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Chemistry of α-Nitrohetero-organic Compounds

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Methods of preparation, problems of the establishment of structure and elementotropism, and chemical reactions are surveyed on the basis of 177 references.

CONTENTS

I.	Introduction	872
II.	Methods of preparation	872
III.	Establishment of structure	876
IV.	Chemical properties	882

I. INTRODUCTION

During recent years we have witnessed vigorous development of the chemistry of organoelementary compounds and of nitro-compounds. The results of these investigations have been summarised in a considerable number of monographs and review papers. Hitherto, however, no attempt has been made to examine from a uniform viewpoint the chemistry of compounds in which both a nitro-group and a heteroatom are attached to the same atom of the molecular framework, i.e. the chemistry of α-nitrohetero-organic compounds.

Yet an analysis of the reactions of this class of compounds is of undoubted interest, both theoretical and applied. Indeed, several methods of preparation involve interaction of an ambident nitro-anion with an electrophile in which the positive charge is concentrated mainly on the heteroatom, which may prove interesting in the study of dual reactivity. Furthermore, these compounds are able to develop elementotropism, a phenomenon well known with carbonyl compounds, which can now be considered on new models. On the other hand, the preparation of these α-nitro-compounds and the investigation of their properties will broaden the opportunities for using both hetero-organic compounds and the nitro-derivatives in organic synthesis. There are indications that α-nitrohetero-organic compounds may be used directly in herbicidal and insecticidal compositions, and also as intermediates for the production of surface-active agents, biologically active products, explosives, and finishing agents in the textile industry. The present review summarises results on methods for the preparation of α-nitrohetero-organic compounds, examines the chief principles on which their structure is established, and describes several chemical reactions. It covers the literature to 1974. It does not include data on α-halogeno-α-nitro-compounds, nor certain earlier results, whose reliability is open to doubt.

II. METHODS OF PREPARATION

1. Reaction of Salts of Nitro-compounds with Halogenated Hetero-Organic Compounds

The chief examples of this reaction that have been studied are sulphenylation, silylation, and diethylborylation. Salts of mononitro-compounds react with sulphenyl halides and thiocyanates to form α-nitroalkyl sulphides[1,2]:

$$RSX + [R'R''C(NO_2)]Na \rightarrow RSCR'R''(NO_2) + NaX \quad (1)$$

R = *p*-MeC_6H_4, *m*-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$; R' = H, Me, Et, n-Pr; R'' = H, Me; X = Cl, Br, SCN.

Furthermore, corresponding disulphides are also formed†. Anions of polynitro-compounds have been successfully sulphenylated by means of sulphenyl halides and sulphenium salts[4-7]:

$$RC(NO_2)_2^-Z^+ + R'SX \rightarrow RC(NO_2)_2SR' \quad \text{or} \quad RC(NO_2)=N\langle^{O}_{OSR'}$$

R = H, Me, NO_2; R' = Me, Ph, *p*-$MeOC_6H_4$, *p*-$NO_2C_6H_4$, 2,4-$(NO_2)_2C_6H_3$; Z = K, Ag, $(CH_2)_5NH_2$; X = Cl, Br, SbF_6, BF_4.

The synthesis of nitromethyl trichloromethyl sulphide[8,9]

$$MeNO_2 + CCl_3SCl \xrightarrow{NaOH/EtOH} (NO_2)CH_2SCCl_3$$

is clearly also a reaction of this type. The preparation of bis-1-nitroalkyl disulphides from the sodium salts of nitroalkanes and sulphur monochloride has been patented[10,11]:

$$RCH(NO_2)^-Na^+ \xrightarrow[ether]{S_2Cl_2} [RCH(NO_2)S]_2$$

R = Alk C_1—C_6, Ar C_6—C_{15}.

Nitro-derivatives containing oxidised sulphur are obtained by the action of sulphonyl chlorides on salts of nitro-compounds. In particular, a convenient method has been proposed[12] for synthesising 1-nitroalkyl *p*-tolyl sulphones:

$$RR'C(NO_2)^-K^+ + p\text{-}MeC_6H_4SO_2X \rightarrow p\text{-}MeC_6H_4SO_2CRR'NO_2$$

R = H, Me; R' = H, Me, Et, Ph‡; *p*-ClC_6H_4, *p*-$MeOC_6H_4$; RR' = $(CH_2)_5$; X = Br, I.

This reaction takes place by a radical-anion mechanism[12]:

$$Tos\,I + Me_2C(NO_2)^- \rightarrow Tos^- + ICMe_2NO_2$$
$$ICMe_2NO_2 \rightleftarrows I^\cdot + Me_2CNO_2^\cdot$$
$$Tos^- + Me_2CNO_2^\cdot \rightleftarrows Tos\,C(NO_2)Me_2^{\cdot-}$$
$$Tos\,C(NO_2)Me_2^{\cdot-} + ICMe_2NO_2 \rightleftarrows Tos\,C(NO_2)Me_2 + ICMe_2NO_2^{\cdot-}$$
$$ICMe_2NO_2^{\cdot-} \rightarrow I^- + Me_2CNO_2^\cdot \text{ etc.}$$

†Reaction (1) will be discussed in detail in Section IV, 1*a*. The products $CH_3CH(NO_2)SR'''$ (where R''' = $Cl[CH_2]_2$ or *m*-$NO_2C_6H_4$) were oxidised to the corresponding sulphones without being isolated[3].

‡The salt of this nitroalkane was treated also with benzenesulphonyl chloride.

where Tos = p-$CH_3C_6H_4SO_2$. N-Nitrosulphonamides can be obtained from salts of nitramines and sulphonyl chlorides: e.g.[13]

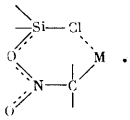
$$Me_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}\underset{\underset{NO_2}{|}}{N}Na + PhSO_2Cl \rightarrow Me_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}\underset{\underset{NO_2}{|}}{N}{-}SO_2Ph \ .$$

Nitro-silyl derivatives are also obtained from salts of nitro-compounds. In contrast to α-sulphur-substituted nitro-compounds, however, the only final products are O-esters of nitronic acids:

$$M^+[C(NO_2)RR']^- + R''_3SiCl \rightarrow RR'C{=}N{-}O{-}SiR''_3$$

R = R' = CO_2Me[14], NO_2[15,16]; R = NO_2, R' = CN[17]; R" everywhere Me or Ph.

The potassium salt of trinitromethane and the sodium salt of dimethyl nitromalonate do not react with trimethylchlorosilane§. From this it is concluded[14,16] that the silylation of salts of nitro-compounds by trimethylchlorosilane requires electrophilic assistance in abstracting the leaving group, perhaps in a cyclic transition complex of the type



The silver salts of methylnitramine, N-nitrotoluene-p-sulphonamide, and ethyl N-nitrocarbamate are also silylated by trialkylhalogenosilanes:

$$[RN(NO_2)]Ag + Me_2SiClR' \rightarrow [RN(NO_2)]SiMe_2R'$$

R = Me, R' = H, Me, iso-Pr[20];
R = EtOCO[21], p-$MeC_6H_4SO_2$[22], R' = Me.

Diethylboryl derivatives of nitroalkanes have been isolated or detected when diethylboryl chloride acts on salts of the nitroalkanes and functionally substituted nitro-compounds in inert aprotic solvents:

$$[RR'C(NO_2)]M \xrightarrow[-MCl]{Et_2BCl} RR'C{=}N{-}O{-}OBEt_2$$

R = Me, R' = Me, CHMeEt, M = Na[23];
R = H, R' = Me, n-Pr, CO_2Me, $CONH_2$;
R' = Ph, CO_2Me, $CONH_2$; R = R' = CO_2Me, M = Na, K[24].

Similarly, diethylboryl derivatives of N-nitro-compounds have been obtained by the action of diethylboron chloride on silver salts of several nitramines and N-nitroamides[25,26]:

$$[RN(NO_2)]Ag + Et_2BCl \xrightarrow[-AgCl]{} [RN(NO_2)]BEt_2 \ .$$

Reaction between silver salts of nitramines and trialkyltin halides yields organotin derivatives of the nitramines[27]:

$$[R'N(NO_2)]Ag + R_3SnX \xrightarrow[-AgX]{} R'N(NO_2)SnR_3$$

R = Me, Et, Ph; R' = Me, Et, iso-Pr, t-Bu, Ph; X = Cl, Br.

Mercuric chloride reacts with the sodium salt of nitromethane to give the mercury salt of the latter[28-30]:

$$2CH_2NO_2Na + HgCl_2 \rightarrow Hg[CH_2NO_2]_2 \ .$$

§There has been a report[18] (without any experimental data) that α-nitroalkyl-trimethylsilyl derivatives are formed by the interaction of sodium salts of primary and secondary nitroalkanes "under specific conditions". Also without experimental support Manzur and Zamudio[19] postulate the intermediate formation of trimethylsilyl methanenitronate in the reaction of trimethylchlorosilane with nitromethane in pyridine.

2. Nitration of Hetero-organic Compounds

This method is used only to obtain compounds that are resistant to hydrolysis and do not undergo any great oxidative degradation under the influence of nitrating agents. Mainly the nitration of organosulphur compounds has been reported, with the use of acidic nitrating agents and also alkyl nitrates in the presence of bases.

Many N-nitrosulphonamides have been obtained by the nitration of arenesulphonamides with nitric acid or a mixture of sulphuric and nitric acids:

$$ArSO_2NHR \rightarrow ArSO_2NRNO_2$$

Ar = Ph, R = Me, Et[31]; Ar = Ph, p-BrC_6H_4, m-$NO_2C_6H_4$, R = Alk C_3—C_7,
$(CH_2)_9N(NO_2)SO_2Ph$[32,33]; Ar = Ph, p-MeC_6H_4, 4-Me-3-$NO_2C_6H_3$, R = H, Me, Et[34-36]; Ar = 4-Me-3-$NO_2C_6H_3$,
R = CH_2CH_2Br, $CH_2CHBrMe$, $MeCHCH_2Br$[37] .

Nitrogen pentoxide has been used to nitrate the sodium salts of N-alkylsulphonamides[38]:

$$[RSO_2NR']Na + N_2O_5 \rightarrow RSO_2N(NO_2)R' + NaNO_3$$

R = Me, Ph, p-MeC_6H_4; R' = Me, n-Bu, s-Bu, Allyl .

Trismethylsulphonylmethane on treatment with a mixture of nitric and sulphuric acids gives the nitro-derivative in 68% yield[39]:

$$CH(SO_2Me)_3 \xrightarrow{HNO_3+H_2SO_4} NO_2C(SO_2Me)_3 \ .$$

α-Nitro-sulphones are obtained in good yield by nitrating alkyl and aryl sulphones with alkyl nitrates in the presence of bases[40,41]:

$$RCH_2SO_2R' \xrightarrow[Nu]{R''ONO_2} RCH(NO_2)SO_2R'$$

R = H, Et, n-Pr, Ph, p-$MeOC_6H_4$, p-ClC_6H_4;
R' = Alk C_1—C_4, Ph, $PhCH_2$, p-MeC_6H_4;
R" = Et, C_5H_{11}; Nu = t-BuOK, KNH_2/NH_3.

The nitration of sulphonates with alkyl nitrates in the presence of bases has been studied in detail[42,43]. In the suggested reaction scheme

$$RCH_2SO_3CH_2\underset{|}{C}H \xrightarrow[Nu]{R'ONO_2} \left[H_A{-}\underset{\vdots}{\overset{-}{C}}RSO_3CH_2\underset{|}{C}H_B\right] \rightleftarrows \underset{(I)}{\overset{\vdots}{O_2}NOR'}$$

$$\rightleftarrows \left[H_ACR(NO_2)SO_3CH_2\underset{|}{C}H_B + R'O^-\right] \qquad (2)$$

$$\overset{Nu}{\swarrow}\ (II)\ \overset{Nu}{\searrow}$$

$$\left[H_B\underset{|}{C}CH_2OSO_2C(NO_2)R\right]^- \qquad RCH_A(NO_2)SO_3^- + CH_2{=}C\!\!<$$

(III) (IV) (V)

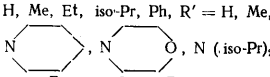
either the normal nitration product (III) or a mixture of compounds (IV) and (V) is formed depending on which proton (H_A or H_B) is attacked by the nucleophile Nu^-. The composition of the reaction mixture is, of course, determined by the structure of the radical CH_2CH_B. In agreement with this, neopentyl sulphonates not containing H_B are smoothly converted into the corresponding nitro-derivatives, whereas the nitration of ethyl and octyl butane-1-sulphonates yields secondary products (potassium 1-nitrobutane-1-sulphonate and oct-1-ene). In full agreement with scheme (2) the nitration of ethyl butane-2-sulphonate does not give the expected ethyl 2-nitrobutane-2-sulphonate but a >50% yield of potassium 2-nitrobutane-2-sulphonate, together with ethyl 3-methylpentane-3-sulphonate[43]:

$$EtCHMeSO_3Et \xrightarrow[2.NH_4Cl]{1.KNH_2/NH_3/EtONO_2} EtC(Me)(NO_2)SO_3K + Et_2CMeSO_3Et \ .$$

Alkyl nitrates can be used also to obtain *NN*-dialkylated α-nitro-sulphonamides¶:

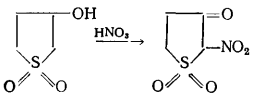
$$RR'CHSO_2NR''_2 + B \xrightarrow[0^\circ]{\text{oxolan}} RR'C^-SO_2NR''_2 \xrightarrow{EtONO_2} \rightarrow RR'C(NO_2)SO_2NR''_2 + EtO^-$$

R = Ph, R′ = H, R″ = Me, B = KH[44];
R = H, Me, Et, iso-Pr, Ph, R′ = H, Me,

NR''_2 = 

B = t-BuOK, n-BuLi[45].

Nitration is sometimes accompanied by partial oxidation or degradation of the initial organosulphur compound. Thus when acyclic or cyclic 3-hydroxy-sulphones are treated with nitric acid (at 60–90°C), the corresponding 3-keto-2-nitro-sulphones are obtained: e.g. [46]



Several β-keto-sulphides are converted by ethyl nitrate followed by oxidation into the corresponding nitromethyl sulphones [47,48]:

$$RSCH_2COMe + EtONO_2 \xrightarrow{EtONa} RSCH{=}NO_2Na \xrightarrow[AcOH]{H_2O_2} RSO_2CH_2NO_2$$

R = Me, *p*-MeC$_6$H$_4$.

α-Nitroalkylphosphonates have been obtained by nitrating phosphorylated aldehydes, ketones, and β-alkoxy-vinylphosphonates with acetyl nitrate in acetic anhydride[49]:

$$(RO)_2P(O)CH_2COX + AcONO_2 \longrightarrow (RO)_2P(O)CH_2NO_2$$
$$(RO)_2P(O)CH{=}CHOEt + AcONO_2 \longrightarrow \uparrow$$

R = Alk C_1—C_4; X = H, Me.

3. Action of Nitro-compounds on Hetero-organic Derivatives

α-Nitro-derivatives of hetero-organic compounds of many elements—silicon, mercury, thallium, indium, tin, lead, boron, etc.—have been obtained by this method.

Free nitro-compounds and nitramines can be silylated by means of many silylating agents. In particular, functionally substituted mono- and poly-nitro-compounds are silylated in inert aprotic solvents by *NN′*-diphenyl-*N*-trimethylsilylurea:

$$RR'CHNO_2 + PhNHCON(SiMe_3)Ph \rightarrow RR'C{=}N{-}C(=O){-}OSiMe_3 + (PhNH)_2CO$$

R=R′=CO_2Me[14]; R=CO_2Me, R′=H, NO_2[50];
R=R′=NO_2[16]; R=Me, R′=NO_2[17].

This agent was unsuitable for silylating nitroalkanes, for which purpose the stronger donor of a trimethylsilyl group, *NO*-bistrimethylsilylacetamide, was used [17,52]†:

$$RR'CHNO_2 + MeC(OSiMe_3){=}NSiMe_3 \rightarrow RR'C{=}N{-}C(=O){-}OSiMe_3 + AcNHSiMe_3$$

R = H, Me, Et, Ph; R′ = H, Me.

Trimethylsilyl derivatives of methylnitramine and *N*-nitro-toluene-*p*-sulphonamide are formed by silylation of the free *N*-nitro-derivatives:

$$RNHNO_2 + Me_3SiX \rightarrow [RN(NO_2)]SiMe_3$$

R = Me[20]; *p*-MeC$_6$H$_4$SO$_2$[22]; X = MeNH, PhNHCONPh, AcNSiMe$_3$.

Lovett [53] patented a method for preparing salts of light metals with trinitromethane, of general formula $MR_n[C(NO_2)_3]_x$ (where M = Li, Be, Mg, B, or Al and R = Alk, C_6H_5, aralkyl, or cycloalkyl), to several of which he assigned a covalent structure. These compounds are formed by the action of the metal alkyls on trinitro-methane or halogenotrinitromethanes. However, the absence of experimental data or evidence of the structure of the products casts doubt on the correctness of these results.

Much attention has been paid to the preparation of organomercury nitro-derivatives. Aryl and alkyl derivatives of nitromethylmercury are obviously extremely unstable. Their formation was postulated [54] by the action of nitromethane on phenylmercury hydroxide or bismethyl-mercury oxide, and also by the action of mercury dialkyls on the product of the reaction between mercuric oxide and nitromethane‡. Nevertheless, alkylmercury deriva-tives of polynitroalkanes proved to be comparatively stable compounds [54,55]:

$$R_2Hg + HC(NO_2)_3 \rightarrow RHgC(NO_2)_3$$

R = n-Bu, Ph.

Mercury and silver oxides are convenient starting materials for the preparation of bistrinitromethylmer-cury [56–58], bisfluorodinitromethylmercury [59], and silver derivatives of trinitromethane [60–62]:

$$M_mO + p\text{-}X(NO_2)_2CH \rightarrow M[C(NO_2)_2X]_n$$

M = Hg, X = NO_2, F, *m* = 1, *n* = 2;
M = Ag, X = NO_2, *m* = 2, *n* = 1.

Intermediate formation of α-nitroalkylplatinates is assumed in the reaction of tetrakistriphenylphosphine-platinum with nitroalkanes [63,64]:

$$Pt(PPh_3)_4 \rightleftarrows Pt(PPh_3)_2 + 2PPh_3$$

$$Pt(PPh_3)_2 \xrightarrow{RR'CHNO_2} \left[PPh_3,\ C(RR'),\ H{-}Pt,\ O,\ N{=}O,\ PPh_3 \right]$$

R = H, Me; R′ = H, Me.

The preparation has been described of α-mono- and α-poly-nitroalkyl derivatives of thallium [65–67], and also that of α-mononitroalkyl derivatives of indium [68]:

$$R_3M + HC(NO_2)R'_2 \rightarrow R_2MC(NO_2)R'_2 + RH$$

M = Tl, In, R = Me, Et, R′ = H, Me;
M = Tl, R = Et, R′ = NO_2, Cl, F.

Good yields of organotin derivatives of nitramines are obtained by the action of a tetra-alkylstannane or bis-trialkylstannyl oxide on primary nitramines [27]:

$$2R'NHNO_2 + (R_3Sn)_2O \rightarrow 2R'N(NO_2)SnR_3 + H_2O$$

R = iso-Pr, R′ = Me, t-Bu;

$$R'NHNO_2 + R_4Sn \rightarrow R'N(NO_2)SnR_3 + RH$$

R = Et, R′ = Me, iso-Pr.

¶ Yet *NN*-dialkyl-α-nitroalkanesulphonamides could not be obtained by nitrating alkanesulphonamides with nitric acid or ethylenesulphonamides with nitrogen sesquioxide [44].

†On silylating nitromethane with *NN′*-diphenyl-*N*-tri-methylsilylurea, Klebe [51] isolated bistrimethylsilyl methazonate. He assumed that trimethylsilyl methane-nitronate was an intermediate in this reaction.

‡The nitromethyl-phenylmercury described by Petukhov [30] was actually phenylmercury fulminate [54]:

$$PhHgOH + MeNO_2 \rightarrow [PhHgCH_2NO_2] \rightarrow PhHgONC + H_2O.$$

Several hetero-organic derivatives of amines react with nitro-compounds[69-71]§:

$$L_mM(NR_2)_n + nR'R''CHNO_2 \rightarrow L_mM(O{-}N{=}CR'R'')_n + nR_2NH$$
$$\downarrow O$$

R = Me, Et, $SiMe_3$; R′ = H, Me; R″ = H, Me; L = Me, Et; M = Sn, Pb ($n = 1$, $m = 3$), Hg ($n = m = 1$).

Triethylboron reacts with α-nitroalkenes to form diethylboryl alkanenitronates[73]:

$$2R'CH{=}C(NO_2)R + 2BEt_3 \rightarrow \left[R'CH(Et)CR{=}N\begin{matrix}\nearrow O\\ \searrow OBEt_2\end{matrix}\right]_2$$

R=R′=Me; R=Me, R′=Et; R= iso-Pr, R′=Me.

4. Replacement of Halogen in Halogenated Nitro-compounds

The first synthesis of an α-nitrohetero-organic compound from a halogenonitro-compound was accomplished in 1872, when nitromethanedisulphonic acid $NO_2CH(SO_3H)_2$ was obtained[74] from picryl chloride and potassium sulphite. The formation of this product was probably due to development of the properties of a "positive" halogen by one of the chlorine atoms. Reaction between chloronitro-compounds and sodium or ammonium sulphite has been successfully used also to obtain salts of other sulphonic acids[44,75]:

$$RR'C(NO_2)Cl + M_2SO_3 \rightarrow RR'C(NO_2)SO_3M \xrightarrow{HCl} RR'C(NO_2)SO_3H$$

where M = K or NH_4 and R, R′ = H, Alk, cycloalkyl, C_6H_5, or a heterocyclic radical.

Studies have been made on the reactions of picryl chloride and bromide with mercapto-derivatives of thiazole and thiadiazole[76,77], aliphatic and aromatic thiols[78], and also alkali-metal sulphides and sodium hydrogen sulphide[79]. It was assumed that derivatives of nitrotrithio-orthoformic esters $(RS)_3CNO_2$ or mercapto-derivatives of the type $(HS)_3CNO_2$ were formed as intermediates. Mono- and di-bromonitro-methane and also -ethane react similarly with arenethiols in alkaline medium[80]. However, intermediate sulphur-containing α-nitro-derivatives were neither isolated nor identified[76-80].

Halogenonitroalkanes have been successfully used to obtain α-nitro-sulphones[1,81-84]:

$$RR'C(NO_2)X + R''SO_2Na \rightarrow R''SO_2CRR'(NO_2) \qquad (3)$$

R and R′=H, Alk C_1–C_3, $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$; R″ = Ph, p-MeC_6H_4, p-BrC_6H_4, $C_{10}H_7$; X=Cl, Br, I.

It is interesting that one of the nitro-groups in a polynitro-compound may play the part of a halogen[84]:

$$Me_2C(NO_2)_2 + PhSO_2Na \rightarrow Me_2C(NO_2)SO_2Ph \quad . \qquad (4)$$

Kornblum et al. have shown[84] that reactions (3) and (4) have a radical-anion mechanism:

$$Me_2CI(NO_2) + PhSO_2^- \rightarrow Me_2CI(NO_2)^{\cdot-} + PhSO_2^{\cdot}$$
$$Me_2CI(NO_2)^{\cdot-} \rightarrow Me_2C(NO_2)^{\cdot} + I^-$$
$$Me_2C(NO_2)^{\cdot} + PhSO_2^- \rightarrow [Me_2C(NO_2)SO_2Ph]^{\cdot-}$$
$$[Me_2C(NO_2)SO_2Ph]^{\cdot-} + Me_2C(NO_2)I \rightarrow Me_2C(NO_2)SO_2Ph + Me_2CI(NO_2)^{\cdot-} \quad .$$

§Products of undetermined structure had earlier been isolated[72] from the reaction of a dialkylaminotrialkyltin with nitromethane.

The one-electron oxidation of diphenylmercury by tetranitromethane or a halogenotrinitromethane in solvents of various polarities—acetonitrile, sulpholan, chloroform—yields phenyltrinitromethylmercury[85]:

$$Ph_2Hg + C(NO_2)_4 \rightarrow [Ph_2Hg^{+}C(NO_2)_4^{\cdot-}] \rightarrow Ph^{\cdot} + NO_2^{\cdot}$$
$$\downarrow RH \qquad\qquad \downarrow$$
$$PhHgC(NO_2)_3 \qquad C_6H_6\ N_2O_4 \quad .$$

Reaction of triphenylphosphine with a bromonitroalkane involves intermediate formation of an α-nitroalkylphosphonium bromide, but different workers interpret differently the further changes undergone by these products[80,86-89].

Trialkyl phosphites and dialkyl phosphorohalidites obviously form with halogenonitroalkanes unstable products of the type $>P(:O).O.N(\rightarrow O):CCR'$,[90] but no evidence has been given[80,89,90] for the structure of the unstable nitro-derivatives.

5. Other Methods of Preparation

Other reactions are known that result in the formation of α-nitrohetero-organic compounds. Thus nitromethane and nitrocyclohexane are sulphonated by the dichloroethane, pyridine, and dioxan complexes of sulphur trioxide[91] to give insignificant yields of sulphonated products.

α-Nitroalkanesulphonyl chlorides were obtained[92] by the photochemical chlorosulphonation of C_{1-10} aliphatic nitro-compounds:

$$RCH_2NO_2 + SO_2 + Cl_2 \xrightarrow{h\nu} NO_2CHR(SO_2Cl) \quad .$$

However, no physical constants of the products isolated were given, and attempts to repeat this reaction have been unsuccessful[44].

Acyl esters of dinitromethanenitronic acid are converted by treatment with 2,4-dinitrobenzenesulphenyl chloride into 2,4-dinitrophenyl trinitromethyl sulphide[93]:

$$(NO_2)_2C{=}N\begin{matrix}\nearrow O\\ \searrow OCOR\end{matrix} + (NO_2)_2C_6H_3SCl \rightarrow (NO_2)_2C_6H_3SC(NO_2)_3 \quad .$$

Reaction of sodium toluene-*p*-sulphinate with the potassium salts of nitroalkanes and iodine in dimethylformamide yields α-nitro-sulphones[12]:

$$p\text{-}MeC_6H_4SO_2Na + RR'C{=}NO_2K + I_2 \rightarrow p\text{-}MeC_6H_4SO_2C(NO_2)RR'$$

R=H, Me, R′=H, Me, Et; RR′=$(CH_2)_5$.

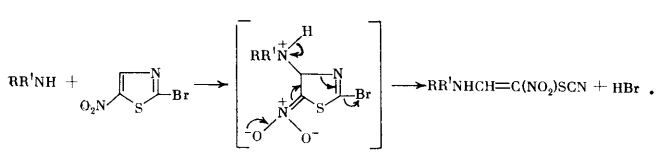
A simple method for obtaining α-nitroisoalkylphosphonates is to oxidise the α-aminoisoalkylphosphonates[49]:

$$(RO)_2P(O)CRMeNH_2 \xrightarrow{KMnO_4} (RO)_2P(O)CRMeNO_2 \quad .$$

R=Me, Et

Silver salts of polynitroalkanes are obtained from other salts of these compounds by the action of silver nitrate[60,94-97].

Sterically hindered secondary aliphatic amines open the ring of a substituted nitrothiazole to give 2-dialkylamino-1-nitrovinyl thiocyanates[98]:



Several workers have postulated the formation of unstable α-nitrohetero-organic compounds. This has

been assumed in particular in the reaction between nitromethane and aluminium tribromide [99]:

$$AlBr_3 \cdot MeNO_2 + MeNO_2 \rightleftarrows \left\{ CH_2{=}N^{+}\!\!<^{O}_{OAlBr_2} \cdot MeNO_2 + HBr \right\}.$$

A mixture of products $(NO_2CH_2)_nSnCl_{4-n}$ (n = 1–3) is supposed to be formed when nitromethane acts on tin tetrachloride in a primary amine [100]. Formation of the radical-anions

$$O_3SCH_2NO_2^{\cdot-}, SCH_2NC_2^{\cdot-}$$

$$O_3PCH_2NO_2^{\cdot-}, O_2P(H)CH_2NO_2^{\cdot-}, O_2AsCH_2NO_2^{\cdot-}.$$

has been recorded [101] when certain radicals add to the anion of aci-nitromethane.

6. Synthesis of α-Nitro-ylides

α-Nitro-ylides of triphenylarsenic have been obtained by the reactions [102,103]

$$\begin{aligned} &Ph_3AsCl_2 + PhCH_2NO_2 \xrightarrow[C_6H_6]{Et_3N} Ph_3As{=}C(NO_2)Ph \\ &Ph_3AsO + MeNO_2 \xrightarrow[P_2O_5]{Et_3N} \begin{cases} \xrightarrow{Ac_2O} Ph_3As{=}C(NO_2)Ac \\ \xrightarrow[P_2O_5]{Et_3N} Ph_3As{=}CH(NO_2) \end{cases} \end{aligned} \qquad (5)$$

for which the mechanism

$$Ph_3AsO + Ac_2O \rightarrow [Ph_3As^{+}OAc] \xrightarrow{CH_2NO_2^{-}} [Ph_3As^{+}CH_2NO_2] + OAc^{-}$$
$$\downarrow -H^{+}$$
$$Ph_3As^{+}-\bar{C}HNO_2 \leftrightarrow Ph_3As{=}CHNO_2$$

has been suggested. The corresponding α-nitro-ylides of phosphorus were unstable compounds [102]. The product of the decomposition of trimethylsilyl dinitromethanenitronate $[C(NO)NO_2]$ has been detected as the ylide with triphenylphosphine [16]:

$$Ph_3P + [C(NO)NO_2] \rightarrow Ph_3P^{+}[C(NO_2)NO]^{-}.$$

When dimethyl sulphoxide was treated with dinitromethane in the presence of acetic anhydride, the corresponding αα-dinitro-ylide of sulphur $(CH_3)_2S^{+}-C^{-}(NO_2)_2$ was obtained [104].

III. ESTABLISHMENT OF STRUCTURE

Elementotropism is now known in many classes of organic compounds. Therefore any α-nitrohetero-organic compound can in principle exist as an equilibrium tautomeric mixture:

$$\underset{\text{"O-form"}}{>C{=}N^{+}\!\!<^{O}_{OElR_n}} \text{ or } \underset{\text{"O-form"}}{-N{=}N^{+}\!\!<^{O}_{OElR_n}} \rightleftarrows \underset{\text{"C" or "N-form"}}{>C(NO_2)ElR_n} \text{ or } \underset{\text{"C" or "N-form"}}{-N(NO_2)ElR_n} \qquad (6)$$
$$\rightarrow \left[>C(NO_2) \right]^{-} ElR_n^{+} \text{ or } [-N(NO_2)]^{-}ElR_n^{+} \leftarrow$$

The presence of a particular form and the position of the equilibrium (6) are, of course, determined both by the nature of the element and by the structure of the nitro-containing group. Furthermore, it must be borne in mind that the compound isolated may be either kinetically or thermodynamically preferred. In most cases the nature of the product has not been firmly established¶.

¶Products of the sulphenylation of mono- and polynitro-compounds are kinetically preferred, since their structure depends on the nature of the sulphenylating reagents as well as on the process conditions [2,7].

In view of the above considerations neither the chemical reactions nor the method of preparation can be a criterion in establishing the structure of α-nitrohetero-organic compounds, but at best merely enable one form to be identified. Therefore only a combined study by physicochemical methods will establish the structure. Confirmation of a structure is obtained by comparing spectroscopic characteristics with corresponding properties of model compounds. However, such correspondence must be approached extremely cautiously, since the introduction of an element in the α position with respect to a nitro-group may itself distort appreciably the properties of the model. The choice of method for proving the structure is, of course, determined by the nature of the element adjacent to the nitro-group. Much published information on this question appears to be incorrect, and requires critical review.

1. Physicochemical Methods

Papers have appeared during recent years on the use of ultraviolet, infrared, and nuclear magnetic resonance spectroscopy to investigate the structure of α-nitrohetero-organic compounds. Reports of the use of Mössbauer spectroscopy, mass spectrometry, or nuclear quadrupole resonance are considerably less frequent.

(a) Electronic absorption spectra

Polynitro-compounds and functionally α-substituted nitro-compounds exhibit marked differences in the ultraviolet spectra of anions, *O*-derivatives (alkyl esters of the corresponding nitronic acids), and true nitro-compounds [105,106], which may be used to determine the structure of α-nitrohetero-organic compounds derived from them. Nevertheless, the differences between the ultraviolet spectra of anions and *O*-derivatives have largely levelled off with mononitroalkanes and nitramines, so that it is difficult to use ultraviolet spectroscopy to determine the structure of α-nitrohetero-organic compounds obtained from them.

Kharasch and Cameron [3] regarded 2-chloroethyl and *p*-tolyl 1-nitroethyl sulphones as true nitro-compounds, having shown that their far ultraviolet spectra were similar to the ultraviolet spectrum of nitroethane. The intense absorption maximum in the range 290–320 nm, characteristic of alkyl esters of substituted nitromethanenitronic acids, is absent from the ultraviolet spectra of sulphides of general formula $RC(NO_2)_2SR'$ (R = H, CH_3, NO_2 and R' = H, CH_3, 2,4-$(NO_2)_2C_6H_3$, *p*-$CH_3OC_6H_4$, *p*-$NO_2C_6H_4$) [6,7], which indicates that the above polynitroalkyl sulphides are *C*-nitro-derivatives. When the sulphenylating agent was changed, however, other products were isolated, regarded as *O*-derivatives on the basis of their ultraviolet spectra [7].

Electronic absorption spectra have been used to investigate trialkylsilyl derivatives of aliphatic nitro-compounds. These products can be regarded as nitronic esters, since the ultraviolet spectra of $RR'C{:}NO.OSi(CH_3)_3$ contain a characteristic absorption maximum (λ_{max} = 240 nm for R, R' = H, Alk [17,52] and 265–315 nm for R, R' = $COOCH_3$, NO_2, CN [14–16,50], with lg ε = 3.7–4.0), coinciding with a maximum in the corresponding standard alkyl nitronates [107–109].

The ultraviolet spectra of diethylboryl derivatives of nitroalkanes contain a maximum at λ = 228–235 nm (ε = 10200–10700), [23,73] which is consistent with their suggested structure as dialkylboron nitronates.

Degrees of ionisation in solution have been determined for several α-nitrohetero-organic compounds from their molar extinction coefficients. It has been shown in particular that bistrinitromethylmercury has a covalent structure in solvents of low polarity[110,111]. Its complexes may be either *C*-derivatives or ionic compounds depending on the nature of the ligand[112,113]. Bisfluorodinitromethylmercury is almost completely unionised in solvents of various polarities (dimethylformamide, acetonitrile, acetone, alcohol).[111] Silver salts of polynitroalkanes are assumed[60,114,115] also to be covalent in several aprotic solvents†

Trinitromethyl derivatives of diethylthallium are completely ionised both in protic and in aprotic solvents. However, equilibrium between ionic and covalent forms is assumed[67] for diethylthallium derivatives of *gem*-dinitroalkanes in weakly ionising solvents:

$$Et_2Tl^+A^- \rightleftarrows Et_2Tl{-}A$$
$$A{=}CH(NO_2)_2,\quad C(NO_2)_2Me.$$

Ultraviolet spectra have been determined[103] for α-nitro-ylides of triphenylarsenic. The ultraviolet spectrum of $(C_6H_5)_3As:CHNO_2$ contains three maxima—at 223 nm (lg ε = 4.39), 265 nm (3.76), and 298 nm (3.81)—and that of $(C_6H_5)_3As:C(NO_2).COCH_3$ has two maxima—at 222 nm (4.40) and 315 nm (4.06).

(*b*) Infrared and Raman spectra

The method of infrared and Raman spectroscopy enables the structure of an α-nitrohetero-organic compound to be established not only in solution but also in the crystalline state. A rigorous choice between true nitro-compounds and anions or nitronic esters can be based on the infrared spectra of derivatives of nitroalkanes[109,117-119]. In true nitroalkanes the ν_{as} band of the nitro-groups lies in the range 1530–1560 cm^{-1}, whereas the C=N stretching vibration lies between 1585 and 1620 cm^{-1}‡. In the Raman spectra of nitroalkanes the ν_{as} vibration of the nitro-group is usually apparent as a weak depolarised line, whereas $\nu_{C:N}$ is seen as a strong polarised band. From this it may be concluded that infrared spectroscopy permits *C*-derivatives of α-nitrohetero-organic compounds to be distinguished from nitronic esters or ionic compounds§. Nevertheless, it is difficult on the basis of the infrared spectra to choose between hetero-organic *O*-derivatives of nitroalkanes and ionic structures.

Introduction of an electronegative functional substituent (including a nitro-group) in an α position with respect to the nitro-group in a nitroalkane shifts the ν_{as} band of the latter group to higher frequencies[119,120], while the C:N stretching vibration in an *O*-alkyl derivative may move to lower frequencies[14]. As a result the ν_{as,NO_2} and $\nu_{C:N}$ ranges overlap, and sharp demarcations can no longer be made from the infrared spectra between *C*- and *O*-derivatives of such nitro-compounds (including α-nitro-hetero-organic compounds). It may be supposed that the Raman spectra preserve the difference between these structures, but this question has not yet been examined experimentally. With functionally substituted α-nitro-hetero-organic compounds, on the other hand, infrared spectroscopy enables a clear choice to be made between ionic and covalent structures, since very significant differences are evident in the infrared and Raman spectra of corresponding nitro-compounds and their salts[117].

In the infrared spectra of silyl alkanenitronates the $\nu_{C:N}$ band is located in the range 1617–1622 cm^{-1}, which differs by 40–60 cm^{-1} from ν_{as} for the nitro-group in the corresponding nitroalkanes. The $\nu_{C:N}$ band is strongly developed also in the Raman spectra of the products[17,52]. The introduction of electronegative substituents into methanenitronic acid shifts the $\nu_{C:N}$ band to shorter wavelengths (1595–1605 cm^{-1}), where it almost coincides with ν_{as,NO_2} in the corresponding nitro-compounds. Several silyl derivatives of functionally substituted nitro-compounds exhibit an intense $\nu_{C:N}$ band in the Raman spectra[14,15,17,50].

The infrared and Raman spectra of trialkylmetal nitronates of general formula $R'R''C:NO.OMR_3$ (where $R = CH_3$, C_2H_5, n-C_4H_9; $R' = R'' = H$, CH_3; $R' = H$, $R'' = CH_3$; and M = Sn, Pb) are almost identical with those of salts of the corresponding nitro-compounds[121], so that the structure of *C*-derivatives was rejected for these products. Analysis of the spectra of compounds in which $R = CH_3$ established[121] that the MC_3 group has D_{3h} symmetry.

In the infrared spectra of diethylboron dialkylated methanenitronates the C:N stretching band appears at 1630–1645 cm^{-1}.[23,73] The infrared spectrum of the diethylboron derivative of methyl α-nitropropionate indicates that the boron atom is attached to the carbonyl oxygen atom by a donor–acceptor bond[24], which moves $\nu_{C:O}$ by more than 150 cm^{-1} to lower frequencies. Yet coordination of boron with the carbonyl group is probably absent from diethylboron derivatives of amides of α-nitro-acids, the boron being coordinated with the amide nitrogen atom[24].

Bands characteristic of anions of nitro-compounds are absent from the infrared spectra of the mercury salts of nitromethane[122] and trinitromethane[110,123,124] and from those of many complexes of the mercury salt of trinitro-methane[112]; all these products are regarded as *C*-derivatives. Yet the infrared spectra of crystalline polynitro-methyl derivatives of thallium[66,67] and silver[60,114,115] are almost identical with those of the potassium salts, which indicates that the products have an ionic structure. However, infrared spectroscopic data suggest that the silver salts of polynitroalkanes are not ionised in certain solvents[60].

Bands characteristic of covalent true nitro-compounds are present in the infrared spectra of α-nitroalkyl sulphones[40,43,84,125] and poly-α-nitroalkyl sulphides[6]. Bands due to the nitro-group and to carbonyl have shifted to lower frequencies in the infrared spectra of nitro-ylides of arsenic having the general formula $(C_6H_5)_3As:CR.NO_2$ (where $R = H$, $COCH_3$): ν_{s,NO_2}, ν_{as,NO_2}, and $\nu_{C:O}$ are respectively 1208, 1395, and 1595 cm^{-1}.[103] Spectral data are available also for trichloromercapto-derivatives of arylhydrazones of nitroformaldehyde[8] and for thio-cyanates of general formula $R'RNCH:C(NO_2)SCN$ in which R, R' = n-C_3H_7, iso-C_3H_7, $C_6H_5CH_2$, $[CH_2]_5$, $[CH_2]_7$, etc.[98].

For alkylnitramine derivatives infrared spectroscopy in principle enables a choice to be made between *O*-forms, *N*-forms, and ionic compounds. The infrared spectra of primary and secondary nitramines contain ν_{s,NO_2} bands at

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†Nielsen[116] cites several references to the preparation of covalent salts of heavy metals, but these results cannot be regarded as entirely reliable.

‡This conclusion cannot be extended to derivatives of nitromethane[117].

§It may be assumed that, under the influence of electropositive elements—boron, silicon, tin, etc.—the ν_{as} vibration of the nitro-group will undergo further displacement to lower frequencies, which should facilitate identification of the α-nitrohetero-organic compound.

1310–1340 cm^{-1} and ν_{as,NO_2} bands at 1570–1590 and 1510–1550 cm^{-1} respectively [117,126,127]. Furthermore, those of *O*-alkyl derivatives of alkylnitramines are characterised by two intense bands at 1240–1260 cm^{-1} and 1545–1570 cm^{-1}.[128] The presence of two stereoisomers splits the shorter-wavelength band, whose shorter-wavelength shoulder corresponds to the *cis*-isomer of the *O*-derivative [129]. Anions of alkylnitramines are characterised by the ν_{s,NNO_2} band in the range 1400–1500 cm^{-1}.[127] It is thus obvious that ionic structures of derivatives of nitramines are easily distinguished by means of the infrared spectra from covalent structures, and a choice between *O*- and *N*-forms can be based on the ν_s band of the nitro-group. It must be remembered, however, that the positions of characteristic bands in the infrared spectra of nitramine derivatives depend significantly on the conditions under which the spectra are determined¶, so that special attention must be paid to comparing the spectra of specimens recorded under closely similar conditions.

It may be expected from general considerations that the characteristic bands of the *O*-forms and ionic structures of α-nitrohetero-organic compounds will not differ significantly from the corresponding bands in the analogous alkyl derivatives, whereas the introduction of a heteroatom α to the nitro-group in the *N*-form may produce considerable shifts in the ν_s and ν_{as} bands of the nitro-group.

In conformity with this the *O*-trialkylsilyl derivatives of methylnitramine exhibit intense bands at 1250–1270 and 1550–1560 cm^{-1}.[20,130] In the *N*-trialkylsilyl derivatives, however, the ν_{as,NO_2} band appears in the range 1500–1510 cm^{-1}: i.e. it has undergone a low-frequency shift of >70 cm^{-1} in comparison with methylnitramine†. The low-frequency shift of ν_{s,NO_2} in these compounds is considerably smaller: in trialkylsilyl derivatives of methylnitramine this band appears around 1300 cm^{-1}.[20,130] Similarly, in the pyridine complex of diethylborylmethylnitramine the ν_{as} band of the nitro-group has been displaced to lower frequencies than in methylnitramine by about 100 cm^{-1}.[25]

Organotin derivatives of alkylnitramines of general formula $R'N(NO_2)SnR_3$ (R = Alk, C_6H_5, and R′ = Alk) are assumed [27] to have the structure of *N*-derivatives with the tin atom coordinated with an oxygen atom of the nitro-group. The infrared spectra of these compounds do not contain in the region of 1550 cm^{-1} bands due to N=N(→O).O–vibrations, nor bands typical of alkali-metal salts of primary nitramines‡.

The structure of an *O*-derivative has been assigned to the trimethylsilyl derivative of *N*-nitrotoluene-*p*-sulphonamide, since its infrared spectrum does not contain the ν_{s,NO_2} band (1280–1290 cm^{-1}) characteristic of *N*-alkyl-*N*-nitrosulphonamides, while bands found with the standard *O*-isopropyl derivative of *N*-nitrotoluene-*p*-sulphonamide are present [22].

¶In solvents ν_{as,NO_2} shifts to higher frequencies, but ν_{s,NNO_2} to lower frequencies.

†The spectra of the trialkylsilyl derivatives of methylnitramine were determined in dichloromethane.

‡According to the infrared spectra data, however, an ionic structure cannot be completely excluded for these products.

(*c*) Nuclear magnetic resonance spectroscopy

This method is probably the most informative with respect to the structure of α-nitrohetero-organic compounds, but hitherto has not been sufficiently widely used, and then mainly as proton magnetic resonance. Analysis of hetero-organic derivatives of aliphatic nitro-compounds is usually based on the chemical shifts of protons δ_H attached to α- and β-carbon atoms (relative to the nitro-group), the J_{El-H} constants in the El–$CH(NO_2)$– group, and also the shifts δ_H of protons attached to the heteroatom. The principal ^1H n.m.r. spectroscopic data for the hetero-organic derivatives of aliphatic nitro-compounds are listed in Table 1, which includes corresponding values for model nitro-compounds. The signals from protons attached to α- and β-carbon atoms in nitronic esters and nitroalkane salts exhibit down-field shifts relative to the analogous signals in the corresponding *C*-nitro-derivatives.

It may be assumed that the introduction, at an α position with respect to the nitro-group in the *C*-form, of an element of electronegativity less than that of hydrogen–lead, tin, mercury, thallium, silicon, boron—will produce an up-field shift in the signals of corresponding protons [131], whereas the introduction of such groups into the *O*-form or especially into an ionic structure should not significantly change the δ_H of the protons in comparison with the model compounds. Hence it should be easy by means of ^1H n.m.r. data to distinguish covalent *C*-derivatives of α-nitrohetero-organic compounds from the corresponding *O*-derivatives, provided that they contain one of the above six elements, as is confirmed by Table 1. Compounds No. 1–24 are *O*-derivatives, and therefore in most of them the signals due to protons attached to α- and β-carbon atoms are displaced down-field relative to those of the corresponding nitro-compounds§. Compound No. 4 was regarded [65] as a *C*-derivative, but the methylene proton chemical shifts and certain other criteria indicate that it is undoubtedly an *O*-derivative.

The introduction of hetero-organic groups of electronegativity exceeding that of hydrogen into an α position relative to the nitro-group should shift the signals of α or β protons down-field [131]. In agreement with this the signals of these protons in α-nitroalkyl sulphones [40,44,45,84,125] and α-nitroalkanesulphonates [43] are considerably displaced down-field relative to those of analogous protons in nitro-compounds, and almost coincide in the value of δ_H with the signals of α and β protons in *O*-alkyl derivatives of closely related nitronic acids. In the spectra of *C*-derivatives of α-nitrohetero-organic compounds containing thallium, mercury, and certain other elements a spin–spin interaction should be evident between the element and the α or β proton [138]. The absence of such an interaction for compounds No. 2, 4, 6, 11, and 13 in Table 1 finally eliminates the *C*-derivative structure for them.

Study of the dependence of δ_H for trimethylstannyl on the nature of the element with which this group is combined reveals [71] that the shift in compounds No. 2, 6, and 11 corresponds exactly with δ_H for $(CH_3)_3Sn–O–$ and differs considerably from that for $(CH_3)_3Sn–C$. However, a cautious approach must be adopted towards such analogies, since the introduction of the very electronegative and anisotropic nitro-groups may distort the picture.

§The abnormally low value of δ_{CH_3} for compound No. 9 was noted by the authors themselves [71].

Table 1. Proton magnetic resonance data for α-nitrohetero-organic compounds.

No.	Compound*	δ, ppm** CH=N or CH—NO_2	δ, ppm** CH_3C=N or CH_3C—NO_2	Ref.	Model cpd.	δ, ppm	Ref.
1	$R_3PbON(O)$=CH_2; R=Me, Et	5.4—5.5	—	71	CH_3NO_2	4.28	133
2	$R_3SnON(O)$=CH_2; R=Me, Et	5.5—5.6	—	71	$[CH_2NO_2]^-$ in H_2O	5.83	133
3	$Me_3SiON(O)$=CH_2	5.55	—	52, 132			
4	$Et_2Tl(CH_2)(NO_2)$***	5.35	—	65			
5	$R_3PbON(O)$=$CHCH_3$; R=Me, Et	5.7	1.7—1.9	71	$CH_3CH_2NO_2$	1.48 (CH_3); 4.38 (CH_2)	134
6	$R_3SnON(O)$=$CHCH_3$; R=Me, Et	5.96	1.83	71	$[CH_3CHNO_2]^-$	1.73 (CH_3); 6.14 (CH)	135
7	$Me_3SiON(O)$=$CHCH_3$	6.05	1.84	52, 132	CH_3CH=N(O)OCH_3	1,9 and 1.8 (CH_3)	
8	$Et_2BON(O)$=$CHCH_3$****	6.95	2.0	24		5,9 and 3.2 (CH)	135
9	$Me_3PbON(O)$=$C(CH_3)_2$	—	1.35	71	$(CH_3)_2CHNO_2$	1.57 (CH_3); 4.58 (CH)	134
10	$Et_3PbON(O)$=$C(CH_3)_2$	—	1.95	71			
11	$R_3SnON(O)$=$C(CH_3)_2$; R=Me, Et	—	1.9	71			
12	$Me_3SiON(O)$=$C(CH_3)_2$	—	1.9	5, 132			
13	$EtHgON(O)$=$C(CH_3)_2$	—	1.95	71			
14	$Et_2BON(O)$=$C(CH_3)_2$ *****	—	2.1	23			
15	$Me_3SiON(O)$=CHPh	6.74	—	52, 132			
16	$Et_2BON(O)$=C(CH)$_3$Ph	—	2.49	24			
17	$Me_3SiON(O)$=CHBr	6.96	—	132			
18	$Me_3SiON(O)$=$CH(CO_2Me)$	6.33	—	50, 132	$CH_2(NO_2)CO_2CH_3$	5.35 (CH_2)	24
19	$Et_2BON(O)$=$CH(CO_2Me)$	6.82	—	24	$CH(CH_3)(NO_2)CO_2CH_3$	1.75 (CH_3); 5.15 (CH)	24
20	$Et_2BON(O)$=$C(CH_3)(CO_2Me)$	—	2.1	24	$CH(NO_2)(CH_3)CONH_2$	1.7 (CH_3); 5.45 (CH)	24
21	$Et_2BON(O)$=$CH(CONH_2)$	6.85	—	24	$CH(CO_2Me)$=N(O)OCH_3	6.43 and 6.79 (CH)	136
22	$Et_2BON(O)$=$C(CONH_2)CH_3$	—	2.13	24			
23	$Me_3SiON(O)$=$CHNO_2$	8.25	—	50, 132	$CH_2(NO_2)_2$	6.1	134
24	$Me_3SiON(O)$=$C(CH_3)NO_2$	—	2.55	132	$CH_3CH(NO_2)$	2.18 (CH_3); 6.28 (CH)	134
25	Ph_3As=$CH(NO_2)$	7 6	—	103	CH_2=$CH(NO_2)$	7.12 (CH)	137

*Solution in tetrachloromethane at 20 or 35°C.

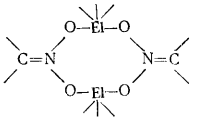
**Here and subsequently chemical shifts are given on the δ scale in all n.m.r. spectra. The standards adopted were tetramethylsilane for δ_H, δ_{13C}, and δ_{29Si}; nitromethane for δ_{14N} and δ_{15N}; and boron trifluoride–diethyl ether for δ_{11B}.

***Solution in acetonitrile; structure according to Ref. 65.

****Solution in dichloromethane at −20°C; the product has a dimeric structure.

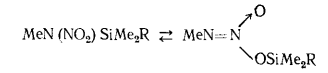
*****The product has a dimeric structure.

It is interesting that the α-nitrohetero-organic compounds listed in Table 1 do not exhibit non-equivalence of protons in α and β positions relative to the C=N(→O).O group, although such non-equivalence is very strongly developed in the corresponding *O*-alkyl derivatives. The averaging of the signals of α and β protons is attributed in trialkylsilyl derivatives to rapid exchange of the trialkylsilyl group between the two oxygen atoms of the O–N → O group[132,139], but in trialkyl-tin and -lead nitronates[71] it is due to the formation of symmetrical dimeric structures.



(see further in this subsection and also under *d*). In diethylboryl derivatives of nitroalkanes the averaging of the signals is also due to the formation of stable dimers[23,73], but in dialkylboryl methoxycarbonyl- and carbamoyl-methanenitronates only the *cis*-isomer of the nitronic ester is present in the reaction mixture, owing to coordination of the boron atom with the functional group[24]. In diethylboryl dimethoxycarbonylmethanenitronate rapid intramolecular transfer of the diethylboryl radical from one methoxycarbonyl group to the other has been established by proton magnetic resonance, and several kinetic parameters of the process have been determined[24].

The proton magnetic resonance spectra of α-nitrohetero-organic derivatives of nitramines do not permit a choice between *O*- and *N*-forms, since the δ_H ranges in the corresponding model compounds overlap[37]. However, use of this method to study dynamic processes in such compounds has established the presence of tautomerism in trialkylsilyl derivatives of methylnitramine[20,130]:



Appreciable displacement of this equilibrium in favour of the *O*-form is produced by rise in temperature and by the substituents R in the sequence t-C_4H_9 ≫ iso-C_3H_7 > CH_3 > H.

Heteronuclear magnetic resonance has hitherto been used mainly to analyse organosilyl and diethylboryl derivatives of nitro-compounds and nitramines. Table 2 shows that the α-carbon-13 signals are located in higher fields in aliphatic mononitro-compounds than in corresponding salts and *O*-alkyl derivatives. Published data suggest that, as in the ^1H n.m.r. spectra, replacement of a proton α to a nitro-group by an element of lower electronegativity should produce a diamagnetic shift in the α-carbon-13 signal[142], whereas the replacement of alkyl in an *O*-derivative by a hetero-organic group should not affect significantly the chemical shift δ_α-^{13}C. The signal from the α-carbon atom will then distinguish covalent *O*- and *C*-derivatives of α-nitrohetero-organic compounds (it is more difficult to distinguish *O*-derivatives from ionic structures). It is evident that this holds for compounds 1–9 in Table 2. However, the α-carbon-13 signal from compound No. 10, which according to ultraviolet spectral data is a *C*-derivative[112,113], is located considerably down-field from the signals for trinitromethane and trinitroethane. This suggests that the proposed criterion cannot be used to interpret the structures of α-nitrohetero-organic derivatives of polynitro-compounds.

Among other peculiarities of the ^{13}C n.m.r. spectra of α-nitrohetero-organic compounds is firstly their temperature dependence determined e.g. for compound No. 4, which indicates rapid exchange of the trimethylsilyl group

Table 2. Carbon-13 n.m.r. data (at 20°C).

No.	Compound	$\delta^{13}C$, ppm				Ref.	Model cpd.	$\delta^{13}C$, ppm.		Ref.
		Me—Si or BEt	α_C	β_C	other signals			α_C	β_C	
1	$MeCH{=}N(O)OSiMe_3$	−0.9	109.8	11.4	—	132	$CH_3CH_2NO_2$	69.3	11.5	140
2	$Me_2C{=}N(O)OSiMe_3$	−0.2	118.3	18.0	—	132	$[CH_3CH(NO_2)]^-$	115.7	—	139
3	$MeC(NO_2){=}N(O)OSiMe_3$	−0.7	wide	14.7	—	132	$(CH_3)_2CHNO_2$	78.4	20.0	141
4	$(MeO_2C)_2C{=}N(O)OSiMe_3$ *	−1.7	114.2	158.8	51.9	132, 139	$CH_3CH(NO_2)_2$	109	14.1	140
5	$MeO_2CC{=}N{\rightarrow}O$ MeO (C, O) $O{\cdots}BEt_2$	—	111.7	170.1 158.1	57.4 52.9	24	$(CH_3OCO)_2CHNO_2$	88.2	160.7	139
6	$HC{=}N{\rightarrow}O$ MeO (C, O) $O{\cdots}BEt_2$	8.1	103.0	171.8	56.0	24	$(CH_3OCO)_2C{=}N(O)OCH_3$	111.8	158.5 159.5	139
7	$MeC{=}N{\rightarrow}O$ MeO (C, O) $O{\cdots}BEt_2$	8.0	111.5	170.9	55.8 10.2	24	$[(CH_3OCO)_2C(NO_2)]^-$	111.7	164.6	139
8	$CH{=}N{\rightarrow}O$ $CONH_2{\cdots}BEt_2$	8.7	105.8	168.9		24	$CH_3OCOCH_2NO_2$	74.9	161.4	24
9	$MeC{=}N{\rightarrow}O$ $CONH_2{\cdots}BEt_2$	8.7	112.4	167.2	10.2	24	$CH_3OCOCH(CH_3)NO_2$	80.4	164.2	24
10	$(O_2N)_2Hg[C(NO_2)_3]_2$	—	151.8	—	—	112, 113	$CH_2(NO_2)CONH_2$	78.8	168.7	24
11	$MeN(NO_2)SiMe_2R$	0 (−3)	34—35	—	—	130	$CH_3CH(NO_2)CONH_2$	80.4	164.2	24
12	$MeN{=}N(O)OSiMe_2R$	0 (−3)	39—40	—	—	130	$HC(NO_2)_3$	113.5	—	141
13	$MeN(NO_2)BEt_2$ **	8.4	38.2	—	—	25	$[C(NO_2)_3]^-$	149	—	140
14	$MeN{=}N(O)OBEt_2$ **	7.2 6.9	40.0 40.2	—	—	25	$CH_3C(NO_2)_3$	128	—	133
15	$MeN(NO_2)BEt_2{\cdot}C_5H_5N$	8.7	36.5	—	125.3 140.4 143.7	25	CH_3NHNO_2	31.7	—	133

*At −80°C the carbonyl carbon atom gives two signals differing in δ values by 1.45 ppm, and the methoxy-carbon atom two signals differing by 0.73 ppm.
**In dichloromethane at −60°C.

between the two oxygen atoms of the O–N → O group. Secondly, analysis of the spectra of diethylboryl derivatives of nitro-compounds shows that in compounds 5–7 the boron atom is coordinated with the carbonyl oxygen atom. This produces a paramagnetic shift in the $^{13}C{=}O$ signal exceeding 10 ppm. In compounds 8 and 9, in which boron is coordinated with an amino-nitrogen atom, the paramagnetic shift is considerably smaller.

The ^{13}C n.m.r. spectra for silyl and diethylboron derivatives of methylnitramine show a sharp difference between the $^{13}CH_3{-}N$ signals for *N*- and *O*-derivatives[25,130]. The ^{14}N n.m.r. spectra of α-nitrohetero-organic derivatives of nitroalkanes and functionally substituted nitro-compounds usually permit reliable differentiation between covalent *C*- and *O*-products: firstly the signals from the O–N → O group in *O*-derivatives are considerably broader than the signals from the nitro-group in *C*-products, and secondly they are appreciably displaced up-field. However, comparison of the nitrogen-14 and nitrogen-15 chemical shifts in $Hg[C(NO_2)_3]_2$ (a *C*-product) and in $(^{15}NO_2)_2C{=}^{15}N(\rightarrow O).O.COCH_3$ shows that the accumulation of nitro-groups tends to level off this difference in chemical shifts[93]. It must be noted that, in the case of α-nitrohetero-organic derivatives of nitroalkanes, it is difficult to distinguish *O*-derivatives from ionic structures by means of the nitrogen-14 spectra without additional investigations.

Table 3 shows appreciable differences between nitrogen-14 chemical shifts for the nitro-group and for O–N → O in *O*- and *N*-hetero-organic derivatives of methylnitramine, without any significant influence of the nature of the heteroatom on the chemical shifts. The half-width of the line due to the nitro-group is considerably smaller than that for the O–N → O group. It is advisable to use ^{15}N n.m.r. at a low temperature in order to analyse labile compounds. Trimethylsilyl and diethylboron derivatives of *N*-nitrotoluene-*p*-sulphonamide are assumed to be *O*-products because the nitrogen-14 signal from the O–N → O group is very broad in their spectra.

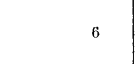
Analysis of n.m.r. spectra on nuclei of the heteroatoms may prove extremely fruitful in elucidating the structure of α-nitrohetero-organic compounds. Such studies have hitherto been made on trialkylsilyl and diethylboron derivatives of nitro-compounds and nitramines. Comparison of the silicon-29 n.m.r. spectra of silyl nitronates (compounds 2 and 3 in Table 4) with those of trialkylsilyl derivatives of the corresponding oximes confirms that silicon is not five-coordinated in nitronic esters. Compounds 5 and 6 show that the ranges of $\delta^{29}Si$ values for *N*- and *O*-forms are sharply delimited in the case of trialkylsilyl derivatives of nitramines. The boron-11 n.m.r. spectra for a series of α-nitrohetero-organic compounds (Table 5) indicate that the boron atom in them is hybridised. Fluorine-19 n.m.r. spectral data have been published[145] for several complexes of bisfluorodinitromethylmercury.

(*d*) Mass spectrometry

The mass spectra of α-nitro-sulphones of general formula $p\text{-}CH_3C_6H_4SO_2C(NO_2)RR'$ have been investigated with R = H, CH_3 and R′ = H, CH_3, C_2H_5, C_6H_5, $p\text{-}ClC_6H_4$, $p\text{-}CH_3OC_6H_4$.[12,84] If R or R′ = H, the mass spectrum contains an intense peak having *m/e* 172 ($C_7H_8SO_3^{+}\cdot$). The fragmentation of nitromethyl *p*-tolyl sulphone is given as example:

$$\left(p\text{-}MeC_6H_4SO_2CH_2N\begin{matrix}O\\O\end{matrix}\right)^{+} \xrightarrow{-HCNO} \underset{m/e\ 172}{(p\text{-}MeC_6H_4SO_3H)^{+}} \begin{cases} \xrightarrow{-SO_2} C_7H_8O^{+} \ m/e\ 108 \\ \xrightarrow{-HSO_3} C_7H_7^{+} \ m/e\ 91 \end{cases}$$

Table 3. Nitrogen-14 n.m.r. data.

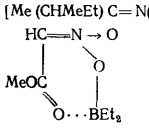
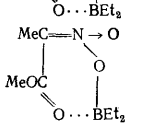
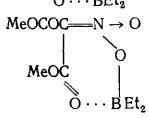
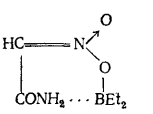
No.	Compound	$\delta^{14}N$, ppm NO_2 or NO.O (half-width, Hz)	Ref.	Model cpd.	$\delta^{14}N$, ppm NO_2 or NO.O (half-width, Hz)	Ref.
1	$MeCH{=}N(O)OSiMe_3$	−83±5 (270±20)	132	$EtNO_2$	12±1 (30)	143
2	$Me_2C{=}N(O)OSiMe_3$	−97± (550±30)	132	$[MeCHNO_2]^-$	−60.5±20	140
3	$(MeOCO)_2C{=}N(O)OSiMe_3$	broadened	132	Me_2CHNO_2	24 (38)	143
4	$MeC(NO_2){=}N(O)OSiMe_3$	−12±2 (NO_2) −74±8 (350±50)	132	$[Me_2CNO_2]^-$	−79±5	140
5	$Hg[C(NO_2)_3]_2$	−25±1 (24±2)	112,113	$[MeOCO]_2CHNO_2$	−16±4 (220±15)	139
6		−23.6±1 (67±3)	112,113	$[(MeOCO)_2CNO_2]^-$	−31±5 (230±20)	139
7	$MeN(NO_2)SiMe_2R$	−25.0	130	$(MeOCO)_2C{=}N(O)OMe$	−70±5 (290±20)	139
8	$MeN{=}N(O)OSiMe_2R$	−55.0	130	$Me_2CH(NO_2)_2$	−11±1 (28)	144
9	$MeN(NO_2)BEt_2$ *	−20±3	25	$[MeC(NO_2)_2]^-$	−22.5±1	140
10	$MeN{=}N(O)OBEt_2$ *	−49±1	25	$HC(NO_2)_3$	−33.5 (11)	143
11	$MeN(NO_2)BEt_2{\cdot}C_5H_5N$	−21±1,5	25	$CH_3C(NO_2)_3$	−26.0	133
	$MeN(NO_2)BEt_2{\cdot}C_5H_5N$ *	−15.8	25	$[C(NO_2)_3]^-$	−28±1	133
12	$n\text{-}MeC_6H_4SO_2N{=}N(O)OSiMe_3$	broadened	22	$C(^{15}NO_2){=}^{15}N(O)OAc$	−35.6 and −31.8	93
13	$n\text{-}MeC_6H_4SO_2N{=}N(O)OBEt_2$	broadened	22	$MeNHNO_2$	−23.2±0.5	133
				$[MeN(NO_2)]^-$	−26.3±1.0	133
				$p\text{-}MeC_6H_4SO_2NRNO_2$ R=H, Alkyl	−40±2 (60±10)	22
				$p\text{-}MeC_6H_4SO_2N{=}N(O)OPr\text{-}iso$	broadened	22

*Nitrogen-15 n.m.r. data at −50°C, with $^{15}NO_2NHCOOC_2H_5$ (δ = −41 ppm) as standard.

Table 4. Silicon-29 n.m.r. data [132].

No.	Compound	$\delta^{29}Si$, ppm	No.	Compound	$\delta^{29}Si$, ppm
1	$MeCH{=}N(O)OSiMe_3$	22.6	6	$MeN{=}N(O)OSiMe_2R$ (R=Me, t-Bu)	28—30
2	$Me_2C{=}N(O)OSiMe_3$	21.1		model cpd.	
3	$(MeOCO)_2C{=}N(O)OSiMe_3$	32.7		$Me_2C{=}NOSiMe_3$	21.2
4	$Me(NO_2)C{=}N(O)OSiMe_3$	32.2		$(MeOCO)_2C{=}NOSiMe_3$	33.8
5	$MeN(NO_2)SiMe_2R$ (R=Me, t-Bu)	13—15			

Table 5. Boron-11 n.m.r. spectral data.

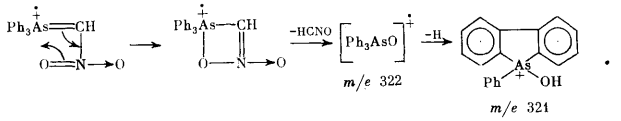
No.	Compound	$\delta^{11}B$, ppm	Ref.
1	$[Me_2C{=}N(O)OBEt_2]_2$	12.0	23
2	$[Me(CHMeEt)C{=}N(O)OBEt_2]_2$	13.6	23
3		15.8	24
4		16.7	24
5		15.9	24
6		12.8	24
7	$MeNBEt_2 \rightleftarrows MeN{=}N(O)OBEt_2$ * NO_2	54	25
8	$MeN(NO_2)BEt_2{\cdot}C_5H_5N$	5.0	25
9	$p\text{-}MeC_6H_4SO_2N{=}N(O)OBEt_2$ *	43.0	22

*At −20°C.

The tropylium cation has been identified in the mass spectrum of benzyl α-nitrobenzyl sulphone [12].

In the opinion of Lorberth and Lange [71] the mass spectra of trialkyltin, trialkyl-lead, and alkylmercury derivatives of nitroalkanes confirm the suggested nitronic ester structure, since the NO_2 and NO peaks are absent. The mass spectra of trialkyl-lead, trialkyltin [71], and diethylboryl [23,73] derivatives of nitroalkanes indicate that these compounds are dimeric, which eliminates the possibility of salt structures.

α-Nitro-ylides of arsenic on electron bombardment undergo the fragmentation [103]



(*e*) Nuclear γ-ray and quadrupole resonance spectroscopy

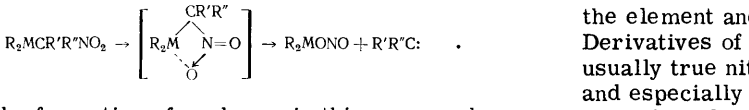
Mössbauer spectroscopy enables the structure of solid specimens containing tin to be elucidated. Lorberth et al. [121] have shown that trialkylstannyl alkanenitronates have a trigonal bipyramidal structure with five-coordinated tin. *N*-Trialkylstannyl derivatives of alkylnitramines also contain tin coordinated to the nitro-group [27].

Chlorine-35 and indium-115 nuclear quadrupole resonance data for the diethylthallium derivative of chloronitromethane and for dialkylindium derivatives of nitroalkanes respectively were regarded [66,68] as showing that these compounds are *C*-derivatives, with intramolecular coordination of the metal to oxygen of the nitro-group. However, this conclusion is not supported by the investigation of organothallium derivatives of certain nitro-compounds by other physicochemical methods—see (*c*) above.

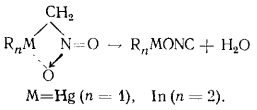
2. Establishment of Structure by Chemical Reactions

Several chemical reactions of α-nitrohetero-organic compounds may give information on their structure. Firstly mention must be made of 1,3-dipolar cycloaddition, by means of which several alkyl nitronates had earlier been detected[146]. However, *O*-acyl nitronates do not undergo this reaction[93], so that it cannot be regarded as common to all *O*-derivatives of nitro-compounds. Only trialkylsilyl nitronates have yet been subjected to such addition with alkenes, and therefore the possibility of detecting in this way *O*-derivatives of α-nitrohetero-organic compounds has so far been examined very roughly. (This reaction will be considered in detail in Section IV.)

The possibility of intramolecular coordination has been suggested[65,66,68] for *C*-derivatives of α-nitrohetero-organic compounds in which the heteroatoms have vacant *d* orbitals, leading to elimination of the corresponding carbene and formation of a nitrite:



However, the formation of carbenes in this process has not been rigorously confirmed, and the structure of the initial nitro-derivatives (especially the diethylthallium derivative of nitromethane) arouses great doubt. Therefore the isolation of nitrites of the type R_2MONO cannot serve as a strict proof of the existence of the corresponding α-nitrohetero-organic compounds in the *C*-form. All the above considerations apply also to the formation of fulminates from hetero-organic derivatives of nitromethane. This reaction has been assumed[54,68] to be characteristic of *C*-derivatives of nitro-compounds and to involve intramolecular coordination of a mercury or an indium atom:



M=Hg ($n = 1$), In ($n = 2$).

Yet Lorberth and Lange[71] observed that methylmercury fulminate is readily formed also by the methylmercury derivative of nitromethane, which is a nitronic ester¶.

It is assumed[2] that the reaction of salts of primary nitroalkanes with 2,4-dinitrobenzenesulphenyl chloride forms *O*-derivatives, which then rearrange into *C*-products or else undergo a series of chemical reactions. The following tests have been suggested[1] for distinguishing α-nitro-sulphides from the corresponding *O*-derivatives — (i) treatment with alkali followed by oxidation, when α-nitro-sulphides undergo no changes, whereas the corresponding nitronic esters should decompose, and (ii) oxidation, which converts α-nitro-sulphides into the corresponding sulphones, whereas *O*-derivatives should be cleaved at the sulphur–oxygen bond (more detailed information on the reactions of *O*- and *C*-derivatives will be found in Section IV, 3 and 6*c*).

Chemical reactions enabling the *N*-form to be distinguished from *O*-derivatives are unknown for α-nitrohetero-organic compounds derived from nitramines. Among possible reactions of this type, mention may be made of the Franchimont test[147], which has been successfully used for the qualitative detection of various nitramines. Furthermore, the action of 40% sulphuric acid on certain *O*-alkyl derivatives of nitramines results in rapid evolution of nitrous oxide[148]. However, it is not clear how effective and specific this reaction is for the *O*-forms of α-nitrohetero-organic compounds.

In the identification of α-nitrohetero-organic compounds by means of chemical reactions it must be borne in mind that many of them are hydrolytically extremely unstable (Section IV, 2), so that reagents having a mobile hydrogen atom cannot be used for their analysis.

Several general conclusions on the structure of α-nitrohetero-organic compounds derived from aliphatic nitro-compounds and nitramines can be drawn from the above discussion. The structure depends on the nature of the element and the residue containing the nitro-group. Derivatives of mercury, phosphorus, and sulphur are usually true nitro-compounds, whereas those of boron and especially silicon are often nitronic esters. Contrary to published views[65-68] thallium and indium derivatives of nitroalkanes are also nitronic esters. The overwhelming majority of α-hetero-organic derivatives of mononitro-compounds exist in the *O*-form. The contribution of ionic structures is increased by the attachment of electronegative substituents to the carbon atom bearing the nitro-group.

Since the majority of α-nitrohetero-organic compounds are most probably not kinetically favoured products, their structure cannot be related to the direction of attack by the heteroatomic group on the ambident nitro-anion. Information on the structure of hetero-organic derivatives of nitramines and nitroamides is insufficient for any significant generalisations to be made, but even in these cases the compounds isolated are thermodynamically favoured products.

It is interesting that trialkylsilyl and diethylboron derivatives of alkylnitramines[20,25,130] are tautomeric mixtures of *N*- and *O*-forms containing the two structural isomers in comparable quantities. However, the pyridine complex of the diethylboryl derivative of methylnitramine is the pure *N*-form[25].

IV. CHEMICAL PROPERTIES

We shall first discuss the properties common to most α-nitrohetero-organic compounds.

1. Thermal Decomposition

On the whole these compounds are less thermostable than the corresponding nitro-compounds or their salts; *O*-derivatives are usually thermally less stable than their *C*- or *N*-analogues.

(*a*) Thermal decomposition of *O*-derivatives

The modes of decomposition of the *O*-forms of α-nitrohetero-organic compounds differ from the rearrangements of alkyl nitronates[108]. The character of the former process and the final products depend on the nature of the nitro-component and the heteroatom. The way in which nitronic esters of the type RCH : N(→O).O.SAr

¶Theoretically the above hetero-organic derivatives of nitro-compounds may exist as an equilibrium tautomeric mixture, with one form present in such minute quantity that it cannot be reliably detected by physicochemical methods. In the equilibrium mixture, however, this particular form may well be responsible for conversion into nitrite or fulminate.

breakdown is supposed[2] to be determined by the structure of the aryl radical. Thus if Ar = 2,4-$(NO_2)_2C_6H_3$ or m-$NO_2C_6H_4$, the O-derivatives rearrange into aryl nitroalkyl sulphides and decompose into bisnitroaryl disulphides: e.g.

$$\left[\mathrm{MeCH{=}N}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OSC_6H_3(NO_2)_2\text{-}2,4}\end{smallmatrix}\right] \rightarrow (2,4\text{-}(NO_2)_2C_6H_3S)_2 + 2,4\text{-}(NO_2)_2C_6H_3SCH(NO_2)Me\ .$$

If, however, Ar = p-ClC_6H_4, quite different decomposition products have been detected[2]:

$$\left[\mathrm{EtCH{=}N}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OSC_6H_4Cl\text{-}}p\end{smallmatrix}\right] \rightarrow [p\text{-}ClC_6H_4SO_2H] \xrightarrow{p\text{-}ClC_6H_4SCl} p\text{-}ClC_6H_4SO_2SC_6H_4Cl\text{-}p\ .$$

O-Thienyl derivatives of polynitroalkanes are also thermally unstable[7].

In the reactions of potassium and sodium salts of thols or of sodium hydrogen sulphide with halogenonitromethanes[76-80] unstable O-alkylthio- or O-mercapto-derivatives of alkanenitronic acids are obviously formed, which decompose to give mixtures of products:

$$RSK + CH_2BrNO_2 \rightarrow \left[\mathrm{CH_2{=}N}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OSR}\end{smallmatrix}\right] \rightarrow (RS)_2 + CO + N_2 + H_2O \quad (R = Alk)$$

$$NaHS + C(NO_2)Cl_3 \rightarrow \left[\mathrm{CCl_3{=}N}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OSH}\end{smallmatrix}\right] \rightarrow CO + NO + H_2S + S + N_2 + H_2O + COS\ .$$

Trialkylsilyl nitronates break down in a different way[15-17,50]:

$$RR'C{=}N\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OSiMe_3}\end{smallmatrix} \rightarrow [RC{\equiv}N \rightarrow O] + Me_3SiOR' \rightarrow [Me_3Si]_2O + R'_2O$$

R=R'=NO_2; R=COOMe, NO_2, Ph; R'=H.

If R' = H, parallel hydrolysis of the nitronic esters by trimethylsilanol takes place. The O-trimethylsilyl derivative of N-nitrotoluene-p-sulphonamide decomposes similarly when heated[22]:

$$p\text{-}MeC_6H_4SO_2N{=}N\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OSiMe_3}\end{smallmatrix} \xrightarrow{>100^\circ} p\text{-}Me{-}C_6H_4{-}SO_3SiMe_3 + N_2O\ .$$

Trialkylsilyl derivatives of methylnitramine are unstable at room temperature, but the way in which they decompose has not been studied[20].

Diethylboron derivatives of alkanenitronic acids, whether in solid form or in solution, undergo rearrangement into a new heterocyclic system, a 4-alkylidene-2,5,5-triethyl-1,3-triethyl-1,3-dioxa-4-aza-2,5-diborolidine[23,24]:

$$\left[RR'C{=}N\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{OBEt_2}\end{smallmatrix}\right]_2 \rightarrow \begin{smallmatrix}&&\mathrm{O}&&\\ &\mathrm{Et_2B}&&\mathrm{BEt}&\\ &\vdots&&\diagup&\\ &RR'C{=}N{-}&&\diagdown&\end{smallmatrix}$$

R = Alk; R' = H or Alk.

(*b*) Conversion into nitrites or fulminates

Certain α-nitrohetero-organic compounds are converted into the corresponding nitrites[65,68]:

$$Et_2MC(NO_2)Me_2 \rightarrow Et_2MONO + :CMe_2 \quad (M=Tl, In.)$$

The mechanism of this rearrangement has already been discussed (Section III, 2).

Diethylthallium derivatives of halogenonitroalkanes decompose with the formation both of nitrites and of diethylthallium halides[66]. In particular, chloro (and fluoro)nitromethyldiethylthallium pass rapidly into diethylthallium nitrite, whereas difluoronitromethyldiethylthallium forms diethylthallium fluoride[66]. Alkylmercury and dialkylindium derivatives of nitromethane are similarly converted into the corresponding fulminates†:

$$R_nMCH_2NO_2 \rightarrow R_nMONC + H_2O$$

M=Hg (n = 1), R=Me, Bu, Ph[54,71]; M=In (n = 2), R=Me, Et[68].

Beck and Schorpp[63,64] assume that in the reaction

$$[(Ph_3P)_2PtH][CR'_2NO_2]_2 \rightarrow \begin{cases}(Ph_3P)_2Pt(ONO)_2 & (R'=Me)\\ (Ph_3P)_2Pt(ONC)_2 & (R'=H)\end{cases}$$

platinum derivatives of nitromethane and of nitroalkanes are formed, and then pass rapidly into the corresponding fulminates or nitrites.

(*c*) Decomposition of hetero-organic *C*-derivatives of nitro-compounds and *N*-derivatives of nitramines

Compounds whose structure as *C*-derivatives has been firmly established are usually stable at ordinary temperatures.

Thermal changes undergone by α-nitro-ylides of phosphorus closely resemble the Wittig reaction[102]:

$$Ph_3\overset{+}{P}{-}C^-(NO_2)Ph \leftrightarrow Ph_3\overset{+}{P}{-}\overset{-}{C}Ph \leftrightarrow Ph_3\overset{+}{P}{-}CPh \rightarrow Ph_3PO + PhC{\equiv}N{\rightarrow}O\ .$$

$$\begin{smallmatrix}&&|&&\\ &&O{-}\overset{+}{N}{=}O&&O{-}\overset{+}{N}{\rightarrow}O\\ &&^-&^+&^-\ \ ^+\end{smallmatrix}$$

The thermal decomposition of hetero-organic *N*-derivatives of nitramines remains almost uninvestigated. Organotin derivatives of nitramines are stable below 150°C.[27] *N*-Nitrobenzenesulphonamide when heated decomposes with the evolution of nitrous oxide[34]:

$$PhSO_2NHNO_2 \rightarrow PhSO_3H + N_2O\ .$$

(*d*) Decomposition of hypothetical α-nitrohetero-organic compounds

Here we consider reactions of α-nitrohetero-organic compounds whose formation has been postulated in studies of the chemical changes undergone by nitroproducts.

The oxidation of triphenylphosphine by bromonitromethane is assumed to involve formation of an unstable triphenylnitromethylphosphonium bromide[80,86-89]‡:

$$Ph_3P + CH_2BrNO_2 \rightarrow \left[Ph_3P\begin{smallmatrix}\nearrow\mathrm{Br}\\ \searrow\mathrm{CH_2NO_2}\end{smallmatrix}\right] \rightarrow \begin{cases}Ph_3PO + HBr + CO + N_2 + H_2O\\ \xrightarrow{CH_2BrNO_2} Ph_3PBr_2 + CO + N_2 + H_2O\ .\end{cases}$$

$$\downarrow$$

$$Ph_3PO + [Ph_3PCH{=}NOH]^+Br^-$$

Dibromonitromethane reacts similarly with triphenylphosphine[80]. Nevertheless, the action of trialkyl

†A review on nitronic acids and esters[116] gives two references[149,150] reporting decomposition of the mercury salt of nitromethane into mercury fulminate. However, it has been shown more recently[122] that the former salt is stable up to 180°C.

‡The corresponding alkanonitriles have been detected in reactions of α-halogenonitroalkanes with triphenylphosphine, and are obviously formed by reduction of the nitrile oxides by the triphenylphosphine[87].

phosphites on α-halogenonitro-compounds gives[90] unstable nitronic esters, which rapidly oxidise the phosphite:

$$(EtO)_3P + R'OCO(R)C(NO_2)X \xrightarrow{-EtX} \left[(EtO)_2P(O)-O-N=C(R)COOR'\right] \rightarrow$$

$$\xrightarrow[-(EtO)_3PO]{(EtO)_3P} (EtO)_2P(O)-ON=C(R)COOR'$$

R=H, F, CF_3; R'=Me, Et, Pr, iso-Pr; X=Cl, Br.

The reaction of nitromethane with aluminium bromide can be represented by the scheme[99]

$$AlBr_3 \cdot MeNO_2 + MeNO_2 \rightleftarrows CH_2=N(O)OAlBr_2 \cdot MeNO_2 + HBr$$

$$HOAlBr_2 + CH_2=NOH \rightleftarrows CH_2=N(O)OAlBr_2 \qquad CHBr=NOH + H_2O$$

$$(NH_2=C=NH_2)^{2+}\,2Br^- \qquad NH_2OH \cdot HBr + CO$$

2. Reaction with Compounds containing a Mobile Hydrogen Atom

The resistance of α-nitrohetero-organic compounds to hydrolysis or solvolysis is governed by the nature of the heteroelement, the structure of the nitro-group, and in several cases also the form of the hetero-organic compound. Among the relatively thermostable α-nitrohetero-organic compounds the most sensitive to hydrolysis and solvolysis are α-organosilicon derivatives of nitro-compounds, which react readily with water, alcohols, acids, and primary and secondary amines[14,16,17,50,52]:

$$RR'C=N(O)OSiMe_3 + HZ \rightarrow RR'CHNO_2 + Z-SiMe_3$$

R=R'=CO_2Me, NO_2; R=H, R'=CO_2Me, NO_2; Z=OMe, OH, Cl, Et_2N.

The reaction probably involves a multicentre transition state of type (*A*) or (*B*)[14]

$$>C=N(O\cdots H)(Z)(O-SiMe_3) \qquad >C=N(O)(O-SiMe_3)\cdots H-Z$$

(*A*) (*B*)

In agreement with this it has been shown that the primary product of the methanolysis of trimethylsilyl phenylmethanenitronate is the aci-form of phenylnitromethane

$$PhCH=N(O)OSiMe_3 \xrightarrow{MeOH} \left[PhCH=N(O)OH\right] \rightarrow PhCH_2NO_2$$

Trimethylsilyl derivatives of methylnitramine[20] and *N*-nitrotoluene-*p*-sulphonamide[22] also react with water and alcohols:

$$[RN(NO_2)]SiMe_3 \xrightarrow{R'OH} RN(NO_2)H + R'OSiMe_3$$

R=Me, *p*-$MeC_6H_4SO_2$; R'=H, Me.

However, the rate of alcoholysis of hetero-organic compounds of this type is significantly retarded by the presence of a t-butyl radical in the trialkylsilyl group[20].

Diethylboryl derivatives of alkanenitronic acids[23,24,73] (including functionally substituted compounds), as well as diethylboryl derivatives of methylnitramine[25] and *N*-nitrotoluene-*p*-sulphonamide[22] are very readily hydrolysed by water, and they react with alcohols. Organotin derivatives of alkylnitramines are perfectly stable in air, but break down fairly slowly on treatment with water[27].

Diethylthallium derivatives of α-nitroalkanes readily undergo solvolysis in protic solvents, but on the addition of hydrochloric acid or a salt thereof the nitroalkyl group is replaced by the halogen:

$$Et_2Tl[RR'C(NO_2)] \underset{}{\overset{H_2O}{\rightleftarrows}} [RR'C(NO_2)]^- + Et_2Tl^+OH_2 \xrightarrow{Cl^-} Et_2TlCl + H_2O$$

R=R'=H, Me[66]; R, R'=H, NO_2, Hal[66].

O-Alkylthio-derivatives of nitro-compounds are extremely unstable in alcohols[2]:

$$\left[RCH=N(O)OSAr\right] \xrightarrow{EtOH} [ArSOH] \rightarrow ArSO_2H + ArSH$$

$$\text{or } ArSOH \text{ or } ArSCl \rightarrow ArSO_2SAr + ArSSAr$$

Nevertheless, α-nitroalkyl[1] and αα-dinitroalkyl[6,7] sulphides are unaffected by proton-containing solvents. In trinitromethyl sulphides, on the other hand, the sulphur–carbon bond is labile towards protic solvents[6]:

$$(NO_2)_3C-SR + MeOH \rightarrow HC(NO_2)_3 + RSOMe$$

R=Me, Ph, 2,4-$(NO_2)_2C_6H_3$.

α-Nitro-sulphones and *N*-nitrosulphonamides are inert towards water and alcohols[1,2,34].

α-Nitroalkylphosphonates of general formula $NO_2CR'(CH_3).PO(OR)_2$ (where R, R' = CH_3, C_2H_5) give the corresponding acids $NO_2CR'(CH_3).PO(OH)_2$ on treatment with an acid§[49]. With dialkyl nitromethylphosphonates the course of this reaction is complicated and involves the nitro-group.

α-Halogeno-α-nitroalkanesulphenyl chlorides react with acids and thiols at the sulphur–halogen bond[11,151]:

$$RC(X)NO_2SHal \xrightarrow{R'SH} RC(X)NO_2SSR'$$

$$RC(X)NO_2SHal \xrightarrow{HX'} RC(X)NO_2SX'$$

R, R' — Alk, Ar; X, X' = Cl, Br.

3. Reaction with Nucleophilic Reagents

The action of alkalis or alkali-methyl alkoxides on certain α-nitrohetero-organic compounds results in the formation of salts of the corresponding nitro-compounds[17,24,73] or nitramines[20,22,25]. With α-organosulphur derivatives of nitro-compounds[1,6,40,45,47,48,82] and with *N*-nitrosulphonamides[34,35], in particular, these alkaline reagents yield the nitronate salts. If an α-nitrohetero-organic compound of this type does not contain a mobile hydrogen atom, other reactions may occur. Thus, under the influence of alkali, trismethylsulphonylnitromethane loses one of its methylsulphonyl groups[39]:

$$NO_2C(SO_2Me)_3 \xrightarrow{2NaOH} [NO_2C(SO_2Me)_2]Na + MeSO_2ONa$$

Sulphonyl groups are similarly detached from *N*-alkyl-*N*-nitrotoluene-*p*-sulphonamides[35]:

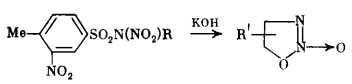
$$RN(NO_2)SO_2C_6H_4Me\text{-}p \xrightarrow{NaOH} [RN(NO_2)]Na + p\text{-}MeC_6H_4SO_2Na$$

R=Me, $PhCH_2$.

The action of alkali on *N*-2′-bromoalkyl-2,*N*-dinitrotoluene-4-sulphonamides also causes elimination of the sulphonyl group, with intramolecular alkylation of anions

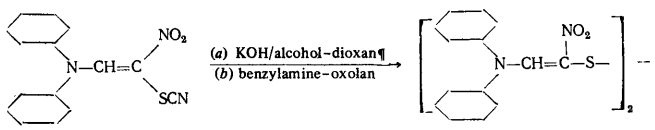
§Nitroalkylphosphonic chlorides are formed by the action of phosphorus pentachloride.

of the nitramines with formation of the 2-oxides of 4,5-dihydro-1,2,3-oxadiazoles [37]:

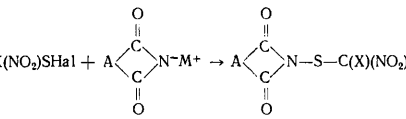


R=CH_2CH_2Br, CH(Me)CH_2Br, $CH_2CHBrMe$; R′=Me.

Certain α-nitro-organosulphur compounds undergo greater breakdown under the influence of alkalis [98]:



α-Nitroalkane-sulphenyl and -sulphonyl chlorides react with nucleophilic reagents at the sulphur–halogen bond:



Hal and X = Br, Cl; M=Na, K;

R= Alk (C_1—C_6); R′=H, Alk (C_1—C_6);

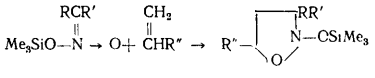
R″=H, Alk [10];

$R_2NH + R'R''C(NO_2)SO_2Cl \rightarrow R'R''C(NO_2)SO_2NR_2$

R=H, Me; R′ and R″=H, Alk, cyclo Alk, or N, O, or S heterocycle [44,75].

4. 1,3-Dipolar Cycloaddition

Among all the α-nitrohetero-organic compounds that exist as the *O*-esters only the silyl nitronates have been studied in this reaction. Styrene and methyl acrylate have been used as model compounds, and in isolated cases ethylene. Silyl nitronates undergo cycloaddition to selected alkenes to give good yields of the corresponding cycloadducts:



for R″=CO_2Me: R=H, Me, Et, R′=H, Me [52];

R=R′=CO_2Me; R=H, CO_2Me, R′=H, NO_2 [14,50];

for R″=Ph: R=H, Me, Et, R′=H, Me [52];

R=R′=CO_2Me [14], NO_2 [15,16,152], R=CO_2Me, H,

R′=H, NO_2 [50];

for R″=H: R=CO_2Me, R′=H [50,153];

R=R′=NO_2 [16].

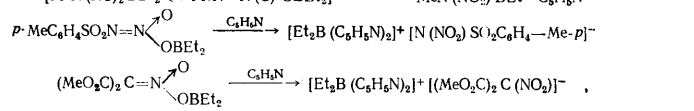
This reaction exhibits strict structural and in most cases also steric regiospecificity.

Silyl nitronates are rather less reactive than their alkyl analogues, but their enhanced thermal stability extends significantly the possibility of using nitro-compounds in the synthesis of heterocyclic structures by 1,3-dipolar cycloaddition. It is noteworthy that silyl dinitromethanenitronates $(NO_2)_2C:NOOSi(CH_3)_n(C_6H_5)_{3-n}$ (n = 0, 1, 3) with methyl acrylate undergo direct silylation, not 1,3-cycloaddition [15,16].

¶Alcoholic hydrogen chloride acts on the starting material of this reaction to give dicyclohexylamine hydrochloride.

5. Complexes of α-Nitrohetero-organic Compounds

Bistrinitromethylmercury [112] and bisfluorodinitromethylmercury [145] readily form complexes with many organic ligands (ethers, dioxan, dimethyl sulphoxide, etc.). Both neutral complexes [25] and boronium salts [22,24,26] have been isolated from the action of pyridine on diethylboryl derivatives of nitro-compounds and nitramines: e.g.



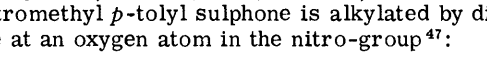
Below we shall discuss reactions undergone only by individual types of α-nitrohetero-organic compounds. The most detailed studies have been made, of course, on the most stable compounds, which include organosulphur and organomercury derivatives of mononitro- and polynitro-compounds.

6. Reactions of α-Organosulphur Derivatives of Nitro-compounds

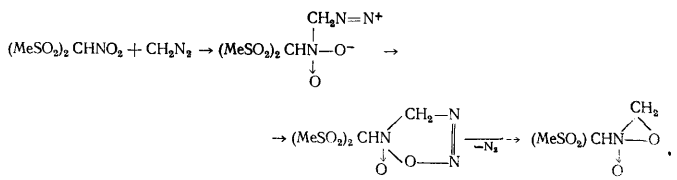
Many reactions well known in the chemistry of aliphatic nitro-compounds have been reported for α-nitroalkyl and α-nitramine derivatives of organosulphur compounds.

(*a*) Alkylation

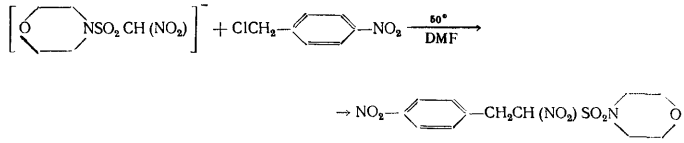
The direction of alkylation depends on the nature of the nitro-component, the alkylating reagent, and the solvent. Thus nitromethyl *p*-tolyl sulphone is alkylated by diazomethane at an oxygen atom in the nitro-group [47]:



The alkylation of dimethylsulphonylnitromethane by diazomethane follows a completely different course [154]:

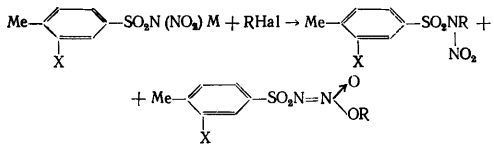


Anions of α-nitroalkanesulphonamides do not react with benzyl chloride, but with *p*-nitrobenzyl chloride they give *C*-alkylated products [45]:



This reaction was regarded as having a radical-anion mechanism. The alkylation of salts of αα-dinitroalkyl sulphides by methyl iodide gives *C*-substituted products [6]:

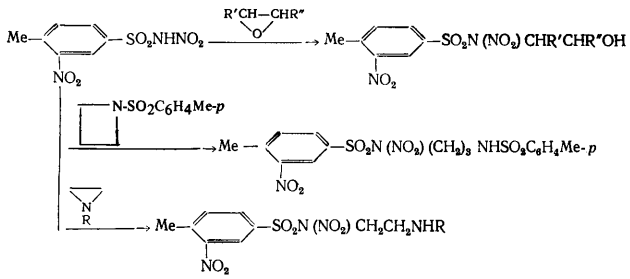
The alkylation of salts of *N*-nitroarenesulphonamides by alkyl halides gives a mixture of *N*- and *O*-alkylated products:



X=H, R=$C_6H_5CH_2$; M=Ag, Hal=Cl[35];
X=H, NO_2, R=Alk, C_1—C_3, adamantyl,
M=Ag, Na, Hal=Br, I[155].

The accumulation of alkyl groups in the alkylating reagent increases the proportion of the *O*-product, while the quantity of the *N*-alkylated product increases in the sequence of solvents—hexane < ether < ethyl acetate < diglyme < acetonitrile < dimethylformamide < acetone < methanol.

Silver and potassium salts of 2,*N*-dinitrotoluene-4-sulphonamide give with methyl iodide only the *N*-alkylated product[35,156]. Diazomethane, adamantyldiazoketone, and triethyloxonium tetrafluoroborate also alkylate nitrosulphonamides at the amino-nitrogen atom[155]. 2,*N*-Dinitrotoluene-4-sulphonamide reacts with oxirans and with aziridines and azetidine containing electronegative *N*-substituents to form *N*-2-hydroxyalkylated and *N*-2-amidoalkylated *N*-nitrosulphonamides[157]†:



R=$COC_6H_4NO_2$-*p*, $SO_2C_6H_4Me$-*p*; R′, R″=H or Alk.

(*b*) Halogenation

Nitro-derivatives of sulphones, sulphonamides, and sulphides in which the nitro-group is accompanied by a mobile hydrogen atom are readily halogenated either in the presence or in the absence of a base. In particular, dimethylsulphonylnitromethane and its sodium salt react in aqueous solution with bromine and chlorine[39]:

$$O_2NCR(SO_2Me)_2 + X_2 \rightarrow O_2NC(X)$$

X=Cl, Br; R=H, Na.

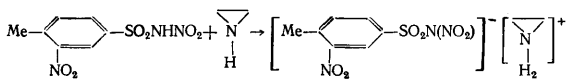
The bromination of α-nitro-sulphones may lead to isolation of the corresponding monobrominated[40,82] or dibrominated[40] derivatives:

$$RCH(NO_2)SO_2R' \xrightarrow[2.\ Br_2]{1.\ R''O^-} RCBr(NO_2)SO_2R'$$

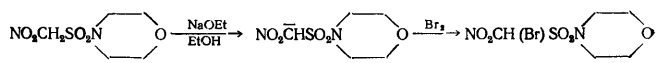
$$CH_2(NO_2)SO_2Me \xrightarrow[2.\ Br_2/CCl_4]{1.\ R''O^-} MeSO_2C(NO_2)Br_2$$

R=Bu, Ph; R′=Ph, CH_2Ph, CH_2CH_2Me;
R=H, R′=*p*-MeC_6H_4; R″=Alk.

†Reaction of 2,*N*-dinitrotoluene-4-sulphonamide with aziridine itself results merely in the formation of an aziridinium salt[157]:



The bromination of primary α-nitro-sulphonamides has been described[45]:



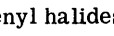
Bis-1-nitroalkyl disulphides are converted by halogens into 1-halogeno-1-nitroalkanesulphenyl halides[10,11]:

$$RCH(NO_2)S—SC(NO_2)RH \xrightarrow{X_2} 2RCX(NO_2)SX$$

R=Alk, Ar; X=Cl, Br.

Salts of dinitromethyl sulphides give 70–95% yields of chloro-derivatives[6]:

$$[RSC(NO_2)_2]^-M^+ + Cl_2 \rightarrow RSC(NO_2)_2Cl + MCl$$

R=Me, 2,4-$(NO_2)_2C_6H_3$; M=K, 

Alkyl 1-nitroalkanesulphonates have been identified by conversion into the corresponding brominated products[43]:

$$RCH(NO_2)SO_2R' \xrightarrow[2.\ Br_2,CCl_4]{1.\ KOH—EtOH} RC(NO_2)BrSO_3R'$$

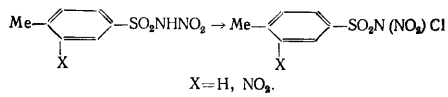
R, R′ = — Alk.

In some cases the halogenation of sulphonyl derivatives is hindered by the presence of a nitro-group. Thus the conversion of α-nitro-sulphonate salts into the acid chlorides requires more severe conditions than does preparation of the unsubstituted sulphonyl chlorides[44,75]:

$$RCH(NO_2)SO_3Na \xrightarrow{PCl_5,POCl_3} RCH(NO_2)SO_2Cl$$

R=H, Alk, cycloAlk, Ar.

N-Chloro-*N*-nitroarenesulphonamides are obtained by the action of t-butyl hypochlorite on the corresponding *N*-nitrosulphonamides[158]:



X=H, NO_2.

(*c*) Oxidation and reduction

Oxidation of the sulphur atom in α-mono- and αα-di-nitroalkyl sulphides has been reported:

$$RSC(NO_2)R'R'' \xrightarrow[AcOH]{H_2O_2} RSO_2CR'R''(NO_2)$$

R=Me, R′=R″=H[48]; R=*p*-MeC_6H_4,
R′=R″=H[47]; R=$ClCH_2CH_2$, 3-$NO_2C_6H_4$,
R′=H, R″=Me[3]; R=Me, Ar, R′=NO_2,
R″=H, Me[7].

The corresponding oximes can be isolated from the reduction of certain α-nitro-sulphides by lithium tetrahydroaluminate[3]:

$$p\text{-}MeC_6H_4SCH(NO_2)Me \rightarrow p\text{-}MeC_6H_4SC(Me)=NOH.$$

Yet the action of this reductant on a sulphone of similar structure is accompanied by cleavage of the carbon–sulphur bond and formation of toluene-*p*-sulphinic acid (in 80% yield)[3]. Reduction of the same sulphone by hydrogen over Raney nickel gives a mixture of products[3]:

$$p\text{-}MeC_6H_4SO_2CH(NO_2)Me \xrightarrow[Ni/Re]{H_2} p\text{-}MeC_6H_4SO_2C(Me)=NOH + p\text{-}MeC_6H_4SO_2NH_4 + p\text{-}MeC_6H_4SO_2H.$$

Dimethylsulphonylnitromethane is reduced by lithium tetrahydroaluminate with the evolution of ammonia[39]:

$$NO_2CH(SO_2Me)_2 \xrightarrow{LiAlH_4} CH_2(SO_2Me)_2 + NH_3.$$

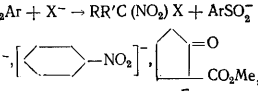
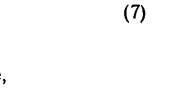
In the catalytic or electrolytic hydrogenation of certain α-nitro-organosulphur compounds the nitro-group may be reduced to amino [75]:

$$RR'C(NO_2)SO_2NR''R''' \rightarrow RR'C(NH_2)SO_2NR''R'''$$
R, R', R'', R'''=H, Alk, cycloAlk, etc.

(*d*) Other reactions

Several anions act on α-nitroalkyl sulphones with elimination of the sulphonyl group [125,159]:

$$RR'C(NO_2)SO_2Ar + X^- \rightarrow RR'C(NO_2)X + ArSO_2^- \quad (7)$$

$X^- = [Me_2C(NO_2)]^-$, , ,

$MeC^-(CO_2Me)_2$, p-$MeC_6H_4SO_2^-$,
p-$ClC_6H_4S^-$.
R, R' = Alk, cycloAlk.

The reaction is accomplished under mild conditions at room temperature. It takes place by a radical-anion mechanism:

$$TosCMe_2(NO_2) + [Me_2C(NO_2)]^- \rightarrow [TosCMe_2(NO_2)]^{\cdot-} + Me_2C(NO_2)^{\cdot}$$
$$[TosCMe_2(NO_2)]^{\cdot-} \rightarrow Tos^- + Me_2C(NO_2)^{\cdot}$$
$$Me_2C(NO_2)^{\cdot} + [Me_2C(NO_2)]^- \rightarrow [Me_2C(NO_2)-C(NO_2)Me_2]^{\cdot-}$$
$$[Me_2C(NO_2)-C(NO_2)Me_2]^{\cdot-} + TosCMe_2(NO_2) \rightarrow [Me_2C(NO_2)]_2 + [TosCMe_2(NO_2)]^{\cdot-},$$

In addition to the products indicated in Eqn. (7) potassium salts of α-nitroalkyl sulphones and iodine are isolated from the reaction of the potassium salt of 2-nitropropane with α-iodo-α-nitroalkyl sulphones [125].

Sodium nitrite acts on α-nitroalkyl sulphones under mild conditions [41]:

$$RSO_2CH(NO_2)R' + NaNO_2 \rightarrow RSO_2C(NO_2)(NO)R' \xrightarrow{B^-}$$
$$\rightarrow [RSO_2\bar{C}(NO)R' \leftrightarrow RSO_2CR'(=N\bar{O})] \xrightarrow{-H_2O} RSO_2CR'(=NOH)$$
R = p-MeC_6H_4, $C_6H_5CH_2$; R' = H, Me, Et, Ph,
p-$MeOC_6H_4$, p-ClC_6H_4.

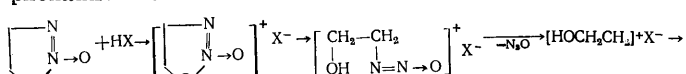
An α-bromo-α-nitroalkyl sulphone reacts with potassamide [40]:

$$PrC(NO_2)(Br)SO_2CH_2Pr \xrightarrow[NH_3]{KNH_2} PrCH=C(SO_2NH_2)Pr.$$

With benzenediazonium salts α-nitro-sulphones of general formula $RSO_2CH_2NO_2$ (R = C_6H_5, p-BrC_6H_4) form hydrazones $RSO_2C(NO_2):NHC_6H_5$. Analogous hydrazones can be obtained also by the interaction of an arenediazonium chloride and nitromethyl trichloromethyl sulphide [8,9]:

$$[RC_6H_4N\equiv N]^+Cl^- + CH_2NO_2(SCCl_3) \xrightarrow{AcONa} RC_6H_4NH-N=C(NO_2)SCCl_3$$
R=H, p-Me, p-MeO, m- and p-NO_2, p-Cl, etc.

An interesting reaction takes place between 4,5-dihydro-1,2,3-oxadiazole 2-oxide and 2,*N*-dinitrotoluene-4-sulphonamide [37]:



$\rightarrow HOCH_2CH_2X$ or $AcH + HX$
$X = Me(NO_2)C_6H_3SO_2N(NO_2)$.

The addition of *N*-chloro-*N*-nitrosulphonamides to unsaturated compounds gives mixtures of *O*- and *N*-halogenoalkylated products [159]:

$$p\text{-}MeC_6H_4SO_2N(Cl)NO_2 + RCH=CHR' \rightarrow p\text{-}MeC_6H_4SO_2N(NO_2)CHRCHR'(Cl) +$$
$$+ p\text{-}MeC_6H_4SO_2N=N(O)OCHRCHR'Cl$$
R=H, Me, Ph; R'=H; R and R'=$(CH_2)_4$.

With butadiene *N*-chloro-*N*-nitrotoluene-p-sulphonamide forms the 1,4(*N*)-adduct p-$CH_3C_6H_4SO_2N(NO_2)CH_2CH:CHCH_2Cl$, and from its reaction with diphenylacetylene p-$CH_3C_6H_4SO_2N(NO_2)C(C_6H_5):CCl.C_6H_5$ is isolated in low yield [159].

7. Reactions of Polynitroalkylmercury Derivatives

The main chemical reactions of trinitromethylmercury derivatives and of bisfluorodinitromethylmercury have been reviewed in detail [112,146,160,161], and only a few additional results will be given here.

Kashutina and Okhlobystin [54] have shown that butyl- and phenyl-trinitromethylmercury can be obtained by the dealkylation of dibutyl- and diphenyl-mercury respectively:

$$Hg[C(NO_2)_3]_2 + R_2Hg \rightarrow 2RHgC(NO_2)_3$$
R=Bu, Ph.

Reaction of bitrinitromethylmercury with vinyltrimethylsilane in solvents varying polarity—water, alcohol, benzene, tetrachloromethane—yields bis-3,3,3-trinitro-1-trimethylsilylpropylmercury [162]:

$$2Me_3SiCH=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow Hg[Me_3SiCHCH_2C(NO_2)_3]_2.$$

A similar reaction occurs with but-3-enyltrimethylsilane [162]. A product of the reaction of bistrinitromethylmercury with allyltrimethylsilane is 2,2-bistrinitromethyl-1,3-bistrinitromethylmercurypropane (VI) [162]:

$$Me_3SiCH_2CH=CH_2 + Hg[C(NO_2)_3]_2 \rightarrow Me_3SiCH_2CH[C(NO_2)_3]CH_2Hg[C(NO_2)_3] \xrightarrow{-Me_3SiH}$$
$$\rightarrow CH_2=C[C(NO_2)_3]CH_2HgC(NO_2)_3 \xrightarrow{Hg[C(NO_2)_3]_2} [(NO_2)_3CHgCH_2]_2C[C(NO_2)_3]_2,$$
(VI)

The reactions of (VI) with halogens and with hydrogen chloride can be represented by the scheme

$$(VI) \begin{cases} \xrightarrow{Br_2} (BrHgCH_2)_2C[C(NO_2)_3]_2 \xrightarrow[(PhCO_2)_2]{Br_2} (BrCH_2)_2C[C(NO_2)_3]_2 \\ \xrightarrow{HCl} [ClHgCH_2]_2C[C(NO_2)_3]_2 + 2HC(NO_2)_3, \end{cases}$$

8. Other Reactions of α-Nitrohetero-organic Compounds

Nitrotriphenylarsenylmethylide reacts with aromatic aldehydes to form the corresponding alkenes—*trans*-β,4-dinitrostyrene with p-nitrobenzaldehyde, and ω-nitrostyrene with benzaldehyde [103]:

$$Ph_3As=CH(NO_2) + RCHO \rightarrow RCH=CH(NO_2) + Ph_3AsO$$
R=Ph, p-$NO_2C_6H_4$.

While the Review was being prepared for press, communications have appeared on the preparation and properties of organosulphur derivatives of nitro-compounds [163,164,176], various nitro-ylides [165-167,172], organophosphorus derivatives of aliphatic nitro-compounds [173-175], and also the mechanism of silatropic rearrangements in trialkylsilyl derivatives of nitramines [168-170] and *N*-nitrourethanes [171], as well as the problem of the structure of various hetero-organic derivatives of nitromethane [177].

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