# 677. *The Reaction of Nickel Carbonyl with Ethynyldimethylcarbinol and* iso*Propenylacetylene.*

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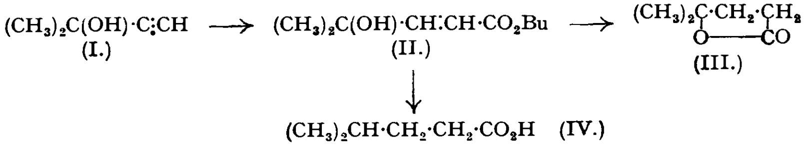
It is shown that carboxylation of the two compounds takes place at the terminal acetylenic carbon atoms. From ethynyldimethylcarbinol, primarily butyl 4-hydroxy-4-methylpent-2-enoate * is formed; the primary product from *iso*propenylacetylene dimerises to (probably) 1-methyl-5-*iso*propenyl*cyclo*hexene-3 : 4-dicarboxylic acid.

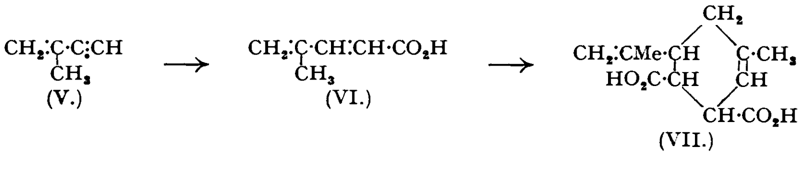
Jones, Shen, and Whiting (*J.*, 1950, 230) have reported observations on the reaction between nickel carbonyl and monosubstituted acetylenic compounds R·C⋮CH. In those cases in which reaction took place, it led to olefinic carboxylic acids of the type $R\cdot C(CO_2H){:}CH_2$ or their derivatives; no significant reaction was observed with tertiary αβ-acetylenic carbinols.

In connection with experiments on the synthesis and chemical behaviour of such carbinols [Zeltner and Genas, U.S.P. 2,345,170 (*Chem. Abstr.*, 1944, **38**, 4273); Weizmann, B.P. 580,921 (*Chem. Abstr.*, 1947, **41**, 2429) and 573,527 (*ibid.*, 1949, **43**, 2219); U.S.P. 2,435,524 (*ibid.*, 1948, **42**, 3772)], their reaction with nickel carbonyl was studied some time ago; it was found that ethynyldimethylcarbinol (I) reacted with the carbonyl in presence of butanolic hydrogen chloride even at room temperature, and more quickly at 40°, and gave a distillable product in reasonable yield. As the structure of this product could not be ascertained, it was hydrogenated. The following observations show that the butyl ester (II) had been formed: the hydrogenation was accompanied by partial hydrogenolysis and gave—after hydrolysis—a mixture of *iso*hexanolactone (III) and *iso*hexanoic acid (IV), which could be separated by means of cold potassium carbonate solution; both were identified by characteristic derivatives. The reaction can be formulated as follows:



It is remarkable that, under the conditions employed, the reaction of ethynyldimethylcarbinol with nickel carbonyl takes a course opposite to that observed by Jones, Shen, and Whiting, and that it does so exclusively, at least as far as can be determined by the isolated product.

*iso*Propenylacetylene (V), too, could easily be induced to react with nickel carbonyl, when a mixture of glacial acetic acid and methanol was used as reaction medium. At 0° to −10°, 7—8% conversion took place in 12 days, at 25° 60% in 5 days, and at 60° almost all of (V) disappeared in about 8 hours. The product, however, was much less characteristic than in the foregoing case. It consisted of a crystalline acid, m. p. 210° (decomp.), small quantities of a methyl ester, and—as main constituent—a resinous acid, softening at 80—90°. Jones, Shen, and Whiting have already observed that free acids are formed in this type of reaction in hydroxylic, but—at least seemingly—anhydrous, solvents.



The crystalline acid had the expected formula $C_6H_8O_2$ [(V) + CO + $H_2O$], but proved to be dimeric and to contain two double bonds. It is, therefore, monocyclic. It may be tentatively assumed that the acid (VI), analogous in its formation to (II), dimerises to 1-methyl-5-*iso*propenyl*cyclo*hexene-3 : 4-dicarboxylic acid (VII), in accordance with reaction mechanisms observed by Kuhn and Deutsch (*Ber.*, 1932, **65**, 43) in similar cases. No proof of the structure beyond this analogy was attempted. It may, of course, be that (V) dimerises before the reaction with carbon monoxide takes place, according to the mechanism outlined by Alder ("New Methods of Preparative Organic Chemistry," p. 389, New York and London, 1948), and by

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* Geneva numbering.

Copenhaver and Bigelow (" Acetylene and Carbon Monoxide Chemistry," p. 253, New York, 1949).

The analogous reaction of vinylacetylene was studied by Reppe (" Neue Entwicklungen der Chemie des Acetylens und Kohlenoxyds," Berlin, 1949, p. 99) as a side reaction in the carboxylation of acetylene.

## EXPERIMENTAL.

*Ethynyldimethylcarbinol and Nickel Carbonyl.*—The carbinol (15·1 g., 0·18 mol.), nickel carbonyl (8·55 g., 0·05 mol.), and a solution of hydrogen chloride (7·3 g., 0·2 mol.) in anhydrous butyl alcohol (30 c.c.) were cautiously heated at 40° in a sealed glass tube, which was immersed in an iron tube, filled with water. When at 40° the exothermic reaction set in, as indicated by precipitation of nickel chloride, the heating was interrupted, and was resumed (for 4 hours) when the spontaneous reaction had subsided. Analysis of the reaction mixture showed that 0·12 mol. of ethynyldimethylcarbinol had disappeared (0·06 mol. unchanged) and that 0·03 mol. of nickel carbonyl had been consumed (determination of nickel chloride). The excess of carbonyl was distilled off, and the reaction product washed with water. The aqueous layer was once extracted with ether, and the combined ethereal and butanolic solutions were freed from solvent and unchanged (I) by distillation under 30 mm. pressure (up to 60°). The residue (15·3 g.) was then separated from some resinous material by distillation *in vacuo* (without fractionation) (yield, 13·9 g.) and directly subjected to hydrogenation at room temperature and atmospheric pressure, palladium being used as catalyst. The quantity of hydrogen consumed was 120% of that calculated for (II).

Distillation under 24 mm. pressure gave fractions: (*a*) 90—91°, 3·3 g., $n_{\mathrm{D}}^{22\cdot5}$ 1·4210; (*b*) 96—102°, 4·3 g., $n_{\mathrm{D}}^{22\cdot5}$ 1·4305; (*c*) 122—142°, 1·1 g., $n_{\mathrm{D}}^{22\cdot5}$ 1·4360; (*d*) 160—174°, 2·1 g., $n_{\mathrm{D}}^{22\cdot5}$ 1·4517.

Fractions (*a*) and (*b*), which were more fully investigated, had approximately the composition and saponification value of the dihydro-derivative of (II) [Found : (*a*) C, 64·3; H, 11·2%; S.V., 309; (*b*) C, 65·4; H, 9·8%; S.V., 348. Calc. for $C_{10}H_{20}O_3$ : C, 63·8; H, 10·6%; S.V. 300]. They were combined and hydrolysed with alkali, and the acids extracted with ether, and the ethereal solution was treated with cold aqueous potassium carbonate solution. (i) The ether-soluble fraction was washed with dilute acid and solidified at 10° [m. p. of (III) : 10°, Noyes, *J. Amer. Chem. Soc.*, 1901, **23**, 392]; it was identified as *iso*hexanolactone (III) by conversion into 2-hydroxy*iso*hexanamide by means of aqueous ammonia; m. p. 100·5° (Stroem, *J. pr. Chem.*, 1893, **48**, 220, gives m. p. 101°) (Found : C, 54·6; H, 9·6. Calc. for $C_6H_{13}O_2N$ : C, 55·0; H, 10·0%). (ii) The carbonate-soluble (acidic) fraction was isolated by acidification, extraction with ether, and distillation under atmospheric pressure [b. p. of *iso*hexanoic acid (IV), 200—201°; Bentley and Perkin, *J.*, 1898, **73**, 49]. The saturated substance gave a well-crystallised *p*-phenylphenacyl ester, m. p. 70·5° (Wrede and Rothhaas, *Ber.*, 1934, **67**, 739, give m. p. 69—70°) (Found : C, 77·2; H, 7·4. Calc. for $C_{20}H_{22}O_3$ : C, 77·4; H, 7·1%). The ester gave no depression with the authentic *p*-phenylphenacyl ester of *iso*hexanoic acid, but its m. p. was lowered by 12·5° upon admixture with the corresponding ester of methyl*iso*propylacetic acid (m. p. 73·5°; Wrede and Rothhaas, *loc. cit.*) (Found : C, 77·1; H, 7·5%).

*iso*Hexanoic acid (IV) was synthesised according to Noyes (*loc. cit.*), and methyl*iso*propylacetic acid as follows : from ethyl malonate and *iso*propyl bromide, ethyl *iso*propylmalonate (b. p. 213—214°/745 mm.) was obtained in 72% yield (*Org. Synth.*, Coll. Vol. I, p. 250). It was methylated in the usual manner to ethyl methyl*iso*propylmalonate, b. p. 221°/752 mm., in quantitative yield. Hydrolysis of this ester and decarboxylation of the corresponding acid (after recrystallisation from benzene) at 160° gave the desired acid, b. p. 189—191° (Levene and Bass, *J. Biol. Chem.*, 1926, **70**, 211).

iso*Propenylacetylene and Nickel Carbonyl.*—The hydrocarbon (b. p. 33·5°) was prepared by distilling a mixture of 200 g. of (I) and 300 g. of 30% (by weight) sulphuric acid in an efficient column, so that the vapour temperature never rose above 40°. The distillate was dried ($Na_2SO_4$) and redistilled (yield : 85 g., 54%).

The reaction between the hydrocarbon (13·2 g., 0·2 mol.) and nickel carbonyl (8·55 g., 0·05 mol.) was carried out in a mixture of acetic acid and methanol at 60°, as described above. Water was added until no more oil (see below) separated. Then the supernatant layer was decanted and acidified, whereupon a colourless *acid* (3·1 g.) separated [VII (?)]. The latter was recrystallised repeatedly from 70% acetic acid and had m. p. 210° (decomp.). It could be sublimed under 2 mm. pressure without decomposition. It did not polymerise when heated for 5 days at 70° in presence of benzoyl peroxide; it is, therefore, unlikely that it contains a conjugated system; it does, however, contain two double bonds [Found : C, 64·5; H, 7·3%; Br no., 155 mg./g.; equiv. (by titration ), 114; *M*, 200 (in glacial acetic acid). $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·1%; Br no., 143; equiv., 112; *M*, 224]. (Farmer, Morrison, and Jones have determined the molecular weight of a similar *cyclo*hexenedicarboxylic acid in glacial acetic acid; *J.*, 1940, 1339.) The di-(*p*-phenylphenacyl) ester, from butanol, had m. p. 150—152°. Some proof for the tentative structure (VII) was found on investigation of the infra-red absorption spectrum of its (oily) dimethyl ester, obtained by use of the theoretical amount of diazomethane and having b. p. 146—148°/8 mm. (Found : C, 66·6; H, 8·0. Calc. for $C_{14}H_{20}O_4$ : C, 66·7; H, 8·0%). Double bonds of the types $R_2C{:}CH_2$ and $R_2C{:}CHR$ should absorb in the 885—900-cm.$^{-1}$ and the 825—250-cm.$^{-1}$ region, respectively (see Barnard and co-workers, *J.*, 1950, 915, also for literature). In fact, a strong band was observed at 897 cm.$^{-1}$, a weak one at 874 cm.$^{-1}$, and a strong one at 842 cm.$^{-1}$. These data do not, of course, exclude other structures similar to (VII).

The oily product (see above) was dissolved in ether and the ethereal layer treated with aqueous sodium hydroxide. The latter solution, on acidification, gave a brown, resinous acid (6·6 g.), and the ethereal layer, on evaporation, left an oily residue, a neutral monomethyl ester (2·4 g.). Its homogeneity could not be definitely established owing to lack of material; it contained two double bonds [Found: equiv. (by hydrolysis), 198; Br no., 140. Calc. for $C_{12}H_{18}O_2$: equiv., 194; Br no., 165]. Possibily, this ester corresponds in structure to (VII), which would have lost one carboxyl group (compare Wicks, Daly, and Lack, *J. Org. Chem.*, 1947, **12**, 713).

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