THE ALIPHATIC NITRO-COMPOUNDS

By N. LEVY, PH.D., and J. D. ROSE, B.A., B.SC.
(IMPERIAL CHEMICAL INDUSTRIES LIMITED)

ALTHOUGH dinitroethane was first prepared in 1864 and a general method for nitro-paraffins devised in 1872, progress was rather restricted until recently by the difficulty and expense of the preparative methods, none of which was suitable for large-scale manufacture. The development during the past decade of a process for the vapour-phase nitration of the lower paraffins, due primarily to the work of H. B. Hass and his collaborators in the United States, has stimulated renewed interest in the chemistry and applications of nitro-paraffins. Comparison of the reviews of T. W. J. Taylor and W. Baker [1] and H. B. Hass and E. Riley [2] shows the substantial advances made. Since the latter review, publication has been sustained and, in particular, the hitherto obscure reaction between olefins and oxides of nitrogen has been elucidated by recent work in this country. New nitro-aliphatic compounds, for example, the lower dinitro-paraffins, have thus become available, and some novel reactions, including those of addition to the nitro-olefins, disclosed. A fresh outline, embodying later work, therefore seems desirable.

Nitro-paraffins

Preparation.—(*a*) *Indirect methods.* Until the advent of the vapour-phase methods described below, the preparation of the lower nitro-paraffins largely depended on the methods of Victor Meyer [3] and H. Kolbe,[4] both of which were published in 1872. The Victor Meyer method makes use of the reaction between alkyl iodides and silver nitrite :

$$\begin{tikzcd} & R\cdot NO_2 + AgI \\ RI + AgNO_2 \arrow[ur] \arrow[dr] & \\ & RO\cdot NO + AgI \end{tikzcd}$$

and was first applied with amyl iodide. The method is a general one, yielding a mixture of nitro-paraffin and alkyl nitrite in proportions which depend on the nature of both the halogen and the alkyl group. Separation of the isomerides is easy because of the appreciably higher boiling point of the nitro-paraffin, as illustrated in Table I :

TABLE I

Nitro-paraffin.	B.p.	Alkyl nitrite.	B.p.
Nitromethane . .	101·2°	Methyl nitrite	− 12°
Nitroethane . . .	114·0	Ethyl nitrite	17
1-Nitropropane . .	131·6	*n*-Propyl nitrite	57

---

[1] Sidgwick's " Organic Chemistry of Nitrogen ", Oxford, 1937, pp. 228—247.

[2] *Chem. Reviews*, 1943, **32**, 373.

[3] V. Meyer and O. Stüber, *Ber.*, 1872, **5**, 203.

[4] *J. pr. Chem.*, 1872, **5**, 427.

The method, which has been extended by R. B. Reynolds and H. Adkins,[5] is applicable to the synthesis of nitro-paraffin derivatives, such as nitro-ketones, nitro-esters, nitro-alcohols and nitro-olefins other than Δ^{α}-nitro-olefins, *e.g.*, 1-nitroprop-2-ene from allyl bromide. The reported preparation of 1 : 2-dinitroethane from ethylene iodide[6] is now questionable.[47] Although silver nitrite is commonly used, the method has been applied to mercury and alkali nitrites. Apart from halides other than iodides, mono- and di-alkyl sulphates and alkyl *p*-toluenesulphonates have been employed, without cheapening the process sufficiently for commercial scale operation.

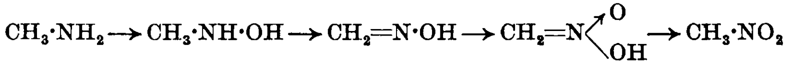
Kolbe's method is based on the reaction between α-halogeno-acids and sodium nitrite in aqueous solution and was first applied to nitromethane :

$$CH_2Cl{\cdot}CO_2Na + NaNO_2 \rightarrow NaCl + CH_2(NO_2){\cdot}CO_2Na \xrightarrow{H_2O} CH_3{\cdot}NO_2 + NaHCO_3$$

Nitromethane can be obtained thereby in 55—70% yield on chloro-acetate, depending on the nitrite : chloroacetate ratio.[7] The main sources of loss appear to be hydrolysis of the chloroacetate to glycollate and decomposition of the nitroacetate first formed. V. Auger [8] has reported 50% yields of the homologous nitro-paraffins, using α-bromopropionic, α-bromobutyric, and α-bromoheptoic acids. The reaction fails when applied to acids in which the bromine is attached to a tertiary carbon atom, small yields of the *pseudo*-nitrole being obtained, for example, from α-bromo*iso*butyric acid :

$$(CH_3)_2CBr{\cdot}CO_2H \rightarrow (CH_3)_2C(NO_2){\cdot}NO$$

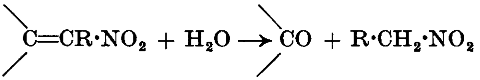
Other early methods include the oxidation of primary amines [9] (methyl-amine, ethylamine, and *tert.*-butylamine):



$$CH_3{\cdot}NH_2 \rightarrow CH_3{\cdot}NH{\cdot}OH \rightarrow CH_2{=}N{\cdot}OH \rightarrow CH_2{=}N\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix} \rightarrow CH_3{\cdot}NO_2$$

and the reaction of halogeno-nitro-paraffins with zinc alkyls ; for example, the formation of *tert.*-nitrobutane from chloropicrin and dimethylzinc.[10, 11] The ease of preparing alkyl nitrites would make isomerisation methods attractive, but the claims made [12, 13] have not been substantiated by extensive repetition of the work both in the vapour phase and in solution.[14]

Means of preparing the higher nitro-paraffins from the lower homologues are described in a later section. Now that alternative routes to nitro-olefins are available, it should be mentioned that they can be converted into lower nitro-paraffins by oxidative or hydrolytic fission :



$$>C{=}CR{\cdot}NO_2 + H_2O \rightarrow\ >CO + R{\cdot}CH_2{\cdot}NO_2$$

For example, nitromethane is formed in almost quantitative yield from

---

[5] *J. Amer. Chem. Soc.*, 1929, **51**, 279.

[6] V. Ipatov, *J. Russ. Phys. Chem. Soc.*, 1917, **49**, 297.

[7] I.C.I., private communication.

[8] *Bull. Soc. chim.*, 1900, **23**, 335.

[9] E. Bamberger and R. Seligman, *Ber.*, 1902, **35**, 4299.

[10] I. Bevad, *ibid.*, 1893, **26**, 129.

[11] *Idem*, *J. pr. Chem.*, 1893, **48**, 345.

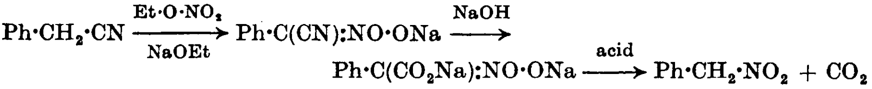
[12] P. Neogi and T. Chowduri, *J.*, 1916, **109**, 701.

[13] *Idem*, *J.*, 1917, **111**, 899.

[14] I.C.I., private communication.

α-nitro*iso*butene,[50] nitroethane from 2-nitrobut-2-ene [50] and nitro*neo*pentane from 3-nitro-2 : 4 : 4-trimethylpent-2-ene.[60]

The only remaining method of any importance for the introduction of the nitro-group into aliphatic compounds is nitration of active methylenic substances with ethyl nitrate and sodium methoxide. The synthesis of phenylnitromethane is the best example of this process : [15]



$$\mathrm{Ph{\cdot}CH_2{\cdot}CN \xrightarrow[\text{NaOEt}]{\text{Et}{\cdot}\text{O}{\cdot}\text{NO}_2} Ph{\cdot}C(CN){:}NO{\cdot}ONa \xrightarrow{\text{NaOH}} Ph{\cdot}C(CO_2Na){:}NO{\cdot}ONa \xrightarrow{\text{acid}} Ph{\cdot}CH_2{\cdot}NO_2 + CO_2}$$

and the reaction has also been used for the synthesis of nitrosulphones.[16]

An interesting paper by W. Steinkopf and M. Kuhnel [17] describes the addition of nitryl chloride (NO_2Cl) to unsaturated compounds. Although ethylene is merely chlorinated by this reagent, vinyl bromide is converted into 1-chloro-1-bromo-2-nitroethane with such vigour that, unless the reaction is carried out at low temperature and in dilute solution, violent explosion occurs. Similarly, 1 : 2-dichloroethylene gives 1 : 1 : 2-trichloro-2-nitroethane, and tetrachloroethylene yields pentachloronitroethane. Phenylacetylene and nitryl chloride afford 1-chloro-2-nitro-2-phenylethylene.

(*b*) *Liquid-phase nitration of paraffins.* The direct nitration of liquid paraffins was first reported with petroleum fractions by F. Beilstein and A. Kurbatov in 1880, since when a great deal of work has been reported on paraffins containing five or more carbon atoms. Procedures have been extremely varied and some confusion has therefore arisen, the main products and side-reactions being affected by the temperature and nitrating agent employed. The reaction has been carried out with various strengths of nitric acid, with sulphuric acid–nitric acid mixture, and with oxides of nitrogen, and the reagents have been refluxed together at atmospheric pressure or heated in sealed tubes at higher temperatures. Certain regularities have nevertheless emerged.

Tertiary carbon atoms are most readily attacked, appreciable reaction occurring at little above room temperature [18] and, in general, ease of formation follows the order tertiary > secondary > primary nitro-paraffin. Usually the reaction is slow due to the low mutual solubility of the acid and the paraffin. Reaction times vary from a few hours to several days, depending on the technique (temperature and pressure) and the hydrocarbon. As would be expected the longer reaction times are associated with atmospheric pressure nitration of the lighter normal paraffins [19] and the shorter reaction times with the higher temperatures obtainable in the nitration of heavier paraffins or in nitration under pressure.[20, 21]

The mononitro-paraffin first formed is more soluble, particularly in concentrated acid, and undergoes further reaction to form, on the one hand, polynitro-paraffins and, on the other hand, decomposition products of

---

[15] *Org. Synth.*, **19,** 73.

[16] F. Arndt and J. D. Rose, *J.*, 1935, 1.

[17] *Ber.*, 1942, **75,** 1323.

[18] W. Markovnikov, *ibid.*, 1899, **32,** 1441.

[19] R. A. Worstall, *J. Amer. Chem. Soc.*, 1898, **20,** 202.

[20] M. Konovalov, *J. Russ. Phys. Chem. Soc.*, 1894, **25,** 472.

[21] *Idem, J.*, 1894, **65,** 265.

secondary and primary nitro-paraffins. Some direct oxidation also occurs. Hence the product consists of a mixture of mono- and poly-nitro-paraffins, together with oxides of carbon, fatty acid, alcohols, etc., arising from oxidation and hydrolysis reactions. Through these side reactions, part of the nitric acid is lost as nitrogen and nitrous oxide, whereas in vapour-phase nitration practically quantitative recovery as nitro-paraffin and nitric oxide is obtained. Dilute nitric acid seems preferable to concentrated since it facilitates the use of pressure and the attendant higher reaction temperatures, faster nitration and better yields being obtained, for example, 60% yield of nitrohexanes from treatment of *n*-hexane at 10°5 in a sealed tube with dilute nitric acid [20, 21] compared with 6% by refluxing at atmospheric pressure with concentrated acid.[19] Mixed acid is less reactive than nitric acid [18, 22] and its sulphuric acid content presumably promotes more rapid hydrolysis of the mononitro-paraffins. Concentrated nitric acid favours oxidation and polynitro-compound formation, as well as the formation of primary and secondary nitro-paraffins at the expense of tertiary.[23, 24] This lends some support to the claims of R. Worstall [19, 25] to have obtained exclusively 1-nitro-paraffins from C_6—C_{10} normal paraffins; on the other hand, the identification has been criticised,[26] and the relatively low temperatures employed should favour secondary derivatives, though these might not persist as mononitro-paraffins.

An interesting method, providing a link with fully vapour-phase nitration, has been employed by C. Grundmann [27] for C_{10}—C_{18} normal paraffins as well as higher petrol fractions. The paraffin is caused to react at 140—210° with aqueous nitric acid vapour or nitrogen dioxide preheated to the same temperature; up to 60% of the paraffin is thus converted into nitro-compounds and only 1—8% into fatty acid for hydrocarbon : acid ratios of 2 : 1 to 1 : 2 and reaction times of 3—5 hours. The proportion of mononitro-paraffin in the product increases sharply with the hydrocarbon : acid ratio. The original claim that the method gave largely 2-nitro-paraffins was later contested and retracted.[28, 29] It is interesting to speculate how much of the reaction in this case, and in the earlier work under pressure, actually occurred in the vapour-phase.

The use of solvents is limited because of attack by the acid at temperatures required for nitration. Nitrates increase the reaction velocity by raising the boiling point of the nitric acid,[30] and reducing agents have been claimed as catalysts for liquid-phase nitration.[31] The introduction of negative groups into a hydrocarbon residue facilitates nitration. M. Konovalov [32, 33] showed that chloro-derivatives of butane and pentane are

[22] W. Markovnikov, *J. pr. Chem.*, 1899, **59**, 556.

[23] M. Konovalov, *J. Russ. Phys. Chem. Soc.*, 1899, **31**, 57.

[24] *Idem, ibid.*, 1906, **38**, 1, 109, 124.

[25] *J. Amer. Chem. Soc.*, 1899, **21**, 210, 223, 233, 237 ; 1900, **22**, 164.

[26] L. Henry, *Rec. Trav. chim.*, 1905, **24**, 352.

[27] *Die Chemie*, 1943, **56**, 159.

[28] F. Asinger, *ibid.*, p. 323.

[29] C. Grundmann, *loc. cit.*

[30] C. Denison, Thesis, Purdue University, 1940.

[31] R. Senkus, U.S.P. 2,332,491.

[32] M. Konovalov, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 220, 537.

[33] *Idem, ibid.*, 1906, **38**, 607.

more reactive than the parent hydrocarbons. Acetoacetic ester is readily nitrated with fuming nitric acid in acetic anhydride to give ethyl nitroacetate,[34] whilst malonic ester with fuming nitric acid alone gives nitromalonic ester in good yield.

The greater reactivity of tertiary carbon atoms and the effect of substituents and of activating groups suggest that the nitration reaction is electrophilic in character. That free radicals are not involved is indicated by the formation of optically active 3-nitro-3-methyloctane by the liquid-phase nitration of *l*-3-methyloctane.[35]

(*c*) *Liquid-phase nitration of olefins.* Since the work of A. Semenov [36, 37] over 80 years ago on the reaction between ethylene and apparently pure dinitrogen tetroxide, persistent attempts have been made to achieve satisfactory preparation of nitro-aliphatic compounds from olefins and oxides of nitrogen or nitric acid. H. Wieland [38, 39] has suggested that nitric acid adds to the double bond as $HO{\cdot}NO_2$, giving rise to the nitro-alcohol which in turn forms the nitrate ester, and the nitro-olefin :

$$(CH_3)_2C{=}CH_2 \xrightarrow{HO\cdot NO_2} (CH_3)_2C(OH){\cdot}CH_2{\cdot}NO_2 \xrightarrow{H\cdot NO_3'}$$
$$(CH_3)_2C(O{\cdot}NO_2){\cdot}CH_2{\cdot}NO_2 \xrightarrow{-HNO_3} (CH_3)_2C{=}CH{\cdot}NO_2$$

Although this is supported by the formation of 2-nitroethanol from ethylene and fuming nitric acid,[40] an alternative mechanism, based on addition of nitrous gases formed *in situ* by the accompanying oxidation reactions, has been proposed by A. Michael and G. H. Carlson.[41] Satisfactory yields with nitric acid still remain to be achieved. The position arising from the use of oxides of nitrogen was until recently no less confused, as indicated in previous reviews.[1, 2, 42] Semenov undoubtedly prepared 1 : 2-dinitroethane, although calling it " ethylene dinitrite." Dinitro-compounds have also been isolated from the product with fully-substituted ethylenes.[43, 44] The formation of nitrosites, nitrosates, and nitro-olefins has been reported and that of dinitro-paraffins inferred,[45, 46] but in general the greater part of the product resisted identification, and dinitro-paraffins had not been previously isolated from the simple olefins.

This situation has been transformed by a recent series of papers [47,48,49,50,51]

---

[34] L. Bouveault and A. Wahl, *Bull. Soc. chim.*, 1904, **31**, 847.

[35] P. G. Stevens and R. W. Schiessler, *J. Amer. Chem. Soc.*, 1940, **62**, 2885.

[36] *Jahresbericht*, 1864, 480.

[37] *Z. Chem. Pharm.*, 1864, **7**, 129.

[38] *Ber.*, 1920, **53**, 201.

[39] *Ibid.*, 1921, **54**, 1770.

[40] J. McKie, *J.*, 1927, 962.

[41] *J. Amer. Chem. Soc.*, 1935, **57**, 1268.

[42] J. L. Riebsomer, *Chem. Reviews*, 1945, **36**, 157.

[43] H. Biltz, *Ber.*, 1902, **35**, 1528.

[44] A. Michael and G. H. Carlson, *J. Org. Chem.*, 1940, **5**, 14.

[45] *Idem, J. Amer. Chem. Soc.*, 1937, **59**, 843.

[46] *Idem, J. Org. Chem.*, 1939, **4**, 169.

[47] N. Levy and C. W. Scaife, *J.*, 1946, 1093.

[48] N. Levy, C. W. Scaife, and A. E. W. Smith, *J.*, 1946, 1096.

[49] N. Levy and C. W. Scaife, *J.*, 1946, 1100.

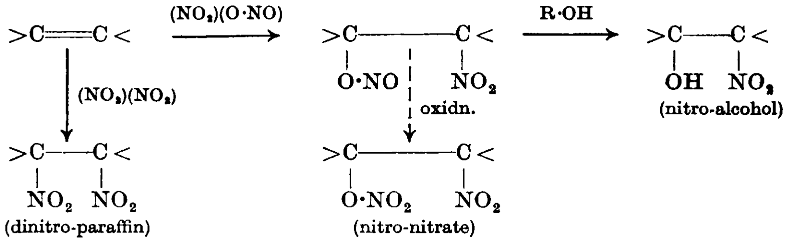
[50] *Idem*, in the press.

[51] *Idem*, in the press.

dealing with the addition of dinitrogen tetroxide to ethylene, propylene, *iso*butene, but-1-ene, but-2-ene, 2 : 4 : 4-trimethylpent-1- and -2-ene, and *cyclo*hexene, in the liquid phase. The work has shown that, under appropriate conditions, high overall yields of dinitro-compound, nitro-alcohol and nitro-nitrate can be obtained and isolated in pure condition by safe methods. It has also been shown that much of the earlier work was vitiated by : (i) the use of impure tetroxide or " nitrous fumes " which gave rise to nitroso-compounds and increased the instability of the mixed product, (ii) failure to control oxidative side-reactions, resulting in formation of dinitrogen trioxide and subsequent addition, (iii) the variable effect of reaction medium, in certain cases decisive, and (iv) decomposition of products, often with violence, during attempted separation of the products, rendering recovery and identification unsatisfactory. The methods used to overcome these difficulties are described below.

The reaction is best carried out in the liquid phase at − 10° to + 25°. Gaseous olefins are absorbed in pure dry dinitrogen tetroxide, as liquid or concentrated solution, the reaction mixture being cooled, and liquid olefins simply mixed by dropwise addition. Ethylene reacts fairly slowly, 10 hours being required for the optimum absorption of 0·4 mole per mole of tetroxide. Higher olefins react more rapidly, and molar equivalents can be made to react completely in 1—2 hours. Propylene, *iso*butene, and the normal butenes require an ether or ester type of solvent since otherwise oxidation supervenes and no dinitro-paraffin can be isolated. Oxidation reactions and interference by dinitrogen trioxide addition can always be avoided by use of excess tetroxide or, where convenient, the addition of gaseous oxygen.

Under such conditions addition of tetroxide to the double bond takes only two forms : (i) as two NO_2 groups to give dinitro-compounds, and (ii) as one NO_2 group and one O·NO group to give nitro-nitrites. Some oxidation of the latter to nitro-nitrate occurs in the presence of oxygen, but the product always contains a substantial proportion of nitro-nitrite which, being unstable, tends to decompose, sometimes explosively, during removal of excess of tetroxide or solvent. It has been found, however, that the nitro-nitrites are readily converted into the quite stable nitro-alcohols by treatment in the cold with water or a lower aliphatic alcohol and this is the most essential feature in safe and efficient recovery of nitrated products. Preferably, solvent and excess of tetroxide are removed by continuous evaporation from a warm falling film, the stripped material falling immediately into cold water or methanol :



Subsequent separation of the dinitro-paraffin, nitro-alcohol, and nitro-nitrate is not difficult and varies to some extent with the olefin ; for example, dinitroethane and dinitro*iso*butane are crystallised by cooling the methyl alcohol solution of the product, water extraction is used for recovery of all nitro-alcohols up to C_6, and vacuum fractional distillation covers all other separations and ultimate purification. Total yields of separated products are 65—85%, the deficiency being mainly due to separation losses inherent in the small scale. Except where dinitrogen trioxide is deliberately used, or allowed to accumulate, nitroso-compounds or their derivatives are not formed.

As a result of this work the following generalisations can be made :

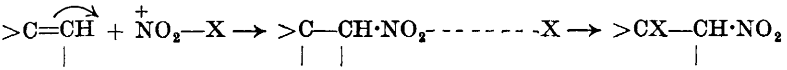
(i) The two modes of initial addition occur to a similar extent and only minor changes are involved in passing from one olefin to another.

(ii) In the formation of nitro-nitrites from unsymmetrical olefins (propylene, *iso*butene, but-1-ene, and the trimethylpentenes) the nitro-group invariably attaches to the carbon atom with the greater number of hydrogen atoms and the nitrite group to the other side of the double bond ; for example :

$$CH_3{\cdot}CH{=}CH_2 \xrightarrow{(NO_2)(O{\cdot}NO)} CH_3{\cdot}CH(O{\cdot}NO){\cdot}CH_2{\cdot}NO_2$$

$$(CH_3)_2C{=}CH_2 \longrightarrow (CH_3)_2C(O{\cdot}NO){\cdot}CH_2{\cdot}NO_2$$

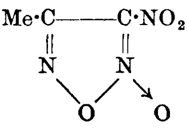
It is therefore suggested that the reaction is electrophilic and concerns polar forms of dinitrogen tetroxide ; initial attack is by the positive nitro-group, followed by release and attachment of the remaining group as $-NO_2$ or $-O{\cdot}NO$:



$$>C{=}CH + \overset{+}{N}O_2{-}X \longrightarrow >C{-}CH{\cdot}NO_2 \text{- - - - - - -} X \longrightarrow >CX{-}CH{\cdot}NO_2$$

($X{=}NO_2$, $O{\cdot}NO$, or NO.)

(iii) Parallel experiments on the behaviour of dinitrogen trioxide in ether showed that it behaves as $(\overset{+}{NO_2})(\overset{-}{NO})$, with the nitroso-group, like the nitrite group, attaching to the carbon atom with fewer hydrogen atoms. The nitrosonitro-paraffin is usually isolated as the solid dimer, although in the case of propylene it appears to be converted into 4-nitro-3-methylfurazan oxide (I). At the same time, the trioxide gives rise to tetroxide by dissociation and hence to dinitro-paraffin and nitro-nitrite.



(I.)

(iv) The solvent effect noted above was most completely studied with *iso*butene. Liquid dinitrogen tetroxide alone, hydrocarbons, and chlorinated solvents promote oxidation, among the products of which the nitrate ester of α-hydroxy*iso*butyric acid $[(CH_3)_2C(O{\cdot}NO_2){\cdot}CO_2H]$ is usually found and the dinitro-paraffin cannot be recognised. Symmetrical ethers, dioxan, benzyl methyl ether, methylal, acetal, tetrahydropyran, tetrahydrofuran, and acetate esters all permit normal addition. Formic esters act as intermediate types, allowing some oxidation as well as normal addition. Substituted ethers, with reduced electron availability at the oxygen atom, are ineffective for normal addition. This gradation of solvent effects, and the isolation of a solid 1 : 1 complex of dioxan with dinitrogen tetroxide, indicate that effective solvents operate through molecular association with the tetroxide and thereby moderate its oxidising tendency.

(v) Nitro-nitrate is formed in relatively small amount unless oxygen is deliberately added to promote stability and obviate the formation of dinitrogen trioxide. Nitro-nitrate appears to be formed at the expense of dinitro-compound as the oxygen rate is increased.

Apart from the importance of this work in clearing up a confused field in organic chemistry, it has made available a series of compounds which were formerly unknown or extremely difficult of access. Their value in further syntheses will be illustrated later in this review.

(*d*) *Vapour-phase nitration of paraffins.* Until 1934, when the first vapour-phase nitration of a saturated paraffin was claimed by H. B. Hass and his collaborators,[52] a process of this type seemed unlikely, the only other positive result being a 2% yield of primary nitro-paraffins from reaction between normal C_5—C_7 paraffins and nitric oxide over an alumina–ceria–thoria catalyst.[53] The Hass process, operated since 1940 by Commercial Solvents Corporation on a moderate works scale, originated with trial of liquid-phase nitration of *iso*butane under pressure, with ultimately greater success at temperatures above the critical for *iso*butane.[2] Succeeding investigations by the Hass school are described in numerous papers since 1936, and a series of patents covering process detail ; the more important of these are referred to below. Developments in this country are indicated in patents assigned to Imperial Chemical Industries Ltd.

Following the nitration of *iso*butane under pressure, ethane, propane, and the butanes were nitrated in a flow apparatus at atmospheric pressure and 420°, using 68% nitric acid, a hydrocarbon : acid ratio of 2 : 1, and a contact time of 2 seconds.[54] Pass conversions of nitric acid into mixed mononitro-paraffins ranged from 9% for ethane to 28% for *iso*butane ; methane was apparently unattacked. It was later found by G. K. Landon [55, 56] that pressures above atmospheric were required for the nitration of methane. Reaction under pressure also gave improved results with ethane,[57] and pressures of 10 atmospheres or more are employed in the commercial process with propane.

Nitration of the lower paraffins gives rise to all the mononitro-paraffins possible by C–H and C–C fission ; thus ethane gives nitromethane as well as nitroethane, propane gives both these as well as 1- and 2-nitropropane, *n*-butane gives nitromethane, nitroethane, 1-nitropropane and 1- and

---

[52] H. B. Hass, E. B. Hodge, and B. M. Vanderbilt, U.S.P. 1,967,667 (1934).

[53] Platonov and Shaikind, *J. Gen. Chem. Russia*, 1934, **4**, 434.

[54] H. B. Hass, E. B. Hodge, and B. M. Vanderbilt, *Ind. Eng. Chem.*, 1936, **28**, 339.

[55] U.S.P. 2,161,475 (1939).

[56] U.S.P. 2,164,774 (1939).

[57] H. J. Hibshman, E. H. Pierson, and H. B. Hass, *Ind. Eng. Chem.*, 1940, **31**, 427.

2-nitrobutane, and *iso*butane give nitromethane, 2-nitropropane and 1- and 2-nitro*iso*butane. Similar results obtain with normal pentane [58] and *iso*-pentane.[59] The proportions of the various nitro-paraffins in the product are affected by temperature, the reaction being more selective at lower temperatures when ease of substitution follows the order tertiary > secondary > primary hydrogen atoms. As the temperature is raised, more primary and lower nitro-paraffins are formed. This is illustrated in the nitration of propane with nitrogen tetroxide at temperatures of 250—800°.[60] Over this range the 2-nitropropane content diminishes from 72% to 23·5%, while the other components increase as follows: nitromethane from 14% to 23·5%, nitroethane from 3% to 23·5%, and 1-nitropropane from 11% to 29·5%. In manufacturing practice this degree of flexibility is limited by considerations of yield, the competing oxidation reaction becoming more marked with rising temperature, and on this account it is necessary to control temperature precisely. Operation under pressure requires higher hydrocarbon ratios and shorter contact times for the same reason; for example, the nitration of ethane at 7 atmospheres and 450—470° was carried out with an ethane : nitric acid ratio of 10 : 1 and a contact time of 0·23—0·33 second [57] compared with a ratio of 2 : 1 and a contact time of 2 seconds at atmospheric pressure.[54]

Dinitrogen tetroxide can be used under similar conditions, but better control and conversions can be achieved at substantially lower temperatures and longer contact times, together with higher partial pressures of nitrating agent.[61] The main advantage of these conditions is that the lower temperatures and moderate rate of heat evolution permit a more positive control of reaction temperature, for example, by heat transfer to a boiling liquid. The process is a cyclic one, that is, after passage of the mixed vapours through the reactor, nitro-paraffins and water are condensed, and the spent gas (containing excess of hydrocarbon, and nitric oxide, oxides of carbon, and other minor constituents) is treated to remove oxides of carbon. Paraffin and nitric oxide, after re-oxidation by suitable means, are returned to the converter with fresh paraffin and nitrating agent. The crude nitro-paraffin mixture may be steam-distilled first and then fractionated in a series of stills operated under partial vacuum. When propane and nitrogen tetroxide are used at about 360° and 10 atmospheres pressure, the product contains 20—25% of nitromethane, 5—10% of nitroethane, 45—55% of 2-nitropropane, and 20% of 1-nitropropane in total yield of 75—80% on the propane consumed in the converter and over 90% on the tetroxide.[61] Acetone is also formed in small amount, and up to 1% of the nitro-paraffin mixture is 2 : 2-dinitropropane. The main source of loss is oxidation of the hydrocarbon, ultimately to carbon monoxide and dioxide, though the reduction of acid or tetroxide stops short at nitric oxide. The oxidation reaction is a chain process, with the reactor walls playing an important part, and it

---

[58] H. B. Hass and J. Patterson, *Ind. Eng. Chem.*, 1938, **30,** 67.

[59] L. W. Siegle and H. B. Hass, *ibid.*, 1939, **31,** 648.

[60] H. B. Hass, J. Dorsky, and E. B. Hodge, *ibid.*, 1941, **33,** 1138.

[61] I.C.I., private communication.

is possible that nitro-paraffins of lower carbon number than the original hydrocarbon are by-products of branching oxidation chains.

The use of stainless steel reaction vessels with nitric acid, although initially satisfactory, leads to progressive increase in the oxidation reaction at the expense of nitration. In a number of patents assigned to Commercial Solvents Corporation, intermittent washing or coating with a number of inorganic salt solutions [62, 63] or the injection of small amounts of sodium or potassium nitrate with the acid [64] is claimed to control this effect, while G. K. Landon [55, 56] mentions precious metals and " Pyrex " for the reaction vessel. The precise rôle of catalysts in this reaction is not known, but arsenic- or antimony-containing glasses,[65] lead or lead-containing glass,[66] aluminium,[67] and borosilicate glass [68] have all been claimed to give improvements. Recent data [69] on German war-time research on the synthesis of nitro-paraffins show no new features.

The formation of dinitro-paraffins in vapour-phase reactions may well be a function of the use of dinitrogen tetroxide and the associated longer contact times, albeit at lower temperature,[70, 71] though it is unlikely that solely 1-nitro- and 1 : 1-dinitro-paraffins are formed.[60, 72] Reaction between *iso*butane and dinitrogen tetroxide at 200—250° yields a product up to half of which is 1 : 2-dinitro*iso*butane, the remainder being tertiary nitrobutane mixed with smaller amounts of lower mononitro-paraffins and 2 : 2-dinitropropane.[73] If the mixed product is steam-distilled, much of the dinitrobutane is lost by conversion *via* α-nitro*iso*butene into acetone and nitromethane.[50] More recently, Hass and his school have extended their investigations to miscellaneous higher paraffins and *cyclo*paraffins up to C_7.[74, 75]

A free-radical mechanism has been proposed for the nitration reaction [76] which accounts for the specific mononitro-paraffins formed in all cases ; small amounts of the expected olefins are also found. On the other hand, it seems unlikely to explain the proportions of the various products or the fact that the nitration of *iso*butyl chloride [77] leads to mononitro-derivatives of the parent substance (1-chloro-3-nitro-, 1-chloro-2-nitro-, and 1-chloro-1-nitro-2-methylpropane), 1-chloro-2-nitropropane, and nitromethane, but no

---

[62] U.S.P. 2,236,905 (1941).

[63] U.S.P. 2,236,906 (1941).

[64] U.S.P. 2,260,258 (1941).

[65] N. Levy and I.C.I. Ltd., B.P. 575,733.

[66] K. W. Gee and I.C.I. Ltd., B.P. 576,129.

[67] M. P. Applebey and I.C.I. Ltd., B.P. 578,044.

[68] N. Levy, A. E. Rout, K. W. Gee, and I.C.I. Ltd., B.P. 586,203.

[69] S. Masterman and D. B. Clapp, C.I.O.S., Item 22, File No. XXXIII—41, H.M.S.O., 1947.

[70] T. Urbanski and M. Slon, *Roczniki Chem.*, 1936, **16**, 466 ; *Compt. rend.*, 1936, **203**, 620.

[71] *Idem, Roczniki Chem.*, 1937, **17**, 161.

[72] M. H. Danzig and H. B. Hass, *J. Amer. Chem. Soc.*, 1944, **66**, 2017.

[73] I.C.I., private communication.

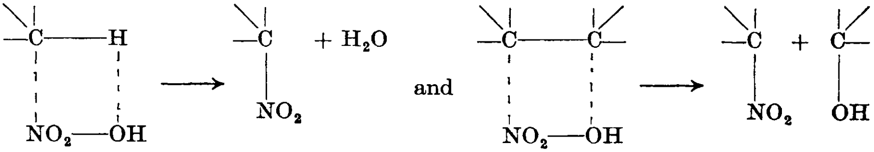
[74] A. P. Howe and H. B. Hass, *Ind. Eng. Chem.*, 1946, **38**, 251.

[75] R. T. Bickerstaff and H. B. Hass, *J. Amer. Chem. Soc.*, 1946, **68**, 1431.

[76] R. F. McCleary and E. F. Degering, *Ind. Eng. Chem.*, 1938, **30**, 64.

[77] T. J. Oleszko and E. T. McBee, Thesis, Purdue University, 1939.

chloronitromethane or 2-nitropropane. The alternative theory mentioned by Hass [2] of complex formation between nitric acid and the hydrocarbon, for example :



while providing for the formation of alcohols, small amounts of which survive, also fails to explain the above case, unless complex formation is itself electrophilic and affected by neighbouring substituents. It would be interesting to see this tried and the decisive test applied by Stevens and Schiessler [35] to liquid-phase nitration used with vapour-phase examples.

N. L.

Physical Properties.—A summary of the physical properties of the commoner nitro-paraffins is given in Table II.[78]

TABLE II

	Nitromethane, $CH_3{\cdot}NO_2$.	Nitroethane, $CH_3{\cdot}CH_2{\cdot}NO_2$.	1-Nitropropane, $CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2$.	2-Nitropropane, $(CH_3)_2CH{\cdot}NO_2$.
$d_{20°}^{20°}$	1·139	1·052	1·003	0·992
M.p.	– 29°	– 90°	– 108°	– 93°
B.p.	101·2°	114·0°	131·6°	120·3°
Vap. press. (mm. at 20°) . . .	27·8	15·6	7·5	12·9
$n^{20°}$	1·3818	1·3916	1·4015	1·3941
Solubility at 20° : c.c. in 100 c.c. of water c.c. of water in 100 c.c.	 9·5 2·2	 4·5 0·9	 1·4 0·5	 1·7 0·6

All the mononitro-paraffins are colourless when pure, and have dipole moments of about 3·2. They are miscible with most organic solvents, and possess considerable solvent power for many organic substances. This will be dealt with more fully in the section of this review dealing with their uses.

Of the mononitro-paraffins, only nitromethane can be detonated with a cap ; the dinitro- and polynitro-compounds, being more in oxygen balance, are more sensitive and explode more easily.

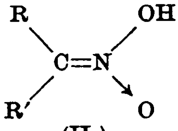
In view of the known considerable toxicity of many aromatic nitro-compounds it is surprising that the nitro-paraffins are comparatively

[78] From " The Nitroparaffins ", Commercial Solvents Corporation, New York.

innocuous ; they are said to be of the same order of toxicity as the normal paraffins of the same boiling point.

Structure of the Nitro-paraffins and their Salts.—Nitro-paraffins are classified as primary, secondary, or tertiary according to the number of hydrogen atoms carried by the carbon atom adjacent to the nitro-group. Thus, nitromethane with three, and nitroethane and 1-nitropropane with two α-hydrogen atoms are primary nitro-compounds, 2-nitropropane with one α-hydrogen atom is secondary, and tertiary nitrobutane has no α-hydrogen atoms.

Primary and secondary nitro-paraffins dissolve in aqueous or aqueous alcoholic solutions of strong alkalis, but tertiary nitro-compounds do not. This difference in behaviour is due to the fact that primary and secondary nitro-paraffins can exist in an *aci-* or *iso*-form (known as nitronic acids), and many of the reactions of the aliphatic nitro-compounds are due to the reactivity of this *aci*-form. The generally accepted structure of the *aci*-nitro-paraffins is (II), and the arguments in favour of this structure are excellently reviewed by Taylor and Baker.[1]



(II.)

The structure of the salts has, until recently, been a matter of considerable controversy. In 1927 it was reported by R. Kuhn and H. Albrecht [79] that optically active 2-nitrobutane gives an active sodium salt when heated with sodium methoxide ; this sodium salt, with bromine, gave an optically active 2-bromo-2-nitrobutane. A similar study on active 2-nitro-octane was carried out by R. L. Shriner and J. H. Young [80] in 1930 ; they demonstrated that an optically active sodium salt was formed, which gave an active 2-bromo-2-nitro-octane, and in which the activity was retained to the extent of 24% and 71% when the parent nitro-paraffin was regenerated at — 10° and — 70° respectively. The acceptance of these results rendered untenable the accepted structure (III) of the nitro-paraffin salts, and many theories were advanced,[1, 79, 80, 81, 82] none of which was completely satisfactory, to account for these phenomena. As far as Shriner and Young's results are concerned the problem has been solved by a recent re-investigation of their work.[83] It has been shown that their active 2-nitro-octane, prepared from active 2-bromo-octane and silver nitrite, contains some active 2-nitro-octyl nitrate which cannot be separated by distillation. Naturally, the activity due to this ester is retained throughout the cycle of sodium salt formation and regeneration, and accounts for the 24% residual activity in the experiments at — 10°. The 71% activity in the lower temperature work is demonstrated as due to (*a*) the octyl nitrate and (*b*) incomplete salt formation at the lower temperature. When pure optically active 2-nitro-

[79] *Ber.*, 1927, **60**, 1297.

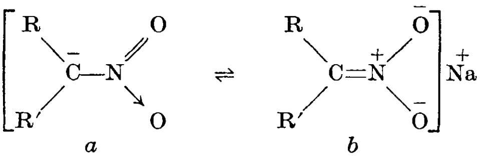
[80] *J. Amer. Chem. Soc.*, 1930, **52**, 3332.

[81] " Organic Chemistry ", ed. H. Gilman, John Wiley & Sons, New York, 1943 ed., Vol. I, p. 391.

[82] H. B. Hass and E. Riley, *Chem. Reviews*, 1943, **32**, 381.

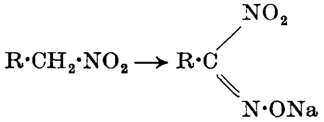
[83] N. Kornblum, N. N. Lichtin, J. T. Patton, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1947, **69**, 307.

octane is converted completely into its salt and regenerated, the resulting nitro-paraffin is inactive. The structure (III) can therefore be accepted with confidence, and it is postulated by L. P. Hammet,[84] that the contribution of form (III*b*) is more important than that of (III*a*).



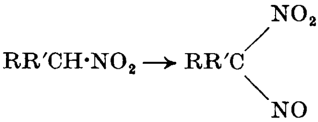
(III.)

Primary, secondary, and tertiary aliphatic nitro-compounds can be differentiated one from another by reaction with nitrous acid in alkaline solution, the so-called " red, white, and blue " reaction. Primary compounds give a red colour due to the formation of a nitrolic acid salt (IV), secondary give a blue colour due to a *pseudo*nitrole (V), whilst tertiary do not react.



$$R\cdot CH_2\cdot NO_2 \longrightarrow R\cdot C\genfrac{}{}{0pt}{}{\diagup NO_2}{\diagdown\!\!\diagdown N\cdot ONa}$$

(IV.)



$$RR'CH\cdot NO_2 \longrightarrow RR'C\genfrac{}{}{0pt}{}{\diagup NO_2}{\diagdown NO}$$

(V.)

Action of Acids and Bases.—Cautious acidification of the aqueous solution of the sodium salt of a nitro-paraffin liberates the free *aci*-form, which can often be isolated in state of purity. Thus, phenylnitromethane, an oil, after dissolution in sodium hydroxide and acidification at 0°, gives *aci*-phenylnitromethane, a white crystalline solid (m.p. 84°) which can be recrystallised from light petroleum ; this reverts slowly to the normal liquid nitro-paraffin. Regeneration of nitro-compounds from alkaline solutions is best carried out either at low temperature, or with a weak acid (carbon dioxide or acetic acid). At higher temperatures alkaline solutions of primary nitro-paraffins may rearrange to hydroxamic acids [85] which by hydrolysis give carboxylic acids and hydroxylamine :

$$R\cdot CH{:}NO\cdot OH \longrightarrow R\cdot C(OH){:}N\cdot OH$$

Excellent yields of hydroxylamine are obtained by heating primary nitro-paraffins with 85% sulphuric acid.[86] Under these conditions, secondary nitro-paraffins give only tars.

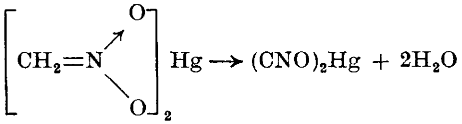
An alternative mode of decomposition of the alkali *aci*-nitro-paraffins is to an aldehyde (from primary) or ketone (from secondary nitro-compounds) and nitrous oxide.[87] This reaction predominates when the aqueous sodium salt is added to excess of dilute sulphuric acid, and aldehydes and ketones

[84] " Physical Organic Chemistry ", McGraw Hill Book Co., New York, 1940, p. 67.
[85] H. L. Yale, *Chem. Reviews*, 1943, **33**, 226.
[86] S. B. Lippincott and H. B. Hass, *Ind. Eng. Chem.*, 1939, **31**, 118.
[87] J. U. Nef, *Annalen*, 1894, **280**, 263.

have been obtained by K. Johnson and E. F. Degering [88] in 85% yield by this method :

$$2CH_3{\cdot}CH{:}NO_2Na + 2H_2SO_4 \longrightarrow 2CH_3{\cdot}CHO + N_2O + NaHSO_4 + H_2O$$
$$2(CH_3)_2C{:}NO_2Na + 2H_2SO_4 \longrightarrow 2(CH_3)_2CO + N_2O + NaHSO_4 + H_2O$$

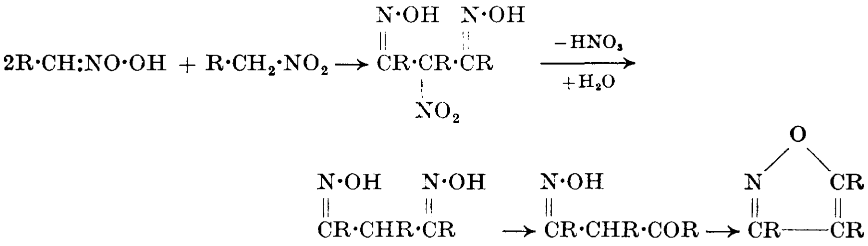
The alkali-metal salts of the nitro-paraffins are unstable to heat or shock, the potassium salts being more sensitive than the sodium salts. Heavy metals form insoluble precipitates with aqueous solutions of the alkali salts, but nitromethane is exceptional in giving mercury fulminate by spontaneous dehydration of the intermediate mercury salt :



With strong alkalis nitromethane gives salts of methazonic acid, which by further hydrolysis gives salts of nitroacetic acid, thus

$$CH_2{:}NO{\cdot}ONa + CH_3{\cdot}NO_2 \longrightarrow [NO_2{\cdot}CH_2{\cdot}CH_2{\cdot}N(OH){\cdot}ONa] \xrightarrow{-H_2O}$$
$$\underset{\text{sodium methazonate}}{N(OH){:}CH{\cdot}CH{:}NO_2Na} \longrightarrow [CN{\cdot}CH{:}NO_2Na] \longrightarrow CO_2Na{\cdot}CH{:}NO_2Na$$

Dehydration of the intermediate methazonic acid with thionyl chloride affords nitromethyl cyanide.[89] The action of basic substances on primary nitro-paraffins higher than nitromethane was investigated by W. R. Dunstan and his co-workers [90] who demonstrated the formation of trialkyl*iso*oxazoles. More recently, S. B. Lippincott [91] has carried out this reaction under milder conditions and shown that β-dioximes are the initial products formed by the action of organic bases, and that these on hydrolysis with dilute acids give the trialkyl*iso*oxazoles. The following reaction mechanism is postulated :



$$2R{\cdot}CH{:}NO{\cdot}OH + R{\cdot}CH_2{\cdot}NO_2 \longrightarrow \overset{N\cdot OH\ \ \ N\cdot OH}{CR{\cdot}\underset{NO_2}{CR}{\cdot}CR} \xrightarrow[+H_2O]{-HNO_3}$$
$$\overset{N\cdot OH\ \ \ \ N\cdot OH}{CR{\cdot}CHR{\cdot}CR} \longrightarrow \overset{N\cdot OH}{CR{\cdot}CHR{\cdot}COR} \longrightarrow$$

Reduction.—The reduction products of nitro-paraffins and their derivatives vary according to the conditions and reducing agent employed. A large number of methods of reduction have been described, and an extensive review of these methods is given by H. B. Hass and E. Riley.[2] K. Johnson

---

[88] *J. Org. Chem.*, 1943, **8**, 10.

[89] W. Steinkopf and L. Bohrmann, *Ber.*, 1908, **41**, 1048.

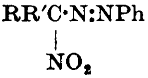
[90] W. R. Dunstan and T. S. Dymond, *J.*, 1891, **59**, 410 ; W. R. Dunstan and E. Goulding, *J.*, 1900, **77**, 1262.

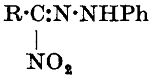
[91] *J. Amer. Chem. Soc.*, 1940, **62**, 2604.

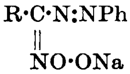
and E. F. Degering[92] conclude that the best yields of amines from nitro-paraffins are obtained with iron and hydrochloric acid, or by catalytic reduction over Raney nickel under pressure. For the reduction of 2-nitro-alcohols, Raney nickel and hydrogen is the preferred method since the alcohols are sensitive to acids and alkalis ; a diluent is necessary to prevent the reduction from getting out of hand, and it is usually preferable to work at superatmospheric pressure and room temperature. Secondary amines have been prepared by reduction of a nitro-compound with zinc dust and dilute acetic acid in presence of an aldehyde. Thus, reduction of nitromethane with benzaldehyde gives benzylmethylamine.[93]

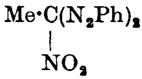
Hydroxylamines are isolated as major products when nitro-paraffins are reduced with zinc dust and water, zinc dust and ammonium chloride,[94] zinc and dilute acetic acid,[95] or sodium amalgam in neutral solution.[96] Carbonyl compounds have been obtained by reduction of primary or secondary nitro-paraffins with acid reducing agents, such as zinc dust and acetic acid ;[97] these are probably formed by hydrolysis of an intermediate oxime, since K. Johnson[92] has shown that zinc dust and glacial acetic acid is a general method for the reduction of nitro-paraffins to oximes. Ketones are also formed by catalytic reduction of α-chloronitro-paraffins with palladium on barium sulphate,[98] and oximes are obtained in excellent yield by reducing the sodium salt of the nitro-paraffin with cold stannous chloride and hydrochloric acid.[99]

Action of Diazo-compounds.—The condensation of aryldiazonium salts with nitro-paraffins was discovered by Victor Meyer,[100] who obtained an orange solid from benzenediazonium sulphate and sodium nitroethane ; similar substances were also prepared from 2-nitropropane. The compounds derived from secondary nitro-compounds are regarded as true azo-compounds (VI), but those from primary nitro-compounds with one molecular proportion of diazo-salt correspond better with the hydrazone structure (VII) for the free nitro-compounds, and the azo-structure (VIII) for the salts.[101, 102, 103]


$$\begin{array}{l}\mathrm{RR'C{\cdot}N{:}NPh}\\ \;\;|\\ \;\mathrm{NO_2}\end{array}$$
(VI.)


$$\begin{array}{l}\mathrm{R{\cdot}C{:}N{\cdot}NHPh}\\ \;\;|\\ \;\mathrm{NO_2}\end{array}$$
(VII.)


$$\begin{array}{l}\mathrm{R{\cdot}C{\cdot}N{:}NPh}\\ \;\;\|\\ \;\mathrm{NO{\cdot}ONa}\end{array}$$
(VIII.)


$$\begin{array}{l}\mathrm{Me{\cdot}C(N_2Ph)_2}\\ \;\;|\\ \;\mathrm{NO_2}\end{array}$$
(IX.)

The salts (VIII) react with a further molecule of aryldiazonium chloride, and the final product of the reaction between, *e.g.*, nitromethane and benzene-

---

[92] *J. Amer. Chem. Soc.*, 1939, **61,** 3194.

[93] S. Kanao, *J. Pharm. Soc. Japan*, 1929, **49,** 42 ; *Chem. Zentr.*, 1929, I, 2974.

[94] E. Beckmann, *Annalen*, 1909, **365,** 205.

[95] W. R. Dunstan and E. Goulding, *J.*, 1900, **77,** 1262.

[96] W. Charlton and J. Kenner, *J.*, 1932, 750.

[97] T. Urbanski and M. Slon, *Compt. rend.*, 1937, **204,** 870.

[98] E. Schmidt and A. Ascherl, *Ber.*, 1925, **58,** 356.

[99] J. v. Braun and E. Danziger, *ibid.*, 1913, **46,** 103.

[100] V. Meyer and G. Ambuhl, *ibid.*, 1875, **8,** 751, 1073.

[101] V. Meyer, *ibid.*, 1888, **21,** 11.

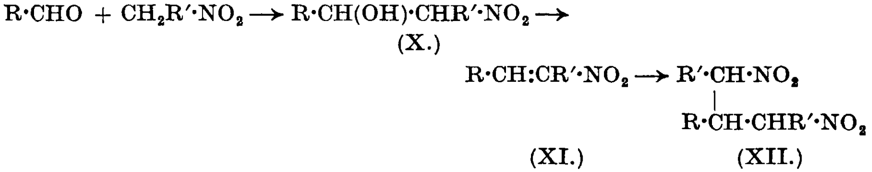
[102] *J.*, 1930, 919.

[103] E. Bamberger, *Ber.*, 1894, **27,** 157.

diazonium chloride is "nitroformazyl," $NHPh{\cdot}N{:}C(NO_2){\cdot}N_2Ph$ [103] and of nitroethane, the bisazo-compound (IX).

E. C. S. Jones and J. Kenner [102] have shown that interaction of 2-nitropropyl alcohol and benzenediazonium chloride gives the phenylhydrazone (VII ; R = Me), formaldehyde being eliminated. Similarly, the alcohol and glycol derived from nitromethane and formaldehyde give "nitroformazyl" on treatment with benzenediazonium chloride. C. F. Feasley and E. F. Degering [104] have recently described the preparation of a series of azo-compounds of type (VI) from 2-nitropropane and 2-nitrobutane with various aromatic amines. If the original amine contains an acidic auxochromic group the product will dye wool and silk directly, and dyeings are also achieved by coupling of the components on the fibre. Such dyes, however, have no commercial value.[105]

Reactions with Aldehydes and Ketones.—Primary and secondary aliphatic nitro-compounds condense readily with aldehydes and ketones. The product from a primary nitro-compound is usually the corresponding alcohol (X), sometimes, particularly in condensations with aromatic aldehydes, the nitro-olefin (XI), and occasionally the dinitro-compound (XII), formed by addition of a further mole of nitro-paraffin to the nitro-olefin (see later):



$$R{\cdot}CHO + CH_2R'{\cdot}NO_2 \longrightarrow \underset{(X.)}{R{\cdot}CH(OH){\cdot}CHR'{\cdot}NO_2} \longrightarrow$$

$$\underset{(XI.)}{R{\cdot}CH{:}CR'{\cdot}NO_2} \longrightarrow \underset{(XII.)}{\begin{array}{l} \quad R'{\cdot}CH{\cdot}NO_2 \\ \qquad | \\ R{\cdot}CH{\cdot}CHR'{\cdot}NO_2 \end{array}}$$

The condensing agents which have been used to effect these reactions are normally basic ones, such as alkali carbonates, hydrogen carbonates, hydroxides, or alkoxides, primary aliphatic amines, and calcium hydroxide, but occasionally, with aromatic aldehydes, acidic agents such as zinc chloride have been employed.

In general, formaldehyde in excess under mildly basic conditions can replace all the α-hydrogen atoms of a nitro-paraffin by hydroxymethyl groups. Thus, nitromethane gives tris(hydroxymethyl)nitromethane, nitroethane gives 2-nitro-2-methylpropane-1 : 3-diol, and 2-nitropropane gives 2-nitro-2-methylpropanol. The nitromethane reaction cannot be restricted to the formation of the diol (2-nitropropane-1 : 3-diol) ; this is prepared by removal of a molecule of formaldehyde from the trihydroxy-compound by treatment with sodium alkoxide.[106]

With the higher primary nitro-paraffins, alkaline condensation with formaldehyde gives a mixture of the alcohol and the glycol, and yields of either can be controlled within certain limits by correct choice of proportion of reactants and experimental conditions. It has recently been found in the laboratories of I.C.I. Ltd. Dyestuffs Division [107] that the yield of alcohol

---

[104] *J. Org. Chem.*, 1943, **8**, 12.

[105] I.C.I. Ltd., private communication.

[106] E. Schmidt and R. Wilkendorf, *Ber.*, 1919, **52**, 389.

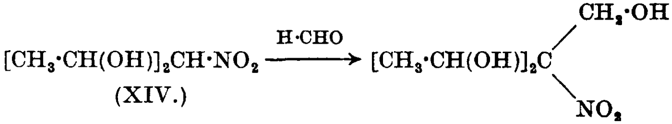
[107] A. Lowe, private communication.

can be considerably increased at the expense of the diol by carrying out the reaction in the presence of a full molecular proportion of caustic alkali.

The condensation of aliphatic aldehydes higher than formaldehyde with nitro-paraffins becomes progressively more difficult with increasing molecular weight of the aldehyde. Acetaldehyde and nitromethane give 2-nitro*iso*propyl alcohol (XIII) in good yield, the diol [3-nitropentane-2 : 4-diol (XIV)] being only a minor by-product in the normal condensation of equimoles of the reactants.[108] Three molecules of acetaldehyde cannot be condensed with nitromethane, but the remaining α-hydrogen atom in the diol (XIV) can be replaced by a hydroxymethyl group, thus :

$$CH_3{\cdot}NO_2 + CH_3{\cdot}CHO \longrightarrow CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2 \longrightarrow$$

(XIII.)



$$[CH_3{\cdot}CH(OH)]_2CH{\cdot}NO_2 \xrightarrow{H{\cdot}CHO} [CH_3{\cdot}CH(OH)]_2C\begin{array}{l} \diagup CH_2{\cdot}OH \\ \diagdown NO_2 \end{array}$$

(XIV.)

Aromatic aldehydes and nitro-paraffins condensed together under alkaline conditions yield monohydric alcohols, which often dehydrate spontaneously to the nitro-olefin unless special precautions are taken. Thus, benzaldehyde and nitromethane yield ω-nitrostyrene directly when the alkaline reaction product is acidified with a mineral acid ; if acetic acid is used, the nitro-alcohol is precipitated [109] and can be isolated.

$$Ph{\cdot}CHO + CH_3{\cdot}NO_2 \longrightarrow Ph{\cdot}CH(OH){\cdot}CH_2{\cdot}NO_2 \longrightarrow Ph{\cdot}CH{:}CH{\cdot}NO_2$$

Nitromethane reacts with ketones, such as acetone or methyl ethyl ketone, under the influence of basic catalysts to give 1 : 3-dinitro-paraffins.[110] H. B. Hass [111] has shown that in the reaction product of acetone and nitromethane 1-nitro-2-methylprop-1-ene (XVI) is present, and that this can react with nitromethane giving 1 : 3-dinitro-2 : 2-dimethylpropane (XVII). An important reaction product isolated by Hass, and not reported by Fraser and Kon,[110] is 5-nitro-4 : 4-dimethylpentan-2-one (XVIII), formed by addition of excess of acetone to the nitro-olefin. By the use of a large excess of acetone, this can be made the main product. Hass postulates these reactions as following the course below, but describes nitro-*tert.*-butanol (XV) as unknown.

It has recently been shown [72] that when sodium methoxide or hydroxide, a quaternary ammonium hydroxide, or trimethylamine is used as catalyst, nitro-*tert.*-butanol is formed in high yield. This nitro-alcohol, kept at room temperature with secondary amines, gives a mixture of the unchanged alcohol, the nitro-olefin (XVI), and the dinitro-paraffin. This indicates that the reaction mechanism proposed by Hass (see above) is essentially correct, but the formation of the nitro-alcohol from acetone and nitromethane

---

[108] G. D. Buckley and (Mrs.) J. L. Charlish, *J.*, 1947, 1472.

[109] K. W. Rosenmund, *Ber.*, 1913, **46**, 1037.

[110] H. B. Fraser and G. A. R. Kon, *J.*, 1934, 604.

[111] *Ind. Eng. Chem.*, 1943, **35**, 1150.

is reversible.[112] The reactions of nitromethane with *cyclo*hexanone and methyl ethyl ketone follow a similar course.

$$(CH_3)_2CO + CH_3\cdot NO_2 \longrightarrow \underset{\text{(XV.)}}{(CH_3)_2C(OH)\cdot CH_2\cdot NO_2} \longrightarrow$$

$$\begin{tikzcd} \underset{\text{(XVI.)}}{(CH_3)_2C{:}CH\cdot NO_2} \arrow[r, "\text{acetone}"] \arrow[d, "CH_3\cdot NO_2"] & \underset{\text{(XVIII.)}}{CH_3\cdot CO\cdot CH_2\cdot C(CH_3)_2\cdot CH_2\cdot NO_2} \\ \underset{\text{(XVII.)}}{(CH_3)_2C(CH_2\cdot NO_2)_2} & \end{tikzcd}$$

Nitro-alcohols and glycols derived from nitro-paraffins and aldehydes or ketones are readily reduced to the corresponding amino-alcohols, which have been extensively investigated as intermediates in the preparation of emulsifying agents, detergents, and dispersing agents, fields in which the ethanolamines (prepared from ethylene oxide and ammonia) have already found considerable application.

The Mannich Reaction.—The Mannich reaction on nitro-paraffins was first investigated by L. Henry,[113] who showed that *N*-hydroxymethylpiperidine condensed with nitromethane and nitroethane yielding respectively 2-nitro-1 : 3-di-*N*-piperidinopropane (XIX) and 2-nitro-1 : 3-di-*N*-piperidino-2-methylpropane (XX).

$$2C_5H_{10}N\cdot CH_2\cdot OH + CH_3\cdot NO_2 \longrightarrow NO_2\cdot CH(CH_2\cdot NC_5H_{10})_2 \quad \text{(XIX.)}$$

$$2C_5H_{10}N\cdot CH_2\cdot OH + CH_3\cdot CH_2\cdot NO_2 \longrightarrow NO_2\cdot C(CH_3)(CH_2\cdot NC_5H_{10})_2 \quad \text{(XX.)}$$

As a result of later work [114, 115] it has been established that although under normal conditions nitromethane and nitroethane condense with two molecules of a secondary hydroxymethylamine, higher nitro-paraffins (nitropropane, 1-nitrobutane) condense with only one. The formation of the nitro-monoamines (XXI) from, *e.g.*, nitroethane and piperidine requires long reaction periods at low temperatures :

$$C_5H_{10}N\cdot CH_2\cdot OH + CH_3\cdot CH_2\cdot NO_2 \longrightarrow C_5H_{10}N\cdot CH_2\cdot CH(CH_3)\cdot NO_2 \quad \text{(XXI.)}$$

and the products are unstable ; (XXI), for example, on being kept precipitates the nitro-diamine (XX).[116] The nitro-diamine (XX) can also be prepared from the nitro-glycol (XXII) by reaction with piperidine, and

$$\underset{\text{(XXII.)}}{NO_2\cdot C(CH_3)(CH_2\cdot OH)_2} + C_5H_{11}N \longrightarrow NO_2\cdot C(CH_3)(CH_2\cdot NC_5H_{10})_2$$

$$CH_3\cdot CH(OH)\cdot CH_2\cdot NO_2 + 2C_5H_{10}N\cdot CH_2\cdot OH \longrightarrow NO_2\cdot CH(CH_2\cdot NC_5H_{10})_2 + CH_3\cdot CHO$$

---

[112] A. Lambert and A. Lowe, *J.*, 1947, 1517.

[113] *Bull. Acad. roy. Belg.*, 1896, **32,** 33 ; *Ber.*, 1905, **38,** 2027.

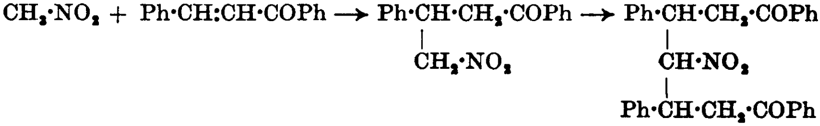
[114] Cerf de Mauney, *Bull. Soc. chim.*, 1937, **4,** 1451, 1460.

[115] M. Zief and J. P. Mason, *J. Org. Chem.*, 1943, **8,** 1.

[116] A. Lambert and J. D. Rose, *J.*, 1947, 1511.

(XIX) is formed from hydroxymethylpiperidine and 2-nitro*iso*propyl alcohol with elimination of acetaldehyde.[116]

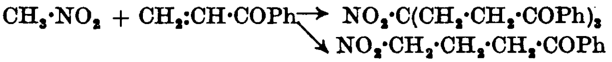
Addition to Activated Ethylenic Compounds.—Closely parallel to the reaction of nitro-paraffins with aldehydes is the addition of primary and secondary aliphatic nitro-compounds to substances containing an activated ethylenic linkage. The reaction is similar to the Michael condensation of the sodium derivative of malonic ester with activated unsaturated compounds. By this method E. P. Kohler and his co-workers [117] condensed nitromethane with benzylideneacetophenone using an alkaline catalyst, and obtained 3-nitro-2-phenylbutyrophenone (XXIII) and the bis-adduct (XXIV):



$$CH_3{\cdot}NO_2 + Ph{\cdot}CH{:}CH{\cdot}COPh \longrightarrow \underset{\displaystyle CH_2{\cdot}NO_2}{Ph{\cdot}\underset{|}{C}H{\cdot}CH_2{\cdot}COPh} \longrightarrow \begin{array}{l} Ph{\cdot}CH{\cdot}CH_2{\cdot}COPh \\ \quad\ | \\ \quad CH{\cdot}NO_2 \\ \quad\ | \\ Ph{\cdot}CH{\cdot}CH_2{\cdot}COPh \end{array}$$

(XXIII.) (XXIV.)

A. Sonn [118] obtained 3-nitrobutyrophenone (XXV) from phenyl vinyl ketone and nitromethane, whilst C. F. Allen and A. B. Bell [119] obtained tris-(2-benzoylethyl)nitromethane (XXVI) from the same reactants:



$$CH_3{\cdot}NO_2 + CH_2{:}CH{\cdot}COPh \begin{array}{l} \nearrow NO_2{\cdot}C(CH_2{\cdot}CH_2{\cdot}COPh)_3 \quad (XXVI.) \\ \searrow NO_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COPh \quad (XXV.) \end{array}$$

Mannich bases derived from methyl ketones react with nitromethane under alkaline conditions and form similar products; thus, 2-dimethylaminopropiophenone affords the nitro-ketone (XXV).[120]

H. Bruson [121] has recently demonstrated the addition of nitro-paraffins to vinyl cyanide. Nitromethane, in presence of a quaternary ammonium hydroxide catalyst, gives tris-(2-cyanoethyl)nitromethane (XXVII), nitroethane gives 3-nitro-1 : 5-dicyano-3-methylpentane (XXVIII), and 2-nitropropane adds only one molecule of cyanide, giving 3-nitro-1-cyano-3-methylbutane (XXIX):

$$CH_3{\cdot}NO_2 + 3CH_2{:}CH{\cdot}CN \longrightarrow NO_2{\cdot}C(CH_2{\cdot}CH_2{\cdot}CN)_3 \quad (XXVII.)$$

$$CH_3{\cdot}CH_2{\cdot}NO_2 + 2CH_2{:}CH{\cdot}CN \longrightarrow NO_2{\cdot}C(CH_3)(CH_2{\cdot}CH_2{\cdot}CN)_2 \quad (XXVIII.)$$

$$(CH_3)_2CH{\cdot}NO_2 + CH_2{:}CH{\cdot}CN \longrightarrow NO_2{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN \quad (XXIX.)$$

It is difficult to restrict this reaction to the condensation of a number of vinyl cyanide molecules less than the number of active hydrogen atoms in the nitro-paraffin, but recently the bis-adduct of vinyl cyanide and nitromethane has been prepared by carrying out the condensation in the presence of a full molecular proportion of caustic alkali.[122]

---

[117] *J. Amer. Chem. Soc.*, 1916, **38**, 889; 1919, **41**, 1644; 1922, **44**, 624, 2144; 1924, **46**, 509, 1274; 1926, **48**, 2425.

[118] *Ber.*, 1935, **68**, 148.

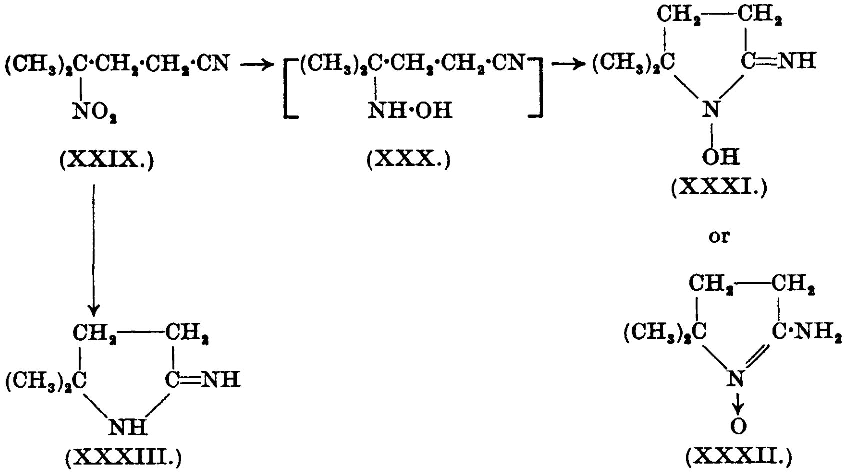
[119] *Canadian J. Res.*, 1934, **11**, 40—46.

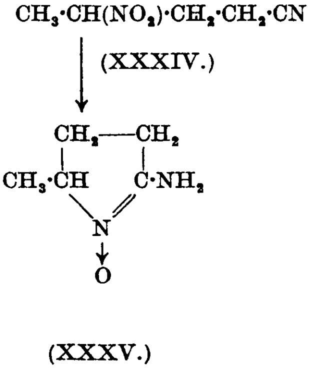
[120] B. Reichert and H. Posemann, *Arch. Pharm.*, 1937, **275**, 67.

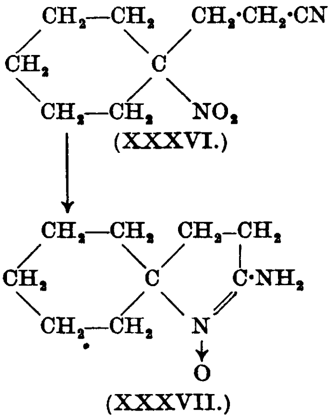
[121] *J. Amer. Chem. Soc.*, 1943, **65**, 23.

[122] G. D. Buckley, T. J. Elliott, F. G. Hunt, and A. Lowe, *J.*, 1947, 1505.

An interesting phenomenon has been observed in attempts to reduce the nitro-cyanide (XXIX) to the corresponding diamine. Reduction with iron and hydrochloric acid gave 5-imino-2 : 2-dimethylpyrrolidine (XXXIII) and a white crystalline substance, $C_6H_{12}ON_2$, formulated as 5-amino-2 : 2-dimethylpyrroline *N*-oxide (XXXII) or its tautomeride, 5-imino-1-hydroxy-2 : 2-dimethylpyrrolidine (XXXI).[123] This substance is also obtained in good yield by reduction of the nitro-cyanide with hydrogen over Raney nickel, or in excellent yield by reduction with zinc dust and ammonium chloride.


(XXIX.) (XXX.) (XXXI.) or (XXXII.) (XXXIII.)


(XXXIV.) (XXXV.)


(XXXVI.) (XXXVII.)

This last method of reduction gives a clue to the mechanism of formation of the *N*-oxide; zinc and ammonium chloride are specific reagents in the nitro-paraffin series for reduction of the nitro- to the hydroxylamino-group, and it is probable that in this case the intermediate product is 3-hydroxylamino-3-methylbutyl cyanide (XXX). A similar case has been reported

---

[123] G. D. Buckley and T. J. Elliott, *J.*, 1947, 1508.

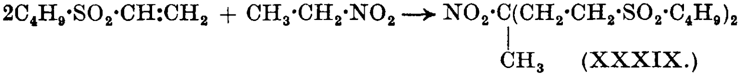
by K. H. Bauer[124] who hydrogenated *o*-nitrostyryl cyanide over a palladium catalyst and obtained 2-aminoquinoline *N*-oxide in 60% yield.

Similar behaviour on reduction was observed with analogues of (XXIX);[83] thus, 3-nitrobutyl cyanide (XXXIV) gave 5-amino-2-methylpyrroline *N*-oxide (XXXV), and 5-amino-2 : 2-pentamethylenepyrroline *N*-oxide (XXXVII) resulted from the reduction of 1-nitro-1-(2-cyanoethyl) *cyclo*hexane (XXXVI).

The behaviour of nitro-paraffins with vinyl cyanide is closely paralleled by that with vinyl sulphones.[125] In the presence of alkaline catalysts, all the α-hydrogen atoms of the nitro-paraffin are replaced, giving nitro-monosulphones from secondary, and nitro-disulphones from primary nitro-paraffins. Nitromethane and methyl vinyl sulphone give tris-(2-methylsulphonylethyl)nitromethane (XXXVIII), and nitroethane with butyl vinyl sulphone in the presence of a small amount of potassium hydroxide gives 3-nitro-1 : 5-di-(*n*-butylsulphonyl)-3-methylpentane (XXXIX); if the quantity of potassium hydroxide is increased to a full molecular proportion, the main product of this reaction is 3-nitrodibutyl sulphone (XL). 2-Nitropropane and divinyl sulphone afford 3 : 3′-dinitro-3 : 3′-dimethyldibutyl sulphone (XLI).

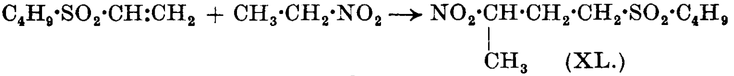
$$3CH_3{\cdot}SO_2{\cdot}CH{:}CH_2 + CH_3{\cdot}NO_2 \longrightarrow NO_2{\cdot}C(CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_3)_3$$

(XXXVIII.)



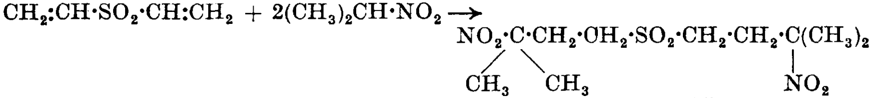
$$2C_4H_9{\cdot}SO_2{\cdot}CH{:}CH_2 + CH_3{\cdot}CH_2{\cdot}NO_2 \longrightarrow NO_2{\cdot}\underset{\displaystyle CH_3}{C}(CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}C_4H_9)_2$$

(XXXIX.)



$$C_4H_9{\cdot}SO_2{\cdot}CH{:}CH_2 + CH_3{\cdot}CH_2{\cdot}NO_2 \longrightarrow NO_2{\cdot}\underset{\displaystyle CH_3}{CH}{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}C_4H_9$$

(XL.)



$$CH_2{:}CH{\cdot}SO_2{\cdot}CH{:}CH_2 + 2(CH_3)_2CH{\cdot}NO_2 \longrightarrow NO_2{\cdot}\underset{\displaystyle CH_3\ \ CH_3}{C}{\cdot}CH_2{\cdot}OH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{\displaystyle NO_2}{C}(CH_3)_2$$

(XLI.)

Reduction of the nitro-sulphones to amino-sulphones proceeds readily and smoothly with Raney nickel and hydrogen at ordinary temperature and pressure.

The Nef hydrolysis[87] (see p. 370) of nitro-paraffins is unusually facile in the nitrosulphone series, and the free nitro-compounds must be regenerated from aqueous solutions of their alkali metal salts with acetic or carbonic acid. Acidification of the potassium salt of (XL) with mineral acid, for example, yields 3-ketodibutyl sulphone.[125]

Reactions with Organometallic Reagents.—The action of organometallic compounds on nitro-paraffins was first examined by C. Moureu[126] who observed that nitro-ethane and two molecules of ethylmagnesium iodide gave *NN*-diethylhydroxylamine. J. Bevad[127] studied the reaction of primary and secondary nitro-paraffins with several alkylzinc and alkyl-

---

[124] *Ber.*, 1938, **71**, 2226.

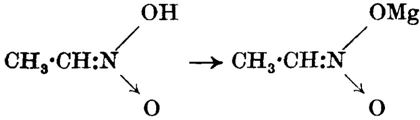
[125] G. D. Buckley, (Mrs.) J. L. Charlish, and J. D. Rose, *J.*, 1947, 1514.

[126] *Compt. rend.*, 1901, **132**, 837.

[127] *Ber.*, 1907, **40**, 3065.

magnesium iodides, and found that nitroethane reacted with ethylmagnesium iodide with evolution of ethane and a little ethylene to give a complex which on hydrolysis gave *NN*-diethylhydroxylamine, together with minor quantities of diethylamine and ethyl-*sec*.-butylhydroxylamine. Ethylzinc iodide reacted similarly, but gave ethyl-*sec*.-butylhydroxylamine as the main product. Similar results were obtained from 1- and 2-nitropropane.

Bevad postulated reaction of the Grignard reagent with the *aci*-nitroparaffin to give the complex (XLII), followed by addition of one or two molecules of Grignard reagent to the ethylenic linkages :

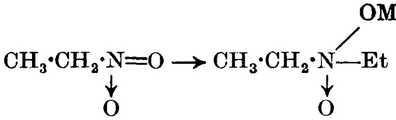


$$\mathrm{CH_3\cdot CH{:}N}\genfrac{}{}{0pt}{}{\diagup\mathrm{OH}}{\searrow\mathrm{O}} \longrightarrow \mathrm{CH_3\cdot CH{:}N}\genfrac{}{}{0pt}{}{\diagup\mathrm{OMgI}}{\searrow\mathrm{O}}$$

(XLII.)

T. Zerewitinoff[128] showed that primary and secondary nitro-paraffins reacted with methylmagnesium iodide to give slightly less than one equivalent of methane, and considered that this arose from reaction of the Grignard reagent with the *aci*-nitro-paraffin. A. B. Wang,[129] from a detailed study of the reaction products of phenylmagnesium bromide and nitromethane, put forward a reaction mechanism differing only in detail from that of Bevad, and also involving a complex of type (XLII). These mechanisms are unlikely since they postulate the preliminary tautomerism of the nitro-paraffin to its *aci*-form, a change normally requiring strongly ionising conditions.

The reaction has been recently re-examined by G. D. Buckley[130] who considers that the first stage is addition of the Grignard reagent to the N=O bond of the nitro-group, giving a complex (XLIII). Complexes of this type



$$\mathrm{CH_3\cdot CH_2\cdot}\underset{\mathrm{O}}{\underset{\downarrow}{\mathrm{N}}}\mathrm{{=}O} \longrightarrow \mathrm{CH_3\cdot CH_2\cdot}\overset{\diagup\mathrm{OMgBr}}{\underset{\mathrm{O}}{\underset{\downarrow}{\mathrm{N}}}}\mathrm{{-}Et}$$

(XLIII.)

have been isolated by interaction of equimoles of the reactants at low temperature. They are white hygroscopic powders which on reduction with zinc and hydrochloric acid give a secondary amine, *e.g.*, diethylamine from (XLIII). The complex may then react with a second molecule of ethylmagnesium bromide with evolution of a molecule of ethane and formation of a second complex which yields *NN*-diethylhydroxylamine on hydrolysis. The mechanism of the second stage of this reaction is still obscure.

Chloro-nitro-paraffins.—The most important of the chlorinated nitroparaffins is chloropicrin (trichloronitromethane, $CCl_3\cdot NO_2$). It is formed when almost any organic compound is treated destructively with " aqua regia ", and was first prepared by R. Preibisch[131] by the action of bleaching powder on nitromethane. Preibisch thought his product was monochloronitromethane, but it has since been shown that he obtained the azeotrope

---

[128] *Ibid.*, 1910, **43**, 3593.

[129] *Trans. Sci. Soc. China*, 1932, **7**, 253.

[130] *J.*, 1947, 1492.

[131] *J. pr. Chem.*, 1873, **8**, 309—327 ; *J.*, 1874, **27**, 462.

of nitromethane and chloropicrin. The literature on chloropicrin up to 1933 has been comprehensively reviewed by K. E. Jackson [132] and little needs to be added. A process for the quantitative conversion of nitromethane into chloropicrin by chlorination in an aqueous suspension of calcium carbonate has been worked out by W. D. Ramage,[133] and similar results are claimed using an alkali or alkaline-earth hypochlorite.[134]

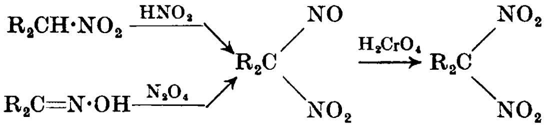
Chloropicrin is an extremely active lung irritant, fatal to man at concentrations of 1 part in 20,000 of air. Although used in 1916 in gas shell, it has been rendered obsolete for military purposes by the efficiency of modern respirators ; it is, however, finding important applications as a soil-sterilising agent.

Other halogenated nitro-paraffins are made very easily by addition of halogen to the *aci*-form or sodium salt of the nitro-compound, and all the α-hydrogen atoms can be substituted in this way. The α-chloro- and α-bromo-nitro-paraffins are more stable than the α-iodo-analogues, some of which decompose on attempted distillation.[135]

Little is known of the chemical reactivity of the α-halogeno-nitro-compounds although the formation of 1 : 2-dinitro-paraffins by interaction of 2-chloro-2-nitropropane with the sodium salts of other nitro-paraffins has been reported.

Chlorination of the nitro-paraffins under the influence of phosphorus pentoxide and intense illumination [2] causes halogenation on carbon atoms other than the α- ; nitro-alcohols can be converted into chloronitro-compounds by treatment with phosphorus pentachloride.

Polynitro-paraffins.—Aliphatic dinitro-compounds in which the two nitro-groups are attached to the same carbon atom can be prepared by chromic acid oxidation of the *pseudo*nitroles, which in turn are formed by the action of nitrous acid on secondary nitro-paraffins [136] or by treatment of oximes with dinitrogen tetroxide : [137]



Certain ketones, notably ethyl ketones, give dinitro-compounds on treatment with concentrated nitric acid. Thus diethyl ketone, methyl ethyl ketone, and ethyl propyl ketone all yield 1 : 1-dinitroethane.[138, 139] The V. Meyer method [3] can also be applied to the synthesis of *gem*-dinitro-compounds, and 1 : 1-dinitropropane has been produced by the interaction of 1-bromo-1-nitropropane and sodium nitrite.[140]

Nitroform (trinitromethane) is formed in small yield by passing acetylene

---

[132] *Chem. Reviews*, 1934, **14**, 251.

[133] U.S.P. 1,996,388.

[134] B. M. Vanderbilt, U.S.P. 2,181,411.

[135] L. W. Seigle and H. B. Hass, *J. Org. Chem.*, 1940, **5**, 100.

[136] V. Meyer, *Annalen*, 1875, **175**, 120.

[137] G. Born, *Ber.*, 1896, **29**, 90.

[138] M. G. Chancel, *Bull. Soc. chim.*, 1879, **31**, 504.

[139] M. Fileti and G. Ponzio, *J. pr. Chem.*, 1897, **55**, 195.

[140] E. ter Meer, *Annalen*, 1876, **181**, 1.

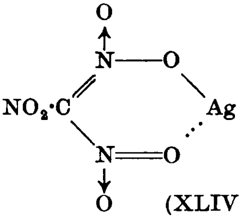
into a mixture of nitric acid and sulphuric acid[141] or from ethylene and fuming nitric acid.[142] Mercuric nitrate is used as a catalyst, and from ethylene some dinitroethyl alcohol is formed. Nitroform, on being heated with fuming sulphuric acid, gives tetranitromethane,[141] from which nitroform can be regenerated by treatment with potassium hydroxide or ethoxide, a reaction which appears from the description of an explosion given by A. K. Macbeth[143] to be extremely dangerous. Safer procedures, however, have been worked out by F. D. Chattaway[144] and by A. K. Macbeth.[145] Tetranitromethane can be prepared in 80% yield by interaction of nitric acid and acetic anhydride for several days at room temperature.[146]

The dinitro-compounds, with the exception of dinitromethane, are relatively stable substances which can be distilled without decomposition. The primary ones (*i.e.*, those containing an α-hydrogen atom) are strong acids, which almost certainly exist in solutions in the *aci*-form. On reduction, one nitro-group is readily lost giving an oxime, which on further reduction yields an amine:[147]

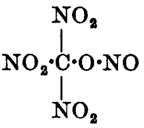
$$R\cdot CH(NO_2)_2 \longrightarrow R\cdot CH{:}N\cdot OH \longrightarrow R\cdot CH_2\cdot NH_2$$

The products of heating dinitromethane with potassium hydroxide are potassium nitrate, ammonia, and a fatty acid. This easy loss of a nitrogen atom has been adduced by G. Ponzio[148] as evidence that dinitromethane is, in fact, a nitro-nitrite; this is unconvincing, since a similar loss of a nitro-group occurs even more readily with tetranitromethane, where the evidence for four nitro-groups is incontrovertible.

Nitroform is a colourless liquid which solidifies at 23°. Its aqueous solutions and salts are yellow, suggesting that in ionising solvents it exists in the *aci*-form. A solid form, m.p. 50°, can be obtained by cautious acidification of the potassium salt with ice-cold concentrated sulphuric acid; this is probably the solid *aci*-form, $(NO_2)_2\cdot C : NO\cdot OH$, the form m.p. 23° being the true trinitro-compound, $CH(NO_2)_3$. The mercury and silver salts are readily soluble in organic solvents, and it is probable that the silver salt exists in the form of the chelate ring compound (XLIV):



(XLIV.)



$$NO_2\cdot\overset{\displaystyle NO_2}{\underset{\displaystyle NO_2}{C}}\cdot O\cdot NO$$

(XLV.)

Tetranitromethane is a liquid boiling unchanged at 126°, and melting at 13°. It forms violently explosive mixtures with aromatic hydrocarbons, and

---

[141] K. J. P. Orton and P. V. McKie, *J.*, 1920, **117**, 283.

[142] P. V. McKie, *J.*, 1927, 962.

[143] *Ber.*, 1913, **46**, 2537.

[144] F. D. Chattaway and J. M. Harrison, *J.*, 1916, **109**, 171.

[145] A. K. Macbeth and W. B. Orr, *J.*, 1932, 538.

[146] F. D. Chattaway, *J.*, 1910, **97**, 2099.

[147] G. Ponzio, *J. pr. Chem.*, 1902, **65**, 197.

[148] *Ibid.*, 1903, **67**, 137.

fatalities from such mixtures have been reported.[149] A marked yellow colour, the origin of which is not known, appears when tetranitromethane is mixed with an unsaturated or aromatic compound, and this colour reaction is often used as a test for unsaturation. The dipole moment of tetranitromethane in carbon tetrachloride is zero; [150] the calculated dipole of a molecule with the structure (XLV), deduced from the individual dipoles of nitromethane and amyl nitrite, would be 0·8 D, a value which is far beyond the limits of error of measurement. The symmetrical tetranitro-structure can therefore be accepted with confidence.

The ease with which tetranitromethane loses a nitro-group makes possible its use as a nitrating agent. Dimethyl-*p*-toluidine and tetranitromethane in alcohol give *m*-nitrodimethyl-*p*-toluidine, but non-basic substances, *e.g.*, phenol, are nitrated only in the presence of a base, such as pyridine. The formation of the 1 : 2-dinitro-paraffins has been referred to earlier in this review (p. 363). These substances show properties which are very different from those of the 1 : 3- and 1 : 4-analogues; in fact the latter behave so " normally " that it is not proposed to consider them at this point, but to deal with them under the reactions of nitro-olefins and nitroparaffins by which they are formed.

The abnormal properties of the 1 : 2-dinitro-paraffins are largely due to the ease with which one nitro-group is lost. In unsymmetrical substances such as 1 : 2-dinitro*iso*butane, the NO_2 group attached to the carbon poorer in hydrogen is readily removed. Thus, by refluxing 1 : 2-dinitro*iso*butane with alcohol, 1-nitro-2-methylprop-1-ene is formed, ethyl nitrite being evolved: [50, 151]

$$(CH_3)_2C(NO_2)\cdot CH_2\cdot NO_2 + C_2H_5\cdot OH \longrightarrow (CH_3)_2C{:}CH\cdot NO_2 + C_2H_5\cdot O\cdot NO + H_2O$$

Alternatively, the nitro-olefin may be formed by stirring the dinitro*iso*butane with a weak alkali such as calcium hydroxide, zinc oxide, or sodium carbonate.[152] This process is, however, limited to the formation of non-polymerisable olefins, and treatment of, *e.g.*, 1 : 2-dinitroethane with weak alkalis gives only a polymer of nitroethylene.[48, 153]

1 : 2-Dinitroethane is a white crystalline solid, m.p. 39—40°, b.p. 88°/1 mm.; it slowly decomposes on storage giving some nitroethylene and nitrous fumes. This decomposition is probably alkali-catalysed, and can be completely inhibited by incorporation of 0·5% of an aromatic sulphonic acid such as naphthalene-1 : 5-disulphonic acid.[48, 154] The structure of 1 : 2-dinitroethane as a true dinitro-compound is rigidly established by reduction to ethylenediamine and by mineral acid hydrolysis to oxalic acid and hydroxylamine: [48, 155]

$$NH_2\cdot CH_2\cdot CH_2\cdot NH_2 \xleftarrow{10H,} NO_2\cdot CH_2\cdot CH_2\cdot NO_2 \longrightarrow (CO_2H)_2 + 2NH_2\cdot OH$$

---

[149] A. Stettbacher, *J. Ind. Hyg.*, (Abstr.), 1943, **25,** 49.

[150] A. Weissberger and R. Sängewald, *Ber.*, 1932, **65,** 701.

[151] A. E. W. Smith, R. H. Stanley, C. W. Scaife, and I.C.I. Ltd., B.P. 583,468.

[152] A. E. W. Smith, C. W. Scaife, and I.C.I. Ltd., B.P. 580,256.

[153] A. E. W. Smith and I.C.I. Ltd., B.P. 572,891.

[154] C. W. Scaife and I.C.I. Ltd., B.P. 578,169.

[155] A. E. W. Smith and I.C.I. Ltd., B.P. 573,630.

Other 1 : 2-dinitro-paraffins are similar to dinitroethane ; 1 : 2-dinitropropane [49] and 1 : 2-dinitrobutane [50] are liquids which on treatment with alkali yield respectively poly-1-nitroprop-1-ene and 1-nitrobut-1-ene. Reduction gives the diamines, and hydrolysis, hydroxylamine.

Nitro-olefins

Preparation.—The formation of the non-polymerisable olefins, and of polymers of nitroethylene and nitropropene, by fission of HNO_2 from the 1 : 2-dinitro-paraffins has already been mentioned. The 2-nitroalkyl nitrates behave in the same way on treatment with alkali, and the nature of the product (monomer or polymer) is determined by the degree of sensitivity of the nitro-olefin to alkali-catalysed polymerisation. Thus 2-nitroethyl nitrate on treatment with weak alkalis gives polynitroethylene [156] and 2-nitro*iso*propyl nitrate yields poly-1-nitropropene.[49] Nitro-*tert.*-butyl nitrate, however, on treatment with sodium hydroxide gives an 83% yield of 1-nitro-2-methylprop-1-ene,[50] as this nitro-olefin is relatively insensitive to alkali.

$$(CH_3)_2C(O{\cdot}NO_2){\cdot}CH_2{\cdot}NO_2 \longrightarrow (CH_3)_2C{:}CH{\cdot}NO_2$$

The direct formation of nitro-olefins by interaction of an aldehyde or ketone with a nitro-paraffin has been mentioned on p. 373. This is limited in its applicability and usefulness to nitro-olefins derived from ketones with nitromethane and those from aromatic aldehydes and primary nitro-paraffins. Examples of these two classes are 1-nitro-2-methylprop-1-ene (nitro*iso*butene) from acetone and nitromethane,[112] and ω-nitrostyrene (2-phenylnitroethylene) from benzaldehyde and nitromethane.

The main standard method of preparation of nitro-olefins is by dehydration, either directly or indirectly, of the 2-nitro-alcohols, which are formed in good yield from aldehydes (and some ketones) and nitro-paraffins.

The direct dehydration is not generally a good method ; powerful dehydrating agents such as phosphoric oxide, thionyl chloride, potassium hydrogen sulphate, or zinc chloride are necessary, and often the nitro-olefin does not survive the conditions necessary for its formation. Yields are poor, and polymeric by-products are common. H. Wieland and E. Sakellarios [157] prepared nitroethylene by dehydration of 2-nitroethyl alcohol with potassium hydrogen sulphate, but this method is suited only to small-scale preparations and fails in larger experiments.[158] A better method of direct dehydration is by heating the nitro-alcohol with phthalican hydride or a substituted phthalic anhydride, the nitro-olefin being removed by distillation as it is formed.[158]

Possibly the best method for all-round applicability and general usefulness is based on that of E. Schmidt and G. Rutz, who reported [159] that the acetates

---

[156] A. E. W. Smith, R. H. Stanley, C. W. Scaife, and I.C.I. Ltd., B.P. 573,785.

[157] *Ber.*, 1919, **52,** 898.

[158] G. D. Buckley and C. W. Scaife, *J.*, 1947, 1471.

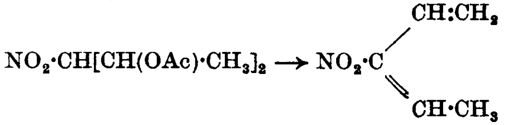
[159] *Ber.*, 1928, **61,** 2142.

of 2-nitro-alcohols, on refluxing with potassium carbonate or hydrogen carbonate in ether solution, lost acetic acid yielding nitro-olefins. This was modified by H. Schwarz and G. Nelles,[160] who obtained excellent yields of α-nitro-olefins by interaction of a 2-nitroalkyl acetate with sodium acetate or potassium carbonate, and distillation of the product.

$$\mathrm{R{\cdot}CH(NO_2){\cdot}CR'R''{\cdot}O{\cdot}CO{\cdot}CH_3 \longrightarrow R{\cdot}C(NO_2){:}CR'R'' + CH_3{\cdot}CO_2H}$$

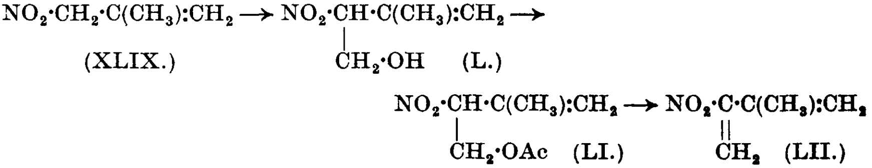
Nitro-dienes. This last method has recently been applied to the synthesis of conjugated nitro-dienes;[161] 3-nitro-2 : 4-diacetoxypentane (XLVI), prepared by acetylation of the glycol (XLVII) from nitromethane and acetaldehyde, on heating with sodium acetate gives a 54% yield of 3-nitropenta-1 : 3-diene (XLVIII):

$$\mathrm{CH_3{\cdot}NO_2 + 2CH_3{\cdot}CHO \longrightarrow \underset{(XLVII.)}{NO_2{\cdot}CH[CH(OH){\cdot}CH_3]_2} \longrightarrow}$$



(XLVI.) (XLVIII.)

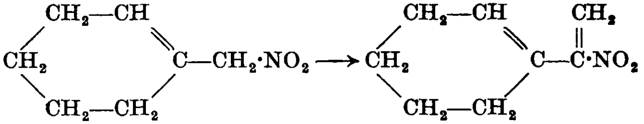
2-Nitro-3-methylbuta-1 : 3-diene (LII) was prepared from 1-nitro-2-methylprop-2-ene (XLIX) by condensation with formaldehyde, acetylation of the nitro-alcohol (L), and distillation of the acetate (LI) with sodium acetate:



$$\mathrm{\underset{(XLIX.)}{NO_2{\cdot}CH_2{\cdot}C(CH_3){:}CH_2} \longrightarrow \underset{\displaystyle\overset{|}{CH_2{\cdot}OH}}{NO_2{\cdot}CH{\cdot}C(CH_3){:}CH_2}\ (L.) \longrightarrow}$$

$$\mathrm{\underset{\displaystyle\overset{|}{CH_2{\cdot}OAc}}{NO_2{\cdot}CH{\cdot}C(CH_3){:}CH_2}\ (LI.) \longrightarrow \underset{\displaystyle\overset{||}{CH_2}}{NO_2{\cdot}C{\cdot}C(CH_3){:}CH_2}\ (LII.)}$$

Starting with 1-nitromethyl*cyclo*hex-1-ene (LIII), a similar series of reactions afforded 1-α-nitrovinyl*cyclo*hexene (LIV), an unstable oil which on keeping gave a crystalline dimeride of unknown structure.



(LIII.) (LIV.)

Properties.—The lower α-nitro-olefins are, when pure, almost colourless or pale yellow liquids, the boiling points of which are of the same order as those of the saturated compounds. Many of the lower members are strongly lachrymatory, and polymerise readily. The polymerisation is catalysed by water and especially by alkalis, and in some cases may be almost explosive

---

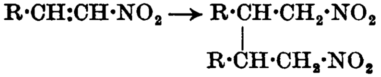
[160] Assgrs. to General Aniline and Film Corporation, U.S.P. 2,257,980.

[161] G. D. Buckley and (Mrs.) J. L. Charlish, *J.*, 1947, 1472.

in its violence. Organic bases catalyse the polymerisation of some substituted nitro-olefins, of which nitrostyrene is a good example.

Little is known of the structure of the polymers, which are usually pale yellow or brown amorphous powders, with low solubility in organic solvents. It has recently been reported [162] that catalytic hydrogenation of the polymer of 2-nitropropene yields a water-soluble polymer containing primary amino-groups.

Reduction.—There is no general method for the reduction of the nitro-olefins to the corresponding nitro-paraffins, although C. de Mauney [163] has reported the quantitative reduction of 1-nitro-oct-1-ene to 1-nitro-octane with hydrogen and platinum. Hydrogenation of nitrostyrene and piperonylidenenitromethane with platinum and hydrogen affords the "hydrodimers", 1 : 4-dinitro-2 : 3-diarylbutanes [164] (LV).



$$R{\cdot}CH{:}CH{\cdot}NO_2 \longrightarrow \begin{array}{l} R{\cdot}CH{\cdot}CH_2{\cdot}NO_2 \\ \quad | \\ R{\cdot}CH{\cdot}CH_2{\cdot}NO_2 \end{array}$$

(LV.)

This was confirmed by E. P. Kohler and N. L. Drake,[165] who found, however, that if the reduction with hydrogen and platinum was conducted in the presence of dry hydrogen chloride, the yield of the dinitrodiphenylbutane (LV; R = Ph) was greatly reduced and the main product was a mixture of the two isomerides of phenylacetaldoxime. Reduction of nitrostyrene with hydrogen and platinum in acetic acid is greatly influenced by the presence of sulphuric acid; [166] 2-phenylethylamine, is obtained in 84% yield by using a mixture of glacial acetic and concentrated sulphuric acid, but in only very low yield if the sulphuric acid is omitted. This phenomenon is attributed by Kindler to the formation of a molecular complex of nitrostyrene and sulphuric acid, and the method has been successfully applied to the reduction of piperonylidenenitromethane to homopiperonylamine.[167]

The reduction of a series of substituted nitrostyrenes to the oximes by hydrogenation in pyridine with a palladium or charcoal catalyst has been reported by B. Reichert and W. Koch.[168] The yields of oximes were high, and substituted phenylethylamines were obtained from them by further reduction with platinum and hydrogen in alcohol containing oxalic acid. Good yields of substituted phenylethylamines have also been obtained from the corresponding nitrostyrenes by electrolytic reduction.[169]

Catalytic hydrogenation of 2-nitro-1-phenylprop-1-ene (LVI) to "benzedrine" (2-phenyl*iso*propylamine) (LVII) is easier than reduction of

---

[162] A. T. Blomquist, W. J. Tapp, and J. R. Johnson, *J. Amer. Chem. Soc.*, 1945, **67**, 1519.

[163] *Bull. Soc. chim.*, 1940, **7**, 133.

[164] A. Sonn and A. Schellenberg, *Ber.*, 1917, **50**, 1513.

[165] *J. Amer. Chem. Soc.*, 1923, **45**, 1281.

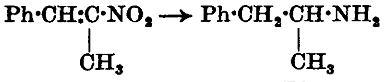
[166] K. Kindler, E. Brandt, and E. Gehlhaar, *Annalen*, 1934, **511**, 209.

[167] O. Schales, *Ber.*, 1935, **68**, 1579.

[168] *Arch. Pharm.*, 1935, **273**, 265.

[169] K. H. Slotta and G. Szyszka, *Ber.*, 1935, **68**, 184.

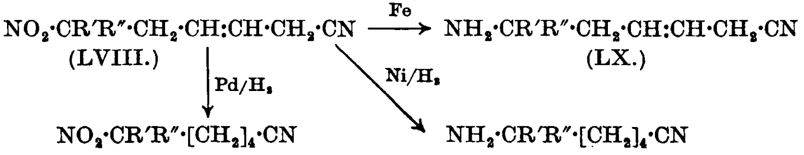
nitrostyrene to phenylethylamine, and has been successfully carried out over Raney nickel.[170]



$$\underset{\text{(LVI.)}}{Ph{\cdot}CH{:}\underset{CH_3}{\underset{|}{C}}{\cdot}NO_2} \longrightarrow \underset{\text{(LVII.)}}{Ph{\cdot}CH_2{\cdot}\underset{CH_3}{\underset{|}{CH}}{\cdot}NH_2}$$

Zinc and acetic acid at 0° are reported [171] to reduce nitro-olefins to the oximes, and iron and hydrochloric acid yield a mixture of ketones and ketoximes, the latter being favoured if the amount of acid present is strictly limited.[172] Since direct reduction of ketoximes or reduction of ketones in presence of ammonia yields the corresponding amines, this represents a two-stage conversion of the nitro-olefin into the amine.

Nitro-olefins in which the nitro-group is not attached to a doubly-bound carbon atom present no difficulties in reduction, either to the saturated nitro-compound or to the saturated amine. Nitropentenyl cyanides (LVIII) can be reduced in high yield with hydrogen and palladium on calcium carbonate to the saturated nitroamyl cyanides (LIX), with iron and acid to the aminopentenyl cyanides (LX), and with nickel and hydrogen to the aminopentyl cyanides (LXI).[173]



$$\begin{tikzcd}
\underset{\text{(LVIII.)}}{NO_2{\cdot}CR'R''{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN} \arrow[r, "Fe"] \arrow[d, "Pd/H_2"] \arrow[dr, "Ni/H_2"] & \underset{\text{(LX.)}}{NH_2{\cdot}CR'R''{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CN} \\
\underset{\text{(LIX.)}}{NO_2{\cdot}CR'R''{\cdot}[CH_2]_4{\cdot}CN} & \underset{\text{(LXI.)}}{NH_2{\cdot}CR'R''{\cdot}[CH_2]_4{\cdot}CN}
\end{tikzcd}$$

Hydration.—α-Nitro-olefins are hydrolysed by water, dilute acids, or alkalis to the original aldehyde or ketone and nitro-paraffin. L. Haitinger [174] showed that 1-nitro-2-methylprop-1-ene (LXII), prepared by nitration of *iso*butene, on hydrolysis with water gave nitromethane and acetone, and B. Priebs [175] demonstrated a similar hydrolysis of ω-nitrostyrene and of 2-nitro-1-phenylpropene to benzaldehyde, and nitromethane and nitroethane respectively.

$$\underset{\text{(LXII.)}}{(CH_3)_2C{:}CH{\cdot}NO_2} \longrightarrow (CH_3)_2CO + CH_3{\cdot}NO_2$$

H. Wieland and E. Sakellarios [157] established that the first step of such hydrolysis is the addition of water to the ethylenic linkage, and by treatment of nitroethylene with cold dilute sulphuric acid they were able to isolate 2-nitroethyl alcohol:

$$CH_2{:}CH{\cdot}NO_2 \longrightarrow CH_2(OH){\cdot}CH_2{\cdot}NO_2$$

Addition of Halogens.—The simple α-nitro-olefins add chlorine and bromine readily in the cold, forming stable 1 : 2-dihalogeno-nitro-paraffins.

---

[170] Unpublished work by J. B. Tindall, quoted in ref. 2, p. 412.

[171] L. Bouveault and A. Wahl, *Compt. rend.*, 1902, **134**, 1145; **135**, 41.

[172] A. G. Susie, Thesis, Purdue University, 1939; quoted in ref. 2, p. 412.

[173] (Mrs.) J. L. Charlish, W. H. Davies, and J. D. Rose (in the press).

[174] *Annalen*, 1878, **193**, 374.

[175] *Ibid.*, 1884, **225**, 319.

L. Haitinger[174] prepared 1 : 2-dibromo-1-nitro-2-methylpropane from nitro*iso*butene, and B. Priebs[175] prepared the dibromide and dichloride from nitrostyrene. Nitro-olefins carrying negative substituents react less readily than the simple ones ; thus, attempts to add bromine to 1-bromo-1-nitro-2-phenylethylene have failed completely.[176] If the addition product of bromine and a nitro-olefin contains an α-hydrogen atom, hydrogen bromide can be removed by mild treatment with alkalis ; thus 1 : 2-dibromo-1-nitro-2-phenylethane with sodium acetate affords 1-bromo-1-nitro-2-phenylethylene :[177]

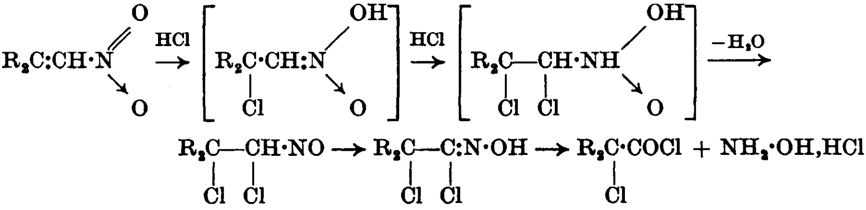
$$\mathrm{Ph{\cdot}CH{:}CH{\cdot}NO_2 \longrightarrow Ph{\cdot}CHBr{\cdot}CHBr{\cdot}NO_2 \longrightarrow Ph{\cdot}CH{:}CBr{\cdot}NO_2}$$

From this product, a further molecule of hydrogen bromide can be abstracted with diethylamine, giving the unstable phenylnitroacetylene.[176]

$$\mathrm{Ph{\cdot}CH{:}CBr{\cdot}NO_2 \longrightarrow Ph{\cdot}C{\vdots}C{\cdot}NO_2}$$

Addition of Hydrogen Chloride.—The early literature on the action of hydrochloric acid on the α-nitro-olefins is not extensive. L. Haitinger[178] reported that 1-nitro-2-methylprop-1-ene (nitro*iso*butene), on treatment with hydrogen chloride at 20° or on being boiled with concentrated hydrochloric acid, gave hydroxylamine hydrochloride, carbon dioxide, ammonia, and an unidentified hydroxy-acid, m.p. 65°, which can now be recognised as impure α-hydroxy*iso*butyric acid. Similar treatment of nitrostyrene enabled B. Priebs[175] to isolate phenylchloroacetic acid.

The subject has recently been reinvestigated by R. L. Heath and J. D. Rose.[179] It is shown that if a nitro-olefin containing an α-hydrogen atom ($\mathrm{R_2C{:}CH{\cdot}NO_2}$) is treated with anhydrous ethereal hydrogen chloride, the products are hydroxylamine hydrochloride and an α-chloro- or α-hydroxy-acid, $\mathrm{R_2C(OH){\cdot}CO_2H}$ or $\mathrm{R_2CCl{\cdot}CO_2H}$. If a nitro-olefin with no α-hydrogen atom ($\mathrm{R_2C{:}CR{\cdot}NO_2}$) is so treated, the product is a dichloronitroso-compound, $\mathrm{RR'CCl{\cdot}CRCl{\cdot}NO}$. The following mechanism is suggested :



$$\mathrm{R_2C{:}CH{\cdot}N}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O} \xrightarrow{\mathrm{HCl}} \left[\mathrm{R_2C{\cdot}CH{:}N}\genfrac{}{}{0pt}{}{\nearrow OH}{\searrow O}\right]_{\mathrm{Cl\ (on\ C)}} \xrightarrow{\mathrm{HCl}} \left[\mathrm{R_2\underset{Cl}{C}{-}\underset{Cl}{CH}{\cdot}NH}\genfrac{}{}{0pt}{}{\nearrow OH}{\searrow O}\right] \xrightarrow{-\mathrm{H_2O}}$$

$$\underset{\text{(LXIII.)}}{\mathrm{R_2\underset{Cl}{C}{-}\underset{Cl}{CH}{\cdot}NO}} \longrightarrow \underset{\text{(LXIV.)}}{\mathrm{R_2\underset{Cl}{C}{-}\underset{Cl}{C}{:}N{\cdot}OH}} \longrightarrow \mathrm{R_2\underset{Cl}{C}{\cdot}COCl + NH_2{\cdot}OH,HCl}$$

(LXIII.) (LXIV.)

The initial step is postulated as 1 : 4-addition ; evidence for this is as follows. If the initial addition were 1 : 2-, the product from, *e.g.*, 1-nitropropene

---

[176] J. Loevenich and H. Gerber, *Ber.*, 1930, **63**, 1707.

[177] J. Thiele and S. Haeckel, *Annalen*, 1902, **325**, 7.

[178] L. Haitinger, *Monatsh.*, 1881, **2**, 287 ; *Wien. Akad. Ber.*, 1878, **77**, 428 ; *A.*, 1879, 700.

[179] *J.*, 1947, 1485.

would be 2-chloro-1-nitropropane, $CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}NO_2$. This product, synthesised unambiguously from the corresponding nitro-alcohol by treatment with phosphorus pentachloride, is completely inert to hydrogen chloride under conditions which convert 1-nitropropene itself into α-chloropropionic acid and hydroxylamine hydrochloride.

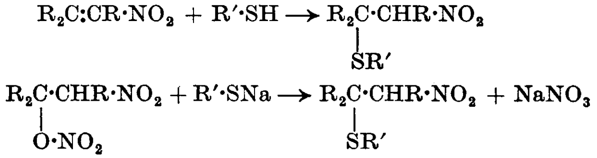
In this mechanism, an important step is the rearrangement of the dichloro-nitroso-compound (LXIII) to the dichloro-oxime (LXIV). If the reaction is carried out on a nitro-olefin, $R_2C{:}CR{\cdot}NO_2$, containing no α-hydrogen atom, the dichloro-nitroso-compound, $R_2CCl{\cdot}CRCl{\cdot}NO$, cannot rearrange and is, therefore, the end product.

Addition of Alcohols and Thiols.—There are many examples of the addition of alcohols to nitro-olefins; thus, ω-nitrostyrene,[180] ω-bromo-ω-nitrostyrene,[177] 1-bromo-1-nitrobut-1-ene, and 1-bromo-1-nitropent-1-ene [181] all add alcohols in the presence of basic catalysts to give 2-nitroalkyl ethers :

$$R_2C{:}CR{\cdot}NO_2 \xrightarrow{R'OH} R_2C(OR'){\cdot}CHR{\cdot}NO_2$$

The formation of 2-nitroalkyl ethers from 1-nitrobut-1-ene and some higher nitro-olefins has also been recently described by C. T. Bahner.[182] A. Lambert *et al.*[183] have described the formation of 2-nitroalkyl ethers from nitro-olefins and alcohols, usually in the presence of basic catalysts. In the case of nitroethylene, a base causes polymerisation, but the addition of alcohol proceeds even in the presence of phosphoric acid, present as a stabiliser for the nitroethylene. The same products are formed from the 1 : 2-dinitro-paraffins on heating them with alcohol, one nitro-group being eliminated as alkyl nitrite, and from 2-nitroalkyl nitrates and sodium alkoxides. The nitro-ethers are smoothly reduced by hydrogen over Raney nickel to the corresponding alkyl 2-aminoalkyl ethers.

A logical extension of the synthesis of 2-nitroalkyl ethers to the preparation of alkyl 2-nitroalkyl sulphides by interaction of a thiol and a nitro-olefin is described by R. L. Heath and A. Lambert.[184] The reaction is a general one, and in many cases the 2-nitro-alcohols or their esters, *e.g.*, nitrates, can be used as convenient laboratory substitutes for the nitro-olefins.



$$R_2C{:}CR{\cdot}NO_2 + R'{\cdot}SH \rightarrow \underset{\displaystyle SR'}{R_2C}{\cdot}CHR{\cdot}NO_2$$

$$\underset{\displaystyle O{\cdot}NO_2}{R_2C}{\cdot}CHR{\cdot}NO_2 + R'{\cdot}SNa \rightarrow \underset{\displaystyle SR'}{R_2C}{\cdot}CHR{\cdot}NO_2 + NaNO_3$$

The thiols add to nitro-olefins with greater ease than do alcohols, and the reaction, carried out in an alcoholic solvent, yields almost exclusively the sulphide.

[180] K. W. Rosenmund, *Ber.*, 1913, **46**, 1034 ; J. Meisenheimer and F. Heim, *ibid.*, 1905, **38**, 467.

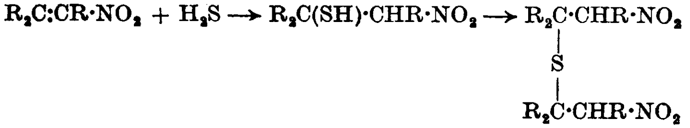
[181] J. Loevenich, J. Koch, and U. Pucknat, *ibid.*, 1930, **63**, 636.

[182] U.S.P. 2,391,815.

[183] A. Lambert, C. W. Scaife, and A. E. W. Smith, *J.*, 1947, 1474.

[184] *J.*, 1947, 1477.

Hydrogen sulphide reacts with nitro-olefins in alcoholic solution, giving a mixture of 2-nitroalkylthiol and di-(2-nitroalkyl) sulphide,[144] thus :



$$R_2C{:}CR{\cdot}NO_2 + H_2S \longrightarrow R_2C(SH){\cdot}CHR{\cdot}NO_2 \longrightarrow \begin{array}{l} R_2C{\cdot}CHR{\cdot}NO_2 \\ \quad | \\ \quad S \\ \quad | \\ R_2C{\cdot}CHR{\cdot}NO_2 \end{array}$$

The nitroalkyl sulphides can be oxidised with hydrogen peroxide to nitroalkyl sulphones, or reduced catalytically to aminoalkyl sulphides ; the latter on oxidation give aminoalkyl sulphones, also formed by catalytic reduction of the nitroalkyl sulphones.

$$\begin{tikzcd}
R'{\cdot}S{\cdot}CR_2{\cdot}CHR{\cdot}NO_2 \arrow[r, "H_2O_2"] \arrow[d, "H_2"] & R'{\cdot}SO_2{\cdot}CR_2{\cdot}CHR{\cdot}NO_2 \arrow[d, "H_2"] \\
R'{\cdot}S{\cdot}CR_2{\cdot}CHR{\cdot}NH_2 \arrow[r, "H_2O_2"] & R'{\cdot}SO_2{\cdot}CR_2{\cdot}CHR{\cdot}NH_2
\end{tikzcd}$$

Addition of Sodium Hydrogen Sulphite.—Although the addition of sodium hydrogen sulphite to such ethylenic systems as acrylic acid, styrene, and allyl alcohol has often been reported, it is only recently that such addition to nitro-olefins has been described. A simple synthesis of 2-nitroalkanesulphonic acids, and, by reduction, of 2-aminoalkanesulphonic acids has been achieved by R. L. Heath and H. A. Piggott.[185] The reaction of nitro-olefins with sodium hydrogen sulphite is general, and proceeds in aqueous or aqueous–alcoholic solution without catalyst, to give good yields of sodium 2-nitroalkanesulphonates. As an example, 1-nitro-2-methylprop-1-ene (LXV) affords sodium 1-nitro-2-methylpropane-2-sulphonate (LXVI), and the reaction is successful with nitroethylene, the isomeric nitropropenes, nitrostyrene, and furylnitroethylene :

$$\underset{\text{(LXV.)}}{(CH_3)_2C{:}CH{\cdot}NO_2} \longrightarrow \underset{\text{(LXVI.)}}{(CH_3)_2C(SO_3Na){\cdot}CH_2{\cdot}NO_2}$$

Sodium sulphite reacts similarly, giving the disodium salt (*i.e.*, the di-salt of the *aci*-form of the nitro-sulphonic acid), whilst sulphurous acid affords the free nitro-sulphonic acid.

$$NO_2{\cdot}CH{:}CH{\cdot}CH_3 \xrightarrow{Na_2SO_3} NaO{\cdot}NO{:}CH{\cdot}CH(CH_3){\cdot}SO_3Na$$

$$NO_2{\cdot}CH{:}CH{\cdot}CH_3 \xrightarrow{H_2SO_3} NO_2{\cdot}CH_2{\cdot}CH(CH_3){\cdot}SO_3H$$

Catalytic reduction of the nitrosulphonic acids in aqueous solution gives aminosulphonic acids. For example, taurine (2-aminoethanesulphonic acid) is formed by reduction of the sodium 2-nitroethanesulphonate resulting from nitroethylene and sodium hydrogen sulphite.

Addition of Amines and Ammonia.—The addition of amines to nitro-olefins has been described in the older literature. H. Wieland and E. Sakellarios[157] added aniline to nitroethylene and obtained 2-nitroethylaniline. D. E. Worrall[186] attempted to add some forty bases, including

---

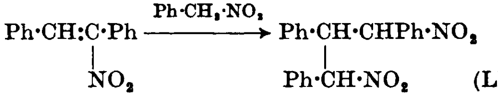
[185] *J.*, 1947, 1481.

[186] *J. Amer. Chem. Soc.*, 1927, **49**, 1598.

aliphatic and aromatic amines and hydrazines, to ω-nitrostyrene, but found that only thirteen gave isolable adducts. Aniline and *p*-toluidine were the only common aromatic bases, and piperidine the only secondary amine, which gave characterised adducts. A recent investigation [187] of the addition of ammonia and primary and secondary aliphatic and aromatic amines to nitro-olefins has shown that in general the reaction proceeds easily, but the yields are variable owing to the inherent instability of the 2-nitroalkylamines. The products from aromatic amines are weaker bases than those from ammonia or aliphatic amines, and are therefore more stable. Hydrogenation of the nitroamines over Raney nickel afforded derivatives of ethylenediamine. Ammonia gave only mononitroalkylamines, but di-2-nitroethylaniline was prepared in two stages from nitroethylene and aniline; it is a very unstable weak base, the hydrochloride of which on being heated with water loses a molecule of nitroethylene and regenerates 2-nitroethylaniline.

$$CH_2{:}CH{\cdot}NO_2 + Ph{\cdot}NH_2 \longrightarrow Ph{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2 \xrightarrow{CH_2:CH\cdot NO_2} Ph{\cdot}N(CH_2{\cdot}CH_2{\cdot}NO_2)_2$$

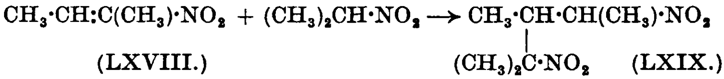
Addition of Nitro-paraffins.—Products derived from the addition of nitro-paraffins with nitro-olefins have occasionally been reported in the literature. D. E. Worrall [188] recorded the addition of phenylnitromethane to α-nitrostilbene giving 1 : 3-dinitro-1 : 2 : 3-triphenylpropane (LXVII).



$$Ph{\cdot}CH{:}\underset{NO_2}{C}{\cdot}Ph \xrightarrow{Ph\cdot CH_2\cdot NO_2} Ph{\cdot}\underset{Ph\cdot CH\cdot NO_2}{CH}{\cdot}CHPh{\cdot}NO_2$$

(LXVII.)

H. B. Hass [189] has recently shown that one of the products from acetone and nitromethane is 1 : 3-dinitro-2 : 2-dimethylpropane, and demonstrated that its formation was due to the addition of the nitromethane to 1-nitro-2-methylprop-1-ene, formed in an earlier stage of the reaction sequence outlined on p. 375. The results of a systematic investigation [190] have shown that the addition of nitro-paraffins to nitro-olefins is a general reaction in which yields are extremely variable and dependent on the nature of the nitro-olefin, nitro-paraffin, and conditions employed. Thus, 2-nitrobut-2-ene (LXVIII) and 2-nitropropane give 47% of 2 : 4-dinitro-2 : 3-dimethylpentane (LXIX) in the presence of sodium ethoxide, but yields are usually much lower.



$$\underset{(LXVIII.)}{CH_3{\cdot}CH{:}C(CH_3){\cdot}NO_2} + (CH_3)_2CH{\cdot}NO_2 \longrightarrow CH_3{\cdot}\underset{(CH_3)_2C\cdot NO_2}{CH}{\cdot}CH(CH_3){\cdot}NO_2 \quad (LXIX.)$$

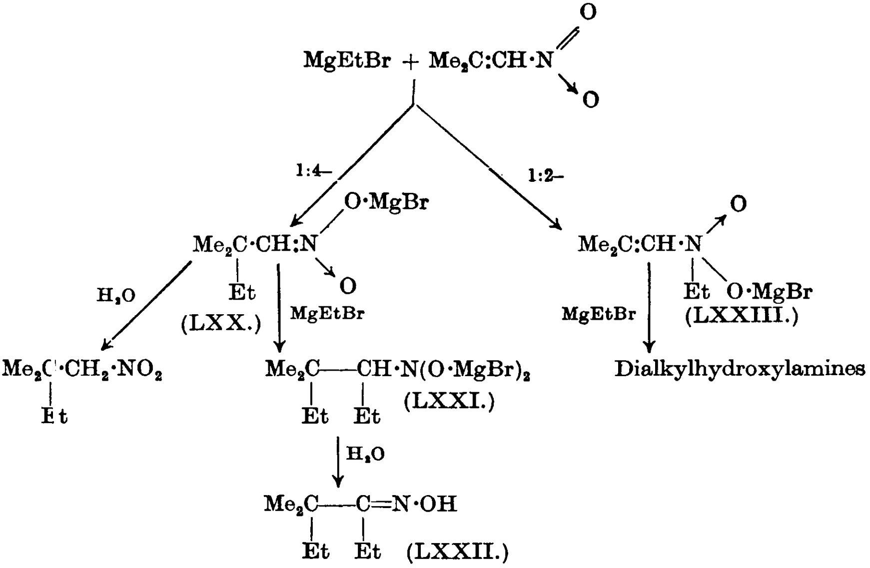
The properties of the 1 : 1- and 1 : 2-dinitro-paraffins have been shown earlier in this review to be " abnormal ". The 1 : 3-dinitro-paraffins, however, have all the normal properties of nitro-paraffins. They dissolve in alkalis, and give di-α-bromo-derivatives which are useful for characterisation

---

[187] R. L. Heath and J. D. Rose, *J.*, 1947, 1486.
[188] *J. Amer. Chem. Soc.*, 1935, **57**, 2299.
[189] *Ind. Eng. Chem.*, 1943, **35**, 1151.
[190] A. Lambert and H. A. Piggott, *J.*, 1947, 1489.

purposes. Reduction, preferably with hydrogen over Raney nickel, affords 1 : 3 diamines.

Addition of Grignard Reagents.—The formation of nitro-paraffin derivatives in high yield by the action of Grignard reagents on di- and tri-phenylnitroethylenes has been described by E. P. Kohler and J. F. Stone.[191] Under similar conditions, the lower nitro-olefins give only poor yields of nitro-paraffins,[192] but, by carrying out the reaction below 10° and avoiding an excess of organometallic halide, secondary reactions are almost completely suppressed and yields are much improved.[193] If an excess of Grignard reagent is used, nitro-paraffins, oximes, and reducing bases are formed, the last being probably hydroxylamines. The initial steps consist of addition, chiefly 1 : 4-, of the Grignard reagent to the conjugated system to produce a complex (LXX) which on hydrolysis with water gives the nitro-paraffin; but since (LXX) contains the system $C = N \rightarrow O$, addition of a second molecule of Grignard reagent occurs to give the complex (LXXI), which on hydrolysis yields the oxime (LXXII). The formation of reducing bases in the reaction can be explained only by the assumption that part of the original nitro-olefin undergoes 1 : 2-addition of Grignard reagent to give a complex (LXXIII) which on further reaction with the Grignard reagent gives *NN*-dialkylhydroxylamines, a reaction quite analogous to the reaction of Grignard reagents on nitro-paraffins (see p. 378). The scheme below outlines the suggested course of the reaction of ethylmagnesium bromide with 1-nitro-2-methylpropene.



By restricting the reaction as outlined above to low temperatures and equimoles of the reactants, a series of new nitro-paraffins has been

---

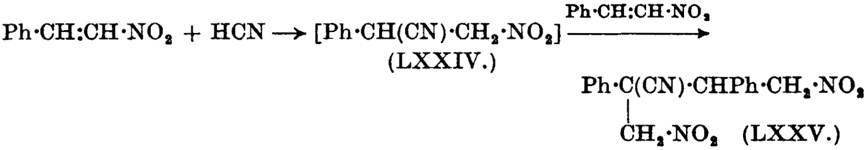
[191] *J. Amer. Chem. Soc.*, 1930, **52**, 761.

[192] G. D. Buckley, *J.*, 1947, 1494.

[193] *Idem*, *J.*, 1947, 1497.

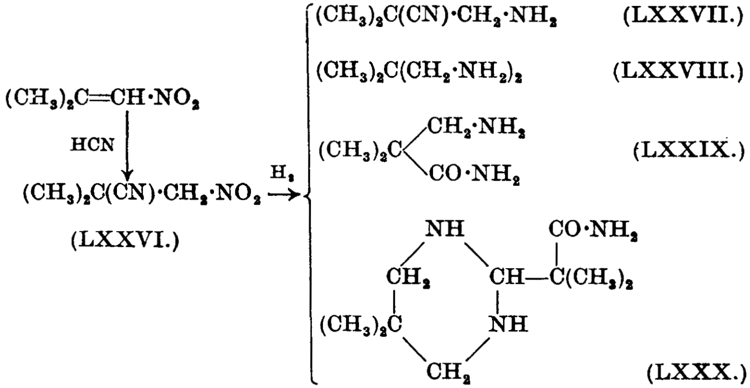
synthesised. These, on reduction with hydrogen over Raney nickel, afford the corresponding amines in high yield, and the chief value of this synthesis is in the preparation of a wide range of hitherto inaccessible primary amines.

Addition of Hydrogen Cyanide.—The addition of potassium cyanide to a nitro-olefin was described by M. Hollemann,[194] who showed that ω-nitrostyrene and potassium cyanide gave two stereoisomerides of 1 : 4-dinitro-2-cyano-2 : 3-diphenylbutane :



$$\mathrm{Ph{\cdot}CH{:}CH{\cdot}NO_2 + HCN \longrightarrow \underset{(LXXIV.)}{[Ph{\cdot}CH(CN){\cdot}CH_2{\cdot}NO_2]} \xrightarrow{Ph\cdot CH:CH\cdot NO_2} Ph{\cdot}\underset{\displaystyle CH_2{\cdot}NO_2}{\underset{|}{C}}(CN){\cdot}CHPh{\cdot}CH_2{\cdot}NO_2 \quad (LXXV.)}$$

Although the intermediate nitro-cyanide (LXXIV) was not isolated by Hollemann, it is clear that this must be formed as a first step in the reaction. A recent investigation has shown that such addition of hydrogen cyanide to nitro-olefins is a general reaction,[195] and is best carried out in the presence of a few moles per cent. of potassium cyanide as catalyst : hydrogen cyanide alone will not react. By this method, a series of 2-nitroalkyl cyanides has been synthesised from nitropropenes and nitrobutenes. A very interesting feature of these substances is their behaviour on reduction. Taking nitro-*tert.*-butyl cyanide (LXXVI) as an example, catalytic reduction with nickel and hydrogen at ordinary temperature and pressure afforded a mixture of four products : (*a*) amino-*tert.*-butyl cyanide (LXXVII) (1·5%), (*b*) 1 : 3-diamino-2 : 2-dimethylpropane (LXXVIII) (1·5%), (*c*) β-amino-αα-dimethylpropionamide (LXXIX) (50%), and (*d*) 5 : 5-dimethyl-2-(1-carbamyl*iso*propyl)hexahydropyrimidine (LXXX) (20%) :



The hexahydropyrimidine (LXXX) was recognised by the fact that with reagents for amines it gave the picrate, hydrochloride, and benzoyl derivative of the dimethylpropylenediamine (LXXVIII), whilst with 2 : 4-dinitrophenylhydrazine hydrochloride it gave the derivative of β-carbamyl*iso*-

---

[194] *Rec. Trav. chim.*, 1904, **23**, 283.

[195] G. D. Buckley, R. L. Heath, and J. D. Rose, *J.*, 1947, 1500.

butaldehyde. The mode of formation of this hexahydropyrimidine and of the amide (LXXIX) is not clear. The latter cannot be formed by a straightforward hydration of the cyano-group by the water formed from reduction of the nitro-group, since an authentic specimen of the amino-cyanide (LXXVII), on treatment with Raney nickel catalyst and two moles of water in methyl alcohol (*i.e.*, the conditions of the hydrogenation, without the hydrogen), was completely unchanged. It is probable that an *iso*-oxazole is formed as an intermediate product and is split by hydrogen to the amino-amide.

Applications of the Aliphatic Nitro-compounds and their Derivatives

The four commonest nitro-paraffins—nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane—have been commercially available in large quantities for the last six years in America, and have recently become available in pilot-plant quantities in this country. Six years is a short time in chemical development, and it is much too early to forecast the extent of their ultimate utilisation. Certain uses have, however, already been described.

Direct Uses of the Nitro-paraffins.—The nitro-paraffins are good solvents for a wide range of organic substances. According to C. L. Gabriel [196] of the Commercial Solvents Corporation, nitro-paraffins have considerable solvent power for organic esters of cellulose, including the difficultly soluble cellulose triacetate and cellulose acetobutyrate—the solvent power of 1- and 2-nitropropanes for the latter being about the same as that of butyl acetate for nitrocellulose. The nitro-paraffins are among the most powerful solvents known for vinyl chloride–vinyl acetate co-polymers (" vinylite " resins), and the solutions have a much lower viscosity than solutions in the more commonly used higher ketones, such as methyl *iso*butyl ketone. Solutions of nitrocellulose in the nitro-paraffins have, in the presence of alcohols, a high tolerance for diluents.

Other solvent uses are for oils, fats, and waxes, and for synthetic rubbers such as " Buna N ", " Chemigum ", and " Hycar OR ". Advantages in their use are low toxicity, mild and non-persistent odour, a medium rate of evaporation (1-nitropropane has the same evaporation rate as *n*-butyl acetate , and comparatively low inflammability. Shell Development Co.[197] have patented their use as selective solvents in the refining of petroleum.

The use of nitro-paraffins in preparing accelerated rubber cements has been described by A. W. Campbell [198] and patented by the Commercial Solvents Corporation.[199]

The use of the nitrates of the nitro-alcohols as explosives will be referred to later. Hercules Powder Co. have patented as explosives mixtures containing simple nitro-paraffins.[200]

Nitro-alcohols.—A great deal of work has been done on the use of the

---

[196] *Chem. Industries*, 1939, **45**, 664.

[197] U.S.P. 2,023,375 ; 2,019,772.

[198] *Ind. Eng. Chem.*, 1941, **33**, 809 ; 1942, **34**, 1106.

[199] U.S.P. 2,251,220 ; 2,297,871.

[200] U.S.P. 2,325,064 ; 2,325,065.

nitrates of the nitro-alcohols, nitro-glycols, and nitro-triols as explosives. Their close structural relationship to glyceryl trinitrate needs no further emphasis. However, the trinitrate of tris(hydroxymethyl)nitromethane is now considered of no value,[201] in spite of the great attention it has received : it does not meet the stability requirements of a modern explosive. Nitro-*iso*butyl nitrate has been described as a sensitiser for safety explosives containing ammonium nitrate,[202] and the dinitrate of 2-nitro-2-methylpropane-1 : 3-diol was patented as an explosive as long ago as 1928.[203]

The esters—particularly the acetates, propionates, butyrates, and lactates—of the nitro-alcohols have been mentioned as plasticisers,[204] and special mention has been made of methyl 2-nitro*iso*butylphthalate as a plasticiser for cellulose acetate.[205]

Other direct applications of the nitro-alcohols which have been described are as heat sensitisers for rubber latex [198] and as finishing agents for textiles.[206]

Amino-alcohols.—The amino-alcohols, amino-glycols, and amino-triols are made from the nitro-alcohols by simple catalytic reduction ; of them, 2-aminobutanol, 2-amino-2-methylpropanol, 2-amino-2-methylpropane-1 : 3-diol, 2-amino-2-ethylpropane-1 : 3-diol, and tris(hydroxymethyl)methylamine are commercially available in America.

The main applications of the amino-alcohols are as emulsifying agents, and considerable use was made in America during the war of 2-amino-2-methylpropanol in the preparation of emulsion camouflage paints.[205] Amino-alcohol soaps (laurates, oleates, stearates) are soluble in water and in a number of organic solvents, such as alcohols, benzene, glycol, and ketones. Such soaps, which are powerful emulsifying agents,[207, 208] may act as stabilisers for either oil-in-water or water-in-oil emulsions,[201] and have been used in the compounding of floor polishes, cosmetics, automobile cleansers, and leather dressings.

Chloronitro-paraffins.—The pesticidal activity of chloropicrin is well known, and, since the commercial production of nitro-paraffins began, chloropicrin in the United States has been made from nitromethane. Any $\alpha\alpha$-dichloronitro-paraffin has insecticidal activity,[209] and an insecticide based on 1 : 1-dichloro-1-nitroethane is marketed under the trade name " Ethide ". It is non-injurious to man, most fabrics, and many foodstuffs, but is as effective as chloropicrin against most insects.[210, 211]

The chloronitro-paraffins are good solvents for a number of synthetic

[201] H. B. Hass, *Ind. Eng. Chem.*, 1943, **35**, 1146.

[202] Hercules Powder Co., U.S.P. 2,330,112.

[203] F. H. Bergeim, U.S.P. 1,691,955.

[204] Commercial Solvents Corporation, U.S.P. 2,233,607 ; 2,177,757 ; B. M. Vanderbilt, assr. to Purdue Research Foundation, U.S.P. 2,233,656.

[205] W. E. Scheer, *Chem. Industries*, 1943, **52**, 473.

[206] H. Robinette, *Amer. Dyestuffs Reporter*, 1942, **31**, 575.

[207] B. M. Vanderbilt, assr. to Commercial Solvents Corporation, U.S.P. 2,281,177.

[208] *Idem*, assr. to Purdue Research Foundation, U.S.P. 2,247,106.

[209] H. B. Hass, assr. to Commercial Solvents Corporation, U.S.P. 2,281,239.

[210] W. C. O'Kane and H. W. Smith, *J. Econ. Entomology*, 1941, **34**, 439.

[211] C. E. Woodworth, *ibid.*, 1943, **36**, 335.

plastics. A list of such substances soluble in 1-chloro-1-nitropropane is given by A. W. Campbell and J. W. Burns,[212] but there is no evidence of commercial application. A patent assigned to Universal Oil Products [213] describes the use of certain chloronitro-paraffins as solvents for the alkylation of aromatic hydrocarbons by olefins catalysed by aluminium chloride. The chloronitro-paraffin dissolves both the aluminium chloride and the aromatic hydrocarbon. 1-Chloro-1-nitropropane has also been described as a stabiliser for rubber cements.[199]

Hydroxylamine.—Most of the hydroxylamine sold in the United States is prepared by acid hydrolysis of primary nitro-paraffins, chiefly 1-nitropropane, and hydroxylamine can logically be considered as a nitro-paraffin derivative. Possible outlets for it are discussed by C. L. Gabriel.[214] The propionic acid simultaneously produced in the hydrolysis of 1-nitropropane has probably found a ready outlet as calcium propionate, an anti-mould agent, or been used in the production of solvents.

J. D. R.

---

[212] *India Rubber World,* 1942, **107**, 169.

[213] U.S.P. 2,302,721.

[214] *Ind. Eng. Chem.*, 1940, **32**, 887.