553. *Addition of Dinitrogen Tetroxide to Olefins. Part V.* cyclo*Hexene and the Octenes.*

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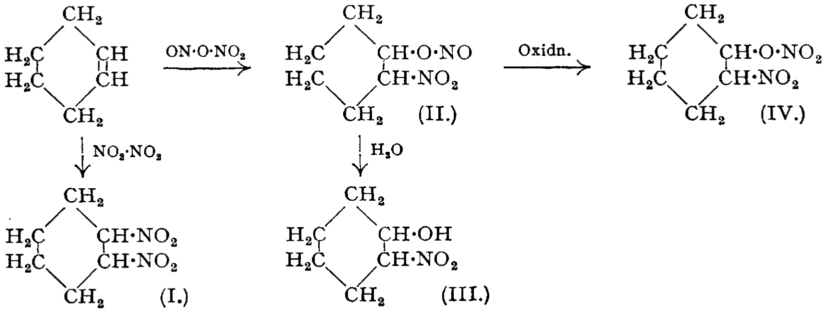
The addition of dinitrogen tetroxide to *cyclo*hexene and to 2 : 4 : 4-trimethylpent-1- and -2-ene is described, together with the isolation of the dinitro-hydrocarbons and the nitro-alcohols in total yields of 75—85% on the olefin. As with the lower olefins, addition occurs both as two nitro-groups and as one nitro- and one nitrite group, the latter being attached in the octenes to the carbon with the fewer hydrogen atoms. The reaction may be carried out without a solvent and the product is treated with water to convert the nitro-nitrite into the nitro-alcohol at an early stage in the separation procedure. Nitro*cyclo*hexanol is water-soluble and may therefore be extracted in the usual manner, but the nitro-octanols are insoluble and require fractional distillation. The three dinitro-compounds and the three nitro-alcohols are new substances, and their properties and reactions are briefly described.

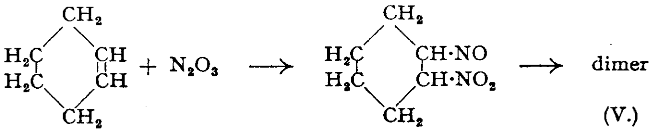
In Part I of this series (*J.*, 1946, 1093) a general introduction was given to the series of papers on addition of dinitrogen tetroxide to olefins, whilst in Parts II (*J.*, 1946, 1096), III (*J.*, 1946, 1100), and IV (*J.*, 1948, 52) the addition to ethylene, propene, and the butenes, respectively, was described. We now report a study of the addition of dinitrogen tetroxide to *cyclo*hexene and to 2 : 4 : 4-trimethylpent-1- and -2-ene.

A. cyclo*Hexene.*—*General.* Previous work on the reaction between *cyclo*hexene and oxides of nitrogen includes the use of nitric oxide, dinitrogen trioxide and tetroxide, usually with isolation of the nitrosite in small yields, the greater part of the product not being identified, or being assessed by indirect means. Baeyer (*Annalen*, 1894, **278**, 110) obtained the nitrosite, m. p. 150°, by adding acetic acid to a mixture of *cyclo*hexene, ligroin, and saturated sodium nitrite solution, and the nitrosate by adding concentrated nitric acid to a mixture of *cyclo*hexene, amyl nitrite, and acetic acid. Wieland and Blumlich (*ibid.*, 1921, **424**, 77) also obtained the nitrosite, m. p. 145°, by causing dinitrogen trioxide (from arsenious oxide and nitric acid) to react with *cyclo*hexene in a mixture of light petroleum and ethyl ether. The mother-liquor yielded nitro*cyclo*hexene on treatment with alkali, and the authors presumed that this arose from dinitro*cyclo*hexane which they were unable to isolate. Addition of the tetroxide to *cyclo*hexene in light petroleum gave similar products. Schaarschmidt and Schlosser (*Ber.*, 1922, **55**, 1103) obtained the nitrosite and a viscous green oil in the same solvent, whilst later work (Schaarschmidt, *Z. angew. Chem.*, 1923, **36**, 565) gave the nitrosate as well as the nitrosite in light petroleum at 0°. Subsequent attempts to isolate other products proved unsuccessful (*idem, ibid.*, 1924, **37**, 333; Schaarschmidt and Hofmeier, *Ber.*, 1925, **58**, 1057) since the materials were extremely unstable, decomposing even before removal of solvent. More recently, Bloomfield and Jeffrey (*J.*, 1944, **120**) studied the reaction between *cyclo*hexene and oxides of nitrogen and obtained the nitrosite, m. p. 153°, together with a mixture of isomeric nitro*cyclo*hexenes and an unstable viscous oil which constituted the main product and was difficult to distil. Jeffrey confirmed by *X*-ray examination the dimeric structure proposed for the nitrosite by Wieland.

In the present work, *cyclo*hexene has been treated with dinitrogen tetroxide alone or in a solvent, with the isolation for the first time of 1 : 2-*dinitro*cyclo*hexane* (I), 2-*nitro*cyclo*hexanol* (III), and 2-*nitro*cyclo*hexyl nitrate* (IV) in high overall yield. Compounds (III) and (IV) are produced from the *nitro*cyclo*hexyl nitrite* (II) first formed, the nitrate by oxidation in the course of reaction, and the nitro-alcohol by hydrolysis at an early stage in the working up :



A slow stream of oxygen added to the reaction mixture gives a product which is more stable to distillation and free from undesirable dinitrogen trioxide addition products. When oxygen is not used, a little di(nitronitroso*cyclo*hexane) (V) is formed, usually to the extent of 3% calc. on the *cyclo*hexene :



(V.)

It is essential to purify the *cyclo*hexene by careful fractional distillation from sodium, otherwise unstable products are obtained whatever nitration procedure is used. Though a solvent is not necessary for formation of the dinitro-compound, in contrast to propene (Part III, *loc. cit.*) and the butenes (Part IV, *loc. cit.*), it is convenient to use ethyl ether as solvent and to bubble oxygen slowly through the cooled mixture.

Yields. The total yield is about 85%, the deficiency occurring largely as extraction losses. The proportions of the three products are markedly affected by the order of mixing the reagents, in effect by that reagent which is in excess for most of the reaction period, as is shown by the two examples detailed in the experimental section. These examples refer to (*a*) the dropwise addition of *cyclo*hexene to excess of dinitrogen tetroxide in ether and (*b*) the dropwise addition of the theoretical amount of the tetroxide to *cyclo*hexene in ether, a slow oxygen stream being used in each case. Yields of distilled materials are compared below :

	(*a*) *cyclo*Hexene added to dinitrogen tetroxide in ether.	(*b*) Dinitrogen tetroxide added to *cyclo*hexene in ether.
Nitro*cyclo*hexanol from aqueous washings, % ...	21·9	47·1
Insoluble oil (calc. as dinitro*cyclo*hexane), %......	62·8	38·5
Totals, %	84·7	85·6

The composition, as well as the quantity, of insoluble oil is changed by reversing the order of addition of the reagents. Thus in (*a*) two-thirds of the oil is dinitro*cyclo*hexane and the remainder nitro*cyclo*hexyl nitrate with a little nitro*cyclo*hexanol, and in (*b*) the amount of nitro*cyclo*hexyl nitrate does not exceed 2%, four-fifths of the insoluble oil consisting of dinitro*cyclo*hexane with most of the remaining one-fifth being nitro*cyclo*hexanol. An approximate allocation of yields between the three components is as follows :

	(*a*) *cyclo*Hexene added to dinitrogen tetroxide in ether.	(*b*) Dinitrogen tetroxide added to *cyclo*hexene in ether.
1 : 2-Dinitro*cyclo*hexane (I), %	42	30
2-Nitro*cyclo*hexanol (III), %	25	54
2-Nitro*cyclo*hexyl nitrate (IV), %	18	2

The formation of nitro*cyclo*hexyl nitrate thus depends on the presence of excess of dinitrogen tetroxide as well as of oxygen. When the order of mixing is reversed, nitro*cyclo*hexyl nitrate formation is virtually suppressed, and addition of the tetroxide as $(-NO_2)(-O\cdot NO)$ is favoured as compared with that as $(-NO_2)(-NO_2)$. Characterisation of the products (detailed below) was : (I) by formation of the diamine on reduction and by formation of 1-nitro*cyclo*hex-1-ene on reaction with aqueous alkali, (III) by formation and deacetylation of the *acetate* to give 1-nitro*cyclo*hex-1-ene, and (IV) by formation of 1-nitro*cyclo*hex-1-ene on reaction with aqueous alkali.

B. 2 : 4 : 4-*Trimethylpent*-1-*ene*.—*General.* There appears to be no previous work on the reaction between oxides of nitrogen and 2 : 4 : 4-trimethylpent-1-ene. Addition of dinitrogen tetroxide to this olefin occurs quite readily both in the absence and the presence of solvents (cf. *cyclo*hexene), with the isolation, in good yield, of the new compounds 1 : 2-*dinitro*-2 : 4 : 4-*trimethylpentane* (VI) and 1-*nitro*-2 : 4 : 4-*trimethylpentan*-2-*ol* (VIII). The addition of oxygen is unnecessary, the *nitro-octyl nitrite* (VII) being much more stable than the lower homologues, and little nitrate is formed :

$$NO_2\cdot CH_2\cdot CMe(NO_2)\cdot CH_2\cdot CMe_3 \xleftarrow{NO_2\cdot NO_2} CH_2{:}CMe\cdot CH_2\cdot CMe_3 \xrightarrow{ON\cdot O\cdot NO_2}$$

(VI.)

$$NO_2\cdot CH_2\cdot CMe(O\cdot NO)\cdot CH_2\cdot CMe_3 \xrightarrow{H_2O} NO_2\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CMe_3$$

(VII.) (VIII.)

Yields. The total yield of the two products usually exceeds 80% calculated on the octene and dinitrogen tetroxide, the deficiency being practically all accounted for as distillation residues and intermediate fractions. Separate and total yields are given in the table below for three examples :

	(*a*) Addition of theoretical amount of dinitrogen tetroxide to liquid octene.	(*b*) Addition of theoretical amount of dinitrogen tetroxide to octene in ether.	(*c*) Addition of octene to excess of dinitrogen tetroxide in ether.
1 : 2-Dinitro-2 : 4 : 4-trimethylpentane (VI), %	32·1	43·9	52·9
1-Nitro-2 : 4 : 4-trimethylpentan-2-ol (VIII), %	42·5	42·9	31·4
Totals, %	74·6	86·8	84·3

It can be seen that addition of octene to excess of dinitrogen tetroxide favours to a moderate extent the formation of the dinitro-compound. In this case, also, there is a high-boiling residue containing a dinitroheptane fraction (about 5%) indicating some fission of the double bond :

$$CH_2{:}CMe{\cdot}CH_2{\cdot}CMe_3 \xrightarrow{2N_2O_4} CH_2O + (NO_2)_2CMe{\cdot}CH_2{\cdot}CMe_3$$

Characterisation of the products (detailed in the experimental section) was : (VI) by reaction with ammonia to give ammonium nitrite and 1-*nitro*-2 : 4 : 4-*trimethylpent*-1-*ene*, which was identified by oxidative fission to 4 : 4-dimethylpentan-2-one, and (VIII) by reaction with formaldehyde to give 4 : 4-dimethylpentan-2-one and nitrotri(hydroxymethyl)methane.

The nitro-nitrite is relatively stable, and the whole of the crude nitration product from 2 : 4 : 4-trimethylpent-1-ene can be converted into the nitro-olefin by reaction with ammonia or urea in non-aqueous solvents. Solid ammonium nitrite is formed simultaneously when ammonia in dry ether is used, and this reaction affords a simple method for the quantitative preparation of this nitrite, normally difficult to obtain in solid form.

C. 2 : 4 : 4-*Trimethylpent*-2-*ene*.—*General.* There appear to be no references in the literature to the addition of oxides of nitrogen to this olefin. Addition of dinitrogen tetroxide occurs readily both in the presence and in the absence of inert solvents, with the formation of the new substances 2 : 3-*dinitro*-2 : 4 : 4-*trimethylpentane* (IX) and 3-*nitro*-2 : 4 : 4-*trimethylpentan*-2-*ol* (XI), the latter being derived from the *nitro-octyl nitrite* (X) first formed.

$$\underset{\text{(IX.)}}{CH_3{\cdot}CMe(NO_2){\cdot}CH(NO_2){\cdot}CMe_3} \xleftarrow{NO_2{\cdot}NO_2} CH_3{\cdot}CMe{:}CH{\cdot}CMe_3 \xrightarrow{ON{\cdot}O{\cdot}NO_2}$$

$$\underset{\text{(X.)}}{CH_3{\cdot}CMe(O{\cdot}NO){\cdot}CH(NO_2){\cdot}CMe_3} \xrightarrow{H_2O} \underset{\text{(XI.)}}{CH_3{\cdot}CMe(OH){\cdot}CH(NO_2){\cdot}CMe_3}$$

Yields. The yield of once-distilled material usually exceeds 90% though some loss occurs in the final fractionation. In the example described, the yields were :

2 : 3-Dinitro-2 : 4 : 4-trimethylpentane (IX), %	48·2
1-Nitro-2 : 4 : 4-trimethylpentan-2-ol (XI), %	31·7
Dinitropentane, %	3·6
Total, %...	83·5

The small fraction, m. p. 52·5—54·5° (3·6%), corresponded closely on analysis to dinitropentane and may have been formed by fission :

$$CH_3{\cdot}CMe{:}CH{\cdot}CMe_3 \xrightarrow{2N_2O_4} (CH_3)_2C(NO_2)_2 + (NO_2)_2CH{\cdot}CMe_3$$

(IX) was characterised by reaction with alcoholic sodium hydroxide, giving 3-*nitro*-2 : 4 : 4-*trimethylpent*-2-*ene* which was identified by oxidative fission to acetone and pivalic acid. A surprising feature of (IX) is its stability towards hot concentrated aqueous solutions of sodium hydroxide or urea, and it can in fact be separated from the nitro-alcohol (XI) by treatment with hot 2N-sodium hydroxide which reacts with the nitro-alcohol and leaves the dinitro-compound unchanged. However, (IX) does give the nitro-olefin satisfactorily with alcoholic sodium hydroxide or ethoxide. (XI) was characterised by hydrolytic fission with water or aqueous alkali to nitro*neo*pentane and acetone :

$$CH_3{\cdot}CMe(OH){\cdot}CH(NO_2){\cdot}CMe_3 \longrightarrow Me_2CO + CMe_3{\cdot}CH_2{\cdot}NO_2$$

EXPERIMENTAL.

Reagents.—Pure liquid dinitrogen tetroxide and dry ether were prepared in the manner previously described (Part II). *cyclo*Hexene was purified before use by fractional distillation from sodium. The trimethylpentenes were obtained by exhaustive fractional distillation of commercial di*iso*butylene and had the following properties: 2 : 4 : 4-trimethylpent-1-ene, b. p. 101·30°, n_D^{20} 1·4089, temp. of miscibility with equal vol. of aniline 45·7°; 2 : 4 : 4-trimethylpent-2-ene, b. p. 104·90°, n_D^{20} 1·4161, temp. of miscibility with equal vol. of aniline 45·7°.

A. cyclo*Hexene.*

Reaction and Separation Procedure.—*cyclo*Hexene was added dropwise to a stirred solution of the tetroxide in ether (or *vice versa*) during *ca.* 1 hour and the reactants were kept at 0°. Ether and tetroxide were then removed, preferably in the falling-film evaporator described in Part I of this series of papers, and the product was added to water. The nitro-alcohol was extracted from the aqueous layer with ether, dried, and distilled. The insoluble oil was dried and distilled to give *dinitro*cyclo*hexane*, *nitro*cyclo*hexanol* and *nitro*cyclo*hexyl nitrate.* The following are accounts of typical experiments.

(a) *Addition to excess of dinitrogen tetroxide in ether with an oxygen stream.* 30 G. of *cyclo*hexene were added during 1½ hours to a stirred solution of 94 g. of dinitrogen tetroxide in 320 g. of ethyl ether at 0°, together with a slow stream of oxygen. Solvent and excess of the tetroxide were then removed and the product poured into 200 c.c. of water. Reaction was vigorous, the temperature rising to 70°. After being kept overnight, the insoluble oily layer was separated and washed successively with 200, 100, and 100 c.c. of water, leaving 44·5 g. of insoluble oil. The combined aqueous layers were continuously extracted with ether for 60 hours, the extract was dried (Na_2SO_4), the solvent removed, and the residual oil fractionally distilled in a vacuum, to give the following fractions: (i) 11·6 g., b. p. 86—94°/<1 mm.; (ii) 1·0 g., b. p. 110—120°/<1 mm.; and a residue, 1·4 g. Redistillation of the first fraction gave 11·2 g of 2-nitro*cyclo*hexanol, b. p. 90—92° <1 mm. (Found: C, 49·3; H, 7·6; N, 9·7. $C_6H_{11}O_3N$ requires C, 49·7; H, 7·6; N, 9·65%). A portion (19·8 g.) of the insoluble oil was dried by addition to 20 c.c. of benzene and removal of the latter in a vacuum. Fractional distillation then gave 17·8 g. of an oil, b. p. 72—120°/1—2 mm., and 1 g. of unstable residue. Redistillation gave 10·9 g., b. p. 76—110°/<1 mm. (the bulk of which boiled at 96—98/<1 mm.), and 4·4 g. of 1 : 2-*dinitro*cyclo*hexane*, b. p. 110—114°/<1 mm. (Found: C, 40·8; H, 5·4; N, 15·7. $C_6H_{10}O_4N_2$ requires C, 41·4; H, 5·7; N, 16·0%). The fraction, b. p. 76—110°/<1 mm., contained a little nitro*cyclo*hexanol but was largely a mixture of dinitro*cyclo*hexane and 2-nitro*cyclo*hexyl nitrate in 60 : 40 molar ratio, determined by analysis and the nitrite-nitrogen content of the aqueous layer after interaction with alkali.

(b) *Addition of the theoretical amount of dinitrogen tetroxide to* cyclo*hexene in ether with an oxygen stream.* 33·6 G. of dinitrogen tetroxide in 36·4 g. of ether were added in 1½ hours to a stirred solution of 30 g. of *cyclo*hexene in 220 g. of ether at 0°, together with a very slow stream of oxygen. The solvent was then removed and the residual product added to 200 c.c. of water. After being kept overnight, the insoluble layer was separated and washed successively with 200-, 100-, and 100-c.c. portions of water, leaving 27 g. of insoluble oil (cf. above). The combined aqueous layers were extracted with ether, the extract was dried, the solvent evaporated under suction, and the residual oil distilled in a vacuum to give (i) 25·0 g., b. p. 58—98°/<1 mm., (ii) 2·0 g. b. p. 130—140°/<1 mm., and (iii) 2·1 g.(residue). The first fraction was redistilled to give 2·1 g., b. p. <94°/<1 mm. (Found: N, 9·5%), and 18·5 g. of nitro*cyclo*hexanol, b. p. 94°/<1 mm. (Found: C, 49·3; H, 7·7; N, 9·8%). The insoluble oil, when dried as before with benzene and distilled, gave 24·5 g., b. p. 82—140/1—2 mm., and 0·9 g. of residue. Two redistillations gave 5·0 g., b. p. 82—101°/<1 mm. (mainly nitro*cyclo*hexanol), and 15·9 g. of dinitro*cyclo*hexane, b. p. 104°/<1 mm. (Found: N, 15·7%).

Properties and Characterisation of Products.—1 : 2-Dinitro*cyclo*hexane (I) is an almost colourless liquid, b. p. 110°/<1 mm.

Reduction to 1 : 2-*diamino*cyclo*hexane.* 0·604 G. of (I) was reduced to the diamine in 30 c.c. of acetic acid with hydrogen at 100 atm. and in the presence of 0·0240 g. of Adams's platinum catalyst. The solution was filtered and then saturated with hydrogen chloride, and the acetic acid removed under suction, to leave 0·8 g. of residue (Found, on the dihydrochloride after reprecipitation from alcohol with ethyl acetate: Cl, 37·8. Calc. for $C_6H_{14}N_2,2HCl$: Cl, 37·8%). The dipicrate was prepared by adding the dihydrochloride in water to picric acid in water at 50° (Found: C, 37·7; H, 3·5; N, 19·4. Calc. for $C_6H_{14}N_2,2C_6H_3O_7N_3$: C, 37·8; H, 3·5; N, 19·6%).

Formation of 1-*nitro*cyclo*hex*-1-*ene.* 44·5 G. of 1 : 2-dinitro*cyclo*hexane were dissolved in 250 c.c. of ether, and 10·25 g. of sodium hydroxide in 200 c.c. water added slowly with stirring. After being stirred for a further 5 hours, the aqueous layer was removed and acidified with 50% acetic acid, some oil separating. The aqueous layer was then extracted with ether, and the ethereal extract added to the original ethereal layer. Ether was removed under suction, and the residue (31·5 g.) was steam-distilled to give a pale yellow oil. The distillate was extracted 3 times with 100-c.c. portions of ether, and the combined extract dried ($CaCl_2$). Vacuum-distillation gave (i) 18·8 g., b. p. 67—69°/<1 mm., and (ii) 3·2 g., b. p. 69—96/<1 mm. Redistillation gave 17·8 g. of 1-nitro*cyclo*hex-1-ene, b. p. 64°/<1 mm. (Found: C, 56·4; H, 6·9; N, 10·8. Calc. for $C_6H_9O_2N$: C, 56·7; H, 7·1; N, 11·0%), and 3·4 g. of unchanged dinitro*cyclo*hexane; yield of nitro*cyclo*hexene, 59%.

The nitro*cyclo*hexene was reduced to *cyclo*hexanone oxime, m. p. 89° (Wieland and Blumlich, *loc. cit.*), in poor yield with zinc dust and acetic acid (Found: C, 63·7; H, 9·8; N, 12·9. Calc. for $C_6H_{11}ON$: C, 63·7; H, 9·7; N, 12·4%).

2-*Nitro*cyclo*hexanol* (III) is a colourless liquid b. p. 92°/<1 mm. which slowly crystallises when kept. After crystallisation from chloroform containing a little light petroleum it melts at 47—48° (Found: C, 50·3; H, 7·6; N, 9·9. $C_6H_{11}O_3N$ requires C, 49·7; H, 7·6; N, 9·7%).

Formation and deacetylation of 2-*nitro*cyclo*hexyl acetate.* Nitro*cyclo*hexanol (7·25 g.) was acetylated with acetic anhydride (12·2 g.) and concentrated sulphuric acid (two drops). Excess of acetic anhydride was distilled off under reduced pressure, and the residue dissolved in benzene and washed twice with

50-c.c. portions of water. After removal of the solvent, the product was distilled to give 7·3 g. of 2-*nitro*cyclo*hexyl acetate* and on re-distillation, 7·1 g., b. p. 96—97°/<1 mm. (Found: C, 51·0; H, 7·1; N, 7·7. $C_8H_{13}O_4N$ requires C, 51·3; H, 6·95; N, 7·5%). 5·9 G. of the acetate were heated with 0·2 g. of anhydrous potassium carbonate for 30 minutes at 105° and then distilled to give 4·6 g. of a substance, b. p. 62—94°/<1 mm. The distillate was heated for a further 45 minutes at 110° with 0·2 g. of carbonate to complete the reaction, and then distilled, to give 3·4 g. of 1-nitro*cyclo*hex-1-ene, which after redistillation, had b. p. 60—64°/<1 mm. (Found: C, 56·7; H, 7·1; N, 10·7%).

2-*Nitro*cyclo*hexyl nitrate* (IV). From an insoluble oil prepared as in (*a*) a first fraction of nitro*cyclo*hexyl nitrate was obtained on fractional distillation (Found: C, 38·4; H, 5·3. $C_6H_{10}O_5N_2$ requires C, 37·9; H, 5·3%). (IV) is an almost colourless liquid, b. p. 98°/<1 mm. It reacts with alkali, like 1 : 2-dinitro*cyclo*hexane to give 1-nitro*cyclo*hex-1-ene.

*cyclo*Hexene "nitrosite" (V) is a white solid, m. p. 152—153°, after recrystallisation from ethyl acetate (Found: C, 45·4; H, 6·5; N, 17·4. Calc. for $C_6H_{10}O_3N_2$: C, 45·6; H, 6·3; N, 17·6%).

B. 2 : 4 : 4-*Trimethylpent*-1-*ene*.

Reaction and Separation Procedure.—The olefin may be added to excess of pure or dissolved tetroxide, or the theoretical amount of liquid tetroxide may be added to the pure or dissolved olefin. In either case the mixture is cooled and thoroughly stirred. After removal of excess of tetroxide and solvent, the product is treated with water to convert the nitro-octyl nitrite into the nitro-octanol. Owing to the greater stability of the nitrite and the insolubility of the resulting nitro-alcohol, this conversion is completed more slowly than in the case of the lower members. The washed oil is dried and fractionally distilled to isolate the dinitro-octane and the nitro-octanol. Distillation proceeds quite smoothly in contrast to the behaviour noted with the lower olefins when oxygen is omitted. The following are accounts of typical experiments.

(a) *Addition of the olefin to excess of dinitrogen tetroxide in ether.* 332 G. of the olefin were added dropwise during 3 hours to a well-stirred solution of 790 g. of dinitrogen tetroxide in 1830 g. of dry ethyl ether at −5°. Solvent and excess of the tetroxide were then removed and the product, a yellow oil, was stirred with two 600-c.c. portions of water for 20 minutes to hydrolyse the nitro-nitrite. The oil was set aside overnight with water and then separated to give 623 g. of washed oil, or 610 g. after drying by azeotropic distillation with benzene. Fractional distillation of the dried oil gave (i) 31·5 g., b. p. 52—58°/0·5 mm., (ii) 137·9 g., b. p. 58—68°/0·5 mm., (iii) 339·3 g., b. p. 80—130°/<1 mm., and a residue, 54·2 g. Fractions (i) and (ii) were bulked and redistilled to give 162·9 g. (31·4%) of 1-*nitro*-2 : 4 : 4-*trimethylpentan*-2-*ol*, b. p. 58—62°/<1 mm. (Found: C, 56·0; H, 9·8; N, 8·2. $C_8H_{17}O_3N$ requires C, 54·9; H, 9·7; N, 8·0%), and 4·2 g. of residue. Fraction (iii) was redistilled to give (iv) 8·3 g., b. p. 78—94°/<1 mm., (v) 319·7 g., b. p. 94—102°/<1 mm., (vi) 6·2 g., b. p. 102—125°/<1 mm., and 1·6 g. of residue. The main fraction (v) was 1 : 2-*dinitro*-2 : 4 : 4-*trimethylpentane* (52·9%) (Found: C, 47·2; H, 7·8; N, 13·6. $C_8H_{16}O_4N_2$ requires: C, 47·1; H, 7·8; N, 13·7%). The distillation residues (60·0 g.) and intermediate fractions (14·5 g.) would account for 12·3% of the octene if calculated as dinitro-octane. The large residue from the initial distillation of the washed and dried oil distilled completely at 130—135°/<1 mm. and gave a fraction for which analytical figures agreed closely with those for dinitroheptane, indicating some fission of the double bond.

(b) *Addition of the theoretical amount of dinitrogen tetroxide to the olefin in ether.* 246 G. of dinitrogen tetroxide were added dropwise during 5 hours to a solution of 300 g. of the octene in 1800 g. of dry ethyl ether at −5°. The product was worked up in the manner described above to give 200·8 g. (42·9%) of pure 1-nitro-2 : 4 : 4-trimethylpentan-2-ol and 239·8 g. (43·9%) of 1 : 2-dinitro-2 : 4 : 4-trimethylpentane. In this case, the oil distilled to dryness without leaving a high-boiling residue.

(c) *Addition of the theoretical amount of dinitrogen tetroxide to the olefin without a solvent.* 46 G. of dinitrogen tetroxide were added dropwise during 2½ hours to 56 g. of the olefin at −5° with stirring. When worked up, 37·2 g. of the nitro-octanol and 32·7 g. of the dinitro-octane were obtained; yields, 42·5% and 32·1%, respectively, calculated on the octene.

Properties and Characterisation of Products.—1 : 2-Dinitro-2 : 4 : 4-trimethylpentane (VI) is a white crystalline solid, m. p. 19·5°, which distils in a vacuum to give a water-white liquid, b. p. 96°/<1 mm., d_D^{20} 1·126, n_D^{20} 1·464. Like 1 : 2-dinitropropane (Part III, *loc. cit.*), it possesses one asymmetric carbon atom and has a m. p. considerably lower than would be expected of a dinitro-octane. It reacts readily with alkali to give 1-nitro-2 : 4 : 4-trimethylpent-1-ene, oxidative fission of which yields 4 : 4-dimethylpentan-2-one. Interaction of (VI) with aqueous alkali or bases is usually accompanied by some hydrolytic fission of the nitro-olefin; thus N-NaOH gives only a 66% yield, and aqueous urea at 95° only a 54% yield. Ammonium hydrogen carbonate in methyl alcohol gives 4 : 4-dimethylpentan-2-one as main product, but practically quantitative yields of the nitro-olefin are obtained by interaction with ammonia or urea in non-aqueous solvents. Solid ammonium nitrite is formed simultaneously with the nitro-olefin when ammonia in dry ether is used.

Formation of 1-*nitro*-2 : 4 : 4-*trimethylpent*-1-*ene*. 30 G. of the dinitro-octane were dissolved in 250 c.c. of dry ether, and dry ammonia gas passed into the solution till ammonium nitrite ceased to be precipitated. The latter was rapidly filtered off and dissolved in water, and occluded nitro-octene extracted with ether. The extract was dried ($CaCl_2$) and added to the original ethereal solution. Removal of solvent under reduced pressure and distillation of the crude nitro-olefin gave 18·4 g. of 1-*nitro*-2 : 4 : 4-*trimethylpent*-1-*ene*, b. p. 57—59°/<1 mm. (Found: C, 61·0; H, 9·6; N, 9·0. $C_8H_{15}O_2N$ requires C, 61·1; H, 9·6; N, 8·9%), d_4^{20} 0·996, n_D^{20} 1·456, and 3·6 g. of unchanged dinitro-octane.

4 : 4-*Dimethylpentan*-2-*one from nitro-olefin by oxidative fission* ($NO_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CMe_3 \longrightarrow O{:}CMe{\cdot}CH_2{\cdot}CMe_3$). To a solution of 15·34 g. of the nitro-octene in 200 c.c. of acetone, kept at 20°, powdered potassium permanganate was added during 2½ hours and stirring was continued for a further 3½ hours. The permanganate was readily reduced in amount equivalent to 4 atoms of oxygen per molecule of nitro-olefin. The reaction mixture was saturated with carbon dioxide, and manganese

dioxide sludge filtered off. After evaporation of the acetone from the filtrate, distillation gave fractions 1·2 g., b. p. 62—126° (mainly 72°), and 6·3 g., b. p. 126—130° (Found: C, 73·4; H, 12·9. Calc. for $C_7H_{14}O$: C, 73·7; H, 12·3%) [Butlerow (*Annalen*, 1877, **189**, 78) prepared 4 : 4-dimethylpentan-2-one, b. p. 125—130°, by oxidation of 2 : 4 : 4-trimethylpentan-2-ol]. The yield of dimethylpentanone was 50%. The 2 : 4-*dinitrophenylhydrazone* had m. p. 101—102° (Found: C, 52·0; H, 5·8; N, 19·0. $C_{13}H_{18}O_4N_4$ requires C, 52·9; H, 6·4; N, 19·0%).

1-Nitro-2 : 4 : 4-trimethylpentan-2-ol (VIII) is a colourless liquid, b. p. 62°/1 mm., d_4^{20} 0·965, n_D^{20} 1·452. Acetylation with acetyl chloride gives the acetate, b. p. 84°/*ca.* 1 mm.

Reaction with formaldehyde. 3·5 G. of the nitro-alcohol were treated with 1·8 g. of paraformaldehyde in alcohol with the addition of a small pellet of sodium hydroxide. Volatile material was removed by evaporation at 25° in a vacuum and collected in a receiver cooled with solid carbon dioxide–methyl alcohol. The residue, a yellow solid, was recrystallised from ethyl acetate to give 2·8 g. of nitrotri-(hydroxymethyl)methane, m. p. 156° (92·7%). The volatile material, on fractional distillation, gave (i) 0·5 g., b. p. 80—112°, and (ii) 1·64 g., b. p. 128—130° (73·2%) (identified as 4 : 4-dimethylpentan-2-one, previously obtained from 1-nitro-2 : 4 : 4-trimethylpent-1-ene). Reaction was as follows: $3CH_2O + NO_2{\cdot}CH_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CMe_3 \longrightarrow NO_2{\cdot}C(CH_2{\cdot}OH)_3 + Me{\cdot}CO{\cdot}CH_2{\cdot}CMe_3$. Reaction of the nitro-alcohol (VIII) with aqueous sodium hydroxide also gives the ketone.

(iii) *Conversion of the Nitration Product from* 2 : 4 : 4-*Trimethylpent*-1-*ene into* 1-*Nitro*-2 : 4 : 4-*trimethylpent*-1-*ene*.—(a) *With urea.* 53·2 G. dinitrogen tetroxide were added during 4 hours to a solution of 66 g. of the olefin in 366 g. of sodium-dried dioxan at −5° and, after a further 15 minutes' stirring, 53 g. of powdered urea were added. Vigorous reaction set in and the mixture was finally heated at 95—100° for 1¼ hours. After removal of the dioxan, distillation of the residual oil gave two fractions corresponding to nitro-olefin and unchanged dinitro-octane. The latter was therefore treated with a further quantity of urea in dioxan at 95—100° for 3½ hours, the solvent removed, and the oil distilled. A total of 71·7 g. of 1-nitro-2 : 4 : 4-trimethylpent-1-ene was obtained; yield, 77·5% calculated on the olefin.

(b) *With ammonia.* In this case 30 g. of the octene were treated with the equivalent amount of dinitrogen tetroxide in ethyl ether, and gaseous ammonia was passed into the resulting mixture until ammonium nitrite was no longer deposited. When the mixture was worked up in the manner already described for this preparation from the pure dinitro-octane, 33·5 g. of 1-nitro-2 : 4 : 4-trimethylpent-1-ene were obtained; yield, 79·5% calculated on the olefin.

C. 2 : 4 : 4-*Trimethylpent*-2-*ene*.

Reaction and Separation Procedure.—Although the various methods described under (B) may be used in this case, the procedure most used has been the addition of the liquid olefin to excess of tetroxide in ether with stirring and cooling. Removal of excess of the tetroxide and solvent then followed in the usual manner and the product was stirred with water to convert the nitro-nitrite into the nitro-octanol. In this case too, the nitrite is fairly stable in the cold and hydrolysis is not as rapid as with the lower members. The washed oil was dried and fractionally distilled to separate the two main products. Vacuum-distillation proceeded quite smoothly, even when oxygen was not used in the reaction. The following is an account of a typical reaction.

200 G. of the liquid olefin were added dropwise during 3 hours to a well-cooled solution of 476 g. of the tetroxide in 1·1 kg. of dry ethyl ether cooled to 0°. After a further ½ hour's stirring, the solvent and excess of the tetroxide were removed by suction, leaving an almost theoretical yield of crude product. The oil was treated with water in the manner described for the isomeric octene and dried with benzene, to give 348 g. of oil, vacuum-distillation of which yielded a total of 321·3 g. of fractions boiling between 52° and 132° at <1 mm. and only 2·5 g. of residue. The fractions boiling below 105°/1 mm. were bulked and redistilled through a high-efficiency column, to give the fractions: (i) 74·1 g., b. p. 44—52° (mainly 48°)/*ca.* 0·5 mm., (ii) 66·6 g., b. p. 52—56° (mainly 54°)/*ca.* 0·5 mm., (iii) 128·5 g., b. p. 56—74° (mainly 68°)/*ca.* 0·5 mm., and a residue, 8·0 g. Fraction (iii), which set to a semi-crystalline mass, was shown to be 2 : 3-*dinitro*-2 : 4 : 4-*trimethylpentane* (Found: C, 48·4; H, 8·2; N, 13·7. $C_8H_{16}O_4N_2$ requires C, 47·1; H, 7·8; N, 13·7%). Fraction (ii) was treated with warm alkali to separate dinitro-octane and was thereby shown to contain 40·8 g. of 2 : 3-dinitro-2 : 4 : 4-trimethylpentane and 25·8 g. of 3-nitro-2 : 4 : 4-trimethylpentan-2-ol (Found: C, 49·3; H, 7·7; N, 11·3. A mixture of 61·3% of $C_8H_{16}O_4N_2$ and 38·7% of $C_8H_{17}O_3N$ requires C, 50·0; H, 8·4; N, 11·5%). Analytical values for fraction (i) corresponded fairly closely to those for nitro-octanol (Found: C, 55·4; H, 9·3. Calc. for $C_8H_{17}O_3N$: C, 54·9; H, 9·7), but the material was shown on treatment with warm alkali to contain 6·0 g. of dinitro-octane. Total estimated yields were thus 48·2% of dinitro-octane and 31·7% of nitro-octanol, calculated on the olefin. Materials from the first distillation boiling above 105°/1 mm. were bulked and redistilled to give 29·6 g., b. p. 105—132° (mainly 126°)/*ca.* 1 mm., the methyl-alcoholic solution of which deposited, on freezing, 10·4 g. (3·6% calc. on the olefin) of a white crystalline solid, m. p. 52·5—54° (Found: C, 38·2; H, 6·0; N, 16·9. Calc. for $C_5H_{10}O_4N_2$: C, 37·0; H, 6·2; N, 17·3%).

Properties and Characterisation of Products.—2 : 3-Dinitro-2 : 4 : 4-trimethylpentane (IX) is a white crystalline solid m. p. 46°. It distils at 68°/*ca.* 0·5 mm. to give a clear colourless liquid which sets to a crystalline mass. Like the 1 : 2-isomer it has an asymmetric carbon atom and the m. p. is lower than expected.

Formation of 3-*nitro*-2 : 4 : 4-*trimethylpent*-2-*ene*. The dinitro-octane (20·4 g.) was allowed to react with an alcoholic solution of sodium hydroxide (4·4 g.), whereupon the quantitative amount of sodium nitrite was precipitated. This was filtered off, and the alcohol was evaporated from the filtrate under reduced pressure. After acidification with 25% acetic acid, the oil was extracted with ether, the ether removed, and the residue distilled in a vacuum, to give 9·7 g. of 3-*nitro*-2 : 4 : 4-*trimethylpent*-2-*ene*, b. p. 82°/12 mm. (Found: C, 61·0; H, 9·3; N, 10·0. $C_8H_{15}O_2N$ requires C, 61·1; H, 9·6; N, 8·9%). Reduction with zinc and acetic acid gave an oxime (Found: C, 66·7; H, 11·9; N, 10·3. Calc. for $C_8H_{17}ON$: C, 67·1; H, 11·9; N, 9·8%).

Formation of acetone and pivalic acid on oxidative fission of the nitro-olefin [$CH_3·CMe{:}C(NO_2)·CMe_3 \longrightarrow Me_2CO + CMe_3·CO_2H$]. 5·55 G. of the nitro-olefin were heated under reflux for 20 hours with potassium permanganate solution, added at intervals, till the colour just persisted. Manganese dioxide sludge was then filtered off, and the aqueous layer which contained small globules of oil was neutralised and extracted with ether. The extract was dried ($CaCl_2$), the ether removed, and the residue distilled, to give 2·9 g. of a liquid, b. p. 70°/17 mm. (Found : C, 60·6; H, 11·1. Calc. for $C_5H_{10}O_2$: C, 58·8; H, 9·8%) (cf. pivalic acid, b. p. 75—78°/20 mm.). Interaction of the aqueous layer (remaining after the ether-extraction above) with 2 : 4-dinitrophenylhydrazine solution gave a hydrazone, m. p. 127° (Found : C, 46·0; H, 4·4; N, 24·0. Calc. for $C_9H_{10}O_4N_4$: C, 45·4; H, 4·2; N, 23·5%), mixed m. p. with acetone 2 : 4-dinitrophenylhydrazone 128°.

3-Nitro-2 : 4 : 4-trimethylpentan-2-ol (XI) is a colourless liquid, b. p. 48°/*ca.* 0·5 mm.

*Formation of acetone and nitro*neo*pentane on hydrolytic fission.* 41·5 G. of (XI) were stirred with 25 g. of sodium hydroxide dissolved in 200 c.c. of water. On acidification with hydrochloric acid at 0°, a greenish oil separated and was extracted with ether. The extract was dried (Na_2SO_4), the solvent removed under suction, and the residue distilled to give 14·8 g. of nitro*neo*pentane, a colourless liquid, b. p. 146°/760 mm. (Found : C, 51·3; H, 8·7; N, 11·9. Calc. for $C_5H_{11}O_2N$: C, 51·3; H, 9·4; N, 12·0%). Acetone 2 : 4-dinitrophenylhydrazone, m. p. 127°, was obtained from the aqueous layer (Found : C, 45·0; H, 4·5; N, 24·1%).

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