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-acetylacetone-osmium(III)

BY F. P. DWYER AND A. SARGESON

RECEIVED NOVEMBER 1, 1954

No osmium acetylacetone derivative is described in the literature. The reaction between Os(IV) complexes such as the hexachloro- or hexabromoosmate ions with acetylacetone yields only osmium dioxide under neutral or weakly alkaline conditions. However, if first reduced with silver wool to Os(III) and then treated with acetylacetone at *p*H 6–7 a fair yield of tris-acetylacetone-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 acetylacetone and adsorption on alumina from benzene solution shows that it is a complex mixture of different colored substances.

Experimental

Tris-acetylacetone-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 hexabromoösmate (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 acetylacetone (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 (*p*H 7). Acetylacetone (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 tervalent 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

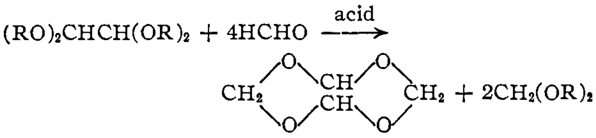
BY O. C. DERMER AND JAMES P. YUK

RECEIVED SEPTEMBER 29, 1954

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), 1,1,2,2-tetra-*n*-butoxyethane[2,3] (II), and 2,3,5,6-tetra-*n*-butoxy-1,4-dioxane[3] (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's[4] 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^{29}_{D} 1.4324, d^{29}_{4} 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^{29}_{4} 0.969, presumed to be 1,1,2,2-tetra-*n*-butoxyethane. However, the literature gives higher boiling points (162°[2] or 159–161°[2] at 10 mm., or 166–167°[5] at 12 mm.; by the Hass–Newton equation these correspond to about 195° at 65 mm.) and a lower density, d^{20}_{4} 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

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

[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. Pflug, *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).

at 10 mm., and then boiled sharply at 139–140°. The purified material had n^{20}_D 1.4350 and d^{20}_4 0.954, whence *MR* 87.0. The literature values therefore are believed somewhat inaccurate.

Fraction c when redistilled comprised 40 g. (14%). It boiled at 198° at 10 mm. and had n^{29}_D 1.4315 and d^{29}_4 0.957; Fiesselmann and Hörndler[3] give the boiling point of 2,3,5,6-tetra-*n*-butoxy-1,4-dioxane as 195–202° at 10 mm.

Anal. Calcd. for $C_{20}H_{40}O_6$: C, 63.8; H, 10.70; mol. wt., 376; *MR*, 101.9. Found: C, 64.3; H, 11.07; mol. wt., 355; *MR*, 102.2.

The compound gave little or no osazone upon standing with an acid solution of 2,4-dinitrophenylhydrazine.

The preparation of 1,1,2,2-tetramethoxyethane by the same method[3] failed, the removal of water by entrainment with methanol being very unsatisfactory, as would be expected.

To obtain 1,2-dichloro-1,2-di-*n*-propoxyethane, 150 ml. of commercial glyoxal was evaporated to half-volume, diluted with 250 ml. of 1-propanol, stirred, and saturated with hydrogen chloride at 0–10° (about 4 hours required). Pouring the mixture into ice-water gave about 200 ml. of a lower layer which was roughly dried over calcium chloride, freed of hydrogen chloride *in vacuo*, further dried at 0–10° (it darkened and evolved hydrogen chloride in 12 hours at room temperature), and fractionally distilled. The portion boiling at 106–107° at 15 mm., n^{29}_D 1.4420, d^{29}_4 1.083 (literature 98–99° at 10 mm.[5] or 97° at 17 mm.,[4] n^{23}_D 1.4448,[4] d^{23}_4 1.0825,[4] *MR* thence 52.88[4]) proved upon analysis to be slightly impure.

Anal. Calcd. for $C_8H_{10}O_2Cl_2$: Cl, 32.6; mol. wt., 215; *MR*, 52.1. Found: Cl, 30.9; mol. wt., 201; *MR*, 52.6.

Redistillation at higher pressures caused even more departure from the theoretical value for chlorine, evidently by loss of hydrogen chloride.

When either 1,1,2,2-tetra-*n*-butoxyethane or *p*-dioxano-[b]-*p*-dioxane was heated with excess trioxane or paraformaldehyde and sulfuric acid catalyst, no definite evidence of the formation of either the desired 1,3-dioxolano[4,5-*d*]-1,3-dioxolane, or the by-products (di-*n*-butoxymethane and 1,3-dioxolane, respectively) could be obtained.

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Preparation of 4-Chlorobutyl *p*-Toluenesulfonate from Tetrahydrofuran and *p*-Toluenesulfonyl Chloride[1]

BY LAMAR FIELD AND JOHN R. HOLSTEN

RECEIVED AUGUST 17, 1954

ω-Haloalkyl sulfonates containing alkyl groups of two or three carbon atoms have been used for alkylation of a variety of substances, and are of interest because the alkyl group introduced is terminated by a halogen atom, which is available for subsequent reaction. The alkylation of a Grignard reagent,[2] which illustrates one such use of these esters and which is referred to in a number of textbooks, is shown by the equation

$$\mathrm{RMgX} + 2p\text{-}\mathrm{CH_3C_6H_4SO_3(CH_2)_3Cl} \longrightarrow \mathrm{R(CH_2)_3Cl} + \mathrm{Cl(CH_2)_3X} + (p\text{-}\mathrm{CH_3C_6H_4SO_3})_2\mathrm{Mg}$$

The synthesis of 4-chlorobutyl benzoate from tetrahydrofuran and benzoyl chloride[3] suggested that 4-chlorobutyl *p*-toluenesulfonate (I), a previously unknown homolog in the series of ω-haloalkyl sulfonates, might be obtained conveniently from *p*-toluenesulfonyl chloride.

When *p*-toluenesulfonyl chloride was heated with tetrahydrofuran and a little zinc chloride, compound I was isolated in 46% yield. 4,4′-Dichlorodibutyl ether (II, 18%) and 1,4-dichlorobutane (III, 12%), the formation of which have been noted previously in related cleavages with inorganic acid halides,[4] were obtained as by-products.

$$p\text{-}\mathrm{CH_3C_6H_4SO_2Cl} + \mathrm{(CH_2)_4O} \xrightarrow{\mathrm{ZnCl_2}} \underset{\mathrm{I}}{p\text{-}\mathrm{CH_3C_6H_4SO_3(CH_2)_4Cl}} + \underset{\mathrm{II}}{[\mathrm{Cl(CH_2)_4}]_2\mathrm{O}} + \underset{\mathrm{III}}{\mathrm{Cl(CH_2)_4Cl}}$$

Variation of the scale of the reaction had little effect, and as much as two moles of the sulfonyl chloride was used successfully and with only minor modifications. Iodine was moderately effective as a catalyst, but aluminum chloride, boron trifluoride etherate and cadmium chloride were unpromising.

The structure I for the product was supported by saponification (which was accompanied by dehydrohalogenation) and by the reactions with inorganic halides discussed below, as well as by physical and chemical evidence of customary character.

In order to ascertain the extent to which the sulfonoxy group of I might react in preference to the chlorine atom in selective alkylation reactions, the reaction of I and sodium iodide was examined. Reaction in acetone at room temperature gave pure 1-chloro-4-iodobutane in 60% yield.

In certain instances, a desired alkylation product may be difficultly separable from unchanged I because of close similarity in physical properties. A method for circumventing this difficulty is suggested by the observation that lithium chloride, which should have no effect on most reaction products, effects virtually quantitative cleavage of the I, with the formation of easily separable III.

The reaction of I with phenylmagnesium bromide yielded 1-bromo-4-chlorobutane (IV, 52%) and 4-chlorobutylbenzene (V, 27%). Although IV and V had physical properties approximating reported values, contamination by difficultly separable impurities resulted in unsatisfactory analyses.

Experimental[5]

4-Chlorobutyl *p*-Toluenesulfonate (I). (a) Preparation.—A mixture of 93.5 g. of tetrahydrofuran, 190.6 g. of *p*-toluenesulfonyl chloride and 12.3 g. of freshly fused zinc chloride was stirred and submerged in an oil-bath preheated to 95°. When the temperature of the mixture reached 80°, a brief but vigorous exothermic reaction began, which resulted in a rise of temperature within about 4 minutes to 168°. The temperature then began to decrease almost immediately, and a viscous oil containing a small amount of solid resulted. The heating bath was removed while the temperature exceeded 100°. When the mixture had cooled again to 100°, it was heated at 85–100° for six hours. The oil, which no longer contained solid, was cooled, and poured into ice-water. Combined ether extracts were washed with saturated aqueous sodium bicarbonate and water until neutral and were dried over anhydrous sodium sulfate–potassium carbonate (1:1). After filtration, the filtrate was distilled through a 25-cm. Vigreux column under reduced pressure until ether had been removed. Anhydrous potassium carbonate (5 g.) was then added, after which distillation with

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[1] This work was supported by the Office of Ordnance Research, U. S. Army. The authors are also indebted to Research Corporation of New York for support during the early phases. Abstracted from the M.A. thesis of John R. Holsten, March, 1955.

[2] (a) H. Gilman and N. J. Beaber, THIS JOURNAL, **45**, 839 (1923); (b) S. S. Rossander and C. S. Marvel, *ibid.*, **50**, 1491 (1928).

[3] M. E. Synerholm, *Org. Syntheses*, **29**, 30 (1949).

[4] K. Alexander and L. E. Schniepp, THIS JOURNAL, **70**, 1839 (1948).

[5] Melting points are corrected and boiling points uncorrected. Analyses, except for sulfur, were by Micro-Tech Laboratories, Skokie, Ill.