[CONTRIBUTION FROM THE STATE AGRICULTURE AND MECHANICAL COLLEGE CHEMICAL LABORATORY]

The Preparation of Methylethylamylcarbinol, Methylethylamyl Iodide, 4-Methyloctanol-3 and 3-Bromo-4-methyloctane

BY J. H. GREEN

This paper reports the synthesis and properties of two new nonyl alcohols, methylethylamylcarbinol, and 4-methyloctanol-3, and their respective iodide and bromide.

Experimental

Methylethyl-*n*-amylcarbinol.—This was prepared by the interaction of 36 g. of methyl *n*-amyl ketone[1] and the ethylmagnesium bromide from 30 cc. of ethyl bromide; b. p. 36–37° (3 mm.); d_{20}^{20} 0.8231; $n_{\text{White light}}^{20.7}$ 1.4101.

Anal. Calcd. for $C_9H_{20}O$: C, 75.44; H, 13.37. Found: C, 75.31; H, 13.19.

The iodide was prepared by allowing a mixture of 10 cc. of the above alcohol, 2 g. of red phosphorus and 17 g. of iodine to stand for thirty-two hours at room temperature and then heating on the steam-bath for fifteen minutes. The product, obtained in 90% yield, boiled at 58° (5 mm.); it decomposes on distillation under atmospheric pressure. The iodine was determined as silver iodide after boiling with alcoholic potash for one hour.

Anal. Calcd. for $C_9H_{19}I$: I, 49.90. Found: I, 49.75.

4-Methyloctanol-3.—2-Bromohexane was prepared by boiling a mixture of 50 g. of methyl-*n*-butylcarbinol, 96.8 g. of 48% hydrobromic acid and 30 cc. of sulfuric acid for two hours. After washing successively with water, sulfuric acid and sodium carbonate, it was dried and distilled, b. p. 142–144°. The yield was 53.9 g. (67% of the theoretical). A mixture of 53.9 g. of the above bromide, 7.8 g. of magnesium, 200 cc. of anhydrous ether and 19.2 g. of propionaldehyde was allowed to react in the cold; after adding the calculated amount of hydrochloric acid in 250 cc. of cold water the resulting alcohol was isolated in the usual way, when a 26% yield of 4-methyl-octanol-3 was obtained; b. p. 132–133° (20 mm.); d_{25}^{25} 0.8462; $n_{\text{White light}}^{21.5}$ 1.4278.

Anal. Calcd. for $C_9H_{20}O$: C, 75.44; H, 13.37. Found: C, 75.21; H, 13.12; O, 11.62.

3-Bromo-4-methyl-octane was prepared by boiling a mixture of 5 g. of the above alcohol, 7.4 g. of 48% hydrobromic acid, and 3 g. of sulfuric acid for two hours under reflux. The yield was 19.8% of the theoretical, b. p. 180°. The bromine was estimated by boiling with alcoholic potash for one hour. *Anal.* Calcd. for $C_9H_{19}Br$: Br, 38.0. Found: Br, 37.8.

ORANGEBURG, S. C.

RECEIVED JANUARY 24, 1934

---

[1] Johnson and Hager, "Organic Syntheses," 1932, Coll. I, p. 343.

[CONTRIBUTION NO. 139 FROM THE EXPERIMENTAL STATION OF THE E. I. DU PONT DE NEMOURS & COMPANY]

The Structure of Divinylacetylene Polymers[1]

BY M. E. CUPERY AND WALLACE H. CAROTHERS

Divinylacetylene, when allowed to stand in contact with a little air, is transformed to a soft, transparent, oxygen-containing jelly which is dangerously explosive.[2] The action of heat in the absence of air yields a quite different type of polymer, a yellow oil which dries to hard, chemically resistant films.[2,3]

We now record some observations concerning the nature of this oily polymer. The reaction involved in its formation is a typically *thermal* polymerization; the rate is but slightly affected by oxidants or antioxidants. In a typical case about 8% of a sample of divinylacetylene was polymerized in three hours at 80°. If the reaction is carried too far (somewhere between 20 and 50%) the mixture sets to a gel. Before this stage is reached, the polymer is easily isolated by evaporation in a vacuum of the unchanged monomer. The properties of the residual oil vary considerably depending upon how far the reaction has progressed. In one experiment a sample taken when 13.4% of the monomer was polymerized (ten hours at 80°) had an apparent molecular weight of 230 ($3 \times C_6H_6 = 216$).

The oil is a mixture partly soluble, and partly insoluble, in alcohol. Attempts to distil it completely in high vacuum lead, in the end, to sudden explosive decompositions, but by careful operation a considerable volatile fraction can be isolated and redistilled. This material has the composition (approximately) and molecular weight $C_{12}H_{12}$. It is thus a dimer of divinyl-

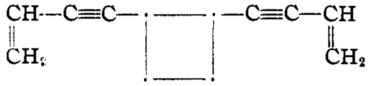
---

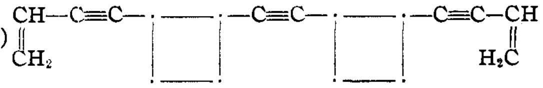
[1] Paper XIX in the series "Acetylene Polymers and their Derivatives."

[2] Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, 53, 4197 (1931).

[3] Collins, U. S. Patents 1,812,849 and 1,812,850.

acetylene which is, in turn, a trimer of acetylene. A fairly pure specimen, when spread out in a layer, dried rapidly to an exceedingly hard, insoluble film with the absorption of considerable oxygen (*e. g.*, 14.3% after two weeks). Bromination of the dimer gave crystalline octa- and deca-bromides. When hydrogenated, the dimer absorbed 12 atoms of hydrogen, and by oxidation it was converted into *trans*-1,2-cyclobutanedicarboxylic acid. Its structure must, therefore, be represented as divinylethynyl-1,2-cyclobutane (I)

(I)


(II)


(The absolute homogeneity of the material is, however, not completely established.) Similar dimerizations of substituted ethylenes are well known (*e. g.*, the truxillic acids), but the above structure was unexpected since most addition reactions of divinylacetylene appear to proceed 1,4.[4]

Attempts similarly to isolate a trimer failed on account of the thermal instability of higher fractions. To increase its stability, the mixed polymer was hydrogenated. Its behavior was peculiar since, with PtO_2 (Adams) and various other catalysts, reaction ceased after 1.5 to 2.9 moles of hydrogen had been absorbed (per C_6). The catalyst was then colloidally dispersed and could not be removed by filtration; fresh catalyst caused no further hydrogenation. The material could, however, be distilled in vacuum without decomposition, and the distillate was easily hydrogenated to saturation with fresh catalyst. From the product a liquid $C_{18}H_{34}$ was isolated. In view of the facts mentioned above the trimer from which it was derived may, with reason, be assigned formula II.

The diversity and the tremendously complex potentialities of polymerization processes are again emphasized by the compound II, which results from two successive steps of self-combination starting with acetylene, and which, in air, is spontaneously transformed into much larger and more complicated molecules.

Experimental

(1) Freshly distilled divinylacetylene was heated at 80° under nitrogen:

Time, hrs.	0	1.5	3	6	9
% non-volatile	0	4.9	8.1	11.6	18.1
n_D^{20} (of mixture)	1.504	1.5074	1.5092	1.5115	1.5173

(2) Polymer from heating of divinylacetylene for ten hours at 80° was isolated by evaporating monomer in vacuum.

	d_4^{20}	n_D^{20}	Mol. wt.
Fresh monomer	0.785	1.504	72 (calcd.)
Isolated polymer	.968	1.581	227, 234 (in freezing benzene)

(3) **Bromide of Polymer.**—A polymer (14.6 g.) similar to that of (2) with 90.5 g. of bromine in cold carbon tetrachloride gave a heavy viscous oil; purified by solution in hot alcohol and precipitation by cooling.

Anal. Calcd. for $C_{12}H_{12}Br_6$: Br, 75.5; mol. wt., 636. Found: Br, 76.65; mol. wt., 591, 608 (in freezing benzene).

(4) **Dimer of Divinylacetylene.**—From 940 g. of divinylacetylene, with 2.5 g. of pyrogallol, heated at 81–82° for five hours, by evaporation of monomer and distillation under nitrogen at 0.1 mm., 10 g. of colorless distillate was isolated. On redistillation it boiled at 53–55° at *ca.* 1 mm.; d_4^{20} 0.9248; n_D^{20} 1.5495; MR_D calcd. (for I) 50.48; MR_D found, 53.73.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 90.27; H, 7.77.

(5) **Bromination of Dimer.**—Freshly distilled dimer (22 g.) with 95 g. of bromine (8.1 atoms per mole) in carbon tetrachloride was allowed to stand for sixteen hours without light and the excess bromine and solvent were removed by evaporation. The residual oil at 0° yielded crystals (27 g.) which after repeated recrystallization from absolute ethyl acetate melted at 211°.

Anal. Calcd. for $C_{12}H_{12}Br_{10}$: C, 15.07; H, 1.27; Br, 83.56. Found: C, 16.05; H, 1.94; Br, 83.86.

Residues from the ethyl acetate mother liquors were recrystallized from alcohol and finally melted at 137°.

Anal. Calcd. for $C_{12}H_{12}Br_8$: C, 18.10; H, 1.52; Br, 80.37; mol. wt., 795.4. Found: C, 18.88; H, 1.95; Br, 80.71; mol. wt. (in freezing benzene), 803.

(6) **Oxidation of Dimer.**—Ozonization in carbon tetrachloride gave much insoluble material. From the water-soluble fraction, after oxidation with permanganate, succinic acid was isolated.

Oxidation with warm (50–60°) alkaline permanganate gave oxalic acid, succinic acid, *trans*-1,2-butanedicarboxylic acid and an oily acid.

Oxidation with cold permanganate: the dimer (9.6 g.) in acetone was slowly added to potassium permanganate (116 g.) in dilute aqueous sodium hydroxide at 5–10°. The mixture was acidified with sulfuric acid and further potassium permanganate (29 g.) added to permanent color. After solution of manganese dioxide by sulfur dioxide, continuous ether extraction gave 7.44 g. of oil from which 3 g. of crystals (m. p. 124–127°) was isolated by filtration. After several crystallizations from benzene the m. p. was 129–130°. A mixed melting point with a sample of *trans*-1,2-butanedicarboxylic acid kindly furnished by Dr. R. C. Fuson gave the same value.

---

[4] Coffman, Nieuwland and Carothers, THIS JOURNAL, **55**, 2048 (1933).

Anal. Calcd. for $C_6H_8O_4$: C, 49.98; H, 5.60; neutral equivalent, 72. Found: C, 49.18; H, 5.65; neutral equivalent, 72.

The oil (above) completely freed of crystals was perhaps a hydroxycyclobutanecarboxylic acid.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.95; neutral equivalent, 116. Found: C, 50.48; H, 6.95; neutral equivalent, 116.8.

The oil was converted into its dry sodium salt and heated with *p*-bromophenacyl bromide. The product, crystallized from 95% alcohol, melted at 145°. Its composition agreed with that calculated for a bromophenacyl ester of a hydroxycyclobutanecarboxylic acid.

Anal. Calcd. for $C_{12}H_{13}O_4Br$: C, 49.84; H, 4.15. Found: C, 49.45, 49.53; H, 3.85, 3.95.

(7) **Hydrogenation of Alcohol-Soluble Polymers.**—Crude polymer in absolute alcohol was hydrogenated (using PtO_2), distilled, and rehydrogenated until no further absorption occurred.

A fraction corresponding to hydrogenated dimer was washed with sulfuric acid, dried over sodium and separated into fractions by distillation through a good column. Physical properties and composition were determined for the first (A, 38 g.) and last (B, 25 g.) fractions as shown below.

(A) B. p. 36–38° at *ca.* 0.1 mm.; d_4^{20} 0.7858; n_D^{20} 1.4342.

(B) B. p. 38–40° at *ca.* 0.1 mm.; d_4^{20} 0.8045; n_D^{20} 1.4432.

Anal. Calcd. for $C_{12}H_{24}$: C, 85.62; H, 14.38; mol. wt., 168.2. Found: (A) C, 85.69, 85.44; H, 14.63, 14.52; mol. wt. (freezing benzene), 170.6, 171. (B): C, 85.80, 85.96; H, 14.18, 14.51; mol. wt. (freezing benzene), 172, 171.

The difference in physical properties between (A) and (B) is sufficient to suggest the presence of stereoisomers in the original dimer.

Further distillation of hydrogenated polymer gave higher boiling fractions, and a fairly sharp cut (7.5 g.) separated at 111–113° under 1–1.5 mm. had d_4^{20} 0.8537; n_D^{20} 1.4682. Analysis showed that it was hydrogenated trimer.

Anal. Calcd. for $C_{18}H_{24}$: C, 86.31; H, 13.48; mol. wt., 250.3. Found: C, 86.23, 85.75; H, 13.48, 13.52; mol. wt. (freezing benzene), 255, 251.

The hydrogenated dimer and trimer both absorbed bromine rapidly with the liberation of hydrogen bromide, and were oxidized slowly by hot alkaline permanganate.

Summary

The thermal polymerization of divinylacetylene yields an oily polymeric mixture, from which the dimer has been isolated and identified as *trans*-1,2-divinylethynyl-cyclobutane. The trimer is probably similarly a *bis*-vinylethynylcyclobutylacetylene. The isolated hydrogenated (saturated) derivatives of the dimer and trimer are described.

WILMINGTON, DEL. RECEIVED JANUARY 25, 1934

[CONTRIBUTION NO. 140 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

The Addition of Alcohols to Vinylacetylene[1]

BY RALPH A. JACOBSON, H. B. DYKSTRA AND WALLACE H. CAROTHERS

Both acetylenic and ethylenic linkages are activated by conjugation with certain polar groups (*e. g.*, carbonyl) in such a manner that they react readily directly with alcohols. Consideration of the formula of vinylacetylene (III) suggested that the acetylenic linkage might here be similarly activated by the vinyl group or conversely the ethylenic linkage by the ethynyl group. Vinylacetylene was accordingly heated at about 105° with methanol and a little sodium methylate. Reaction occurred smoothly and a product having the composition $C_4H_4 \cdot CH_3OH$ was obtained. In view of its origin this material might be expected to have the formula I or II.

$$\underset{\text{(I)}}{CH_2{=}C(OCH_3)CH{=}CH_2} \qquad \underset{\text{(II)}}{CH{\equiv}C{-}CH(OCH_3)CH_3}$$

Examination of its reactions showed, however, that it was V. Hydrogenation converted it to methyl *n*-butyl ether and oxidation gave a mixture of acetic and methoxyacetic acids.

$$\underset{\text{(III)}}{CH{\equiv}C{-}CH{=}CH_2} \longrightarrow \underset{\text{(IV)}}{[CH_2{=}C{=}CHCH_2OCH_3]} \longrightarrow \underset{\text{(V)}}{CH_3C{\equiv}CCH_2OCH_3}$$

The course of the reaction must therefore be interpreted as follows. The alcohol adds 1,4 to the conjugated system, giving rise to the intermediate IV, which is then rearranged by the sodium alcoholate to the acetylenic ether V. It may be recalled that hydrogen chloride similarly adds to vinylacetylene at the ends of the conjugated system, giving rise to a product analogous to IV, but this is capable of being isolated, and subsequent rearrangement follows an entirely different course involving an α,γ-shift.[2] As a matter of observation α,γ-shifts in compounds of

---

[1] Paper XX in the series "Acetylene Polymers and their Derivatives." Paper XIX, THIS JOURNAL, **56**, 1167 (1934).

[2] Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).