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# Aliphatic nitro alcohols. Synthesis, chemical transformations and applications

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**Abstract. The data on the synthesis, chemical transformations and practical use of aliphatic nitro alcohols published over the last 25 years are described systematically and analysed. The bibliography includes 316 references**.

## I. Introduction

Aliphatic nitro-derivatives attract considerable attention from researchers, because they are readily accessible and convenient starting compounds for the synthesis of organic derivatives of various classes. The diversity of chemical transformations of aliphatic nitro-compounds provided the basis for the paper 'Aliphatic nitro-compounds as perfect intermediates' published in 1979.[1] Nitro alcohols of the aliphatic series fully conform to this definition. Furthermore, since nitro alcohols contain the hydroxy group, their reactions can involve simultaneously several reaction sites; hence, the range of chemical transformations of these derivatives is even broader.

The results of numerous studies devoted to the chemistry of aliphatic nitro alcohols and published before 1972 have been surveyed quite comprehensively in reviews and monographs.[2–4] However, no reviews describing systematically the data on the synthesis, transformations and practical use of aliphatic nitro alcohols obtained during the last 25 years have been published so far.

The purpose of this review is to fill this gap. We only briefly outline the preparation of nitro alcohols by nitroaldol condensation (Henry reaction), because its conditions have been described quite comprehensively in previous publications.[3,4] The studies containing some novelty either in the procedure of condensation of nitro-compounds with carbonyl derivatives or in the use of the target compounds are discussed in greater detail. New data about other known methods for the synthesis of nitro alcohols and new information on their chemical transformations are presented. We also consider most of the studies that mention potential practical applications of these compounds, because this aspect has received little attention in earlier reviews.

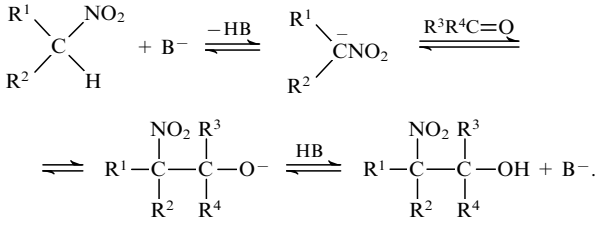
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## II. Methods for the synthesis of aliphatic nitro alcohols

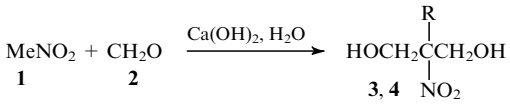
### 1. Nitroaldol condensation (the Henry reaction)

The Henry reaction consisting of condensation of aliphatic nitro-compounds with aldehydes or ketones is the most general method used widely for the synthesis of aliphatic nitro alcohols. The mechanism of this reaction has not yet been completely elucidated. It is generally accepted that nitroalkanes are condensed with carbonyl compounds according to the following scheme:



#### a. Reactions of nitromethane and its derivatives with aldehydes

The reaction of nitromethane **1** with formaldehyde **2** catalysed by $Ca(OH)_2$ makes it possible to prepare both 2-nitropropane-1,3-diol **3** [5] and 2-hydroxymethyl-2-nitropropane-1,3-diol **4**.[6]



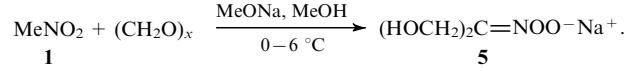
R = H (**3**); $CH_2OH$ (**4**).

The diol **3** has also been prepared from the compounds **1** and **2** at 0 – 10 °C in the presence of sodium carbonate.[7]

The synthesis of **3** from **1** and an aqueous solution of formaldehyde or paraformaldehyde is carried out most often in the presence of alkali, NaOH [8–12] or KOH,[13] as catalysts.

Sodium and potassium hydroxides are also used as catalysts to synthesise the triol **4** from $MeNO_2$ and the aldehyde **2**.[14]

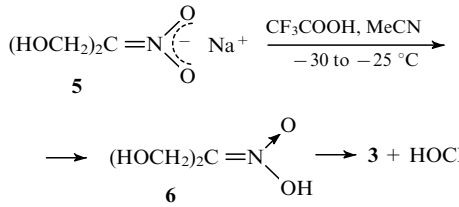
The condensation of nitromethane **1** with paraformaldehyde catalysed by sodium methoxide in methanol gives the sodium salt **5**.[15,16]



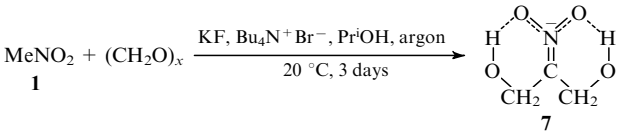
The condensation of $MeNO_2$ with paraform in the presence of $Bu_4N^+Br^-$ and KF under an inert atmosphere at 18 – 22 °C for

72 h affords a mixture of the diol **3** (yield 5% – 10%) and the triol **4** (yield 80% – 85%).[16]

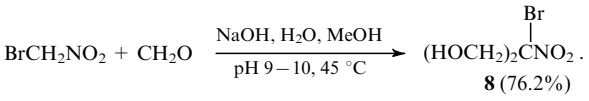
Treatment of the nitronate **5** with trifluoroacetic acid at low temperatures gives rise to the *aci*-form **6**, which is rapidly converted into the diol **3** and 2-nitroprop-2-en-1-ol.[16]



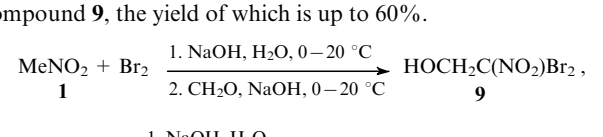
The diol **3** obtained from $MeNO_2$ and paraformaldehyde in the presence of KF and $Bu_4N^+Br^-$ exists as a nitronate **7** stabilised by intramolecular interactions.[17]



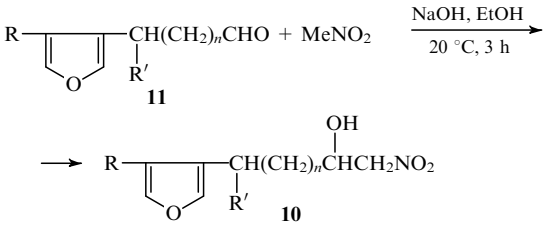
The condensation of bromonitromethane with formaldehyde **2** in the presence of NaOH in methanol gives the diol **8**.[18]



Treatment of nitromethane **1** with bromine in an alkaline medium followed by the reaction with formaldehyde in the presence of NaOH [19] or the condensation of $MeNO_2$ with formaldehyde followed by treatment with bromine [20] afford the same compound **9**, the yield of which is up to 60%.



Nitro alcohols **10** containing a furyl substituent have been obtained by the condensation of $MeNO_2$ with aldehydes **11** in the presence of sodium hydroxide.[21,22]



| R | R′ | *n* | Yield (%) | Ref. |
|---|---|---|---|---|
| H | Me | 2 | 49 | 21 |
| Me | H | 2 | 78 | 22 |
| H | H | 1 | 66 – 73 | 21, 22 |
| H | Me | 1 | 59 – 75 | 21, 22 |

The reaction of chiral complex **12** with nitromethane has been carried out in the presence of NaOH or KF and gave a mixture of diastereoisomeric nitro alcohols **13a** (1*S*,2*S*) and **13b** (1*S*,2*R*) in a high yield. It was found that the ratio of the resulting isomers varies over a wide range depending on the procedure used and the temperature (see Table 1).[23]

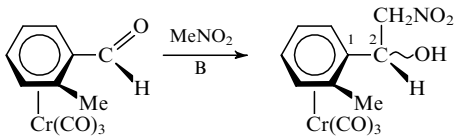
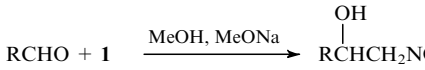


**Table 1**. Reaction conditions and the ratio of the products **13a** and **13b**.

| Base | Temperature /°C | Yield (%) | Ratio **13a** : **13b** |
|---|---|---|---|
| NaOH | 20 | 100 | 64 : 36 |
| NaOH | −20 | 95 | 92 : 8 |
| NaOH | −40 | 90 | 97 : 3 |
| KF/Pr$^i$OH | 20 | 80 | 40 : 60 |
| KF/Pr$^i$OH | 0 | 90 | 88 : 12 |

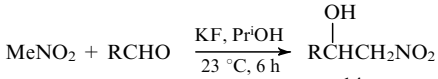
When nitromethane was treated with butyllithium (THF, HMPT, −90 to −60 °C), and the product was made to react with aldehyde **12** (THF, −70 to −60 °C, 1.5 h; −45 to −40 °C, 3 h), the isomer **13a** was obtained as the only product.[23]

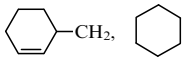
Sodium methoxide has been used as the catalyst in the reactions of nitromethane **1** with both aliphatic [24] and aromatic [25,26] aldehydes.



R = $C_{13}H_{27}$, 3-$MeOC_6H_4$, 4-$PhCH_2OC_6H_4$ (43%), Ph (59%), 4-$MeC_6H_4$ (50%), 4-$ClC_6H_4$ (63%).

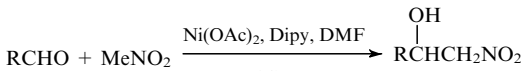
Potassium fluoride is an efficient catalyst of the reaction of $MeNO_2$ with aldehydes.[27]



R = $C_6H_{13}$, $C_7H_{15}$, ,

$Me_2C{=}CH(CH_2)_2C(Me){=}CH(CH_2)_2$.

Study of the condensation of nitromethane with aldehydes carried out using IR and NMR spectroscopy has shown that the process occurs efficiently in DMF at 20 °C in the presence of a complex of nickel acetate with 2,2′-dipyridyl (Dipy) and gives nitro alcohols **15** in 81% – 87% yields.[28]



R = , $PhCH_2CH_2$, 4-$NO_2C_6H_4$, 4-$NCC_6H_4$.

The reaction of $MeNO_2$ with acetaldehyde catalysed by $Rh(PMe_3)_3Cl$ and carried out at 23 °C for 0.5 h affords 1-nitropropan-2-ol in 90% yield.[29]

Nitromethane readily reacts with aromatic aldehydes in liquid ammonia giving rise to nitro alcohols **16** in good yields.[30]

$$\underset{\mathbf{1}}{MeNO_2} + ArCHO \xrightarrow{NH_3(liq.)} \underset{\mathbf{16}}{ArCH(OH)CH_2NO_2}$$

Ar = 2-$H_2NC_6H_4$ (53%), 3,4-$(MeO)_2C_6H_3$ (98%), 4-Br-3,4-$(MeO)_2C_6H_2$ (80%), 4-$MeC_6H_4$ (92%), 3,4-$(CH_2O_2)C_6H_3$ (83%), 4-$BrC_6H_4$ (93%), 3-$BrC_6H_4$ (91%), 3-$ClC_6H_4$ (75%), 4-$MeOC_6H_4$ (82%), 1-naphthyl (53%).

Triethylamine has been used as the catalyst in the reaction of $MeNO_2$ with 4-chloropentanal **17**; this resulted in the formation of nitro alcohol **18** in 42.5% yield.[31]

$$\underset{\mathbf{17}}{\mathbf{1} + MeCH(Cl)(CH_2)_2CHO} \xrightarrow[\substack{5-7\ ^\circ C,\ 48\ h;\\ 20\ ^\circ C,\ 24\ h}]{Et_3N,\ EtOH} \underset{\mathbf{18}}{MeCH(Cl)(CH_2)_2CH(OH)CH_2NO_2}.$$

Difluoronitromethane condenses with trifluoroacetaldehyde on heating in the presence of sodium carbonate. The reaction gives 1,1,1,3,3-pentafluoro-3-nitropropan-2-ol in 38.5% yield.[32]

The condensation of difluoronitromethane with aromatic aldehydes has been carried out using KOH as the catalyst.[33]

$$F_2C(NO_2)H + ArCHO \xrightarrow[150\ ^\circ C,\ 5-15\ h]{KOH,\ DMF} ArCH(OH)C(NO_2)F_2$$

Ar = 2-$HOC_6H_4$ (47%), 2-$ClC_6H_4$ (61%), 2-$O_2NC_6H_4$ (31.5%), 3-$O_2NC_6H_4$ (56%), 4-$MeC_6H_4$ (60%), 2,4-$(MeO)_2C_6H_3$ (53.5%).

It has been reported[34] that chlorofluoronitromethane reacts with aliphatic aldehydes without a catalyst.

$$F(Cl)C(NO_2)H + RCHO \xrightarrow[\text{refluxing, 1 h}]{} RCH(OH)C(NO_2)(Cl)F$$

R = H (83%), Me (55%), Et (73%), Pr (86%).

### b. Reactions of nitromethane homologues and their derivatives with aldehydes

It should be noted that even when primary nitro-compounds are used, the synthesis usually affords products resulting from condensation with one formaldehyde molecule.

2-Nitrobutan-1-ol has been obtained in an almost quantitative yield by the reaction of 1-nitropropane with formaldehyde **2** in the presence of $Ca(OH)_2$ at 30 °C.[35]

In a number of publications,[36–39] synthesis of nitro alcohols **19** from nitroalkane **20** and formaldehyde catalysed by an alkali (NaOH or KOH) or by Amberlites IRA-410 has been described (Table 2).

$$\underset{\mathbf{20}}{RR'CHNO_2} + \underset{\mathbf{2}}{CH_2O} \xrightarrow[20-30\ ^\circ C]{H_2O} \underset{\mathbf{19}}{RR'C(NO_2)CH_2OH}.$$

**Table 2**. Reaction conditions and yields of products in the condensation of the nitro-derivatives **20** with formaldehyde.

| R | R′ | Catalyst | Time /h | Yield (%) | Ref. |
|---|---|---|---|---|---|
| $Bu^t$ | Me | KOH | – | 56.5 | 36 |
| $MeC(NO_2)_2CH_2$ | H | NaOH | 48 | – | 37 |
| Et | H | NaOH | 5 | see [a] | 38 |
| $C_{12}H_{25}-C_{18}H_{37}$ | H | Amberlites IRA-410 | – | 30 | 39 |

[a] The reaction also yields $EtC(NO_2)(CH_2OH)_2$.

Condensation of nitrated butadiene or isoprene oligomers with formaldehyde in the presence of alkaline catalysts gave the corresponding nitro alcohols.[40]

The process of condensation of nitroalkanes with formaldehyde has been optimised by experiment design.[41,42] It was found that the reaction of paraformaldehyde with nitroethane in the presence of KOH occurs over a period of 2–3 min.[41] The highest yields of nitro alcohols in the reaction between an aqueous solution of the aldehyde **2** and a mixture of $C_1-C_4$ nitroalkanes are attained when the process is carried out at an $RNO_2:CH_2O$ ratio of 2.5 : 1 and at a temperature of 50–60 °C for 35–40 min.[42]

The condensation of 2-nitropropane with paraformaldehyde in the presence of KF affords 2-methyl-2-nitropropan-1-ol in 86% yield.[43]

2-Nitropropan-1-ol has been obtained in a yield of 62%–74% by the reaction of nitroethane with the aldehyde **2** in the presence of triethylamine.[44]

Tributylphosphine has been used as the catalyst in the synthesis of 2-methyl-2-nitropropan-1-ol from 2-nitropropane and paraformaldehyde.[45]

$$Me_2CHNO_2 + (CH_2O)_x \xrightarrow[35-40\ ^\circ C,\ 45\ min]{Bu_3P,\ Pr^iOH} Me_2C(NO_2)CH_2OH.$$

As a rule, high yields of nitro alcohols are achieved when formaldehyde is condensed with functionally substituted nitroalkanes **21** in the presence of NaOH (Table 3).[46–48]

$$\underset{\mathbf{2}}{CH_2O} + \underset{\mathbf{21}}{RR'CHNO_2} \xrightarrow{NaOH,\ H_2O} RR'C(NO_2)CH_2OH.$$

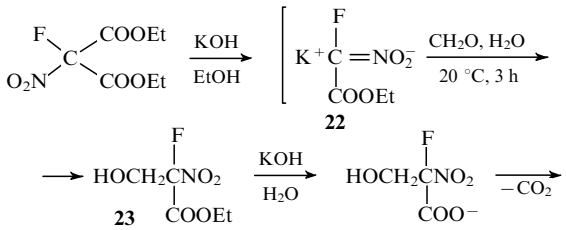
**Table 3**. Reaction conditions and yields of products for the condensation of the nitro-derivative **21** with formaldehyde.

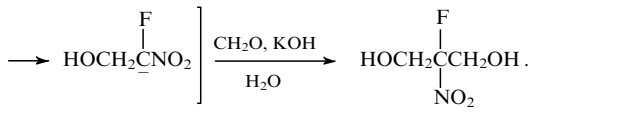
| R | R′ | Temperature /°C, | Time /h | Yield (%) | Ref. |
|---|---|---|---|---|---|
| Et | F | 76–80 | 2–3 | 80 | 46 |
| Pr | F | 76–80 | 2–3 | 87 | 46 |
| Bu | F | 76–80 | 2–3 | 86 | 46 |
| $C_5H_{11}$ | F | 76–80 | 2–3 | 79 | 46 |
| $C_6H_{13}$ | F | 76–80 | 2–3 | 83 | 46 |
| $C_7H_{15}$ | F | 76–80 | 2–3 | 85 | 46 |
| $C_8H_{17}$ | F | 76–80 | 2–3 | 81 | 46 |
| $F_2CCl$ | H | –10 | – | – | 47 |
| COOEt | Me | 20 | 2 | 60 [a] | 48 |
| COOEt | Et | 20 | 2 | 67 [a] | 48 |
| COOEt | Pr | 20 | 2 | 67 [a] | 48 |
| COOEt | $Pr^i$ | 20 | 2 | 79 [a] | 48 |
| COOEt | Bu | 20 | 2 | 82 [a] | 48 |

[a] Found for the acetylated product.

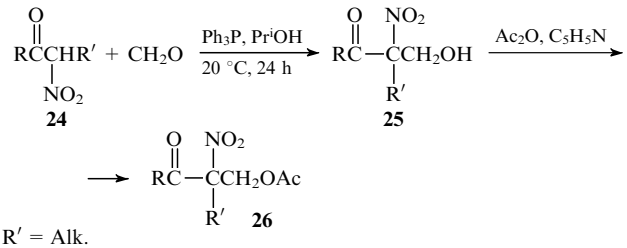
It can be seen from Table 3 that in the case of fluorine-containing nitroalkanes, approximately the same yields of nitro alcohols are obtained when the reaction is carried out with heating. On the other hand, homologues of ethyl nitroacetate readily react with formaldehyde at room temperature.

Treatment of diethyl fluoronitromalonate with potassium hydroxide gives rise to salt **22**, which reacts with the aldehyde **2** to yield compound **23**; the latter reacts with one more molecule of formaldehyde being thus converted into 2-fluoro-2-nitropropane-1,3-diol in a yield of more than 70%.[49]



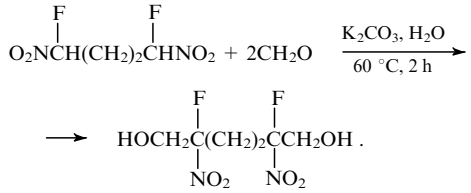


Reactions of aldehydes with nitro ketones carried out in the presence of strong bases are substantially complicated by side reactions of the initial compounds and reaction products. To avoid these problems and to obtain the products of nitroaldol condensation in higher yields, a convenient procedure was developed[48] according to which the condensation of nitro ketones with formaldehyde was carried out in the presence of triphenylphosphine. The intermediate alcohols were isolated as the corresponding acetates after treatment with acetic anhydride. Thus the reaction of nitro ketones **24** with formaldehyde in the presence of triphenylphosphine gave nitro alcohols **25**, which were treated *in situ* with acetic anhydride in the presence of pyridine to give the corresponding acetates **26** (yields 73% – 91%).[48]

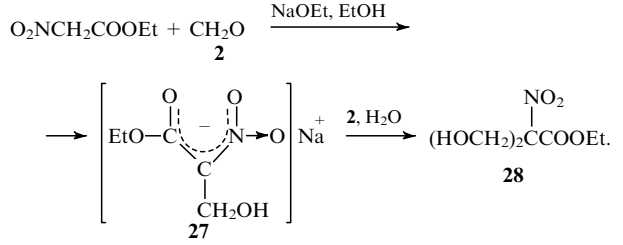


R, R′ = Alk.

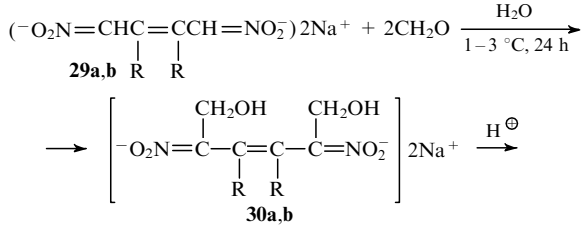
1,4-Difluoro-1,4-dinitrobutane reacts with two molecules of the aldehyde **2** in the presence of potassium carbonate giving 2,5-difluoro-2,5-dinitrohexane-1,6-diol in 75% yield.[50]

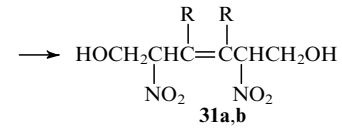


Some researchers have synthesised nitro alcohols by reactions of formaldehyde with the salts of nitro-compounds prepared previously. The sodium salt **27** prepared from ethyl nitroacetate and the aldehyde **2** under the action of sodium ethoxide has been made to react with a second molecule of **2**; this resulted in the synthesis of compound **28**.[51]



The reaction of bis-salts **29** with the aldehyde **2** at 1 – 3 °C gave bis-salts **30**, which were converted into the corresponding diols **31**. Thus treatment of the salt **30b** with $HONH_2 \cdot HCl$ in water at pH 4 gives the diol **31b** in 54.5% yield; treatment of the salt **30a** with 18% hydrochloric acid or with 75% acetic acid affords **31a** in a yield of 9.2% or 6.6%, respectively.[52]

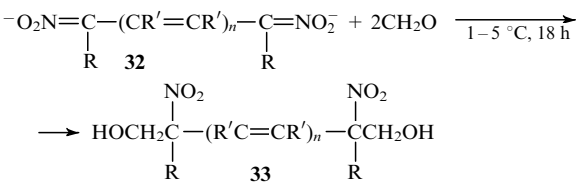




R = H (**a**), Me (**b**).

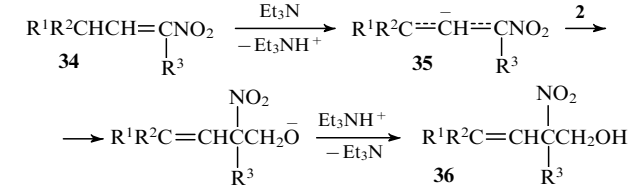
Under the same conditions, the bis-salt ($^-O_2N{=}CHCH_2.CH_2CH{=}NO_2^-$) $2Na^+$ reacts with two molecules of $CH_2O$ and is thus converted into the salt of bis-hydroxymethyl derivative [$^-O_2N{=}C(CH_2OH)CH_2CH_2C(CH_2OH){=}NO_2^-$] $2Na^+$ in 93.6% yield.[52]

Whereas the anions of non-conjugated mononitro-derivatives react with formaldehyde only at pH > 7, the dianions of conjugated dinitroalkanes **32** are able to react with the aldehyde **2** giving rise to diols **33** both at pH > 7 (yields 70% – 90%) and at pH = 4 (yields 40% – 70%).[53]



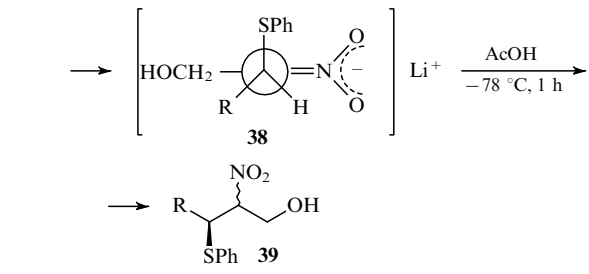
*n* = 0, R = H; *n* = 1: R = H, R′ = H, Me.

The reaction of conjugated nitroalkenes **34** with the aldehyde **2** in the presence of $Et_3N$ in acetonitrile starts with the formation of allylic anions **35**, which are attacked by the aldehyde at the carbon atom carrying the nitro group to give nitro alcohols **36** (yields 60% – 94%).[54]



$R^1$ = H, Bu, $PhCH_2$; $R^2$ = H; $R^3$ = Me, Et, $C_7H_{15}$, $(CH_2)_2COOMe$.

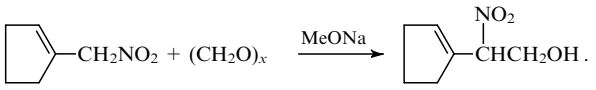
Nitroalkenes **37** react successively with lithium phenylthiolate and the aldehyde **2** to afford salts of *aci*-forms **38**, which are converted, on treatment with acetic acid, into mixtures of *erythro*- and *threo*-isomers (in a ratio ranging from 86 : 14 to 93 : 7) of nitro alcohols **39** (yields 57% – 91%).[55]



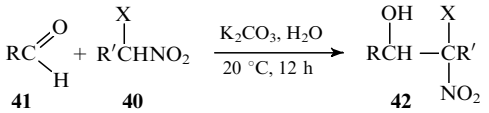
R = Me, Et, Pr, Pr$^i$, Bu, $C_5H_{11}$, Ph, $PhCH_2CH_2$.

The reaction of the nitroalkenes **37** with PhSH and $CH_2O$ in the presence of bases yields mixtures of the *erythro*- and *threo*-isomers of **39** (1 : 1) together with nitro diols RCH(SPh) – $C(CH_2OH)NO_2$.[55]

Sodium methoxide has been used as the catalyst in the reaction of 1-(nitromethyl)cyclopentene with paraformaldehyde.[56]



1-Halo-1-nitroalkanes **40** smoothly react with aldehydes **41** in the presence of potassium carbonate at 20 °C, and this leads to halo-substituted nitro alcohols **42** (yields 37% – 75%).[57]



R = Alk, $CCl_3$; R′ = H, Cl, Br, Me, Et; X = Cl, Br.

Several nitro-compounds **43** have been condensed with aliphatic or arylalkyl aldehydes **44** in the presence of sodium hydroxide in methanol or ethanol; this resulted in the formation of *threo*-isomers of nitro alcohols **45**, as a rule, in good yields.[59, 60] However, the reactions of butyraldehyde with nitrobutane (**43**, $R^1$ = Pr) and nitrooctane ($R^1 = C_7H_{15}$) gave the corresponding nitro alcohols in yields of 26% and 30% (Table 4).[60] When the same nitro-compounds **43** were made to react with aldehydes in the presence of KF, the *erythro*-isomers of **45** were obtained.[59, 60] In some cases, water was added to the reaction mixture.[60]

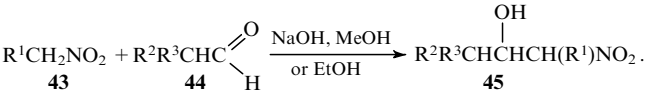
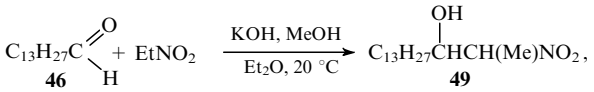


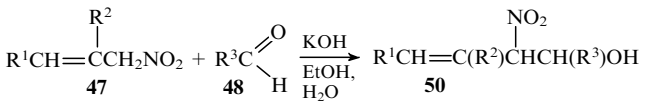
**Table 4**. Reaction conditions and yields of the compounds **45**.

| $R^2$ | $R^3$ | $R^1$ | Temperature /°C | Time /h | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| Me | H | $Cl(CH_2)_3$ | 5 – 10 | – | 65 [a] | 58 |
| Ph | H | H | 30 – 35 | 45 | 67 [a] | 59 |
| Ph | H | Me | 30 – 35 | 45 | 69 [a] | 59 |
| Ph | H | Et | 30 – 35 | 45 | 65 [a] | 59 |
| H | H | Ph | 30 – 35 | 45 | 63 [a] | 59 |
| Me | H | Ph | 30 – 35 | 45 | 58 [a] | 59 |
| Ph | H | Ph | 30 – 35 | 45 | 60 [a] | 59 |
| Me | Me | Ph | 30 – 35 | 45 | 58 [a] | 59 |
| H | Ph | Ph | 20 | 144 | 85 [a] | 59 |
| Me | H | Et | 38 | 65 | 80 [b] | 60 |
| Et | H | Et | 38 | 65 | 63 [b] | 60 |
| Bu | H | Me | 38 | 65 | 52 [b] | 60 |
| Bu | H | Et | 38 | 65 | 58 [b] | 60 |
| Et | H | $C_7H_{15}$ | 38 | 65 | 30 [b] | 60 |
| $C_9H_{19}$ | H | Me | 38 | 65 | 61 [b] | 60 |
| Bu | H | $C_7H_{15}$ | 38 | 65 | 70 [b] | 60 |
| Me | Me | Et | 38 | 65 | 54 [b] | 60 |
| Et | H | $Pr^i$ | 38 | 65 | 26 [b] | 60 |

[a] (*R**,*R**) *threo*-Isomers are formed; if the reaction is carried out in the presence of KF, the nitro alcohols **45** are mostly formed as (*R**,*S**) *erythro*-isomers; [b] water was added to the reaction mixture.

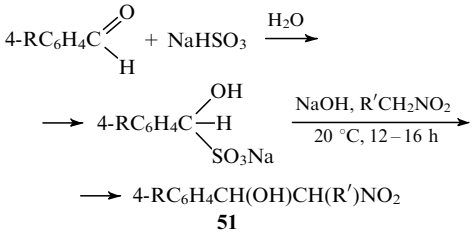
Potassium hydroxide has been used as the catalyst in the reactions of myristaldehyde **46** with nitroethane [61] and of unsaturated nitro-compounds **47** with aldehydes **48**;[62] these reactions gave nitro alcohols **49** and **50** in 64% and 30% – 65% yields, respectively.





$R^1$, $R^2$ = H, Me; $R^3$ = Me, Et, Pr, $Pr^i$.

A method for the synthesis of nitro alcohols **51** by condensation of aromatic aldehydes with nitroalkanes has been patented.[63] According to this method, aldehydes are treated first with sodium hydrogensulfite and then with nitroalkanes in the presence of aqueous sodium hydroxide at 20 °C.[63]



R = $Bu^t$, $Bu^s$; R′ = Me, Et.

In the synthesis of 1,1,1-trichloro-3-nitrobutan-2-ol (yield 30%), the initial chloral was also converted first into the hydrogensulfite derivative, and the latter was made to react with nitroethane in the presence of aqueous sodium hydroxide at 20 °C for 12 h.[64]

In the same study,[64] condensation of primary or secondary nitroalkanes with aliphatic or aromatic aldehydes at 20 °C in the presence of $NaHCO_3$, $K_2CO_3$ or NaOH was studied. The yields of the target nitro alcohols **52** were found to depend crucially on the nature of the initial aldehyde (Table 5).

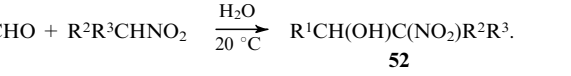
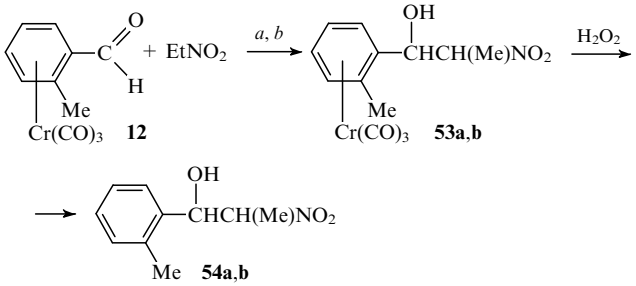


**Table 5**. Reaction conditions and yields of the nitro alcohols **52**.

| $R^1$ | $R^2$ | $R^3$ | Catalyst | Time /h | Yield (%) |
|---|---|---|---|---|---|
| Me | Me | H | $K_2CO_3$ | 5 | 54 |
| $Pr^i$ | Me | H | $K_2CO_3$ | 5 | 40 |
| $CF_3$ | Me | H | NaOH | 5 | 8.2 |
| 4-$O_2NC_6H_4$ | Et | H | $NaHCO_3$ | 5 | 16.3 |
| 4-$O_2NC_6H_4$ | Me | Me | $K_2CO_3$ | 5 | – |
| $Br_3C$ | Me | H | $K_2CO_3$ | 0.5 | 10 |

Synthesis of 2-nitro-1-phenylpropan-1-ol from benzaldehyde and nitroethane under mild conditions in the presence of bases in DMSO or DMF has been reported.[65]

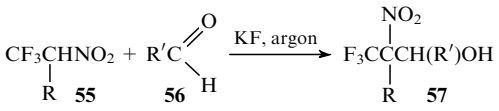
Condensation of the complex **12** with nitroethane in the presence of NaOH yields a mixture of diastereoisomers **53a,b**; on treatment with hydrogen peroxide, this mixture is converted into a mixture of diastereoisomeric nitro alcohols **54a** (1*R**,2*R**) and **54b** (1*R**,2*S**) in a ratio of 36 : 64.[23]



(*a*) NaOH, EtOH, $H_2O$, −40 °C, 0.5 h; (*b*) $NH_4Cl$, $H_2O$.

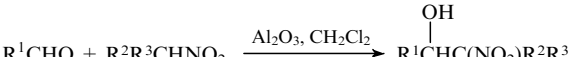
The reaction of **12** with the nitronate prepared previously from nitroethane resulted in the formation of a mixture of diastereoisomers **54a,b** in a ratio of 77 : 23.[23]

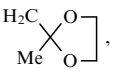
Nitro-compounds **55** containing a $CF_3$ group condense with aldehydes **56** in the presence of potassium fluoride in isopropyl alcohol or without a solvent to give nitro alcohols **57**.[66]

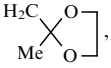


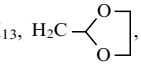
| R | R′ | Solvent | Yield (%) |
|---|---|---|---|
| H | Pr | $Pr^iOH$ | 71 |
| H | Pr | — | 73 |
| H | $C_6H_{13}$ | $Pr^iOH$ | 65 |
| H | $C_6H_{13}$ | — | 71 |
| H | $Ph(CH_2)_2$ | — | 83 |
| H | Me(Ph)CH | — | 46 |
| H | Ph | $Pr^iOH$ | 26 |
| H | Ph | — | 9.5 |
| Me | Pr | $Pr^iOH$ | 54 |
| Me | Pr | — | 35 |
| Me | $C_6H_{13}$ | $Pr^iOH$ | 54 |
| Me | $PhCH_2CH_2$ | — | 40 |

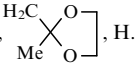
During the last 10–15 years, neutral alumina (Brockmann activity I) has been used as a catalyst in the Henry reaction. In the presence of this catalyst, nitro-compounds **58** condense with various aliphatic aldehydes **59** at ambient temperature.[67]



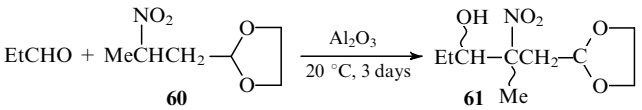
$R^1$, $R^2$, $R^3$ : Me, Et, H; Me, , H; $Pr^i$, Et, H; $C_6H_{13}$, Et, H;

$C_6H_{13}$, , H; $CH_2{=}CH(CH_2)_2$, Me, Me; $Ph(CH_2)_2$,

Me, H; $CH_2{=}CH(CH_2)_2$, Me, H; $C_6H_{13}$, , H;

$C_6H_{13}$, $MeOCO(CH_2)_2$, H; $Ph(CH_2)_2$, , H.

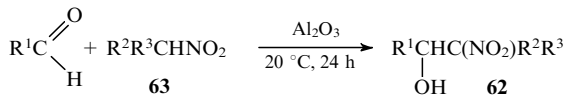
The reaction of nitro-compound **60** with propanal carried out in the presence of $Al_2O_3$ at 20 °C affords condensation product **61** as a mixture of *erythro*- and *threo*-isomers in a 54 : 46 ratio and in 22% overall yield.[68]

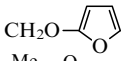
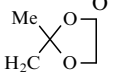
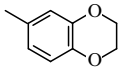


The reaction of nitro-compound **60** with propanal carried out in the presence of $Al_2O_3$ at 20 °C affords condensation product **61** as a mixture of *erythro*- and *threo*-isomers in a 54 : 46 ratio and in 22% overall yield.[68]



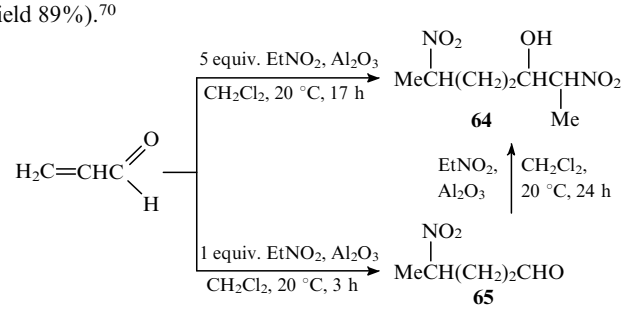
Nitro alcohols **62** have been prepared by the reactions of primary or secondary nitro-compounds **63** with aldehydes in the presence of neutral $Al_2O_3$ without solvents.[66, 69]



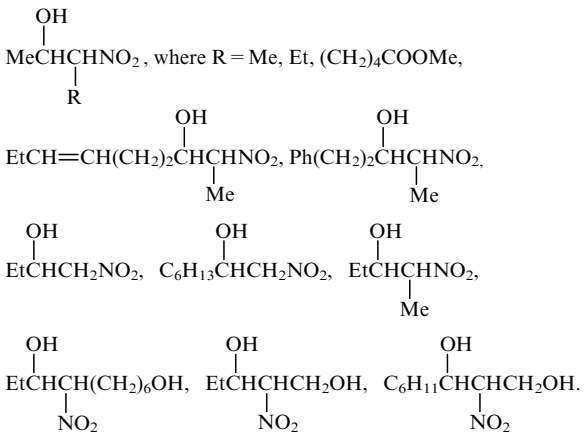
| $R^1$ | $R^2$ | $R^3$ | Yield (%) | Ref. |
|---|---|---|---|---|
| Me | Et | H | 80 | 69 |
| Et | Me | H | 71 | 69 |
| Et | $(CH_2)_2COOMe$ | H | 84 | 69 |
| $Pr^i$ | MeCH(OH) | H | 69 | 69 |
|  | Me | H | 75 | 69 |
| $C_6H_{13}$ |  | H | 86 | 69 |
| $C_6H_{13}$ |  | H | 86 | 69 |
| $Ph(CH_2)_2$ | Me | H | 71 | 69 |
| $Ph(CH_2)_2$ | Me | Me | 69 | 69 |
| $Ph(CH_2)_2$ | see [a] | H | 82 | 69 |
| See [b] | Me | H | 78 | 69 |
| Pr | $CF_3$ | H | 73 | 66 |
| Ph | $CF_3$ | H | 9.5 | 66 |
|  | $CF_3$ | H | 3 | 66 |
| Pr | $CF_3$ | Me | 33 | 66 |

[a] $R^2 = Me(CH_2)_3OCH(Me)OCH_2$; [b] $R^1 = Me_2C{=}CH(CH_2)_2CH(Me)CH_2$.

The product **64** resulting from interaction of acrolein with two molecules of nitroethane has been synthesised by two procedures: by the reaction of the aldehyde with a fivefold excess of $EtNO_2$ (yield 39%) or by the addition of one molecule of $EtNO_2$ to the double bond of the aldehyde followed by condensation of the resulting adduct **65** with a second molecule of the nitro-derivative (yield 89%).[70]



It has been reported [71] that the following nitro alcohols are formed as mixtures of *erythro*- and *threo*-isomers upon reaction of the corresponding aldehydes with nitro-compounds in the presence of $Al_2O_3$ (Brockmann activity I) at 20 °C for 23 h:

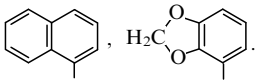


It can be seen from published results [66, 69] that the condensation of nitro-compounds with aromatic aldehydes in the presence of KF or $Al_2O_3$ gives the corresponding nitro alcohols in low yields. When the reactions of nitroalkanes **66** with aromatic aldehydes **67** are conducted [30] in liquid ammonia, the corresponding nitro alcohols **68** are formed in 53%–98% yields.

$$ArCHO + RR'CH_2NO_2 \xrightarrow{NH_3(liq.)} ArCH(OH)CRR'(NO_2)$$

**67** **66** **68**

R = H, Me; R′ = H, Me; Ar = 3-$ClC_6H_4$, 4-$ClC_6H_4$, 3-$BrC_6H_4$, 4-$BrC_6H_4$, 4-$MeOC_6H_4$, 4-$MeC_6H_4$, 2-$O_2NC_6H_4$, 2-$H_2NC_6H_4$, 3,4-$(MeO)_2C_6H_3$, 6-Br-3,4-$(MeO)_2C_6H_2$,



Nitro alcohols have been obtained in good yields by the condensation of nitromethane, nitroethane or 1-nitropropane with the corresponding aliphatic, aromatic or heterocyclic aldehydes in the presence of KF supported on $Al_2O_3$ (Scheme 1).[72]

Scheme 1

$$RCHO + R'CH_2NO_2 \xrightarrow{KF/Al_2O_3} RCH(OH)CH(NO_2)R'$$

| R | R′ | Time /h | Yield (%) |
|---|---|---|---|
| Et | H | 5 | 71 |
| $Pr^i$ | Me | 5 | 75 |
| Et | Me | 5 | 75 |
| $Pr^i$ | Et | 5 | 78 |
| Me | Et | 5 | 77 |
| Bu | Me | 5 | 62 |
| See [a] | Me | 5 | 79 |
| See [a] | H | 5 | 50 |
| Ph | Et | 6 | 55 |
|  | Me | 15($N_2$) | 77 |

[a] R = $Me_2C{=}CH(CH_2)_2CH(Me)CH_2$.

Sodium methoxide [73] and sodium ethoxide [74] have been used as catalysts in the nitroaldol condensation of primary nitroalkanes with functionally substituted aldehydes **69** and **70**.

$$R(R'O)P(O)CH_2CHO + EtNO_2 \xrightarrow[2.\ H_3O^+]{1.\ MeONa,\ 20\ ^\circ C,\ 18\ h} R(R'O)P(O)CH_2CH(OH)CHNO_2Me$$

**69**

R, R′ (yield, %): MeO, Me (66); EtO, Et (60); $Pr^iO$, $Pr^i$ (50); Bu, $Pr^i$ (46); $MeCH{=}CHCH_2$, $Pr^i$ (20); $MeCH{=}CHCH_2$, Pr (20).

$$EtOC(O)CHO + RCH_2NO_2 \xrightarrow[2.\ H_3O^+]{1.\ EtONa,\ EtOH,\ PhH,\ 20\ ^\circ C,\ 12\ h} RCH(NO_2)CH(OH)COOEt$$

**70**

R = Me (52%), Et (51.5%), Pr (54%), $Pr^i$ (28%), Ph (65%).

The reaction of sulfide **71** with acetaldehyde carried out in the presence of potassium *tert*-butoxide (0 °C, 20 min) gives nitro alcohol **72** (yield 95%), whereas the reaction with isobutyraldehyde carried out under the same conditions affords nitroalkene **73** (yield 83%).[75]

$$PhSCH_2NO_2 \xrightarrow[THF]{Bu^tOK,\ Bu^tOH,} \begin{cases} \xrightarrow[0\ ^\circ C,\ 20\ min]{MeCHO} PhSCH(NO_2)CHMeOH \ \mathbf{72} \\ \xrightarrow[0\ ^\circ C,\ 14\ h]{Me_2CHCHO} O_2NCH{=}C(H)SPh\ \mathbf{73}\ Pr^i \end{cases}$$

**71**

Esters of chloronitroacetic acid **74** react with aliphatic aldehydes in the presence of sodium acetate.[76]

$$ClO_2NCHCOOR + R'CHO \xrightarrow[20\ ^\circ C,\ 1-2\ h]{AcONa\cdot 3H_2O,\ EtOH,\ H_2O} R'CH(OH)C(NO_2)(Cl)COOR$$

**74**

R, R′ (yield, %): Me, Me (65); Me, Et (92); Et, Me (98); Et, Et (45); $PhCH_2$, H (71).

The reaction of nitro-compounds **76** with aldehydes in the presence of butyllithium led to γ-nitro alcohols **75** in 75% – 80% yields instead of the normal products of nitroaldol condensation.[77]

$$ArCH_2CH_2NO_2 + RCHO \xrightarrow[-78\ ^\circ C,\ 0.5\ h]{BuLi,\ C_6H_{14},\ THF} RCH(OH)CH(Ar)CH_2NO_2$$

**76** **75**

Ar, R: 4-$ClC_6H_4$, Et; Ph, Ph; Ph, 4-$ClC_6H_4$.

This unusual reaction pathway was explained [77] by the fact that at low temperatures nitro-compounds **76** are doubly deprotonated at the α- and β-positions with respect to the nitro group to give dilithio-derivatives **77**.

$$ArCH_2CH_2NO_2 \xrightarrow[-90\ to\ -78\ ^\circ C]{BuLi} \left[ Ar\text{–}CH\text{–}N(O^-)(O) \leftrightarrow Ar\text{–}CH\text{–}N(O^-)_2 \leftrightarrow Ar\text{–}CH{=}N(O^-)_2 \right] 2Li^+$$

**77**

The formation of γ-nitro alcohols in the condensation of nitro-compounds with aldehydes in the presence of BuLi is not a specific feature peculiar only to 2-arylnitroethanes. It was found that γ-nitro alcohols are also formed in the reactions of some secondary nitro-compounds with aldehydes in the presence of BuLi or $Bu^tLi$. For example, 3-nitro-1-phenylbutan-1-ol was synthesised in 50% yield by the reaction of 2-nitropropane with benzaldehyde in the presence of BuLi and $Bu^tLi$.[77]

The condensation of 1,1,1-trifluoro-2-nitropropane with aliphatic and aromatic aldehydes in the presence of BuLi and $Bu^tLi$ occurs *via* unusual doubly deprotonated products **78** and yields γ-nitro alcohols **79**.[67]

$$F_3CCH(NO_2)Me \xrightarrow[2.\ Bu^tLi,\ THF,\ HMPT,\ -70\ ^\circ C]{1.\ BuLi,\ THF,\ argon,\ -70\ ^\circ C} \left[ LiO\text{–}N(OLi)\text{–}C(F_3C){=}CH_2 \right] \xrightarrow[2.\ H_2O]{1.\ RCHO,\ -80\ ^\circ C} F_3CCH(NO_2)CH_2CH(OH)R$$

**78** **79**

R = $C_6H_{13}$ (12%), $PhCH_2CH_2$ (9%), Ph (21%).

Primary nitro-compounds **80**, doubly deprotonated upon treatment with BuLi, react with aldehydes to give products of nitroaldol condensation, namely, β-nitro alcohols **81**.[66]

$$F_2C(X)CH_2NO_2 \xrightarrow[-90\ ^\circ C]{BuLi,\ DMF,THF,\ argon} \left[ {}^-O\text{–}N(OLi)\text{–}C(F_2X){=}C\text{–}Li \right] \xrightarrow[2.\ H_2O,\ -75\ ^\circ C,\ 1\ h]{1.\ RCHO,\ THF,\ argon} F_2C(NO_2)CH(R)OH(X)$$

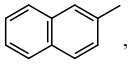
**80** **81**

X, R (yield, %): F, $Bu^t$ (90); H, $Bu^t$ (40); F, Ph (67); H, Ph (32); H, 4-$O_2NC_6H_4$ (52); F, 3,4-$(CH_2O_2)C_6H_3$ (40).

The reactions of primary nitro-compounds **82** with aldehydes in the presence of butyllithium and $TiCl_3(OPr^i)$ at nitroalkane : aldehyde ratios of 1 : 1 or 2 : 1 have been studied in detail. This process was found to afford β-nitro alcohols **83** as mixtures of *erythro*- and *threo*-isomers.[78]

$$RCH_2NO_2 \xrightarrow{a,\,b} R'CH(OH)CH(R)NO_2$$
**82** **83**

R = Et: R′ = 4-$O_2NC_6H_4$, Ph, 4-$MeOC_6H_4$, 2-$CF_3C_6H_4$, 4-$MeOCOC_6H_4$,



, PhCH=CH, Bu, $C_5H_{11}$, Bu$^t$, COOMe;

R = Bu: R′ = 4-$O_2NC_6H_4$.

(*a*) BuLi, THF, −78 °C, 15 min;

(*b*) R′CHO, $TiCl_3(OPr^i)$, $CH_2Cl_2$, −78 °C, 1 h; 20 °C, 3.5 h.

The ratio of the *erythro*- and *threo*-isomers formed varies over a wide range. For a nitroalkane : aldehyde ratio of 1 : 1, it varies from 3.9 : 1 (in the case of R′ = 4-$O_2NC_6H_4$, R = Bu) to 11.2 : 1 (in the case of R′ = $MeOOCC_6H_4$, R = Et); for a nitroalkane : aldehyde ratio of 2 : 1, it ranges from 2 : 1 (R′ = COOMe, R = Et) to 8 : 1 (R′ = PhCH=CH, R = Et).[78]

The reaction of nitroethane with benzaldehyde in the presence of butyllithium has been studied systematically using two approaches.[79] According to one of them, $EtNO_2$ was treated with BuLi in THF and HMPT at various temperatures and various HMPT/BuLi ratios, and after that, the aldehyde was added at a temperature between −78 and −35 °C, and the reaction mixture was quenched with acetic acid (procedure A). The second approach included treatment of the aldehyde with butyllithium in THF and HMPT at −90 °C and subsequent addition of the nitro-compound at various temperatures and various HMPT/BuLi ratios followed by acidification of the reaction mixture (procedure B). It was found that in both cases, the reaction resulted in the formation of a mixture of β-nitro alcohol **84** and γ-nitro alcohol **85**.

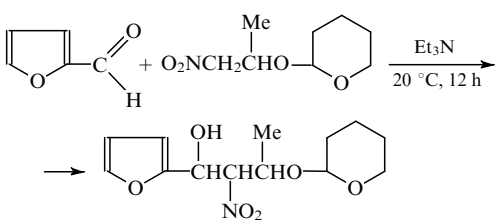
$$MeCH_2NO_2 + PhCHO \longrightarrow \underset{\mathbf{84}}{PhCH(OH)CH(Me)NO_2} + \underset{\mathbf{85}}{PhCH(OH)CH_2CH_2NO_2}.$$

When the reaction was carried out by procedure A at an HMPT/BuLi ratio of 2.6 and at a temperature of −90 to −25 °C, the yields of the compound **84** varied in the range 68.8% – 11.3%. In the absence of HMPT, the yield of **84** was 47.3%, and that of the compound **85** was 3% (at −90 °C). At higher temperatures, the yield of **85** increased, whereas the overall yield decreased. The reaction carried out by procedure B without HMPA afforded only the nitro alcohol **84** (yield 56.8%). At HMPT/BuLi ratios greater than 2, the nitro alcohol **85** was formed as the major product (yields 50.8% – 72.6%, the yields of **84** formed simultaneously being 3.8% – 10.6%.

Triethylamine has been used as the catalyst in the condensation of nitro-compounds with both aliphatic[30] and heteroaromatic[80] aldehydes.

$$Me_2CHNO_2 + MeCH(Cl)(CH_2)_2CHO \xrightarrow[5-7\ ^\circ C,\ 2\ days;\ 20\ ^\circ C,\ 24\ h]{Et_3N,\ EtOH} MeCH(Cl)(CH_2)_2CH(OH)C(NO_2)Me_2,$$

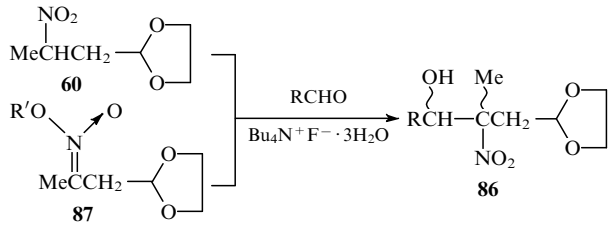
(42.5%)



Mixtures of *erythro*- and *threo*-isomers of nitro alcohols **86** are formed when the nitro compound **60** or its derivative **87** is made to react with acetaldehyde or propionaldehyde in the presence of tetrabutylammonium fluoride trihydrate (Table 6).[69]

**Table 6**. Reaction conditions, yields and isomeric ratios of the nitro alcohols **86**.

| R | Nitro-compound | Temperature /°C | Time /h | Yield (%) | Ratio *erythro* : *threo* |
|---|---|---|---|---|---|
| Me | **87** | −78 – 20 | 15.5 | 20 | 56 : 44 |
| Me | **87** | 0 | 2.3 | 89 | 55 : 45 |
| Et | **87** | 0 | 0.75 | 74 | 54 : 46 |
| Me | **60** | 0 – 6 | 23 | 52 | 62 : 38 |



R′ = Bu$^t$Me$_2$Si.

In a study on the development of the synthesis of β-amino alcohols according to the scheme

$$RCHO + R'CH_2NO_2 \longrightarrow RCH(OH)CH(R')NO_2 \longrightarrow RCH(OH)CH(R')NH_2,$$

it was found[81–83] that the nitroaldol condensation of nitroalkanes with molecular weights much greater than that of nitromethane in the presence of conventional catalysts gives β-nitro alcohols in low yields. In order to increase the yields of the target compounds, the researchers studied the nitroaldol condensation of aldehydes with silyl ethers **88**, which were obtained from nitroalkanes and chlorotrimethylsilane or *tert*-butyl(chloro)dimethylsilane under the action of $Pr^i_2NLi$ (LDA), in the presence of tetrabutylammonium fluoride. This resulted in the formation of nitro alcohol derivatives **89** in good or high yields.

$$R^2CH_2NO_2 \xrightarrow[2.\ Me_3SiCl\ or\ Bu^tMe_2SiCl]{1.\ LDA,\ THF,\ -78\ ^\circ C} \underset{\mathbf{88}}{R^2CH{=}\overset{+}{N}(OR^1)O^-} \xrightarrow[Bu_4N^+F^-]{R^3CHO} \underset{\mathbf{89}}{R^3CH(OH)R^2NO_2}$$

$R^1$ = $SiMe_3$, $SiMe_2Bu^t$: $R^2$ = $C_5H_{11}$, $R^3$ = $C_6H_{13}$ (71 – 80%);
$R^2$ = $C_5H_{11}$, $R^3$ = Bu$^t$ (57%); $R^2$ = $C_5H_{11}$, $R^3$ = Ph (75 – 83%);
$R^2$ = $C_5H_{11}$, $R^3$ = 4-$MeOC_6H_4$ (70%); $R^2$ = $C_5H_{11}$,
$R^3$ = 4-$O_2NC_6H_{11}$ (91%); $R^2$ = Et, $R^3$ = Pr (82%,
*erythro* : *threo* = 20 : 1); $R^2$ = Et, $R^3$ = Pr$^i$; $R^2$ = Pr$^i$, $R^3$ = Pr;
$R^2$ = Me, $R^3$ = $C_5H_{11}$ (*erythro* : *threo* = 20 : 1); $R^2$ = Et,
$R^3$ = $C_5H_{11}$ (*erythro* : *threo* = 20 : 1); $R^2$ = $C_7H_{15}$, $R^3$ = Pr
(*erythro* : *threo* = 20 : 1); $R^2$ = Me, $R^3$ = $C_{10}H_{21}$; $R^2$ = Me,
$R^3$ = $C_9H_{19}$; $R^2$ = Et, $R^3$ = Ph (*erythro* : *threo* = 3.5 : 1).

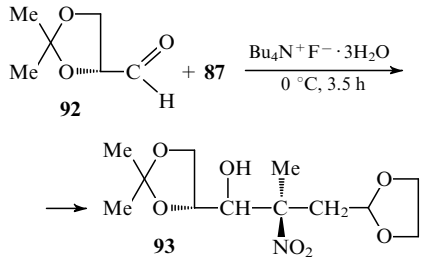
Silyl ethers of nitro alcohols **90** have been prepared in 30% – 40% yields by treatment of 2-nitropropane derivative **91** with aldehydes.[81]

$$Me_2CHNO_2 \xrightarrow[2.\ Bu^tMe_2SiCl]{1.\ LDA,\ THF,\ -78\ ^\circ C} \underset{\mathbf{91}}{Me_2C{=}\overset{+}{N}(OSiMe_2Bu^t)O^-} \xrightarrow[RCHO,\ Bu_4N^+F^-]{} \underset{\mathbf{90}}{Me_2C(NO_2)CH(R)OSiMe_2Bu^t}$$

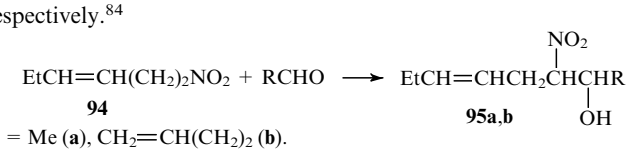
R = $C_6H_{13}$, Bu$^t$, Ph, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$.

The reaction of the silyl ether **87** with aldehyde **92** gives rise to four isomeric nitro alcohols (overall yield 59%, isomer ratio

58 : 28 : 12 : 2). The isomer **93** was isolated from this mixture in a pure state in a yield of 34%.[69]



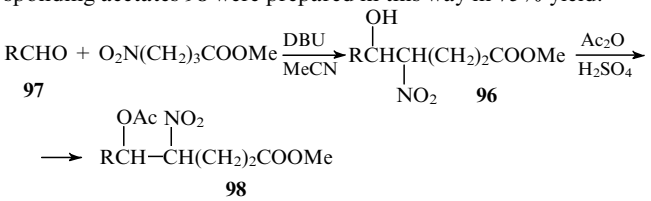
The condensation of 1-nitrohex-3-ene **94** with aldehydes catalysed by Amberlyst A-21 occurs successfully at 20 °C; this gives nitro alcohols **95a**,**b**, their yields being 74% and 71%, respectively.[84]



R = Me (**a**), $CH_2{=}CH(CH_2)_2$ (**b**).

The reactions of nitroalkanes $RCH_2CH(R')NO_2$ with 4-ethoxybenzaldehyde carried out in the presence of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) give rise to the corresponding nitro alcohols $4\text{-}EtOC_6H_4CH(OH)C(R')(NO_2)CH_2R$ (R, R′ : H, H; H, Me; Me, H).[85]

Nitro alcohols **96** resulting from the condensation of aldehydes **97** with methyl 4-nitrobutyrate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) have been treated *in situ* with acetic anhydride in the presence of sulfuric acid; the corresponding acetates **98** were prepared in this way in 75% yield.[86]



R = Me, $(CH_2)_2COOMe$.

The reaction of nitroalkenes $MeCH(R)CH{=}CHNO_2$ (R = H, Me) with propionaldehyde in the presence of DBN is accompanied by isomerisation of the double bond in the nitroalkene and gives unsaturated β-nitro alcohols $EtCH(OH)CH(NO_2){-}CH{=}C(Me)R$ (R = H, Me).[54]

To synthesise nitro alcohols **99**, a mixture of nitroethane and aldehydes was treated with a mixed acetal of dimethylketene in the presence of $[Rh(C_5Me_5)Cl]_2(\mu\text{-}Cl)_2$ and then with tetrabutylammonium fluoride. The reaction conditions and the product yields are listed in Table 7.[87]

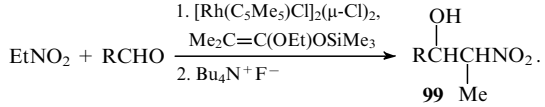


**Table 7**. Reaction conditions and yields of the nitro alcohols **99**.

| R | Solvent | Number of equivalents of $EtNO_2$ | Yield (%) |
|---|---|---|---|
| Ph | $CH_2Cl_2$ | 5 | – |
| Ph | THF | 10 | 16 |
| Ph | THF | 43 | 82 [a] |
| PhCH=CH | THF | 43 | 48 |
| $PhCH_2CH_2$ | THF | 43 | 54 |

[a] The ratio *syn* : *anti* = 39 : 61.

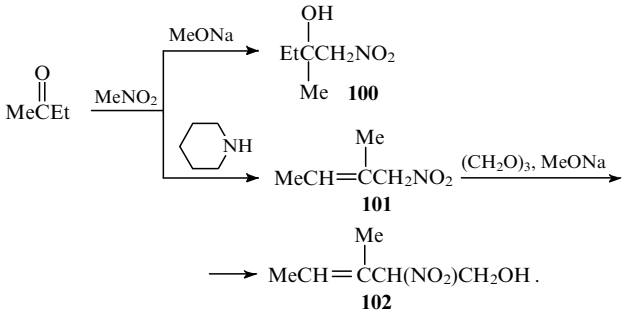
**c. Reactions of nitroalkanes with ketones**

Reactions of nitro-compounds with ketones have been much less studied than the nitroaldol condensation involving aldehydes. This is due to some features peculiar to the reactions with ketones. These reactions are often accompanied by spontaneous dehydration of the adducts yielding nitroalkenes, which enter into the Michael reaction with the initial nitro-derivatives.

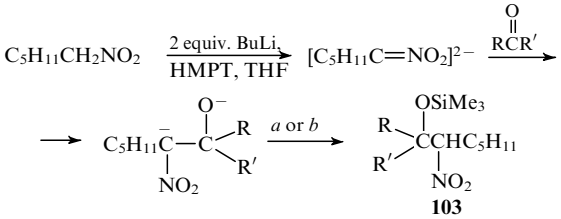
Only few studies dealing with the reactions of nitro-compounds with ketones have been published over the last 25 years.

The reaction of phenylnitromethane with acetone in the presence of sodium methoxide at 20 °C for 50 h gave the corresponding nitro alcohol, 2-methyl-1-nitro-1-phenylpropan-2-ol, in a yield of only 10%.[59]

When nitromethane **1** was made to react with ethyl methyl ketone in the presence of sodium methoxide, the product of nitroaldol condensation, 2-methyl-1-nitrobutan-2-ol **100**, was obtained. When this reaction was carried out in the presence of piperidine, 2-methyl-1-nitrobut-2-ene **101** was isolated from the reaction mixture. In the presence of sodium methoxide, **101** reacted with 1,3,5-trioxane being thus converted into nitro alcohol **102**.[56]

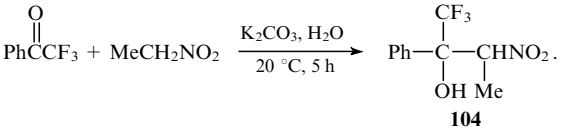


The method for the synthesis of β-nitro alcohols from aldehydes and nitroalkanes developed by Colvin *et al.*[81,82] and described above proved to be inapplicable to nitroaldol condensation between nitroalkanes and ketones. Therefore, a modified procedure for the synthesis of silyl ethers of β-nitro alcohols **103** from 1-nitrohexane and ketones RCOR′ was proposed.[81]

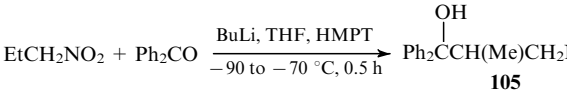


R = R′ = Ph, R,R′ = $(CH_2)_5$;
(*a*) $Me_3SiCl$; (*b*) 1. AcOH; 2. $Me_3SiCl{-}(Me_3Si)_2NH$.

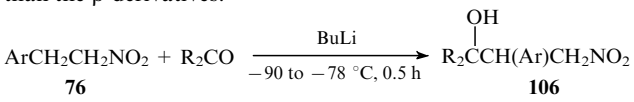
When trifluoroacetophenone was treated with nitroethane in the presence of an aqueous solution of potassium carbonate for 5 h, nitro alcohol **104** was formed.[6]



γ-Nitro alcohol **105** was synthesised in 77% yield by condensation of 1-nitropropane with benzophenone in the presence of butyllithium in THF and HMPT at low temperatures.[79]



The reactions of 2-arylnitroethanes **76** with ketones in the presence of butyllithium also afford γ-nitro alcohols **106** rather than the β-derivatives.[77]

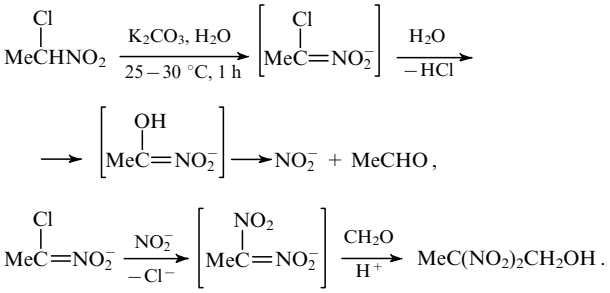


R, Ar (yield, %): Me, Ph (70); Ph, 4-$ClC_6H_4$ (67); $(CH_2)_5$, Ph (69).

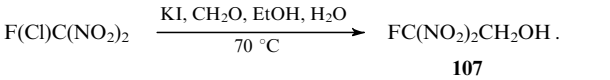
### d. Reactions of 1,1-dinitro- and 1,1,1-trinitro-derivatives with aldehydes

In a study dealing with the kinetics and mechanism of the condensation of acetaldehyde with 1,1-dinitroethane or with methyl 2-nitropropionate in DMSO,[88] it has been found that the addition of the anions derived from nitro-compounds to the carbonyl group of the aldehyde is the rate-determining step of this reaction. The researchers determined the equilibrium and rate constants of the process, which characterise the basicity and nucleophilicity of the nitronate anions. It was found that there exists a normal correlation between the basicity and nucleophilicity of the two anions in DMSO: the more basic anion reacts faster than the less basic one. In the presence of alkali, 1,1-dinitroethane reacts with an aqueous solution of formaldehyde to give 2,2-dinitropropan-1-ol in 80% yield.[89]

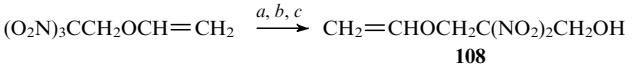
Condensation of the potassium salt of 1,1-dinitroethane, formed upon treatment of 1-chloro-1-nitroethane with an aqueous solution of potassium carbonate for 1 h at 25–30 °C, with excess formaldehyde resulted in the formation of 2,2-dinitropropan-1-ol in 20%–25% yield.[90]



2-Fluoro-2,2-dinitroethanol **107** was prepared by the reaction of chlorofluorodinitromethane with potassium iodide and formaldehyde at 70 °C.[91]

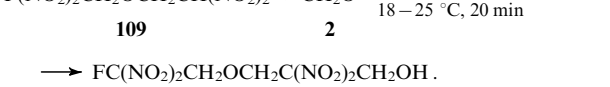


2,2-Dinitro-3-vinyloxypropan-1-ol is formed in 19.2% yield when 2,2,2-trinitroethyl vinyl ether is treated successively with alkaline hydrogen peroxide and with formaldehyde in the presence of sodium hydroxide, and the reaction mixture is then acidified by HCl to pH 2.[92]

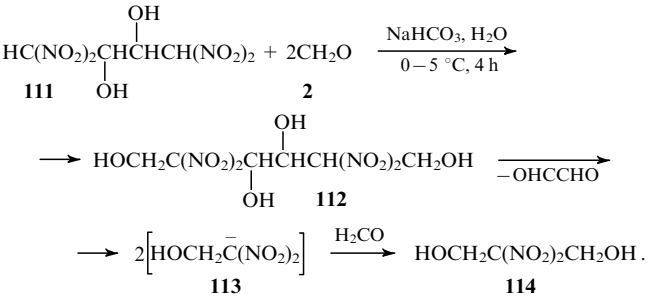


(*a*) $H_2O_2$, NaOH, $H_2O$, MeOH, −4 °C; (*b*) $CH_2O$, $H_2O$; (*c*) HCl, MeOH, 40 °C.

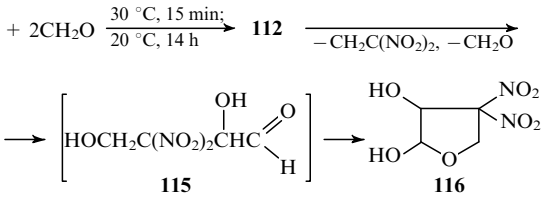
The ether **109** containing an $HC(NO_2)_2$ group reacts readily and rapidly with formaldehyde in the presence of sodium hydroxide and is thus converted into hydroxymethyl derivative **110**.[93]



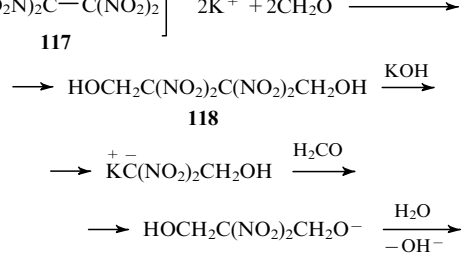
Compound **111** containing two $HC(NO_2)_2$ groups reacts with two molecules of formaldehyde in the presence of sodium hydrogencarbonate to give tetrol **112**; under the action of a base, it eliminates a glyoxal molecule giving rise to salt **113**. The latter reacts with the aldehyde **2** to give 2,2-dinitropropane-1,3-diol **114** in an overall yield of 74%.[94]



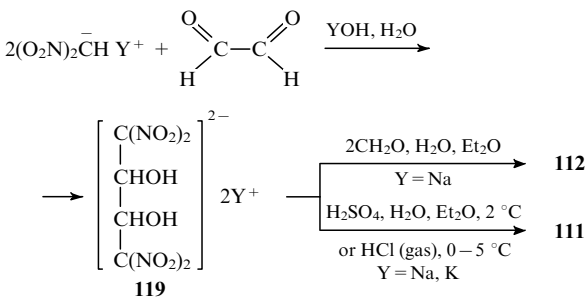
The compound **111** can also react with formaldehyde without a catalyst yielding the tetrol **112**, which eliminates a dinitromethane molecule and $CH_2O$ even at 20–30 °C being thus converted into aldehyde **115**, which cyclises *in situ* into tetrahydrofuran derivative **116**.[94]



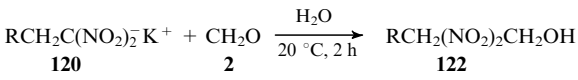
When the dipotassium salt of 1,1,2,2-tetranitroethane **117** is made to react with formaldehyde, this gives tetranitrodiol **118**, which is cleaved on treatment with KOH to give 2,2-dinitroethane salt. This salt reacts with the aldehyde **2** yielding diol **114**.[95]



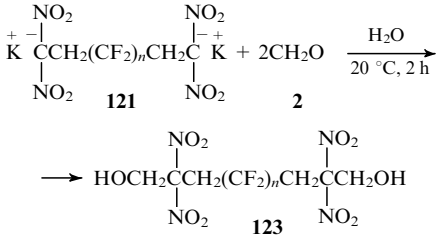
The sodium[95] or potassium[96] salts of dinitromethane react with glyoxal to give salts of 1,1,4,4-tetranitrobutane-2,3-diol **119**. The salt **119** (Y = Na) is converted into the tetrol **112** by the reaction with formaldehyde.[95] Treatment of the salts **119** (Y = Na or K) with 10% sulfuric acid[95] or hydrogen chloride[96] results in the formation of the diol **111** in a yield of 71.8% or 57.2%, respectively.



Potassium salts of fluoro-containing dinitroalkanes **120** or tetranitroalkanes **121** react readily with formaldehyde to give the corresponding nitro alcohols **122** or tetranitro-diols **123**.[97]



R = $C_6F_{13}$ (36%); $C_{10}F_{21}$ (62%);



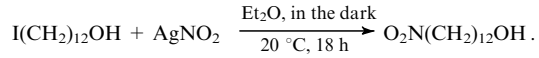
*n* = 4 (55%), 6 (75%).

Synthesis of 2,2,2-trinitroethanol by the condensation of trinitromethane with formaldehyde in the presence [98] or in the absence [99] of $CuSO_4$ has been reported.

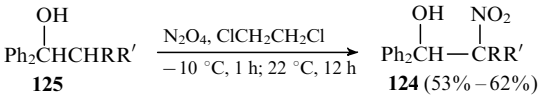
## 2. Synthesis of nitro alcohols by introduction of a nitro group into hydroxyl-containing compounds

This route for the preparation of nitro alcohols has not found wide application, because the two existing methods for the introduction of a nitro group into compounds containing a hydroxy group suffer from serious drawbacks restricting their use. One of these methods, namely, treatment of halo-substituted alcohols with some metal nitrites, normally permits preparation only of nitro alcohols containing a primary nitro group. In addition, there are some limitations as regards the use of the initial halohydrins and solvents. The second method, namely, nitration of alcohols, has also found limited use, because only in some cases does it permit the target compounds to be obtained in reasonable yields. The main reaction pathway in this case is the oxidation of alcohols yielding carboxylic acids and the corresponding nitroalkanes.

During the last 25 years, the former method has hardly been used to synthesise aliphatic nitro alcohols. It was not until 1987 that the synthesis of 12-nitrododecan-1-ol (yield 79.5%) by the Meyer reaction of 12-iodododecan-1-ol was reported.[100]



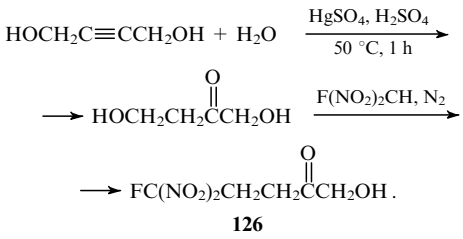
Over the period of time considered, only in rare cases has nitration of alcohols been used to prepare nitro alcohols; for example, nitro alcohols **124** have been obtained in this way by treating alcohols **125** with dinitrogen tetroxide.[101]



R = H: R′ = Me, Et, Bu; R = R′ = Me.

The reaction of $Ph_2C(OH)Et$ with $N_2O_3$ or $N_2O_4$ at 20 – 25 °C in chloroform affords nitro alcohol $Ph_2C(OH)CH(Me)NO_2$ in a yield of 47% or 62%. When the same alcohol is treated with $N_2O_5$ in chloroform or with $HNO_3$ (20 °C, 1 h; 80 °C, 4 h), nitration involves not only the side chain but also the aromatic ring and the hydroxy group and results in the formation of $O_2NC_6H_4C(Ph)(O\text{-}NO_2)CH(Me)NO_2$ (yields 35% and 70%, respectively).[102]

An original method for the synthesis of nitro alcohol **126** reported in a patent [103] consists of the transformation of butyne-1,4-diol into 1,4-dihydroxybutan-2-one by the Kucherov reaction followed by replacement of the β-hydroxyl with respect to the carbonyl group by a fluorodinitromethyl group by treatment with fluorodinitromethane.

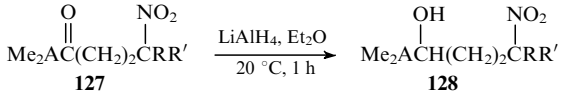


## 3. Synthesis of nitro alcohols by introduction of a hydroxy group into compounds containing a nitro group

Syntheses of nitro alcohols by this route can be clearly divided into two groups: (*a*) formation of a hydroxy group in nitro-compounds from other oxygen-containing groups incorporated in the initial molecule and (*b*) the formation of nitro alcohols from nitro-compounds containing no oxygen-containing groups.

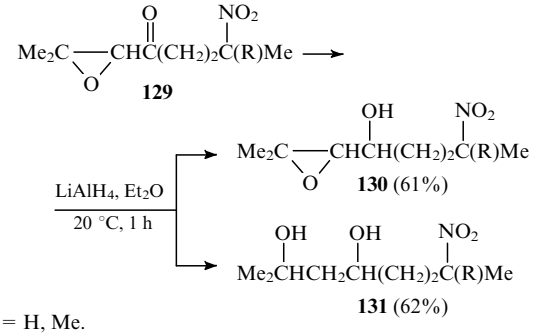
### a. The formation of a hydroxy group from other oxygen-containing groups present in nitro-compounds

The reaction of unsaturated nitro ketones **127** (A = C=CH) or saturated nitro ketones (A = $CHCH_2$) with lithium aluminium hydride at 20 °C and at a $LiAlH_4$ : **127** ratio of 1 : 4 involves only transformation of the carbonyl group into a hydroxy group and affords nitro alcohols **128** (yields 64% – 95%).[104]



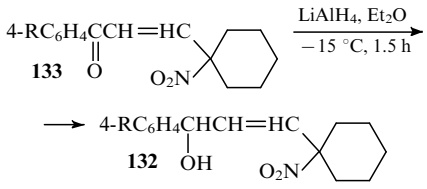
R = H, Me; R′ = H, Me, Et, Pr; A = C CH, $CHCH_2$.

When nitro ketones **129** containing an epoxy group are reduced with lithium aluminium hydride, the structure of the reaction product depends on the $LiAlH_4$ : **129** ratio. When this ratio is 1 : 4, only the carbonyl group is reduced, and nitro alcohols **130** are formed (yields 67% and 74%); at a ratio of 1 : 2, cleavage of the epoxide ring occurs, in addition to the reduction of the carbonyl group, and the process gives nitro-diols **131**.[104]



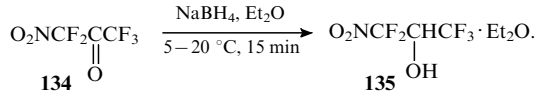
R = H, Me.

Unsaturated nitro alcohols **132** have been synthesised in 62% – 68% yields by the reduction of nitro ketones **133** with lithium aluminium hydride at −15 °C and at an $LiAlH_4$ : **132** ratio of 1 : 4.[105]

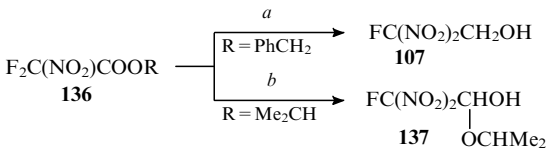


R = H, Me, Cl, Br.

Ketone **134** is converted into nitro alcohol **135** in 71% yield on treatment with sodium tetrahydridoborate.[32]

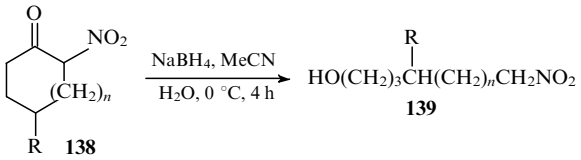


The outcome of the reduction of esters **136** with sodium tetrahydridoborate depends on the nature of the radical R; if R = $PhCH_2$, the reaction gives rise to the nitro alcohol **107** (yield 70%), whereas with R = $Me_2CH$, hemiacetal **137** is formed.[106]



(*a*) $NaBH_4$, THF, $H_2O$, 10–12 °C, 0.5 h;
(*b*) $NaBH_4$, $(MeOCH_2)_2$, 20–25 °C, 0.5 h.

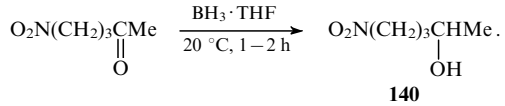
When cyclic α-nitro ketones **138** are treated with sodium tetrahydridoborate, the reduction is accompanied by ring opening and yields nitro alcohols **139**.[107]



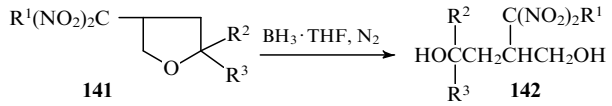
R = H, *n* = 0–10 (50%–85%); R = $Bu^t$, *n* = 1 (75%).

3-Nitropropanal was converted into 3-nitropropan-1-ol in 89% yield by treatment with the complex $BH_3 \cdot SMe_2$ in $Et_2O$ at 20 °C for 4 h under a nitrogen atmosphere.[108]

Nitro alcohol **140** was synthesised in 77.5% yield by the reduction of 5-nitropentan-2-one with diborane in THF.[31]

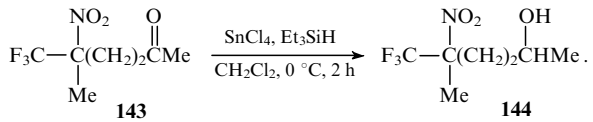


The reaction of tetrahydrofuran derivatives **141** with borane in THF results in ring opening and formation of diols **142**.[109, 110]



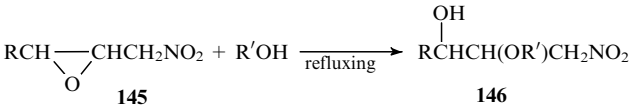
$R^1 = NO_2$, $R^2 = H$, $R^3 = OH$ (35 °C, 72 h, 98%);[109]
$R^1 = F$, $R^2 = H$, $R^3 = OH$ (25 °C, 24 h, 100%);[109]
$R^1 = NO_2$, $R^2$, $R^3 = O$ (35 °C, 72 h, 98%).[110]

Nitro ketone **143** was converted into nitro alcohol **144** in 72% yield on treatment with $SnCl_4$ and $Et_3SiH$ at 0 °C.[66]



The reduction of the compounds $RCOCH(R')(CH_2)_2NO_2$ (R, R′ = Me, H;[111] Ph, H; MeO, 2-$MeOC_6H_4$ [112]) in the presence of baker's yeast occurs stereoselectively to give (*S*)-nitro alcohols as the major products; the highest stereoselectivity (99%) is observed in the case of R = MeO, R′ = 2-$MeOC_6H_4$.[111, 112]

When epoxide **145** (R = Me) is heated in water at 50 °C, the corresponding diol $MeCH(OH)CH(OH)CH_2NO_2$ is formed in 56% yield.[113] Heating of **145** in aliphatic alcohols leads to ethers **146** (yields 55%–68%).[113]



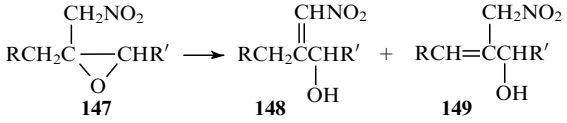
R = H; R′ = Me, Et, $Pr^i$; R = Me, R′ = Me, $Pr^i$.

In the presence of triethylamine at 18–20 °C, the epoxide **145** (R = Me) isomerises into the unsaturated nitro alcohol $MeCH(OH)CH=CHNO_2$ (yield 62%).[113]

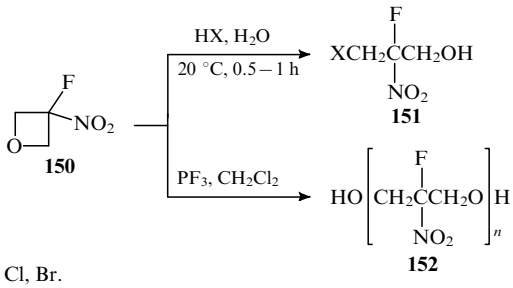
2,3-Epoxy-1-nitropropane reacts with hydrazines $RC_6H_4NHNH_2$ (R = 2-$NO_2$, 4-$NO_2$) at 20 °C in aqueous ethanol affording 2- or 4-$O_2NC_6H_4NHNHCH(CH_2OH)-CH_2NO_2$ in 86% yield.[114]

Epoxides **147** with a more complicated structure have been converted into mixtures of unsaturated nitro alcohols **148** and **149** in four ways: by treatment with triethylamine in aqueous acetonitrile (procedure A); in the presence of alumina in diethyl ether and in dichloromethane (procedure B); at 25 °C over silica gel (procedure C); over aluminium isopropoxide (procedure D) (Scheme 2).[115] The reaction conditions and the yields of the alcohols **148** and **149** are listed in Table 8.

Scheme 2



On treatment with hydrohalic acids, 3-fluoro-3-nitrooxetane **150** is converted into nitro alcohols **151** in high yields (96.5% and 93.1%), whereas on treatment with phosphorus trifluoride, it is converted into polymer **152** (yield 82.6%).[49]

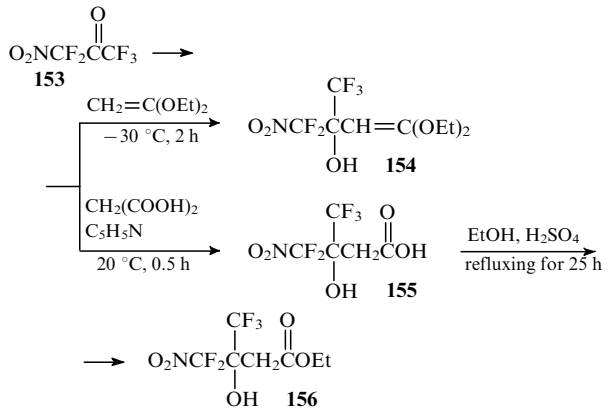


X = Cl, Br.

**Table 8**. Reaction conditions and yields of the nitro alcohols **148** and **149**.

| R | R′ | Time/ h | | | | Yield of (**148** + **149**) (%) | | | | Yield of **148** (%) | | | | *E*/*Z* Ratio in **148** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | A | B | C | D | A | B | C | D | A | B | C | D |
| H | Me | 2 | 2 | 2 | – | 97 | 92 | 92 | – | 16 | 15 | 0 | – | – | – | 78/22 | – |
| H | Et | 2 | 4 | 4 | – | 82 | 96 | 96 | – | 15 | 11 | 0 | – | – | – | 78/22 | – |
| H | $C_5H_{11}$ | 2 | 4 | 5 | – | 89 | 82 | 84 | – | 33 | 18 | 0 | – | – | – | 80/20 | – |
| H | $Pr^i$ | 2 | 3 | 3 | – | 90 | 87 | 83 | – | 17 | 15 | 0 | – | – | – | 84/26 | – |
| Me | Me | – | 3 | 2 | – | – | 85 | 85 | – | – | 9 | 0 | – | – | – | 65/35 | – |
| Et | Et | – | 4 | 48 | 1 | – | 86 | 0 | 80 | – | – | – | traces | – | – | – | 70/30 |
| Bu | Bu | – | 5 | 48 | 1 | – | 80 | 0 | 83 | – | 2 | – | traces | – | 83/17 | – | 71/29 |

Ketone **153** has been treated with ketene diethyl acetal at −30 °C; this gave compound **154** (yield 88%). Acid **155** was synthesised by reaction of the ketone **153** with malonic acid in the presence of pyridine. This acid was converted *in situ* into ester **156** (yield 48%) by reaction with ethanol in the presence of sulfuric acid.[116]



When the trinitromethane derivative $Hg[C(NO_2)_3]_2$ is refluxed with an aqueous solution of formaldehyde, the $HgC(NO_2)_3$ group is substituted resulting in the formation of 2,2,2-trinitroethanol in 95% yield.[117]

On heating with formalin at 60–70 °C for 20 h, compounds of the formula $(O_2N)_3CCH(R)CH_2HgC(NO_2)_3$ (R = H, Me) eliminate an alkene and are thus converted into 2,2-dinitropropane-1,3-diol **114** in 91% yield.[117]

**b. Formation of a hydroxy group in nitro compounds containing no oxygen-containing groups**

The rates of hydration of $CH_2{=}CHNO_2$, $MeC(NO_2){=}CH_2$, $MeCH{=}CHNO_2$ and $MeC(NO_2){=}CHMe$ have been studied by spectrophotometry at 40 °C and pH 6 in an AcOH–$Me_2CO$ buffer solution. The effective pseudo-first-order rate constants for these reactions were found to be $(78.8\pm2.2)\times10^{-3}$, $(6.5\pm0.1)\times10^{-3}$, $(57.8\pm1.0)\times10^{-3}$ and $(5.7\pm0.15)\times10^{-3}$ $min^{-1}$, respectively. The rate of formation of the corresponding nitro alcohol depends on the charge on the β-carbon atom in the π-system and also on the steric effect of the β-substituent.[118]

Having studied the kinetics of hydration of nitroethylene in buffer solutions by spectrophotometry, Fakhrutdinov *et al.*[119] proposed the following scheme for this process:

$$CH_2{=}CHNO_2 + H_2O \rightleftharpoons CH_2(\overset{+}{O}H_2)\overset{-}{C}HNO_2,$$
$$CH_2(\overset{+}{O}H_2)\overset{-}{C}HNO_2 + B \rightleftharpoons CH_2(OH)\overset{-}{C}HNO_2 + BH^+,$$
$$CH_2(OH)\overset{-}{C}HNO_2 + BH^+ \rightleftharpoons HOCH_2CH_2NO_2 + B.$$

It was found that the rate of hydration increases with an increase in the pH, and at a constant pH it increases with an increase in the concentration of the base in the solution. At low pH, the reaction rate is limited by deprotonation of $CH_2(^+OH_2)^-CHNO_2$, whereas at high pH, it is limited by the interaction of the nitroalkene with water. It was found that at pH = 0.96, 2.01, 2.98, 6.00 and 7.15, the activation energies of hydration are 10.9, 14.1, 15.2, 13.5 and 11.1 kcal $mol^{-1}$, respectively, and the corresponding activation entropies are −43.0, −30.1, −29.2, −26.4 and −35.4 e.u., respectively.[119]

The kinetics and mechanism of hydration of 1-nitroprop-1-ene have been studied.[120] The researchers proposed the following scheme for this process:

$$MeCH{=}CHNO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{+}{O}H_2\,|\,MeCH\overset{-}{C}HNO_2,$$

$$\overset{+}{O}H_2\,|\,MeCH\overset{-}{C}HNO_2 + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} OH\,|\,MeCH\overset{-}{C}HNO_2 + BH^+,$$

$$OH\,|\,MeCH\overset{-}{C}HNO_2 + BH^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} OH\,|\,MeCHCH_2NO_2 + B.$$

At low pH and a low buffer capacity, the reaction rate is limited by proton abstraction, and when these parameters are increased, the interaction of the nitroalkene with water becomes the rate-determining step of the process.[120]

γ-Nitro alcohols **157** have been synthesised by radical addition of aliphatic alcohols to nitroalkenes **158** in the presence of *tert*-butyl peroxide at 150 °C.[121]

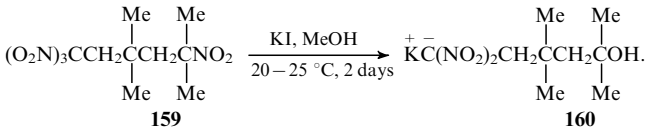
$$\underset{\mathbf{158}}{RCH_2OH} + O_2NCH{=}CHR' \xrightarrow[150\ ^\circ C,\ 12-15\ h]{(Bu^tO)_2} \underset{\mathbf{157}}{RCHCH(R')CH_2NO_2}\ (OH)$$

R′ = Me: R = $C_5H_{11}$ (28%), Pr (11%), Bu (20%);
R′ = Et: R = Pr (6%).

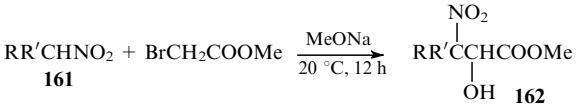
Treatment of 3-fluoro-3,3-dinitropropylammonium sulfate with sodium nitrite in an acid medium yields 3-fluoro-3,3-dinitropropan-1-ol in 56% yield.[122]

$$FC(NO_2)_2CH_2CH_2NH_2\cdot H_2SO_4 \xrightarrow[60\ ^\circ C,\ 1.5\ h]{NaNO_2,\ H_2O\ (pH\ 1.2-1.5)} FC(NO_2)_2CH_2CH_2OH.$$

When tetranitroalkane **159** reacts with potassium iodide in methanol, in parallel with the replacement of one of the nitro groups by potassium, replacement of one more nitro group by a hydroxy group occurs, and the reaction affords the nitro alcohol salt **160**.[123]

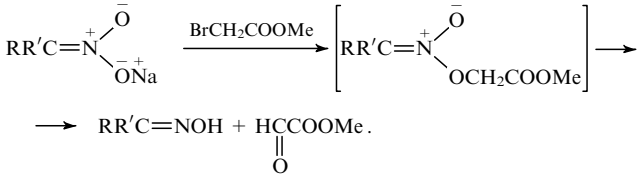


Unexpectedly, the reaction of an excess of nitroalkanes **161** with methyl bromoacetate in the presence of sodium methoxide in dimethylacetamide resulted in the formation of compounds **162**.[124]



R = Me: R′ = Me (48%), Et (52%); R = H: R′ = Et (11%), Ph (68%).

Evidently, the compounds **162** result from the condensation of nitroalkanes $RR'CHNO_2$ with methyl glyoxylate generated according to the following scheme:[124]



## 4. Synthesis of nitro alcohols by simultaneous introduction of nitro and hydroxy groups

Reactions of alkenes with nitrogen oxides are used most often for the synthesis of nitro alcohols with simultaneous introduction of $NO_2$ and OH groups to vicinal positions.

The nitro alcohol $C_{12}H_{25}CH(OH)CH_2NO_2$ (yield 10%) and its nitrate $C_{12}H_{25}CH(ONO_2)CH_2NO_2$ (yield 86%) have been prepared by the reaction of $C_{12}H_{25}CH=CH_2$ with $N_2O_4$ in $CCl_4$ in the presence of sulfuric acid at 0–5 °C for 0.5 h.[125]

The nitro alcohol $Ph_2C(OH)CH(Me)NO_2$ has been synthesised by the reactions of the alkene $Ph_2C=CHMe$ with $N_2O_4$ ($CHCl_3$, 20–25 °C, 6 h), $N_2O_3$ ($CHCl_3$, 20 °C, 17 h) or $HNO_3$ (*d* 1.51, $CHCl_3$, 100 °C, 4 h), the yields of the product being 56%, 46% or 50.8%, respectively.[103] When the same alkene was treated with $N_2O_5$ ($CHCl_3$, 18 °C, 12 h), the product $O_2NC_6H_4$–$(Ph)C(ONO_2)CH(Me)NO_2$ containing a nitro group instead of a hydrogen atom in one of the benzene rings was obtained in 32.2% yield.[102]

The reactions of various alkenes with $NO_2$ in hexane at 20 °C have been studied in detail. Nitro alcohols and their derivatives **163**–**170** were synthesised in this way.[126]

$$Me_2C{=}CMe_2 \xrightarrow[20\ ^\circ C,\ 5\ min]{NO_2^\cdot} Me_2\overset{NO_2}{\overset{|}{C}}C(ONO)Me_2 + \underset{\mathbf{163}\ (17\%)}{}$$

$$+ Me_2\overset{NO_2}{\overset{|}{C}}C(ONO_2)Me_2 + O_2NCH_2\overset{OH}{\overset{|}{C}}(Me)C(NO_2)Me_2,$$

**164** (3%) **165** (3%)

$$Me_2C{=}CHEt \xrightarrow[20\ ^\circ C,\ 5\ min]{NO_2^\cdot}$$

$$\longrightarrow O_2NCH_2\overset{OH}{\overset{|}{C}}(Me)\overset{NO_2}{\overset{|}{C}}HEt + Me_2\overset{NO_2}{\overset{|}{C}}CH(OH)Et,$$

**166** (8%) **167** (36%)

$$CH_2{=}CEt_2 \xrightarrow[20\ ^\circ C,\ 5\ min]{NO_2^\cdot}$$

$$\longrightarrow O_2NCH_2\overset{OH}{\overset{|}{C}}(Et)\overset{NO_2}{\overset{|}{C}}HMe + O_2NCH_2\overset{OH}{\overset{|}{C}}Et_2,$$

**168** (4%) **169** (47%)

$$CH_2{=}CHBu \xrightarrow[20\ ^\circ C,\ 5\ min]{NO_2^\cdot} O_2NCH_2\overset{OH}{\overset{|}{C}}HBu.$$

**170** (48%)

The formation of the compounds **165**, **166** and **168** was explained [126] in terms of the following scheme:

$$-\overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}}-CH_2R \xrightarrow{NO_2^\cdot} -\overset{NO_2}{\overset{|}{C}}-\overset{\cdot}{\underset{|}{C}}-CH_2-R \xrightarrow{NO_2^\cdot}$$

$$\longrightarrow -\overset{NO_2}{\overset{|}{C}}-\underset{|}{C}{=}CH-R \xrightarrow{NO_2^\cdot} -\overset{NO_2}{\overset{|}{C}}-\overset{NO_2}{\overset{|}{C}}-CH-R \xrightarrow{NO_2^\cdot}$$

$$\longrightarrow -\overset{NO_2}{\overset{|}{C}}-\overset{ONO}{\overset{|}{C}}-\overset{NO_2}{\overset{|}{C}}H-R \longrightarrow -\overset{NO_2}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-\overset{NO_2}{\overset{|}{C}}H-R.$$

Diethyl vinylphosphonate **171** readily reacts with $N_2O_4$ in dichloromethane to give nitro alcohol **172** (yield 34%).[127]

$$(EtO)_2\overset{O}{\overset{\|}{P}}CH{=}CH_2 \xrightarrow[0-20\ ^\circ C,\ 3\ h]{N_2O_4,\ CH_2Cl_2} (EtO)_2\overset{O}{\overset{\|}{P}}CHCH_2NO_2.$$

**171** **172**

2-Hydroxy-3-nitropropionic acid was synthesised in 60% yield by the reaction of acrylic acid with $N_2O_4$ in dichloroethane at 18–20 °C over a period of 10 h.[128]

Nitro alcohol **173** is formed in 23%–25% yield in the reaction of nitrogen oxide with 4-phenylbut-1-ene in various solvents (dichloroethane, tetrachloromethane or benzene) at 20 °C.[129]

$$Ph(CH_2)_2CH{=}CH_2 \xrightarrow[20\ ^\circ C]{NO} Ph(CH_2)_2\overset{OH}{\overset{|}{C}}HCH_2NO_2.$$

**173**

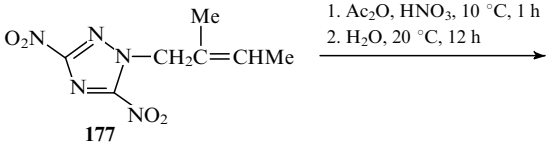
Simultaneous introduction of $NO_2$ and OH groups into alkenes **174** was accomplished by treating them with alkyl nitrites with heating in acetic acid under an inert atmosphere; the yields of nitro alcohols **175** were 20%–33%.[130]

$$R^1R^2C{=}CHR^3 \xrightarrow[115\ ^\circ C,\ 30-50\ min]{AlkONO,\ AcOH,\ N_2} R^1R^2\overset{OH}{\overset{|}{C}}-\overset{NO_2}{\overset{|}{C}}HR^3$$

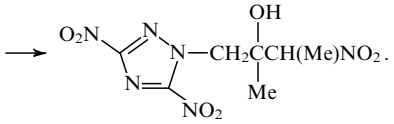
**174** **175**

$R^1$, $R^2$, $R^3$: Ph, Ph, H; Me, Ph, H; Me, COOMe, H; Et, Et, Me.

The synthesis of compound **176** (yield 55%) from alkene **177** was carried out using acetyl nitrate formed *in situ* from $Ac_2O$ and $HNO_3$.[131]




**177**



**176**

The reaction of isoprene with acetyl nitrate at 20 °C affords a mixture of nitroalkenyl acetates **178** and **179** in a ratio of 7 : 3.[132]

$$CH_2{=}\overset{Me}{\overset{|}{C}}-CH{=}CH_2 \xrightarrow[20\ ^\circ C,\ 1\ h]{AcONO_2}$$

$$\longrightarrow O_2NCH_2\overset{Me}{\overset{|}{C}}{=}CHCH_2OAc + O_2NCH_2\overset{Me}{\overset{|}{C}}CH{=}CH_2.$$

**178** **179** OAc

Treatment of unsaturated ketones **180** with nitronium tetrafluoroborate at −30 °C in a solution in $SO_2$ followed by treatment with water gives compounds **181** in low yields.[133]

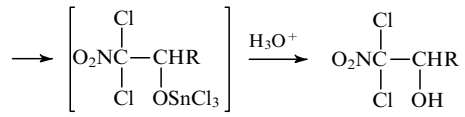
$$RC(CH_2)_2\overset{O}{\overset{\|}{C}}\overset{Me}{\overset{|}{C}}{=}CH_2 \xrightarrow[2.\ H_2O]{1.\ \overset{+}{N}O_2BF_4^-,\ SO_2,\ CH_2Cl_2\ -30\ ^\circ C,\ N_2} RC(CH_2)_2\overset{OH}{\overset{|}{C}}\overset{Me}{\overset{|}{C}}H_2NO_2$$

**180** **181**

R = Me (4%), Pr (17%), $Pr^i$ (34%).

An original method has been proposed [134] for the synthesis of dichloro-substituted nitro alcohols **182**. It is based on the reaction of trichloronitromethane with aldehydes in the presence of $SnCl_2$.

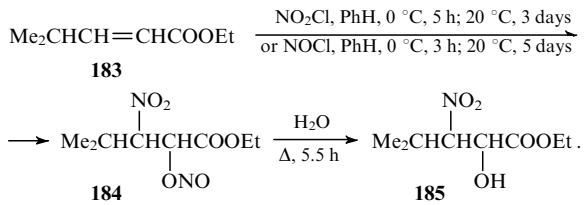
$$Cl_3CNO_2 \xrightarrow[0\ ^\circ C]{SnCl_2,\ Et_2O} \left[\begin{array}{c} Cl \\ | \\ ClCNO_2 \\ | \\ SnCl_3 \end{array}\right] \xrightarrow[4\ h]{RCHO}$$



**182**

R = H (67%), Me (76%), Et (82%), Pr (83%), Bu (92%), $C_5H_{11}$ (85%), Ph (52%), $CCl_3$ (77%), 4-$MeC_6H_4$ (57%), 4-$ClC_6H_4$ (59%), 2-furyl (53%), 2-thienyl (61%).

The reaction of ethyl 4-methylpent-2-enoate **183** with nitryl chloride or nitrosyl chloride yields nitrite **184**, which is converted into compound **185** on refluxing with water, the overall yield of the latter being 34%.[74]



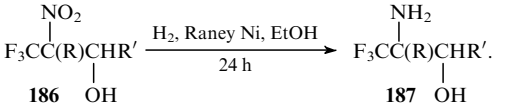
**183** **184** **185**

## III. Chemical transformations of nitro alcohols

### 1. Reactions involving the nitro group

The reduction of 2-nitrobutan-1-ol in the presence of Raney nickel at 35–40 °C under a hydrogen pressure of 10 atm results in the formation of 2-aminobutan-1-ol in 62%–74% yield.[44, 135]

The same catalyst is effective in the reduction of nitro alcohols **186** to amino alcohols **187** (Table 9).[66]



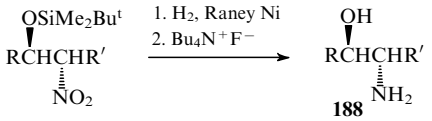
**186** **187**

**Table 9**. Reaction conditions and yields of the amino alcohols **187**.

| R | R′ | Pressure /atm | Temperature /°C | Yield (%) |
|---|---|---|---|---|
| H | Pr | 1 | 20 | 52 |
| H | $C_6H_{13}$ | 25 | 50 | 76 |
| H | $Ph(CH_2)_2$ | 1 | 20 | 79 |
| H | PhCHMe | 25 | 50 | 82 |
| H | Pr | 30 | 50 | 59 |
| Me | Pr | 30 | 50 | 5 |
| Me | $C_6H_{13}$ | 25 | 50 | 22 |
| Me | $Ph(CH_2)_2$ | 25 | 50 | 53 |

Raney nickel has also been used to reduce the compounds $PhCH(OH)(CH_2)_2NO_2$ and $Ph_2CHCH(OH)CH_2NO_2$ to amino alcohols $PhCH(OH)(CH_2)_2NH_2$ (yield 49%) and $Ph_2CH$–$CH(OH)CH_2NH_2$ (yield 18%).[79]

The reduction of the *erythro*-isomers of silyl ethers of nitro alcohols in the presence of Raney nickel occurs stereoselectively; treatment of the reaction mixture with $Bu_4N^+F^-$ gives the *erythro*-isomers of amino alcohols **188**.[82]



**188**

R, R′: Pr, Et; Pr$^i$, Et; $C_5H_{11}$, Me; $C_5H_{11}$, Et; Pr, $C_7H_{15}$; $C_{10}H_{21}$, Me; $C_9H_{19}$, Me; Ph, Et.

2-Hydroxymethyl-2-nitropropane-1,3-diol **4** is converted into the amine $H_2NC(CH_2OH)_3$ (yield 89%) by hydrogenation in the presence of the Pd/C catalyst at 59–63 °C for 4.5 h.[136]

When 4-$MeOC_6H_4CH_2C(OH)(Et)NO_2$ is reduced with ammonium formate in the presence of Pd/C in THF and MeOH, the amino alcohol 4-$MeOC_6H_4CH_2C(OH)(Et)NH_2$ is formed in 73% yield.[137]

The amino-diols $HOCH_2C(R)(NH_2)CH(OH)C_{13}H_{27}$ (R = H, Me) have been synthesised in high yields (83% and 86%) by the reduction of the corresponding nitro-diols with ammonium formate in the presence of Pd/C in MeOH at 20 °C for 16 h under an atmosphere of nitrogen.[61]

An active catalyst of reduction, $Ni_2B$, which is formed *in situ* from $NiCl_2 \cdot 6H_2O$ and $NaBH_4$, has been used to convert the nitro alcohol $O_2NCMe_2(CH_2)_2CH(OH)Me$ into the corresponding amino alcohol (yield 76%). The reaction occurs in MeOH at 20 °C over a period of 5 min.[138]

Reduction of nitro alcohols to amino alcohols with hydrogen has also been carried out in the presence of a number of rhodium-containing catalysts. For example, 2-nitrobutan-1-ol has been converted into 2-aminobutan-1-ol by hydrogenation in the presence of di(rhodiumnorbornadienechloride) and $Ph_2PCH_2CH(PPh_2)Me$ at 60 °C under a hydrogen pressure of 67 atm for 20 h.[139]

The reduction of 2-nitrobutan-1-ol to 2-aminobutan-1-ol catalysed by rhodium-, iridium- and palladium-containing systems has been studied in detail (Table 10).[140]

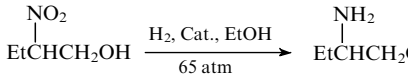
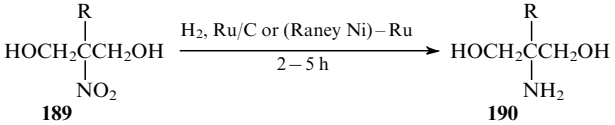


**Table 10**. Hydrogenation of 2-nitrobutan-1-ol.[140]

| Catalyst | Phosphine | Catalyst: phosphine | Time/h | Temperature/ ° | Yield (%) |
|---|---|---|---|---|---|
| $Rh_2Cl_2(NBD)_2$ [a] | see [b] | 1 : 1 | 20 | 60 | 78 |
| $Rh_2Cl_2(NBD)_2$ | $PPh_3$ | 1 : 1 | 16 | 50 | 36 |
| $Rh_2Cl_2(NBD)_2$ | DIOP [c] | 1 : 1 | 65 | 80 | 57 |
| $Ir_2Cl_2(COD)_2$ [d] | PPFA [e] | 1 : 2 | 16 | 50 | 67 |
| $Ir_2Cl_2(COD)_2$ | BPPFA [f] | 1 : 2 | 16 | 50 | 56 |
| $Ir_2Cl_2(COD)_2$ | DIOP | 1 : 2 | 16 | 50 | 54 |
| $Ir_2Cl_2(COD)_2$ | DIPHOS [g] | 1 : 2 | 16 | 50 | 47 |
| $PdCl_2(COD)_2$ | DIPHOS | 1 : 2 | 18 | 75 | 24 |
| $PdCl_2(PhCN)_2$ | BPPFOH [h] | 1 : 1 | 18 | 75 | 41 |

[a] NBD — norbornadiene; [b] $Ph_2PCH_2CH(Me)PPh_2$; [c] DIOP — (*S*,*S*)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane; [d] COD — cyclooctadiene; [e] PPFA — (*R*)-α-[(*S*)-2-(diphenylphosphino)-ferrocenyl]ethyldimethylamine; [f] BPPFA — (*R*)-α-[(*S*)-2,1′-bis(diphenylphosphino)ferrocenyl]ethyldimethylamine; [g] DIPHOS — bis(1,2-diphenylphosphino)ethane; [g] BPPFOH — (*R*)-α-[(*S*)-2,1′-bis(diphenylphosphino)ferrocenyl]ethane.

Nitro glycols **189** have been hydrogenated at 80–100 atm in the presence of Ru/C catalyst or Raney Ni–Ru for 2–5 h; this gave amino glycols **190** in 78%–96% yields.[141]

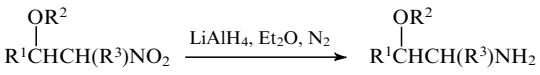


**189** **190**

R = H, Me, Et, $CH_2OH$.

Hydrogenation of the nitro alcohols 4-$RC_6H_4CH(OH).CH_2NO_2$ (R = H, Me, Cl) in the presence of $PdO_2$ in 80% AcOH at 1 atm gives rise to the corresponding amino alcohols $RC_6H_4CH(OH)CH_2NH_2$ in 59%, 50% and 63% yields, respectively.[26]

The nitro groups in nitro alcohols and their derivatives **191** and **192** have been reduced to amino groups using $LiAlH_4$.[23, 25, 81, 83, 142]

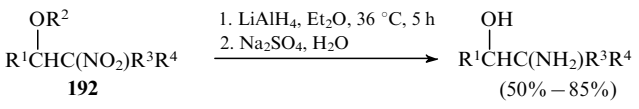


**191**

$R^1$ = Ph, $R^2$ = H, $R^3$ = H (55%);[23] $R^1$ = Ph, $R^2$ = H, $R^3$ = Me;[23]

$R^1$ = PhCH$_2$–(4-MeO-C$_6$H$_4$), $R^2$ = H, $R^3$ = H (28%);[25]

$R^1$ = 2-furyl, $R^2$ = 2-tetrahydropyranyl, $R^3$ = H (80%);[142]

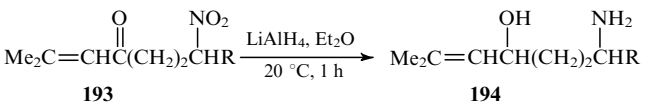


**192**

$R^1$ = $C_6H_{13}$, Bu$^t$, Ph, 4-MeO$C_6H_4$, 4-$O_2NC_6H_4$;

$R^2$ = $SiMe_3$ or $SiMe_2Bu^t$; $R^3$ = H, Me; $R^4$ = $C_5H_{11}$, Me.[81,83]

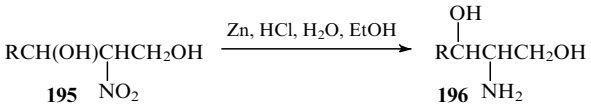
When unsaturated nitro ketones **193** are reduced with a twofold excess of lithium aluminium hydride, the nitro groups are converted into amino groups, whereas the carbonyl groups are reduced to hydroxy groups; thus, the reaction yields amino alcohols **194**.[104]



**193** **194**

R = H (35%), Me (37%), Et (38%).

Nitro-diols **195** have been converted into amino-diols **196** by treatment with zinc and hydrochloric acid in ethanol.[143]

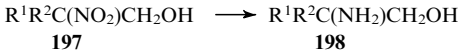


**195** **196**

R = $C_7H_{15}$ (25%), $C_9H_{19}$ (33%), $C_{11}H_{23}$ (38%), $C_{13}H_{27}$ (40%).

Electroreduction of 2-methyl-2-nitropropane-1,3-diol giving 2-amino-2-methypropane-1,3-diol in 99% yield has been patented.[144]

Nitro alcohols or nitro-diols **197** have been converted into the corresponding amino-derivatives **198** by electroreduction at bimetallic electrodes consisting of copper deposited on zinc or cadmium.[145]



**197** **198**

$R^1$, $R^2$: H, Me; Me, $CH_2OH$; H, Et; Et, $CH_2OH$.

Electroreduction of the triol **4** in the presence of sulfuric acid at 75–80 °C and at a current density of 0.1 A cm$^{-2}$ for 12–13 h affords amino-derivative $H_2NC(CH_2OH)_3$ in 40%–50% yield.[6]

The hydrochloride $(HOCH_2)_3CNH_2 \cdot HCl$ has been synthesised by electroreduction of the triol **4** at a perforated palladium cathode at 75–80 °C in the presence of 6.5% HCl.[146]

Electroreduction of methyl 3-hydroxy-2-nitrobutyrate giving rise to the DL-threonine ester **199** (substance yield 72%–77%; current yield 7%–10%) can be described by the following scheme:[147,148]



**199**

Treatment of nitro alcohol acetates **200** with tributylstannane in the presence of azobis(isobutyronitrile) in boiling benzene results in the replacement of the nitro group by a hydrogen atom.[48]



**200**

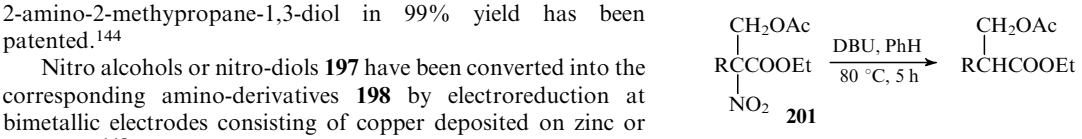
| R | R′ | Yield (%) |
|---|---|---|
| PrCO | Et | 74 |
| Pr$^i$CO | Et | 75 |
| $C_5H_{11}$CO | Me | 83 |
| $C_6H_{13}$CO | Me | 84 |
| EtCO | $C_5H_{11}$ | 83 |
| $C_6H_{13}$CO | $(CH_2)_2$COMe | 85 |
| $C_6H_{13}$CO | $(CH_2)_2$COOMe | 80 |
| COOMe | $(CH_2)_2$CH(OAc)Me | 88 |
| COOMe | $(CH_2)_2$COOEt | 83 |

The reduction of the nitro group in an acetate of a more complicated structure occurs under the same conditions.[48]



(83%)

The researchers cited [48] proposed yet another method for the introduction of a hydrogen atom instead of the nitro group in nitro alcohol acetates **201**. The method involves treatment of **201** with 1,8-diazabicyclo[5.4.0]undec-7-ene in boiling benzene.



**201**

R = Me (66%), Et (71%), Pr (88%), Pr$^i$ (83%), Bu (78%).

## 2. Reactions involving hydrogen atoms attached to a carbon atom carrying nitro groups

Nitro alcohols containing one or two hydrogen atoms at the carbon atom carrying the nitro group are able to enter into nitroaldol condensation. The reaction of the salt $[^-O_2N{=}CHCH(OH)CH(OH)CH{=}NO_2^-]\,2Na^+$ with formaldehyde at 0–5 °C and pH = 10 in $Et_2O$ gives the tetrol $HOCH_2C(NO_2)_2CH(OH)CH(OH)C(NO_2)_2CH_2OH$.[95]

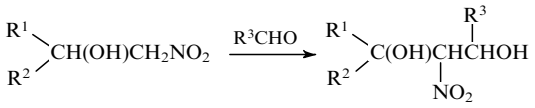
The reactions of salts derived from 2-nitropropane-1,3-diol **3** or from 2-nitropropan-1-ol with an aqueous solution of formaldehyde have been studied.[149] Reversible reactions give 2-hydroxymethyl-2-nitropropane-1,3-diol **4** or 2-methyl-2-nitropropane-1,3-diol, respectively.



**4**

The equilibrium constants $K_1$ and $K_2$ are $(4.3\pm0.4)\times10^{-3}$ and $(3.6\pm0.2)\times10^{-2}$, respectively. The characteristics of these reactions are retained over a broad range of concentrations: $[CH_2(OH)_2]$ = 0.058 – 3.06 M and $[OH^-]$ = $1.8\times10^{-2}$ – 0.36 M.

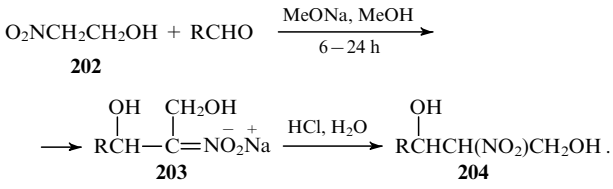
In the presence of Dowex-1 anion-exchange resin, the condensation of nitro alcohols with formaldehyde or acetaldehyde at 20 °C is completed over a period of 1 – 2 h.[150]



$R^1 = R^2 = Me$, $R^3 = H$ (63%); $R^1 = Bu$, $R^2 = H$, $R^3 = Me$ (79%);

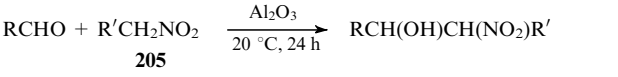
$R^1 = Me$, $R^2 = H$, $R^3 = H$ (91%).

2-Nitroethanol **202** reacts with aliphatic aldehydes in the presence of sodium methoxide to give salts **203** (yields 67% – 99%), which are converted into nitro-diols **204** (yields 91% – 98%) on treatment with hydrochloric acid.[143]



R = $C_7H_{15}$, $C_9H_{19}$, $C_{11}H_{23}$, $C_{13}H_{27}$.

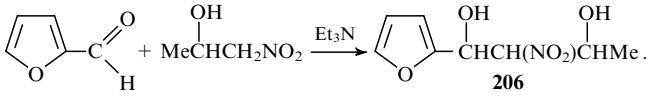
Alumina (Brockmann activity I) has been used as the catalyst in the condensation of nitro alcohols **205** with aldehydes.[69]



R, R′: Me, MeCH(OH)$CH_2$; Et, $(CH_2)_6OH$; Et, $CH_2OH$.

The reaction of the nitro alcohol **202** with benzaldehyde in the presence of triethylamine at 0 °C is completed over a period of 23 h resulting in the formation of DL-*threo*-2-nitro-3-phenylpropane-1,3-diol (yield 98.7%).[151]

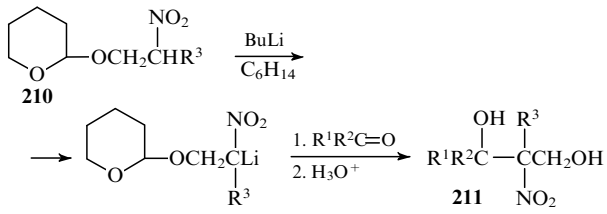
The reaction of furfural with 1-nitropropan-2-ol in the presence of triethylamine gave the corresponding nitro-diol **206** in a yield of only 35%.[152]



The condensation of the nitro alcohol **202** with hexadec-2-enal in the presence of $K_2CO_3$ or $Et_3N$ at 20 °C affords nitro-diol **207** and a minor quantity of the product of its cyclisation **208**.[153]

When this reaction is carried out in methanol in the presence of $K_2CO_3$ at 20 °C, the tetrahydropyran derivative **208** (yield 50%) is formed together with compound **209** (yield 12%) (see Scheme 3).[153]

On treatment with butyllithium, compounds **210** were converted into the corresponding lithio-derivatives. Condensation of the latter with carbonyl compounds $R^1R^2C=O$ followed by hydrolysis of the condensation products gave nitro-diols **211** in 52% – 88% yields.[154]



$R^1$, $R^2$, $R^3$: H, $Pr^i$, H; H, Br, H; H, , H;

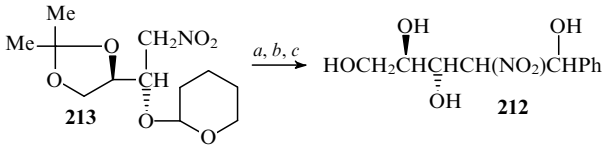
*trans*-PhCH CH, H, H; H, $C_{13}H_{27}C$ C, H; H, Ph, H;

H, 4-$MeOC_6H_4$, H; Me, Ph, H; H, (*S*)-$MeCH_2CH(Me)$, H;

H, $Pr^i$, Me; H, 4-$CNC_6H_4$, H; H, , Me; H, Ph, Me;

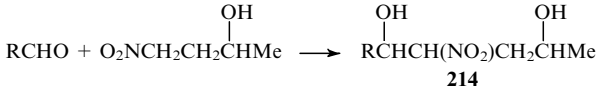
$R^1$,$R^2$ = $(CH_2)_5$, $R^3$ = H, Me.

A single diastereoisomer of nitro-tetrol **212** was obtained in a similar way from compound **213** and benzaldehyde (yield 73%).[154]



(*a*) BuLi, THF, HMPTA −90 to −40 °C, 3 h;
(*b*) PhCHO, −90 to −60 °C, 1.5 h; (*c*) AcONa, $H_2O$.

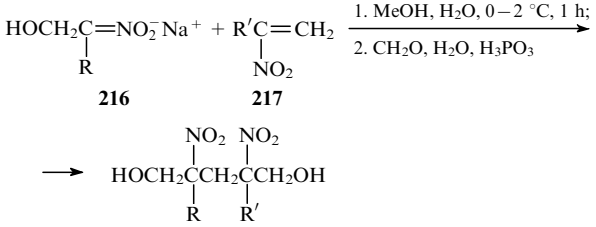
Aldehydes have been made to condense with 4-nitrobutan-2-ol in the presence of the Amberlyst A-21 ion-exchange resin at 0 °C for 15 h. This resulted in the formation of nitro-diols **214** (yields 45% – 70%).[155]



R = Me, $Pr^i$, $C_5H_{11}$, $C_{10}H_{21}$, , $Ph(CH_2)_2$,

(*Z*)-$Me(CH_2)_7CH=CH(CH_2)_7$, $Me(CH_2)_4CH(NO_2)(CH_2)_2$.

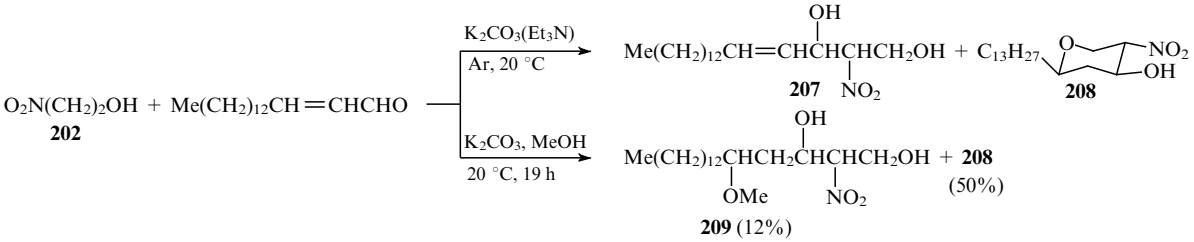
Dinitro-diols **215** have been prepared in two stages, namely, by the reaction of salts **216** with nitroalkenes **217** and subsequent treatment of the resulting reaction mixtures with formaldehyde in the presence of phosphorous acid at pH 6 – 5.5.[156]



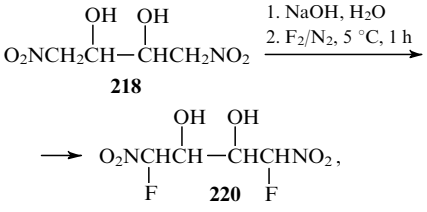
R = Me: R′ = Me (45%), Et (42%); R = R′ = Et (31%).

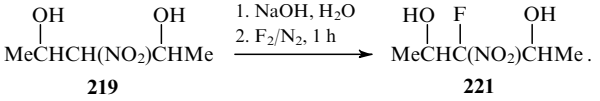
The reaction of 1-nitropropane with formaldehyde in the presence of $Ca(OH)_2$ in water at 30 °C for 1 h followed by treatment of the reaction mixture with bromine in $CCl_4$ at 20 °C gives rise to 2-bromo-2-nitrobutan-1-ol in 90% yield.[35]

Scheme 3



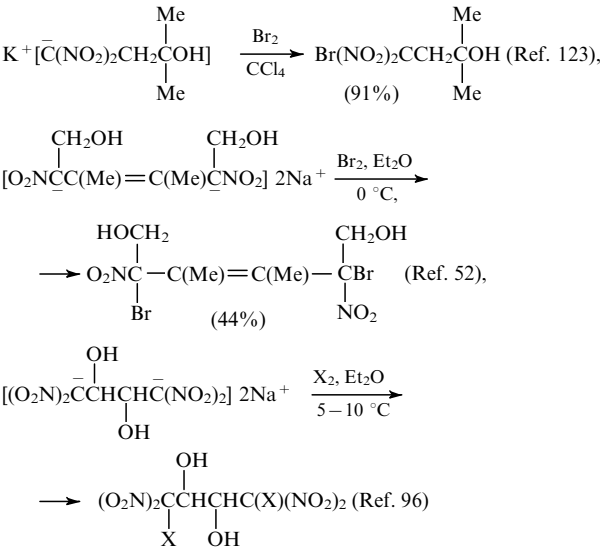
When nitro-diol **218** or **219** is treated with an aqueous solution of sodium hydroxide and then with a mixture of fluorine and nitrogen, fluoro-derivative **220** or **221** is formed in a yield of 71% or 68%, respectively.[50]





The potassium salt of 2,2-dinitroethanol is converted into 2-chloro-2,2-dinitroethanol on treatment with chlorine in water at 0–5 °C.[157]

When salts of nitro alcohols react with chlorine or bromine, halogenation products are formed:



X = Cl (73.8%), Br (75%).

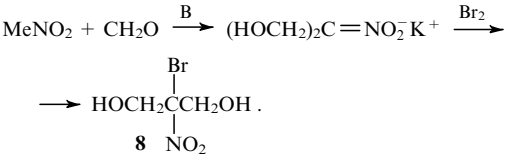
When the products resulting from reactions of $MeNO_2$ with aldehydes ($CH_2O$ or $Cl_3CCHO$) were treated with bromine, 2,2-dibromo-2-nitroethanol[158] or 3-bromo-1,1,1-trichloro-3-nitropropan-1-ol[35] were synthesised.

**Table 11**. Reaction conditions and yields of the compound **8**.

| Conditions of nitroaldol condensation | | | | Conditions of bromination | | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| Base | Solvent | $T$ /°C | $t$/min | $T$ /°C | $t$ /h | | |
| $Ca(OH)_2$ | $H_2O$ | 0 | 30 | 0 | 1 | 74 | 5 |
| $Na_2CO_3$ | | 0–10 | | 10 | 1 | 80 | 7 |
| NaOH | $H_2O$ | 5–10 | | 5–10 | | 86 | 9 |
| NaOH | MeOH | | | 20 | 0.5 | 83 | 10 |
| NaOH | $H_2O$, DEG[a] | 20 | 60 | 5–20 | | 98 | 11 |
| MeONa | MeOH | 5 | | 5 | | 86[b] | 20 |
| NaOH | $H_2O$ | | | see[c] | | | 12 |

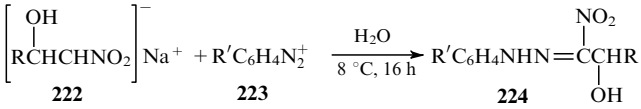
[a] DEG — diethyleneglycol; [b] $CHCl_3$, [c] paraform, $CCl_4$, BrCl.

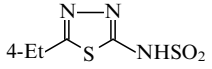
In a number of patents,[5,7,9–12,20] it has been proposed to synthesise 2-bromo-2-nitropropane-1,3-diol **8**, which is a known bactericide agent 'Biocide', according to the following scheme (the reaction conditions and product yields are listed in Table 11):



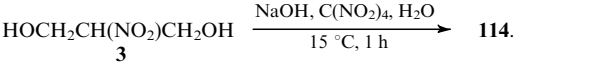
Similarly, $Cl_3CCH(OH)C(NO_2)Br$ was prepared from $MeNO_2$ and $Cl_3CCHO$;[5,7] $MeCH(OH)C(NO_2)BrCH(OH)Me$ was synthesised from $MeNO_2$ and MeCHO;[10] and $MeCH(OH)C(Me)(NO_2)BrCH(OH)Me$ was obtained from $EtNO_2$ and MeCHO.[11]

The reactions of salts of nitro alcohols **222** with aryldiazonium cations **223** in water at low temperatures yield arylhydrazones **224**.[159]

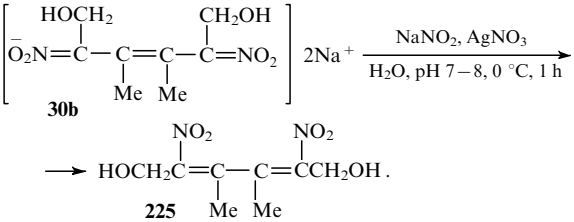


| R | R′ | Yield (%) |
|---|---|---|
| H | 4-Me | 51 |
| Me | H | 60 |
| Me | 4-Me | 45 |
| Me | 4-Cl | 23 |
| Ph | 4-Cl | 22 |
| H | 4-Br | 31 |
| Me | 4-Br | 20 |
| H | 4-$NO_2$ | 20 |
| H | 4-$NH{=}C(NH_2)NHSO_2$ | 25 |
| H | 3-$NO_2$ | 17 |
| Me | 4-$NO_2$ | 35 |
| H | 4-$H_2NSO$ | 22 |
| H | 4-$MeCONHSO_2$ | 20 |
| H | 4-$H_2NCONHSO_2$ | 21 |
| H |  | 56 |

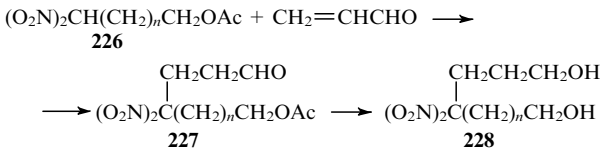
2-Nitropropane-1,3-diol **3** is nitrated with tetranitromethane in an alkaline medium giving 2,2-dinitropropane-1,3-diol **114**.[8]



However, an attempt to carry out alkaline nitration of the salt **30b** was unsuccessful; the reaction resulted in the formation of diene **225** (yield 21.4%).[52]

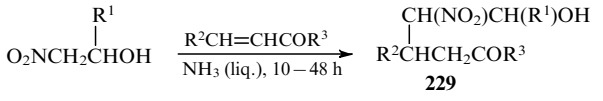


Dinitro alcohol acetates **226** [the compound **226** with $n = 3$ has been obtained by catalytic oxidative nitration of the nitro alcohol $O_2NCH(CH_2)_3OH$] have been introduced into the Michael reaction with acrolein. This afforded compounds **227**, which were then converted into dinitro-diols **228**.[160]



$n$ = 1, 3.

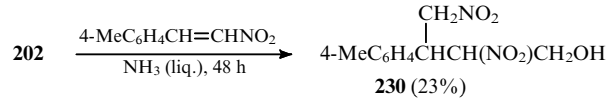
The nitro alcohols $O_2NCH_2CH(R')OH$ add to α,β-unsaturated ketones in liquid ammonia to give adducts **229** (yields 45% – 96%).[161]



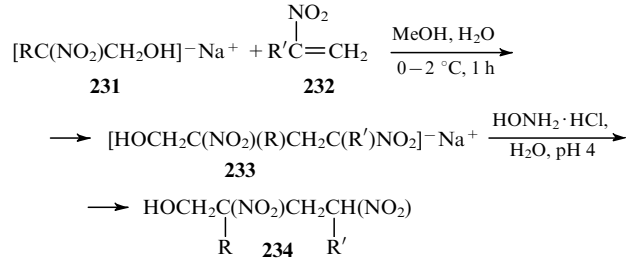
$R^1$ = H, $R^2$ = Ph, 4-$BrC_6H_4$, 4-$O_2NC_6H_4$, ;

$R^3$ = Me, Ph, 4-$MeC_6H_4$, 4-$MeOC_6H_4$; $R^1$ = Me, $R^2$ = $R^3$ = Ph.

Adduct **230** was synthesised by the reaction of the nitro alcohol **202** with 2-(4-methylphenyl)-1-nitroethene under similar conditions (yield 23%).[161]

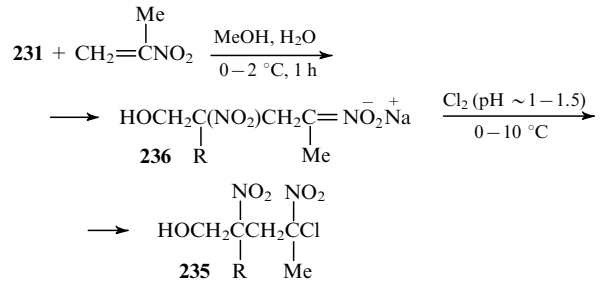


The reaction of salts of nitro alcohols **231** with nitroalkenes **232** in aqueous methanol gives adducts **233** in quantitative yields. On treatment with an aqueous solution of hydroxylamine hydrochloride, the adducts **233** are converted into dinitro alcohols **234** in 37% – 55% yields.[162]



R, R′ = Me, Et.

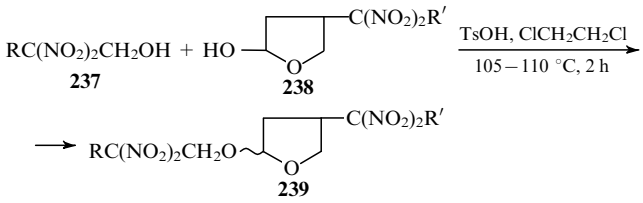
Chloro-substituted dinitro alcohols **235** have been synthesised by the reaction of the salts **231** with 2-nitroprop-1-ene in aqueous methanol followed by treatment of the resulting adducts **236** with chlorine.[163]



R = Me, Et.

## 3. Reactions involving the hydroxy group

When dinitro alcohols **237** react with compound **238** in the presence of toluene-*p*-sulfonic acid, intermolecular elimination of water occurs to give acetals **239** (yields 73% – 100%) as mixtures of *cis*- and *trans*-isomers (in a ratio of 15 – 35 : 85 – 65).[109]

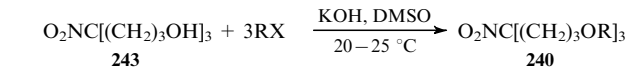


R = F, Me, $NO_2$; R′ = F, $NO_2$.

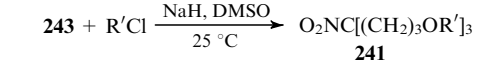
Ethers derived from nitro alcohols are often synthesised by reactions of nitro alcohols with halo-derivatives in the presence of bases.

The reaction of 3-nitropropan-1-ol with $Bu^tMe_2SiCl$ carried out in DMF in the presence of imidazoline at 20 °C for 15 h gave the ether $O_2N(CH_2)_3OSiMe_2Bu^t$ in 91% yield.[108]

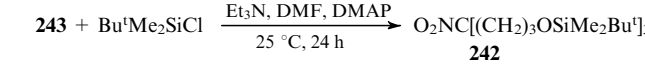
Ethers **240**, **241** and **242** have been prepared in high yields by the reactions of triol **243** with various halo-derivatives at 20 – 25 °C in the presence of KOH, NaH or $Et_3N$.[164]

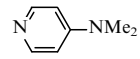


| R | X | Time /h | Yield (%) |
|---|---|---|---|
| Me | I | 2 | 89 |
| Bu | Br | 0.5 | 78 |

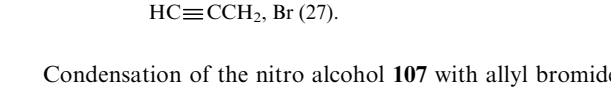


R′ = Bu (78%); 4-$ClC_6H_4$ (63%);



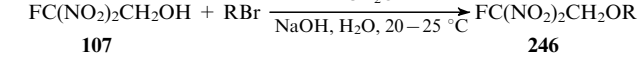
DMAP = .

The reaction of 2,2-difluoro-2-nitroethanol **244** with compounds RX in the presence of 5% aqueous sodium hydroxide at 25 – 30 °C affords ethers **245**.[165]



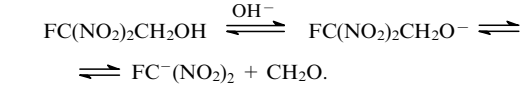
R, X (yield, %): Me, $MeOSO_2$ (78); $CH_2CHCH_2$, Cl (75.5); $HC{\equiv}CCH_2$, Br (27).

Condensation of the nitro alcohol **107** with allyl bromide or propargyl bromide catalysed by sodium hydroxide has been carried out in the presence of formaldehyde; this led to ethers **246** in 66% or 55% yield, respectively.[93]



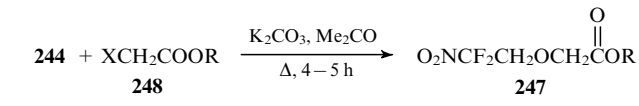
R (time /h): $CH_2CH{=}CH_2$ (45); $HC{\equiv}CCH_2$ (30).

The role of formaldehyde was to prevent the nitro alcohol **107** from decomposing in the alkaline medium.[93]



1,3-Dichloropropan-2-ol reacts with two molecules of the nitro alcohol **244** in the presence of 20% aqueous sodium hydroxide to give the diether $(NO_2CF_2CH_2OCH_2)_2CHOH$ in a yield of 78.6%.[166]

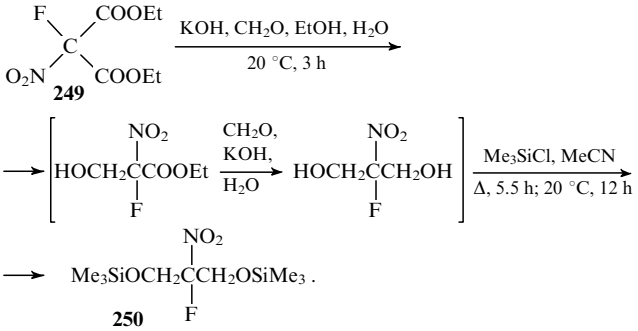
Ethers **247** containing ester groups have been prepared by the reaction of the nitro alcohol **244** with alkyl haloacetates **248** in boiling acetone in the presence of potassium carbonate.[167]



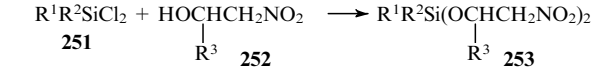
X = Cl, Br; R = Me (74%), Et (67%), Bu (65%).

The reaction of the nitro alcohols **237** with bis(chloromethyl) ether involves the replacement of only one chlorine atom and gives products $RC(NO_2)_2CH_2OCH_2Cl$ (R = Me, F, Cl, $NO_2$).[168]

2-Fluoro-2-nitropropane-1,3-diol resulting from the reaction of diethyl 2-fluoro-2-nitromalonate **249** and the aldehyde **2** in the presence of potassium hydroxide has been introduced *in situ* in the reaction with chlorotrimethylsilane in boiling acetonitrile; this gave bis-silyl ether **250**.[49]

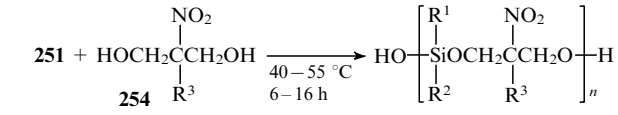


The reactions of dichlorosilanes **251** with nitro alcohols **252** giving rise to compounds **253** (yields 10%–69%) have been studied in detail.[169]



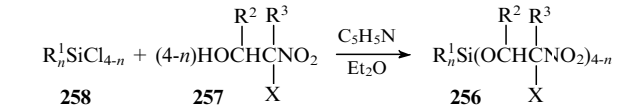
$R^1$ = Me, Et, MeO, EtO; $R^2$ = Me, Et, Ph, MeO, EtO; $R^3$ = H, Me.

Polysiloxanes **255** have been synthesised by the condensation of dichlorosilanes **251** with nitro-diols.[169]



*n* = 3, 4; $R^1$ = Et, Ph, MeO; $R^2$ = Me, Et, MeO; $R^3$ = Me, Et.

Compounds **256** containing one, two or three residues of nitro alcohols **257** are formed in the condensation of **257** with chlorosilanes **258** in the presence of pyridine.[170]



| *n* | $R^1$ | $R^2$ | $R^3$ | X | Yield (%) |
|---|---|---|---|---|---|
| 3 | Me | H | Me | Cl | 44 |
| 2 | Me | H | Me | Cl | 66 |
| 2 | Me | Me | H | Cl | 40 |
| 3 | Me | $CCl_3$ | H | H | 14 |
| 2 | Me | $CCl_3$ | H | H | 15 |
| 1 | H | H | Me | Cl | – |
| 1 | H | $CCl_3$ | H | H | 30 |
| 3 | Me | Et | Et | Br | 12 |

The reaction of the nitro alcohol **107** with epibromohydrin has been carried out at 0–2 °C in the presence of sodium hydroxide for 48 h; the ether $FC(NO_2)_2CH_2OCH_2\overline{CHOCH_2}$ resulting from the replacement of bromine in epibromohydrin was obtained in 32% yield.[171]

The reaction of the nitro alcohol **107** with epichlorohydrin has been described in two publications. In a patent,[172] ether $FC(NO_2)_2CH_2OCH_2\overline{CHOCH_2}$ was reported as the reaction product (yield 31%). However, in another study[171] the same process gave a different compound containing two nitro-alcohol residues, namely, $FC(NO_2)_2CH_2OCH_2CH(OH)CH_2OCH_2-C(NO_2)_2F$.

The nitro alcohol **244** reacts with ethylene oxide or propylene oxide in the presence of aqueous sodium hydroxide at 0 °C for 16 h to give ethers $RCH(OH)CH_2OCH_2C(NO_2)F_2$ (R = H, Me) (yields 32% and 67%); in the case of ethylene oxide, the compound $F_2C(NO_2)CH_2O(CH_2)_2OCH_2CH_2OH$ is also formed (yield 4%).[173]

The reaction of the nitro alcohol **202** with epoxides **259** at 50 °C in the presence of boron trifluoride etherate or sulfuric acid results in the formation of ethers **260** (yields 51% and 46.4%).[174]



R = Et, $CCl_3$.

The compounds $CH\equiv C(R)C(OH)CH(R')-OCH_2CH_2NO_2$ have been obtained by the reaction of the nitro alcohol **202** with epoxides $HC\equiv C(R)-\overline{COCH(R')}$ (R and R′ are H or lower alkyls) in the presence of 4-$MeC_6H_4SO_3H$ or the KU-2 ion-exchange resin.[175]

Nitro alcohols **261** react with trifluoromethanesulfonic acid to give cations **262**, which add *in situ* to nitro alcohols **263** yielding compounds **264** (Table 12).[176]

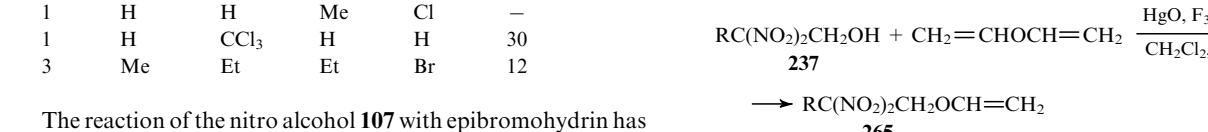


The ether $Me_3SiCH_2OCH_2C(NO_2)_2F$ has been prepared in 45% yield by the reaction of the nitro alcohol **107** with $Me_3SiCH_2OSO_2CF_3$ in dichloromethane in the presence of $K_2CO_3$ at 20 °C for 16 h.[177]

**Table 12**. Reaction condition and yields of the compounds **264**.

| R | R′ | *n* | Temperature /°C | Time /h | Yield (%) |
|---|---|---|---|---|---|
| Me | F | 2 | 60 | 20 | 9 |
| Me | Me | 2 | 60 | 20 | 80 |
| F | F | 2 | 60 | 96 | 15 |
| $NO_2$ | $NO_2$ | 2 | 65–70 | 72 | 16 |
| F | F | 1 | 30–35 | 168 | 20 |
| $NO_2$ | Me | 1 | 70–75 | 72 | 46 |
| $NO_2$ | F | 1 | 60–70 | 72 | 48 |

Refluxing of the nitro alcohols **237** with divinyl ether in the presence of HgO and trifluoroacetic acid leads to transetherification yielding vinyl ethers **265**.[92]



R = Me (64.2%), F (64%), $NO_2$ (25.9%).

The addition of nitro alcohols to alkenes or to buta-1,3-diene and the addition of alcohols to nitroalkenes have been used to synthesise ethers of nitro alcohols. For example, the reaction of 3-nitropropan-1-ol with 2-methylpropene in $CH_2Cl_2$ in the presence of sulfuric acid (20 °C, 12 h) gave the ether $Bu^tO(CH_2)_3NO_2$ (yield 95%).[108]

Adduct **266** was obtained by reaction of **107** with 2-methylpent-1-ene at 20 °C in the presence of $HgSO_4$ or $Hg_2SO_4$ (yields 74% and 58%, respectively).[178]

$$\underset{\mathbf{107}}{FC(NO_2)_2CH_2OH} + CH_2{=}\overset{\overset{Me}{|}}{C}Pr \longrightarrow \underset{\mathbf{266}}{FC(NO_2)_2CH_2OCH_2\overset{\overset{Me}{|}}{C}HPr}.$$

The reaction of the nitro alcohol **107** with buta-1,3-diene affords a mixture of 1,2-addition product **267** and 1,4-addition product **268** in a ratio of 77 : 23, their total yield being 53%.[178]

$$\underset{\mathbf{107}}{FC(NO_2)_2CH_2OH} + CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[55\ ^\circ C,\ 16\ h]{HgSO_4,\ CCl_4,\ \text{sealed tube}}$$

$$\longrightarrow \underset{\mathbf{267}}{CH_2{=}CH\overset{\overset{Me}{|}}{C}HOCH_2C(NO_2)_2F} + \underset{\mathbf{268}}{MeCH{=}CHCH_2OCH_2C(NO_2)_2F}.$$

Two products **269** and **270** resulting from radical *C*- and *O*-addition (yields 28% and 70%, respectively) have been synthesised by the reaction of hexan-1-ol with 1-nitroprop-1-ene in the presence of *tert*-butyl peroxide.[179]

$$Me(CH_2)_4CH_2OH + MeCH{=}CHNO_2 \xrightarrow{(Bu^tO)_2}$$

$$\longrightarrow \underset{\mathbf{269}}{C_5H_{11}\overset{\overset{OH}{|}}{C}HCH_2NO_2} + \underset{\mathbf{270}}{C_6H_{13}O\overset{\overset{Me}{|}}{C}HCH_2NO_2}.$$

1,1,1-Trinitroethanol adds to the C=N bond in perfluoroguanidine at ambient temperature to give compound **271**.[180]

$$(O_2N)_3CCH_2OH + (F_2N)_2C{=}NF \xrightarrow[23\ ^\circ C,\ 72\ h]{H_2NCONH_2,\ MeCN}$$

$$\longrightarrow \underset{\mathbf{271}}{(O_2N)_3CCH_2OC(NF_2)_2NHF}.$$

Acyclic and cyclic acetals containing one or two nitro-alcohol residues are promising compounds for practical purposes.

Acetals **272** have been synthesised by the reactions of the nitro alcohols **237** with 1,3,5-trioxane or with paraldehyde in the presence of sulfuric acid [181, 182] or sodium hydroxide. The reaction conditions and the yields of products are presented in Table 13.[89]

$$\underset{\mathbf{237}}{RC(NO_2)_2CH_2OH} + (R'CHO)_3 \longrightarrow \underset{\mathbf{272}}{[RC(NO_2)_2CH_2O]_2CHR'}.$$

Mixed acetals **273** [182, 183] and **274** [184] have been prepared by condensation of three components.

**Table 13**. Reaction condition and yields of the compounds **272**.

| R | R′ | Catalyst | Yield (%) | Ref. |
|---|---|---|---|---|
| F | H | $H_2SO_4$ | – | 181 |
| Me | H | NaOH | 78 | 89 |
| Me | H | $H_2SO_4$ | 78 | 182 |
| Me | Me | NaOH | 35 | 89 |
| $NO_2$ | H | $H_2SO_4$ | – | 182 |

$$\mathbf{237} + (CH_2O)_x + MeC(NO_2)_2CH_2OH \xrightarrow{80\%\ H_2SO_4}$$

$$\longrightarrow \underset{\mathbf{273}}{RC(NO_2)_2CH_2OCH_2OCH_2C(NO_2)_2Me}$$

R = $NO_2$,[182] F;[183]

$$(NO_2)_3CCH_2CH_2OH + FC(NO_2)_2CH_2CH_2OH + F_5SN{=}CCl_2 \longrightarrow$$

$$\longrightarrow \underset{\mathbf{274}}{F_5SN{=}C[OCH_2CH_2C(NO_2)_3]OCH_2C(NO_2)_2F}.$$

The acetal **273** (R = F) was synthesised by the reaction of the nitro alcohol $FC(NO_2)_2CH_2OH$ with the ether $MeC(NO_2)_2CH_2OCH_2Cl$ in the presence of $TiCl_4$.[183]

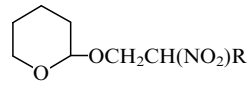
Polycondensation of formaldehyde with the diol $HOCH_2C(NO_2)_2CH_2CH_2C(NO_2)_2CH_2OH$ in the presence of sulfuric acid affords poly(nitroformal).[185]

Nitro alcohols add to acyclic [178, 186] or cyclic [108, 142, 178] vinyl ethers **275** in the presence of catalysts to give acetals **276** (see Table 14).

$$R^1OH + \underset{\mathbf{275}}{R^2OCH{=}CHR^3} \xrightarrow{20\ ^\circ C} \underset{\mathbf{276}}{R^2OCH(OR^1)CH_2R^3}.$$

The addition of nitro alcohols **277** to 2,3-dihydropyran in THF and HMPT in the presence of butyllithium at a temperature between −90 °C and −40 °C leads to the compounds **209**.[154]

$$\underset{\mathbf{277}}{RCH(NO_2)CH_2OH} + \text{} \xrightarrow[-90\ \text{to}\ -40\ ^\circ C,\ 3\ h]{BuLi,\ THF,\ HMPT}$$

$$\longrightarrow \text{}$$

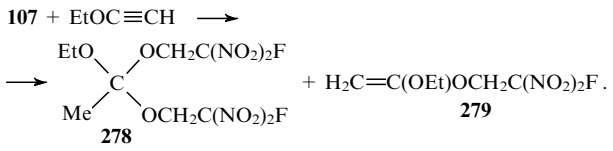
$$\mathbf{209}$$

R = H, Me.

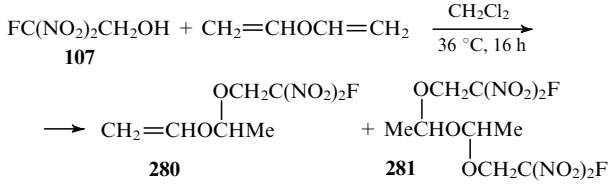
The nitro alcohol **107** adds to ethoxyacetylene in $CH_2Cl_2$ at 20 °C in the presence of $HgSO_4$ [187] or $Hg(OAc)_2$ [178] or in the presence of HgO in $CF_3COOH$ [92] giving rise to 2 : 1 adduct **278** (yields 100%, 95%, or 70%, respectively). When this reaction is carried out in the presence of $Hg(OAc)_2$ in $CH_2Cl_2$ and hexane at 20 °C, the 1 : 1 adduct **279** is produced in 73% yield in addition to the adduct **278** (yield 27%).[178]

**Table 14**. Conditions for the formation of the acetals **276**.

| $R^1$ | $R^2$ | $R^3$ | Catalyst | Solvent | *T* /°C | Time /h | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| $O_2N(CH_2)_3$ | $-(CH_2)_3-$ | | TsOH | $Et_2O$ | 20 | 5 | 95 | 108 |
|  | $-(CH_2)_3-$ | | TsOH | $Et_2O$ | 20 | 12 | 90.5 | 142 |
| $FC(NO_2)_2CH_2$ | Et | H | $Hg(OAc)_2$ | $CH_2Cl_2$ | 20 | 16 | 73 | 178 |
| $FC(NO_2)_2CH_2$ | $-(CH_2)_3-$ | | $Hg(OAc)_2$ | $CH_2Cl_2$ | 42 | 17 | 100 | 178 |
| $FC(NO_2)_2CH_2$ | $FC(NO_2)_2CH_2$ | H | $Hg(OAc)_2$ | $CH_2Cl_2$ | 20 | 24 | 61 | 178 |
| $(O_2N)_3CH_2CH_2$ | $FC(NO_2)_2CH_2$ | H | $BF_3 \cdot Et_2O$ | – | 0 | 12 | – | 186 |
| $MeC(NO_2)_2CH_2$ | $FC(NO_2)_2CH_2$ | H | Mol. sieve 5 Å | – | 0 | 12 | – | 186 |
| $FC(NO_2)_2CH_2$ | $FC(NO_2)_2CH_2$ | H | Mol. sieve 5 Å | – | 0 | 12 | – | 186 |



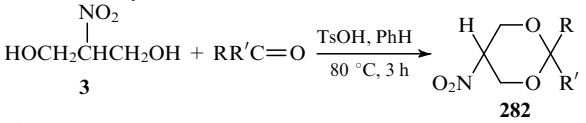
Two compounds, 1 : 1 adduct **280** and 2 : 1 adduct **281**, were obtained by refluxing the nitro alcohol **107** and divinyl ether in $CH_2Cl_2$ in the presence of $HgSO_4$ or $Hg_2SO_4$. It was found that the ratio of **280** to **281** depends appreciably on the **107** : ether ratio. For example, when this ratio is 1 : 1, reaction in the presence of $HgSO_4$ gives **280** in 12% yield and **281** in 58% yield; at 2 : 1 ratio, the yield of **280** is 70%, while that of **281** is 20%. When this reaction is carried out in the presence of $Hg_2SO_4$ and **107** : ether = 1 : 2 (refluxing for 26 h), the yields of **280** and **281** are 40% and 34%, respectively.[178]



The orthoformate $HC[OCH_2C(NO_2)_3]_3$ or orthocarbonate $C[OCH_2C(NO_2)_3]_4$ have been synthesised from 2,2,2-trinitroethanol and $CHCl_3$ or $CCl_4$ in the presence of $FeCl_3$.[188]

Cyclocondensation of nitro-diols of various structures with aldehydes or ketones in the presence of acid catalysts has found wide application as a method for the preparation of nitro-derivatives of 1,3-dioxane.

2-Nitropropane-1,3-diol **3** reacts with acetone or with aromatic aldehydes in boiling benzene in the presence of toluene-*p*-sulfonic acid to yield 5-nitro-1,3-dioxane derivatives **282**.[189]



R, R′: Me, Me; H, 4-$Cl_6H_4$; H, Ph; H, 4-$BrC_6H_4$.

2-Bromo-2-nitropropane-1,3-diol **8** has been involved in the condensation with acetone or aliphatic aldehydes in the presence of various catalysts; this resulted in the formation of 5-bromo-5-nitro-1,3-dioxane derivatives **283**. The reaction conditions and the yields of reaction products are listed in Table 15.[190–192]

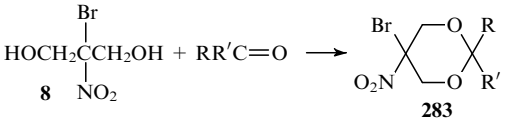
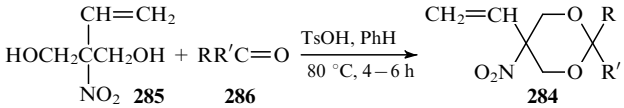


**Table 15**. Reaction conditions and yields of the compounds **283**.

| R | R′ | Catalyst | Solvent | *T* /°C | *t* /h | Yield (%) | Ref. |
|---|---|---|---|---|---|---|---|
| H | Me | *p*-TsOH | PhH | 80 | 0.5 | – | 190 |
| H | Et | *p*-TsOH | PhH | 80 | 0.5 | – | 190 |
| H | Pr | *p*-TsOH | PhH | 80 | 0.5 | – | 190 |
| H | Pr$^i$ | *p*-TsOH | PhH | 80 | 0.5 | – | 190 |
| H | H | $H_2SO_4$ | DCE [a] | 83 | – | – | 191 |
| Me | Me | $BF_3 \cdot Et_2O$ | – | ⩽47 | – | 40 | 192 |
| H | Me | $BF_3 \cdot Et_2O$ | – | ⩽47 | – | 85 | 192 |
| H | Et | $BF_3 \cdot Et_2O$ | – | ⩽47 | – | – | 192 |
| H | Pr | $BF_3 \cdot Et_2O$ | – | ⩽47 | – | – | 192 |
| H | Pr$^i$ | $BF_3 \cdot Et_2O$ | – | ⩽47 | – | – | 192 |

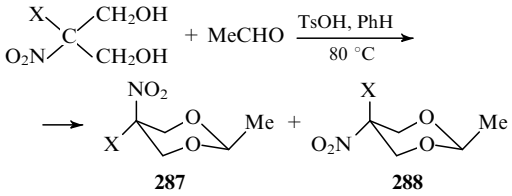
[a] DCE — dichloroethane.

Acetals **284**, which are promising as monomers, have been synthesised from diol **285** and carbonyl compounds **286** in the presence of toluene-*p*-sulfonic acid.[193]



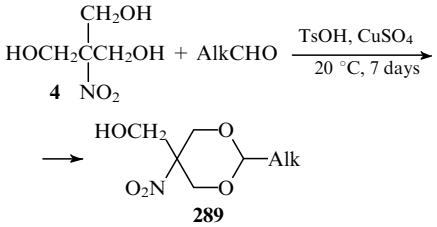
R, R′ (yield, %): H,  (47); H, Ph (65); H, 4-$O_2NC_6H_4$ (70); H, 3,4-$(CH_2O_2)C_6H_3$ (56); H, PhCH = CH (67); Me, Me (71); $(CH_2)_5$ (62).

The stereochemistry of the reactions of halo-2-nitropropane-1,3-diols with acetaldehyde in the presence of toluene-*p*-sulfonic acid has been studied.[194] It was found that these reactions yield mixtures of diastereoisomers **287** and **288**.

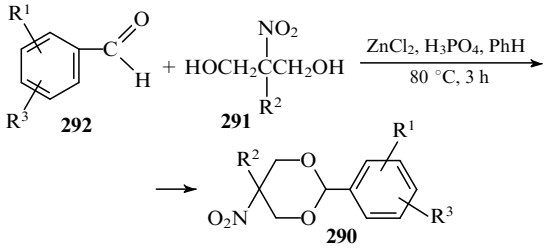


the ratio **287** : **288** = 16 : 83 (X = Cl), 5.5 : 94 (X = Br).

2-Alkyl-5-hydroxymethyl-5-nitro-1,3-dioxanes **289** were prepared in ~90% yields by cyclocondensation of 2-hydroxymethyl-2-nitropropane-1,3-diol **4** with aliphatic aldehydes in the presence of toluene-*p*-sulfonic acid and $CuSO_4$ at 20 °C.[194]

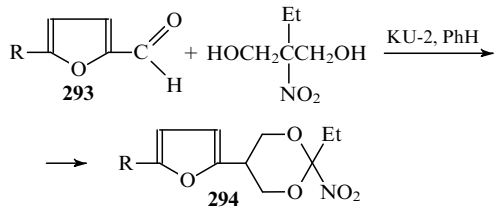


A series of 5-nitro-1,3-dioxane derivatives **290** have been synthesised by cyclocondensation of nitro-diols **291** with esters of aldehydo acids **292** in the presence of zinc chloride and orthophosphoric acid in boiling benzene.[195]



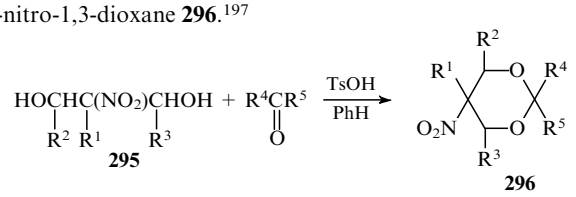
| $R^1$ | $R^2$ | $R^3$ | Yield (%) |
|---|---|---|---|
| H | Me | 2-$OCH_2COOEt$ | 90 |
| H | Et | 2-$OCH_2COOEt$ | 96 |
| H | Br | 2-$OCH_2COOEt$ | 95 |
| H | Me | 3-$OCH_2COOEt$ | 92 |
| H | Br | 3-$OCH_2COOEt$ | 84 |
| H | Me | 4-$OCH_2COOEt$ | 92 |
| H | Et | 4-$OCH_2COOEt$ | 90 |
| H | 3-$O_2NC_6H_4$ | 4-$OCH_2COOEt$ | 50 |
| H | Br | 4-$OCH_2COOEt$ | 75 |
| 2-MeO | Me | 4-$OCH_2COOEt$ | 74 |
| 2-MeO | Cl | 4-$OCH_2COOEt$ | 88 |
| 2-MeO | Br | 4-$OCH_2COOEt$ | 87 |
| 2-EtO | Me | 4-$OCH_2COOEt$ | 92 |
| 2-EtO | Et | 4-$OCH_2COOEt$ | 91 |
| 2-EtO | Br | 4-$OCH_2COOEt$ | 78 |

The rate of the reaction of 5-substituted furfural derivatives **293** with 2-ethyl-2-nitropropane-1,3-diol in the presence of the KU-2 ion-exchange resin (H-form) has been shown to decrease in the series $NO_2 > I > Br > H > Me$. It was assumed that attack by the diol on the protonated formyl group is the rate-determining step of the reaction.[196]



R = H (66%), Me (70%), Br (84%), I (79%), $NO_2$ (82%).

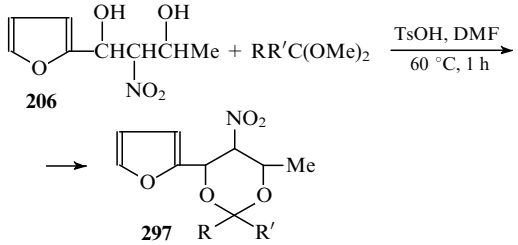
Cyclocondensation of mono- and disubstituted 2-nitropropane-1,3-diol derivatives **295** with aldehydes or ketones in the presence of TsOH gave di-, tri- or tetra-substituted derivatives of 5-nitro-1,3-dioxane **296**.[197]



$R^1$ = H, Me, $CH_2OH$; $R^2$ = H, Me, Pr, $Pr^i$; $R^3$ = H, Me, Pr, $Pr^i$;
$R^4$ = H, Me; $R^5$ = H, Me, Et, $Pr^i$, Bu, Ph, 2-$HOC_6H_4$, 4-$O_2NC_6H_4$, PhCH=CH; $R^4$, $R^5$ = $(CH_2)_5$.

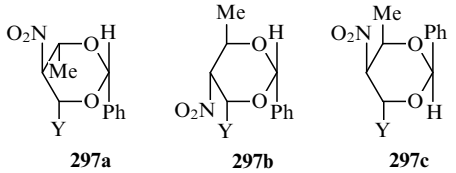
The compounds **296** were obtained in low yields for $R^1$ = H, $R^2$ = $R^3$ = $R^4$ = $R^5$ = Me (27%); $R^1$ = H, $R^2$ = $R^3$ = Me, $R^4$ = $R^5$ = H (30%) and $R^1$ = $R^4$ = $R^5$ = H, $R^2$ = $R^3$ = $Pr^i$ (32%).[197]

1,3-Dioxane derivatives **297** were synthesised from the nitrodiol **206** using acetone dimethyl ketal or benzaldehyde dimethyl acetal as the second reactant.[152, 198]



R = H, R′ = Ph; R = R′ = Me.

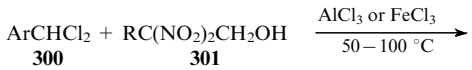
The reaction of **206** with benzaldehyde dimethyl acetal affords three diastereoisomers **297a**,**b**,**c** in 55.5% overall yield and in a ratio of 4 : 1 : 1.[152]

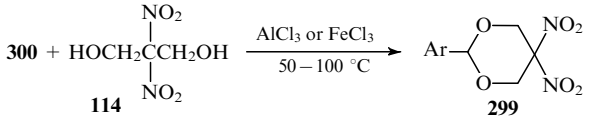


Y =  .

Refluxing of the nitro-diol $HOCH_2CH(NO_2)CH(OH)C_{13}H_{27}$ with acetone dimethyl ketal in acetone in the presence of toluene-*p*-sulfonic acid results in the formation of 2,2-dimethyl-5-nitro-4-tridecyl-1,3-dioxane in 61.5% yield.[61]

Yet another method for the synthesis of acyclic and cyclic acetals of aromatic aldehydes and nitro alcohols consists of the reaction of dichloromethyl arenes with alcohols or 1,3-diols. This procedure was used, for example, to prepare acetals **298** or **299** from dichloromethylarenes **300** and polynitro alcohols **301** or 2,2-dinitropropane-1,3-diol **114**.[199]

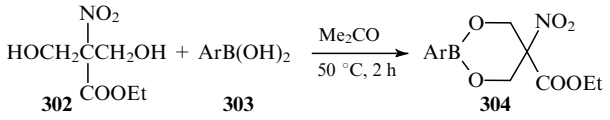




Ar = Ph, 3-$O_2NC_6H_4$ ($AlCl_3$,), 4-$O_2NC_6H_4$ ($FeCl_3$).

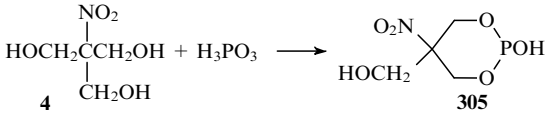
The reactivity of nitro alcohols decreases in the order $NO_2 > Cl > HCCH_2 > Me$, *i.e.* in parallel with their acidity.[199]

By refluxing nitro-diol **302** with arylboronic acids **303** in acetone, 2-bora-1,3-dioxane derivatives **304** have been synthesised.[200]

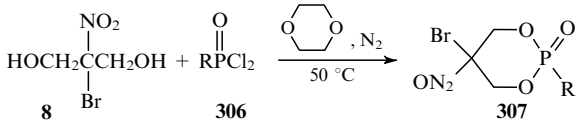


Ar = Ph (90.5%), 4-$ClC_6H_4$ (67%).

Cyclic compound **305** containing two oxygen atoms and a phosphorus atom in the six-membered ring has been obtained by cyclocondensation of the triol **4** with phosphorous acid.[201]

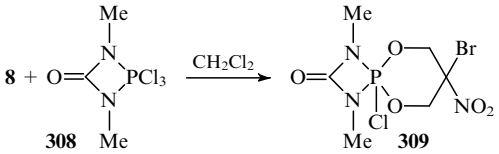


2-Bromo-2-nitropropane-1,3-diol **8** reacts with dichloroderivatives **306** at 50 °C to give 5-bromo-5-nitro-2-R-2-oxo-1,3,2-dioxaphosphorinanes **307**.[202]

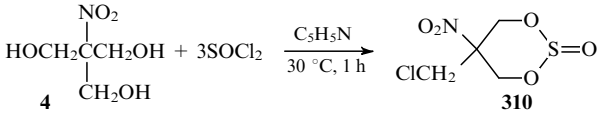


R = Me (60%), Cl (28%), PhO (56%), 4-$MeC_6H_4O$ (49%), 3-$MeC_6H_4O$ (42%), 4-$O_2NC_6H_4O$ (60%), OH (39%).

Cyclocondensation of the diol **8** with 2,2,2-trichloro-1,3-dimethyl-1,3,2$\lambda^5$-diazaphosphetidin-4-one **308** gives rise to compound **309**.[203]



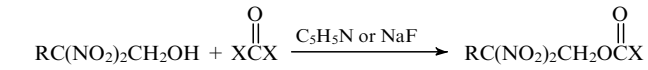
5-Chloromethyl-5-nitro-1,3,2-dioxathian-2-one **310** was synthesised by the reaction of the triol **4** with thionyl chloride in the presence of pyridine.[204]



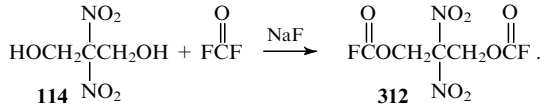
Esters derived from nitro alcohols are usually synthesised either by reactions of nitro alcohols with acid chlorides or anhydrides or by reactions of nitro alcohols with carboxylic acids in the presence of anhydrides of other acids. The preparation

of nitro alcohol acetates has been described in numerous publications. There is no need to consider these studies in detail, because the acetates have been synthesised by conventional procedures, which have been described fairly comprehensively in monographs.[3,4]

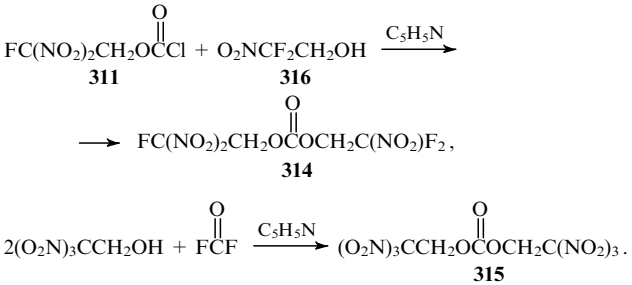
Syntheses of halocarbonates **311** and **312** (yield 91%) by the reactions of nitro alcohols **313** with carbonyl dichloride or difluoride or by the reaction of 2,2-dinitropropane-1,3-diol **114** with carbonyl difluoride have been reported in patents [205,206] and papers.[207,208]



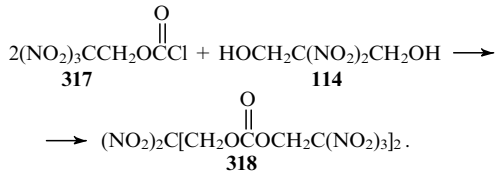
R, X: F, Cl; F, F; Me, F; $NO_2$, F; $FCOOCH_2$, F;



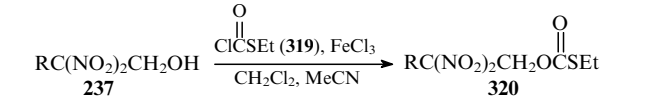
Carbonates **314** [205] or **315** (yield 64%) [208] were prepared by the reaction of nitro alcohol **316** with the chloroformate **311** (R = F, X = Cl) or of 2,2,2-trinitroethanol with carbonyl difluoride.



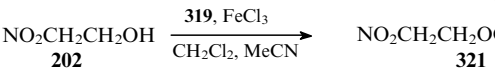
2,2-Dinitropropane-1,3-diol **114** reacts with two molecules of chloroformate **317** giving rise to diester **318** (yield 83%).[209]



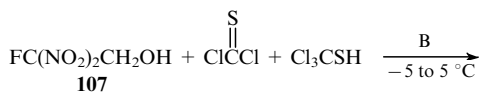
The exothermic reaction of the nitro alcohols **237** or **202** with chloride **319** in the presence of iron(III) chloride has led to the synthesis of *O*-alkyl *S*-ethyl thiocarbonates **320** [210] or **321**.

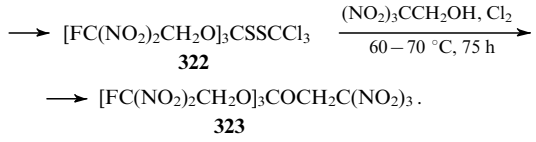


R = F, Me, $NO_2$;

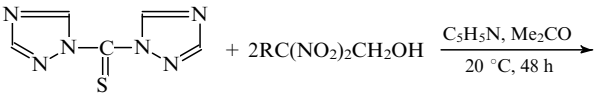


The three-component reaction involving the nitro alcohol **107**, thiophosgene and $Cl_3CSH$, taken in a ratio of 3 : 1 : 1, carried out in the presence of a base under conditions of phase transfer catalysis affords compound **322**, which is converted into compound **323** (yield 81%) upon treatment with 1,1,1-trinitroethanol and chlorine.[211]



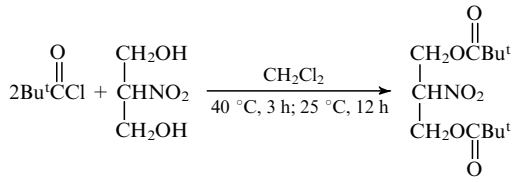


When 2,2-dinitropropanol is made to react with bis(1,2,4-triazol-1-yl) thioketone in acetone in the presence of pyridine at 20 °C, the ester $[MeC(NO_2)_2CH_2O]_2C=S$ is formed in 83% yield over a period of 2 days.[212] Similarly, the reaction of $(O_2N)_3CCH_2OH$ or the alcohol **107** with bis(1,2,4-triazol-1-yl) sulfoxide yields the corresponding esters.[212]

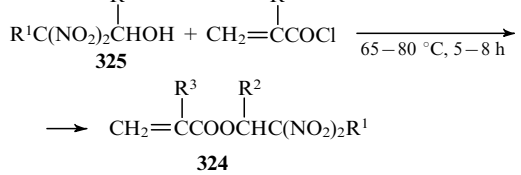


R = F, Me, $NO_2$.

The reaction of 2-nitropropane-1,3-diol with trimethylacetyl chloride in dichloromethane carried out for 3 h at 40 °C and then for 12 h at 25 °C affords the corresponding bis-ester in 95% yield.[15]



Esters **324**, which are of interest as monomers, have been synthesised in 60%–70% yields by the reactions of dinitro alcohols **325** with chlorides of α,β-unsaturated acids.[213–215]



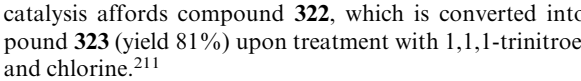
$R^1$ = H, F, Me; $R^2$ = H, Me; $R^3$ = H, Me.

It should be noted that the yield of **324** ($R^1$ = F, $R^2$ = $R^3$ = Me) was as low as 5%.[214] The reaction of the nitro alcohol **325** ($R^1$ = Me, $R^2$ = H) with acryloyl chloride carried out for 3 h at 20 °C in the presence of $TiCl_4$ affords the corresponding ester **324** ($R^1$ = Me, $R^2$ = $R^3$ = H) in 93% yield.[213]

The reaction of perfluoroacryloyl chloride with the nitro alcohol **244** in the presence of triethylamine at −40 to −35 °C follows two competing pathways: esterification of the nitro alcohol giving the ester $F_2C=CFCOOCH_2C(NO_2)F_2$ (yield 7.9%) and the addition of the nitro alcohol to the double bond of the chloride leading to the ether $F_2C(NO_2)CH_2OCF_2$–CH(F)COCl (yield 7%).[216]

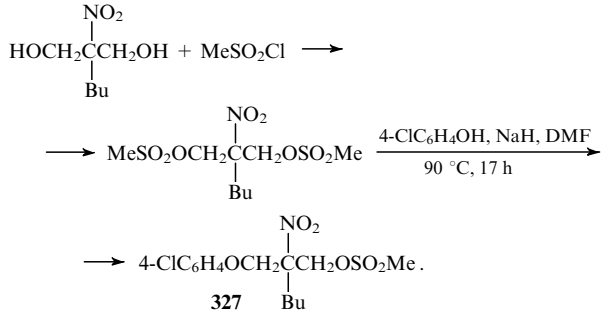
Esters derived from nitro alcohols and unsaturated dicarboxylic acids have been described in the literature.[217,218]

Tris-esters **326** have been prepared by the reactions of the nitro-triol **4** with benzoyl, 4-chlorobenzoyl and toluene-*p*-sulfonyl chlorides in the presence of pyridine.[164]

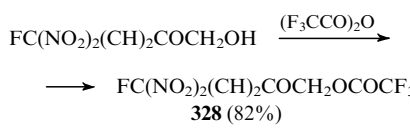


| Ar | Y | *T* /°C | Time /h | Yield (%) |
|---|---|---|---|---|
| Ph | CO | 70 | 15 | 51 |
| 4-$ClC_6H_4$ | CO | 20 | 30 | 93 |
| 4-$MeC_6H_4$ | $SO_2$ | 0 | 12 | 47 |

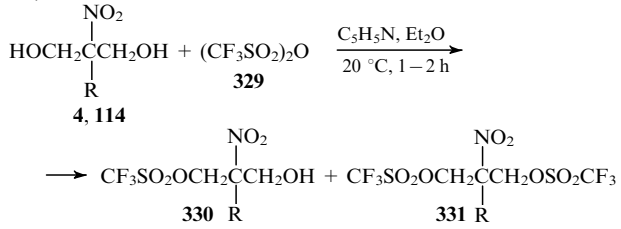
Compound **327** has been obtained in 40% yield by treatment of the bis-ester, resulting from the reaction of 2-butyl-2-nitropropane-1,3-diol with methanesulfonyl chloride, with chlorophenol in the presence of sodium hydride.[219]



Synthesis of hydroxy ketone **328** has been accomplished using trifluoroacetic anhydride.[103]

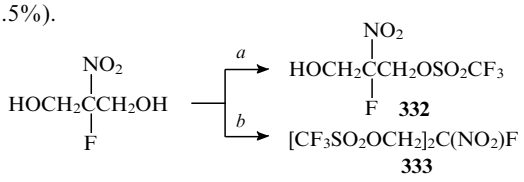


The reaction of the dinitro-diol **114** or the nitro-diol **4** with trifluromethanesulfonic anhydride **329** at 20 °C in the presence of pyridine results in the formation of mixtures of mono-triflates **330** (yields 46.8% or 44.4%) and bis-triflates **331** (yields 14% or 16.2%).[49]



R = $NO_2$ (**114**) ; R = $CH_2OH$ (**4**).

The researchers cited [49] also proposed conditions under which the reaction of 2-fluoro-2-nitropropane-1,3-diol with **329** gives either mono-triflate **332** (yield 78.9%) or bis-triflate **333** (yield 75.5%).

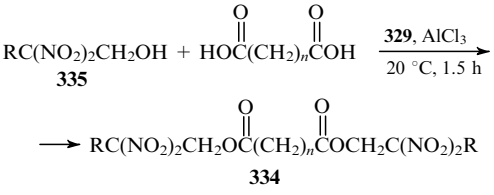


(*a*) 1 equiv. $(CF_3SO_2)_2O$, $C_5H_5N$, $Et_2O$, 20 °C, 16 h;

(*b*) 2 equiv. $(CF_3SO_2)_2O$, $C_5H_5N$, $CHCl_3$, 5 °C, 3 h.

The nitro-diol $HOCH_2C(NO_2)(Br)(CH_2OH)$ has been esterified with formic acid in the presence of acetic anhydride and pyridine at 40 °C to give the corresponding bis-ester $(HCOOCH_2)_2C(NO_2)Br$.[220]

Esters **334** (yields 47% – 100%) have been synthesised from polynitro alcohols **335** and dicarboxylic acids in the presence of the anhydride **329** and aluminium chloride.[221]



*n* = 1, 3, 4, 5, 6, 8, 10; R = F, $NO_2$.

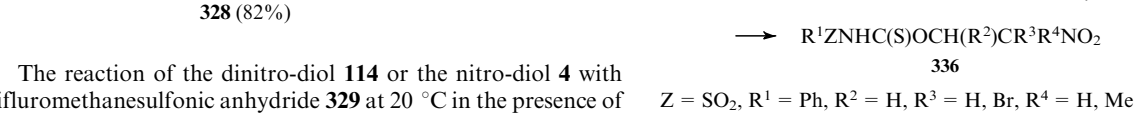
Under the same conditions, the following esters were obtained: $(NO_2)_2(R)CCH_2O_2CCH(Et)CO_2CH(R)(NO_2)_2$ (R = $NO_2$, 63%; R = F, 100%) and $RCOOCH_2C(NO_2)_2F$ (R = Ph, 92%; R = PhCH=CH, 100%).[221]

The urethane $FC(NO_2)_2CH_2CH_2OCONHCH_2CH_2C(NO_2)_2F$ is formed in 72% yield when the isocyanate $FC(NO_2)_2CH_2CH_2NCO$ and the alcohol $FC(NO_2)_2CH_2CH_2OH$ are refluxed for 6 h in chloroform in the presence of iron acetylacetonate.[122]

Study of the kinetics of the reactions of 2-R-2-nitropropane-1,3-diols with the bis-isocyanate $CH_2(C_6H_4NCO)_2$ has shown that the nitro group adjacent to the hydroxy group decreases the reaction rate owing to its inductive effect and also owing to the formation of intra- and intermolecular $OH\cdots O_2N$ hydrogen bonds.[222]

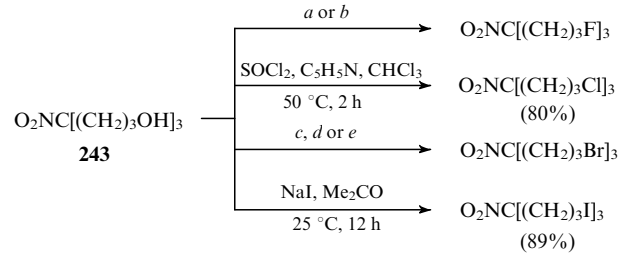
It has been found that the reaction between 2-methyl-2-nitropropane-1,3-diol and *o*-phenylene diisocyanate yielding polyurethane follows second-order kinetics, its rate constant being 0.685 $mol^{-1}\,h^{-1}$ at 20 °C or 1.127 $mol^{-1}\,h^{-1}$ at 30 °C.[223]

Compounds **336** have been synthesised from isothiocyanates and nitro alcohols.[224]



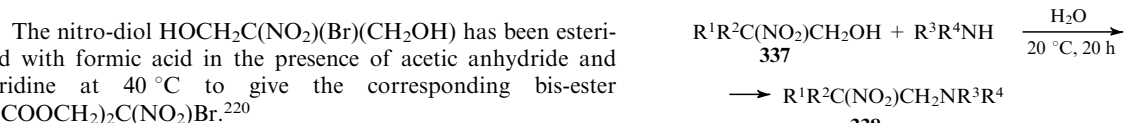
Z = $SO_2$, $R^1$ = Ph, $R^2$ = H, $R^3$ = H, Br, $R^4$ = H, Me (23% – 31%);
Z = CO, $R^1$ = Ph, 4-$ClC_6H_4$, 4-$O_2NC_6H_4$, 2-furyl, $R^2$ = H, Me, $R^3$ = H, Br, $R^4$ = H, Me, Et (18% – 75%).

Substitution of the hydroxy group in nitro alcohols has been studied fairly comprehensively. The replacement of all three hydroxy groups in the triol **243** by fluorine, chlorine, bromine or iodine atoms has been described.[164]



(*a*) $Bu_4\overset{+}{N}F^-$, THF, MeCN, 90 °C, 12 h (75%);
(*b*) $Bu_4\overset{+}{N}F^-$, 4-$MeC_6H_4SO_2F$, THF, 4 Å mol. sieve (86%);
(*c*) $PBr_3$, $C_5H_5N$, PhH, 50 – 70 °C, 2 h (69%);
(*d*) $SOBr_2$, $C_5H_5N$, $CH_2Cl_2$, refluxing for 2 h (64%);
(*e*) NaBr, $(HOCH_2CH_2)_2O$, 150 – 170 °C, 3 h (55%).

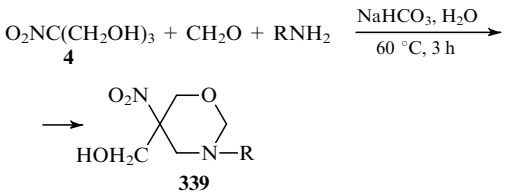
The hydroxy group in nitro alcohols **337** is substituted by an amine residue on treatment with primary or secondary amines in water; this gives compounds **338** in 60% – 89% yields.[225 – 227]



$R^1$ = F, Me; $R^2$ = H, Me, $NO_2$; $R^3$ = Me, Et, $Pr^i$, Bu, $Me_2CH(CH_2)_2$; $R^4$ = H, Me.

If the reaction of formaldehyde with trinitromethane is carried out in water in the presence of urea at 70 °C for 2 h, the resulting $(O_2N)_3CCH_2OH$ reacts *in situ* with urea, and $[(O_2N)_3CCH_2NH]_2CO$ is formed as the reaction product.[98]

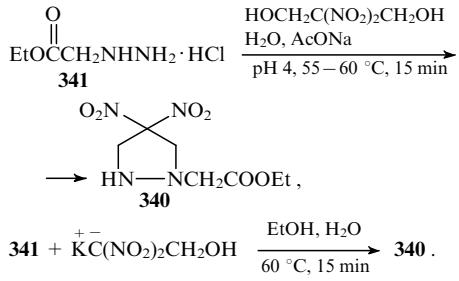
Three-component condensation of the nitro-triol **4**, formaldehyde and primary amines in the presence of sodium hydrogencarbonate gives rise to tetrahydro-1,3-oxazine derivatives **339**.[228]



R = Me (32%); Pr$^i$ (22%); Bu$^t$ (77%).

The compounds **339** (R = Me, Et, Pr, Pr$^i$, Bu and Bu$^t$) have also been obtained by another method, namely, the reaction of the nitro-triol **4** with the corresponding 1,3,5-trialkylhexahydro-1,3,5-triazines.[229]

The pyrazolidine derivative **340** has been synthesised by the reaction of hydrochloride **341** with 2,2-dinitropropane-1,3-diol **114** (yield 86%) or with the potassium salt of 2,2-dinitroethanol (yield 23.5%).[230]



Cyclocondensation of the nitro-diols **302** or **114** with formaldehyde and primary amines leads to hexahydropyrimidine derivatives **342**. The reaction conditions and the yields of reaction products are listed in Table 16.[200, 231, 232]

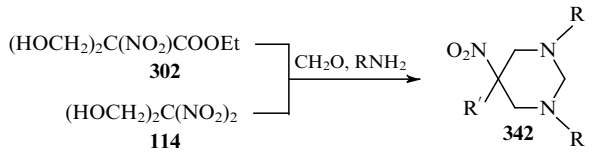
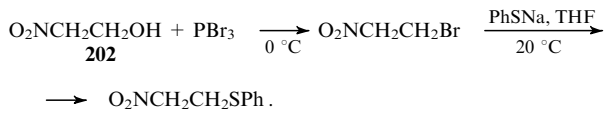


**Table 16**. Reaction conditions and yields of the compounds **342**.

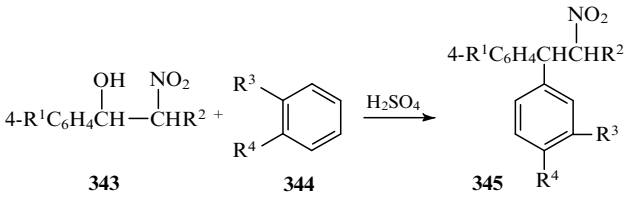
| R | R′ | Solvent | *T* /°C | Time /h | Yield (%) | Ref. |
|---|---|---|---|---|---|---|
| Bu$^t$ | COOEt | EtOH | 78 | 2 | 25 | 200 |
| Me | $NO_2$ | EtOH | 5–20 | | 19 | 231 |
| Bu$^t$ | $NO_2$ | MeOH | 20 | 1 | 29 | 231 |
| Me [a] | $NO_2$ | see [b] | 20 | 24 | 35 | 232 |
| $CH_2COOMe$ [a] | $NO_2$ | see [b] | 20 | 18 | 22 | 232 |
| $CH_2COOEt$ [a] | $NO_2$ | see [b] | 20 | 18 | 15 | 232 |

[a] Hydrochlorides of the amines were used; [b] in the presence of AcONa, pH 4.

When the nitro alcohol **202** is treated successively with phosphorus tribromide and sodium thiophenoxide, the corresponding thioether is formed in an overall yield of 73%.[233]

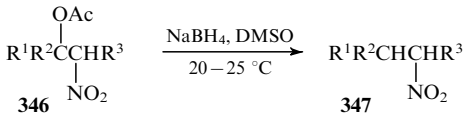


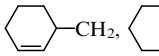
The hydroxy group in nitro alcohols **343** is replaced by aryl groups when **343** are treated with arenes **344** in the presence of sulfuric acid; this yields diphenylmethane derivatives **345**.[63, 234–236]



| $R^1$ | $R^2$ | $R^3$ | $R^4$ | Ref. |
|---|---|---|---|---|
| Bu$^t$ | Me | H | EtO | 63 |
| EtCHMe | Et | H | EtO | 63 |
| Bu$^i$ | Me | $OCH_2O$ | | 234 |
| EtCHMe | Et | $OCH_2O$ | | 234 |
| EtO | H | H | EtS | 234 |
| Cl | H | H | EtS | 235 |
| $HC\equiv CCH_2O$ | Me | H | H, F, Me, Pr$^i$ | 236 |
| | Et | H | MeO, PrO, $HC\equiv CCH_2O$ | |

On treatment of acetates **346** with sodium tetrahydridoborate in DMSO or ethanol at 20–25 °C for 1.5 h, the acetoxy group is substituted by a hydrogen atom giving nitro-compounds **347** (yields 41%–90%).[27, 237]



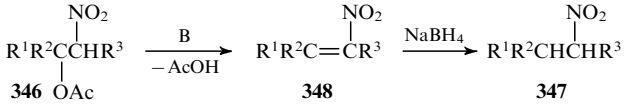
$R^1 = C_6H_{13}$, $C_7H_{15}$, ,

$Me_2C{=}CH(CH_2)_2C(Me){=}CH(CH_2)_2$; $R^2 = R^3 = H$;[27]

$R^1$ = Me, Et, Bu, Ph, $MeCH(Et)(CH_2)_3$; $R^2$ = H, Me;

$R^3$ = H, Me, Et, Pr; $R^2$, $R^3 = (CH_2)_5$.[237]

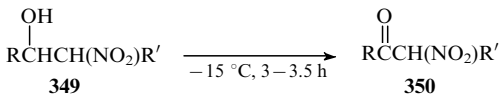
The formation of **347** from the acetates **346** involves the intermediate formation of nitroalkenes **348**.[237]



## 4. Reactions involving several sites

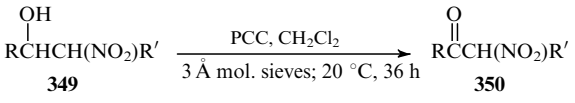
Oxidation of nitro alcohols to nitro-carbonyl derivatives can involve simultaneously two reaction sites, namely, the hydroxy group and the hydrogen atom attached to the carbon atom carrying the hydroxy group.

Nitro alcohols **349** have been converted into nitro ketones **350** by treatment with chromium(VI) oxide supported on montmorillonite at −15 °C accompanied by ultrasonic treatment.[72]



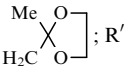
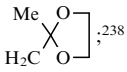
R, R′ (yield, %): Me, Me (90); Et, H (76); Pr$^i$, Me (93); Pr$^i$, Et (90).

Pyridinium chlorochromate has proved to be a good reagent for the transformation of nitro alcohols into nitro ketones. Treatment of nitro alcohols **349** with this reagent in the presence of molecular sieves at 20 °C gave nitro ketones **350** (yields 61%–87%).[83, 238]




**349** **350**

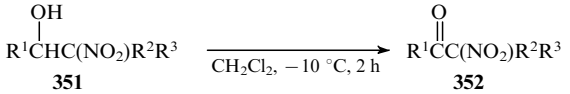
R = Me, $CH_2{=}CH(CH_2)_2$; R′ = $EtCH{=}CHCH_2$;[83] R = Me, Pr$^i$,

Ph$(CH_2)_2$, ; R′ = Me, Et, $(CH_2)_2COOMe$, ;[238]

PCC is pyridinium chlorochromate.

It has been found[239] that both the rate of the oxidation of $EtCH(OH)CH(NO_2)Et$ with pyridinium chlorochromate on silica gel in $CH_2Cl_2$ and the yield of the nitro ketone $EtCOCH(NO_2)Et$ formed in this reaction markedly increase upon ultrasonic treatment: without ultrasound the yield of the product is 60% over a period of 1.5–2.5 h at 25 °C, whereas the reaction carried out with sonication is completed over a period of 20 min at −18 °C (yield 71%).

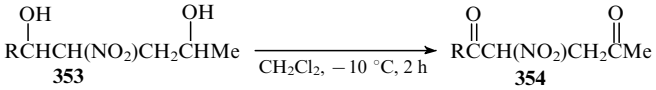
On treatment with $K_2Cr_2O_7$ or $K_2CrO_4$ in the presence of $Bu_4N^+HSO_4^-$, $H_2SO_4$ and $FeSO_4$ at −10 °C, nitro alcohols **351** are readily oxidised to give nitro ketones **352** in high yields (70%–93%),[67] and nitro-diols **353** are easily oxidised to nitro diketones **354**.[155]



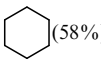

**351** **352**

$R^1$ = Me, Pr$^i$, $C_6H_{13}$, $Ph(CH_2)_2$, $CH_2{=}CH(CH_2)_2$;

$R^2$ = Me, Et, , , $(CH_2)_2COOMe$; $R^3$ = H, Me.



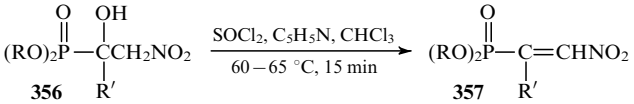

**353** **354**

R = Me (53%), Pr$^i$ (45%), $C_5H_{11}$ (47%), $C_{10}H_{21}$ (58%), (58%), $PhCH_2CH_2$ (70%), $Z$-$Me(CH_2)_7CH{=}CH(CH_2)_7$ (58%), $Me(CH_2)_4CH(NO_2)(CH_2)_2$ (65%).

3-Chloro-6-nitrohexan-2-one has been synthesised in 75% yield by the oxidation of 3-chloro-6-nitrohexan-2-ol with a solution of $Na_2Cr_2O_7$ in $H_2SO_4$ at 10–20 °C for 10 h.[58]

Heating of 1-nitropropan-2-ol with hydrochloric acid (18%–36%) at 95–107 8C for 5–30 h affords lactic acid in 14%–16% yield.[240]

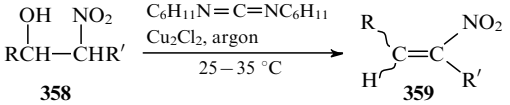
Attempts to dehydrate compounds **356** with phthalic anhydride, $P_2O_5$ or MeCOCl were unsuccessful: the reactions were accompanied by rupture of the C–P bond. Dehydration of these compounds was accomplished by heating them with thionyl chloride in the presence of pyridine. This gave the corresponding unsaturated compounds **357**.[127]




**356** **357**

R, R′ (yield, %): Me, Me (58); Me, Et (69); Et, Pr$^i$ (59); Pr$^i$, Et (53).

Primary and secondary nitro alcohols **358** are readily dehydrated on treatment with cyclohexylcarbodiimide, being converted into mixtures of diastereoisomeric nitroalkenes **359**.[241]

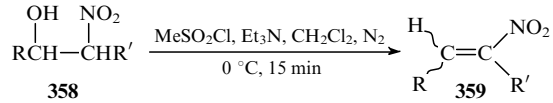



**358** **359**

| R | R′ | Time /h | Yield (%) | Isomeric ratio $Z/E$ |
|---|---|---|---|---|
| H | Me | 3.5 | 35 | |
| Me | Me | 17 | 82 | 70 : 30 |
| H | $C_6H_{13}$ | 2.5 | 60 | |
| Bu | H | 10 | 90 | 83 : 17 |
| see [a] | H | 14 | 75 | |
| Bu$^t$ | H | 17 | 94 | |
| MeCH = CH | H | 60 | 70 | |
| Bu | Me | 17 | 99 | 55 : 45 |
| 2-Furyl | H | 24 | 66 | |

[a] $Me_2C{=}CH(CH_2)_2CH(Me)CH_2$.

The methanesulfonyl chloride–triethylamine system has also been used for the transformation of nitro alcohols **358** into nitroalkenes **359** (yields 30%–80%).[70, 242]

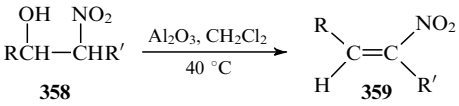



**358** **359**

R = Me, Et, R′ = Me, Et;[242] R = Me, R′ = PhS.[75]

The nitroalkene $Z$-$MeCH(NO_2)CH_2CH_2CH{=}C(NO_2)Me$ is formed in 80% yield when the nitro alcohol $MeCH(NO_2)CH_2CH_2CH(OH)CH(NO_2)Me$ is refluxed with $MeSO_2Cl$ and $Et_3N$ in dichloromethane under nitrogen.[75]

The $E$-isomers of nitroalkenes **359** were synthesised by dehydration of the nitro alcohols **358** over alumina (Brockmann activity I) at 40 °C.[71]

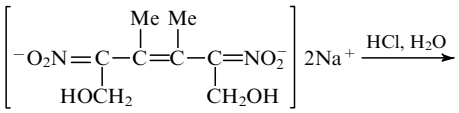



**358** **359**

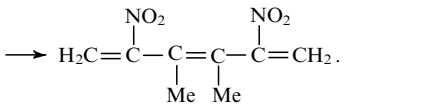
| R | R′ | Time /h | Yield (%) |
|---|---|---|---|
| Me | Me | 8 | 75 |
| Me | Et | 7 | 77 |
| Me | $(CH_2)_4COOMe$ | 7 | 76 |
| Me | $CH_2CH(OH)Me$ | 7 | 73 |
| $EtCH{=}CH(CH_2)_2$ | Me | 7 | 85 |
| $Ph(CH_2)_2$ | Me | 9 | 68 |
| Et | H | 48 | 60 |
| $C_6H_{13}$ | H | 50 | 61 |
| Et | $(CH_2)_6OH$ | 7 | 68 |
| cyclo-$C_6H_{11}$ | $C_5H_{11}$ | 24 | 72 |

The dehydration occurs selectively: when the molecule contains both primary and secondary hydroxy groups, the secondary group is eliminated preferentially.[71]

It is of interest that the dinitro-diol resulting from acidification of the solution of the salt **30** with hydrochloric acid to pH 1 is dehydrated under the reaction conditions to give triene **360** in 26.7% yield.[52]

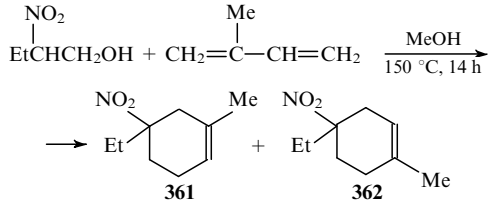



**30**



**360**

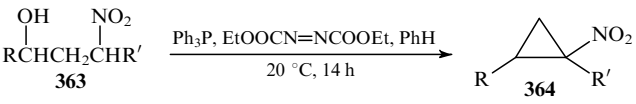
When a mixture of 2-nitrobutan-1-ol and isoprene is kept at 150 °C, the nitro alcohol is dehydrated, and the resulting 2-nitrobut-2-ene reacts *in situ* with isoprene to give a mixture of [4 + 2]-adducts **361** and **362**.[243]



On treatment with potassium hydroxide in $Et_2O$ for 2 h at −15 to −20 °C, the nitro alcohol $O_2NCH_2CH(OH)CH_2Cl$ is converted into the aldehyde $O_2NCH_2CHCH_2CHO$ (yield 21%).[244]

The reactions of 1,1,1-trinitroethanol or trinitromethane with formaldehyde in the presence of $CuSO_4$ followed by treatment of the reaction products with ammonia at 100–105 °C for 8–9 h lead to the same product, 2,2-dinitroethylamine.[98, 245]

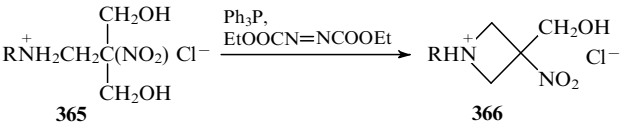
Under conditions of the Mitsunobu reaction (treatment with triphenylphosphine and diethyl azodicarboxylate under an inert atmosphere),[246] γ-nitro alcohols **363** are converted into nitroderivatives of cyclopropane **364**.[247]



| R | R′ | Yield (%) | Ratio *trans* : *cis* |
|---|---|---|---|
| $C_5H_{11}$ | H | 82 | 10 : 1 |
| $C_5H_{11}$ | Me | 87 | 10 : 1 |
| 4-$PhC_6H_4$ | H | 75 | *trans* |
| 4-$MeOC_6H_4$ | H | 92 | 7 : 1 |
| $PhCH_2OCH_2CH=CH$ | H | 64 | *trans* |

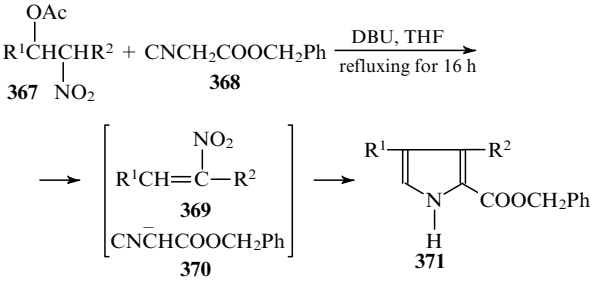
Under the same conditions, $PhCH_2OCH_2CH(OH)$–$CH(CH_2OCH_2Ph)CH_2NO_2$ is converted into 1,3-bis(benzyloxy)-2-nitrocyclopropane in 98% yield (the ratio of the isomers was not determined).[247]

When hydrochlorides **365** are introduced into the Mitsunobu reaction, they are converted into hydrochlorides of 1-alkyl-3-hydroxymethyl-3-nitroazetidines **366**.[229]



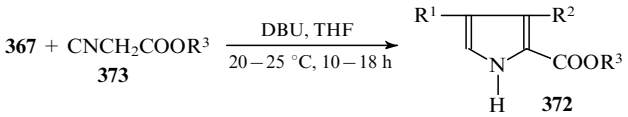
R = Me, Et, Pr, Pr$^i$, Bu, Bu$^t$.

When acetates of nitro alcohols **367** and isonitrile **368** are heated in the presence of DBU, **367** are converted into nitroalkenes **369**, while the isonitrile is deprotonated to give carbanion **370**. The nitroalkenes and the carbanion react to give pyrrole derivatives **371**.[248]



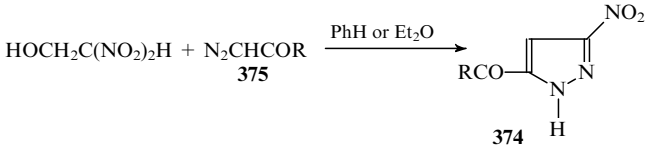
R, R′ (yield, %): Me, Me (72); Et, Me (74); Me, Et (76); Et, Et (74); $(CH_2)_2COOMe$, Me (60); Me, $(CH_2)_2COOMe$ (53).

Pyrrole derivatives **372** have been obtained in high yields (70%–86%) by cyclocondensation of the acetates **367** with alkyl cyanoacetates **373** in the presence of DBU at 20–25 °C.[107]



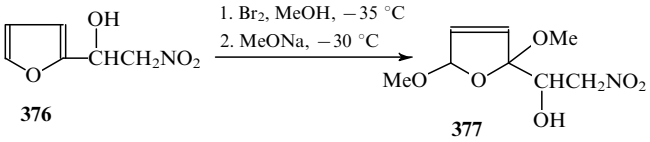
$R^1$ = Et, $(CH_2)_2COOMe$; $R^2$ = Me, Et, $(CH_2)_2COOMe$; $R^3$ = Et, Bu$^t$.

Pyrazole derivatives **374** are formed in the reaction of 2,2-dinitroethanol with diazo compounds **375** in benzene or ether.[249]



R = OEt (PhH, 50 °C, 6 h, 46%); Me (PhH, 50 °C, 4 h, 64%); Ph ($Et_2O$, 36 °C, 14 h, 63%).

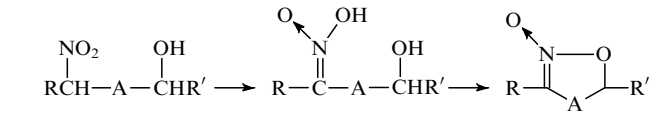
2-(1-Hydroxy-2-nitroethyl)furan **376** reacts with bromine and sodium methoxide to give 2,5-dihydrofuran derivative **377** in 77.5% yield.[142]



2,4,4-Trimethyl-2-nitromethyltetrahydrofuran (yield 30%) is formed when the nitro alcohol $BrCH_2CMe_2CH_2C(OH)(Me)$. $.CH_2NO_2$ is kept over $Al_2O_3$ in benzene at 25 °C.[250]

Treatment of (*S*)-1-nitropentan-1-ol with 30% $H_2O_2$ and $K_2CO_3$ in methanol (0 °C, 24 h) followed by the addition of hydrochloric acid results in the formation of (*S*)-4,5-dihydro-5-methylfuran-2(3*H*)-one (yield 7%).[111]

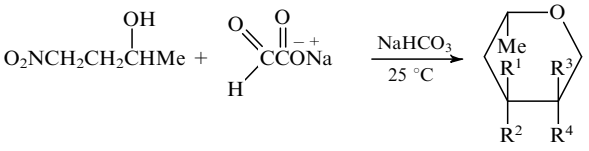
Under the conditions of the Mitsunobu reaction, nitro alcohols **378** cyclise to give either isoxazoline *N*-oxides or dihydro-1,2-oxazine *N*-oxides **379** depending on the mutual arrangement of the nitro and hydroxy groups. When R = $PhSO_2$, the yield of the corresponding isoxazoline is relatively low; in this case, 1-nitro-1-phenylsulfonylcyclopropane is formed as the main reaction product. For the cyclisation products to be formed in high yields, it is necessary that an electron-withdrawing group or a double bond, which stabilise the *aci*-form **380** of the initial compounds, be present in the α-position with respect to the nitro group.[251]



| R | R′ | A | Yield (%) |
|---|---|---|---|
| Ph | H | $CH_2$ | 98 |
| Ph | H | $CH_2CH_2$ | 93 |
| EtOCO | Me | $CH_2CH_2$ | 94 |
| Me | H | $COCMe_2$ | 81 |
| $NO_2$ | H | $CH_2$ | 98 |
| $PhSO_2$ | H | $CH_2$ | 15 |

2-Hydroxy-6-methyl-5-nitrotetrahydropyran has been synthesised in 68% yield by cyclocondensation of acrolein with 1-nitropropan-2-ol in the presence of diethylamine and formic acid at 60–62 °C for 20 h.[252]

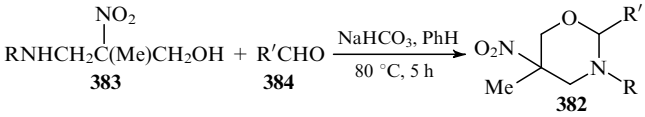
The reaction of 4-nitrobutan-2-ol with sodium glyoxylate in the presence of $Na_2CO_3$ resulted in the isolation of compound **381** as two isomers (**a** and **b**), their yields being 32% and 10%, respectively.[253]



**381a**: $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = OH$;

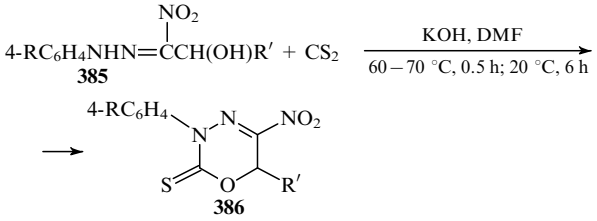
**381b**: $R^1 = NO_2$, $R^3 = OH$, $R^2 = R^4 = H$.

Tetrahydro-1,3-oxazine derivatives **382** have been prepared by refluxing compounds **383** with aldehydes **384** in benzene in the presence of sodium hydrogencarbonate.[254]



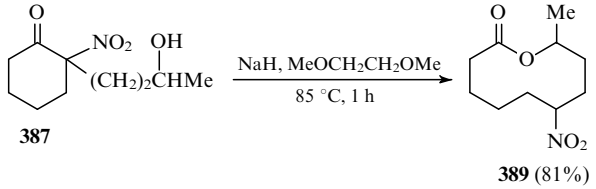
R, R′ (yield, %): $PhCH_2$, Me (80); cyclo-$C_6H_{11}$, Me (60); $PhCH_2$, Ph (60).

Hydrazones **385** react with carbon disulfide in the presence of potassium hydroxide to give 1,3,4-oxadiazine-2-thiones **386**.[159]

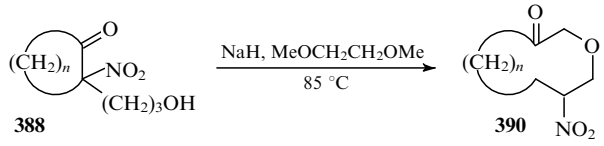


R = H, R′ = Me (71%); R = Me, R′ = H (88%), Me (78%).

On heating with sodium hydride, cyclic ketones **387** or **388** containing nitro and 3-hydroxyalkyl groups in the α-position with respect to the oxo group isomerise with ring expansion giving rise to compounds **389** or **390**.[255]



**389** (81%)

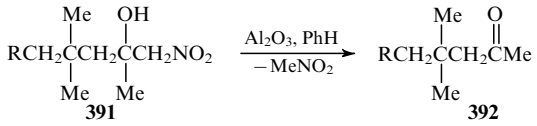


| *n* | Time /min | Yield (%) |
|---|---|---|
| 4 | 45 | 91 |
| 10 | 30 | 87 |

## 5. Cleavage of nitro alcohols

Under certain conditions, β-nitro alcohols (or β-nitro-diols) are cleaved to give the initial carbonyl derivatives and nitro-compounds (or their salts).

In the presence of alumina at ambient temperature, nitro alcohols **391** are cleaved to nitromethane and ketones **392**.[250, 256]



R = Br (20%),[250] $NO_2$ (72%).[256]

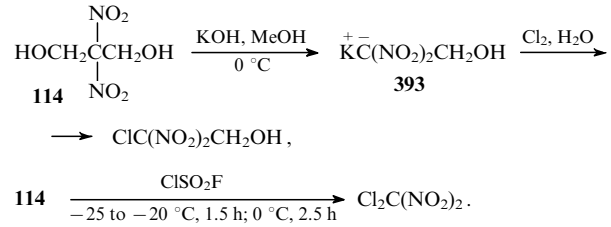
AcONa, BaO or $KNaHPO_4$ can be used instead of $Al_2O_3$.[256]

Benzyltrimethylammonium hydroxide cleaves the nitro alcohol $Me_2C(OH)CH(NO_2)(CH_2)_2NO_2$ on refluxing in methanol for 6 h to give acetone and 1,3-dinitropropane (yield 50%).[257] This process can be carried out in ethanol, dioxane, THF or DMF in the presence of $Na_2CO_3$, $Na_3BO_3$, MgO or $BaCO_3$.[257]

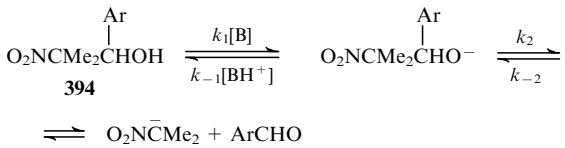
Treatment of the alcohol **107** with sodium dichromate and sulfuric acid results in its cleavage giving formaldehyde and fluorodinitromethane (yield 65%).[258]

When the dinitro-diol **114**[157] or 2,2-dinitropentane-1,3-diol[259] is treated with potassium hydroxide in methanol, the salt $K^+C^-(NO_2)_2CH_2OH$ and $CH_2O$ or MeCHO are formed.

The reaction of compound **114** with potassium hydroxide and sodium carbonate yields salt **393**, which reacts with chlorine to give 2-chloro-2,2-dinitroethanol (overall yield 48%).[157] Treatment of the dinitro-diol **114** with chlorine fluorosulfonate affords dichlorodinitromethane (yield 15%).[260]



The decomposition of nitro alcohols **394** in an aqueous buffer solution with $\mu$ 1.0 D and pH 6.5–8.4 has been studied at 25.3 °C by spectrophotometry. The rate constants for the reaction were determined. It was postulated that deprotonation occurs rapidly, while the rupture of the C–C bond is the rate-determining step of the process.[261]

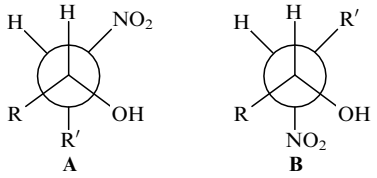


Ar, $10^4\,k$ (litre $mol^{-1}\,s^{-1}$): Ph, 3.02 (pH 4.6–8.4); 4-$MeC_6H_4$, 3.37; 4-$MeOC_6H_4$, 5.09; 4-$ClC_6H_4$, 4.22; 4-$O_2NC_6H_4$, 4.54; 3-$ClC_6H_4$, 3.79; 3-$MeC_6H_4$, 3.07.

## 6. Intramolecular hydrogen bonds in nitro alcohols and nitro-diols

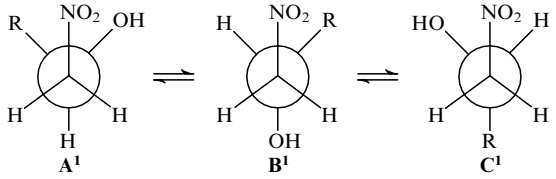
Studies discussing the problems concerning intramolecular hydrogen bonding in nitro alcohols and published before 1977 have been surveyed in a review.[262]

The configurations of the *erythro*- and *threo*-isomers of the nitro alcohols $RCH(OH)CH(NO_2)R'$ (R, R′ = Me, Me; $Pr^i$, Me; $CF_3$, Me; $CCl_3$, Me; $CBr_3$, Me; 4-$O_2NC_6H_4$, Et; 4-$O_2NC_6H_4$, $Pr^i$) have been established by IR and $^1H$, $^{13}C$ and $^{15}N$ NMR spectroscopy. It was found that the *erythro*-isomers occur mostly in the *gauche* conformation **A**, and the *threo*-isomers exist predominantly in the *gauche* conformation **B**. These conformers predominate because they are stabilised by intramolecular hydrogen bonds between OH and $NO_2$ groups.[64]



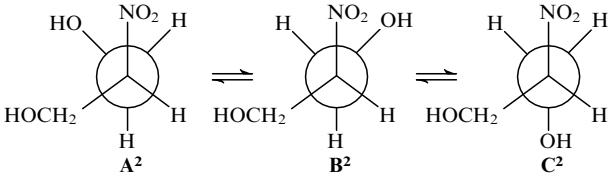
**A** **B**

The conformation equilibria for the alcohols $RCH(OH)CH_2NO_2$ [R = H (**202**), Me, Ph, $CCl_3$] and for 2-nitropropane-1,3-diol **3** have been studied. In the case of the alcohols, equilibrium conformations $\mathbf{A}^1$, $\mathbf{B}^1$ and $\mathbf{C}^1$ were considered.[263]



$\mathbf{A}^1$ $\mathbf{B}^1$ $\mathbf{C}^1$

For the diol **3**, equilibrium conformations $\mathbf{A}^2$, $\mathbf{B}^2$ and $\mathbf{C}^2$ were discussed.



$\mathbf{A}^2$ $\mathbf{B}^2$ $\mathbf{C}^2$

It was found that the nitro alcohol **202** (R = H) exists predominantly in conformations $\mathbf{A}^1$ and $\mathbf{C}^1$. In other cases (R = Me, Ph, $CCl_3$), conformation $\mathbf{C}^1$ predominates. The dihedral angle of 100 – 125 ° is in agreement with the synclinal arrangement of the OH and $NO_2$ groups and with the formation of a hydrogen bond between them.

In the case of the nitro-diol **3**, conformer $\mathbf{A}^2$ with the synclinal arrangement of the $CH_2OH$ and OH groups predominates in the equilibrium. Thus, the interaction between the two hydroxy groups is stronger than that between the OH and $NO_2$ groups.[263]

## IV. Practical use of aliphatic nitro alcohols

Possible applications of aliphatic nitro alcohols have been discussed in a large number of publications. Aliphatic monoatomic and polyatomic nitro alcohols and their derivatives both in a pure state and in various compositions are used most widely as biologically active compounds and as components of rocket fuels or explosives. Other applications of these compounds have also been proposed.

2-Bromo-2-nitropropane-1,3-diol **8** is used most often as a biologically active compound known as 'Biocide'. This nitro-diol as well as nitro alcohols of the general formula $R^1R^2C(OH)CR^3(Br)NO_2$ ($R^1$ = H, alkyl, phenylalkyl; $R^2$ = H; $R^1R^2$ = cycloalkyl; $R^3$ = H, Me, Et, Br) are active against *Staphylococcus aureus* and *Pseudomonas aeruginosa*.[264 – 266] The nitro-diol **8** has been used as an antimicrobial additive [267] and as a component of agents controlling the amount of slime in wood pulp during the manufacture of paper,[265, 268] antimicrobial compositions controlling Chlorella,[269] antiulcer compositions [270] and compositions controlling the development of *Cosmarium*.[271]

It has been proposed to use the bis-formate of nitro-diol **8** and 5-bromo-5-nitro-1,3-dioxane and its 2-substituted derivatives, resulting from condensation of **8** with aldehydes, as bactericides and fungicides;[190, 191, 220] the mixed ester $4\text{-}ClC_6H_4OCH_2$–$C(NO_2)(Br)CH_2OSO_2Me$ has been used as a component of an agent that fully controls the growth of *Erysiphe gramin*.[219]

The nitro-diol **8** has been patented as a deodorant for the toilets of buses and campers,[272] as a deodorant for refuse bins [273] and as a component of compositions removing $NH_3$, $H_2S$ and MeSH from aircraft toilet waste waters.[274]

The use of the nitro-diol **8** and 2-chloro-2-nitropropane-1,3-diol as inhibitors of light- and heat-induced paint changes has been patented.[275]

The polyester obtained by polycondensation of **8** with terephthaloyl dichloride has been claimed as an agent for cotton processing in order to make cotton fabrics resistant against *Escherichia coli* JFO 3134 and *Staphylococcus aureus* JFO 12732 and more comfortable for wearing.[276]

The nitro alcohols $R^1C(NO_2)(X)CH(OH)R^2$ ($R^1$, $R^2$ = H, halogen, substituted alkyl; X = halogen) have been patented as components of microbicide agents, in particular, of those active against *Alternaria tenuis*,[47] *Pseudomonas aeruginosa*,[277] *Plasmodiophora brassicale* [278] and *Baccillus subtilis*.[279]

The nitro alcohols $Cl_3CCH(OH)CH(Br)NO_2$,[7] 2-nitro-1-(2- and 4-pyridyl)propan-1-ols,[280] $EtC(NO_2)(Br)CH_2OH$,[35] 2-nitro-1-(2- and 4-quinolyl)propan-1-ols and 2-nitro-1-(2 and 4-quinolyl)propane-1,3-diols [281] have been used as bactericides and fungicides.

2-Hydroxymethyl-2-nitropropane-1,3-diol **4** has been recommended as an agent for treating water infected with *Streptococcus*.[282]

$FC(NO_2)_2CH_2OH$ **107** suppresses the growth of *Escherichia coli* or *Staphylococcus aureus*, while 2-chloro-2,2-dinitroethanol exhibits antispasmodic activity.[283]

2-Methyl-4-nitropent-3-en-2-ol has been reported to improve blood circulation.[284]

A broad spectrum of biological activities is exhibited by the nitro alcohols $R,R'CH(OH)C(NO_2)(X)$ (R, R′, X = $CCl_3$, Me, Cl; H, Pr, Cl; Me, Cl, Cl; $Pr^i$, H, Br; Bu, H, Br; $C_5H_{11}$, H, Br; $C_6H_{13}$, H, Br; Me, Me, Br; Et, Me, Br; $CCl_3$, Me, Br; H, Et, Br; Me, Et, Br; Me, Br, Br; Et, Br, Br; $Pr^i$, Br, Br.[57]

It has been proposed to use formate, methyl carbonate and some other esters of nitro alcohols $RC(NO_2)_2CH_2OH$ (R = Cl, Br, Me) as bactericides and fungicides.[157, 285]

The compounds $R^1ZNHC(S)OCH(R^2)CR^3R^4NO^2$ ($R^1$, Z, $R^2$, $R^3$, $R^4$ = Ph, $SO_2$, H, H, H; Ph, $SO_2$, H, Br, Me; Ph, CO, H, H, H; $4\text{-}O_2NC_6H_4$, CO, H, Br, Me; $4\text{-}O_2NC_6H_4$, CO, Me, H, Et; $4\text{-}ClC_6H_4$, CO, H, H, H; Ph, CO, H, H, Et; $4\text{-}O_2NC_6H_4$, CO, Me, H, Me; 2-furyl, CO, H, H, H) have been patented as fungicides and bactericides for deodorants, creams and cleaning compositions,[224] while the esters (2-thienyl)$COOCHRCHR'NO_2$ (R = H, Me, Pr, $Pr^i$; R′ = H, Me, Et) have been used as fungicides and bactericides for deodorants, soaps and creams.[286]



R = H, Me, Pr, $Pr^i$; R′ = H, Me, Et.

The nitro alcohols $RR'C(NO_2)(CH_2)_nOH$ (R, R′ = H, Cl, Br, Br; *n* = 1 – 3) and their acetates have been recommended as components of compositions improving the properties of paper, dyes, cosmetics and adhesives.[287]

The addition of the nitro-diol **8** to a mixture used for the development of photographic materials inhibits contamination of waste waters.[288]

The nitro alcohols $RC(NO_2)BrCH(R')OH$ (R = $CH_2OH$, lower alkyls; R′ = H, lower alkyls) increase the stability of dyes in photographic materials with improved photosensitive layers.[289] These nitro alcohols combined with isothiazol-3-one derivatives permit high-quality development of photographic materials even at low pH without decreasing the sensitivity.[290]

The nitro alcohols $RC(NO_2)(Br)CH(OH)R'$ (R, R′ = H, Me, Et) are added to paper pulp in order to improve the properties of photographic paper.[291]

A film coated by a composition of polyamide with 2-hydroxymethyl-2-nitropropane-1,3-diol **4** becomes more resistant to abrasive wear.[292]

The use of the nitro alcohols $R^1R^2C(NO_2)CH(OH)R^3$ [$R^1$, $R^2$ = H, $C_{1-5}$ alkyl, $CH_2OH$; $R^3$ = H, alkyl ($C_{1-5}$)] as components of toning agents protecting colloidal photographic materials from X-rays has been patented.[293]

The nitro-diol **4** has been used as a stabiliser of developers for colour photography.[294] The compound **4** and 2-methyl-2-nitropropane-1,3-diol have been recommended as agents increasing light resistance of dyes.[295]

2-Methyl-2-nitropropan-1-ol can be used for the preparation of polymerisation inhibitors for esters of unsaturated carboxylic acids.[296]

The nitro alcohols $XX'C(NO_2)CH(R)OH$ (X, X′ = Hal; R = H, alkyl) are used to prevent fur formation.[297]

2-Methyl-3-nitropropan-2-ol has been used as a plasticiser for cellulose triacetate.[298] The same nitro alcohol blended with the product of condensation of urea and formaldehyde imparts permanent-press and wrinkle-resistant characteristics to cotton textiles.[299]

The nitro-diols $O_2NC(R)(CH_2OH)_2$ (R = Me, Et, $CH_2OH$) react with melamine at 70 °C and pH 9.5–10 to give adhesive resins that join surfaces under elevated pressures at 250–300 °C.[300]

2-Methyl-2-nitropropan-1-ol has been used to improve adhesion of rubber to a steel cord.[301]

The product of reaction between 2-ethyl-2-nitropropane-1,3-diol and tetraethylenepentamine, which solidifies over a period of 15 min at room temperature, has been recommended as a coating for steel sheets.[302]

The nitro alcohols $RC(NO_2)(X)CH(OH)R'$(R = H, $CH_2OH$, lower alkyls; R′ = H, lower alkyls; X = Hal) have been patented as agents protecting metal working fluids from bacteria and fungi.[303, 304]

2-Nitropropan-1-ol increases the covering power, the time of hardening and the strength of cements.[305]

3-Nitrobutan-2-ol has been used as a selective solvent for dearomatisation of directly distilled petrols.[306]

The nitrate $MeCH(ONO_2)CH(NO_2)Me$ increases the cetane number of diesel fuels.[307]

Halo-substituted nitro alcohols of the general formula $R^1[CH(OH)]_nC(NO_2)(X)CR^2R^3OH$ [$R^1$, $R^2$, $R^3$ = H, alkyl ($C_{1-7}$); X = Cl, Br, I; $n$ = 0, 1], in particular, the nitro-diol **8** have been claimed as antimicrobial agents for hydrocarbon fuels.[308]

Polynitro alcohols and their derivatives are important components of rocket fuels and explosives.

The compound $(O_2N)_2C(F)CH_2OCOOCH_2CF_3$ has been used as a plasticiser for plastic explosives.[205]

The formate, methyl carbonate and some other esters of $MeC(NO_2)_2CH_2OH$ have been used as plasticisers for rocket fuels;[157] the compound $[FC(NO_2)_2CH_2]_2NCOOCH_2C(NO_2)_2F$ has been patented as a plasticiser for explosive compositions.[309]

Among the derivatives of polynitro alcohols proposed as plasticisers for high-energy compositions, the following compounds should be noted: $[EtOCOCH_2C(NO_2)_2F]_2Me$,[187] $(RO)_2CHMe$, $MeCH(OR)OCH_2C(NO_2)_2R'$ [R = $CH_2C(NO_2)_2F$, R′ = F, Me, $NO_2$][186] $[RC(NO_2)_2CH_2O]_2CH_2$ (R = Me,[182, 310] F,[311] $NO_2$[182]), $[RC(NO_2)_2CH_2O]-CH_2[OCH_2C(NO_2)_2R']$ (R, R′ = $NO_2$, Me;[182] Me, Et[310]), $RC(NO_2)_2CH_2OC[=CHCOOCH_2C(NO_2)_2R]COOCH_2(NO_2)_2R'$ (R = R′ = H, F, Me, $NO_2$).[218]

The use of the orthoester $[FC(NO_2)_2CH_2O]_2CH-[OCH(Me)C(NO_2)_2F]$ as a co-plasticiser in high-energy compositions has been patented;[312] the orthocarbonate $[FC(NO_2)_2CH_2O]_3COCH_2C(NO_2)_3$ has been used as a plasticiser and as an energetic explosive.[211]

2-Fluoro-2,2-dinitroethanol **107** can be used as a plasticiser and a binding agent for rocket fuels and explosive compositions;[91] the ether $(O_2N)_3CCH_2OC(NF_2)_3$ can be used as a plasticiser and an oxidant for rocket fuels.[180]

The following compounds have been patented as energetic binding agents for high-energy compositions: the vinyl ethers $RC(NO_2)_2CH_2OCH=CH_2$ (R = F, $NO_2$)[313] and $FC(NO_2)_2-CH_2C(NF_2)_2CH_2OCH=CH_2$,[213] nitroformals synthesised by polycondensation of the tetranitro-diol $[HOCH_2C(NO_2)_2CH_2]_2$ with formaldehyde[185] or by polymerisation of the epoxide $FC(NO_2)_2CH_2OCH_2\underline{CHOC}H_2$,[314 314] and esters formed by 2,2-dinitropropane-1,3-diol **114** with oxalic, malonic or fumaric acids.[315]

The polyester resulting from the reaction of the dichloride $[ClCOCH_2CH_2]_2C(NO_2)_2$ with the diol $[HOCH_2C(NO_2)_2CH_2]_2O$ has been patented as a component of energy-producing compositions.[316]

The nitro-derivatives $[RC(NO_2)_2CH_2O]_2C=S$ (R = F, Me, $NO_2$) have been used as intermediate compounds in the synthesis of energetic explosives.[212]

## References


1. D Seebach, E W Colvin, F Lehr, T Weller *Chimia* **33** 1 (1979)
2. G A Shvekhgeimer, N F Pyatakov, S S Novikov *Usp. Khim.* **28** 466 (1959)
3. L M Kozlov, V I Burmistrov *Nitrospirty i Ikh Proizvodnye* (Nitro Alcohols and Its Derivatives) (Kazan': Kazan' Chemical Engineering Institute, 1960)
4. S S Novikov, G A Shvekhgeimer, V V Sevost'yanova, V A Shlyapochnikov, in *Khimiya Alifaticheskikh i Alitsiklicheskikh Nitrosoedinenii* (The Chemistry of Aliphatic and Alicyclic Nitro Compounds) (Moscow: Khimiya, 1974) p. 56
5. Jpn. Appl. 73-72 108; *Chem. Abstr.* **80** 59 447 (1974)
6. R Yang, B Wu, Zh Ji *Huaxue Shiji* 116 (1982); *Chem. Abstr.* **97** 109 517 (1982)
7. Jpn. Appl. 77-03 011; *Chem. Abstr.* **87** 52 745 (1977)
8. US P. 3 652 686; *Chem. Abstr.* **76** 139 919 (1972)
9. Jpn. Appl. 74-70 911; *Chem. Abstr.* **81** 119 937 (1974)
10. Pol. P. 100 819; *Chem. Abstr.* **92** 75 835 (1980)
11. Jpn. Appl. 81-113 745; *Chem. Abstr.* **96** 51 803 (1982)
12. Pol. P. 120 287; *Chem. Abstr.* **99** 157 826 (1983)
13. BDR P. 3 814 772; *Chem. Abstr.* **112** 216 218 (1990)
14. Eur. P. 3460; *Chem. Abstr.* **92** 6045 (1980)
15. D Seebach, P Knochel *Helv. Chim. Acta* **67** 261 (1984)
16. L T Eremenko, G V Oreshko, G V Lagodzinskaya, V A Zabrodin *Izv. Akad. Nauk SSSR, Ser. Khim.* 634 (1990)[a]
17. L W Herman, J W ApSimon *Tetrahedron Lett.* **26** 1423 (1985)
18. US P. 4 922 030; *Chem. Abstr.* **113** 151 820 (1990)
19. Jpn. Appl. 01-132 549; *Chem. Abstr.* **111** 173 606 (1989)
20. Czech. P. 229 101; *Chem. Abstr.* **106** 32 360 (1987)
21. T I Gibina *Tr. Molodykh Uchenykh Saratovsk. Univ., Vyp. Khim.* (2) 177 (1971) (Transactions of Young Scientists of Saratov University, Issue Chem.); *Ref. Zh. Khim.* 2 Zh 272 (1973)
22. I A Markushina, T I Gibina *Metody Polucheniya Khim. Reakt. Prep.* (26) 297 (1974)
23. A Solladie-Cavallo, G Lapitais, P Buchert, A Klein, S Colonna, A Manfred *J. Organomet. Chem.* **330** 357 (1987)
24. Czech. P. 164 305; *Chem. Abstr.* **86** 105 929 (1977)
25. V Simanek, V Preininger, A Klasek, J Jurina *Heterocycles* **4** 1263 (1976)
26. L Kniezo, P Kristian, S Velebny *Collect. Czech. Chem. Commun.* **43** 1917 (1978)
27. R H Wollenberg, S J Miller *Tetrahedron Lett.* 3219 (1978)
28. K Irie *Nippon Kagaku Kaishi* (1) 150 (1983); *Chem. Abstr.* **98** 160 318 (1983)
29. US P. 4 581 178; *Chem. Abstr.* **105** 78 533 (1986)
30. N P Rumyantsev, K S Rumyantseva *Uch. Zap. Mordovsk. Univ.* (81) 70 (1971); *Chem. Abstr.* **78** 57911 (1973)
31. I S Korsakova, A I Ivanov, R A Sadykov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **17** 1174 (1974)
32. A V Fokin, V A Komarov, A I Rapkin, K V Frosina, K I Posevina, O V Verenkin *Izv. Akad. Nauk SSSR, Ser. Khim.* 1922 (1978)[a]
33. A V Fokin, A I Rapkin, T M Potarina, K I Posevina, O V Verenkin *Izv. Akad. Nauk SSSR, Ser. Khim.* 1661 (1980)[a]

34. V P Solov'ev, D B Kireev, O A Raevskii, L A Chepakova, V K Brel', I V Martynov *Zh. Obshch. Khim.* **61** 212 (1991) [b]
35. BRD P. 2 054 887; *Chem. Abstr.* **77** 33 974 (1972)
36. B Kedzierski, H Piotrowska *Rocz. Chem.* **46** 1421 (1972)
37. M A Ishchenko, I V Troitskaya, M D Boldyrev, B V Gidaspov *Zh. Org. Khim.* **12** 1128 (1976) [c]
38. Rum. P. 62 580; *Chem. Abstr.* **98** 106 789 (1983)
39. S K Ishkina *Neft' i Gaz* (Oil and Gas) (Moscow: Moscow Institute of Petrochemical and Gas Industry, 1974) p. 143
40. M Karaivanova *God. Vissh. Khim.-Teknol. Inst., Burgas, Bulg.* **13** 81 (1979)
41. V K Polovnyak, M V Kolpashchikov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **18** 497 (1978)
42. P Toromanova, I Mladenov, M Bosukova *God. Vissh. Khim.-Teknol. Inst., Burgas, Bulg.* **17** 43 (1982)
43. Jpn. Appl. 71-43 368; *Chem. Abstr.* **76** 45 713 (1972)
44. BRD P. 2 603 076; *Chem. Abstr.* **86** 4928 (1977)
45. US P. 4 496 772; *Chem. Abstr.* **102** 148 725 (1985)
46. L T Eremenko, F Ya Natsibullin, G V Oreshko *Izv. Akad. Nauk SSSR, Ser. Khim.* 832 (1973) [a]
47. BRD P. 3 622 976; *Chem. Abstr.* **108** 182 219 (1988)
48. N Ono, H Miyake, M Eujii, A Kaji *Tetrahedron Lett.* **24** 3477 (1983)
49. Ph T Berkowitz, K Baum *J. Org. Chem.* **45** 4853 (1980)
50. L T Eremenko, G V Oreshko *Izv. Akad. Nauk SSSR, Ser. Khim.* 1174 (1973) [a]
51. L A Bocharova, A S Polyanskaya, L D Zhuchkova, in *XXVI Gertsenovskie Chteniya. Khimiya* (XXVI Gertsen's Readings. Chemistry) (Leningrad: Leningrad State Pedagogical Institute, 1973) No. 2, p. 44
52. L Ya Zagibalova, E S Lipina, G A Berkova, T Ya Paperno, V V Perekalin, V P Pozdnyakov *Zh. Org. Khim.* **17** 2302 (1981) [c]
53. R I Brodina, E S Lipina, V V Perekalin *Zh. Org. Khim.* **12** 2095 (1976) [c]
54. N Ono, I Hamamoto, A Kamimura, A Kaji, R Tamura *Synthesis* 258 (1987)
55. A Kamimura, N Ono *J. Chem. Soc., Chem. Commun.* 1278 (1988)
56. A Barco, S Benetti, G P Pollini, G Spalluto, V Zanirato *Tetrahedron Lett.* **32** 2517 (1991)
57. N G Clark, B Croshaw, B E Leggetter, D J Spooner *J. Med. Chem.* **17** 977 (1974)
58. I E Chlenov, N S Morozova, V A Tartakovskii *Izv. Akad. Nauk SSSR, Ser. Khim.* 216 (1973) [a]
59. J Kochany, H Piotrowska *Bull. Acad. Pol. Sci., Ser. Sci. Chem.* **24** 861 (1976)
60. D Seebach, A K Beck, T Mukhopadhyay, E Thomas *Helv. Chim. Acta* **65** 1101 (1982)
61. Th Kotler, G Echten-Deckert, K Sandhoff *Tetrahedron* **50** 13425 (1994)
62. Yu Baskov, D Aleksiev, I Mladenov, E Lipina *God. Vissh. Khim.-Teknol. Inst., Burgas, Bulg.* **9** 347 (1972); *Chem. Abstr.* **82** 124 645 (1975)
63. US P. 4 004 023; *Chem. Abstr.* **86** 155 357 (1977)
64. Ch A Kingsbury, A E Sopchik, S Rajan *J. Chem. Soc., Perkin Trans. 2* 867 (1982)
65. Th G Dekker, F O Snyckers, J L Du Preez *S. Afr. J. Chem.* **37** 198 (1984); *Chem. Abstr.* **102** 131606 (1985)
66. A K Beck, D Seebach *Chem. Ber.* **124** 2897 (1991)
67. G Rosini, R Ballini, P Sorrenti, M Petrini *Synthesis* 607 (1984)
68. R Ohrlein, V Jager *Tetrahedron Lett.* **29** 6083 (1988)
69. G Rosini, R Ballini, P Sorrenti *Synthesis* 1014 (1983)
70. W R Bowman, S W Jackson *Tetrahedron* **46** 7313 (1990)
71. R Ballini, R Castagnani, M Petrini *J. Org. Chem.* **57** 2160 (1992)
72. J-M Melot, F Texier-Boullet, A Foucaud *Tetrahedron. Lett.* **27** 493 (1986)
73. A I Razumov, B G Liorber, Z M Khamatova, M P Sokolov, T V Zykova, M P Alparova *Zh. Obshch. Khim.* **47** 567 (1977)
74. Ch-Qi Shin, Ya Yonezawa, H Narukawa, K Nanjo, J Yoshimura *Bull. Chem. Soc. Jpn.* **45** 3595 (1972)
75. G M Barrett, G G Graboski, M A Russell *J. Org. Chem.* **51** 1012 (1986)
76. I V Martynov, E V Stoyankova, A I Yurtanov *Zh. Org. Khim.* **18** 1849 (1982)
77. R Henning, F Lehr, D Seebach *Helv. Chim. Acta* **59** 2213 (1976)
78. G M Barrett, Ch Robyr, Ch D Spilling *J. Org. Chem.* **54** 1233 (1989)
79. S Tanaka, Sh Kohmoto, M Yamamoto, K Yamada *Nippon Kagaky Kaishi* 1742 (1989); *Ref. Zh. Khim.* 10 Zh 57 (1990)
80. Pol. P. 96 715; *Chem. Abstr.* **90** 103 804 (1979)
81. E W Colvin, D Seebach *J. Chem. Soc., Chem. Commun.* 689 (1978)
82. D Seebach, A K Beck, F Lehr, Th Weller, E W Colvin *Angew. Chem.* **93** 422 (1981)
83. E W Colvin, A K Beck, D Seebach *Helv. Chim. Acta* **64** 2264 (1981)
84. R Ballini, M Petrini *Synthesis* 849 (1986)
85. US P. 3 657 357; *Chem. Abstr.* **77** 48 041 (1972)
86. N Ono, H Kawamura, M Bougauchi, K Marujama *Tetrahedron* **46** 7483 (1990)
87. S-i Kiyooka, T Tsutsui, H Maeda, Yu Kaneko, K Isobe *Tetrahedron Lett.* **36** 6531 (1995)
88. V M Belikov, Yu N Belokon', N G Faleev, V A Maksakov *Tetrahedron* **28** 3789 (1972)
89. B Stojakovic, N Stojanovic, S Petrovic *Naucno-Tekn. Pregl.* **40** (10) 41 (1990)
90. F M Mukhametshin *Zh. Org. Khim.* **7** 1993 (1971) [c]
91. US Appl. 1223; *Chem. Abstr.* **120** 54 184 (1994)
92. S A Shackelford, R R Mc Guire, R E Cochoy *J. Org. Chem.* **57** 2950 (1992)
93. V Grakauskas *J. Org. Chem.* **38** 2999 (1973)
94. B S Fedorov, N I Golovina, L S Barinova, V V Arakcheeva, G V Lagodzinskaya, M V Loginova, R F Trofimova, V Z Laishev, V F Lazarev, S P Smirnov, I Sh Abdrakhmanov, A I Firkin, L O Atovmyan *Izv. Akad. Nauk SSSR, Ser. Khim.* 2755 (1992) [a]
95. G V Nekrasova, E S Lipina, L Ya Zagibalova, V V Perekalin *Zh. Org. Khim.* **17** 711 (1981) [c]
96. B S Fedorov, N I Golovina, L S Barinova, R F Trofimova, V A Arakcheeva, L O Atovmyan *Izv. Akad. Nauk SSSR, Ser. Khim.* 830 (1991) [a]
97. A A Malik, T G Archibald, D Tzeng, L S Garver, K Baum *J. Fluorine Chem.* **43** 291 (1989)
98. USSR P. 1 696 424; *Chem. Abstr.* **116** 255 172 (1992)
99. M Kwasny, M Syczewski *Bull. Wojsk. Akad. Tech.* **29** 165 (1980); *Chem. Abstr.* **95** 61 164 (1984)
100. T A Ainscow, M R Belmont, J L Henshall, R M Hooper, D J Simmonds *Tetrahedron* **43** 115 (1987)
101. A I Sitkin, O Z Safiulina, R F Chernyaeva, A D Nikolaeva *Zh. Org. Khim.* **11** 452 (1975) [c]
102. A I Sitkin, G M Rotova, A D Nikolaeva, in *Sb. Nauch. Tr. Kuzbassk. Politekh. In-ta* (Collection of Scientific Works of Kuzbas Polytechnic Institute) (36) 62 (1971); *Ref. Zh. Khim.* 15 Zh 221 (1972)
103. US P. 3 759 998; *Chem. Abstr.* **79** 125 813 (1973)
104. I G Tishchenko, V V Berezovskii, V N Lapko *Vestn. Belorussk. Univ., Ser. 2* (3) 11 (1973)
105. V F Belyaev, V I Grushevich, V P Prokopovich *Zh. Org. Khim.* **12** 32 (1976) [c]
106. US P. 3 783 144; *Chem. Abstr.* **80** 70 328 (1974)
107. R Ballini, M Petrini, G Rosini *Tetrahedron* **46** 7531 (1990)
108. R Ohrlein, W Schwab, R Ehrler, V Jager *Synthesis* 538 (1986)
109. M E Sitzmann, W H Gilligan *J. Heterocycl. Chem.* **23** 81 (1986)
110. US Appl. 875 159; *Chem. Abstr.* **107** 25 638 (1987)
111. Th Hafner, H-U Reissig *Liebigs Ann. Chem.* 937 (1989)
112. A Guarna, E G Occhiato, L M Spinetti, M E Vallecchi, D Scarpi *Tetrahedron* **51** 1755 (1995)
113. I F Sokovishina, V V Perekalin *Zh. Org. Khim.* **10** 724 (1974) [c]
114. I F Sokovishina, in *Sinteticheskie Issledovaniya Nitrosoedinenii Aminokislot* (Synthetic Investigation of Nitro Compounds of Amino Acids) (Leningrad: Leningrad State Pedagogical Institute, 1983) p. 7; *Chem. Abstr.* **99** 212 217 (1983)
115. R Schneider, Ph Gerardin, B Loubinoux *Tetrahedron* **49** 3117 (1993)
116. E A Avetisyan, L A Simonyan, N P Gambaryan *Izv. Akad. Nauk SSSR, Ser. Khim.* 2742 (1972) [a]
117. A L Fridman *Zh. Org. Khim.* **12** 237 (1976) [c]

118. R Z Fakhrutdinov, V A Voronkova, T R Bankovskaya, L M Kozlov, in *Neftepererabotka i Neftekhimiya* (Petroleum Processing and Petroleum Chemistry) (Kazan': Kazan' Chemical Engineering Institute, 1975) No. 3, p. 61; *Ref. Zh. Khim.* 21 B 918 (1976)
119. R Z Fakhrutdinov, V A Voronkova, L M Kozlov, G A Prostokvashina, in *Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov* (The Chemistry and Technology of Organoelement Compounds and Polymers) (Kazan': Kazan' Chemical Engineering Institute, 1976) No. 5, p. 62; *Ref. Zh. Khim.* 13 B 1061 (1977)
120. V I Burmistrov, R Z Fakhrutdinov, V A Voronkova *Zh. Org. Khim.* **8** 1349 (1972) [c]
121. USSR P. 407 883; *Ref. Zh. Khim.* 24 N 47 (1974)
122. L T Eremenko, R G Gafurov, L A Lisina *Izv. Akad. Nauk SSSR, Ser. Khim.* 724 (1972) [a]
123. V L Golod, E L Golod, B V Gidaspov, L I Bagal *Zh. Org. Khim.* **12** 542 (1976) [c]
124. E Kaji, A Igarashi, Sh Zen *Bull. Chem. Soc. Jpn.* **49** 3181 (1976)
125. US P. 3 950 385; *Chem. Abstr.* **85** 20 610 (1976)
126. P Golding, J L Powell, J H Ridd *J. Chem. Soc., Perkin Trans. 2* 813 (1996)
127. G M Baranov, V V Perekalin *Zh. Obshch. Khim.* **57** 793 (1987) [b]
128. USSR P. 228 013; *Chem. Abstr.* **77** 19 197 (1972)
129. T Mukaiyama, E Hata, T Yamada *Chem. Lett.* 505 (1995)
130. V N Yandovskii, I I Ryabinkin, I V Tselinskii *Zh. Org. Khim.* **16** 2084 (1980) [c]
131. A A Stotskii, N P Tkacheva *Zh. Org. Khim.* **12** 235 (1976) [c]
132. P A Wehrli, B Schaer *J. Org. Chem.* **42** 2939 (1977)
133. I G Mursakulov, A A Azimzadze, A G Talybov, M R Aslanova *Zh. Org. Khim.* **26** 909 (1990) [c]
134. A S Demir, C Tanyeli, A S Mahasneh, H Aksoy *Synthesis* 155 (1994)
135. Rum. P. 60 029; *Chem. Abstr.* **88** 190 067 (1978)
136. D Kreile, L Krumina, K Ziemelis, A Gutmanis, U Tomsons, V A Slavinskaya *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 464 (1982)
137. US P. 5 099 067; *Chem. Abstr.* **116** 255 300 (1992)
138. J O Osby, B Ganem *Tetrahedron Lett.* **26** 6413 (1985)
139. US P. 4 924 029; *Chem. Abstr.* **113** 171 484 (1990)
140. S G Harsy *Tetrahedron* **46** 7403 (1990)
141. A A Ponomarev, V N Dyukareva *Zh. Org. Khim.* **8** 527 (1972) [c]
142. O Achmatowicz, G Grynkiewicz *Rocz. Chem.* **50** 719 (1976)
143. H Hirata, S Nakasato, K Higushi, M Okimura, T Shimada *Yukagaku* **29** (5) 336 (1980); *Ref. Zh. Khim.* 15 Zh 68 (1981)
144. Fr. P. 2 577 242; *Chem. Abstr.* **108** 111 810 (1988)
145. Eur. P. 287 419; *Chem. Abstr.* **110** 47 418 (1989)
146. E K Ostis, L A Kotok, L N Ozerova, in *VIII Vsesoyuzn. Soveshch. po Elektrokhimii Organicheskikh Soedinenii* (The VIII All-Union Meeting on Electrochemistry of Organic Compounds) (Riga: Zinatne, 1973) p. 104; *Chem. Abstr.* **82** 36 578 (1975)
147. V T Novikov, I A Avrutskaya, M Ya Fioshin, V M Belikov, K K Babievskii *Elektrokhimiya* **12** 1061 (1976) [d]
148. V T Novikov, L A Ratnikova, I A Avrutskaya, M Ya Fioshin, V M Belikov, K K Babievskii *Elektrokhimiya* **12** 1066 (1976) [d]
149. Ya I Tur'yan *Zh. Obshch. Khim.* **45** 2106 (1975) [b]
150. N A Sokolov, Z S Baranova, M A Sevost'yan *Vestn. Akad. Nauk Bel. SSR, Ser. Khim.* 107 (1972)
151. Jpn. Appl. 76-04 980; *Chem. Abstr.* **86** 16 404 (1977)
152. O Achmatowicz, G Grynkiewicz, A Zamojski *Rocz. Chem.* **49** 1549 (1975)
153. T Hino, K Nakakyama, M Taniguchi, M Nakagawa *J. Chem. Soc., Perkin Trans. 1* 1687 (1986)
154. M Eyer, D Seebach *J. Am. Chem. Soc.* **107** 3601 (1985)
155. R Ballini, G Bosica *J. Org. Chem.* **59** 5466 (1994)
156. USSR P. 379 557; *Ref. Zh. Khim.* 9 N 26 (1974)
157. US P. 3 901 974; *Chem. Abstr.* **83** 178 290 (1975)
158. Eur. P. 206 173; *Chem. Abstr.* **106** 137 930 (1978)
159. A I Dychenko, P S Pel'kis *Ukr. Khim. Zh.* **47** 634 (1981)
160. K H Chung, I G Park *J. Korean. Chem. Soc.* **37** 244 (1993); *Chem. Abstr.* **118** 213 587 (1993)
161. K S Rumyantseva, N P Rumyantsev, G E Chekmaeva, R P Kirlyanova *Uch. Zap. Mordovsk. Univ.* (81) 75 (1971); *Chem. Abstr.* **78** 57 948 (1973)
162. I V Troitskaya, M D Boldyrev, B V Gidaspov *Zh. Org. Khim.* **10** 1626 (1974) [c]
163. USSR P. 434 080; *Ref. Zh. Khim.* 16 O 396 (1975)
164. G R Newkome, G R Baker, R K Behera, A L Johnson, C N Moorefield, C D Weis, W-J Cao, J K Young *Synthesis* 839 (1991)
165. A V Fokin, A N Voronkov, V I Shevchenko, V A Komarov *Izv. Akad. Nauk SSSR, Ser. Khim.* 461 (1976) [a]
166. A V Fokin, V I Shevchenko, A N Voronkov, E I Lyubimova *Izv. Akad. Nauk SSSR, Ser. Khim.* 455 (1979) [a]
167. A V Fokin, A N Voronkov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2620 (1979) [a]
168. USSR P. 492 513; *Chem. Abstr.* **84** 58 623 (1976)
169. E V Chirkunov, L M Kozlov, M M Kukovitskii, T V Konstantinova, in *Khimicheskaya Pererabotka Nefti i Gaza* (Chemical Processing of Oil and Gas) (Kazan': Kazan' Chemical Engineering Institute, 1978) No. 6, p. 56
170. L M Kozlov, L A Koroleva *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **18** 1191 (1975)
171. US P. 3 636 060; *Chem. Abstr.* **76** 994 92 (1972)
172. US P. 3 652 600; *Chem. Abstr.* **76** 153 560 (1972)
173. A V Fokin, V A Komarov, A N Voronkov, V I Shevchenko, E I Lyubimova *Izv. Akad. Nauk SSSR, Ser. Khim.* 1448 (1975) [a]
174. M S Malinovskii, A M Korchagina, A G Yudasina, V A Zinovkina *Ukr. Khim. Zh.* **39** 365 (1973)
175. USSR P. 334 816; *Chem. Abstr.* **78** 124 024 (1973)
176. D A Cichra, W M Koppes, H G Adolph *J. Chem. Eng. Data* **31** 372 (1986)
177. K Baum, D A Lerdal, J S Horn *J. Org. Chem.* **43** 203 (1978)
178. R E Cochoy, R R Mc Guire, S A Shackelford *J. Org. Chem.* **55** 1401 (1990)
179. S K Petrova, R Z Fakhrutdinov, L M Kozlov, P T Belikov *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **17** 1116 (1974)
180. US P. 3 692 837; *Chem. Abstr.* **77** 151 449 (1972)
181. K Klager, R R Rindon *Int. Jahrestag.-Fraunhofer-Inst. Treib-Explosivst.* (18) 28/1 (1987); *Chem. Abstr.* **108** 78 232 (1988)
182. US Appl. 43 268; *Chem. Abstr.* **108** 24 189 (1988)
183. US Appl. 45 3674; *Chem. Abstr.* **99** 178 418 (1983)
184. M E Sitzmann, R D Gilardi *J. Fluorine Chem.* **63** 203 (1993); *Chem. Abstr.* **120** 30 446 (1994)
185. US Appl. 343 810; *Chem. Abstr.* **98** 74 898 (1983)
186. US P. 3 962 349; *Chem. Abstr.* **85** 62 649 (1976)
187. US P. 4 424 398; *Chem. Abstr.* **100** 88 196 (1984)
188. K Shiino, Sh Fujiwara, M Kusakabe *Kogyo Kayaku* **35** 113 (1974); *Chem. Abstr.* **85** 194 924 (1976)
189. B A Arbuzov, E N Klimovitskii, L K Yuldasheva, A V Remizov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2746 (1975) [a]
190. US P. 4 025 533; *Chem. Abstr.* **87** 68 370 (1977)
191. BRD P. 2 263 206; *Chem. Abstr.* **82** 120 643 (1974)
192. BRD P. 2 407 289; *Chem. Abstr.* **81** 152 240 (1974)
193. Yu V Baskov, V V Perekalin, H Piotrovska, T Urbanski *Bull. Acad. Pol. Sci., Ser. Sci. Chem.* **19** 681 (1971)
194. B Kedzierski, H Piotrovska, T Urbanski, A Borys *Rocz. Chem.* **46** 1559 (1972)
195. B Krassowska, M Stec, Z Eckstein *Pol. J. Chem.* **52** 2483 (1978)
196. A I Shkrebets, Z I Zelikman, V G Kul'nevich, G N Soltovets, R Z Fakhrutdinov *Khim. Geterotsikl. Soedin.* 1159 (1972) [e]
197. N A Sokolov, N A Voishnits, L S Nemtsova, A G Zhuravlev *Vestn. Belorussk. Univ., Ser. 2* (2) 20 (1973)
198. Pol. P. 96 714; *Chem. Abstr.* **90** 103 969 (1979)
199. S F Mel'nikova, I N Aizenshtadt, L I Bagal *Zh. Org. Khim.* **7** 2136 (1971) [c]
200. H Piotrowska, T Urbanski, I Wolochowicz *Bull. Acad. Pol. Sci., Ser. Sci. Chem.* **19** 591 (1971)
201. A Kamars, A Terauda, E Svarks *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* 136 (1978)
202. R Vilceanu, I Neda *Phosphorus Sulfur Relat. Elem.* **8** 131 (1980); *Chem. Abstr.* **93** 204 756 (1980)
203. I Neda, Th Kaukorat, A Fischer, P G Jones *Phosphorus Sulfur Silicon Relat. Elem.* **85** 153 (1993); *Chem. Abstr.* **121** 83 470 (1994)
204. A A Bolotov, K A V'yunov, A I Ginak, I V Krauklish *Zh. Prikl. Khim.* **54** 1656 (1981) [f]
205. US Appl. 641 320; *Chem. Abstr.* **87** 67 846 (1977)
206. Fr. P. 2 327 228; *Chem. Abstr.* **88** 89 135 (1978)
207. H M Peters, R L Simon, L O Ross, D L Ross, M E Hill *J. Chem. Eng. Data* **20** 113 (1975); *Chem. Abstr.* **82** 86 042 (1975)

208. H M Peters, R L Simon, L O Ross, D L Ross, M E Hill *J. Chem. Eng. Data* **20** 118 (1975); *Chem. Abstr.* **82** 86 046 (1975)
209. US Appl. 224 776; *Chem. Abstr.* **96** 34 590 (1982)
210. W H Gilligen, S L Stafford *Synthesis* 600 (1979)
211. US Appl. 467 713; *Chem. Abstr.* **100** 9526 (1984)
212. US Appl. 235 305; *Chem. Abstr.* **96** 54 805 (1982)
213. US P. 3 700 723; *Chem. Abstr.* **78** 15 549 (1973)
214. G V Oreshko, L I Berezina, L T Eremenko *Izv. Akad. Nauk SSSR, Ser. Khim.* 1175 (1973) [a]
215. US P. 3 770 806; *Chem. Abstr.* **82** 158 367 (1975)
216. US P. 3 781 335; *Chem. Abstr.* **80** 70 364 (1974)
217. Can. P. 977 363; *Chem. Abstr.* **84** 164 187 (1976)
218. US P. 3 872 159; *Chem. Abstr.* **83** 118 054 (1975)
219. BRD P. 3 835 742; *Chem. Abstr.* **114** 23 969 (1991)
220. Eur. P. 34 684; *Chem. Abstr.* **96** 68 312 (1982)
221. R E Cochoy, R R Mc Guire *J. Org. Chem.* **37** 3041 (1972)
222. S Abe, K Namba *Koguo Kayaku* **35** 19 (1974); *Chem. Abstr.* **86** 15 994 (1977)
223. L M Kozlov, N A Solodova, M M Zabarko *Reaktsiya 1,3-Fenilendiizotsianata s 2-Nitro-2-metilpropan-1,3-diolom* (The Reaction of 1,3-Phenylenediisocyanate with 2-Methylpropane-2-nitro-1,3-diol) Article deposited at the ONIITEKhIM, No. 643khp-D82, Cherkassy, 1982; *Chem. Abstr.* **100** 192 353 (1984)
224. BRD P. 2 304 581; *Chem. Abstr.* **81** 135 773 (1974)
225. N Egger, L Hoesch, A S Dreiding *Helv. Chim. Acta* **65** 2558 (1982)
226. S Grudzinski, M Gronek, U Zalega *Acta Pol. Pharm.* **33** 571 (1976); *Chem. Abstr.* **86** 170 767 (1977)
227. L T Eremenko, D A Nesterenko, O M Savchenko *Izv. Akad. Nauk SSSR, Ser. Khim.* 1661 (1974) [a]
228. H Piotrowska, T Urbanski, W Sienicki *Rocz. Chem.* **47** 193 (1973)
229. US P. 5 336 784; *Chem. Abstr.* **121** 300 750 (1994)
230. L S Simonenko, I S Korsakova, S S Novikov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2333 (1972)
231. H Piotrowska, T Urbanski, K Wejroch-Matacz *Rocz. Chem.* **45** 1267 (1971)
232. H Piotrowska, T Urbanski, K Wejroch-Matacz *Rocz. Chem.* **45** 2107 (1971)
233. D Ranganathan, S Ranganathan, Sh Bamesai, S Mehrotra, P Ramachandran, P Veeraraghavan *J. Chem. Res. (S)* 78 (1983)
234. BRD P. 2 142 653; *Chem. Abstr.* **76** 140 175 (1972)
235. Aust. P. 478 873; *Chem. Abstr.* **87** 151 843 (1977)
236. BRD P. 2 404 951; *Chem. Abstr.* **81** 135 723 (1974)
237. G B Bachman, R J Maleski *J. Org. Chem.* **37** 2810 (1972)
238. G Rosini, R Ballini *Synthesis* 543 (1983)
239. L L Adams, F A Luzzio *J. Org. Chem.* **54** 5387 (1989)
240. V I Burmistrov, F G Nasybullina *Zh. Prikl. Khim.* **45** 2579 (1972) [f]
241. P Knochel, D Seebach *Synthesis* 1017 (1982)
242. J Melton, J E Murry *J. Org. Chem.* **40** 2138 (1975)
243. US P. 4 861 925 SShA; *Chem. Abstr.* **112** 550 72 (1990)
244. USSR P. 408 545; *Byull. Izobret.* (53) 181 (1976)
245. USSR P. 1 696 425; *Byull. Izobret.* (45) 91 (1991)
246. O Mitsunobu *Synthsis* 1 (1981)
247. Yu Yu, J R Falck *J. Org. Chem.* **57** 3757 (1992)
248. T D Lash, J R Bellettini, J A Bastian, K B Couch *Synthesis* 170 (1994)
249. USSR P. 367 097; *Ref. Zh. Khim.* 22 N 328 (1973)
250. US P. 3 631 181; *Chem. Abstr.* **76** 85 687 (1972)
251. J R Falck, Yu Yu *Tetrahedron Lett.* **33** 6723 (1992)
252. Jpn. Appl. 75-88 016; *Chem. Abstr.* **83** 193 651 (1975)
253. T Kinoshita, Yo Kawashima, K Hayashi, T Miwa *J. Chem. Soc., Chem. Commun.* 766 (1979)
254. H Piotrowska, T Urbanski, S K Vasudeva *Bull. Acad. Pol. Sci, Ser. Sci. Chem.* **25** 779 (1977)
255. N Ono, H MIyake, A Kaji *J. Org. Chem.* **49** 4997 (1984)
256. US P. 3 941 846; *Chem. Abstr.* **85** 32 415 (1976)
257. US P. 3 760 012; *Chem. Abstr.* **79** 125 810 (1973)
258. US P. 3 629 342; *Chem. Abstr.* **76** 58 955 (1972)
259. US P. 3 632 733; *Chem. Abstr.* **77** 4956 (1972)
260. A V Fokin, Yu N Studnev, A I Rapkin, L D Kuznetsova, V A Komarov *Izv. Akad. Nauk SSSR, Ser. Khim.* 489 (1976) [a]
261. G Guanti, G Petrillo, S Thea, G Cevasco *Tetrahedron Lett.* **21** 4735 (1980)
262. E Lipczynska-Kochany *Wiad. Chem.* **32** 843 (1978); *Chem. Abstr.* **90** 151 126 (1979)
263. A Zschunke, Th Heyer *Z. Chem.* **25** 259 (1985)
264. Br. P. 2 014 848; *Chem. Abstr.* **92** 116 435 (1980)
265. Jpn. Appl. 04-01 104; *Chem. Abstr.* **116** 189 607 (1992)
266. US P. 4 199 602; *Chem. Abstr.* **93** 101 498 (1980)
267. BRD P. 2 113 209; *Chem. Abstr.* **77** 148 546 (1972)
268. Jpn. Appl. 01-61 402; *Chem. Abstr.* **111** 148 872 (1989)
269. Jpn. Appl. 05-331 002; *Chem. Abstr.* **121** 101 971 (1994)
270. Br. P. 2 263 063; *Chem. Abstr.* **119** 167 785 (1993)
271. Jpn. Appl. 04-202 101; *Chem. Abstr.* **117** 247 136 (1992)
272. Jpn. Appl. 05-138 154; *Chem. Abstr.* **119** 209 806 (1993)
273. Jpn. Appl. 06-154 547; *Chem. Abstr.* **120** 269 647 (1994)
274. Jpn. Appl. 05-15 896; *Chem. Abstr.* **118** 240 082 (1993)
275. Jpn. Appl. 60-181 200; *Chem. Abstr.* **104** 20 968 (1986)
276. Jpn. Appl. 02-307 977; *Chem. Abstr.* **114** 209 205 (1991)
277. Jpn. Appl. 02-53 703; *Chem. Abstr.* **113** 186 578 (1990)
278. Jpn. Appl. 60-48 903; *Chem. Abstr.* **103** 49 761 (1985)
279. Jpn. Appl. 61-44 803; *Chem. Abstr.* **105** 74 426 (1986)
280. M Yoshinaka *Shikoku Igaku Zasshi* **28** 261 (1972); *Chem. Abstr.* **83** 53 180 (1975)
281. J Osimi *Shikoku Igaku Zasshi* **28** 245 (1972); *Chem. Abstr.* **81** 145 628 (1974)
282. Eur. P. 4217; *Chem. Abstr.* **92** 116 211 (1980)
283. A L Fridman, O B Kremleva, V S Zalesov, Z V Platonova, F A Gabitov, L A Rubinshtein, A N Plaksina *Khim.-Farm. Zh.* **11** 73 (1977) [g]
284. Jpn. Appl. 81-147 714; *Chem. Abstr.* **96** 174 397 (1982)
285. US P. 3 632 756; *Chem. Abstr.* **77** 4954 (1972)
286. BRD P. 2 304 580; *Chem. Abstr.* **81** 135 940 (1974)
287. Jpn. Appl. 07-53 775; *Chem. Abstr.* **123** 85 052 (1995)
288. Jpn. Appl. 05-333 486; *Chem. Abstr.* **121** 22 406 (1994)
289. Jpn. Appl. 05-331 379; *Chem. Abstr.* **121** 95 875 (1994)
290. Jpn. Appl. 04-194 928; *Chem. Abstr.* **118** 90 712 (1993)
291. Jpn. Appl. 04-299 336; *Chem. Abstr.* **119** 128 313 (1993)
292. US P. 4 298 638; *Ref. Zh. Khim.* 14 T 657 P (1982)
293. Jpn. Appl. 62-231 956; *Chem. Abstr.* **109** 14 601 (1988)
294. R Cowell, P J Devine, G A P Tuey *Res. Discl.* **129** 11 (1975); *Chem. Abstr.* **83** 186 233 (1975)
295. BRD P. 2 034 563; *Chem. Abstr.* **76** 155 965 (1972)
296. BRD P. 2 502 530; *Chem. Abstr.* **83** 179 888 (1975)
297. Jpn. Appl. 06-202 286; *Chem. Abstr.* **121** 267 704 (1994)
298. V G Timofeeva, L M Marchenko, P V Kozlov *Vysokomol. Soedin., Ser. B* **18** 474 (1976) [h]
299. Br. P. 2 058 099; *Chem. Abstr.* **95** 170 945 (1981)
300. US P. 4 235 763; *Chem. Abstr.* **94** 85 102 (1981)
301. US P. 3 897 583; *Chem. Abstr.* **84** 60 909 (1976)
302. US P. 4 243 800; *Chem. Abstr.* **95** 8966 (1981)
303. US P. 4 101 433; *Chem. Abstr.* **90** 25 868 (1979)
304. Jpn. Appl. 07-80 468; *Chem. Abstr.* **122** 310 562 (1995)
305. USSR P. 625 022; *Chem. Abstr.* **90** 8696 (1979)
306. I N Diyarov, L M Kozlov, A N Sadykov *Tr. Kazansk. Khim.-Tekhnol. In-ta* (Transactions of Kazan' Chemical Engineering Institute, (52) 140 (1973)
307. Eur. P. 146 381; *Chem. Abstr.* **103** 90 218 (1985)
308. US P. 4 113 444; *Chem. Abstr.* **90** 74 212 (1979)
309. US P. 3 845 105; *Chem. Abstr.* **82** 97 685 (1975)
310. US P. 4 997 499; *Chem. Abstr.* **114** 250 264 (1991)
311. US P. 3 629 338; *Chem. Abstr.* **76** 58 982 (1972)
312. US Appl. 46 474; *Chem. Abstr.* **108** 170 278 (1988)
313. US P. 4 426 540; *Chem. Abstr.* **100** 121 764 (1984)
314. Can. P. 967 972; *Chem. Abstr.* **93** 195 952 (1975)
315. US P. 3 904 674; *Chem. Abstr.* **83** 192 593 (1975)
316. US P. 3 878 004; *Chem. Abstr.* **83** 100 323 (1975)

[a] — *Russ. Chem. Bull. (Engl. Transl.)*
[b] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[c] — *Russ. J. Org. Chem. (Engl. Transl.)*
[d] — *Russ. J. Electrochem. (Engl. Transl.)*
[e] — *Chem. Heterocycl. Compd. (Engl. Transl.)*
[f] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[g] — *Pharm. Chem. J. (Engl. Transl.)*
[h] — *Polym. Sci. (Engl. Transl.)*