666. *Oxidation of Organic Compounds by Nitrous Oxide. Part I.**

By F. S. BRIDSON-JONES, G. D. BUCKLEY, L. H. CROSS, and A. P. DRIVER.

Nitrous oxide fails to react with most types of organic compound at 200—350° and pressures up to 2000 atm., but oxidises benzaldehyde to benzoic acid, and certain secondary aromatic alcohols to the corresponding ketones.

Olefins are readily oxidised to carbonyl compounds, the reactions being of three types :

(i) Oxidation at the double bond to give a carbonyl compound containing the same number of carbon atoms as the original olefin.

$$CR^1R^2{=}CR^3R^4 + N_2O \longrightarrow CR^1R^2R^3{\cdot}CO{\cdot}R^4 + N_2$$

(ii) Oxidative fission at the double bond to give two carbonyl compounds.

$$CR^1R^2{=}CR^3R^4 + 2N_2O \longrightarrow CR^1R^2{=}O + CR^3R^4{=}O + 2N_2$$

(iii) Reaction of two molecules of the olefin with one molecule of nitrous oxide to give one molecule of a carbonyl compound and one molecule of a *cyclo*propane derivative.

$$2CR^1R^2{=}CR^3R^4 + N_2O \longrightarrow CR^1R^2{=}O + R^1R^2C\left\langle\begin{matrix}CR^3R^4\\ |\\ CR^3R^4\end{matrix}\right. + N_2$$

Ethylene, and monosubstituted and 1 : 2-disubstituted ethylenes react mainly according to reaction (i), but in many cases reactions (ii) and (iii) also occur to some extent. 1 : 1-Disubstituted ethylenes, except methylene*cyclo*butane, react exclusively according to reaction (iii).

The initial step in the reaction of nitrous oxide with an olefin is believed to be addition of the nitrous oxide to the double bond to form a Δ^2-1 : 2 : 3-oxadiazoline which then undergoes decomposition either to give nitrogen and a carbonyl compound containing the same number of carbon atoms as the original olefin or to give an aliphatic diazo-compound and a carbonyl compound containing a smaller number of carbon atoms than the olefin. When the diazo-compound produced is diazomethane or ω-diazotoluene it reacts with a second molecule of the olefin to form a *cyclo*propane derivative, but when it is a higher diazoparaffin it reacts with a second molecule of nitrous oxide to give a carbonyl compound.

NITROUS OXIDE supports the combustion of hydrocarbons, ethers, and alcohols yielding nitrogen, carbon dioxide, and water, and in some cases the inflammability limits have been determined, but no attempt appears to have been made to use the gas as an agent for the controlled oxidation of organic compounds under milder conditions.

The action of nitrous oxide on a wide range of organic compounds at 200—400° and pressures up to 2000 atm. has now been studied. Under these conditions no reaction occurred with paraffins and *cyclo*paraffins (*n*-hexane, *cyclo*hexane, methyl*cyclo*hexane, methyl*cyclo*pentane), aromatic hydrocarbons (benzene, toluene, diphenylmethane, anthracene, phenanthrene), amines (aniline, dimethylaniline, triethylamine, pyridine), esters (ethyl acetate, ethyl malonate), azobenzene, deoxybenzoin, benzophenone, benzil, and furan. Acetanilide, acetylacetone, and dimedone gave tars, presumably owing largely to their own thermal instability. Of the alcohols tried, ethanol and benzyl alcohol were recovered unchanged, but benzhydrol gave a small yield of benzophenone in 4 hours at 300° and 400—500 atm., the remainder of the alcohol being recovered unchanged. Under similar conditions benzoin gave an 18% yield of benzil.

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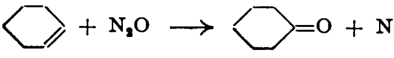
* Brief accounts of this and the succeeding two papers were presented to the International Congress of Pure and Applied Chemistry at New York, September, 1951.

Olefins, on the other hand, reacted readily with nitrous oxide at 250—300° and 100—500 atm. giving carbonyl compounds, the reactions being mainly of three types :

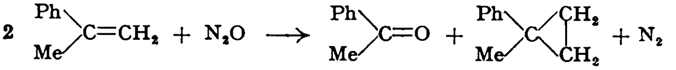
(i) Oxidation at the double bond to an aldehyde or ketone containing the same number of carbon atoms as the original olefin, *e.g.*,



(ii) Oxidative fission at the double bond to give two molecules of carbonyl compound, *e.g.*,

$$CH_3{\cdot}CH{=}CH{\cdot}CH_2{\cdot}CH_3 + 2N_2O \longrightarrow CH_3{\cdot}CHO + CH_3{\cdot}CH_2{\cdot}CHO + 2N_2$$

(iii) Reaction of two molecules of olefin with one molecule of nitrous oxide to give one molecule of a carbonyl compound and one molecule of a *cyclo*propane derivative, *e.g.*,



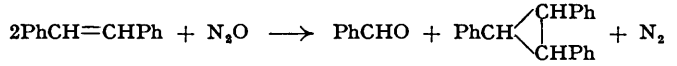
$$2\,PhMeC{=}CH_2 + N_2O \longrightarrow PhMeC{=}O + PhMeC{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + N_2$$

Attack was invariably at the double bond and in most cases there were no side reactions apart from self-condensation of the carbonyl compounds to give higher unsaturated bodies. Some loss of yield by this type of condensation was inevitable at the high temperatures used, especially when the primary products were aldehydes.

Ethylene, monosubstituted ethylenes, and most 1 : 2-disubstituted ethylenes reacted wholly or mainly according to reaction (i). Ethylene gave acetaldehyde together with a little crotonaldehyde and higher condensation products, but no formaldehyde. Propylene gave a mixture of acetone and propaldehyde together with their condensation products; small amounts of acetaldehyde and methyl*cyclo*propane, arising from a type (iii) reaction, were also detected, but formaldehyde was absent. Hept-1-ene similarly gave a mixture of heptanal (50%), hexanal (24%), and heptan-2-one (26%). The hexanal probably arose from a type (iii) reaction, since formaldehyde was absent from the products, although the amyl*cyclo*propane which was presumably formed in the reaction was not isolated.

*cyclo*Hexene gave only *cyclo*hexanone, and acenaphthylene gave acenaphthenone. Pent-2-ene reacted to give 39% of pentan-2-one and 32% of pentan-3-one, together with traces of acetaldehyde and propaldehyde which arose from a type (ii) reaction; no *cyclo*propane derivatives were detected.

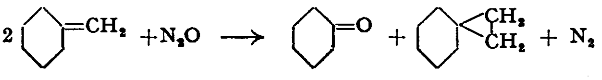
Stilbene behaved differently; deoxybenzoin, the product expected from reaction (i), was formed only in 20% yield, and considerable amounts of benzaldehyde, benzoic acid, and 1 : 2 : 3-triphenyl*cyclo*propane were isolated. The benzaldehyde and the triphenyl*cyclo*propane evidently arose from a type (iii) reaction.



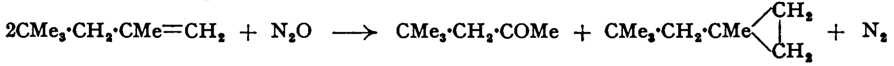
$$2PhCH{=}CHPh + N_2O \longrightarrow PhCHO + PhCH{<}\begin{matrix}CHPh\\ |\\ CHPh\end{matrix} + N_2$$

It was thought likely that the benzoic acid was formed by the further action of nitrous oxide on the benzaldehyde, and this was confirmed by the reaction of pure benzaldehyde with nitrous oxide under the conditions used for the stilbene reaction; the aldehyde was largely converted into benzoic acid.

1 : 1-Disubstituted ethylenes, with one exception, reacted exclusively according to reaction (iii), *e.g.*, methylene*cyclo*hexane gave equimolecular amounts of *cyclo*hexanone and *spiro*[2 : 5]-octane; formaldehyde was absent and no other products were detected :

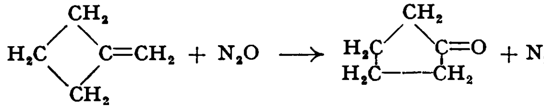


Similarly 2-phenylpropene gave a mixture of equimolecular proportions of acetophenone and 1-methyl-1-phenyl*cyclo*propane, and 2 : 4 : 4-trimethylpent-1-ene gave 4 : 4-dimethylpentan-2-one and 1-methyl-1-*neo*pentyl*cyclo*propane.



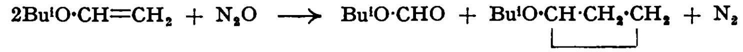
$$2CMe_3{\cdot}CH_2{\cdot}CMe{=}CH_2 + N_2O \longrightarrow CMe_3{\cdot}CH_2{\cdot}COMe + CMe_3{\cdot}CH_2{\cdot}CMe{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + N_2$$

*iso*Butene gave the expected 1 : 1-dimethyl*cyclo*propane but behaved abnormally in giving a mixture of acetone and propaldehyde instead of acetone only. 1 : 1-Diphenylethylene and 1 : 1-bis-*p*-methoxyphenylethylene gave good yields of benzophenone and *pp'*-dimethoxybenzophenone respectively, but the isolation of the corresponding *cyclo*propanes in a pure state was extremely difficult. 1 : 1-Bis-*p*-methoxyphenyl*cyclo*propane was isolated in very small yield and 1 : 1-diphenyl*cyclo*propane was not isolated at all, although the presence of a *cyclo*propane derivative was established by infra-red spectrography. The only 1 : 1-disubstituted ethylene which was examined and which failed to undergo a type (iii) reaction was methylene*cyclo*butane, which gave *cyclo*pentanone as the only identifiable product.



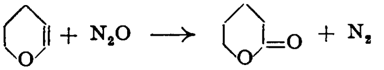
A few olefins having other types of substituent adjacent to the double bond were treated with nitrous oxide. The 1- and 2-chloropropenes gave only tars and hydrogen chloride owing to their instability under the conditions used. αβ-Unsaturated ketones failed to react with nitrous oxide, but αβ-unsaturated ethers readily gave esters.

*iso*Butyl vinyl ether reacted exclusively according to reaction (iii) giving equimolecular amounts of *iso*butyl formate and *iso*butyl *cyclo*propyl ether; no *iso*butyl acetate was detected.



$$2Bu^iO{\cdot}CH{=}CH_2 + N_2O \longrightarrow Bu^iO{\cdot}CHO + Bu^iO{\cdot}\underbrace{CH{\cdot}CH_2{\cdot}CH_2} + N_2$$

On the other hand 2 : 3-dihydropyran reacted only according to reaction (i) giving δ-valerolactone in small amount.



Butyl vinyl sulphide gave a mixture of products containing oxygen, but no identifiable compound was isolated.

No evidence for the formation of olefin oxides was found in any of the reactions, although in the cases of *iso*butene and *cyclo*hexene a particularly careful search was made for evidence of their presence. It was thought possible that olefin oxides might be formed initially and then rearrange to carbonyl compounds under the conditions of the reaction. *cyclo*Hexene oxide was therefore treated with nitrous oxide at 300° and 500 atm. for 4 hours. It was however recovered unchanged.

In an attempt to find a catalyst for the reaction of nitrous oxide with olefins the effect of small amounts of Raney nickel, Raney cobalt, copper, silver, pyridine, triethylamine, sulphuric acid, acetic acid, and iodine was tried, but they all failed to bring about any increase in the rate of reaction between *cyclo*hexene and nitrous oxide.

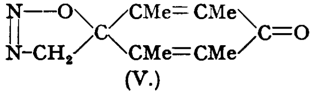
The reaction of nitrous oxide with olefins, although apparently taking very different courses in different cases, was usually quite clear-cut, giving good yields of one or two products, and attack invariably occurred at the double bond. This contrasts sharply with the oxidation of olefins by oxygen, and provides a strong argument against a free-radical mechanism. Since the oxidising action of nitrous oxide is, apart from a few special cases, a specific reaction of the double bond, since the reaction is not catalysed by iodine which is an efficient catalyst for the decomposition of nitrous oxide (Musgrave and Hinshelwood, *Proc. Roy. Soc.*, 1932, *A*, **137**, 25), and since nitrous oxide does not decompose into its elements to any appreciable extent under the conditions used, it is probable that the initial step in the reaction involves addition of the nitrous oxide molecule to the double bond.

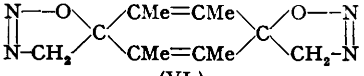
The nitrous oxide molecule is linear, with the oxygen atom at one end, and various structures differing only in electron distribution have been formulated. Pauling ("The Nature of the Chemical Bond," Cornell University Press, 1944, pp. 126, 199) considers that the normal state of the molecule corresponds to resonance between structures (I) and (II), with minor contributions from other mesomeric forms, and spectroscopic (Plyler and Barker, *Phys. Review*, 1931, **38**, 1827) and electron-diffraction evidence (Maxwell, Mosley, and Deming, *J. Chem. Phys.*, 1934, **2**, 331) is consistent with this conclusion.

$$\text{(I.)}\quad \overset{-}{N}{=}\overset{+}{N}{=}O \qquad\qquad \text{(II.)}\quad N{\equiv}\overset{+}{N}{-}\overset{-}{O}$$

Nitrous oxide is therefore seen to be closely analogous in structure to diazomethane and phenyl azide, and like them it may be expected to add to olefinic double bonds under suitable conditions to form a 5-membered heterocyclic ring.

It is accordingly considered likely that the primary product of the reaction of nitrous oxide with an olefin is a Δ^2-1 : 2 : 3-oxadiazoline (III). There is strong evidence that this ring system, commonly formulated as the open-chain diazonium betaine (IV), is also formed as an intermediate step in the reaction of aldehydes and ketones with aliphatic diazo-compounds (Arndt and Eistert, *Ber.*, 1935, **68**, 193), and in the reaction of β-amino-alcohols with nitrous acid (McKenzie and Richardson, *J.*, 1923, **123**, 79), and in one or two cases the 1 : 2 : 3-oxadiazolines have been isolated; *e.g.*, the spirans (V) and (VI) can be obtained in a pure state by the action of diazomethane on duroquinone (Smith and Pings, *J. Org. Chem.*, 1937, **2**, 95).

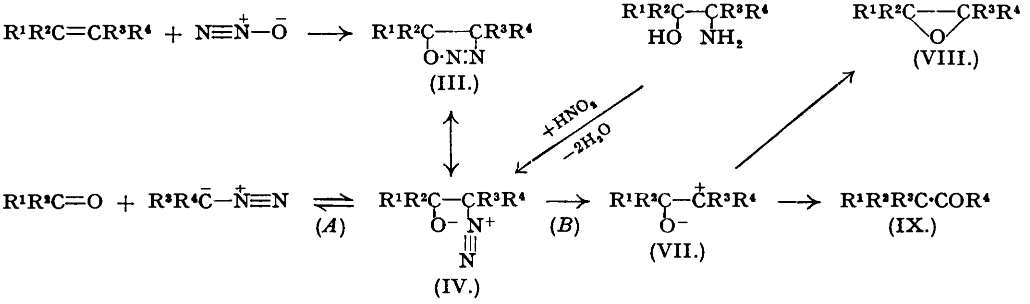

(V.)


(VI.)

The 1 : 2 : 3-oxadiazolines formed by either of these two types of reaction decompose irreversibly either spontaneously or on warming, losing nitrogen to give an intermediate of type (VII), which then either cyclises to the olefin oxide (VIII) or undergoes anionotropic rearrangement to an aldehyde or ketone (IX). This breakdown of the ring will occur very rapidly under the conditions obtaining in the reaction of nitrous oxide with olefins, but it is not the only mode of decomposition which must be taken into consideration. The 1 : 2 : 3-oxadiazolines can be formed from three diverse pairs of starting materials by three very different types of reaction, and one or more of these reactions may be reversible.

The possibility of decomposition to an amino-alcohol and nitrous acid may be dismissed because in the nitrous oxide system the water required for the decomposition is absent. On the other hand, the reaction of an aliphatic diazo-compound with an aldehyde or ketone is a typical example of a nucleophilic addition to the carbonyl group, and such reactions are normally readily reversible (*e.g.*, addition of hydrogen cyanide or sodium hydrogen sulphite, the aldol reaction, etc.). This reversibility has not hitherto been detected in the addition of diazo-compounds because the addition product is rapidly and irreversibly decomposed, whereas the starting materials are relatively stable under the conditions of the reaction. But if a 1 : 2 : 3-oxadiazoline dissociates in this manner at 250—300°, the diazoparaffin formed will be rapidly removed either by thermal decomposition or by reaction with one of the other components of the reaction mixture. We may therefore conclude that the primary product of the addition of nitrous oxide to an olefin may break down either to give nitrogen and a residue (VII) which will rearrange to a carbonyl compound or an olefin oxide containing the same number of carbon atoms as the original olefin (reaction *A*), or to give a diazoparaffin and a carbonyl compound containing a smaller number of carbon atoms than the olefin (reaction *B*).

The relative importance of these two modes of decomposition will depend on the position of the equilibrium in reaction *B* and on the relative rates of reaction *A* and of the elimination of the diazoparaffin, and these factors will in turn depend largely on the number and nature of the substituent groups.



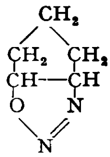
The experimental results are consistent with this interpretation. Ethylene is assumed to form Δ^2-1 : 2 : 3-oxadiazoline (III; $R^1 = R^2 = R^3 = R^4 = H$), which breaks down exclusively to nitrogen and acetaldehyde.

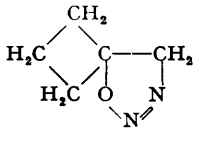
The monosubstituted ethylenes may similarly be supposed to give a mixture of the 4-substituted and the 5-substituted oxadiazoline. The 4-substituted compound (III; $R^1 = R^2 = R^3 = H$, $R^4 = R$) evidently breaks down exclusively by the *A*-type reaction to give nitrogen and the aldehyde, but the 5-substituted compound (III; $R^1 = R$, $R^2 = R^3 = R^4 = H$), although it undergoes mainly the *A*-type decomposition to nitrogen and the ketone, must also break down to a small extent by the *B*-type reaction. The products from this reaction are an aldehyde and diazomethane, which evidently combines with unchanged olefin to give a *cyclo*propane in the known manner. In the case of *iso*butyl vinyl ether, it appears that only 5-*iso*butoxy-Δ^2-1 : 2 : 3-oxadiazoline is formed in the first step and that it then decomposes only by reaction *B*.

The 1 : 1-disubstituted ethylenes appear to give exclusively 5 : 5-disubstituted 1 : 2 : 3-oxadiazolines; the absence of formaldehyde and of aldehydes containing the same number of carbon atoms as the original olefins shows that the 4 : 4-disubstituted oxadiazolines are not formed. The former evidently undergo *B*-type decomposition only to give a ketone and diazomethane, which again reacts with the olefin to give a *cyclo*propane derivative.

Methylene*cyclo*butane is exceptional because of the instability of the 4-membered ring. It seems likely that ring expansion occurs when the olefin is attacked by nitrous oxide, with the result that 4 : 5-trimethylene-Δ^2-1 : 2 : 3-oxadiazoline (X) is formed instead of the expected 4 : 4-trimethylene-Δ^2-1 : 2 : 3-oxadiazoline (XI).

(X.)





(XI.)

A less plausible alternative is that (XI) is first formed and then undergoes rearrangement to (X). By analogy with the corresponding tetramethylene derivative, it is to be expected that (X) will break down exclusively according to reaction *A*.

The 1 : 2-disubstituted ethylenes will form the 4 : 5-disubstituted 1 : 2 : 3-oxadiazolines, and in the case of symmetrical olefins, *e.g.*, *cyclo*hexene and stilbene, only one oxadiazoline can be formed and hence the *A*-type decomposition produces only a single ketone. On the other hand in unsymmetrical olefins, as in pent-2-ene, two isomeric oxadiazolines and hence two isomeric ketones are formed. *B*-Type decompositions, as well as the *A*-type, apparently occur when the olefins are open-chain and result in the formation of an aldehyde R·CHO and a diazocompound $R'\cdot CHN_2$. It has already been shown that diazomethane produced under these conditions reacts with the parent olefin to give a *cyclo*propane derivative. The formation of 1 : 2 : 3-triphenyl*cyclo*propane from stilbene indicates that a similar reaction occurs when R′ is aryl, but when R′ is alkyl, as in the diazoethane and 1-diazopropane which may be assumed to be formed in the fission of the oxadiazolines from pent-2-ene, the diazo-compound is apparently eliminated by reaction with nitrous oxide to form an aldehyde.

$$R'\cdot CHN_2 + N_2O \longrightarrow R'\cdot CHO + 2N_2$$

There remains one anomaly in the experimental results which is not susceptible of explanation in terms of the theory outlined above, *viz.* the formation of a small amount of propaldehyde together with the acetone in the reaction of nitrous oxide with *iso*butene, where the theory predicts the formation of acetone alone. Although this observation is as yet unaccountable it does not appear to invalidate the general thesis.

The reaction of nitrous oxide with olefins affords a simple method of preparing many carbonyl compounds and *cyclo*propane derivatives, but precautions must be taken when carrying out the reaction since nitrous oxide forms explosive mixtures with hydrocarbons. Such mixtures are liable to explode even at room temperature when compressed. Before the full extent of this hazard was properly appreciated several explosions occurred in reaction vessels, and in one case when *cyclo*hexene (25 c.c.) was being treated with nitrous oxide at 300° and 1000 atm. in a vessel of 75-c.c. capacity, capable of withstanding 5000 atm. pressure, a detonation split the vessel lengthways and destroyed the surrounding furnace. The danger was reduced by using a sufficient volume of the organic reagent so that the reaction vessel was half-filled, and by ensuring that the stirring was efficient. As a further precaution the maximum reaction pressure was restricted to 500 atm.

A further risk arises in compressing the nitrous oxide which is liable to escape from the compressor (Fig. 1) past the mercury seal into the pressure-transmitting medium. When this is water no harm results, but if a hydrocarbon oil is used serious explosions may occur in the compression system, and indeed have done so.

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

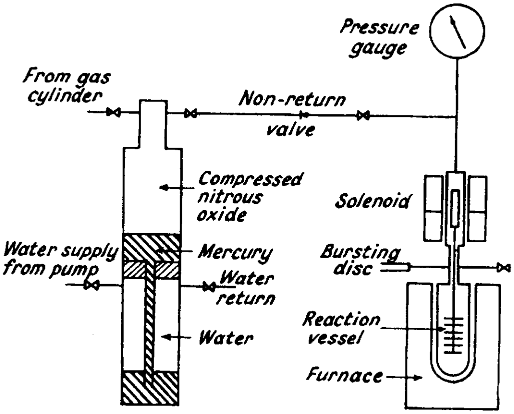
EXPERIMENTAL.

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

Apparatus and Procedure.—All reactions were carried out in a stainless-steel autoclave of 75-c.c. capacity and 3000 atm. maximum working pressure, fitted with a bursting disc (1000 atm.) close to the head of the vessel (Fig. 1). The vessel was heated by a copper-block electric furnace, and stirred by a magnetically operated reciprocating stirrer. The temperatures measured were the furnace temperatures adjacent to the outer surface of the vessel. The nitrous oxide was introduced into the reaction vessel by means of a compressor, consisting of two cylinders, one above the other, with a dip pipe from the upper cylinder reaching almost to the bottom of the lower. Initially the lower cylinder was full of mercury and the upper contained nitrous oxide. Water was then forced into the upper portion of the lower cylinder by means of a piston-type pump. Mercury was thus transferred to the upper cylinder and the gas was compressed and passed through the outlet valve into the reaction vessel.

The vessel was charged with 30—40 c.c. of the organic liquid, closed after the air had been displaced by nitrous oxide at atmospheric pressure, and heated to the required temperature. The stirrer was then started and nitrous oxide admitted until the required pressure was attained. When the reaction was completed, the vessel was cooled to room temperature and the pressure released. The gases were usually passed through a trap cooled in liquid air. The trap was then allowed to warm slowly to room temperature and the residual contents were combined with the contents of the reaction vessel.

FIG. 1.



Nitrous Oxide.—The nitrous oxide used was found to have the following percentage composition : N_2O, 99·8 ; non-condensables, 0·2% ; higher oxides of nitrogen, trace. After 18 hours at 300°/1000 atm. the non-condensables had increased to 1·5%.

Infra-red Spectrography.—A Grubb–Parsons model S3 spectrometer, equipped with a rock-salt prism, thermal detector, A.C. amplifier, and pen recorder, was used for the infra-red examinations.

Reaction of Nitrous Oxide with Olefins.—*Ethylene.* The autoclave was charged with *cyclo*hexane (20 c.c.), closed, and heated to 300°. Ethylene was admitted to a pressure of 230 atm., followed by nitrous oxide until the pressure rose to 500 atm., and the contents were then stirred under these conditions for 4 hours. After the vessel had been cooled the pressure was released slowly and the gases were passed through a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid (500 c.c.). The precipitate (1·1 g.) was collected, washed, and crystallised from ethanol, and was identified as acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°.

The liquid product was distilled. The first fraction (1·7 c.c.), b. p. 20—30°, consisted largely of acetaldehyde. The remainder, b. p. mainly about 80°, was chiefly *cyclo*hexane, and there remained a high-boiling residue (3·1 g.). The *cyclo*hexane fraction, on treatment with a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, gave a small amount of crotonaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 187—188°.

Propylene. The reaction vessel was cooled to −180° and evacuated, and propylene (30 c.c.) was allowed to distil into it. The temperature was then raised to 300°, nitrous oxide was admitted to a pressure of 500 atm., and the mixture was stirred under these conditions for 2 hours. The vessel was cooled to −180° and the pressure slowly released. The contents of the vessel were allowed to warm to −60°, kept at this temperature until no more gas was evolved, and then distilled. A fraction, b. p. 0—5°, was collected as a gas (350 c.c. at N.T.P.) and analysed by infra-red spectrography. It was proved to consist mainly of methyl*cyclo*propane by the similarity of its spectrum with that published by Condon and Smith (*J. Amer. Chem. Soc.*, 1947, **69**, 965). The presence of approximately 16% of acetaldehyde, 10% of propylene, and 1·5% of nitrous oxide was also established.

A small fraction, b. p. 5—23°, was treated with 2 : 4-dinitrophenylhydrazine and yielded acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°.

The main fraction (6·3 c.c.) b. p. 45—56°, reacted with benzaldehyde to give dibenzylideneacetone, m. p. and mixed m. p. 110·5—111·5°, and with dimedone to give propaldehyde dimethone, m. p. and mixed m. p. 155°.

The approximate proportions of acetone and propaldehyde in the mixture were determined by infra-red spectrography. Known mixtures of acetone and propaldehyde were examined in the form of 10% solutions in *n*-hexane; the optical densities for the 8·3-μ band in a 0·09-mm. cell were measured by a base-line density method and plotted against the concentration. By using the curve so obtained the acetone content of the unknown mixture was determined. Propaldehyde was determined by measurement of the optical density of the 5·82-μ band and calculation of the carbonyl content from the known molar extinction coefficient; part of the absorption at 5·82 μ was of course due to acetone, but an appropriate correction was applied by use of the known molar extinction coefficient for acetone at 5·82 μ and the figure for the acetone content derived from measurement of the 8·3-μ band. These determinations showed that the mixture contained 66% of acetone and 32% of propaldehyde.

The material of b. p. >56° (4·8 c.c.) appeared to be a complex mixture of unsaturated carbonyl compounds and a little undistillable resin.

Hept-1-*ene*. The olefin (28 c.c.) was treated with nitrous oxide at 350°/200 atm. for 1 hour. Distillation of the product (25 c.c.) gave fractions: (i) b. p. 78—86°, 7·8 c.c.; (ii) b. p. 86—123°, 1·3 c.c.; (iii) b. p. 123—127°, 1·0 c.c.; (iv) b. p. 127—146°, 0·7 c.c.; (v) b. p. 146—155°, 4·7 c.c.; and (vi) residue, 9·5 c.c. Fraction (i) was mainly unchanged olefin. From fraction (iii) were prepared hexanal semicarbazone, m. p. 105·5° (Found: C, 53·5; H, 9·4. Calc. for $C_7H_{15}ON_3$: C, 53·5; H, 9·6%), and 2 : 4-dinitrophenylhydrazone, m. p. 107°.

Fraction (v) reacted with dimedone to give heptanal dimethone, m. p. and mixed m. p. 99·5°, and with semicarbazide to give heptan-2-one semicarbazone, m. p. and mixed m. p. 121°. The residue (vi) was a complex mixture of condensation products which was not further investigated.

Inspection of the distillation curve and comparison of the infra-red absorption spectra of known mixtures with those of fractions (ii)—(v) indicated that the carbonyl compounds were present in the approximate proportions: hexanal (24%), heptanal (50%), and heptan-2-one (26%).

Pent-2-*ene*. The olefin (2 × 30 c.c.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. After the vessel had been cooled the pressure was released slowly and the gases were passed through a saturated solution of 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid. The precipitate was collected and identified as acetaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 167°.

The liquid product was distilled and gave fractions: (i) b. p. 30—38°, 2 c.c.; (ii) b. p. 38—96°, 6 c.c.; (iii) b. p. 96—102°, 2·8 c.c.; and (iv) b. p. 102—103·5°, 31 c.c.; there remained a small high-boiling residue. Fractions (i) and (ii) were shown to contain aldehydes by Schiff's reaction, and fraction (ii) gave propaldehyde dimethone, m. p. and mixed m. p. 152—154°, and 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 149·5—151°. Fraction (iv) was a mixture of pentan-2-one and pentan-3-one; it reacted with benzaldehyde to give propyl styryl ketone dimer, m. p. and mixed m. p. 196—197·5°. Comparison of the infra-red absorption spectrum of fraction (iv) with those of mixtures of known composition showed that it contained pentan-2-one (*ca.* 56%) and pentan-3-one (*ca.* 44%).

cyclo*Hexene*. The olefin (40 c.c.) was treated with nitrous oxide at 300°/500 atm. for 2 hours, and the product was distilled, yielding fractions: (i) b. p. <90°, 3·5 c.c.; (ii) b. p. 90—153°, 2·6 c.c.; (iii) b. p. 153—156°, n_D^{20} 1·4505, 23·5 c.c.; and (iv) high-boiling residue, 11·5 c.c. Fraction (i) consisted of unchanged *cyclo*hexene and a little water; fraction (iii) was *cyclo*hexanone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 161·5°; semicarbazone, m. p. and mixed m. p. 168·5°); and fraction (iv) appeared to be a complex mixture of condensation product of *cyclo*hexanone.

The infra-red absorption spectra of the fractions showed no bands attributable to *cyclo*hexene oxide.

Stilbene. The olefin (40 g.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. The product was dissolved in ether and washed with 10% potassium carbonate solution and then with water. The washings were acidified with hydrochloric acid, and the precipitate was collected (5·2 g.) and identified as benzoic acid, m. p. and mixed m. p. 122°. The ethereal solution was then washed repeatedly with a 5% sodium hydrogen sulphite solution; the washings were saturated with potassium carbonate and extracted with ether, and the extract was dried ($MgSO_4$). After removal of the ether by distillation there remained benzaldehyde (4·3 g.) (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 238°; semicarbazone, m. p. and mixed m. p. 234—235°).

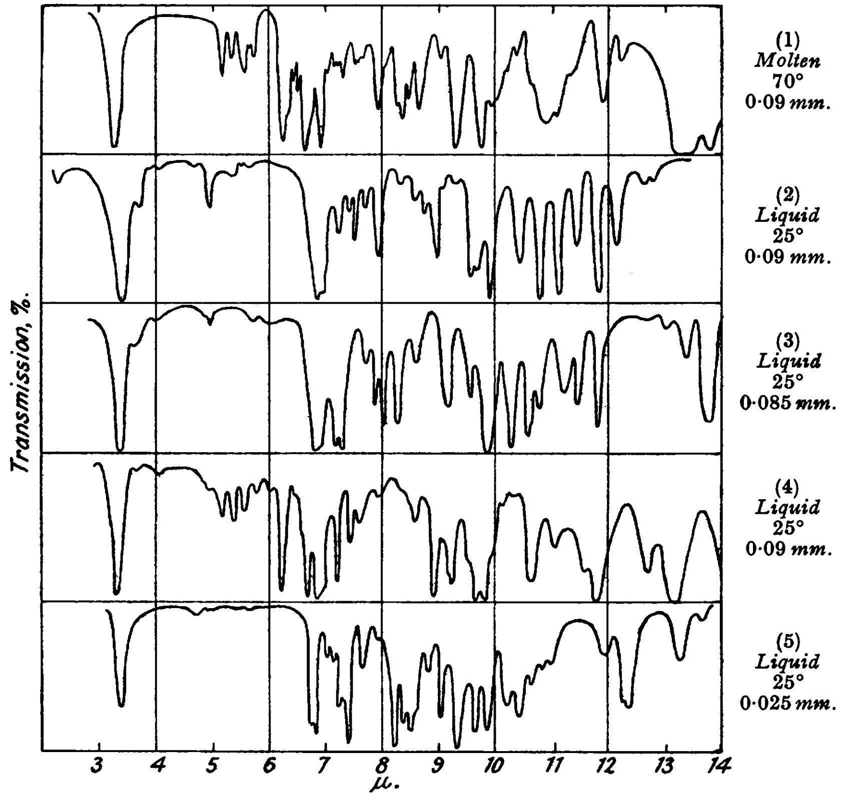
The original ethereal solution, after the treatment described above, was freed from ether by distillation and distilled with steam; the distillate was extracted with ether, and the extract was dried ($MgSO_4$) and evaporated. The residue, a low-melting solid, was crystallised from methanol, giving stilbene (7·2 g.), m. p. and mixed m. p. 122—123°. The mother-liquors were evaporated and the residue crystallised from light petroleum (b. p. 60—80°) giving deoxybenzoin (3·2 g.), m. p. and mixed m. p. 55—56° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 201—203°).

The steam-distillation residue was extracted with ether, and the extract was dried ($MgSO_4$) and evaporated. The residue (21 g.) was distilled *in vacuo* and gave two fractions. Fraction (i) (4·5 g.), b. p. mainly 140—150°/2 mm., solidified on cooling; crystallisation from light petroleum (b. p. 100—120°) gave deoxybenzoin, m. p. and mixed m. p. 55—56°. Fraction (ii) (13·1 g.), b. p. mainly 185—190°/2 mm., was a viscous oil which solidified after several hours; crystallisation from ethanol gave needles of 1 : 2 : 3-*triphenyl*cyclo*propane*, m. p. 63° (Found: C, 93·15; H, 6·5%; *M*, 270. $C_{21}H_{18}$ requires C, 93·35; H, 6·65%; *M*, 270). Its infra-red absorption spectrum (Fig. 2) showed bands at 6·25 and 6·68 μ, attributable to phenyl groups. The absorption at 9·75 μ—which was shown by the compound when examined as a solid film, in the liquid state, and in solution in hexane—was ascribed to the *cyclo*propane ring, although the diagnostic band usually lies in the range 9·8—10 μ.

Acenaphthylene. A solution of acenaphthylene (5 g.) in *cyclo*hexane (30 c.c.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. The resulting solution was evaporated and the residue distilled with steam. Crystals (2 g.) which formed in the distillate were collected and identified as acenaphthenone, m. p. and mixed m. p. 119°.

iso*Butene.* The reaction vessel was cooled to $-180°$ and evacuated, and *iso*butene (35 c.c.) was distilled into it and treated with nitrous oxide at 250°/500 atm. for 2 hours. After the vessel had been cooled the pressure was released and the exit gases were passed through a series of traps immersed in liquid air. The non-condensable gas contained nitrogen (97·8%), oxygen (1·83%), and traces of carbon monoxide and hydrocarbons.

FIG. 2.



(Mm. in the right-hand margin are cell-lengths.)

(1) 1 : 2 : 3-*Triphenyl*cyclo*propane.*
(2) spiro[2 : 5]*Octane.*
(3) 1-*Methyl*-1-neo*pentyl*cyclo*propane.*
(4) 1-*Methyl*-1-*phenyl*cyclo*propane.*
(5) iso*Butyl* cyclo*propyl ether.*

The products from six experiments were combined for working up. The contents of the liquid-air traps were kept at $-50°$ to $-60°$ until no more nitrous oxide was evolved. The residue was then distilled through a train of wash-bottles containing sodium hydrogen sulphite solution followed by sodium carbonate solution, through calcium chloride drying tubes, and finally condensed in a receiver cooled to $-20°$. The condensate was fractionally distilled and gave *iso*butene (38 c.c.), b. p. $-8°$, and a fraction (11·6 c.c.), b. p. 6—22°; most of the latter distilled at 19—22° and had m. p. $-100°$, n_D^0 1·3785 (Found : C, 85·5; H, 14·2%; *M*, 71·6. Calc. for C_5H_{10} : C, 85·7; H, 14·3%; *M*, 70). Gustavson and Popper (*J. prakt. Chem.*, 1898, **58**, 458) give b. p. 21°, m. p. $-108·4$ to $-107·3°$, n_D^{17} 1·3659 for 1 : 1-dimethyl*cyclo*propane. The infra-red absorption spectrum of the sample was identical with that of 1 : 1-dimethyl*cyclo*propane (Derfer, Pickett, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 2482).

The liquid products from the reaction were fractionally distilled; the main fraction, b. p. 54—58°, consisted of acetone (dibenzylidene derivative, m. p. and mixed m. p. 113·5°). A small fraction, b. p. 36—48°, contained propaldehyde (dimethone, m. p. and mixed m. p. 152°). A high-boiling residue contained unsaturated carbonyl compounds but no *iso*butaldehyde was detected. The infra-red absorption spectra of the fractions showed no bands atributable to *iso*butene oxide.

*Methylene*cyclo*hexane.* The olefin (40 c.c.) was treated with nitrous oxide at 300°/400 atm. for 4 hours. The combined products from three runs (96 c.c.) were distilled and the fraction, b. p.

75°/760 mm.—140°/25 mm., (68 c.c.) was washed repeatedly with 5% sodium hydrogen sulphite solution, then with water and 10% sodium carbonate solution. The combined washings were treated with excess of sodium carbonate and distilled in steam. The organic portion of the distillate was separated, dried ($CaCl_2$), and distilled. It consisted almost entirely of *cyclo*hexanone, b. p. 156—157° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 161°; semicarbazone, m. p. and mixed m. p. 165°).

The oil (32·5 c.c.) which had remained undissolved in the sodium hydrogen sulphite solution was dried ($CaCl_2$) and fractionally distilled; the main fraction, b. p. 125—127·5°, n_D^{20} 1·4469, was *spiro*-[2 : 5]octane (Found : C, 87·3; H, 12·6%; *M*, 109. Calc. for C_8H_{14} : C, 87·3; H, 12·7%; *M*, 110). Its infra-red absorption spectrum (Fig. 2) was identical with that of an authentic specimen, b. p. 125·7°, n_D^{20} 1·4468, prepared by the method used by Shortridge *et al.* (*J. Amer. Chem. Soc.*, 1948, **70**, 949).

The infra-red spectrum of the original mixture, b. p. 75°/760 mm.—140°/25 mm., showed that it contained 45 ± 5% of *spiro*[2 : 5]octane, estimated from the optical density of the 11·87-μ band, and 48 ± 5% of *cyclo*hexanone, estimated from the 11·56-μ band.

2 : 4 : 4-*Trimethylpent*-1-*ene*. The olefin (2 × 50 c.c.) was treated with nitrous oxide at 300°/500 atm. for 2 hours, and the product (85 c.c.) was distilled. This gave fractions : (i) b. p. <105°, 20 c.c.; (ii) b. p. 105—119°, 5 c.c.; (iii) b. p. 119—120·5°, 13 c.c.; (iv) b. p. 120·5—124°, 12 c.c.; (v) b. p. 124—124·5°, 6·5 c.c.; (vi) b. p. 124·5—131°, 3·5 c.c.; and (vii) b. p. 131—144°, 6 c.c.

Fraction (i) was mainly unchanged olefin. Fraction (v) had n_D^{20} 1·4041 and was identified as 4 : 4-dimethylpentan-2-one (Found : C, 73·5; H, 12·6. Calc. for $C_7H_{14}O$: C, 73·7; H, 12·3%); it formed a semicarbazone, m. p. 176° (Found : C, 56·6; H, 9·6; N, 24·7. Calc. for $C_8H_{17}ON_3$: C, 56·15; H, 9·9; N, 24·45%), and a 2 : 4-dinitrophenylhydrazone, m. p. 102° [Whitmore *et al.* (*J. Amer. Chem. Soc.*, 1941, **63**, 2035) give b. p. 124°, n_D^{20} 1·4030, for the ketone, m. p. 176° for the semicarbazone, and m. p. 100° for the ddinitrophenylhydrazone].

Fraction (vi) was also essentially 4 : 4-dimethylpentan-2-one, and fractions (iii) and (iv) contained this ketone mixed with a hydrocarbon. Fractions (iii) and (iv) were combined and added rapidly to a stirred solution of sodium hypochlorite which had been freshly prepared by chlorination of sodium hydroxide (43·6 g.) in water (310 c.c.). The temperature rose to 70° and was kept at 65—70° by occasional cooling until the reaction was complete. The excess of hypochlorite was then destroyed by addition of sodium hydrogen sulphite solution, and the mixture was made strongly alkaline with sodium hydroxide, and distilled with steam. The organic layer of the distillate was separated, dried (Na_2SO_4), and distilled. The main fraction, b. p. 128—128·5°, n_D^{20} 1·4179, was 1-*methyl*-1-neo*pentyl*-cyclo*propane* (Found : C, 85·5; H, 14·3%; *M*, 125. C_9H_{18} requires C, 85·7; H, 14·3%; *M*, 126). Its infra-red absorption spectrum (Fig. 2) showed a strong band at 9·86 μ, characteristic of the *cyclo*propane ring.

The steam-distillation residue was acidified with sulphuric acid and distilled in steam. The distillate (140 c.c.) was extracted several times with ether, and the extract dried (Na_2SO_4) and fractionally distilled. This gave $\beta\beta$-dimethylbutyric acid (6·7 g.), b. p. 176—180°, n_D^{20} 1·4110, which was characterised as the anilide, m. p. 132°. Homeyer, Whitmore, and Wallingford (*J. Amer. Chem. Soc.*, 1933, **55**, 4211) give b. p. 183°, n_D^{20} 1·4096, for the acid and m. p. 131° for the anilide.

The infra-red absorption spectra of fractions (ii)—(vi) showed that 4 : 4-dimethylpentan-2-one, estimated from the optical density of the 5·81-μ. band, and 1-methyl-1-*neo*pentyl*cyclo*propane, estimated from the 9·86-μ. band, were present in the mixture in approximately equimolecular proportion.

2-*Phenylpropene*. The olefin (40 c.c.) was treated with nitrous oxide at 280°/500 atm. for 4 hours, and the combined products from four runs (151 c.c.) were distilled under reduced pressure. This gave two main fractions : (i) b. p. 69—69·5°/20 mm., n_D^{20} 1·5156, 27·5 c.c.; and (ii) b. p. 91·5—92°/20 mm., 52 c.c.; a very high-boiling residue (36 c.c.) remained.

Fraction (i) was 1-methyl-1-phenyl*cyclo*propane (Found : C, 90·8; H, 9·2. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%). Whitmore, Weisgerber, and Shabica (*J. Amer. Chem. Soc.*, 1943, **65**, 1469) give b. p. 91°/50 mm., n_D^{20} 1·5160, for this hydrocarbon. Its infra-red absorption spectrum (Fig. 2) showed a band at 9·83 μ. An absorption band between 9·8 and 10 μ. is normally exhibited by *cyclo*propane derivatives.

Fraction (ii) was acetophenone (semicarbazone, m. p. and mixed m. p. 201—202°; 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 248°).

1 : 1-*Diphenylethylene*. The olefin (40 c.c.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. The products from two experiments (70 g.) were combined and distilled in steam. The distillation residue was extracted with benzene, the benzene removed by distillation, and the residue distilled under reduced pressure. Most of it distilled at 128—175°/2 mm. leaving a tarry residue. The distillate was set aside at 0° for 24 hours, and the crystals which formed were then collected and washed with pentane at −20°. They were identified as benzophenone, m. p. and mixed m. p. 41—42·5° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 233—234°).

The mother liquor and washings from the crystallisation were combined with the organic layer of the steam-distillate and added to a mixture of ethanol (36 c.c.), water (7 c.c.), and hydroxylamine hydrochloride (11 g.). Sodium hydroxide (20 g.) was added gradually, and the mixture was then boiled under reflux for 5 minutes, cooled, and diluted with water (200 c.c.). The oil (10·6 g.) was separated, washed with dilute aqueous sodium hydroxide, dried ($CaCl_2$), and distilled under reduced pressure. It was obviously a mixture and boiled mainly at 132—145°/12 mm. Its infra-red absorption spectrum indicated that it was free from benzophenone and showed a prominent band at 9·87 μ. attributable to the *cyclo*propane ring. By applying to measurements of this band a molar extinction coefficient of 50, derived from a study of the spectra of known *cyclo*propanes, it was estimated that the mixture contained approximately 20% of 1 : 1-diphenyl*cyclo*propane.

Acidification of the aqueous alkaline solution from the hydroxylamine reaction gave benzophenone oxime, m. p. 142°.

1 : 1-*Bis*-p-*methoxyphenylethylene.* The olefin (44 g.) was treated with nitrous oxide at 280°/500 atm. for 4 hours, and the product (45 g.) was dissolved in light petroleum (400 c.c.; b. p. 60—80°), and the solution boiled with charcoal and filtered. On cooling, the solution deposited crystals (8·3 g.) of *pp'*-dimethoxybenzophenone, m. p. 143·5° (Found: C, 74·5; H, 5·6. Calc. for $C_{15}H_{14}O_3$: C, 74·4; H, 5·8%). It formed a 2 : 4-dinitrophenylhydrazone, m. p. 199·5° (Found: N, 12·5. Calc. for $C_{21}H_{18}O_6N_4$: N, 13·2%).

The light petroleum solution was evaporated and the residue dissolved in ethanol (50 c.c.); water (7·5 c.c.), hydroxylamine hydrochloride (7·5 g.), and potassium hydroxide (8 g.) were added, and the mixture was boiled under reflux for 15 minutes, cooled, diluted with water (200 c.c.), and extracted with benzene. The benzene was removed by distillation and the residue distilled in a vacuum (0·002 mm.). The pale yellow, semi-solid distillate (2 g.) was crystallised from ethanol giving 1 : 1-*bis*-p-*methoxyphenyl*cyclo*propane* as needles, m. p. 59·5—60·5° (Found: C, 80·0; H, 7·2. $C_{17}H_{18}O_2$ requires C, 80·3; H, 7·1%).

*Methylene*cyclo*butane.* A solution of the olefin (13 c.c.) in decalin (27 c.c.) was treated with nitrous oxide at 300°/450 atm. for 4 hours, and the product was fractionally distilled. There was obtained a small fraction, b. p. 118—135°, which reacted with 2 : 4-dinitrophenylhydrazine to give *cyclo*pentanone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 141—142°.

iso*Butyl vinyl ether.* The olefin was treated with nitrous oxide at 280°/500 atm. for 4 hours, and the product from a series of runs (157 c.c.) was distilled. This gave fractions: (i) b. p. 60—97°, 4 c.c.; (ii) b. p. 97—97·5°, n_D^{20} 1·3865, 45 c.c.; (iii) b. p. 97·5—110°, 6 c.c.; (iv) b. p. 110—113°, n_D^{20} 1·4000, 34 c.c.; and (v) b. p. 113—150°, 11 c.c.; there remained an undistillable residue, probably a polymer of *iso*butyl vinyl ether.

Fraction (ii) was *iso*butyl formate; on hydrolysis with potassium hydroxide solution it gave potassium formate and *iso*butyl alcohol, which was characterised as the α-naphthylcarbamate, m. p. 99—100°.

Fraction (iv) had a saponification value of 62 and therefore probably contained about 10% of *iso*butyl formate. Fractions (iii)—(v) were therefore combined, added to a solution of potassium hydroxide (50 g.) in methanol (200 c.c.), and boiled under reflux for 2·5 hours. The solution was cooled and diluted with water, and the oil was separated, washed with water, dried ($CaCl_2$), and fractionally distilled. The main fraction (20 c.c.), b. p. 112—115°, was boiled under reflux with sodium (2·7 g.) for 2 hours and redistilled. This gave iso*butyl* cyclo*propyl ether* (15 c.c.), b. p. 114·5°, n_D^{20} 1·4032 (Found: C, 74·5; H, 12·6%; *M*, 113. $C_7H_{14}O$ requires C, 73·7; H, 12·3%; *M*, 114). Its infra-red absorption spectrum (Fig. 2) showed a prominent band at 9·88 μ characteristic of the *cyclo*propane ring.

2 : 3-*Dihydropyran.* The olefin (50 c.c.) was treated with nitrous oxide at 300°/500 atm. for 2 hours, and the product (44·8 g.) was freed from unchanged dihydropyran by distillation at atmospheric pressure. The residue was distilled in a vacuum and gave a fraction (3·6 g.), b. p. 112—118°/19 mm., b. p. 212—214°/760 mm., which appeared to be δ-valerolactone (Found: sap. value, 555. Calc. for valerolactone: sap. value, 560). Oxidation with sodium dichromate and sulphuric acid gave glutaric acid, m. p. 94° (Found: equiv., 65·5. Calc. for glutaric acid: equiv., 66). The acid was characterised by conversion into the phenacyl ester, m. p. 104—105°.

Reaction of Nitrous Oxide with Miscellaneous Organic Compounds.—*Benzhydrol.* The carbinol (35 g.) was treated with nitrous oxide at 300°/400—500 atm. for 4 hours. The product was distilled in a vacuum and had b. p. mainly 133—138°/1·5 mm. The distillate partly crystallised on storage, and the crystals were collected and washed with pentane. This gave unchanged benzhydrol, m. p. and mixed m. p. 63—65°. Treatment of the filtrate with 2 : 4-dinitrophenylhydrazine gave a small amount of benzophenone 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 239—241°.

Benzoin. Benzoin (18 g.) was treated with nitrous oxide at 300°/500 atm. for 4 hours. The product was distilled in a vacuum and gave benzil (3·5 g.), b. p. 160—164°/2 mm., m. p. and mixed m. p. 94—96° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 239—241°).

Benzaldehyde. The aldehyde (40 c.c.), carefully purified by washing it with sodium carbonate solution, drying it, and distilling it in a vacuum, was treated with nitrous oxide at 300°/500 atm. for 4 hours. After the reaction vessel had been cooled, the product (39·7 g.) was immediately dissolved in chloroform (250 c.c.) and extracted with 10% sodium carbonate solution. Acidification of the alkaline extract yielded benzoic acid (34·9 g.), m. p. and mixed m. p. 120—121°.

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