668. *Oxidation of Organic Compounds by Nitrous Oxide. Part III.* Acetylenes.*

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Acetylenic hydrocarbons react readily with nitrous oxide at 200—300°/100—500 atm. When the reaction is carried out in inert solvents the products are keten dimers, but carboxylic acids are formed in water, esters in alcohols, and amides in the presence of ammonia or amines. But-3-yn-1-ol reacts with nitrous oxide to give γ-butyrolactone, but $\beta\gamma$-acetylenic alcohols decompose under the conditions used.

It is thought that the primary product of the reaction of nitrous oxide with an acetylene is an α-diazo-ketone or α-diazo-aldehyde, which then loses nitrogen and undergoes anionotropic rearrangement to a ketene.

Since olefins react readily with nitrous oxide to give aldehydes and ketones (Part I), it was thought possible that acetylenes might react similarly to give ketens:

$$CR{\equiv}CH + N_2O \longrightarrow CHR{=}CO + N_2$$

Experiments showed that acetylenes did in fact react readily with nitrous oxide at 200—300°/100—500 atm., but, owing to the instability of the ketens under these conditions, it was usually desirable to carry out the reaction in the presence of substances which would rapidly combine with the keten to produce stable compounds. Thus nitrous oxide reacted with hex-1-yne in ethyl alcoholic solution to give a good yield of ethyl hexanoate; hept-1-yne similarly gave methyl heptanoate when it reacted in the presence of methanol, and *N-cyclo*hexylheptanoamide in the presence of *cyclo*hexylamine. Phenylacetylene reacted with nitrous oxide in ethanol to give ethyl phenylacetate, in water to give phenylacetic acid, and in an alcoholic solution of ammonia to give phenylacetamide. In inert solvents nitrous oxide reacted with hex-1-yne to give a compound, $C_{12}H_{20}O_2$, presumed to be butylketen dimer, and with phenylacetylene to give a tar from which no definite products could be isolated.

Disubstituted acetylenes behaved in a precisely similar manner:

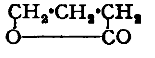
$$CR{\equiv}CR + N_2O \longrightarrow CR_2{=}CO + N_2$$

Nitrous oxide reacted with dec-5-yne to give ethyl 2-butylhexanoate † in ethanol solution, and with diphenylacetylene to give methyl diphenylacetate in methanol solution and diphenylketen dimer in *cyclo*hexane solution.

Acetylene itself reacted with nitrous oxide in ethanol to give ethyl acetate and a trace of *n*-butaldehyde. The ester was presumably formed by the reaction of keten with ethanol but the source of the aldehyde is unknown; no aldehydes or ketones were detected in the reaction products from substituted acetylenes.

Diphenyldiacetylene apparently failed to react with nitrous oxide, and the product consisted of high-molecular weight hydrocarbons of an unknown nature. Attempts were also made to cause nitrous oxide to react with several hydroxyacetylenic compounds. But-3-yn-1-ol reacted readily with nitrous oxide in inert solvents to give γ-butyrolactone, presumably by formation and cyclisation of 2-hydroxyethylketen:

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}C{\equiv}CH + N_2O \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CH{=}CO \longrightarrow$$



$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH_2\\ O{-\!-\!-\!-}CO\end{array}$$

On the other hand, $\beta\gamma$-acetylenic alcohols (propargyl alcohol, 2-methylbut-3-yn-2-ol, 1-phenylprop-2-yn-1-ol, and but-2-yn-1 : 4-diol) gave only complex mixtures of decomposition products.

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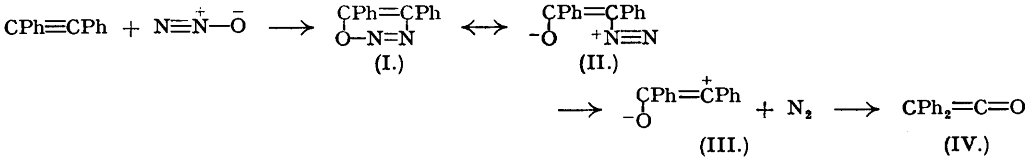
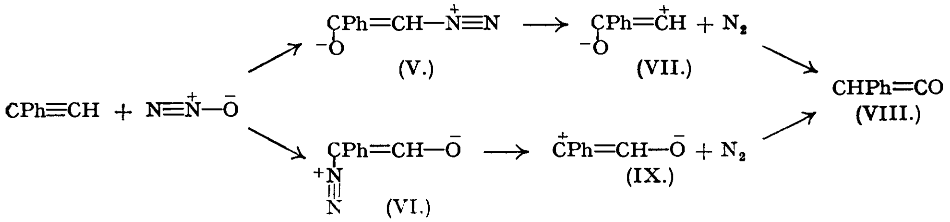
[*] Part II, preceding paper. † Geneva nomenclature, $CO_2H = 1$.

By analogy with the interpretation previously advanced for the reaction of nitrous oxide with olefins, it may be supposed that the initial step in the reaction of nitrous oxide with an acetylene is the formation of a 1 : 2 : 3-oxadiazole. Thus diphenylacetylene would yield 4 : 5-diphenyl-1 : 2 : 3-oxadiazole (I), which is merely a mesomeric form of α-diazodeoxybenzoin (II).



The thermal decomposition of (II) has been studied by Schroeter (*Ber.*, 1909, **42**, 2346, 3361) who found that it decomposed in boiling benzene to give diphenylketen (IV) and in boiling methanol to give methyl diphenylacetate. The formation of diphenylketen dimer by the reaction of nitrous oxide with diphenylacetylene and of methyl diphenylacetate in the presence of methanol is therefore consistent with the theory that (II) is formed as an intermediate. The initial step in the decomposition is presumably loss of nitrogen to form the unstable residue (III), which is then stabilised by anionotropic migration of the phenyl group.

A similar series of reactions must occur when acetylene itself and the monosubstituted acetylenes react with nitrous oxide. Phenylacetylene may react to give either ω-diazoacetophenone (V) or the unknown α-diazophenylacetaldehyde (VI) :



Elimination of nitrogen from (V) leaves the residue (VII) which may be expected to rearrange to phenylketen (VIII) by migration of the phenyl anion; (VIII) may similarly be formed from (VI) by loss of nitrogen and migration of the hydrogen anion.

The products isolated from the interaction of phenylacetylene and nitrous oxide in the presence of water, alcohol, and ammonia are consistent with this interpretation. The decomposition of ω-diazoacetophenone at low temperatures to give phenylketen or its addition products takes place only in the presence of a silver catalyst or under alkaline conditions (Arndt and Eistert, *Ber.*, 1935, **68**, 200). In neutral or acid media in the absence of the catalyst nitrogen is eliminated, but the residue (VII) reacts further without rearrangement. Thus the diazoketone decomposes in water at 70—80° to give ω-hydroxyacetophenone by direct addition of water to (VII) (Arndt and Amende, *Ber.*, 1928, **61**, 1122), and in boiling di*iso*amyl ether it gives 1 : 2 : 3-tribenzoyl*cyclo*propane, which is a trimer of (VII) (Grundmann, *Annalen*, 1938, **536**, 29). It must be assumed that, at the high temperature used in the nitrous oxide reaction, the rearrangement takes place even in the absence of a catalyst.

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EXPERIMENTAL.

Microanalyses are by Dr. A. F. Colson, and infra-red spectrography by Mr. L. H. Cross. All m. p.s are corrected.

Reaction of Acetylenes with Nitrous Oxide.—The apparatus and procedure were as described in Part I.

Acetylene. Acetylene (7·5 g.) was dissolved in ethanol (40 c.c.) at −50° and the vessel was then closed and heated to 300°. Nitrous oxide was admitted until the pressure was 500 atm. and the mixture was stirred under these conditions for 1 hour. The product had sap. value 169, equivalent to an ester content of 26·5% calculated as ethyl acetate, *i.e.*, 41% conversion. The solution was distilled and gave a fraction, b. p. 71·4—72·5°, which had sap. value 435, equivalent to 68·4% of ethyl acetate. According to Horsley (*Ind. Eng. Chem. Anal.*, 1947, **19**, 508) ethyl acetate and ethanol form an azeotrope, b. p. 71·8°, containing 69·2% of the ester. Reaction of this fraction with *o*-phenylenediamine gave 2-methylbenziminazole, characterised as the picrate, m. p. 212° (Found : N, 19·1. Calc. for $C_8H_8N_2,C_6H_3O_7N_3$: N, 19·35%).

The higher-boiling fraction, consisting mainly of unreacted ethanol, gave a small amount of *n*-butaldehyde 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 123°, on treatment with 2 : 4-dinitrophenylhydrazine and hydrochloric acid.

Hex-1-*yne*. (a) A solution of hex-1-yne (7 c.c.) in *cyclo*hexane (33 c.c.) was treated with nitrous oxide at 300°/500 atm. for 1 hour. After the vessel had been cooled the pressure was released, the *cyclo*hexane was removed by distillation, and the residue was distilled under reduced pressure to give *butylketen dimer*, b. p. 170°/12 mm. (Found : C, 73·7; H, 10·2%; *M*, 238. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%; *M*, 196).

(*b*) The reaction was repeated with a solution of hex-1-yne (4 c.c.) in ethanol (36 c.c.). Fractional distillation of the product gave ethyl hexanoate (3 g.), b. p. 164° (Found : C, 66·5; H, 10·9%; sap. value, 394. Calc. for $C_8H_{16}O_2$: C, 66·65; H, 11·1%; sap. value, 389). Reaction with aqueous ammonia gave hexanoamide, m. p. 99°.

Hept-1-*yne*. (*a*) A solution of hept-1-yne (5 c.c.) in methanol (35 c.c.) was treated with nitrous oxide at 200°/300 atm. for 1 hour. The infra-red absorption spectrum of the resulting solution showed a band at 5·79 μ., characteristic of the carbonyl group; this was attributed to the presence of methyl heptanoate, and the ester content of the solution was calculated from the intensity of this band; the conversion was 8·5%.

The experiment was repeated at 250° (conversion 57·0%) and again at 300° (conversion 87·0%).

(*b*) A mixture of hept-1-yne (10 c.c.) and *cyclo*hexylamine (20 c.c.) was treated with nitrous oxide at 250°/500 atm. for 1 hour. The crude product was triturated with dilute hydrochloric acid, collected, and washed with water. There remained crude N-cyclo*hexylheptanoamide* (30·5 g.; 94% of theory), which crystallised from aqueous ethanol in plates, m. p. 82—83° (Found : C, 73·7; H, 11·8; N, 6·4. $C_{13}H_{25}ON$ requires C, 73·95; H, 11·85; N, 6·65%).

Phenylacetylene. (*a*) A solution of phenylacetylene (6·5 g.) in ethanol (33·5 c.c.) was treated with nitrous oxide at 300°/500 atm. for 1 hour. The product was fractionally distilled, giving ethyl phenylacetate (3·5 g.), b. p. 226—228°, n_D^{20} 1·4983 (Found : sap. value, 341. Calc. for $C_{10}H_{12}O_2$: sap. value, 338). Treatment with aqueous ammonia gave phenylacetamide, m. p. and mixed m. p. 158° (Found: C, 71·2; H, 6·7; N, 10·4. Calc. for C_8H_9ON : C, 71·1; H, 6·65; N, 10·35%).

(*b*) Phenylacetylene (5 c.c.) was added to a 16% solution of ammonia in ethanol (35 c.c.) and treated with nitrous oxide at 250°/200 atm. for 2 hours. The alcohol was removed by distillation, and the residue was crystallised from benzene, giving phenylacetamide, m. p. and mixed m. p. 159° (Found : C, 70·9; H, 7·0; N, 10·1. Calc. for C_8H_9ON : C, 71·1; H, 6·65; N, 10·35%).

(*c*) Water (5 c.c.) was added to a solution of phenylacetylene (10 c.c.) in *cyclo*hexane (25 c.c.) and the mixture was treated with nitrous oxide at 300°/500 atm. for 1 hour. The product was extracted with dilute sodium carbonate solution, the extract was acidified, and the precipitated phenylacetic acid (2·0 g.), m. p. 76°, was collected (Found : C, 70·4; H, 5·9%; equiv., 140. Calc. for $C_8H_8O_2$: C, 70·6; H, 5·9%; equiv., 136).

Dec-5-*yne*. A solution of dec-5-yne (8 c.c.) in ethanol (32 c.c.) was treated with nitrous oxide at 300°/500 atm. for 1 hour. After removal of the alcohol by distillation the residue was fractionally distilled under reduced pressure. This gave ethyl 2-butylhexanoate, b. p. 90—95°/6 mm., n_D^{20} 1·4240 (Found : C, 72·3; H, 11·7%; sap. value, 286. Calc. for $C_{12}H_{24}O_2$: C, 72·0; H, 12·0%; sap. value, 280). Reaction with ammonia gave 2-butylhexanoamide, m. p. 135°. Levene and Cretcher (*J. Biol. Chem.*, 1918, **33**, 508) give b. p. 114—115°/15 mm. for the ester, and Dolique (*Ann. Chim.*, 1941, **15**, 425) gives m. p. 134·5° for the amide.

Diphenylacetylene. (*a*) Diphenylacetylene (15 g.) and *cyclo*hexane (25 c.c.) were treated with nitrous oxide at 300°/500 atm. for 1 hour. The product was a dark brown solution which deposited a solid. The solid, apparently a diphenylketen dimer (14 g.; 87% of theory), was collected, washed with *cyclo*hexane, and recrystallised from acetic acid to give crystals, m. p. 173° (Found : C, 87·2; H, 5·1%; *M*, 400. Calc. for $C_{28}H_{20}O_2$: C, 86·6; H, 5·15%; *M*, 388). Staudinger (*Ber.*, 1911, **44**, 530) describes a polymer, m. p. 176°, of diphenylketen.

(*b*) Diphenylacetylene (10 g.) and methanol (30 c.c.) were treated with nitrous oxide at 300°/500 atm. for 1 hour. The solid product was collected and crystallised from methanol, giving methyl diphenylacetate, m. p. 57—58° (Found : C, 79·8; H, 6·3%; sap. value, 253. Calc. for $C_{15}H_{14}O_2$: C, 79·65; H, 6·2% sap. value, 243). Hydrolysis gave diphenylacetic acid, m. p. 148—149° (Found : C, 79·1; H, 6·1. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·65%).

But-3-*yn*-1-*ol*. A solution of but-3-yn-1-ol (4·3 g.) in *cyclo*hexane (35 c.c.) was treated with nitrous oxide at 300°/300 atm. for 1 hour. The *cyclo*hexane was removed by distillation and the residue was distilled under reduced pressure. This gave γ-butyrolactone (3·2 g.), b. p. 49—50°/3 mm., 204—206°/760 mm., n_D^{20} 1·4353 (Found : C, 55·5; H, 7·2%; sap. value, 608. Calc for $C_4H_6O_2$: C, 55·8; H, 7·0%; sap. value, 651). Reaction with phenylhydrazine gave γ-hydroxybutyric phenylhydrazide, m. p. and mixed m. p. 92—93°.

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