Dauben and Harold D. McDowell[23] during the progress of the work.

Summary

1. Crystalline 6-β-D-mannosido-β-D-mannose octaacetate has been synthesized and characterized; m. p. 152–153° (cor.); $[\alpha]^{25}D$ +19.6°.

2. Amorphous 6-β-D-mannosido-mannose has been prepared from the corresponding octaacetate. This sugar began to soften at 70° and caramelized at 90–95°; $[\alpha]^{31}D$ +61.5°. The crystalline 6-β-D-mannosido-mannose phenylosazone has been prepared, m. p. 122–128°.

3. A series of two orthoester forms and one normal form of a glycoside (6-D-mannosido-β-D-glucose octaacetate) has been prepared for the first time.

4. The crystalline positively (m. p., 168–169° (cor.); $[\alpha]^{30}D$ + 17.1°) and negatively (m. p. 174.0–174.5° (cor.); $[\alpha]^{32}D$ −27.6°) rotating orthoester forms of 6-mannosido-β-D-glucose octaacetate have been synthesized and characterized. The action of dry hydrogen halide–chloroform on them has been studied.

5. The normal form of 6-β-D-mannosido-β-D-glucose octaacetate $[\alpha]^{19}D$ +38.9°) has been isolated and purified by chromatographic adsorption and its properties determined.

6. α - Acetobromo - 6 - β - D - mannosido - D - glucose has been prepared crystalline and its properties determined, m. p. 172.0–172.5° (cor.); $[\alpha]^{30}D$ +151.5°.

COLUMBUS, OHIO RECEIVED DECEMBER 17, 1942

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[23] The Ohio State University W.P.A. project.

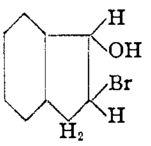
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Indene and Styrene Bromohydrins with Sodium Sulfite. Cleavage of Alkali Sulfonates with Sodium in Liquid Ammonia

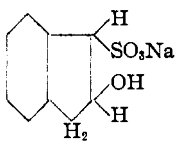
BY C. M. SUTER[1] AND H. BAYARD MILNE

Some time ago von Braun and co-workers[2] reported that the reaction of indene bromohydrin (1-hydroxy-2-bromoindane) with methylamine or dimethylamine gives a derivative of 2-hydroxy-1-aminoindane, presumably through the intermediate formation of indene oxide.[3] On the other hand, styrene bromohydrin (1-phenyl-1-hydroxy-2-bromoethane) reacts with ammonia without rearrangement,[4] and a third bromohydrin, 1-phenyl-1-hydroxy-2-bromopropane,[5] with methylamine yields a mixture of *pseudo* and *iso*-ephedrine.

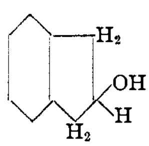
The diverse behavior of these bromohydrins with ammonia and amines suggested the present study of the reaction of indene and styrene bromohydrins with sodium sulfite and other alkaline reagents. Indene bromohydrin, I, reacts rapidly with an excess of hot aqueous sodium sulfite solution to give a high yield of a sodium hydroxyindanesulfonate, II, together with a small amount of *trans*-indene glycol. The hydroxysulfonate undergoes rapid cleavage by sodium in liquid ammonia to give 2-indanol, III, thus indicating its structure.



I



II



III

The reaction of indene oxide with sodium bisulfite yields chiefly *cis*- and *trans*- indene glycols but the oxide and sodium sulfite give the same hydroxysulfonate that is obtained from the bromohydrin. Since in the bromohydrin reaction an excess of sodium sulfite was present the assumption that the oxide is an intermediate in the reaction is not contradicted. The hydroxysulfonate, II, is readily identified by its acetate which has a definite melting point.

The reaction of styrene bromohydrin, IV, with sodium sulfite gives a mixture of three products: styrene glycol, sodium 2-phenylethane-1-sulfonate, and sodium 1-hydroxy-1-phenylethane-2-sulfonate, V. The 2-phenylethane-1-sulfonate presumably comes from unchanged styrene or 1-phenyl-1-bromoethane present in the bromohydrin, as both of these yield this sulfonate.[6]

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(1) Present address, Winthrop Chemical Company, Rensselaer, New York.

(2) von Braun and Weissbach, *Ber.*, **63**, 3052 (1930); von Braun, Braunsdorff and Kirschbaum, **55**, 3652 (1922).

(3) von Braun, Anton and Weissbach, *ibid.*, **63** 2847 (1930).

(4) Read and Reid, *J. Chem. Soc.*, 1488 (1928).

(5) Stevens, Allenby and Du Bois, THIS JOURNAL, **62**, 1424 (1940).

(6) Kharasch, May and Mayo, *J. Org. Chem.*, **3**, 188 (1938); Kharasch, Schenck and Mayo, THIS JOURNAL, **61**, 3092 (1939).

The hydroxysulfonate, V, gives an acetate which decomposes on heating to form sodium styrenesulfonate, VII. The hydroxysulfonate, V, unlike sodium hydroxyindanesulfonate, II, is not cleaved by sodium in liquid ammonia.

$$\underset{\text{IV}}{C_6H_5CHOHCH_2Br} \longrightarrow \underset{\text{V}}{C_6H_5CHOHCH_2SO_3Na} \longrightarrow$$

$$\underset{\text{VI}}{C_6H_5CHOAcCH_2SO_3Na} \xrightarrow{180\text{–}200^\circ} \underset{\text{VII}}{C_6H_5CH{=}CHSO_3Na}$$

The action of aqueous sodium cyanide upon indene bromohydrin yields a mixture from which only 1-indanone and *cis*- and *trans*-indene glycols were isolated.

Because of the ease with which the carbon–sulfur bond in the sodium hydroxyindanesulfonate was cleaved with sodium in liquid ammonia, the behavior of indene oxide and indene bromohydrin as well as other sulfonates with this reagent was investigated. The oxide and bromohydrin give 2-indanol in good yields. The conversion of the bromohydrin to 2-indanol probably occurs through the intermediate formation of the oxide. Previously it has been reported that styrene oxide with sodium and water yields β-phenylethyl alcohol[7] and that the catalytic reduction of indene oxide or of indene bromohydrin in an alkaline medium produces 2-indanol.[8]

Kraus and White[9] have reported that sodium benzenesulfonate reacts with sodium in liquid ammonia to yield benzene, a trace of biphenyl and sodium sulfite; apparently the action of sodium on other sulfonates has not been studied. It has now been found that sulfonates with a benzyl or allyl type of group attached to the sulfur are rapidly cleaved with sodium whereas the β-phenylethyl type of sulfonate does not react. Sodium ω-toluenesulfonate gives toluene, a small percentage of dibenzyl, and sodium sulfite. Similarly sodium 1-phenylethane-1-sulfonate yields ethylbenzene, and 2-methyl-2-propene-1-sulfonate is converted into sodium sulfite and presumably isobutylene. On the other hand sodium 2-phenylethane-1-sulfonate and 2-(*p*-tolyl)-2-methylethane-1-sulfonate were unchanged. This lack of activity probably extends to all saturated aliphatic sulfonic acids.

Experimental

Sodium 2-Indanol-1-sulfonate, II.—A mixture of 38 g. (0.18 mole) of indene bromohydrin and a solution of 40 g. (0.32 mole) of sodium sulfite in 500 ml. of water was heated with stirring on the steam-bath until the bromohydrin dissolved. This required about twenty minutes. The solution was evaporated to dryness under reduced pressure and extracted with hot alcohol. Upon cooling, there crystallized from the alcohol 35 g. (83%) of the pure sodium sulfonate. By evaporation of the alcohol filtrate to dryness and extraction with benzene, 1 g. of *trans*-indene glycol, m. p. 158–159°, was isolated.

From the reaction of 9 g. of indene oxide with 15 g. of sodium bisulfite in 100 ml. of water at 80–90° for about one hour were obtained 2 g. of *trans*-indene glycol (soluble in ether, insoluble in toluene) 6 g. of the *cis*-isomer (soluble in toluene) and 1 g. of the sodium indanolsulfonate, identified as the acetate (see below). A similar reaction using sodium sulfite gave chiefly the sulfonate.

Anal. Calcd. for $C_9H_9O_4SNa$: Na, 9.78. Found: Na, 9.73, 9.70.

Refluxing 5 g. of the hydroxysulfonate for twenty minutes with 60 ml. of acetic anhydride, evaporating the clear solution to dryness under reduced pressure, and crystallizing the residue from alcohol gave sodium 2-acetoxy-1-indanesulfonate as needles, m. p. 235–236° (cor.).

Anal. Calcd. for $C_{11}H_{11}O_5SNa$: Na, 8.25. Found: Na, 8.21, 8.17.

Reduction of Sodium 2-Indanol-1-sulfonate.—To an excess of sodium in 200 ml. of liquid ammonia was added 21.6 g. of the sulfonate. After standing for one and one-half hours, ammonium chloride was added and the solution allowed to evaporate to dryness. Continuous extraction of the solid residue with ether gave 7.9 g. of 2-indanol, m. p. 70°, acid phthalate m. p. 130–131°.

Sodium Sulfonates from Styrene.—To 64 g. (0.61 mole) of styrene emulsified in 300 ml. of hot water was added 32 ml. (0.62 mole) of bromine dissolved in 200 ml. of water containing 50 g. of sodium bromide. To the slightly yellow solution was added 180 g. of sodium sulfite, and the mixture was stirred on the steam-bath for twelve hours, cooled and filtered. The wet filter cake was stirred with an ether–water mixture, and the original filtrate was also extracted with ether. From the combined ether extracts was obtained 9 g. of an oil from which was isolated 1 g. of styrene glycol, m. p. 66–67°. The solid residue from evaporation of the water solutions was extracted with hot 80% alcohol. Evaporation gave 60 g. of solid which, upon repeated recrystallization from 95% alcohol, gave 7 g. of sodium 2-phenylethane-1-sulfonate, identified by sodium analysis and comparison of its *p*-chlorobenzylthiuronium salt (m. p. 197°) with that of the sulfonate made from β-phenylethyl bromide. The main product, 26 g., was sodium 1-phenyl-1-hydroxyethane-2-sulfonate.

Anal. Calcd. for $C_8H_9O_4SNa$: Na, 10.3. Found: Na, 10.3.

The *p*-chlorobenzylthiuronium salt melting at 182–183°, further served to characterize this compound.

Two grams of the sodium salt was acetylated with acetic anhydride, the acetate crystallized from alcohol, and then pyrolyzed by heating in an oil-bath to 180–200°. The acetate liquefied above 165° and acetic acid was evolved. The residue was dissolved in water and converted into the *p*-chlorobenzylthiuronium salt, m. p. 199°. This was

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[7] Tiffeneau and Fourneau, *Compt. rend.*, **146**, 697 (1908).

[8] Willet F. Whitmore and Gebhart, THIS JOURNAL, **64**, 912 (1942).

[9] Kraus and White, *ibid.*, **45**, 768, 779 (1923).

found to be identical with the salt prepared from an authentic sample of barium ω-styrenesulfonate.

Addition of excess sodium to a liquid ammonia solution of 1-phenyl-1-hydroxyethane-2-sulfonate gave no detectible amount of sodium sulfite, and the hydroxysulfonate was recovered unchanged.

Reduction of Indene Oxide and Bromohydrin.—Sodium was added to a solution of 6.3 g. of indene oxide in 100 ml. of liquid ammonia until the blue color persisted. After one-half hour ammonium chloride was added, the ammonia was evaporated, and the residue extracted with ether. From the ether there was obtained 3.1 g. of crude 2-indanol, which, upon recrystallizing from ligroin, melted at 70°.

To 3 g. of sodium dissolved in 300 ml. of ammonia indene bromohydrin was added slowly with stirring until the blue color disappeared; this required 13 g. Evaporation of the ammonia gave 6.2 g. of 2-indanol, m. p. 70°. This is 75% of the theoretical amount.

Reduction of Sodium Sulfonates in Ammonia Solution.—To the sodium sulfonate dissolved in liquid ammonia was added a liquid ammonia solution of sodium until a permanent blue color resulted. After evaporation of the ammonia the residue was examined for sodium sulfite, unchanged sodium sulfonate, and hydrocarbon or alcohol. The results have been given in the discussion part of the paper.

Summary

1. The reaction of indene bromohydrin with sodium sulfite yields sodium 2-hydroxyindane-1-sulfonate, whereas styrene bromohydrin gives the 1-phenyl-1-hydroxyethane-2-sulfonate.

2. Indene bromohydrin and oxide are reduced by sodium in liquid ammonia to 2-indanol.

3. Sodium sulfonates having a benzyl or allyl type carbon attached to the sulfur are readily cleaved by sodium in ammonia to give sodium sulfite, the sulfonate group being replaced by hydrogen.

Evanston, Illinois Received January 2, 1943

[Contribution from the Chemistry Laboratory of The Johns Hopkins University]

Trivalent Carbon. II. Unsymmetrical Hexaaryldimethylperoxides[1]

By Emmett L. Buhle, Sr. Mary Louis Whalen, S.S.N.D., and F. Y. Wiselogle

A recently published note from Marvel and Himel prompts us to record some observations on oxygen absorption by solutions containing mixtures of dissociating hexaarylethanes (Equations 1–6).[2] Marvel and Himel, from studies of

$$\mathrm{R{-}R} \rightleftarrows 2\mathrm{R}\cdot \tag{1}$$
$$\mathrm{R'{-}R'} \rightleftarrows 2\mathrm{R'}\cdot \tag{2}$$
$$\mathrm{R}\cdot + \cdot\mathrm{R'} \rightleftarrows \mathrm{R{-}R'} \tag{3}$$
$$2\mathrm{R}\cdot + \mathrm{O_2} \longrightarrow \mathrm{R{-}O{-}O{-}R} \tag{4}$$
$$2\mathrm{R'}\cdot + \mathrm{O_2} \longrightarrow \mathrm{R'{-}O{-}O{-}R'} \tag{5}$$
$$\mathrm{R}\cdot + \mathrm{O_2} + \cdot\mathrm{R'} \longrightarrow \mathrm{R{-}O{-}O{-}R'} \tag{6}$$

dissociation equilibria in mixtures of hexaarylethanes (Equations 1–3), have concluded that the radical concentration in a mixture is in general lower than the average of the radical concentrations of the two single, symmetrical ethanes in corresponding formal concentrations. Although this appears to be the first quantitative study of a long discussed problem,[3] it is in agreement with other evidence that unsymmetrical dissociating systems are usually more stable than their symmetrical counterparts.[4]

We have found that the action of oxygen on mixtures of dissociating hexaarylethanes gives surprisingly high yields of unsymmetrical peroxides (Equation 6). Thus, in a representative experiment, a benzene solution 0.2 formal with respect to triphenylmethyl and diphenyl-*p*-biphenylmethyl was exposed to air until the colors of the radicals had disappeared. Removal of the solvent and recrystallization of the residue gave a 60% yield of the unsymmetrical 4-phenylhexaphenyldimethylperoxide, $(C_6H_5)_3C{-}O{-}O{-}C(C_6H_5)_2(C_6H_4{-}C_6H_5{-}p)$. Neither of the two symmetrical peroxides could be isolated although both are quite insoluble substances and are readily recovered.

The structures of the new unsymmetrical peroxides were confirmed by cleavage with sodium amalgam to the carbinols (Equation 7), or by

$$\mathrm{R{-}O{-}O{-}R'} + 2\mathrm{Na} \longrightarrow \mathrm{R{-}O^-} + 2\mathrm{Na^+} + {}^-\mathrm{O{-}R'} \tag{7}$$

cleavage with hydrogen iodide in acetic acid which gave the methanes (Equation 8).

$$\mathrm{R{-}O{-}O{-}R'} + 6(\mathrm{H}) \longrightarrow \mathrm{RH} + 2\mathrm{H_2O} + \mathrm{HR'} \tag{8}$$

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(1) Most of the work reported herein was taken from the Essay of Sister Mary Louis Whalen submitted in partial fulfillment of the requirements for the degree of Master of Arts in The Johns Hopkins University, 1937. We are indebted to the Hynson, Westcott and Dunning Research Fund for a grant-in-aid covering a part of the cost of this research.

(2) Marvel and Himel, This Journal, **64**, 2227 (1942).

(3) Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1914, p. 101; Bachmann, This Journal, **55**, 2135 (1933).

(4) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1939, p. 58 ff.