It was found to be slightly soluble in water and cold alcohol and rather strongly soluble in benzene. It dissolved readily in dilute or concentrated sulfuric acid. It was insoluble in aqueous hydrochloric acid but in benzene solution with hydrogen chloride it formed a salt, m.p. 223–225°, which was insoluble in water. A picrate could not be isolated from alcohol solution. The methiodide formed rapidly in boiling methanol and melted at 210–215° dec.

Anal. Calcd. for $C_7H_{12}NS_3I$: C, 25.22; H, 3.63. Found: C, 25.10, 25.38; H, 3.63, 3.63.

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The Reaction of Cumyl Hydroperoxide with Sodium Hydrosulfide

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Cumyl hydroperoxide has been shown[1] to undergo reduction by various routes, depending upon the nature of the reducing agent employed. Boardman[1a] has shown that reduction with ferrocyanide *via* a one-electron transfer gives rise to the α,α-dimethylbenzyloxy radical[2] which decomposes to give acetophenone and methyl radical. An alternative mechanism is a two-electron transfer process, represented by the reduction of cumyl hydroperoxide to α,α-dimethylbenzyl alcohol by iodide ion.[1b] A process involving two consecutive one-electron transfers is a third alternative. This last mechanism would also give rise to α,α-dimethylbenzyl alcohol.

The reaction of cumyl hydroperoxide with alkaline sodium hydrosulfide was investigated in an effort to elucidate the mechanism of reduction by the latter reagent.[3] Under the conditions employed the organic products of this reaction were α,α-dimethylbenzyl alcohol and α-methylstyrene. The latter product is believed to have resulted from dehydration of the initially formed tertiary alcohol. Unfortunately, the formation of these products excludes only one mechanistic concept, namely, reduction by a one-electron transfer to α-cumoxy radical, followed by decomposition to acetophenone and methyl radical, but they do not exclude either a simple two-electron transfer to give cumoxide ion or a rapid reduction of cumoxide radical to cumoxide ion.

It seemed of some interest to attempt to determine the fate of the sulfur in the reaction under consideration, particularly in view of a transitory yellow coloration of the reaction mixture which appeared momentarily after the addition of each drop of sodium hydrosulfide solution to an ethanolic solution of cumyl hydroperoxide. Subsequent investigation showed that polysulfide solutions undergo immediate decoloration when treated with cumyl hydroperoxide and that the acidified aqueous extracts of such solutions showed qualitative tests for sulfate ion.

Analysis of the inorganic products of the reaction of cumyl hydroperoxide with sodium hydrosulfide disclosed that 37% of the theoretical amount of sulfate ion (determined as barium sulfate) based on the equation

$$4\,\mathrm{ROOH} + \mathrm{HS}^- + \mathrm{OH}^- \longrightarrow 4\,\mathrm{ROH} + \mathrm{SO_4}^{=} + \mathrm{H_2O}$$

was formed. Acidification of the aqueous extracts of the reaction mixture led to deposition of sulfur and to the evolution of large amounts of sulfur dioxide. Formation of the latter compound indicates that a portion of the hydrosulfide was oxidized to sulfite and/or thiosulfate. No attempt was made to determine these latter ions in a quantitative manner. In view of the excess hydrosulfide present in the reaction mixture and the isolation of sulfate as a product,[5] it is conceivable that the aqueous extracts from the reaction mixture may have contained sulfur in other valence states.

The reduction of cumyl hydroperoxide to the alcohol by sodium hydrosulfide is, therefore, analogous to the results reported in the reduction by sodium sulfide of methyl 9-hydroperoxydehydroabietate and methyl 9-oxo-14-hydroperoxydehydroabietate.[6]

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Experimental

Materials.—Sodium hydrosulfide reagent was prepared by saturating an approximately 6 *N* sodium hydroxide solution with hydrogen sulfide gas. Dilutions were made as required, and the resulting solutions were standardized by potentiometric titration against standard silver nitrate solutions. Cumyl hydroperoxide was a Hercules Powder Company product containing 70% hydroperoxide.

Procedure.—To cumyl hydroperoxide dissolved in a large volume of 95% ethanol (usually 10 g. of 70% cumyl hydroperoxide in *ca.* 400 ml. of 95% ethanol) was added dropwise with stirring an equimolar quantity of 0.5 *M* sodium hydrosulfide solution. The reaction was conducted in an atmosphere of nitrogen and proceeded vigorously at room temperature. Following the addition of sodium hydrosulfide the mixture was stirred for an hour and allowed to stand overnight. After removal of ethanol by distillation at a pressure of 20 mm., the mixture was extracted with ether; the ether extracts were washed with water and dried over anhydrous sodium sulfate. Removal of ether left a colorless liquid which distilled at 63–102° (18 mm.). Fraction 1, b.p. 63–64° (18 mm.), was shown to be α-methylstyrene by its reaction with an equivalent amount of bromine and the identity of its infrared spectrum with that of an authentic sample.[7] Fraction 3, b.p. 101–102° (18 mm.), which was shown to be α,α-dimethylbenzyl alcohol by the identity of its infrared spectrum with that of the authentic alcohol (b.p., 101–102° (18 mm.), $n^{20}D$ 1.5216), comprised the major portion of the distillate. A small intermediate fraction

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[1] (a) H. Boardman, THIS JOURNAL, **75**, 4268 (1953); (b) H. Boardman and G. E. Hulse, *ibid.*, **75**, 4272 (1953).

[2] M. S. Kharasch, W. Nudenberg and F. S. Arimoto, *Science*, **113**, 392 (1951).

[3] It has been shown[4] that alkaline hydrosulfides reduce alkyl nitrates to the corresponding alcohols. We were interested in the possibility of finding a single one-electron transfer reaction in this medium, in view of the polysulfide catalysis of the nitrate ester reduction.[4]

[4] R. T. Merrow, S. J. Cristol and R. W. Van Dolah, THIS JOURNAL, **75**, 4259 (1953).

[5] H. Hock and S. Lang, *Ber.*, **77B**, 257 (1944), showed that cumyl hydroperoxide may be reduced to α,α-dimethylbenzyl alcohol by sodium sulfite.

[6] P. F. Ritchie, T. F. Sanderson and L. F. McBurney, THIS JOURNAL, **75**, 2610 (1953); **76**, 723 (1954).

[7] α-Methylstyrene was prepared by dehydration of α,α-dimethylbenzyl alcohol by the method of K. Matsubara and W. H. Perkin, Jr., *J. Chem. Soc.*, **87**, 672 (1905).

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

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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

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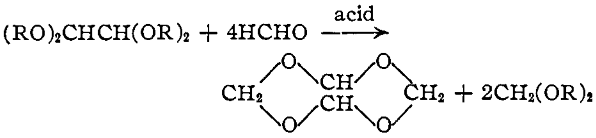
In excellent agreement with the findings of Duval, Hall and Howe,[1] the acid-catalyzed reaction of excess 1-butanol with commercial aqueous glyoxal solution gave 2,3-di-*n*-butoxy-1,4-dioxane (I), 1,1,2,2-tetra-*n*-butoxyethane[2,3] (II), and 2,3,5,6-tetra-*n*-butoxy-1,4-dioxane[3] (III). The formation 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).

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