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SELECTIVE REDUCTION OF ALIPHATIC NITRO-COMPOUNDS WITH OTHER FUNCTIONAL GROUPS

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I. INTRODUCTION

In recent years there has been a great development of the chemistry of aliphatic nitro-compounds. The improvement of old and the discovery of new methods of synthesis has led to a sharp increase in the number of nitro-products that have become readily available; some of these are already produced on the industrial scale.

The nitroalkanes, which are now manufactured in tens of thousands of tons a year, are used as starting materials in the production of many aliphatic nitro-compounds.

In this connection, the attention of chemists has been increasingly attracted to the possibility of using nitro-derivatives of the aliphatic series for the needs of industry and agriculture, both directly and as a relatively cheap chemical material for the synthesis of various products with important applications.

Reduction occupies a special position in the chemical transformations of nitro-compounds. There is no need to dwell on the tremendous importance of this reaction in the aromatic series. However, the reduction of aliphatic nitro-compounds has been studied in a less detailed manner and the literature on this question has not been specially systematised. Isolated information on some particular problems may be found in a number of monographs and review articles on the nitro-compounds[1-7].

Since the question of the reduction of nitro-compounds containing other functional groupings in addition to the nitro-group is of fundamental chemical and pratical interest, only examples of selective reduction of aliphatic functional nitro-compounds will be considered in this review. This question is considered in two aspects. Thus, in the first part the reduction of the nitro-group to the amino-group without change of other functions is considered, and in the second the reduction of functional groups without changing the nitro-group.

It was not our purpose to produce an exhaustive review of all instances of selective reduction of nitro-compounds, and the material of the review has been selected in such a way as to illustrate the use of various reducing agents or catalysts, suitable for the selective (in the above sense) reduction of functional aliphatic nitro-derivatives.

II. SELECTIVE REDUCTION OF THE NITRO-GROUP IN ALIPHATIC NITRO-COMPOUNDS WITH OTHER FUNCTIONAL GROUPS

1. Reduction of Nitro-Alcohols to Amino-Alcohols

Of all aliphatic nitro-compounds, the reduction of the nitro-alcohols has been most fully studied. The leading motive of many investigations in this field is the wide use

of amino-alcohols in a number of branches of industry and also their great importance as physiologically active compounds.

The selective reduction of nitro-alcohols does not present particular difficulties, because the hydroxyl group is inert to the action of the majority of chemical reagents usually employed for reducing the nitro-group.

Hydrogenation with Raney nickel is one of the main methods of selectively reducing nitro-alcohols. Change of temperature between 30° and 100° and of pressure between 1 and 130 atm has no material effect on the yields of amino-alcohols [8-20]; however, carrying out the hydrogenation in the presence of carbon dioxide leads to a significant increase in the yield of amino-alcohols [11,14]. In an acid medium, as a rule, the hydrogenation of the nitro-group is not accompanied by side-reactions. On the other hand, when the reaction is carried out in an alkaline medium, the reduction is frequently accompanied by side-reactions connected with the instability of nitro-alcohols under these conditions. Thus in the reduction of 2-methyl-2-nitropropan-1-ol with Raney nickel in liquid ammonia, Johnson separated 1,2-diamino-2-methylpropane, the appearance of which the author explains by the exchange of a hydroxyl group of the reduced alcohol for an amino-group [21]. Moreover, in an alkaline medium methyl groups are easily eliminated from tertiary carbon atoms. For example, in the reduction of 2-ethyl-2-nitropropan-1,3-diol, 2-aminobutanol and methanol are formed [22]. In an acid medium the reaction proceeds normally and leads to the formation of 2-amino-2-ethylpropan-1,3-diol.

In a number of papers the reduction of nitro-alcohols (monohydroxy- and polyhydroxy-) to amino-alcohols in the presence of platinum oxide [23-25] and palladium [26-29] is described. Usually the yield of amino-alcohols is 80–95%. The process is best carried out in an acid medium.

Fundamental information on the selectively catalytic hydrogenation of nitro-alcohols is collected in Table 1.

There are many papers on the reduction of nitro-alcohols by chemical reagents. The reduction of nitro-alcohols with nascent hydrogen has been studied in great detail. Various combinations of metals and acids have been proposed as a source of hydrogen (for example, Fe + H_2SO_4, HCl, or H_3PO_4 [10,30,31]; Zn + HCl [14]; $SnCl_2$ + HCl [15]).

TABLE 1.

Initial nitro-alcohol	Catalyst*	Hydrogenation conditions (temp., H_2 pressure)	Solvent	Yield of amino-alcohol, %	Ref.
2-Methyl-2-nitropropan-1-ol	Ni/Re	70°; 30–35 atm	water–methanol	95.8	9
2-Nitro-1-phenylpropan-1-ol	Ni/Re	50–70°; 20–120 atm; CO_2	alcohol	87.45 (no CO_2)	14
1-Cyclohexyl-2-nitroethan-1-ol	Ni/Re	25–35°; 4–6 atm; CO_2	–	91	16
$CH_2OH{-}C(NO_2)(C_nH_{2n+1})CH_2OH$	Ni/Re	125°; 1–135 atm	water–methanol	–	18
1,4-Dinitrobutan-2,3-diol	Ni/Re	40–80°; 200 atm	dioxan	–	19
1-Deoxy-1-nitro-D-*manno*-D-galaheptanol	Ni/Re	20°; 1 atm	–	90	16
1,4-Dideoxy-1,4-dinitroneoinositol	Ni/Re	20°; 1 atm	acetic acid–dimethylformamide	89.6	20
2-Nitrooctadecan-1,3-diol	PtO_2	20°; 1 atm	acetic acid	71	24
3-Nitropentan-2,4-diol	5% Pd on $BaSO_4$	20°; 1 atm	H_2O + pyridine	86.5	28
2-Nitropropan-1,3-diol	Pd on $BaSO_4$	20°; 1 atm	in the presence of COOH–COOH	93	2, 9

* Ni/Re presumably denotes Raney nickel (Ed. of Translation).

Evidently, the action on β-nitro-alcohols of iron in sulphuric acid at a pH of 3–3.5, and the use of 1–1.1 equivalents of acid for each nitro-group give the most favourable conditions for the reduction of β-nitro-alcohols by this method; the yields of amino-alcohols is 92–98%.

Lower β-amino-alcohols (C_3–C_5) are conveniently obtained by the action of aluminium in weak acid on nitro-alcohols [32]; the yield varies between 50 and 70%. The method is particularly recommended for nitro-alcohols sensitive to strong alkalis and acids, but the effectiveness of the method is greatly reduced in the reduction of higher nitro-alcohols ($>C_5$).

The reduction of β-nitro-α-phenyl-alcohols to the corresponding amino-derivatives by sodium amalgam [33] and lithium tetrahydroaluminate [34] has also been described.

As has been shown by the investigations of Jenny and Druey [35], and also by Grob and Gadient [36], lithium tetrahydroaluminate, or zinc and hydrochloric acid, or aluminium and acetic acid may be used for the simultaneous reduction of nitro-groups and multiple carbon bonds in higher aliphatic unsaturated nitrodiols. The yields of saturated amino-alcohols vary between 40 and 70%. According to Takagi and coworkers [37], ammonium amalgam reduced nitrodiols to hydroxylaminodiols [37].

Examples are known of the selective electrochemical reduction of nitro-alcohols and diols [17,38]. The authors used a lead cathode and dilute sulphuric or hydrochloric acid as electrolytes. The yield of amino-derivatives was 75–94%.

2. Reduction of Alkyl Ethers of Nitro-Alcohols to Alkyl Ethers of Amino-Alcohols

The alkoxy-group in the β-position to the nitro-group is much more stable than the hydroxyl group. Thus, when lithium tetrahydroaluminate acts on β-nitro-α-phenyl-alcohols the carbon–carbon bond is ruptured, but when the analogous alkoxy-compounds are reduced with this reagent, the corresponding β-alkoxy-β-phenylamines are formed in quantitative yield [34].

It is very easy to reduce 1-alkoxy-2-nitro-1-phenylalkanes by zinc in organic acids. For example, by using zinc and formic acid, it is possible to obtain β-amino-ethers in ~90% yield [39]. Lambert and coworkers, who made a detailed study of the action of various reducing agents on lower aliphatic β-nitro-ethers, showed that the highest yields of amino-ethers are obtained by catalytic hydrogenation [40]:

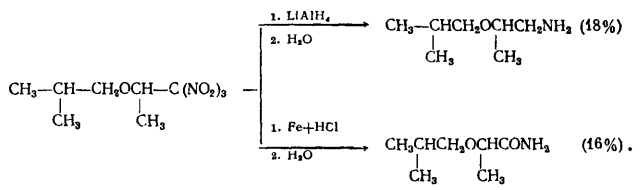
$$C_2H_5OCH_2CH_2NO_2 \xrightarrow[20^\circ,\ 100\ \text{atm, alcohol}]{H_2/PtO_2} C_2H_5OCH_2CH_2NH_2 \quad (52\%),$$

$$CH_3CH(NO_2)CH(OCH_3)CH_3 \xrightarrow[50^\circ,\ \text{alcohol}]{H_2,\ \text{Raney Ni}} \underset{(I)}{CH_3CH(NH_2)CH(OCH_3)CH_3} \quad (50\%).$$

When iron filings in hydrochloric acid are used as reducing agent the yield of (I) falls to 30%.

Thompson and coworkers [41] studied the conversion of chloro-substituted β-nitro-ethers ($Cl_3C{-}CHOR{-}CH_2NO_2$) into the corresponding amines under the action of tin and hydrochloric acid in alcohol at 90–100°. The yield of alcohols largely depends on the radical R and varies from 16% when R = 4-methylcyclohexyl to 65% when R = $(CH_3)_2.CHCH_2$.

Schechter and Cates reduced isobutyl 1-trinitromethylethyl ether to the corresponding amine by the action of lithium tetrahydroaluminate, and to α-isobutoxypropionamide by the action of iron in hydrochloric acid[42].



3. Reduction of Nitro-Ketones and Nitro-Aldehydes to Amino-Ketones and Amino-Aldehydes

The presence of a carbonyl group in nitro-compounds makes selective reduction of the nitro-group difficult, because many hydrogenation catalysts and chemical reagents (for example, lithium tetrahydroaluminate) first reduce the carbonyl group. Moreover, reduction is often accompanied by cyclisation through the carbonyl group of the amino-ketones and -aldehydes formed.

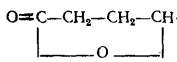
Using 4-keto-6-nitrohexanoic acid (II) and its esters as examples, Moldenhauer[43] and Grundmann[44] showed the possibility of selectively reducing the nitro-group in β-nitro--ketones. When (II) was hydrogenated with palladium on charcoal in hydrochloric acid under normal conditions, the yield of amino-acid reached 96.4%.[44]

$$\underset{\text{(II)}}{CH_2(NO_2)CH_2CO[CH_2]_2COOH} \rightarrow \underset{\text{(III)}}{CH_2(NH_2)CH_2CO[CH_2]_2COOH}.$$

However, hydrogenation of (II) with palladium on barium sulphate in acetic acid leads to (III) in lower yield (67%).

The authors point out the instability in an alkaline medium of compounds containing the β-amino-ketone grouping.

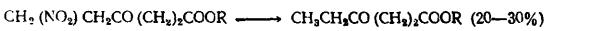
The possibility of selectively reducing the nitro-group in esters of (II) has also been studied and it has been shown that it may be effected by hydrogenation with 5% palladium on charcoal in water[43]. The yield of the corresponding esters of the amino-keto-acid mounted to ~30%. The use in this reaction of Raney nickel as hydrogenation catalyst at low hydrogen pressures leads to the formation of (III) in 20% yield, but at a pressure of 100 atm and a temperature of 225–240° the lactone



is formed in 33.7% yield[44].

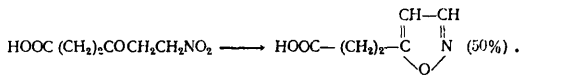
Hydrogenation of (II) with platinum dioxide in water brings about reduction of the keto-group as well as the nitro-group and leads to 6-amino-4-hydroxyhexanoic acid[43].

When palladium on aluminium oxide is used as catalyst, deamination of the reduction products occurs[43]:

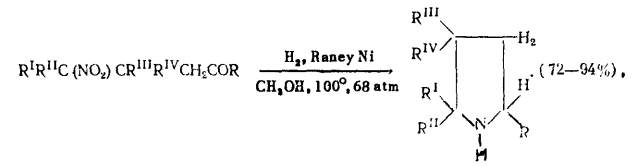


where R = H or alkyl.

When lithium tetrahydroaluminate acts on (II), all the functional groups are reduced[43]. Reduction of (II) with tin(II) chloride in hydrochloric acid leads to the formation of an isoxazole ring[45]:

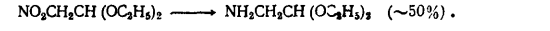


According to Kloetzel[46], on reduction γ-nitro-ketones undergo ring closure to pyrrolidine rings:

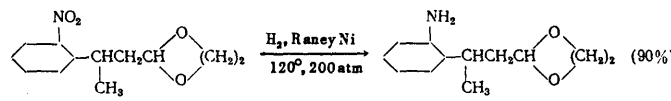


where R, R^I, R^{II}, R^{III}, R^{IV} = H or alkyl.

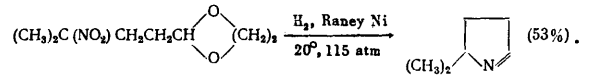
In connection with the difficulties arising in the direct reduction of nitro-ketones and nitro-aldehydes, it is useful to first protect the keto-group by the formation of acetals. Losanitsch[47] has described the reduction of the nitro-group in β-nitroacetals by sodium in boiling alcohol:



However, when acetals of γ-nitro-ketones are reduced, the final product largely depends on the structure of the initial nitro-acetal. Thus, in particular, reduction of the acetal† of ethylene glycol and γ-(2-nitrocyclohexyl)butyraldehyde is not accompanied by cyclisation of the final product[48]:



On the other hand, hydrogenation of the acetal‡ of ethyleneglycol and γ-methyl-γ-nitrovaleraldehyde is accompanied by cyclisation[49]:



4. Reduction of Nitro-Acids and Their Derivatives to Amino-Acids and Derivatives

The tremendous practical interest in the selective reduction of the nitro-group in α-nitro-acids and their derivatives as a method of synthesis of α-amino-acids should be mentioned.

The world demand for some amino-acids now reaches some hundreds of thousands of tons per year; for this reason at the present time intensive searches are being

† 2-[2-(2-Nitrocyclohexyl)propyl]-1,3-dioxolane (Ed. of Translation).

‡ 2-(3-Methyl-3-nitrobutyl)-1,3-dioxolane (Ed. of Translation).

made for cheap chemical materials which could be used in their synthesis. In particular, great attention has been paid to the possibility of using nitromethane for this purpose. Nitroacetic esters can easily be obtained from nitromethane, and from these the synthesis of many amino-acids can be effected. Thus, glycine was obtained by the reduction of nitroacetic ester on Raney nickel[50].

In a general way the synthesis of α-amino-acids from nitromethane may be represented by the following scheme:

$$CH_3NO_2 \rightarrow CH_2NO_2COOR' \rightarrow RCH(NO_2)COOR' \rightarrow RCH(NH_2)COOH,$$

where R = alkyl, or substituted alkyl; R′ = CH_3 or C_2H_5. Using this scheme, Weisblat and coworkers[51] synthesised DL-tryptophan and leucine.

In recent years the selective reduction of α-nitro-acids obtained from nitroacetic ester has been studied in detail by Belikov and coworkers[52-54]. In particular, in a study of the hydrogenation of methyl esters of α-nitro-$\alpha\beta$-unsaturated acids with Raney nickel in methanol, it was shown that sometimes there is first addition of the elements of the solvent through the activated double bond, which is probably catalysed by traces of alkali present in the catalyst[52]:

$$CH_3CH{=}C(NO_2)COOCH_3 \xrightarrow{CH_3OH} CH_3\underset{\underset{OCH_3}{|}}{C}HCH(NO_2)COOCH_3 \rightarrow$$

$$\xrightarrow[55^\circ,\,75\ atm]{H_2} CH_3\underset{\underset{OCH_3}{|}}{C}HCH(NH_2)COOH \quad (41\%).$$

Esters of sterically hindered α-nitro-acids are normally reduced under these conditions:

$$(CH_3)_2CH{-}CH{=}C(NO_2)COOCH_3 \xrightarrow[50^\circ,\,68\ atm]{H_2,\,CH_3OH} (CH_3)_2CHCH_2\underset{\underset{NH_2}{|}}{C}HCOOCH_3 \quad (61\%).$$

Another example is the synthesis of proline from nitroacetic ester[54]:

$$CH_3NO_2COOCH_3 \xrightarrow{CH_2{=}CH{-}CHO} HC(O)CH_2CH_2CH(NO_2)COOCH_3 \rightarrow$$

$$\rightarrow (CH_3O)_2CHCH_2CH_2CH(NO_2)COOCH_3 \xrightarrow[2.\ H_2O]{1.\ H_2/PtO_2} \text{NH-ring-COOH}.$$

Reduction of α-nitro-acids or their derivatives to amino-acids with the aid of chemical reagents is carried out much less frequently; as a rule, the amino-acids are obtained in a lower yield than by catalytic hydrogenation. Information on the reduction of nitro-acids and their derivatives is given in Table 2.

Sometimes the hydrogenation of nitro-acids is accompanied by side reactions. Thus, the reduction of esters of dibasic γ-nitro-acids on platinum oxide or Raney nickel leads to lactams[61] and other cyclic products[62]:

$$CH_3OOC(CH_2)_2CH(CH_2)_2COOCH_3 \;(NO_2) \xrightarrow[25^\circ,\,2-3\ atm]{H_2,\,PtO_2} (CH_2)_2{-}COOCH_3,\ CH{-}NH,\ CH_2{-}CH_2,\ C{=}O$$

$$\xrightarrow[275^\circ,\,250-350\ atm]{H_2,\ Raney\ Ni} \text{N-ring} \quad (57\%).$$

When the ethyl 3,4-dehydro-5-nitrohexanoate is hydrogenated on Raney nickel at high temperatures and pressures, caprolactam is obtained instead of ethyl 6-aminohexanoate[62].

Isolated information on the reduction of nitro-acids containing other functional groups is given in preceding and subsequent parts of Section II (see pp. 21,23).

5. Reduction of Nitro-Nitriles to Amino-Nitriles

The selective reduction if the nitro-group in nitro--nitriles to the amino-group is of considerable interest, since in the end it opens the way to the synthesis of amino--acids.

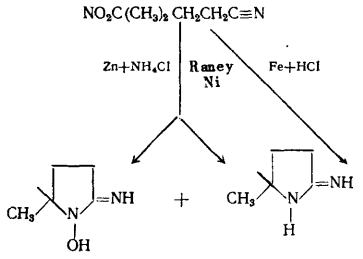
Using nitro-t-butyl cyanide as an example, Buckley and coworkers[63] showed that the selective reduction of β-nitro--nitriles is usefully carried out with iron in dilute hydrochloric acid. The yield of amino-t-butyl cyanide was 65%. When the starting material and other β-nitro-nitriles were catalytically hydrogenated (Raney nickel, palladium on calcium carbonate), instead of amino-nitriles the authors obtained amino-acid amides, diamines, and other secondary products.

As Buckley and Elliott showed[64], when γ-nitro-nitriles are reduced both by chemical and catalytic methods amino--nitriles are generally not obtained. Instead of them,

TABLE 2.

Initial nitro-acid or its derivative	Reducing agent or hydrogenation catalyst	Reaction conditions	Solvent	Reduction product	Yield, %	Ref.
Ethyl β-indolyl-α-nitropropionate	Raney Ni	100°, ~100 atm	alcohol	DL-tryptophan	50	55
Diethyl α-nitroglutarate	Raney Ni *	100°, 150 atm	alcohol	DL-glutamic acid	–	56
$(CH_3O)_2CH(CH_2)_2\underset{\underset{NO_2}{|}}{C}HCOOCH_3$	skeleton Ni	70°, 62 atm	absolute methanol	$(CH_3O)_2CH(CH_2)_2\underset{\underset{NH_2}{|}}{C}HCOOCH_3$	75	54
Ethyl $\alpha\alpha$-dimethyl-β-nitropropionate	Raney Ni	90°, 95 atm	water + $Ba(OH)_2$	β-amino-$\alpha\alpha$-dimethylpropionic acid	65	57
$(CH_3)_2C(NO_2)(CH_2)_2$–CONRR′	Raney Ni	125°, 68 atm	–	$(CH_3)_2C(NH_2)(CH_2)_2$CONRR′	45–89	58
Methyl β-hydroxy-α-nitrobutyrate	5% Pd/C	20°, 40–50 atm	acetic acid	DL-threonine	74	53
$CH_3CH{=}C(NO_2)COOCH_3$	PtO_2	5°, 1 atm	ethyl acetate	$CH_3CH_2CH(NH_2)COOCH_3$	63	53
γ-Nitropentanoic acid	PtO_2	20°, 1 atm	alcohol	γ-aminopentanoic acid	98	59
$(CH_3O)_2CH(CH_2)_2\underset{\underset{NO_2}{|}}{C}HCOOCH_3$	PtO_2	20°, 60 atm	70% CH_3COOH	DL-proline	65	54
Ethyl β-indolyl-α-nitropropionate	Fe + HCl	20°	–	DL-tryptophan	25	55
Ethyl nitromalonate	Zn + CH_3COOH	50–80°	$(CH_3CO)_2O$	$CH_3CONHCH(CO_2C_2H_5)_2$	30	60

mixtures of the corresponding *N*-hydroxy-5-iminopyrrolidines and 5-iminopyrrolidines are obtained. For example:



6. Reduction of Nitro-Amines to Polyamines

Information in the literature relates to the reduction of β-nitro-amines, products readily obtained by the Mannich reaction from nitro-compounds, formaldehyde, and amines. The most selective reduction of the nitro-group in nitro--amines should, of course, not present any difficulties. However, in selecting the reaction conditions it should be noted that the process is often complicated by side-reactions which are connected with the instability of the initial compounds and to a large degree depend on the structure of the latter, the pH the medium, and other factors.

Johnson[65] reduced a series of β-nitro-amines on Raney nickel at 30–50° and a hydrogen pressure of 70 atm in methanol; the yield of diamines was 65–80%. A few other papers have been published on the selective reduction of nitro-amines and nitro-diamines on Raney nickel under similar conditions[66,67,70-72]. However, Senkus hydrogenated *NN*-diisopropyl-2-methyl-2-nitropropylamine under the same conditions and obtained a mixture of lower amines instead of the diamine[69]. The author explains this result by the instability of the initial nitro-amine. Some β-nitro-amines may be reduced to diamines by the action of tin(II) chloride in hydrochloric acid at 0° in yields of ~30%.[68]

When esters of α-nitro-β-alkylamino-acids are catalytically hydrogenated, esters of the αβ-diamino-acids are not obtained; the bond between the α- and β-carbon atoms is ruptured[70]:

$$\begin{matrix}RCH{-}CH(NO_2)COOR'\\ \quad\quad|\\ \quad NHR'\end{matrix} \xrightarrow[PtO_2]{H_2} RCH_2NHR' + CH_2(NH_2)COOR'.$$

Dornow and Gellrich[34] observed similar cleavage of the initial α-nitro-β-alkyl aminoester under the action of lithium tetrahydroaluminate:

$$\begin{matrix}Cl{-}C_6H_4{-}CHCH(NO_2)COOC_2H_5\\ \quad\quad\quad|\\ \quad\quad NHC_6H_5\end{matrix} \xrightarrow{LiAlH_4} Cl{-}C_6H_4{-}CH_2NHC_6H_5 + CH_2NH_2CH_2OH.$$

Obviously, this reaction is general for all β-nitro-amines in which the nitro-group is on the carbon atom connected to the ester grouping.

The reduction of the nitro-group in *N*-nitro-amines has been studied in the literature with nitroguanidine as an example. The catalytic reduction has been described of nitroguanidine to aminoguanidine with the aid of Raney nickel[71], platinum oxide[71,72], sodium with the addition of ammonium chloride in liquid ammonia[73], zinc dust[74-76], titanium trichloride[77,78]; an electrolytic method has also been used[79,80].

Moreover, it has been shown that nitroguanidine can be converted into nitrosoguanidine[71,81].

There are also reports on the electrolytic reduction of nitrourea to semicarbazide on a platinum cathode[82].

7. Reduction of Halogeno-Nitro-Compounds to Halogeno--Alkylamines

Catalytic hydrogenation is generally used for the selective reduction of the nitro-group in γ-fluoronitroalkanes. In particular, Cook smoothly reduced 2-heptafluoropropyl--1-nitrobutane to the corresponding amine under mild conditions (20°, 4 atm) with the aid of Adams' catalyst[83]. In the same paper it is shown that selective hydrogenation of the nitro-group in fluoronitroalkanes, including those containing hydroxyl groups in the β-position to the nitro-group, can be effected with the aid of Raney nickel. It has also been noted that lithium tetrahydroaluminate in the reduction of the nitro-group and some other functions does not generally affect the C–F bond and permits the preparation of the corresponding polyfluoroamines in good yield.

The reduction of monochloro-β-nitroalkanes is most efficiently carried out with tin(II) chloride in hydrochloric acid[88]. Under these conditions 2-chloro-3-methyl-1--nitrobutane gave the corresponding β-chloroamine in 57% yield. However, when the starting compound is hydrogenated on Raney nickel, a mixture of amines and hydroxylamines difficult to separate is formed.

As already mentioned, β-alkoxy-γ-trichloronitroalkanes[41] and γ-trichloro-β-hydroxynitroalkanes[15] may also be selectively reduced to amines in high yields (50–70%) by tin(II) chloride and hydrochloric acid.

3-Amino-1,1,1-trichloropropan-2-ol was obtained[85] by the reduction of 1,1,1-trichloro-3-nitropropan-2-ol on Raney nickel at room temperature and pressures up to 10 atm. However, at a higher pressure (50 atm) and increased temperature (106°), one chlorine atom may be reduced in addition to the nitro-group[15]:

$$CCl_3CH(OH)CH_2NO_2 \xrightarrow[\text{in HCl}]{H_2} CHCl_2CH(OH)CH_2NH_2\cdot HCl \quad (34.7\%).$$

In the light of these results, it may be concluded that Raney nickel is unsuitable for the selective reduction of the nitro-group in γγγ-trichloronitroalkanes.

8. Selective Reduction of Nitro-Groups in Aliphatic Sulphur-Containing Compounds

Several papers have been published on the selective reduction of the nitro-group in β-nitroalkyl sulphides[86], β-nitroalkyl sulphones[86,87] and β-nitrosulphonic acids[88] by hydrogenation of the initial compounds in methanol on Raney nickel at room temperature, or slightly higher, and at atmospheric or higher hydrogen pressure. In a number of cases the corresponding amines are obtained in close to quantitative yield.

Gold and coworkers made a detailed study of the reduction of the nitro-group in salts of β-nitrosulphonic acids of the type $CH_2(NO_2)CHRSO_3H$ (R = H, CH_3, C_6H_5); $CH(NO_2)R{-}CH_2SO_3H$ (R = H, CH_3, C_2H_5); $CH(NO_2)(C_2H_5)CH(C_3H_7)SO_3H$.[89] The authors consider that the most efficient conditions of hydrogenation of the initial salt are with Raney nickel in

water at 30° and low pressures; the yield of β-aminosulphonic acids is greater than 90%. At increased hydrogenation temperature there is a reduction in the yield of β-aminosulphonic acids. Reduction of the above-mentioned compounds may also be carried out by iron in water in the presence of catalytic quantities of hydrochloric acid (the yield of β-aminosulphonic acids is greater than 80%), and also electrolytically on a lead cathode with 15% sulphuric acid as an electrolyte (the yield of β-aminosulphonic acids is 60%).

The reduction of 1-nitroethyl *p*-tolyl sulphide (IV) and sulphone (V) proceed anomalously[90]. When treated with Raney nickel or Adams' catalyst, (IV) is recovered unchanged, but (V) gives a mixture of products:

$$p\text{-}CH_3C_6H_4SO_2CH(NO_2)CH_3 \xrightarrow[\text{Raney Ni}]{H_2} \begin{cases} p\text{-}CH_3C_6H_4SO_2C(NOH)CH_3 & \text{(VI) (10\%)} \\ p\text{-}CH_3C_6H_4SO_2NH_4 & \text{(28\%)} \\ p\text{-}CH_3C_6H_4SO_2H & \text{(50\%).} \end{cases}$$
(V)

When (IV) is treated with lithium tetrahydroaluminate, (VIa) is obtained in low yield:

$$p\text{-}CH_3C_6H_4SCH(NO_2)CH_3 \xrightarrow{LiAlH_4} p\text{-}CH_3C_6H_4SC(NOH)CH_3 \quad (14\text{—}16\%).$$
(IV) (VIa)

It should be emphasised that the reduction of aliphatic nitro-compounds with lithium tetrahydroaluminate is hardly mentioned in the literature. From this point of view the example given here is of undoubted interest.

9. Reduction of Nitro-Alkynes to Amino-Alkynes

The selective reduction of the nitro-group in aliphatic acetylene nitro-diols is described in papers by Jenny[35] and by Grob[36]

$$R\text{—}C{\equiv}CCH(OH)CH(NO_2)CH_2OH \rightarrow R\text{—}C{\equiv}C\text{—}CH(OH)CH(NH_2)CH_2OH,$$
(VII, *a—f*) (VIII, *a—f*)

(*a*) R = n-C_6H_{17}; (*b*) R = n-$C_{10}H_{21}$; (*c*) R = n-$C_{12}H_{25}$; (*d*) R = n-$C_{14}H_{29}$; (*e*) R = $C_{16}H_{33}$; (*f*) R = $C_{18}H_{37}$.

With the action of zinc and hydrochloric acid on (VII, *c*), the yield of (VIII, *c*) amounted to 72%. When (VII, *f*) was reduced by aluminium in ether with the addition of a little water and acetic acid at room temperature, the yield of (VIII, *f*) did not exceed 45%. Aluminium amalgam was found to be unsuitable for the reduction of (VII). Hydrogenation of (VII) with palladium on lead carbonate, with palladium on carbon, or with lithium tetrahydroaluminate involves the triple bond§.

By the action of zinc or aluminium in acid on optically active (VII, *f*), the authors obtained (VIII, *f*) in optically active form.

10. Reduction of Nitro-Alkenes to Amino-Alkenes

There is evidently no general method for the selective reduction of the nitro-group in nitro-alkenes. The selection of the reducing agent and the reaction conditions depends entirely on the structure of the initial nitro-alkene. It is entirely understandable that special difficulties should be encountered in attempts to reduce the nitro-group without affecting the double bond in α-nitro-alkenes. The instability of the corresponding amino-derivatives considerably complicates the study of this reaction. However, even with exhaustive reduction of α-nitro-alkenes, it is necessary to choose carefully the reducing agent and the conditions of the reaction, since frequently oximes are obtained as the final product of the expected alkylamines. Thus, when aluminium and amalgam[91], zinc dust in an alkaline medium[92], or iron filings in hydrochloric acid[93] acts on α-nitro-alkenes only the oximes of the corresponding aldehydes and ketones are obtained. Ammonium sulphide reduces α-nitro-alkenes to acid amides[94]. When hydride reducing agents, for example, lithium tetrahydroaluminate, act on α-nitro-alkenes the double bond is first reduced[83]. The same result was obtained in attempts at selective electrolytic reduction[84].

Until recently only one α-nitro-unsaturated compound (ethyl β-methyl-α-nitrocrotonate) had been described in which the nitro-group had been successfully reduced selectively:

$$(CH_3)_2C{=}C(NO_2)COOC_2H_5 \rightarrow (CH_3)_2C{=}C(NH_2)COOC_2H_5 \text{ or } (CH_3)_2C{=}C(NHCOCH_3)COOC_2H_5.$$
(IX) (X) (XI)

Obviously, the stability of the C=C bond in (IX) to reduction is related to the steric hindrance caused by its substituents.

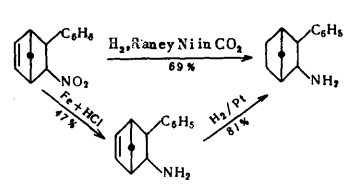
Bouveault[95] obtained (X) in 60–62% yield by the action of aluminium amalgam in ether on (IX), having shown that acid and alkaline reagents were not suitable for the selective reduction of (IX). However, these results were not confirmed by the later work of Süs, who only obtained the acetyl derivative (XI).[96] Moreover, he showed that the catalytic reduction of (IX) on Raney nickel at 70° and 50 atm in the presence of acetic anhydride leads to (XI) in over 90% yield[97].

In recent years Kuhn proposed a reducing agent which apparently can be used for the selective reduction of the nitro-group in α-nitro-alkenes[98]. According to the author, hydrazine in the presence of catalytic platinum or palladium is a very effective reducing agent for nitro- and nitrate-groups, and it does not affect the carbon–carbon double bond. In particular, 2-amino-1-phenylprop-1-ene can be obtained from 2-nitro-1-phenylprop-1-ene. Replacement of the platinum or palladium by nickel reduces the effectiveness and selectivity of the reagent and leads to hydrogenation of the double bond.

The selective reduction of the nitro-group in β-nitro-alkenes has not been described in the literature.

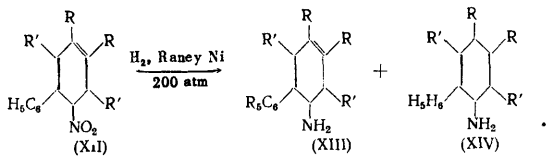
Work on the reduction of the nitro-group in γ-nitro-alkenes does not permit of any general recommendations on the choice of reducing agent.

Parham and coworkers[99] studied the reduction of 3-nitro-2-phenylbicyclo[1,2,2]hept-5-ene by various agents, and they showed that only iron in hydrochloric acid has a selective action:



§ For more details see the next Section.

As the results of the work show, catalytic methods do not permit the selective reduction of the nitro-group in this γ-nitro-alkene. However, Nightingale and Tweedie [100], who studied the hydrogenation of some phenylnitrocyclohexenes on Raney nickel, obtained different results:



(XII) (XIII) (XIV)

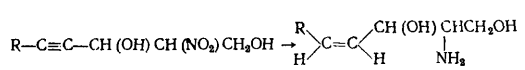
a, R = R′ = H; *b*, R = CH_3, R′ = H; *c*, R = H, R′ = C_6H_5.

The authors found that in (XII, *a–c*), at low temperature and with Raney nickel as catalyst, the nitro-group is first reduced and then the double bond. Thus, at 26° (XII, *a*) gives an almost quantitative yield of (XIII, *a*).

The introduction of methyl groups still further hinders the reduction of the double bond, which in (XII, *b*), for example, cannot be reduced at a temperature below 165°. The introduction of phenyl radicals hinders the reduction of both functional groups; therefore (XII, *c*) is reduced more slowly than (XII, *a*).

The use of other reagents for the selective reduction of (XII, *a–c*) gives less satisfactory results. Thus, when tin(II) chloride and hydrochloric acid in alcohol act on (XII, *a*) the unsaturated amine (XIII, *a*) is formed in 50% yield; however, under the same conditions (XII, *b*) gives a complex mixture of products. The authors also do not recommend zinc in acetic acid of iron(II) sulphate for the selective reduction of the nitro-group in these compounds.

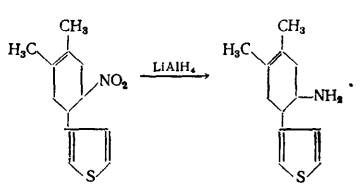
The most effective catalytic method for the selective reduction of unsaturated nitro-compounds uses Lindlar catalyst (palladium on lead carbonate). With the aid of this, Jenny and Druey [35] obtained a series of *cis*-unsaturated aliphatic amines:



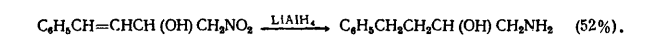
R = n-C_8H_{17}; n-$C_{10}H_{21}$; n-$C_{12}H_{25}$; n-$C_{14}H_{29}$; n-$C_{16}H_{33}$.

When lithium tetrahydroaluminate was used as a reducing agent, the corresponding *trans*-unsaturated amines were obtained.

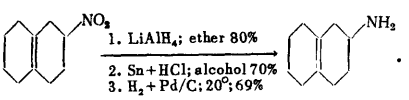
In some γ-nitro-alkenes lithium tetrahydroaluminate reduces only the nitro-group, but in others it reduces both the nitro-group and the double bond. Thus, Nightingale and coworkers [101] described the selective reduction by lithium tetrahydroaluminate of the nitro-group in 1,2-dimethyl-4-nitro-5-thien-3-ylcyclohex-1-ene:



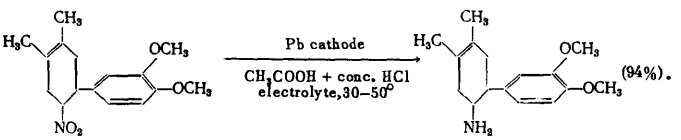
On the other hand, Dornow and Gellrich [34] showed that 3-hydroxy-4-nitro-1-phenylbut-1-ene cannot be selectively reduced with lithium tetrahydroaluminate:



Obviously, the possibility of selectively reducing the nitro-group in γ-nitro-alkenes largely depends on the structure of the initial compound. If the double bond is screened and not activated by other substituents, it is not affected by many reducing agents. For example, Bailev and Golden reduced 2-nitro-9,10-octalin and 2-amino-9,10--octalin by three different methods [102]:



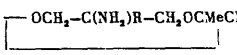
A successful electrochemical method for the selective reduction of γ-nitro-alkenes has been described [103]:



11. Reduction of Nitro-Groups in Compounds with Other Functional Groups

In this section we shall give some examples of the selective reduction of nitro-groups in functional compounds not considered in previous Sections.

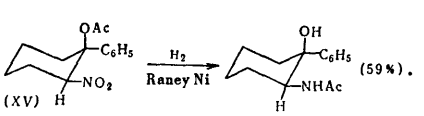
There are two United States patents on the reduction of the nitro-group in nitrodioxans. Morey described a method for the preparation of substituted 5-amino-1,3-dioxans:



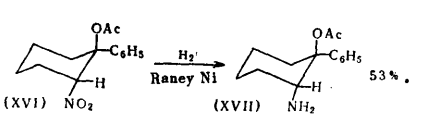
by the catalytic reduction of the corresponding nitro-compounds [104]. The catalyst is not indicated in the patent.

Senkus obtained substituted 5-amino-1,3-dioxans by the catalytic hydrogenation of 5-nitro-1,3-dioxans on Raney nickel at 25° and 130 atm in methanol [105]. The author notes the insecticidal activity of the products obtained.

Interesting information on the reduction of acetates of the stereoisomeric 2-nitro-1-phenylcyclohexan-1-ols and 2-nitro-1-phenylcyclopentan-1-ols is contained in a paper by Bordwell and Garbisch [106]. These workers showed that the reduction of 1-acetoxy-*cis*-2-nitro-1-phenylcyclohexane on Raney nickel is accompanied by transacylation and leads to 2-acetamino-1-hydroxy-1-phenylcyclohexane:

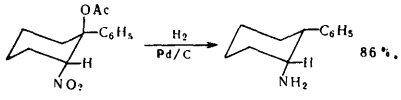


Reduction of the *trans*-isomer proceeds normally:



When (XVI) is electrolytically reduced on a platinum cathode at 50°, (XVII) is also formed. Hydrogenation

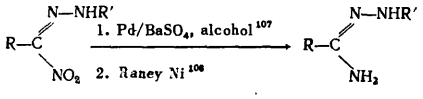
of (XVI) on palladium is accompanied by elimination of the acetyl group:



86 %.

Analogous results were obtained with 1-acetoxy-2--nitro-1-phenylcyclopentenes.

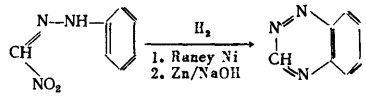
There are hardly any examples in the literature on the selective reduction of aliphatic α-substituted nitro-compounds. Generally, reduction of such compounds proceeds in a complex manner[90]. However, a few instances are known of the selective reduction of hydrazones of alkyl- or aryl-nitroformaldehydes to the corresponding amidrazones[107,108]:



(80%),

where R = alkyl or aryl.

If R = H and R' = phenyl, the reaction does not stop at the amidrazone stage and leads to triazines[108]:



However, it was not possible to separate the amidrazone as an intermediate product.

Table 3 shows the applicability of various reducing agents to the reduction of the nitro-group in aliphatic nitro--compounds with other functional groups.

Table 3 makes clear the field of application of a given reducing agent for the selective reduction of nitro-compounds; it also shows to what extent the reduction of various classes of nitro-compounds has been studied.

Raney nickel is the most widely used catalyst for the reduction of various nitro-compounds with other functional groups. The reaction is carried out over a wide range of temperature and pressure and, as a rule, in polar solvents (generally alcohols, water, or acetic acid). Other hydrogenation catalysts have not the same general importance; however, of these palladium on lead acetate should be mentioned; hydrogenation on this catalyst does not effect the double bond.

TABLE 3.

Reducing agent for nitro-groups	Functional groups														
	C=C	C≡C	OH	C=O	COOH & COOR	C≡N	C—Cl	C—F	SO_3H	SO_2	—S—	OR	C—NH_2	O=C—NH_2	N—NO_2
Raney nickel	±	—	+	—	+	—	±	+	+	+	+	+	+	+	+
Palladium on carbon	+	—	+	+	+										
Palladium on $PbCO_3$	+	—	+			—									
Palladium on $BaSO_4$			+	+	+										
Adams catalyst		—	+	—	+			+				+			+
Colloidal Pt	—		+												
Na amalgam			+		+									+	
Al amalgam	+				+										
Zn dust	—														+
Fe + acid	±		+		+	+			+			+			
Zn + acid	—	+	+		+							+			
Sn or $SnCl_2$ + HCl	±		+	—			+	+				+	+		
Na in boiling alcohol			+												
N_2H_4 with addition of Pt or Pd	+														
Lithium tetrahydroaluminate	±	—	+	—	—		+	+				+			

+ selective reduction.
- non-selective reduction.

In work with catalysts other than Raney nickel, low pressures and temperatures close to room temperature are used.

Of chemical reducing agents, iron filings and iron(II) salts should be mentioned; with these the reduction usually proceeds in the presence of catalytic quantities of protons:

$$R—NO_2 + 3\,Fe + 4\,H_2O \xrightarrow{H^+} R—NH_2 + 3\,Fe(OH)_2,$$

or

$$R—NO_2 + 2\,Fe + 4\,H_2O \xrightarrow{H^+} R—NH_2 + 2\,Fe(OH)_3$$

This permits reduction with iron to be carried out in weakly acid, almost neutral, solution[109].

In spite of the selectivity of tin and tin(II) chloride in hydrochloric acid (they do not attack multiple C–C bonds), they generally give lower yields than catalytic methods and the reduction is sometimes complicated by side-reactions¶.

The use of lithium tetrahydroaluminate, which, as a rule, readily reduces the aliphatic nitro-group to the amino-group, is largely affected by the interaction of this agent with many functional groups (carbonyl, carboxyl, ester, nitrile, triple bond, etc.).

It is of interest to note that when optically active nitro--compounds are reduced with lithium tetrahydroaluminate, optically active amines are obtained[110].

Aluminium amalgam and zinc dust are extremely weak reducing agents. In reduction with zinc in an acid solution, it is sometimes useful to employ copper-coated or amalgamated zinc[111,112].

Until recently the possibility of selectively reducing nitro-groups in aliphatic compounds by such reagents as hydrazine with the addition of platinum or palladium, titanium sulphate[113], NH_4–Hg amalgam[114], etc. was not considered. However, these agents reduce the nitro--group in aromatic nitro-compounds extremely rapidly and easily.

The electrochemical method has also not been sufficiently used for the selective reduction of nitro-groups in polyfunctional aliphatic compounds.

III. SELECTIVE REDUCTION OF FUNCTIONAL GROUPS IN NITRO-COMPOUNDS

There is relatively little information in the literature on the selective reduction of functional groups in nitro--compounds. This may be explained by the difficulty of this problem, since the nitro-group is one of the functions most sensitive to reduction, and also by the fact that the object of the majority of workers is to find conditions for the reduction of the nitro-groups in order to synthesise the corresponding amines, oximes, or alkylhydroxylamines.

¶ This applies to a greater extent to aromatic nitro-compounds.

In recent years, in connection with the increasing part played by nitro-compounds in industrial practice and theoretical investigations, the attention of chemists has been more and more attracted to the possibility of synthesising nitro-products (mainly nitroalkanes, nitro-alcohols, and nitro-amines) by the selective reduction of the corresponding polyfunctional compounds.

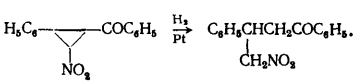
The material in this part of the review is grouped according to general methods of reduction, catalytic, chemical, and electrochemical.

1. Catalytic Reduction of Functional Groups in Nitro--Compounds

Multiple carbon–carbon bonds can usually be easily reduced by catalytic hydrogenation. This obviously explains why most work on the catalytic reduction of polyfunctional nitro-compounds has been done on the reduction of nitro-alkenes.

As early as 1917, work was carried out on the reduction of the double bond conjugated with a nitro-group; this work was done on the nitrostyrenes. Sonn and Schellenberg observed that when nitrostyrenes are hydrogenated on platinum black or colloidal palladium in alcohol at room temperature, selective reduction of the double bond occurs[115]. However, instead of the desired phenylnitroethanes, products formed by the addition of phenylnitroethane to unreduced nitrostyrene were obtained.

Similar results were obtained somewhat later by Kohler and Drake, who showed, moreover, that Kelber nickel cannot be used as a catalyst for the selective reduction of α-nitro-alkenes because the rate of reduction of the nitro--group is similar to the rate of reduction of the double bond[116]. These workers opened the cyclopropane ring of 3-benzoyl-1-nitro-2-phenylcyclopropane without affecting the carbonyl or nitro-group:

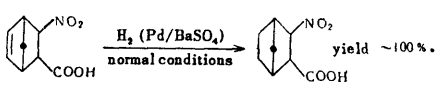


Hurd developed a satisfactory method of selective hydrogenation, not accompanied by dimerisation, for 1-aryl-2--nitroalk-1-enes[117]. He carried out the reduction at 15–40° on platinum or palladium in water, alcohols, ketones or aromatic hydrocarbons and obtained the corresponding 1-aryl-2-nitroalkanes in 25–60% yield. The author noted ketones or oximes as possible secondary products.

It is much easier to reduce a double bond not conjugated with a nitro-group. For this it is expedient to use platinum dioxide in acetic acid at room temperature. Examples are known of the successful selective reduction of the C=C bond with the aid of this catalyst in nitro-alkenes[118], phenylnitrocyclohexenes[119,120] nitronorbornylenes[121] and other nitro-cyclenes of the terpene series[122]. Raney nickel is less suitable for the selective hydrogenation of the double bond, since in a number of instances the double bond is reduced on this catalyst only after reduction of the nitro--group[100].

It should be mentioned that the structure of the nitro--compound undergoing reduction frequently affects the nature of the products of catalytic hydrogenation. Thus, Young and Snyder succeeded in hydrogenating the phenyl ring of ethyl 3-(2-nitrobutyl)indole-2-carboxylate without affecting the nitro- or the ester group[123]. The catalyst was 30% palladium on charcoal, and the reaction was carried out at room temperature under a hydrogen pressure of 3 atm in acetic acid. The authors consider that the course of this reaction is explained by a combination of steric and electronic factors that protect the nitro-group in this compound. It is also known that the double bond conjugated with the nitro-group can be selectively reduced in 1,2-dideoxy-1-nitro-D-*arabo*-hexitoltetraacetate, the molecule of which contains several ester groups[124]; the reaction was carried out on palladium black in absolute alcohol under normal conditions.

Recently Yur'ev and coworkers[125] described the selective reduction of 2-nitro-3,6-*endoxo*-Δ^4-tetrahydrobenzoic acid in acetone with palladium on barium sulphate:



There are no references whatever in the literature on the possibility of the catalytic selective reduction of carbonyl-containing functional groups in aliphatic nitro-compounds.

On the contrary, as is shown in Section II, in a number of instances the nitro-group is first reduced[44]. Catalytic reduction of the sulpho-group is also impossible in the presence of a nitro-group[88].

The examples given therefore exhaust all information on the catalytic selective reduction of functional groups in aliphatic nitro-compounds. It is clearly obvious that this method is not general, and in effect can only be used for the reduction of multiple bonds in nitro-alkenes; even here the reaction is sometimes complicated by the formation of secondary products. It should also be noted that the catalytic hydrogenation of functional groups in polynitro-compounds is not described in the literature, and it may be supposed that this would be a still more complicated process.

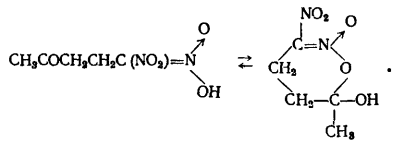
2. Chemical Reduction of Functional Groups in Nitro--Compounds

As is shown in Section II, reduction by atomic hydrogen, obtained by the interaction of metals with acids and alkali metals with alcohols, is one of the most widely used methods for the chemical reduction of the nitro-group and cannot be used for the selective reduction of functional groups in nitro-compounds. In the same way, chlorides of metals of variable valency which react with the nitro--group must also be excluded.

In the past decade the method of chemical reduction with complex hydrides of the alkali and alkaline earth elements has been widely developed. This method was very promising for the selective reduction of functional groups in nitro--compounds, because of the relative stability of nitro--groups to hydride anions. Moreover, at present there is a great selection of hydride reducing agents with the most diverse sensitivity to a number of functional groups.

Shechter[126] showed that nitro-ketones and nitro-aldehydes may be reduced in good yield to nitro-alcohols with sodium tetrahydroborate in aqueous-methanolic solution at pH 3–10.5. and a temperature from 0° to 25°. 1,1-Dinitropentan-4-one formed an exception; even with a considerable excess of reducing agent this gave a low yield of

nitro-alcohol. The author explains this by the existence of the initial compound as an equilibrium mixture:



Shechter suggests that sodium tetrahydroborate is particularly useful for the selective reduction of the most labile nitro-ketones and nitro-aldehydes. He also recommends the reduction of the carbonyl group in more stable nitro-ketones and nitro-aldehydes by aluminium isopropoxide† in isopropyl alcohol or toluene (for more "acid compounds"); aldehydes are reduced more rapidly than ketones, and the yields of nitro-alcohols are connected in the following manner with the nature of the nitro-group in the initial compounds:

$$t\text{-}NO_2 > s\text{-}NO_2 > primary\text{-}NO_2.$$

It is known that at room temperature lithium tetrahydroaluminate reduces the nitro-group in nitro- [36,58] and polynitro-compounds [42]. However, it has beenshown by Feuer and Kucera [129] that in ether at -30° and -60° this is a stronger reducing agent than sodium tetrahydroborate and may be used for the selective reduction of esters containing secondary and tertiary nitro-groups and even *gem*-dinitro-groups. The yields of nitro-alcohols are 53–76%. Hence, Shechter [126] and Feuer [129] have developed a new method of obtaining nitro-alcohols, greatly extending the range of these compounds, which are of practical interest.

In 1963, Gold and Klager published a paper on the reduction with sodium tetrahydroborate of the chlorides of a number of nitro-acids, including trinitrobutyric acid [130]; the corresponding nitro-alcohols were always obtained (see Table 4).

The authors also describe the reduction of some ketones containing $C(NO_2)_3$ groups, but they do not give yields, constants of the alcohols obtained, or experimental methods:

$$C(NO_2)_3CH_2CH_2COCH_3 \xrightarrow{NaBH_4} C(NO_2)_3CH_2CH_2CH(OH)CH_3,$$

$$C(NO_2)_3CH_2CH_2COCH_2OH \xrightarrow{NaBH_4} C(NO_2)_3CH_2CH_2CH(OH)CH_2OH.$$

TABLE 4.

Initial acid chloride	Alcohol obtained	Yield, %
$CH_3—C(NO_2)_2(CH_2)_2COCl$	$CH_3C(NO_2)_2(CH_2)_2CH_2OH$	63
$CH_3—C(CH_3)NO_2(CH_2)_2COCl$	$CH_3C(CH_3)NO_2(CH_2)_2CH_2OH$	70
$C(NO_2)_3(CH_2)_2COCl$	$C(NO_2)_3CH_2CH_2CH_2OH$	65
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2COCl$	$CH_3C(NO_2)_2CH_2N(NO_2)CH_2CH_2OH$	82
$(NO_2)_2C(CH_2CH_2COCl)_2$	$(NO_2)_2C(CH_2CH_2CH_2OH)_2$	50
$(NO_2)_2C[CH_2C(NO_2)_2CH_2CH_2COCl]_2$	$(NO_2)_2C[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	63
$(NO_2)HC[CH_2C(NO_2)_2CH_2CH_2COCl]_2$	$NO_2CH[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	85
$N(NO_2)—[CH_2C(NO_2)_2CH_2CH_2COCl]_2$	$N(NO_2)[CH_2C(NO_2)_2CH_2CH_2CH_2OH]_2$	85

† It should be mentioned that isolated instances of selective reduction of the carbonyl group in nitrocyclopropyl ketones had previously been known [127,128]. However, the authors of these papers did not aim at developing a general method of preparing nitro-alcohols.

Recently, a number of patents appeared on the preparation of the latter polynitrodiol from hydroxymethyl 3,3,3-trinitropropyl ketone with the aid of sodium tetrahydroborate. [131-134] The authors point out that this diol may be used as an intermediate in the synthesis of components of solid rocket propellents.

Ioffe and coworkers [135] showed that a solution of diborane in tetrahydrofuran (THF) may be used for the reduction of aliphatic mononitro-acids:

$$CH_2NO_2CH_2COOH + B_2H_6 \xrightarrow{THF} (NO_2)CH_2CH_2CH_2OH.$$

Diborane in tetrahydrofuran is also suitable for the reduction of esters of nitro-acids, but the presence of such electronegative substituents as nitro-groups sharply reduces the rate of reduction of the ester group.

Alkali metal tetrahydroborates (for example, sodium tetrahydroborate or sodium hydrotrimethoxyborate), which are reducing agents of the nucleophilic type, may be used very successfully also for the preparation of nitroalkanes and conjugated nitroalkenes [136], since the influence of the nitro-group ensures the possibility of nucleophilic attack of the BH_4^- and $BH(OCH_3)_3^-$ anions on the double bond. According to Shechter, the reduction mechanism includes nucleophilic attack of the relatively positive carbon atom of the C=C group of the conjugated nitro-alkene. Evidently, the initially formed metal trihydro(monoalkanenitronato)-borate Li or $Na(R_2CHCR'=NO_2)BH_3$ enters into further reactions giving a metal tetrakis(alkylnitronato)borate which is converted into the nitroalkane after hydrolysis. The course of the reactions may be represented by the following equations:

$$R_2C=CR'NO_2 + NaBH(OCH_3)_3 \rightarrow R_2CHCR'NO_2Na + B(OCH_3)_3,$$

or

$$4R_2C=CR'NO_2 + BH_4^- \xrightarrow[Na^+]{Li^+} [(R_2CHCR'=NO_2)_4B]^-.$$

The yield of nitroalkanes is 50–80%. The introduction of electronegative substituents, which increase the electron deficiency of the double bond, accelerates reduction. For this reason, the reaction with sodium and lithium tetrahydroborates is suitable for the selective reduction of conjugated fluoronitroalkenes (for example, 4,4,5,5,6,6,6-heptofluoro-2-nitrohex-2-ene). The reduction of nitroalkenes is usefully carried out at the lowest possible temperatures (-50°, -70°); the alkene is added to the metal tetrahydroborate to reduce the dimerisation side reaction:

$$R_2CHCR'=NO_2^- + R_2C=CR'NO_2 \rightarrow R_2CHCR'(NO_2)CR_2CR'=NO_2^-.$$

The reduction of sterically hindered nitroalkenes (for example, 3-nitrohept-4-ene) cannot be fully effected even at 0°. The reaction with such alkenes is carried out at room temperature.

The C=C bond in conjugated nitroalkenes may be reduced in the presence of ester groups by means of alkali tetrahydroborates [136]. In particular, the double bond in 1,2-dideoxy-1-nitro-D-*arabo*hexitol tetraacetate has been reduced with sodium tetrahydroborate [136]; the yield of product was 55–65% (for the catalytic reduction see Sowden and Fischer [124].) It has also been observed that, because of the strong inductive effect, closely situated nitro-groups activate ester groups to such an extent that they are reduced by metal tetrahydroborates [136]. Both sodium tetrahydroborate and sodium hydrotrimethoxyborate successfully reduce 2-nitrobutyl acetate at 3–5° to the corresponding alcohol, although generally under these conditions these reagents do not affect the ester gruup.

Cook and coworkers[83] showed that α-nitro-alkenes (including those containing fluorine) may be reduced to fluoronitro-alkanes in 35–55% yield by the action of lithium tetrahydroaluminate in anhydrous ether at -50°. Shechter and coworkers, who studied this reaction, also observed that it proceeds smoothly at temperatures below -40° after addition of lithium tetrahydroaluminate to the alkene undergoing reduction[136]. If the reagents are mixed in a different order, polymerisation occurs.

There are some very interesting results on the chemical reduction of the halogen in α-halogenonitro-compounds. In 1893, Duden showed that dibromodinitromethane is reduced to dinitromethane in 70–80% yield by the action of arsenic trioxide in potassium hydroxide solution[137]. Similar results are obtained by treatment of dibromodinitromethane with aqueous ammonia solution of hydrogen sulphide. Somewhat later, Pratt observed that the halogen in nitromethane derivatives can be reduced by an alkaline solution of hydrazine[138]‡:

$$CX(NO_2)_3 + NH_2{-}NH_2 \xrightarrow{KOH} CH(NO_2)_3,$$

$$RCHBrNO_2 + NH_4{-}NH_2 \xrightarrow{KOH} RCH_2NO_2,$$

$$CBr_2(NO_2)_2 + NH_2{-}NH_2 \xrightarrow{KOH} CHBr(NO_2)_2,$$

$$CCl_3NO_2 + NH_2{-}NH_2 \xrightarrow{KOH} CCl_2H(NO_2),$$

where X = Cl or Br, R = H or C_6H_5.

Iffland proposed the reduction of α-bromonitro-compounds of the aliphatic and alicyclic series to the corresponding nitro-alkanes (yield 15–80%) by sodium tetrahydroborate in aqueous methanol solution[139,140]. Although ordinary halogenoalkanes are inert to sodium tetrahydroborate, the reduction of α-bromonitro-compounds becomes possible, evidently because of the strong inductive effect of the nitro-groups, which facilitates nucleophilic attack of the tetrahydroborate anion on the carbon atom carrying the halogen and the nitro-group. As a result of his investigations, Iffland[139,140] proposed a new method of preparing nitroalkanes from the corresponding carbonyl compounds:

$$R_2C{=}O \rightarrow R_2C{=}NOH \xrightarrow{\text{bromosuccinimide}} \left[R_2{-}\underset{Br}{C}{-}N{=}O\right] \rightarrow$$

$$\rightarrow R_2CBrNO_2 \xrightarrow{NaBH_4} R_2CHNO_2.$$

Klager has described the reduction of αα-tetrabromodinitro-compounds by sodium tetrahydroborate[141]:

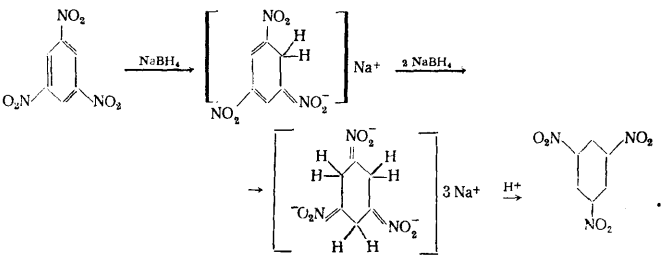
$$CBr_2NO_2CH_2CH_2CBr_2NO_2 \xrightarrow{NaBH_4} CH_2NO_2CH_2CH_2CH_2NO_2.$$

Thus, α-halogenonitro-alkanes may be reduced in several ways to nitro-alkanes. However, as has been shown in Section II.7, only the nitro-group is usually reduced in other halogenonitro-compounds.

Although the present review is concerned with aliphatic nitro-compounds, the work of Severin and Schmitz should be briefly mentioned[142-147]; they showed that the aromatic ring in polynitrobenzenes could be selectively reduced with sodium tetrahydroborate.

‡ It is interesting to note that aromatic nitro-groups, in contrast to aliphatic, are readily reduced by hydrazine.

The alkali tetrahydroborates are, as a rule, inert to aromatic systems, but because of the strong electron-acceptor activity of the nitro-groups, BH_4^- can attack the carbon atoms of the ring, for example:



More detailed information on this question is given in the literature[142-147].

It can be concluded from the material discussed here that the use of complex metal hydrides has substantially extended the possibility of selectively reducing functional groups in nitro-compounds; in particular it has, for the first time, permitted the preparation of a large number of nitro-alcohols from the corresponding carbonyl-containing compounds.

3. Electrochemical Reduction of Functional Groups in Nitro-Compounds

The only work on the selective reduction of functional groups in aliphatic nitro-compounds by an electrochemical method is that of Mairanovskii and coworkers[148], who investigated α-halogenonitroalkanes. These workers found that the effect of the nitro-groups facilitates the polarographic reduction of the C–Hal bond, and the wave corresponding to this process precedes the wave corresponding to the reduction of the nitro-group. This order of the waves was observed for mononitro-, dinitro-, and trinitro-alkanes containing chlorine, bromine, or iodine in the α-position to the nitro-groups.

There is some indirect information indicating the possibility of selectively reducing the carbonyl group in nitro-compounds by an electrochemical method. Shikata and Tacho established that the reduction potentials of ketones, azo-, and nitro-compounds are proportional to the electronegativity of the substituents linked to the group undergoing reduction[149]. Obviously, it should be possible to select substituents such that their carbonyl group is reduced by an electrochemical method before the nitro-group. However, there is no information on this question in the literature

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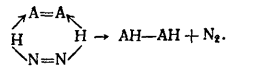
In conclusion, some hydrogenation catalysts will be briefly discussed that do not reduce the nitro-group, and also reagents that weakly react (or do not react at all) with the nitro-group, but are capable of reducing some functional groups. However, these have not yet been used for the selective reduction of polyfunctional nitro-compounds.

According to Japanese workers, the hydrogenation of 1-nitropropane on a catalyst of metal formates (for example, Ni and Zn, or Zr and V formates) is difficult[150].

A silk–palladium catalyst, generally used for the hydrogenation of multiple bonds in alkenes, aldehydes and nitriles, has similar properties[151].

Broadbent and Johnson[152] recently described a catalyst based on rhenium oxide ($Re_2O_7.3C_4H_8O$) with a wide spectrum of activity. It can be used for readily hydrogenating aromatic systems, but it also reduces carbonyl and carboxyl groups to alcohols groups, and nitriles to amines; this catalyst is inert to aliphatic nitro-compounds (for example, 2-nitropropane) and reduces aromatic nitro-compounds (for example, nitrobenzene) with difficulty. However, m-nitroacetophenone is very inert to its action, and, thus, the introduction of the nitro-group may render the carbonyl group and the atomatic nucleus passive.

Diimide readily reduces symmetrical multiple bonds (C=C, C≡C, N=N, O=O, etc.) with which it apparently forms a transition complex[153,154]:



However, the formation of such a complex with two unlike charged atoms is difficult, and therefore the reduction of groups of the type C=N, NO_2, C≡N, S=O, and C=O proceeds much more slowly. In particular, nitroethane is comparatively stable to the action of azodiimide[153].

It should be noted that some nitro-compounds are not affected by calcium hydride[155].

Some neutral complexes of borine and alkylborines that do not react with the nitro-group should also be mentioned[156]; these have hardly been used for the reduction of polyfunctional aliphatic nitro-compounds.

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POLYMER SYNTHESIS BY CYCLIC POLYMERISATION

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CONTENTS

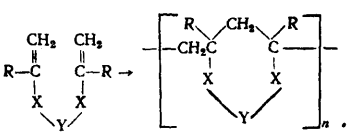
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I. INTRODUCTION

In connection with studies on the synthesis of polymers with valuable technical properties, in particular high thermal stability, there has been a considerable increase of interest in recent years in polymeric compounds containing cyclic groupings in the main chain [1-3]. At the present time extensive experimental data have been accumulated on the synthesis of various cyclic polymers, their structure, and their properties.

When the information available in the literature is generalised and systematised, it becomes clear that introduction of cyclic groupings, carbocyclic and heterocyclic units, into the main polymer chain can be achieved in three principal ways: by cyclic polymerisation, polycondensation, and chemical modification of polymeric compounds. Cyclic polymerisation can in turn be subdivided into two classes according to the mode of formation of the rings: chain polymerisation and stepwise polymerisation. The latter class includes polymerisation by the Diels–Alder reaction [4], thermal polymerisation of allene hydrocarbons [5], and others.

In the present review only cyclic polymers obtained by cyclic chain polymerisation are considered. In the field of cyclic polymerisation the so called intermolecular–intramolecular polymerisation of non-conjugated dienes has at present undergone the greatest development [6]. This type of cyclic polymerisation was discovered as a result of studies by several investigators [7-11], in particular Butler and coworkers [12,13]. It consists essentially in intramolecular ring closure of non-conjugated dienes, in particular 1,6-dienes, with simultaneous intermolecular chain growth, according to the following general mechanism:

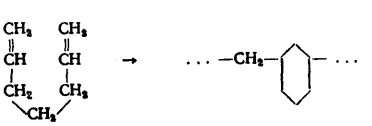


The polymerisation of other unsaturated systems, cyclodiene, triene, and vinylacetylene compounds and bifunctional compounds (dialdehydes, diepoxides) has also been investigated, using all known methods of initiation, with the aim of synthesising cyclic polymers. It was established that cyclic units in the polymer chain can form by intramolecular cyclisation of the monomer and interaction of two or several monomeric units of various types. For this reason, we shall give the name cyclic polymerisation to any type of polymerisation which leads to the introduction into the main polymer chain of cyclic groupings, regardless of the structure and nature of the monomer.

II. SYNTHESIS OF CARBOCYCLIC POLYMERS

1. Polymerisation of Non-Conjugated Dienes.

A. Polymerisation of diene hydrocarbons. Marvel and Stille [14] were the first to show the possibility of the cyclic polymerisation of non-conjugated diolefins under the influence of complex metal alkyl catalysts. A solid, benzene-soluble polymer with cyclohexane rings in the chain, melting at 210–230° and having an intrinsic viscosity $[\eta] = 0.2–0.4$, was obtained from hepta-1,6-diene under the action of the $Al(iso\text{-}C_4H_9)_3$–$TiCl_4$ catalytic system:



Rigid rubberlike polymers, the degree of cyclisation in the soluble fraction of which reaches 87%, are obtained under similar conditions from hexa-1,5-diene and 2,5-dimethylhexa-1,5-diene. Recently Makowski et al. [15] obtained in