14. Addition of Dinitrogen Tetroxide to Olefins. Part IV. The Butylenes.

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This paper deals mainly with the addition of dinitrogen tetroxide to *iso*butylene, and the application of the same procedure to the *n*-butylenes is described.

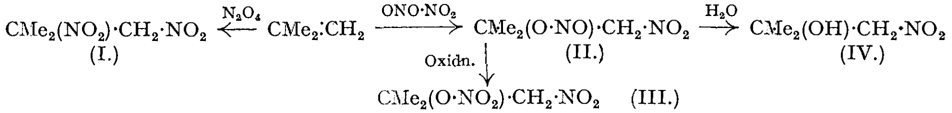
Normal addition to give dinitrobutanes and nitrobutyl nitrites requires an ether or ester solvent. The nitro-nitrites are partly oxidised to nitro-nitrates in the reaction, and the remainder are converted into nitrobutanols by water treatment at an early stage for safe and efficient separation of products. Total yields of pure products from *iso*butylene average 70—80%, made up of 35—42% of 1 : 2-*dinitro*isobutane, 25—30% of *nitro*-tert.-*butanol*, 2% of *nitro*-tert.-*butyl nitrate*, and 5—9% 1 : 3-*dinitro-2-methylpropan-2-ol*, the last three compounds being derived from nitro-*tert*.-butyl nitrite first formed. Addition of oxygen with the *iso*butylene sharply increases the proportion of the nitrate at the expense of the dinitro-paraffin. Only two modes of addition of dinitrogen tetroxide in ether type solvents were found: (i) as two nitro-groups, and (ii) as one nitro- and one nitrite group, the latter always being attached to the carbon atom with fewer hydrogen atoms. Addition of dinitrogen trioxide follows a similar rule in forming nitronitroso*iso*butane, the nitroso-group becoming attached to the tertiary carbon atom of *iso*butylene.

Part I (Levy and Scaife, *J.*, 1946, **1093**) gave a general introduction to the series of papers on addition of dinitrogen tetroxide to olefins, while Parts II (Levy, Scaife, and Wilder-Smith, *J.*, 1946, 1096) and III (Levy and Scaife, *J.*, 1946, 1100) referred to the addition to ethylene and propylene respectively. The present paper extends the investigation to a study of the addition of dinitrogen tetroxide to the butylenes.

iso*Butylene*.

Previous work on the reaction between *iso*butylene and nitrogen oxides, including the tetroxide, is not extensive and has two outstanding deficiencies: (i) isolation and direct identification of products was incomplete; (ii) the rôle of reaction medium was insufficiently studied. The instability of the product, particularly when prepared from or in the presence of dinitrogen trioxide and the oxidising character of the tetroxide itself, present further difficulties. Sidorenko (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 955) treated *iso*butylene in ether with nitrous fumes (from arsenious oxide and nitric acid) obtaining *iso*butylene " nitrosite ", m. p. 80°, and a blue liquid. The solid gave a blue melt and could be reduced to the diamine. He also found that nitrogen tetroxide and *iso*butylene in ether gave a small amount of the bisnitrosate [dimeric $CMe_2(O{\cdot}NO_2){\cdot}CH_2{\cdot}NO$], m. p. 104°, and, as main product, a blue liquid which could be reduced in small yield to *iso*butylenediamine, but Strack and Fanselow (*Z. physiol. Chem.*, 1929, **180**, 153) failed to confirm this reduction. Ipatieff and Solonina (*J. Russ. Phys. Chem. Soc.*, 1901, **33**, 496) prepared the oxime $CMe_2(O{\cdot}NO_2){\cdot}CH{:}NOH$, m. p. 114—115°, from the reaction between *iso*butylene and amyl nitrite in acetic acid with the addition of nitric acid; the compound reacted with potassium cyanide to give 2-cyano*iso*butaldoxime, $CMe_2(CN){\cdot}CH{:}NOH$. More recently Michael and Carlson (*J. Org. Chem.*, 1940, **5**, 1) examined the reaction with nitrous fumes in both the gas and the liquid phase. The gas-phase reaction was accompanied by pronounced oxidation, and reaction in liquid dinitrogen tetroxide or light petroleum gave bis(*iso*butylene nitrosate) in varying small yields not exceeding 13%. The liquid product from reaction in ether was apparently more stable to distillation at low pressure but, other than a small amount of bis(nitronitroso*iso*butane), no pure products were isolated and therefore reduction was used as a means of identification. Both the crude mixture and the distilled portion gave *iso*butylamine assumed to have arisen from 1-nitro*iso*butylene, and di*iso*butylamine, supposed to have been formed together with *iso*butylamine from 1 : 2-dinitro*iso*butane. As in the work of Strack and Fanselow (*loc. cit.*) no *iso*butylenediamine was obtained, though it has now been obtained from 1 : 2-dinitro*iso*butane. Part of the distilled oil gave on reduction practically equimolar amounts of amino-*tert*.-butanol and ammonia, thought to have been formed from nitro-*tert*.-butyl nitrite. Michael and Carlson deduced from this that 1-nitro*iso*butylene constituted 5—12%, nitro-*tert*.-butyl nitrite 16—23%, and 1 : 2-dinitro*iso*butane at least 12% of the addition product.

The present investigation has shown that the course of reaction as in the case of propylene (Part III, *loc. cit.*) is profoundly affected by the solvent in that normal addition requires an ether or ester medium. Under appropriate conditions, oxidation reactions and nitronitroso*iso*butane formation can be suppressed. The primary products are 1 : 2-*dinitro*iso*butane* (I) and nitro-*tert.*-butyl nitrite (II), and part of the latter is oxidised to nitro-*tert.*-butyl nitrate (III) :



$$\begin{tikzcd} \underset{(I.)}{\mathrm{CMe_2(NO_2)\cdot CH_2\cdot NO_2}} & \mathrm{CMe_2{:}CH_2} \arrow[l, "N_2O_4"'] \arrow[r, "ONO\cdot NO_2"] & \underset{(II.)}{\mathrm{CMe_2(O\cdot NO)\cdot CH_2\cdot NO_2}} \arrow[r, "H_2O"] \arrow[d, "Oxidn."'] & \underset{(IV.)}{\mathrm{CMe_2(OH)\cdot CH_2\cdot NO_2}} \\ & & \mathrm{CMe_2(O\cdot NO_2)\cdot CH_2\cdot NO_2}\ \text{(III.)} & \end{tikzcd}$$

The nitrite (II) is less stable than its lower homologues (*e.g.*, nitroethyl and nitropropyl nitrites can be prepared from the nitro-alcohol and nitrous acid, but nitro-*tert.*-butyl nitrite has not been formed in this manner), and it decomposes during distillation, forming some 1-nitro*iso*butylene. Isolation of pure substances by distillation of the crude product is very difficult, as well as hazardous. The decomposition of the nitrite and the induced decomposition of accompanying products makes difficult the assessment of substances originally present. The action of bases on the materials (*q.v.*) also affects inferences drawn from reduction experiments. Conversion of the unstable nitrite (II) into *nitro*-tert.-*butanol* (IV) by treatment with cold water, however, permits safe and efficient separation of pure products in total yield of 70—80% on the *iso*butylene consumed.

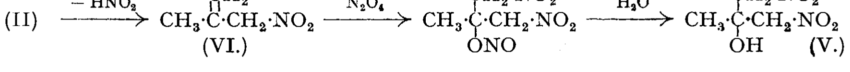
The yields summarised below are taken from examples in which ether was used as solvent. Two of the examples are described in detail later.

Product.	Yield without oxygen, %.	Yield with oxygen, %.		
		O_2/C_4H_8 = 0·27.	O_2/C_4H_8 = 1·09.	O_2/C_4H_8 = 3·2.
	(*a*)		(*b*)	
1 : 2-Dinitro*iso*butane	42·6 (45·9)	36·2	25·7 (31·8)	18·3
Nitro-*tert.*-butanol	27·8 (36·5)	26·5	28·7 (35·9)	26·7
Nitro-*tert.*-butyl nitrate	1·9 (2·3)	7·8	11·8 (14·6)	30·0
1 : 3-Dinitro-2-methylpropan-2-ol	6·1 (8·0)	4·5	3·8 (9·0)	3·0
Total	78·4 (92·7)	75·0	70·0 (91·3)	78·0

Additional figures, shown in parenthesis, are the yields in the reaction mixture before separation, and have been given to show how completely the reported products account for *iso*butylene concerned. The corrected values shown in parenthesis for (*a*) are based on experimentally determined losses in extraction and separation of a synthetic mixture of that composition. For (*b*) a different procedure for obtaining the corrected values was employed. For the nitro-alcohols extracted from the aqueous layer an experimentally determined extraction efficiency of 80% was used and no account was taken of losses occurring during this distillation, while for the other materials the values were based on losses during the distillation of the insoluble oil which is accompanied by some decomposition and is incomplete. For calculation it was assumed that the decomposition losses for (I) and (III) were in proportion to their actual yields, and the distillation residue was taken as 1 : 3-*dinitro*-2-*methylpropan*-2-*ol* (V), as this compound was isolated when the residue was carefully distilled.

With no oxygen the corrected total yield on tetroxide is 94% and the ether loss is about 3%. The product (I) was characterised by formation of *iso*butylenediamine on reduction and by formation of 1-nitro*iso*butylene on reaction with aqueous alkali, ammonia, and other bases, (III) by formation of 1-nitro*iso*butylene on reaction with aqueous alkali and by comparison with the nitrate ester prepared by nitration of nitro-*tert.*-butanol, (IV) by formation and de-acetylation of the acetate, giving 1-nitro*iso*butylene, and by hydrolytic fission to nitromethane and acetone, and (V) by hydrolytic fission to nitroacetone. Dehydration of (IV) by phosphoric oxide in benzene gives some 1-nitro*iso*butylene but largely the isomeric nitro-butylene, 3-*nitro*-2-*methyl*-1-*propylene* (VI).

As (V) has been prepared by the addition of dinitrogen tetroxide and then water to (VI) it probably arises from (II) in the following manner :

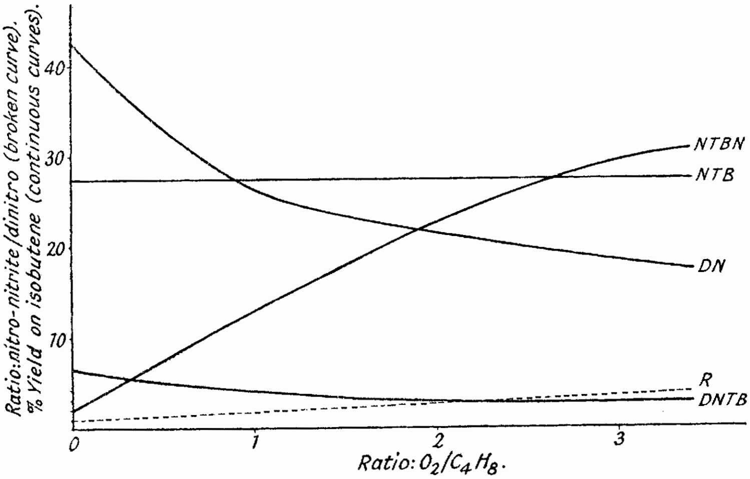


$$\text{(II)} \xrightarrow{-HNO_2} \underset{(VI.)}{\mathrm{CH_3\cdot \overset{CH_2}{\overset{\|}{C}}\cdot CH_2\cdot NO_2}} \xrightarrow{N_2O_4} \mathrm{CH_3\cdot \overset{CH_2\cdot NO_2}{\underset{ONO}{C}}\cdot CH_2\cdot NO_2} \xrightarrow{H_2O} \mathrm{CH_3\cdot \overset{CH_2\cdot NO_2}{\underset{OH}{C}}\cdot CH_2\cdot NO_2}\ \text{(V.)}$$

The table clearly shows that modes of addition other than as two nitro-groups or as one nitro- and one nitrite group do not occur to any substantial extent.

Discussion.—(a) *Effect of reaction medium* (cf. Parts I and III, *locc. cit.*). The reaction medium has been varied by the use of several classes of solvent, and by reaction in liquid dinitrogen tetroxide, in liquid *iso*butylene, and in the gas phase in a few experiments. In the gas phase, although it is possible to control the accompanying oxidation reaction even at 150° and to collect in good yield an oil which is fairly stable to distillation, dinitro*iso*butane has not been isolated, in contrast to the results with ethylene at 100°. Liquid media were more promising but the addition to give dinitro-formation only took place when ethers or esters were employed as solvents. Reaction in other solvents (*e.g.*, carbon tetrachloride, methylene chloride, light petroleum) or in the absence of a solvent gives rise to oxidation, and the main products isolated are the nitrate of α-hydroxy*iso*butyric acid (VII) and the nitrate of α-hydroxy*iso*butaldoxime.

Oxidation reactions are largely suppressed and the desired reaction favoured by the following solvents: diethyl ether, di-*n*-propyl ether, dioxan, benzyl methyl ether, methylal, acetal, tetrahydropyran, tetrahydrofuran, ethyl acetate, and amyl acetate. There is some attack on the solvent in certain cases, and of the solvents mentioned the first three and the last two are the most suitable. These solvents are thought to moderate the oxidising tendency of N_2O_4 through molecular complex formation between the N_2O_4 and the free electrons of the oxygen atom, and this view is supported by the actual separation of a labile solid complex, $C_4H_8O_2,N_2O_4$, from dioxan. With methyl 2-nitroethyl ether and 2 : 2′-dichlorodiethyl ether as solvents the nitrate of α-hydroxy*iso*butyric acid is produced, and, as with these ethers there is reduced electron-availability at the oxygen atom due to their electron-attracting substituents, it is apparent that the greater the electron availability the less the oxidising tendency of the dinitrogen tetroxide. Formic esters (ethyl and *iso*butyl formate), as would be expected on this theory, do not give as effective control of the oxidising tendency of N_2O_4 as do the acetates, and act as intermediate types giving rise both to dinitro*iso*butane, etc. (p. 58), and to the nitrate of α-hydroxy*iso*butyric acid.



Variation of yield with O_2/C_4H_8 *ratio.*

DN = *Dinitro*iso*butane.* NTB = *Nitro*-tert.-*butanol.* NTBN = *Nitro*-tert.-*butyl nitrate.* DNTB = *Dinitro*-tert.-*butanol.*

R = *Ratio of nitro-nitrite to dinitro-addition corrected for* 20% *extraction loss of nitro*-tert.-*butanol.*

Diethyl ether and dioxan have been examined in the greatest detail. The former is preferable because its low boiling point makes separation easier. Dioxan has given slightly higher yields of dinitro*iso*butane (45%), but gives the disadvantages of high boiling point and ready condensation of the solid complex in vapour lines.

(b) *Effect of oxygen.* The addition of oxygen during the reaction gives products more stable to distillation and prevents the formation of bis(nitronitroso*iso*butane) (VIII) which arises from any dinitrogen trioxide produced in the reaction (see p. 59). (VIII) is formed as one of the main products, together with dinitro*iso*butane and nitro-*tert.*-butanol when N_2O_3 reacts with *iso*butylene in ether.

With increasing partial pressure of oxygen in the inlet gas the yield of (III) rises and that of

(I) falls. As a result of the large change in composition of the product mixture, separation of dinitro*iso*butane by freezing becomes more difficult and fractional distillation becomes necessary. Yields of the four products with varying oxygen–*iso*butylene ratios are plotted in the figure. Taking nitro-*tert.*-butanol, nitro-*tert.*-butyl nitrate and 1 : 3-dinitro-2-methylpropan-2-ol as all derived from the nitro-nitrite, the ratio of $(^-NO_2)(^-ONO)$ addition to $(^-NO_2)(^-NO_2)$ addition has been calculated and plotted against the oxygen–*iso*butylene ratio in the figure, which shows a linear relationship between the two ratios. For this purpose the nitro-alcohol yields are corrected for 20% extraction loss but no correction is made for distillation losses.

The following approximate relation holds :

$$\frac{A_{(-NO_2)(-ONO)}}{A_{(-NO_2)(-NO_2)}} = 1 + \frac{P_{O_2}}{P_{C_4H_8}}$$

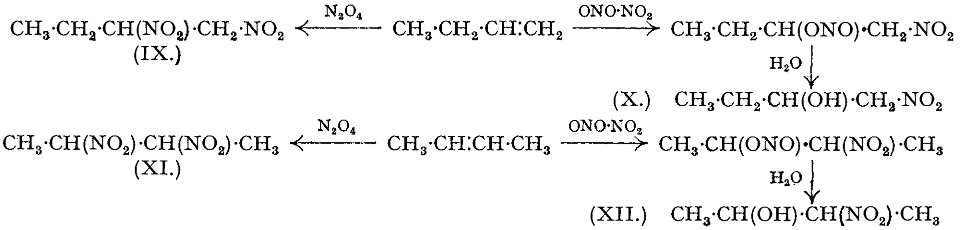
where $A_{(-NO_2)(-ONO)}$ = % C_4H_8 converted into nitro-nitrite,
$A_{(-NO_2)(-NO_2)}$ = % C_4H_8 converted into dinitro*iso*butane,
P_{O_2} and $P_{C_4H_8}$ = partial pressures of oxygen and *iso*butylene respectively.

Addition of oxygen thus influences the balance between nitro-nitrite and dinitro-compound in a regular manner.

It has been shown that the lower nitro-nitrites are readily oxidised to nitro-nitrates by dinitrogen tetroxide and oxygen in ether, and this suggests a means of formation of nitro-*tert.*-butyl nitrate. However, this does not explain the concurrent diminution of dinitro*iso*butane yield, and it seems probable that oxygen acts in a more direct fashion. Furthermore, the amount of *iso*butylene absorbed is not affected by the presence of oxygen, and mere dilution of the tetroxide does not show any marked influence on the proportions of products, so that concentration changes are not the deciding factor. Formation of olefin oxide, followed by tetroxide addition to give nitro-nitrate, does not seem likely since, apart from other considerations, attempts to form nitroethyl nitrate from ethylene oxide and tetroxide under similar conditions gave only water-soluble oxidation products. The suggestion is therefore made that dissolved oxygen gives rise to $\overset{+}{N}O_2$–ONO_2 assemblies, either immediately or in the course of addition, leading to nitro-nitrate formation in place of dinitro*iso*butane. One further result related to this observation is that if the reaction is carried out by passing nitric oxide and a large excess of oxygen into a 10% solution of *iso*butylene in ether at — 10°, the products isolated by the usual separation procedure are mainly nitro-*tert.*-butanol and nitro-*tert.*-butyl nitrate, with only 5% yield of dinitro*iso*butane.

Normal Butylenes.

The same procedure has been applied to 1- and 2-butylenes with formation of the dinitrobutanes and the nitrobutanols as expected. Thus, 1-butylene gives 1 : 2-*dinitrobutane* (IX) and 1-nitrobutan-2-ol (X), while 2 : 3-dinitrobutane (XI) and 2-nitrobutan-3-ol (XII) are obtained from 2-butylene.



$$\underset{\text{(IX.)}}{CH_3\cdot CH_2\cdot CH(NO_2)\cdot CH_2\cdot NO_2} \xleftarrow{N_2O_4} CH_3\cdot CH_2\cdot CH{:}CH_2 \xrightarrow{ONO\cdot NO_2} CH_3\cdot CH_2\cdot CH(ONO)\cdot CH_2\cdot NO_2 \xrightarrow{H_2O} \underset{\text{(X.)}}{CH_3\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NO_2}$$

$$\underset{\text{(XI.)}}{CH_3\cdot CH(NO_2)\cdot CH(NO_2)\cdot CH_3} \xleftarrow{N_2O_4} CH_3\cdot CH{:}CH\cdot CH_3 \xrightarrow{ONO\cdot NO_2} CH_3\cdot CH(ONO)\cdot CH(NO_2)\cdot CH_3 \xrightarrow{H_2O} \underset{\text{(XII.)}}{CH_3\cdot CH(OH)\cdot CH(NO_2)\cdot CH_3}$$

Demjanov (*Ber.*, 1907, **40**, 245) previously investigated the reaction between 1-butylene and nitrous fumes (from arsenious oxide and nitric acid), obtaining butylene " nitrosite ", and he also isolated a similar compound from the reaction between 2-butylene and dinitrogen pentoxide (*Ann. Inst. Agron. Moscow*, 1894, **4**, 155). A 2 : 3-dinitrobutane has been reported as a solid, m. p. 41°, from the spontaneous decomposition of the silver salt of nitroethane (Angeli and Allessandri, *Atti R. Accad. Lincei*, 1886, **19**, 784). Both nitro-alcohols have been prepared before, 2-nitrobutan-3-ol from nitroethane and acetaldehyde (*e.g.*, Henry, *Ber.*, 1900, **33**, 3169) and 1-nitrobutan-2-ol from nitromethane and propaldehyde (*e.g.*, Jones and Kenner, *J.*, 1930, 919).

Yields are as follows : (*a*) from 1-butylene, 33% of 1-nitrobutan-2-ol and 39·3% of insoluble oil (largely 1 : 2-dinitrobutane); (*b*) from 2-butylene, 34·5% of 2-nitrobutan-3-ol and 30% of insoluble oil (largely 2 : 3-dinitrobutane). The nitrobutanol obtained from 1-butylene is derived from the expected nitro-nitrite, that is, with the nitrite group attached to the carbon with fewer hydrogen atoms. The amounts of nitrobutyl nitrate formed are quite small, oxygen not being used in the reaction. Characterisation of the products is detailed on p. 60 : (IX) by formation of 1 : 2-diaminobutane on reduction and by formation of propaldehyde on reaction with aqueous alkali accompanied with oxidation hydrolysis, (X) by formation and de-acetylation of the acetate giving 1-nitro-1-butylene, (XI) by formation of 2 : 3-diaminobutane on reduction and by formation of acetaldehyde on reaction with aqueous alkali accompanied by hydrolysis, (XII) by formation and de-acetylation of the acetate giving 2-*nitro*-2-*butylene*. The nitro-alcohols (X) and (XII) were also characterised by hydrolysis to the aldehydes in a similar way to the dinitro-compounds.

EXPERIMENTAL.

Reagents.—Pure liquid dinitrogen tetroxide and dry ether were prepared as previously described (Part II, *loc. cit.*). *iso*Butylene of high purity was prepared by dehydration of *tert.*-butanol over active alumina, and the normal butylenes by dehydration of *iso*butanol followed by fractional distillation. Nitric oxide was prepared by addition of concentrated sulphuric acid to a well-stirred paste of sodium nitrite and water, and was dried by passage through concentrated sulphuric acid and over calcium chloride. Dinitrogen trioxide was prepared by passing nitric oxide through pure liquid dinitrogen tetroxide at −10° until no more was absorbed, and purified by distillation in a rapid stream of nitric oxide. The vapours were passed through a trap to collect any trace of nitric acid and then through a cooling coil at −20° where the trioxide collected as a blue liquid in a cooled receiver. Moisture was excluded from the apparatus by calcium chloride tubes.

iso*Butylene.*

Diethyl Ether as Solvent. Dinitrogen Tetroxide Addition.—The reaction procedure is similar to that described for propylene (Part III, *loc. cit.*), but because of the higher boiling point of *iso*butylene the liquid tetroxide may be slowly added to a stirred 10% solution of *iso*butylene in ether at −10°. *iso*Butylene reacts somewhat more rapidly than propylene. Oxides of carbon in the exit vapours correspond to less than 0·1% on the *iso*butylene. In the absence of oxygen, interference by nitrogen trioxide addition is prevented by absorbing no more than 0·8 mol. of *iso*butylene per mol. of tetroxide and by not exceeding tetroxide concentrations of 40% by weight in ether for batch reactions. Circumstances which may give high general or local ratios of *iso*butylene to tetroxide should be avoided; *e.g.*, temperatures below −10° when gaseous *iso*butylene is passed into dissolved tetroxide, or high concentrations of *iso*butylene in ether when tetroxide is added dropwise. Prevention of the formation of nitronitroso-*iso*butane (VIII) is advisable since even in small quantities it interferes with the crystallisation of pure 1 : 2-dinitro*iso*butane. Oxygen, when used, is mixed with the *iso*butylene before absorption.

The separation procedure is similar to that described previously (Parts I and III, *locc. cit.*). *Nitro*-tert.*-butanol* is recovered from the aqueous extract together with a subsidiary fraction of 1 : 3-*dinitro*-2-*methylpropan*-2-*ol* and small amounts of 1 : 2-*dinitro*iso*butane* and nitro-*tert.*-butyl nitrate. Neutralisation of the aqueous layer with chalk before ether extraction gives pure nitro-*tert.*-butanol on first distillation and simplifies separation from the dinitro-alcohol. The separation of 1 : 2-dinitro*iso*butane obtained on cooling a methyl alcohol solution of the water-insoluble oil is not complete owing to the presence of other components, and, for full recovery, fractional distillation of the oil obtained from the filtrate is necessary. Considerable care is required, and the distillation flask must be cooled with a methyl alcohol solution containing solid carbon dioxide whenever gas evolution is marked. When oxygen is used, even in small amount, for the reaction much of the dinitro*iso*butane remains in solution on cooling because of the increased content of nitro-*tert.*-butyl nitrate, and a somewhat laborious fractional distillation is then the only satisfactory means of separation. The oil, however, is much more stable than that obtained in the absence of oxygen. With no oxygen the main loss occurs in the recovery of nitro-*tert.*-butanol, which is about 75% efficient mainly owing to incomplete extraction and hydrolytic fission of the nitro-alcohol. With oxygen, besides the loss of nitro-*tert.*-butanol there is also appreciable loss of product in the distillation of the water-insoluble oil due to some decomposition and unstable distillation residue. The following are accounts of typical experiments showing the procedure in the absence, and in the presence, of oxygen.

(*a*) Dry *iso*butylene (270 g. or 107 l. at N.T.P.) was passed into a solution of tetroxide (750 g.) in dry diethyl ether (1750 g.) at 0° during 3½ hours. Ether and excess of tetroxide were removed in the continuous film evaporator, the reaction product falling dropwise into 1 l. of water. Recovered ether weighed 1690 g. (97% of original weight) and recovered tetroxide 300 g. After the oil–water mixture had been stirred, the oil was separated and further washed with successive quantities of 800 c.c., 400 c.c., and 400 c.c. of water, leaving 431 g. of insoluble oil. The bulked aqueous layers were continuously extracted with ether for 48 hours, the extract dried (Na_2SO_4), the ether removed under reduced pressure, and the residue distilled to give the following fractions : (i) 8·25 g., b. p. 42—50°/1 mm.; (ii) 138·9 g., b. p. 50—70°/1 mm.; (iii) 17·3 g., b. p. 70—106°/1 mm.; (iv) 33·5 g., b. p. 106—120°/1 mm. The first three fractions were mixed and redistilled to give 147·8 g. of nitro-*tert.*-butanol, b. p. 56°/<1 mm. (Found : C, 40·0; H, 7·4; N, 11·7. $C_4H_9O_3N$ requires C, 40·3; H, 7·6; N, 11·8%), and 14·9 g., b. p. 69—70°/<1 mm., shown by estimation as in (*b*) to contain 6·0 g. of nitro-*tert.*-butyl nitrate and 8·9 g. of 1 : 2-dinitro*iso*butane. Fraction (iv) was crystallised from ether to give 1 : 3-dinitro-2-methylpropan-2-ol (Found C, 29·5; H, 4·8; N, 16·9. $C_4H_8O_5N_2$ requires C, 29·2; H, 4·9; N, 17·1%).

The 431 g. of insoluble oil were dissolved in 700 ml. of methyl alcohol and cooled with stirring in a jacket at −70° to give 261 g. of solid 1 : 2-dinitro*iso*butane (Found : C, 32·3; H, 5·6; N, 18·5. $C_4H_8O_4N_2$

requires C, 32·4; H, 5·4; N, 18·9%). After removal of the methyl alcohol from the filtrate, the oil was dried by azeotropic distillation with 180 ml. of benzene, giving 132·2 g. of dry oil. Fractional distillation, with occasional cooling of the boiler to check decomposition, gave the following fractions: (i) 14·3 g., b. p. 30—60°/1—2 mm.; (ii) 44·7 g., b. p. 60—90°/1—2 mm.; (iii) 13·6 g., b. p. 90—134°/1—2 mm.; residue, 25·5 g.; distillation loss as gaseous decomposition products and volatile material containing some 1-nitro*iso*butylene, 34·1 g. Freezing fraction (ii) in methanol at $-70°$ gave a further 24·6 g. of 1 : 2-dinitro*iso*butane and a residual oil which, after admixture with fractions (i) and (iii) was redistilled to give 11·4 g. of nitro-*tert.*-butanol, 9·4 g. of nitro-*tert.*-butyl nitrate, 9·0 g. of dinitro*iso*butane, and 16·4 g. of 1 : 3-dinitro-2-methylpropan-2-ol. The total quantities of the four compounds and the yields on *iso*butylene were 303·5 g. of dinitro*iso*butane (42·6%), 159·2 g. of nitro-*tert.*-butanol (27·8%), 15·4 g. of nitro-*tert.*-butyl nitrate (1·9%), and 49·9 g. of 1 : 3-dinitro-2-methylpropan-2-ol (6·1%).

(*b*) The quantities used were *iso*butylene 127 g. (53·5 l.), oxygen 58·7 l., dinitrogen tetroxide 301 g., dry diethyl ether 700 g., requiring 1 hour's absorption time at 0°. Removal of ether and excess of tetroxide followed by treatment of the product with 500 c.c. and 400 c.c. portions of water gave 177 g. of insoluble oil. Neutralisation of the aqueous layers followed by extraction and distillation gave two sharp fractions: (i) 77·4 g., b. p. 50—56°/<1 mm.; (ii) 14·1 g., b. p. 108—111°/<1 mm.; (iii) 0·9 g., intermediate fraction; residue, 1·8 g. Fraction (i) solidified in the receiver and was pure nitro-*tert.*-butanol. Fraction (ii) was practically pure 1 : 3-dinitro-2-methylpropan-2-ol.

The insoluble oil gave only a little dinitro*iso*butane on freezing in methanol at $-70°$ and was therefore distilled under reduced pressure without difficulty and with a residue of 16·1 g. Redistillation gave two fractions: (i) 77·4 g., b. p. 74—77°/<1 mm.; (ii) 52·8 g., b. p. 80—82°/1 mm. Fraction (ii) solidified in the receiver and was pure 1 : 2-dinitro*iso*butane. Fraction (i) was a mixture of dinitro*iso*butane and nitro-*tert.*-butyl nitrate which was analysed by reaction with aqueous alkali, removal of 1-nitro*iso*butylene with benzene, and determination of total nitrogen and nitrite nitrogen in the aqueous layer. Two such analyses in agreement gave 43·4% of dinitro*iso*butane and 56·6% of nitro-nitrate. Thus, total amounts and yields on *iso*butylene were 86·4 g. of dinitro*iso*butane (25·7%), 43·8 g. of nitro-*tert.*-butyl nitrate (11·8%), 77·4 g. of nitro-*tert.*-butanol (28·7%), and 14·1 g. 1 : 3-dinitro-2-methylpropan-2-ol (3·8%).

(*c*) Dry nitric oxide and a large excess of oxygen were passed into a solution of *iso*butylene (29 g.) in ether (326 g.) at $-5°$. Removal of ether and excess of tetroxide followed by treatment of the product with water (200 c.c.) gave 44·6 g. of insoluble oil. Distillation of this oil, after drying by distillation with benzene, gave 41·0 g., b. p. 74—78°/<1 mm., which was analysed as before and shown to contain 39·7 g. of nitro-*tert.*-butyl nitrate (46·7% yield) and 1·3 g. of dinitro*iso*butane (1·7% yield). The aqueous layer yielded 12·6 g. of nitro-*tert.*-butanol (20·2% yield) and a residue containing 1 : 3-dinitro-2-methylpropan-2-ol.

Properties and Characterisation of Products—1 : 2-*Dinitro*iso*butane* (I). This is a white crystalline solid, m. p. 52—53° after recrystallisation from methyl alcohol. It distils in a vacuum to give a colourless liquid, b. p. 92°/*ca.* 1 mm., which readily solidifies on cooling. Although it is an explosive of moderate power (51·1% blasting gelatin in the mortar test), it is very insensitive to friction and impact, stable to storage at room temperature and at 50°, and withstands heating in vacuum at 100° for more than 40 hours.

iso*Butylenediamine.* (I) was reduced in glacial acetic acid with hydrogen at 80—100 atm. and Adams's platinum catalyst. As with the lower dinitro-paraffins dilute solutions were necessary and, hence, 0·5 g. of dinitro*iso*butane in 300 c.c. of glacial acetic acid was reduced at 80 atm. in the presence of 0·0234 g. of catalyst to give, after saturation with hydrogen chloride and evaporation of the acetic acid, 0·525 g. of crude hydrochloride (96%). This was dissolved in the minimum amount of alcohol, and 0·320 g. of pure iso*butylenediamine dihydrochloride* precipitated with ether (59% yield). After recrystallisation it melted at 302° (Found: Cl, 43·7; N, 17·8. $C_4H_{12}N_2,2HCl$ requires Cl, 44·1; N, 17·4%).

1-*Nitro*iso*butylene from* 1 : 2-*dinitro*iso*butane.* A solution of sodium hydroxide (81 g.) in water (300 c.c.) was added during ½ hour to a stirred suspension of dinitro*iso*butane (300 g.) in water (450 c.c.). The nitro-olefin separated as an oil, and together with a small amount extracted with ether from the aqueous layer was dried (Na_2SO_4) and distilled under reduced pressure to give 180 g. (88% yield) of nitro*iso*butylene, b. p. 56°/11 mm., $d_{4^\circ}^{20^\circ}$ 1·048, $n_D^{20^\circ}$ 1·468 (Found: C, 47·4; H, 6·9; N, 12·9. Calc. for $C_4H_7O_2N$: C, 47·5; H, 6·9; N, 13·9%).

Nitro-tert.-*butyl nitrate* (III). This was isolated on careful fractional distillation of fraction (i) of the insoluble oil (*b*) (Found: C, 29·5; H, 5·1; N, 17·3. Calc. for $C_4H_8O_5N_2$: C, 29·3; H, 4·9; N, 17·1%). The nitrate crystallises at about 6° and distils in a vacuum to give a colourless liquid, b. p. 78°/*ca.* 1 mm., $d_{4^\circ}^{20^\circ}$ 1·283; $n_D^{20^\circ}$ 1·449. The same nitrate is obtained by nitration of nitro-*tert.*-butanol. The nitration gives much better yields if nitrogen tetroxide is used in place of the usual nitric acid–sulphuric acid mixture. A slow stream of oxygen was passed through a mixture of nitro-*tert.*-butanol (130 g.) and dinitrogen tetroxide (950 g.) for 60 hours. The excess of nitrogen tetroxide was removed in a stream of oxygen, and the product (214 g.) stirred with 660 c.c. of water. The residue (93 g.) on distillation gave 2·7 g., b. p. <74°/*ca.* 1 mm., and 80·4 g. of nitro-*tert.*-butyl nitrate, b. p. 78—80°/*ca.* 1 mm. (Found: C, 29·4; H, 4·9; N, 17·1%). From the aqueous layer 50·5 g. of nitro-*tert.*-butanol were recovered. (Yield of nitrate on nitro-*tert.*-butanol converted, 73·4%.)

1-*Nitro*iso*butylene from nitro*-tert.-*butyl nitrate.* The method was the same as that used for 1 : 2-dinitro*iso*butane, except that stirring was continued for 3 hours and the solution made just acid before ether extraction. Quantities used were nitro-*tert.*-butyl nitrate (50 g.) in water (500 c.c.) and sodium hydroxide (12·5 g.) in water (500 c.c.); 25·7 g. (yield 83·5%) of 1-nitro*iso*butylene, b. p. 65°/14 mm., were obtained (Found: C, 47·5; H, 6·9; N, 14·2%).

Nitro-tert.-*butanol* (IV). This crystallises in needles, m. p. 26°. It distils under vacuum to give a colourless liquid, b. p. 66°/*ca.* 1. mm., $d_{4^\circ}^{20^\circ}$ 1·132, $n_D^{20^\circ}$ 1·443, and is somewhat hygroscopic.

Formation and de-acetylation of nitro-tert.-*butyl acetate. Nitro*-tert.-*butyl acetate* is prepared in almost theoretical yield by adding acetyl chloride to nitro-*tert.*-butanol in the cold and distilling the product under reduced pressure (Found: C, 44·4; H, 7·0; N, 8·9. $C_6H_{11}O_4N$ requires C, 44·7; H, 6·8; N, 8·7%). It has b. p. 60°/<1 mm., $d_{4^\circ}^{20^\circ}$ 1·123, n_D^{20} 1·432. The acetate (30 g.) was heated with 2% potassium carbonate for 1 hour at 65° and then distilled at 14 mm. The distillate was added to 1·5 vols. of ether, washed with water to remove acetic acid, dried, and distilled. This gave 14·8 g. (78% yield) of nitro-olefin (Found: C, 47·4; H, 6·9; N, 13·8%). Careful fractionation showed it to contain 1·05 g. of 3-*nitro*-2-*methyl*-1-*propylene* (VI), b. p. 40—43°/13 mm., while the remainder was 1-nitro*iso*butylene, b. p. 56°/11 mm. Unlike the α-nitro-olefins, 3-nitro-2-methyl-1-propylene is not lachrymatory.

*Hydrolytic fission of nitro-*tert.*-butanol to nitromethane and acetone.* Nitro-*tert.*-butanol (40·5 g.) was heated with 1000 c.c. of distilled water in a stainless steel autoclave at 130—150° for 2 hours. The product was cooled and drained off and the autoclave washed with distilled water. The product was combined with the washings and fractionally distilled through a vacuum-jacketed silvered column (6 in. × 1 in. diameter, packed with 1/16 in. × 1/16 in. stainless steel gauze rings), using a reflux ratio of approximately 30 : 1. Acetone (12·96 g.) was collected, b. p. 56—58°, followed by a small intermediate fraction (2·1 g.), b. p. 58—62°, the nitromethane–water azeotrope, b. p. 82°, and a small aqueous fraction boiling up to 100°. The acetone fraction was pure (yield 66%). The nitromethane–water fraction contained 22 g. of water and 17·8 g. of nitromethane (yield 85·7%).

*Dehydration of nitro-*tert.*-butanol by phosphoric oxide.* Nitro-*tert.*-butanol (70 g.) and phosphoric oxide (120 g.) in benzene (500 c.c.) were heated on the water-bath for 40 minutes. The pale brown supernatant liquid was decanted, and the residual phosphoric oxide washed with 50 c.c. of hot benzene and the latter added to the benzene already decanted. The benzene was recovered through a column and the residue was distilled under reduced pressure through an efficient column to give (i) 22·8 g. (41·0%) of 3-nitro-2-methyl-1-propylene, b. p. 40—43°/13 mm. (Found: C, 47·4; H, 6·9; N, 14·2. $C_4H_7O_2N$ requires C, 47·5; H, 6·9; N, 13·9%), (ii) 12·1 g. (21·7%) of 1-nitro*iso*butylene, b. p. 57—60°/13 mm. (Found: C, 47·2; H, 6·9; N, 14·2%), and (iii) 4·45 g. of unchanged nitro-*tert.*-butanol.

1 : 3-*Dinitro*-2-*methylpropan*-2-*ol* (V). This is a white crystalline solid, m. p. 31°; it distils in a vacuum to give a colourless liquid, b. p. 108°/<1 mm., which is very difficult to crystallise.

Hydrolytic fission of (V) *to nitroacetone.* (V) (10 g.) was added slowly to stirred aqueous alkali (30·6 c.c. of 4·25N-sodium hydroxide) at room temperature, and after 1 hour the mixture was slowly acidified at 0° with 7·8N-hydrochloric acid; some white solid then separated. The aqueous solution was continuously extracted with ether, and the ether removed, leaving an oil which crystallised on cooling. Recrystallisation at −70° from ether gave 4·32 g. (69%) of nitroacetone, m. p. 51° (Found: C, 34·4; H, 5·2; N, 13·5. Calc. for $C_3H_5O_3N$: C, 35·0; H, 4·9; N, 13·6%). The nitroacetone was also identified by mixed melting point with material made from 2-nitro*iso*propanol (Part III, *loc. cit.*), and by preparation of the anil.

Synthesis of (V) *from* 3-*nitro*-2-*methyl*-1-*propylene.* The nitro-olefin (30 g.) in diethyl ether (300 c.c.) was added dropwise during 1 hour to dinitrogen tetroxide (30 g.) in ether (200 c.c.) at −10° and allowed to stand for 2 hours. The solvent was removed under reduced pressure, and the residual oil added to a little water. The aqueous mixture was extracted with ether and the extract distilled to give 22·1 g. of oil, b. p. 130—145°/2 mm., with gas evolution and a large residue. Redistillation gave 1 : 3-dinitro-2-methylpropan-2-ol, b. p. 106—108°/1 mm. (Found: C, 29·3; H, 5·0; N, 17·0%).

Miscellaneous Solvents. Dinitrogen Tetroxide Reaction.—(a) *Ethers and esters.* With dioxan, di-*n*-propyl ether, benzyl methyl ether, methylal, acetal, tetrahydropyran, ethyl acetate, and amyl acetate, using the same reaction and separation procedure as described under diethyl ether, (I), (III), (IV), and (V) were again obtained. Their yields were (1) for dioxan, of the same order as for diethyl ether as solvent, total 69%, (2) for ethyl acetate and amyl acetate, total 60%, that for (IV) being only about 10%, (3) for acetal, total about 50%, that for (IV) being 21%, (4) for the other solvents, total less than 50%, but only small-scale experiments were carried out. With the acetates and acetal, only small amounts of 1 : 2-dinitro*iso*butane (I) could be obtained on freezing, and distillation of the insoluble oil was necessary.

(I), (III), (IV), and (V) were not obtained on applying the same reaction and separation procedure with methyl 2-nitroethyl ether and 2 : 2′-dichlorodiethyl ether as solvents. The nitrate of α-hydroxy-*iso*butyric acid (VII) was formed, and was isolated in small yield by the procedure outlined in the account of the following experiment. *iso*Butylene (18 g.) was passed into a solution of tetroxide (61 g.) in dichlorodiethyl ether (150 g.) at −5°. The solvent and excess of tetroxide were removed under suction leaving 49·8 g. of oil, which was washed with 100 c.c. of water; a little oil (7·3 g.) then dissolved. The insoluble oil was distilled and gave the following fractions: (i) 18·25 g., b. p. <60°/1 mm., (ii) 0·3 g., b. p. 62—100°/1·5 mm., (iii) 10·6 g., b. p. 100—110°/1·5 mm., and 6·3 g. residue. Fraction (iii) solidified in the receiver and after recrystallisation from light petroleum had m. p. 77° (Found: C, 31·7; H, 4·4; N, 9·5. Calc. for $C_4H_7O_5N$: C, 32·2; H, 4·7; N, 9·4%); cf. Duval (*Bull. Soc. chim.*, 1904, **31**, 246) who obtained the nitrate of α-hydroxy*iso*butyric acid as a solid, m. p. 78°, by the action of mixed nitric and sulphuric acids on the zinc salt of α-hydroxy*iso*butyric acid. The aqueous washings, after extraction with ether and distillation, gave a further 4 g. of (VII), making a total yield of 30·5%.

Using formic esters as solvents, (I), (III), (IV), (V), and (VII) were obtained. An account of an experiment using ethyl formate as solvent is given. *iso*Butylene (23 g.) was passed into a solution of tetroxide (57 g.) in ethyl formate (138 g.) at 0°. The solvent and excess of tetroxide were removed under suction leaving 50·0 g. of oil, which was washed with 700 c.c. and 250 c.c. of water, and left 27 g. undissolved. The aqueous washings were extracted with ether and the extract distilled to give 9·8 g., b. p. 50—130°/0·5—2·0 mm., and 3·5 g. of residue. Fractionation of the distillate gave 5·3 g. of nitro-*tert.*-butanol and 0·9 g. of the nitrate of α-hydroxy*iso*butyric acid. The insoluble oil was added to methyl alcohol (40 c.c.) and cooled to −70°; only a little dinitro*iso*butane separated. The oil was therefore distilled, and the distillate on redistillation gave the following fractions: (i) 1·3 g., b. p. 34—40°/<1 mm., (ii) 5·9 g., b. p. 65—94°/1 mm., (iii) 3·1 g., b. p. 94—108°/1 mm., (iv) 4·4 g., b. p. 108—114°/<1 mm. Fraction (ii) was added to methyl alcohol and cooled to −70°; dinitro*iso*butane was thus obtained, m. p. 52—53°. Fractions (iii) and (iv) were dissolved in benzene, light petroleum (b. p. 60—80°) added, and the mixture cooled; then the nitrate of α-hydroxy*iso*butyric acid separated, m. p. 75°. All products were characterised by analysis, mixed m. p. if solid, and reactions.

(b) *Liquid dinitrogen tetroxide.* Passage of *iso*butylene into cold dinitrogen tetroxide, followed by removal of excess of the latter, gave a yellow oil which on cooling to −70° deposited the nitrate of α-hydroxy*iso*butyric acid in 22% yield. The residual oil, from which no (I), (III), (IV), or (V) could be separated, represented about 40% of the *iso*butylene.

(c) *Liquid* iso*butylene.* Passage of gaseous tetroxide into liquid *iso*butylene at −10°, followed by removal of excess of *iso*butylene, gave a green oil in good yield which deposited a small amount of the nitrate of α-hydroxy*iso*butaldoxime, m. p. 110° (Found : C, 31·8; H, 5·1; N, 19·3. Calc. for $C_4H_8O_4N_2$ C, 32·4; H, 5·4; N, 18·9%) (Ipatieff and Solonina, *loc. cit.*, give m. p. 114—115°). From the remaining oil no (I), (III), (IV), or (V) could be separated.

(d) *Carbon tetrachloride.* Rapid absorption took place when *iso*butylene (56 g.) was passed into a cooled solution of tetroxide (100 g.) in carbon tetrachloride (300 g.). Sufficient oxidation occurred to form a small separate layer of aqueous nitric acid. The solvent was removed under reduced pressure and the oil mixed with an equal volume of methyl alcohol and cooled; a little of the nitrate of α-hydroxy*iso*butaldoxime then separated. The remaining oil was washed three times with 2 vols. of water and a 5% yield of (VII) isolated from the aqueous extract. Subsequent distillation of the washed oil caused decomposition with the formation of 4 g. of 1-nitro*iso*butylene. No (I), (III), (IV), or (V) could be separated.

(e) *Methylene chloride.* Rapid absorption took place when *iso*butylene (75 g.) was passed into a cooled solution of tetroxide (120 g.) in methylene chloride (270 g.). Two phases separated as with carbon tetrachloride. The solvent was removed under reduced pressure and a methyl alcohol solution of the oil cooled; a little (VII) but no (I) then separated. The residual oil was unstable to distillation. No (I), (III), (IV), or (V) could be separated using the procedure described under diethyl ether as solvent.

(f) *Light petroleum* (*b. p.* 60—80°). *iso*Butylene (103 g.) was passed into a solution of tetroxide (240 g.) in petroleum (722 g.) at 0°. Two layers were formed. The solvent and excess of tetroxide were removed under reduced pressure, and the oil washed with 600 c.c., 250 c.c., and 250 c.c. of water. The aqueous extract yielded 22·6 g. of distillate, b. p. <91°/2 mm., which fractionation and analysis showed contained mainly non-nitrogenous compounds, although a small amount of nitro-*tert.*-butanol was isolated. No deposit was obtained on cooling a methyl alcohol solution of the insoluble oil, nor was any pure product obtained on distillation.

Diethyl Ether as Solvent. Dinitrogen Trioxide Addition.—*iso*Butylene (29 g.) and ether (216 g.) were stirred to −5° in a flask (fitted with a reflux condenser through which methyl alcohol, cooled to −70°, circulated) and a solution of dinitrogen trioxide (43 g.) in ether (110 g.) added over 1½ hours. The trioxide solution was freshly prepared and was stored at −70° before use. The ether solution turned bright blue, and crystals separated. The solvent was removed under reduced pressure and the residue stirred with 200 c.c. of water and left for 48 hours. On filtration, a solid (16·6 g.) was obtained, which gave white crystals on crystallisation from alcohol, m. p. 81°, giving a blue melt (Found : C, 36·3; H, 6·2; N, 21·2. Calc. for $C_4H_8O_3N_2$: C, 36·3; H, 6·1; N, 21·2%.) The aqueous layer was separated, extracted with ether for 48 hours, and the ether extract distilled to give 8·9 g. of nitro-*tert.*-butanol and 3·0 g. of 1 : 3-dinitro-2-methylpropan-2-ol. The insoluble oil (21 g., after drying by azeotropic distillation with benzene) gave only a little dinitro*iso*butane (I) on cooling a methyl alcohol solution, and therefore the content of (I) was estimated by interaction of the oil (10 g.) with aqueous alkali when (I) gave 1-nitro*iso*butylene (3·3 g.).

The solid, m. p. 81°, was characterised as bis-(1-nitro-2-nitroso*iso*butane) (VIII) (cf. Sidorenko, *loc. cit.*) by (*a*) reaction with acetic anhydride in the presence of concentrated sulphuric acid to give nitro-*tert.*-butyl acetate which was de-acetylated as before to 1-nitro*iso*butylene, and (*b*) reaction with alcoholic potash or aniline to give 1-nitro*iso*butylene. Details are given below.

*Conversion of Bis(nitronitroso*iso*butane) into Nitro*iso*butylene.*—(a) via *Nitro-*tert.*-butyl acetate.* The nitroso-compound (10 g.) was added slowly to 20 c.c. of acetic anhydride (20 c.c.) and concentrated sulphuric acid (4 drops), the temperature being maintained at 40—45°. A further 15 c.c. of anhydride and a few drops of acid were added to complete the reaction. Excess of anhydride was removed under reduced pressure, the residue dissolved in benzene and washed with water, dried, and then distilled to give 4·2 g. of nitro-*tert.*-butyl acetate, b. p. 44°/<1 mm., which when de-acetylated as before gave 2·0 g. of 1-nitro*iso*butylene, b. p. 56—58°/12 mm., yield 26%.

(b) *By reaction with alcoholic potash.* The nitroso-compound (5·0 g.) was added with stirring to 10% alcoholic potash (36 c.c.), followed by water (50 c.c.), and acidification with concentrated hydrochloric acid at 0°. The solution was extracted with ether to give 1·6 g. of nitro*iso*butylene, yield 42%.

(c) *By reaction with aniline.* The nitroso-compound (4·0 g.) was added to a boiling solution of aniline (2·8 g.) in alcohol (10 c.c.) under reflux, the solution turning olive-green and then pale yellow. After 2 hours, the alcohol was removed and the residue distilled under reduced pressure to give 1·9 g. of nitro*iso*butylene, yield 62%.

Normal Butylenes.

Diethyl Ether as Solvent. Dinitrogen Tetroxide Addition.—The procedures for reaction, removal of solvent and excess of tetroxide, treatment of crude oil with water, and extraction of nitro-alcohol from the aqueous layer are all identical with those used for *iso*butylene. On the other hand, the insoluble oil from 1-butylene deposits no solid when cooled in methyl alcohol solution and gives liquid 1 : 2-*dinitrobutane* on distillation. In the case of 2-butylene, only a small amount of a solid form of 2 : 3-dinitrobutane comes out on cooling, and distillation gives a liquid form, from which some more of the solid can be obtained by freezing. The amounts of nitrobutyl nitrate formed in both cases are quite small, oxygen not being used in the reaction. The following are accounts of typical experiments.

1-*Butylene.* The quantities used were 45·8 g. (18·9 l.) of 1-butylene, 94 g. of dinitrogen tetroxide, and 314 g. of diethyl ether, requiring 1 hour's absorption time at 0°. Removal of ether and excess of tetroxide left 126 g. of product (almost theoretical for $C_4H_8O_4N_2$), which, after being stirred successively with 400, 120, and 60 c.c. portions of water, gave 61 g. of insoluble oil. The aqueous layers yielded 32·1 g., b. p. 56—62°/*ca.* 1 mm., of 1-nitrobutan-2-ol (Found after redistillation : C, 39·9; H, 7·8·

N, 12·0. Calc. for $C_4H_9O_3N$: C, 40·3; H, 7·6; N, 11·8%), and only 1·8 g. of distillation residue. No solid could be isolated from the insoluble oil on cooling in methyl alcohol to $-70°$, and, after being dried by distillation with benzene, it gave 47·5 g. boiling over a wide range and 3·0 g. of residue. Two further distillations gave 1 : 2-dinitrobutane, b. p. 90—92°/1 mm. (Found : C, 31·9; H, 5·3; N, 19·0. $C_4H_8O_4N_2$ requires C, 32·4; H, 5·4; N, 18·9%).

2-*Butylene*. The quantities used were 51·9 g. (22·2 l.) of 2-butylene, 197 g. of dinitrogen tetroxide, and 365 g. of ether, requiring $1\frac{1}{2}$ hours' absorption time at 0°. Removal of ether and excess of tetroxide left 139 g. of product (practically theoretical for $C_4H_8O_4N_2$). Extraction successively with 500 and 100 c.c. of water left 58 g. of insoluble oil. Treatment of the aqueous layers as before gave 35·1 g. of 2-nitrobutan-3-ol, b. p. 60—61°/1 mm. The insoluble oil was dissolved in 88 g. of alcohol and cooled to $-70°$; crystals then separated. All but 2·7 g. disappeared into the filtrate on warming to room temperature. This solid, after recrystallisation from methyl alcohol, melted at 48—49° (Found : C, 32·6; H, 5·4; N, 18·8%). The solvent was removed from the filtrate under reduced pressure, the residual oil dried with benzene, and then distilled under reduced pressure to give 38·5 g., b. p. 64—92°/*ca.* 1 mm., collected in fractions, the higher-boiling part of which gave a further 1·1 g. of the solid form on cooling in methyl alcohol. Redistillation of the remaining oil gave liquid 2 : 3-dinitrobutane, b. p. 76—77°/<1 mm. (Found : C, 32·5; H, 5·6; N, 18·9%).

Properties and Characterisation of Products.—1 : 2-*Dinitrobutane* (IX). This is a colourless liquid, b. p. 90—92°/<1 mm. Like 1 : 2-dinitropropane (Part III, *loc. cit.*) it has one asymmetric carbon atom and has not been obtained solid at room temperature.

Reduction to 1 : 2-diaminobutane was carried out as for 1 : 2-dinitro*iso*butane. From 0·447 g. of (IX) in 30 c.c. of glacial acetic acid in the presence of 0·025 g. of Adams's platinum catalyst at 100 atm., 0·233 g. of diamine dihydrochloride was obtained, m. p. 182° (Found : N, 17·4; Cl, 43·8. Calc. for $C_4H_{12}N_2,2HCl$: N, 17·4; Cl, 44·1%), yield 48%. The dipicrate was prepared by adding dihydrochloride (0·0325 g.) in water (5 c.c.) to picric acid (0·10 g.) in water (70 c.c.); 0·072 g. of dipicrate then crystallised, m. p. 244·5° (decomp.) (Found : C, 35·5; H, 3·9; N, 20·0. Calc. for $C_4H_{12}N_2,2C_6H_3O_7N_3$: C, 35·2; H, 3·3; N, 20·5%).

Formation of propaldehyde. The nitro-olefin solution, prepared by adding (IX) (0·75 g.) to potassium hydroxide (0·2 g.) in water (5 c.c.), was added dropwise to a boiling solution of potassium permanganate (2-g.) in water (40 c.c.) under reflux in a stream of carbon dioxide. The issuing gas was passed to a bubbler containing 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. After 1 hour the propaldehyde was allowed to distil into the bubbler and the 2 : 4-dinitrophenylhydrazone formed recrystallised from alcohol (Found : C, 45·9; H, 4·4; N, 24·1. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·2; N, 23·5%).

1-*Nitrobutan*-2-*ol* (X). This is a colourless mobile liquid, b. p. 60—61°/<1 mm. It is identical with the synthetic material (Jones and Kenner, *loc. cit.*).

1-*Nitro*-1-*butylene formation* via *acetate*. The acetate was prepared in 86% yield by interaction of (X) and acetyl chloride. It had b. p. 62°/<1 mm. (Found : C, 45·1; H, 6·8; N, 9·0. Calc. for $C_6H_{11}O_4N$: C, 44·7; H, 6·8; N, 8·7%). The acetate (5 g.) was heated with potassium carbonate (0·1 g.) at 80°/100 mm., and then distilled at 20 mm. to give the nitro-olefin which, after being washed to remove acetic acid and dried ($CaCl_2$), distilled at 65°/19 mm. (Found: C, 47·4; H, 6·7; N, 13·9. Calc. for $C_4H_7O_2N$: C, 47·5; H, 6·9; N, 13·9%).

2 : 3-*Dinitrobutane* (XI). This exists in two forms, a solid, m. p. 48—49° (Angeli and Alessandri, *loc. cit.*, give m. p. 41°), and a liquid, b. p. 76—77°/<1 mm. Since (XI) has two asymmetric carbon atoms, the solid is possibly the *meso*-form and the liquid the *dl*-form. The diamine dihydrochloride and the dipicrate of the diamine from the solid form have melting points which differ from those of the derivatives from the liquid form.

Reduction to 2 : 3-*diaminobutane*. (a) Reduction of the solid form (0·441 g.), as before, gave 0·65 g. of crude dihydrochloride, which, after recrystallisation from alcohol, had m. p. 240—241° (Found : N, 17·7; Cl, 42·6%). The dipicrate, prepared as above, had m. p. 230° (decomp.) (Found : C, 35·3; H, 3·2; N, 20·4%).

(b) The liquid form (0·449 g.) gave 0·192 g. of *dihydrochloride*, which was washed with alcohol (Found : N, 17·5; Cl, 43·7%). This dihydrochloride was much less soluble in acetic acid and alcohol than that obtained from the solid and had a much higher melting point, darkening at 275—280°. The dipicrate also had a higher melting point, darkening at 240—250°. The acetic acid remaining after separation of the above dihydrochloride gave a further 0·068 g. of the dihydrochloride obtained from the solid form, confirmed by m. p., mixed m. p., and formation of identical dipicrate.

Formation of acetaldehyde. (a) The solid form (0·51 g.) was dissolved in an aqueous solution of potassium hydroxide (0·46 g.) and added to water (40 c.c.) under reflux. The reaction was carried out in a stream of nitrogen and the acetaldehyde vapour passed into 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. The dinitrophenylhydrazone was recrystallised from alcohol (Found : C, 42·0; H, 3·0; N, 25·3. Calc. for $C_8H_8O_4N_4$: C, 42·8; H, 3·6; N, 25·0%).

(b) The liquid form (0·75 g.) treated as for the solid with 0·60 g. potassium hydroxide gave acetaldehyde 2 : 4-dinitrophenylhydrazone (Found : C, 42·6; H, 3·6; N, 25·3%).

2-*Nitrobutan*-3-*ol* (XII). This, when pure, is a colourless mobile liquid, b. p. 60—61°/<1 mm.

2-*Nitro*-2-*butylene formation* via *the acetate*. 2-Nitrobutyl 3-acetate, b. p. 61°/1 mm., was prepared in 89% yield by interaction of the nitro-alcohol and acetyl chloride. By heating 5 g. with 0·1 g. of potassium carbonate at 70°/25 mm. for 2 hours and distilling at 14 mm., followed by washing, drying and distilling, 2-*nitro*-2-*butylene* was obtained, b. p. 58°/18 mm. (Found : C, 49·6; H, 6·8; N, 13·5. $C_4H_7O_2N$ requires C. 47·5; H, 6·9; N, 13·9%).

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