

## NEW REACTIONS OF PENTAERYTHRITOL

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Pentaerythritol,  $C(CH_2OH)_4$ , was manufactured in large quantities during the last war for conversion to its explosive tetranitrate. It has also a considerable market as a component of resinous compositions for the paint and varnish industry, and is becoming important for manufacturing surface-active agents. This increased importance has suggested further study of its reactions.

The monoformal, for instance, has been prepared only by acid-catalyzed reaction of equimolar amounts of pentaerythritol and formaldehyde (7), the monoformal being separated from the accompanying diformal by the smaller solubility of the monoformal — the more polar form — in benzene. In the present work pentaerythritol diformal (60g, 0.375 mole), pentaerythritol (51g, 0.375 mole) and 85% phosphoric acid (0.5 ml) were refluxed for 2 hours, cooled to about 100°, and exactly neutralized with concentrated aqueous sodium hydroxide. Distillation of the mixture at 0.25 mm gave 17.5 g of recovered diformal, b.p. 92–100°, and 61 g (55% of the theoretical amount) of pentaerythritol monoformal, b.p. 150–152°. After one recrystallization from benzene the product melted at 59°; the literature value is 60° (7).

Treatment of the monoformal with benzaldehyde and concentrated hydrochloric acid gave no visible reaction, showing that the monoformal is converted neither to the dibenzal nor to an insoluble monoformal monobenzal derivative. The monoformal resists alkaline hydrolysis, as expected, but is totally destroyed by aqueous alkaline permanganate rather than being converted to a *m*-dioxane-5, 5-dicarboxylic acid. The diformal is similarly attacked by aqueous permanganate.

Pentaerythrityl tetraacrylate is unrecorded in the literature, but would probably find use as a monomer for making cross-linked plastics. In view of the ready availability of methyl acrylate and the difficulties of using the free acid, alcohol exchange was chosen as a route to this ester. Essentially the procedure of Rehberg (4) was followed but sulfuric acid was used as catalyst (2). The alcoholysis was performed in a three-necked, round-bottomed flask fitted with an inlet tube for carbon dioxide, a mechanical stirrer, and an 8-ball Snyder fractionating column. Washing the distillate with water served both to recover methyl acrylate and to indicate (by loss in volume) the amount of methanol produced. When the catalyst was sulfuric acid, up to 86% of the theoretical amount of methanol was collected, in several trials, but phosphoric acid, *m*-nitrobenzenesulfonic acid, and sodium methoxide were ineffective. After the distillation with sulfuric acid the brown residue was dissolved in water, neutralized with sodium bicarbonate, and extracted with ether. Distillation of the brown oil at 0.3–0.4 mm failed repeatedly because of sudden polymerization at 190°, which occurred in spite of the presence of inhibitors; recrystallization also failed.

Although ethers of pentaerythritol are known, they have not been prepared by splitting out water with other alcohols or with phenols. Since this is a familiar procedure for making ethers of aliphatic alcohols and of naphthols, both preparations were tried. The attempted alkylation of pentaerythritol with boiling isopropyl alcohol and concentrated sulfuric acid, however, gave no evidence of any involvement of the polyalcohol. Refluxing pentaerythritol and 2-naphthol (molar ration 1:4) in xylene solution in the presence of sulfuric acid (soon converted to xylenesulfonic acids) produced water, which was removed azeotropically, and a dark solution. This by evaporation, washing with alkali solutions, and exhaustive recrystallization from benzene and petroleum gave a neutral white crystalline product (A) melting at 158–159°, soluble in cold alcohol or benzene. Several attempts to repeat this preparation

gave only a different substance (B), white cotton-like needles from benzene or acetone + petroleum ether, of melting point 146.5-147°. B was soluble in alcohol but virtually insoluble in cold benzene. Analyses for carbon and hydrogen showed that neither A nor B was one of the naphthyl ethers of pentaerythritol nor a mixture of them.

In order to find out whether the solvent was participating in the reaction, two runs were made in ethylbenzene. Both gave a third white crystalline product (C), m.p. 172.5-173° after recrystallization from alcohol-water or acetone-ligroin, soluble in benzene but not in cold alcohol. A trial run in ethylbenzene *without* pentaerythritol gave 2-naphthyl ether, recrystallizable from alcohol and recognized by its melting point of 105°, as the only insoluble product. To complete the trials pentaerythritol, ethylbenzene and sulfuric acid were heated together without 2-naphthol; no product was obtained.

Neither A, B, nor C contained sulfur nor decolorized a cold aqueous solution of potassium permanganate. The results of analyses are recorded here, but no reasonable structures have been devised to fit them.

	CARBON, %		HYDROGEN, %		OXYGEN, % (BY DIFFERENCE)	
A	81.99,	82.09	6.50,	6.43	11.51,	11.48
B	77.85,	77.30	6.72,	6.53	15.43,	16.17
C	89.25,	89.05	5.93,	5.75	4.82,	5.20

Like ethers of pentaerythritol, the amines derived therefrom have not been prepared from the polyalcohol and ammonia or primary or secondary amines by intermolecular dehydration. Since the alkylation of aniline with methanol is well known, an analogous reaction was attempted with pentaerythritol as the alcohol in the hope of obtaining tetrakis(phenylaminomethyl)methane,  $C(CH_2NHC_6H_5)_4$ . Boiling aniline containing a little zinc chloride or aniline hydrochloride gave no evidence of reacting with pentaerythritol, but freshly distilled aniline hydrochloride refluxed with pentaerythritol gradually produced the theoretical amount of water, collected by distillation. Addition of excess alkali, removal of aniline by steam distillation, and extraction with ether produced a small amount of a water-insoluble orange oil, soluble in all organic solvents tried except ligroin but non-crystallizable. It was therefore distilled at 210-230° at 3 mm, but still would not crystallize; and since a solid product was expected, the oil was abandoned.

Since simple alcohols react at their boiling points with urea to give urethans, it was supposed that pentaerythritol might analogously be converted to  $C(CH_2OOCNH_2)_4$ , of possible use in making nylon-type fibers. However, Dittmar and Loder (3) obtained ethyleneurea and not the diurethan by heating ethylene glycol and urea together at 200-300°. In present experiments pentaerythritol and urea (mole ratio 1:4) were heated in sealed tubes for 5 hours at 200° and 230° for 2 hours more. The crystalline yellow product gave evidence of containing a compound other than the reagents, but solubility differences of the components of the mixture were too small to permit separation.

Known means (1, 4) of preparing the tetrathio derivative of pentaerythritol,  $C(CH_2SH)_4$ , are roundabout and inconvenient. The direct preparation from pentaerythritol, hydrobromic acid, and thiourea, modeled after the conversion thus of simpler alcohols to thiols (5), was therefore tried, but without success. Presumably pentaerythritol behaves more like a neopentyl alcohol than an ordinary one here.

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