

[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 ketone¹ and the ethylmagnesium bromide from 30 cc. of ethyl bromide; b. p. 36–37° (3 mm.); d_{20}^{20} 0.8231; n_{D}^{20} 1.4101.

Anal. Calcd. for $C_{10}H_{20}O$: 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 $C_{10}H_{19}I$: I, 49.90. Found: I, 49.75.

(1) Johnson and Hager, "Organic Syntheses," 1932, Coll. I, p. 343.

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; $n_{D}^{21.5}$ 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

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

The Structure of Divinylacetylene Polymers¹

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 reac-

tion 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.