

was shown to be a mixture of the above two products by like methods. The yield of organic products was 95%.

The absence of acetophenone from the reaction mixture was established by the failure of any fraction to yield acetophenone semicarbazone under conditions which gave rise to a 92% yield of this derivative from authentic acetophenone.

Infrared spectra were run on a Perkin-Elmer infrared spectrophotometer. Sulfate was determined quantitatively by usual methods.

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Tris-acetylacetonate-osmium(III)

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No osmium acetylacetonate derivative is described in the literature. The reaction between Os(IV) complexes such as the hexachloro- or hexabromo-osmate ions with acetylacetonate yields only osmium dioxide under neutral or weakly alkaline conditions. However, if first reduced with silver wool to Os(III) and then treated with acetylacetonate at pH 6-7 a fair yield of tris-acetylacetonate-osmium(III) results. During the reaction or the working up of the product a purple substance also is formed. This is diamagnetic and hence contains Os(IV) or Os(VI). It contains halogen as well as acetylacetonate and adsorption on alumina from benzene solution shows that it is a complex mixture of different colored substances.

Experimental

Tris-acetylacetonate-osmium(III).—Water (30 ml.), 47% hydrobromic acid (2 ml.) and silver wool (1 g.) in a small flask were agitated with a current of nitrogen for 15 min., and ammonium hexabromoosmate (2 g.) added and the passage of gas continued for 12 hr. The resulting pale orange-yellow solution was treated with potassium bicarbonate (1.2 g.), and acetylacetonate (5 ml.) and heated under reflux for 15 min. More potassium bicarbonate (1.5 g.) was added, the color changing from dark orange to purplish-red (pH 7). Acetylacetonate (2 ml.) then was added and the heating continued for an hour. After cooling, the mixture was extracted with chloroform, which was then washed with 2% sodium hydroxide. The chloroform was evaporated and the solid crystallized from aqueous alcohol. The substance (0.7 g., 50%) gave dark red plates and needles, m.p. 251, sparingly soluble in methanol and petroleum ether, but easily soluble in benzene and chloroform. The magnetic moment (1.81 B.M.) is consistent with trivalent osmium. Since there does not appear to be a reliable method for C, H analysis in the presence of Os, analysis for the metal only was done. The purple compound is found in the mother liquors.

Anal. Calcd. for $C_{15}H_{21}O_6Os$: Os, 39.02; mol. wt., 488. Found: Os, 39.06; mol. wt. (Rast, in camphor), 450.

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Glyoxal Acetals

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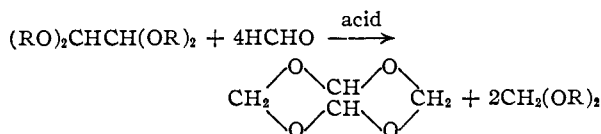
In excellent agreement with the findings of Duval, Hall and Howe,¹ the acid-catalyzed reaction of excess 1-butanol with commercial aqueous glyoxal solution gave 2,3-di-*n*-butoxy-1,4-dioxane (I), 1,1-

(1) B. Duval, R. H. Hall and B. K. Howe, *J. Appl. Chem. (London)*, **2**, 546 (1952).

2,2-tetra-*n*-butoxyethane^{2,3} (II), and 2,3,5,6-tetra-*n*-butoxy-1,4-dioxane³ (III). The formation of I depended on the presence of ethylene glycol in the glyoxal solution, and was enhanced by addition of that glycol to the reaction mixture. However, commercial glyoxal solution could not be made to yield 1,1,2,2-tetramethoxyethane by distillation with methanol.²

Since the formation of α -chloro ethers from glyoxal by Henry's⁴ method has never been reported, it was tested with methanol and 1-propanol. Methanol, aqueous glyoxal and hydrogen chloride gave no non-aqueous layer, but 1-propanol used as the alcohol produced what was probably the expected 1,2-dichloro-1,2-di-*n*-propoxyethane,^{5,6} not fully purified because of its instability. This instability has been noted in 1,2-dihalo-1,2-dialkoxyethanes otherwise prepared.⁷

Efforts to prepare 1,3-dioxolano[4,5-d]-1,3-dioxolane, which may be regarded as a mixed polymer of glyoxal and formaldehyde, by the reaction



were unsuccessful.

Experimental

Aqueous 30% glyoxal solution (200 ml.), 1-butanol (400 ml.), and 1 ml. of concentrated sulfuric acid as catalyst were distilled together, the alcohol layer being returned to the reaction mixture as long as any water phase appeared in the distillate. The residue was washed thoroughly with water to remove acid, dried over calcium sulfate, and rapidly distilled up to 225° at 25 mm. pressure. The distillate was fractionally distilled at 65 mm. through either an Oldershaw or a Todd column, yielding a small fraction (a) boiling at 140° and a larger one (b) at 177°; further distillation at 5 mm. gave a third fraction (c) boiling at 187-188°. All three fractions were yellow and required at least redistillation.

Fraction a, comprising 3.3 g. (1%) after redistillation, proved to be 2,3-di-*n*-butoxy-1,4-dioxane, n_D^{20} 1.4324, d_4^{20} 0.984.

Anal. Calcd. for $C_{12}H_{24}O_4$: C, 62.1; H, 10.34; mol. wt., 232; glyoxal, 25.0; *MR*, 60.0. Found: C, 61.6; H, 10.43; mol. wt. (cryoscopically in benzene), 227; glyoxal (gravimetrically, as the 2,4-dinitrophenylosazone), 24.5; *MR*, 61.2. The yield of 2,3-di-*n*-butoxy-1,4-dioxane was increased substantially when ethylene glycol was added to the 1-butanol initially used.

Redistillation of fraction b at 177° at 65 mm. gave 95.5 g. (20%) of a colorless liquid, d_4^{20} 0.969, presumed to be 1,1,2,2-tetra-*n*-butoxyethane. However, the literature gives higher boiling points (162° or 159-161° at 10 mm., or 166-167° at 12 mm.; by the Hass-Newton equation these correspond to about 195° at 65 mm.) and a lower density, d_4^{20} 0.890.² The sample had about the proper molecular weight (calcd. 318, found 308) but not satisfactory molecular refraction (calcd., 87.1, found 85.1). It therefore was purified by diluting with toluene, refluxing with sodium until reaction ceased, filtering, and refractionating

(2) L. G. MacDowell and R. W. McNamee, U. S. Patent 2,360,959 (1944), *via* C. A., **39**, 2080 (1945); British Patent 559,362 (1944), *via* C. A., **40**, 355 (1946).

(3) H. Fiesselmann and F. Hörndler, *Chem. Ber.*, **87**, 906 (1954); *cf.* H. C. Chitwood, U. S. Patent 2,361,456 (1944), *via* C. A., **39**, 2078 (1945).

(4) L. Henry, *Bull. soc. chim. Belg.*, [2] **44**, 458 (1885).

(5) H. Baganz, W. Hohmann and J. Pfug, *Chem. Ber.*, **86**, 615 (1953).

(6) H. Fiesselmann and F. Hörndler, *ibid.*, **87**, 911 (1954).

(7) S. M. McElvain and C. H. Stammer, *THIS JOURNAL*, **73**, 915 (1951); **75**, 2154 (1953); R. C. Schreyer, *ibid.*, **73**, 2962 (1951).