667. *Oxidation of Organic Compounds by Nitrous Oxide. Part II.* Tri- and Tetra-substituted Ethylenes.*

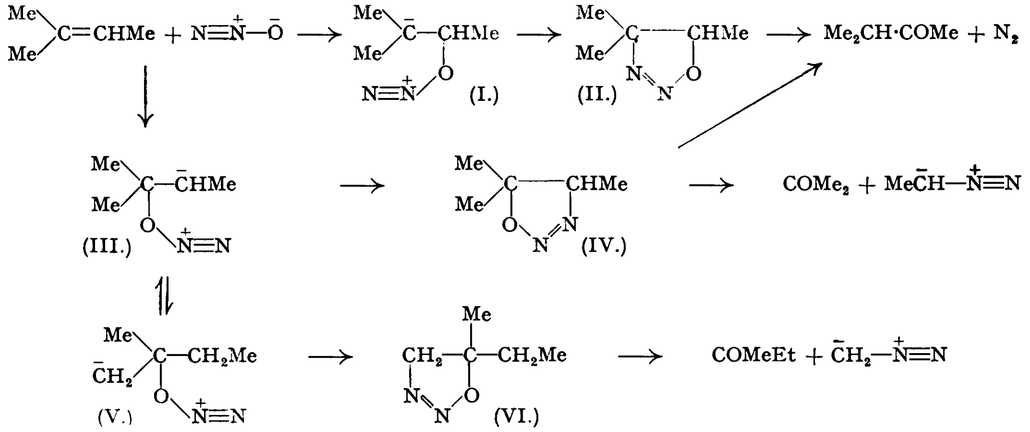
By F. S. Bridson-Jones and G. D. Buckley.

The reaction of nitrous oxide with nine trisubstituted and two tetrasubstituted ethylenes has been studied at 250—300°/100—500 atm. Tri- and tetra-phenylethylenes failed to react, but the remaining examples readily gave carbonyl compounds. The fundamental reactions were the same as with simpler olefins (cf. Part I), but the additional substituents increased the number of possible reactions and resulted in the formation of more complex mixtures of products.

The results were consistent with the reaction mechanism advanced in Part I.

Tri- and tetra-substituted ethylenes, with two exceptions, reacted readily with nitrous oxide at 250—300°/100—500 atm., in many cases with the formation of complex mixtures. It is evident that an olefinic hydrocarbon CHX=CYZ may react with nitrous oxide to form two isomeric 1 : 2 : 3-oxadiazolines, and when X, Y, and Z are all different the *A*-type decomposition (cf. Part I) of the two isomers may lead to three isomeric ketones. Even in the simplest case (X = Y = Z) the simultaneous occurrence of *A*- and *B*-type decompositions may lead to a mixture of several products.

Two examples of the simple cases were studied. Triphenylethylene failed to react with nitrous oxide, but 2-methylbut-2-ene reacted readily. The main product was the expected 3-methylbutan-2-one, which is the only ketone which can be formed by the *A*-type decomposition of either 4 : 5 : 5-(IV) or 4 : 4 : 5-trimethyl-1 : 2 : 3-oxadiazoline (II); small amounts of acetaldehyde, acetone, butan-2-one, ethylene, 1 : 1 : 2-trimethyl*cyclo*propane, and a hydrocarbon, C_7H_{14}, which was probably the unknown 1 : 1 : 2 : 3-tetramethyl*cyclo*propane, were however also formed.



B-Type decomposition of (IV) would lead to the production of acetone and diazoethane. The production of diazoethane may be inferred from the appearance of ethylene, arising by thermal decomposition, and of acetaldehyde and 1 : 1 : 2 : 3-tetramethyl*cyclo*propane, arising from the reaction of diazoethane with nitrous oxide and 2-methylbut-2-ene, respectively.

It is also possible, though less probable, that some of the acetone and acetaldehyde arose from *B*-type decomposition of (II).

All the products, except butan-2-one and 1 : 1 : 2-trimethyl*cyclo*propane, may therefore be accounted for as decomposition products of the two oxadiazolines (II and IV) which would be formed by direct addition of nitrous oxide to the double bond. The presence of butan-2-one and trimethyl*cyclo*propane appears to be explicable only by postulation of the formation of a small amount of 5-ethyl-5-methyl-1 : 2 : 3-oxadiazoline (VI), which like all other 5 : 5-disub-

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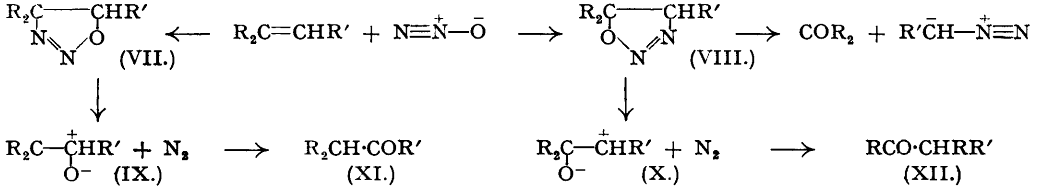
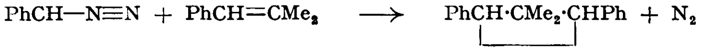
* Part I, preceding paper.

stituted 1 : 2 : 3-oxadiazolines (cf. Part I) would undergo only *B*-type decomposition to give butan-2-one and diazomethane; the diazomethane would then react with 2-methylbut-2-ene to give 1 : 1 : 2-trimethyl*cyclo*propane. (VI) might have been formed by the reaction of nitrous oxide with 2-methylbut-1-ene, but care was taken to ensure that the 2-methylbut-2-ene was free from isomers, and no isomerisation occurs when the olefin is heated alone at 300°. It must therefore be assumed that rearrangement occurs when the olefin is attacked by nitrous oxide. Attack may occur either at the 2- or the 3-position to give (III) and (I), respectively. (I), if it is formed, evidently cyclises to (II), and (III) must largely cyclise normally to (IV). But in order to account for the formation of (VI) it must be assumed that part of (III) isomerises to (V) by migration of a proton from the 1-position to the 3-position, and that (V) then undergoes a normal cyclisation to (VI).

Three examples of the case $Y = Z \neq X$, which can yield two isomeric ketones by *A*-type decomposition of the two isomeric oxadiazolines, were studied.

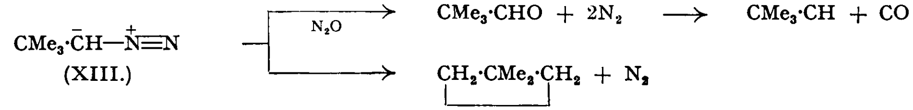


2-Methyl-1-phenylprop-1-ene reacted with nitrous oxide to give 3-phenylbutan-2-one (XII; R = Me, R′ = Ph) and small amounts of *iso*butyrophenone (XI; R = Me, R′ = Ph), acetone, propaldehyde, and 1 : 1-dimethyl-2 : 3-diphenyl*cyclo*propane. It may therefore be inferred that nitrous oxide reacted with the olefin to give mainly 5 : 5-dimethyl-4-phenyl-1 : 2 : 3-oxadiazoline (VIII; R = Me, R′ = Ph), together with a small amount of 4 : 4-dimethyl-5-phenyl-1 : 2 : 3-oxadiazoline (VII; R = Me, R′ = Ph). (VII) evidently underwent only *A*-type decomposition to *iso*butyrophenone, whereas (VIII) underwent both types of decomposition to give 3-phenylbutan-2-one on the one hand and acetone and ω-diazotoluene on the other. The diazo-compound must then have been eliminated by reaction with the olefin:



$$\mathrm{PhCH{-}N{\equiv}N + PhCH{=}CMe_2 \longrightarrow PhCH{\cdot}CMe_2{\cdot}CHPh + N_2}$$

The reaction of nitrous oxide with 2 : 4 : 4-trimethylpent-2-ene and with 4-propylhept-3-ene followed a similar pattern. The carbonyl compounds formed from 2 : 4 : 4-trimethylpent-2-ene were 2 : 2 : 4-trimethylpentan-3-one (XI; R = Me, R′ = Bu^t), acetone, and a trace of propaldehyde; there was also evidence of the presence of a minor amount of a second C_8 ketone which may have been 3 : 4 : 4-trimethylpentan-2-one (XII; R = Me, R′ = Bu^t). It must therefore be assumed that this olefin yields the two isomeric oxadiazolines in approximately equal proportions, and that the 5-*tert.*-butyl-4 : 4-dimethyl-1 : 2 : 3-oxadiazoline breaks down exclusively by reaction *A* to give (XI) whereas the 4-*tert.*-butyl-5 : 5-dimethyl-1 : 2 : 3-oxadiazoline breaks down by both reaction *A* to give (XII) and reaction *B* to give acetone and diazo*neo*pentane (XIII). By analogy with other examples it was thought that (XIII) would react either with the olefin to give 2 : 3-di-*tert.*-butyl-1 : 1-dimethyl*cyclo*propane or with nitrous oxide to give pival-aldehyde, but a careful examination of the reaction products showed that neither of these compounds was present.



However, Conant, Webb, and Mendum (*J. Amer. Chem. Soc.*, **1929**, **51**, 1246) have shown that pivalaldehyde slowly decomposes to carbon monoxide and *iso*butane even at 20°, and both these compounds and also 1 : 1-dimethyl*cyclo*propane were identified among the gaseous products of the nitrous oxide reaction. It must therefore be concluded that the diazo*neo*pentane is eliminated partly by thermal decomposition to nitrogen and 1 : 1-dimethyl*cyclo*propane and partly by reaction with nitrous oxide to give pivalaldehyde which then decomposes at the high temperature.

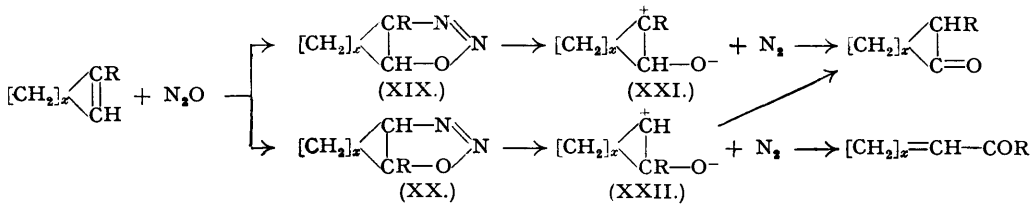
4-Propylhept-3-ene reacted with nitrous oxide to give propaldehyde, heptan-4-one, and a mixture of ketones, $C_{10}H_{20}O$. Degradation of the C_{10} ketones by the Schmidt reaction gave a mixture of amides, $C_{10}H_{21}ON$, which on hydrolysis gave a complex mixture of amines and carboxylic acids. Propylamine, 3-aminohexane, 4-aminoheptane, and butyric acid were identified, and the presence of a higher carboxylic acid was also established. The amide mixture must therefore have contained 3-butyramidohexane (XV), 4-propionamidoheptane (XVI) and 1-α-ethylvaleramidopropane (XIV). The ketones must therefore have been a mixture of 5-ethyloctan-4-one (XVII) and 4-propylheptan-3-one (XVIII).

$$\begin{tikzcd}[column sep=large] & \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHEt{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3}\ \text{(XIV.)} \\ \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHEt{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3}\ \text{(XVII.)} \arrow[ur] \arrow[dr, "\mathrm{N_3H}"'] & \\ & \mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHEt{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3}\ \text{(XV.)} \end{tikzcd}$$

$$\underset{\text{(XVIII.)}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHPr{\cdot}CO{\cdot}CH_2{\cdot}CH_3}} \xrightarrow{\mathrm{N_3H}} \underset{\text{(XVI.)}}{\mathrm{CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CHPr{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_3}}$$

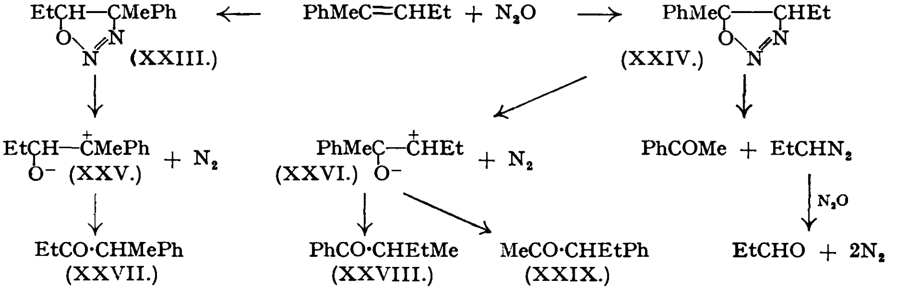
The three examples studied of the case $X{=}Y{\neq}Z$ were all 1-substituted *cyclo*alkenes. 1-Methyl*cyclo*hexene gave approximately equal amounts of 2-methyl*cyclo*hexanone and methyl *cyclo*pentyl ketone, and no other products were detected. 1-Phenyl*cyclo*hexene similarly gave 2-phenyl*cyclo*hexanone and *cyclo*pentyl phenyl ketone, but 1-methyl*cyclo*pentene gave only 2-methyl*cyclo*pentanone.

It is probable that the two isomeric 1 : 2 : 3-oxadiazolines (XIX and XX) were formed in each case, and evidently only *A*-type decomposition occurred.



The intermediate (XXI), arising from the breakdown of (XIX), rearranges to a stable form by migration of the hydrogen anion, but (XXII), arising from the breakdown of (XX), may become stabilised either by migration of the R anion or by ring-contraction. Ring-contraction evidently occurs to a large extent in the *cyclo*hexene series, but cannot occur in the *cyclo*pentene series since it would involve the formation of a highly strained four-membered ring from a strain-free five-membered ring.

One example of the case X ≠ Y ≠ Z was studied. 2-Phenylpent-2-ene reacted with nitrous oxide to give acetophenone, propaldehyde, and a small amount of one or more ketones, $C_{11}H_{14}O$. It must therefore be supposed that the main initial reaction was the formation of 4-ethyl-5-methyl-5-phenyl-1 : 2 : 3-oxadiazoline (XXIV), but it is possible that the isomeric 5-ethyl-4-methyl-4-phenyl-1 : 2 : 3-oxadiazoline (XXIII) was also formed to a minor extent. It is presumed that (XXIII) broke down by reaction *A* to give nitrogen and (XXV), and that (XXIV) broke down partly by reaction *A* to give nitrogen and (XXVI) but mainly by reaction *B* to give acetophenone and 1-diazopropane which was then oxidised to propaldehyde. (XXV) would then rearrange to 2-phenylpentan-3-one (XXVII) by migration of the hydrogen anion, and (XXVI) would rearrange either to α-methylbutyrophenone (XXVIII) by migration of the methyl anion or to 3-phenylpentan-2-one (XXIX) by migration of the phenyl anion.



Tetrasubstituted ethylenes may give rise to mixtures which are simpler or more complex than those derived from trisubstituted ethylenes according as the substituents are all the same or are different. In the two examples studied the four substituents were identical. Tetraphenylethylene failed to react with nitrous oxide, but 2 : 3-dimethylbut-2-ene readily gave 3 : 3-dimethylbutan-2-one; in addition a trace of propaldehyde was found, but no acetone. Tetramethyl-1 : 2 : 3-oxadiazoline therefore decomposes almost exclusively by the *A*-type reaction.

$$CMe_2{=}CMe_2 + N_2O \longrightarrow CMe_3{\cdot}COMe + N_2$$

The results now described are entirely consistent with the theory of the reaction mechanism advanced in Part I and it becomes possible to formulate tentative generalisations which enable the course of the reaction to be predicted in certain cases.

Since no formaldehyde was detected amongst the products of the reaction of nitrous oxide with any olefin it is evident that substitution in position 5 of the oxadiazoline ring is a necessary, though not a sufficient, condition for the occurrence of *B*-type decomposition. Thus *iso*butyl vinyl ether yields exclusively *iso*butyl formate with no detectable amount of *iso*butyl acetate, but propylene yields a trace only of acetaldehyde, and hept-1-ene yields approximately equimolecular amounts of hexanal and heptan-2-one. On the other hand 5 : 5-disubstituted oxadiazolines decompose only by the *B*-type reaction. Furthermore, 5 : 5-disubstituted oxadiazolines only must be formed from 1 : 1-disubstituted ethylenes, since in no case have there been found reaction products which could arise only by decomposition of 4 : 4-disubstituted oxadiazolines.

With trisubstituted ethylenes the point of attachment of the oxygen atom is in most cases predominantly the tertiary carbon, resulting in the formation of 4 : 5 : 5-trisubstituted oxadiazolines which decompose predominantly by the *A*-type reaction with migration of one of the 5-substituents.

Tetramethyl-1 : 2 : 3-oxadiazoline decomposes almost entirely by the *A*-type reaction with migration of one of the methyl groups.

It may therefore be concluded that the presence of an alkyl group in the 5-position favours *B*-type decomposition and that the magnitude of this effect is increased by a second alkyl group in the 5-position and diminished by an alkyl group in the 4-position.

This work is the subject of B.P. Applns. 24780/48, 822/49, and 19509/49.

EXPERIMENTAL.

(Microanalyses are by Dr. A. F. Colson. All m. p.s are corrected.)

Reaction of Olefins with Nitrous Oxide.—The apparatus and procedure are described in Part I.

2-*Methylbut-2-ene*. The olefin was prepared by dehydration of *tert.*-amyl alcohol with 35% (*v*/*v*) sulphuric acid, and purified by fractional distillation through a 50-plate column packed with stainless-steel gauze rings. This gave pure 2-methylbut-2-ene, b. p. 38·2—38·5°, n_D^{20} 1·3872; the infra-red absorption spectrum of the vapour was identical with that given in the " Catalogue of Selected Infra-Red Absorption Spectrograms " (Amer. Petr. Inst. Research Project 44, Nat. Bur. Standards).

The olefin was treated with nitrous oxide at 300°/500 atm. for 4 hours. After the vessel had been cooled to 20° the pressure was released and the gases were passed through a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, a calcium chloride drying tower, and finally a trap cooled in liquid air. The non-condensable gases consisted almost entirely of nitrogen. The contents of the liquid-air trap were vaporised and examined by infra-red spectrography in a gas cell at 34 cm. pressure. They consisted mainly of nitrous oxide, but the presence of 1·5% of ethylene was established by comparison of the optical density of the 10·5-μ band with the values given by mixtures of known composition.

A precipitate which formed in the 2 : 4-dinitrophenylhydrazine solution was collected, crystallised from glacial acetic acid, and identified as acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°.

The combined liquid products from a series of experiments (120 c.c.) were fractionally distilled, and gave fractions : (i) b. p. 20—30°, 1 c.c. ; (ii) b. p. 30—45°, 21 c.c. ; (iii) b. p. 45—54°, 7·5 c.c. ; (iv) b. p. 54—79°, 5·5 c.c. ; (v) b. p. 79—80°, 6 c.c. ; (vi) b. p. 80—94°, 4 c.c. ; and (vii) b. p. 94—95°, 45 c.c. ; there remained a small high-boiling residue which was not further investigated. Fraction (i) contained acetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°). Fraction (v) was water-soluble and consisted mainly of butan-2-one (semicarbazone, m. p. and mixed m. p. 137·5—139·5°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 110—111°). Fraction (vii) had n_D^{20} 1·3915, and was identified as 3-methylbutan-2-one (*p*-nitrophenylhydrazone, m. p. 107°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 121—122°).

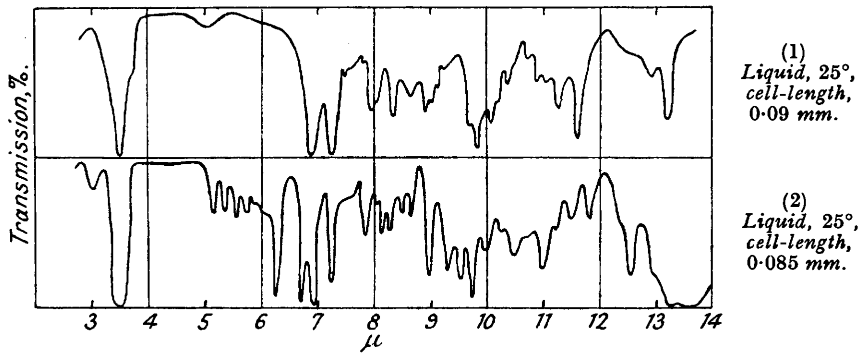
Fractions (ii)—(iv) were not completely water-soluble, but fraction (iii) was shown to contain acetone (dibenzylideneacetone, m. p. and mixed m. p. 109·5°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed

m. p. 124°). The three fractions were combined and washed with water and then with sodium hydrogen sulphite until free from carbonyl compounds. The residual oil (12 c.c.) was dried (CaCl$_2$) and fractionally distilled to give fractions (*a*) b. p. 34—37°, 3·9 c.c.; (*b*) b. p. 37—50°, 3·1 c.c.; (*c*) b. p. 50—53°, 2·85 c.c.; (*d*) b. p. 53—76°, 1·35 c.c.; and (*e*) b. p. 76—81°, 0·65 c.c.

Fraction (*a*) had n_D^{20} 1·3832, and was essentially unchanged 2-methylbut-2-ene. Fraction (*c*) had n_D^{20} 1·3835 and consisted of 1 : 1 : 2-trimethyl*cyclo*propane (Found: C, 85·8; H, 14·1. Calc. for C_6H_{12}: C, 85·7; H, 14·3%) (Kishner, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 169, gives b. p. 52·8°, n_D^{20} 1·3866). The infra-red absorption spectrum of the vapour was identical with that of 1 : 1 : 2-trimethyl*cyclo*propane (Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482). Fraction (*e*) had n_D^{20} 1·3975 and was probably 1 : 1 : 2 : 3-*tetramethyl*cyclo*propane* (Found: C, 85·3; H, 14·7. C_7H_{14} requires C, 85·7; H, 14·3%). Its infra-red absorption spectrum (see figure) did not agree with the spectrum of any known *cyclo*propane derivative, but the occurrence of prominent absorptions at 9·83 and 7·26 μ were consistent with the material being a *cyclo*propane derivative with a high methyl-group content.

2 : 4 : 4-*Trimethylpent*-2-*ene*. The olefin (40 c.c.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. The vessel was then cooled, the pressure released, and the gaseous products passed through a series of traps cooled in liquid air. The non-condensable gases (4·89 l. at N.T.P.) were analysed in a constant volume gas analysis apparatus (Gooderham, *J. Soc. Chem. Ind.*, 1938, **57**, 388) and found to contain nitrogen (94·5%) and carbon monoxide (3·47%) together with traces of carbon dioxide, oxygen, and hydrogen.

The traps were then allowed to warm to −60° and kept at this temperature until no more gas was evolved; the gas consisted only of nitrous oxide and nitrogen. The residue in the traps was combined with the contents of the reaction vessel and fractionally distilled to give fractions: (i) b. p. −10°—+21°; (ii) b. p. 21—47°, 0·2 c.c.; (iii) b. p. 47—50°, 1 c.c.; (iv) b. p. 50—57°, 3·5 c.c.; (v) b. p. 57—95°, 1·3 c.c.; (vi) b. p. 95—132°, 5·3 c.c.; (vii) b. p. 132—138°, 6·4 c.c.; and (viii) b. p. 138—158°, 4·9 c.c.; there remained a small high-boiling residue.



(1) 1 : 1 : 2 : 3-*Tetramethyl*cyclo*propane*. (2) 1 : 1-*Dimethyl*-2 : 3-*diphenyl*cyclo*propane*.

Fraction (i) was collected as a gas (420 c.c. at N.T.P.), and found by infra-red spectrography to contain approximately 40% by volume of nitrous oxide, 26% of 1 : 1-dimethyl*cyclo*propane, and 35% of *iso*butane.

Fraction (iii) contained propaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 154—155°); fraction (iv) was mainly acetone (dibenzylidene derivative, m. p. and mixed m. p. 111—112°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 123—124°); and fraction (vi) was largely unchanged olefin.

Fraction (vii) had n_D^{20} 1·4081 and its infra-red absorption spectrum showed a prominent band at 5·81 μ, indicative of the carbonyl group (Found: C, 75·0; H, 12·6. Calc. for $C_8H_{16}O$: C, 75·0; H, 12·5%). It was identified as 2 : 2 : 4-trimethylpentan-3-one [semicarbazone, m. p. 135—136°; 2 : 4-dinitrophenylhydrazone, m. p. 159° (Found: C, 54·5; H, 6·0; N, 18·4. Calc. for $C_{14}H_{20}O_4N_4$: C, 54·55; H, 6·5; N, 18·2%) (Locquin and Leers, *Compt. rend.*, 1924, **179**, 55, give m. p. 132° for the semicarbazone; Byers and Hickinbottom, *J.*, 1948, 284, give m. p. 163—164° for the 2 : 4-dinitrophenylhydrazone)]. Reduction of the ketone with sodium and alcohol gave 2 : 2 : 4-trimethylpentan-3-ol, b. p. 145—148°, n_D^{20} 1·4289 (Found: C, 74·2; H, 14·0. Calc. for $C_8H_{18}O$: C, 73·85; H, 13·85%). This was characterised as the phenylurethane, m. p. 75·5—76·5° (Found: N, 5·7. Calc. for $C_{15}H_{23}O_2N$: N, 5·6%), and the 3 : 5-*dinitrobenzoate*, m. p. 101—102° (Found: N, 8·7. $C_{15}H_{20}O_6N_2$ requires N, 8·65%) (Whitmore and Houk, *J. Amer. Chem. Soc.*, 1932, **54**, 3714, give b. p. 148—150°, n_D^{20} 1·4288, for the alcohol; Haller and Bauer, *Compt. rend.*, 1910, **150**, 584, give m. p. 79° for the phenylurethane).

Fraction (viii) appeared to be a mixture of C_8 ketones (Found: C, 74·9; H, 12·4. $C_8H_{16}O$ requires C, 75·0; H, 12·5%). Attempts to prepare derivatives gave only oils or mixtures of indefinite melting point.

2-*Methyl*-1-*phenylprop*-1-*ene*. A solution of the olefin (19 c.c.) in *cyclo*hexane (20 c.c.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. The product was distilled to give fractions: (i) b. p.

<52·5°, 1 c.c.; (ii) b. p. 52·5—53°, 1·4 c.c.; (iii) b. p. 53—79°, 2 c.c.; (iv) b. p. 79—83°, 18·6 c.c.; (v) b. p. <82°/3 mm., 1·3 c.c.; (vi) b. p. 82—87°/3 mm., 1·9 c.c.; (vii) b. p. 87—125°/3 mm., 0·7 c.c.; and (viii) b. p. 125—170°/3 mm., 4·2 c.c.; a small residue remained.

Fraction (i) contained propaldehyde (dimethone, m. p. and mixed m. p. 155°); fraction (ii) was essentially acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 123—124°); and fraction (iv) was unchanged *cyclo*hexane.

Fraction (vi) was a C_{10} ketone (Found : C, 80·7; H, 7·8. Calc. for $C_{10}H_{12}O$: C, 81·1; H, 8·1%). It was shown to be a methyl ketone by the iodoform reaction, and was characterised as the semicarbazone, m. p. 170—171° after repeated recrystallisation from ethanol (Found : N, 20·4. Calc. for $C_{11}H_{15}ON_3$: N, 20·5%). Darzens (*Compt. rend.*, 1905, **141**, 768) gives m. p. 172—173° for 3-phenylbutan-2-one semicarbazone. A portion of fraction (vi) was treated several times with alkaline sodium hypochlorite solution; most of the ketone reacted, but after separation of the oil and removal of the chloroform there remained a small amount of oil, which reacted with semicarbazide to give *iso*butyrophenone semicarbazone, m. p. 181—182° (depressed on admixture with the semicarbazone, m. p. 170—171°, above) (Found : N, 20·3. Calc. for $C_{11}H_{15}ON_3$: N, 20·5%).

The infra-red absorption spectrum of fraction (viii) showed that it contained carbonyl compounds. After removal of these by reaction with Girard's reagent P, the residual oil was redistilled to give 1 : 2-*dimethyl*-2 : 3-*diphenyl*cyclo*propane*, b. p. 102—112°/3·5 mm., n_D^{20} 1·5502 (Found : C, 92·3; H, 7·8. $C_{17}H_{18}$ requires C, 91·9; H, 8·1%). Its infra-red absorption spectrum (see figure) showed strong absorptions at 6·26, 7·26, and 9·74 μ which were consistent with the material's being a methylphenyl*cyclo*propane.

4-*Propylhept*-3-*ene*. The olefin (40 c.c.), prepared by Church, Whitmore, and McGrew's method (*J. Amer. Chem. Soc.*, 1934, **56**, 176), was treated with nitrous oxide at 300°/525 atm. for 4 hours. Distillation of the product gave fractions : (i) b. p. 50—53°, 0·3 c.c.; (ii) b. p. 53—145°, 3·7 c.c.; (iii) b. p. 145—145·5°, 5 c.c.; (iv) b. p. <95°/30 mm., 6 c.c.; (v) b. p. 95—96·5°/30 mm., 13·3 c.c.; and (vi) b. p. 96·5—160°/30 mm., 2 c.c.

Fraction (i) was identified as propaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 150—151°); fraction (iii) had n_D^{20} 1·4090 and was identified as heptan-4-one (semicarbazone, m. p. 135·5°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 74—75°); and fraction (iv) contained unreacted olefin.

Fraction (v) had n_D^{20} 1·4243 and was a mixture of C_{10} ketones (Found : C, 77·3; H, 12·8. Calc. for $C_{10}H_{20}O$: C, 76·9; H, 12·8%). Its infra-red absorption spectrum showed a strong band at 5·81 μ, indicative of the carbonyl group, but all attempts to prepare crystalline derivatives with the usual reagents were unsuccessful. The ketone (7 g.) was therefore dissolved in chloroform (100 c.c.) and cooled to 0°; concentrated sulphuric acid (35 c.c.) was added to the stirred solution at 0—10°, followed by sodium azide (2·8 g.). After the mixture had been stirred at 20° for 1 hour it was poured on ice, and the chloroform solution was separated, washed with water, and evaporated. The semi-solid residue (4·7 g.) was hydrolysed by heating it in a sealed tube with concentrated hydrochloric acid at 190—200° for 12 hours. The mixture was diluted with water and extracted with ether; after the extract had been dried ($CaCl_2$) the ether was removed by distillation and the residue distilled under reduced pressure to give two main fractions. One of these, b. p. 55—69°/15 mm., formed *p*-bromophenacyl butyrate, m. p. and mixed m. p. 60—61° after repeated recrystallisation from ethanol. The second fraction, b. p. 109—115°/15 mm., was soluble in dilute aqueous sodium hydroxide, but attempts to prepare crystalline derivatives were unsuccessful (Found : equiv., 131. Calc. for $C_7H_{14}O_2$: equiv., 130).

The amines were isolated from the hydrochloric acid solution by treatment with sodium hydroxide and extraction with ether. The ethereal solution was dried (KOH) and fractionally distilled to give two basic fractions. One of these, which passed over with the ether, was treated with 2 : 4-dinitrophenylnitrourea; repeated recrystallisation of the product from ethanol gave *N*-2 : 4-dinitrophenyl-*N'*-propylurea as long yellow needles, m. p. 147° not depressed on admixture with an authentic specimen (Found : C, 44·9; H, 4·4; N, 20·8. Calc. for $C_{10}H_{12}O_5N_4$: C, 44·75; H, 4·45; N, 20·9%). The second fraction, b. p. 121—130°, reacted with phenyl *iso*cyanate to give a mixture of ureas; crystallisation of the mixture from methanol gave N-*phenyl*-N'-1-*propylbutylurea*, m. p. 137—138° not depressed on admixture with an authentic specimen (see below) (Found : C, 71·3; H, 9·1; N, 11·8. $C_{14}H_{22}ON_2$ requires C, 71·8; H, 9·4; N, 11·95%). The alcoholic mother liquors were evaporated to dryness and the residue crystallised from light petroleum (b. p. 60—80°) to give N-1-*ethylbutyl*-N'-*phenylurea*, m. p. 78° not depressed on admixture with an authentic specimen (see below) (Found : C, 70·8; H, 9·0; N, 12·3. $C_{13}H_{20}ON_2$ requires C, 70·9; H, 9·1; N, 12·75%). The base reacted with 2 : 4-dinitrophenylnitrourea to form a derivative which after repeated recrystallisation from ethanol gave N-2 : 4-*dinitrophenyl*-N'-1-*propylbutylurea*, m. p. 129—130° not depressed on admixture with an authentic specimen (see below).

An authentic specimen of 3-aminohexane, prepared by hydrogenation of hexan-3-one oxime, had b. p. 116—118°. With phenyl *iso*cyanate it gave *N*-1-ethylbutyl-*N'*-phenylurea (from light petroleum), m. p. 79° (Found : N, 12·8. Calc. for $C_{13}H_{20}ON_2$: N, 12·75%). It also reacted with 2 : 4-dinitrophenylnitrourea to give N-2 : 4-*dinitrophenyl*-N'-1-*ethylbutylurea*, small yellow needles (from a small volume of ethanol), m. p. 130·5—131° (Found : C, 50·2; H, 5·8; N, 17·7. $C_{13}H_{18}O_5N_4$ requires C, 50·3; H, 5·8; N, 18·05%).

An authentic specimen of 4-aminoheptane, prepared by hydrogenation of heptan-4-one oxime, had b. p. 134—136°. With phenyl *iso*cyanate it gave *N*-phenyl-*N'*-1-propylbutylurea, needles (from ethanol), m. p. 137—138° (Found : N, 11·8. Calc. for $C_{14}H_{22}ON_2$: N, 11·95%). Reaction with 2 : 4-dinitrophenylnitrourea gave *N*-2 : 4-dinitrophenyl-*N'*-1-propylbutylurea, yellow needles (from ethanol), m. p. 130° (Found: C, 51·6; H, 5·9; N, 17·3. $C_{14}H_{20}O_5N_4$ requires C, 51·85; H, 6·15; N, 17·3%).

1-*Methyl*cyclo*pentene*. The olefin (35 c.c.) was treated with nitrous oxide at 300°/350—700 atm. for 3 hours. The product was distilled with steam, and the volatile oil was separated, dried ($CaCl_2$), and distilled to give fractions: (i) b. p. 72—90°, 3·2 c.c.; (ii) b. p. 90—133°, 2·6 c.c.; (iii) b. p. 133—138·5°, 1·4 c.c.; (iv) b. p. 138·5—139°, 6·1 c.c.; and (v) b. p. 139—152°, 1·6 c.c.

Fraction (i) was mainly unchanged olefin. Fraction (iv) had n_D^{20} 1·4320, and was identified as 2-methyl*cyclo*pentanone (Found: C, 72·8; H, 10·4. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·2%) [2 : 4-*dinitrophenylhydrazone*, m. p. 155—157° (Found: C, 51·8; H, 5·3. $C_{12}H_{14}O_4N_4$ requires C, 51·8; H, 5·05%); semicarbazone, m. p. 180° (Found: N, 27·1. Calc. for $C_7H_{13}ON_3$: N, 27·1%)]. Van Rysselberge (*Bull. Acad. roy. Belg.*, 1926, **11**, 171) gives b. p. 139·5°, n_D^{20} 1·4347, for 2-methyl*cyclo*pentanone, and m. p. 184° for its semicarbazone.

Fractions (iii) and (v) also consisted largely of 2-methyl*cyclo*pentanone.

1-*Methyl*cyclo*hexene*. The olefin was treated with nitrous oxide at 300°/500 atm. for 5 hours, and the products from several experiments (243 g.) were combined and distilled to give fractions: (i) b. p. 105—115°, 81 c.c.; (ii) b. p. 115—157·5°, 11 c.c.; (iii) b. p. 157·5°, 17·5 c.c.; (iv) b. p. 157·5—162°, 29 c.c.; (v) b. p. 162—162·5°, 12·5 c.c.; (vi) b. p. 162·5—165°, 12·5 c.c.; (vii) b. p. 165°, 36 c.c.; and (viii) b. p. 165—210°, 19 c.c.

Fraction (i) was mainly unchanged olefin. Fractions (iii)—(vi) were shown to contain a methyl ketone by the iodoform reaction, and fraction (iii) reacted with semicarbazide to give methyl *cyclo*pentyl ketone semicarbazone, m. p. and mixed m. p. 144—145·5°, and with 2 : 4-dinitrophenylhydrazine to give the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 122·5—124°. Fraction (vii), which had n_D^{20} 1·4480, was identified as 2-methyl*cyclo*hexanone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 137—138°).

Comparison of the infra-red absorption spectra of fractions (iii)—(vii) with those of synthetic mixtures showed that the two ketones were present in the following proportions:

Fraction:	(iii)	(iv)	(v)	(vi)	(vii)
Methyl *cyclo*pentyl ketone, %	84	76	50	29	0
2-Methyl*cyclo*hexanone, %	16	24	50	71	100

1-*Phenyl*cyclo*hexene*. The olefin (40 c.c.) was treated with nitrous oxide at 300°/500 atm. for 3 hours, and the combined products from four experiments (165 g.) were distilled *in vacuo*. The material boiling up to 200°/2 mm. (114·5 g.) was distilled to give fractions: (i) b. p. <84°/2 mm., 5·3 c.c.; (ii) b. p. 84°/2 mm., 15 c.c.; (iii) b. p. 84—102·5°/2 mm., 15 c.c.; (iv) b. p. 102·5—107·5°/2 mm., 37 c.c.; (v) b. p. 107·5—123°/2 mm., 6·5 c.c.; and (vi) b. p. 123°/2 mm., 5·3 c.c.

Fraction (ii) was substantially pure 1-phenyl*cyclo*hexene, and fractions (i) and (iii) also contained considerable amounts of the olefin. Fraction (iv) had n_D^{20} 1·5426 and was identified as cyclo*pentyl phenyl ketone* (Found: C, 83·0; H, 8·7. $C_{12}H_{14}O$ requires C, 82·75; H, 8·05%) [p-*nitrophenylhydrazone*, m. p. 98° (Found: C, 70·0; H, 6·0; N, 13·6. $C_{18}H_{19}O_2N_3$ requires C, 69·9; H, 6·15; N, 13·6%); 2 : 4-*dinitrophenylhydrazone*, m. p. 143—144° (Found: N, 15·6. $C_{18}H_{18}O_4N_4$ requires N, 15·8%)]. Its structure was confirmed by degradation. Concentrated sulphuric acid (48 c.c.) was added to a stirred, ice-cooled solution of the ketone (12 g.) in chloroform (140 c.c.). Sodium azide (6 g.) was then added at 0—5° during 30 minutes. After a further 30 minutes' stirring the mixture was poured on ice, and the chloroform layer separated and washed with dilute sodium carbonate solution and with water. The chloroform was removed by distillation and the residue washed with pentane and crystallised from aqueous ethanol. This gave an amide (7·5 g.), m. p. 142—145°, which on further purification by solution in concentrated hydrochloric acid, and fractional precipitation by gradual addition of water, gave *N-cyclo*pentylbenzamide, m. p. and mixed m. p. 158—159°. The low m. p. of the crude amide was presumably attributable to the presence of a little of the isomeric *N*-phenyl*cyclo*pentanecarboxyamide, but its presence was not proved. Hydrolysis of the crude amide with concentrated hydrochloric acid at 200° gave as the main products benzoic acid, m. p. and mixed m. p. 122·5°, and *cyclo*pentylamine [*picryl* derivative, m. p. and mixed m. p. 105° (Found: N, 19·3. $C_{11}H_{12}O_6N_4$ requires N, 18·9%)].

Fraction (vi) was a solid which crystallised from light petroleum (b. p. 60—80°) to give 2-phenyl*cyclo*hexanone, m. p. 57° (Found: C, 82·7; H, 8·0. Calc. for $C_{12}H_{14}O$: C, 82·75; H, 8·05%) [oxime, m. p. 169° (Found: N, 7·35. Calc. for $C_{12}H_{15}ON$: N, 7·4%); semicarbazone, m. p. 179—181° (Found: N, 18·1. Calc. for $C_{13}H_{17}ON_3$: N, 18·2%)].

2-*Phenylpent*-2-*ene*. A solution of the olefin (20 c.c.) in *cyclo*hexane (20 c.c.) was treated with nitrous oxide at 280°/350 atm. for 4 hours. The product was fractionally distilled and in addition to *cyclo*hexane and unchanged olefin two main fractions were obtained. One of these, b. p. *ca.* 50°, was shown to contain propaldehyde [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 155° (Found: N, 24·0. Calc. for $C_9H_{10}O_4N_4$: N, 23·6%)]. The other fraction, b. p. 68—74°/10 mm., was identified as acetophenone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 241—243·5°).

A small ketonic fraction, b. p. 85°/3 mm., was also obtained (Found: C, 81·6; H, 8·1. Calc. for $C_{11}H_{14}O$: C, 81·5; H, 8·65%). It formed a semicarbazone which, after recrystallisation from ethanol, had m. p. 183° (Found: N, 19·5. Calc. for $C_{12}H_{17}ON_3$: N, 19·2%).

2 : 3-*Dimethylbut*-2-*ene*. The olefin (40 c.c.) was treated with nitrous oxide at 300°/500 atm. for 4 hours, and the product distilled to give fractions: (i) b. p. 48—50°, 1 c.c.; (ii) b. p. 50—71°, 1·1 c.c.; (iii) b. p. 71—72°, 2·9 c.c.; (iv) b. p. 72—110°, 2 c.c.; and (v) b. p. 110—110·5°, 24 c.c.

Fraction (i) was identified as propaldehyde (dimethone, m. p. and mixed m. p. 153°); fraction (iii) was unchanged olefin; and fraction (v) was 2 : 2-dimethylbutan-3-one (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 125·5°; semicarbazone, m. p. and mixed m. p. 156—157°). No other products were detected.

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