sulfate and the most probable course of the reaction is

$$C_6H_5CH_2{-}S{-}CH_2C_6H_5 + H_2SO_4 \longrightarrow$$
$$C_6H_5CH_2{-}S{-}H + C_6H_5CH_2{-}O{-}SO_2{-}O{-}H \quad (1)$$
$$2C_6H_5CH_2{-}S{-}H + O[\text{from } H_2SO_4] \longrightarrow$$
$$C_6H_5CH_2{-}S{-}S{-}CH_2C_6H_5 + H_2O \quad (2)$$

and more complex products.

$$C_6H_5CH_2{-}S{-}CH_2C_6H_5 +$$
$$C_6H_5CH_2{-}O{-}SO_2{-}O{-}H \longrightarrow$$
$$(C_6H_5CH_2)_3S{-}OSO_2OH \quad (3)$$

Based on this explanation of the process the yields are nearly quantitative.

The tribenzylsulfonium hydrogen sulfate like the chloride and iodide was found to be fairly stable in water but decomposed on heating in water solution in the usual way to the sulfide and benzyl alcohol. Attempts to prepare the nitrate from the sulfate by treating the latter with silver nitrate in 95% alcohol resulted unexpectedly in the formation of tribenzylsulfonium hydroxide. Apparently, the nitrate was easily hydrolyzed to the hydroxide and since this behavior is unusual in the case of sulfonium salts, the point was investigated further. Tribenzylsulfonium nitrate was prepared by the method of Renshaw and Searle[1] and it was found that it was in fact very readily converted to the hydroxide when heated with water. By a slight modification of the procedure of Renshaw and Searle the tribenzylsulfonium hydroxide was formed directly in nearly quantitative yields from tribenzylsulfonium iodide–mercuric iodide. This constitutes a convenient and very efficient preparation method for the hydroxide.

Tribenzylsulfonium Sulfate.—Three grams of dibenzyl sulfide was added to 6 g. of concentrated sulfuric acid. Little solution occurred at room temperature, but on warming to 70–80° and shaking vigorously, solution of the sulfide was complete in about ten minutes. This dissolving was accompanied by the evolution of sulfur dioxide. After the reaction mixture had cooled, it was poured into 25 cc. of cold water. This caused the precipitation of a white crystalline product, which was washed by decantation with two 25-cc. portions of water. A crude yield of 3 g. of tribenzylsulfonium sulfate, melting at 130–135°, was obtained. Crystallization from alcohol gave pure tribenzylsulfoniumsulfate, m. p. 171°. (The reported melting points of this salt vary from 170 to 175°.)[2]

Anal. Calcd. for $C_{21}H_{22}O_4S_2$: SO_4^{--}, 24. Found: (by addition of barium chloride solution to the water solution of the sulfonium sulfate), 21. This sulfonium salt forms a trinitrophenoxide (m. p., 140°) which is identical with that prepared from known tribenzylsulfonium salts and picric acid. These are easily formed by mixing hot alcohol or water solutions of the reactants. Tribenzylsulfonium sulfate may be changed into the hydroxide by silver nitrate, if the reaction is carried out in 95% alcohol.

Tribenzylsulfonium Hydroxide.—Tribenzylsulfonium hydroxide was prepared in almost quantitative yields by the action of dilute aqueous silver nitrate (0.05 *N*) on an acetone solution of tribenzylsulfonium iodide–mercuric iodide. This addition complex was prepared by the general method of Smiles,[3] and was obtained in the form of glistening yellow plates, m. p. 137–138°.

Anal. Calcd. for $C_{21}H_{21}SI_3Hg$: S, 3.61; I, 43.0. Found: S, 3.58; I, 42.5.

After the addition of the silver nitrate, the solution was warmed to coagulate the silver iodide, which was then removed by filtration. The excess acetone was evaporated, and on cooling the residual solution, tribenzylsulfonium hydroxide separated as a white solid. When this was recrystallized from water, the hydroxide was obtained in the form of thick, white needles, which were stable and non-hygroscopic, and which melted at 133°.

Anal. Calcd. for $C_{21}H_{22}OS$: S, 9.94. Found: S, 9.84.

This sulfonium hydroxide was also prepared from tribenzylsulfonium chloride[4] and moist silver oxide. It may be converted into the trinitrophenoxide, sulfate, iodide (m. p. 78°), chloride, etc., by metathesis with the acids (or salts) in water solutions. On heating, the hydroxide decomposed into dibenzyl sulfide and benzyl alcohol.

Tribenzylsulfonium nitrate was prepared according to the method of Renshaw. The oily product obtained was converted into the sulfonium hydroxide by heating it with water.

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[1] Renshaw and Searle, This Journal, **55**, 4951 (1933).

[2] Fichter and Sjöstedt, *Ber.*, **43**, 3428 (1910).

[3] Smiles, *J. Chem. Soc.*, **77**, 160 (1900).

[4] Lee and Dougherty, *J. Org. Chem.*, **4**, 48 (1939).

FRICK CHEMICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.

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Contribution to the Theory of Racemism

BY C. S. HUDSON

Let the enantiomorphic forms of an optically active substance S be designated *d*-S and *l*-S. Assume that a solution containing equal quantities of *d*-S and *l*-S deposits crystals of S.

Case 1.—If these crystals are found by suitable measurements to be different from the separately and similarly prepared crystals of the single *d*-S and *l*-S components, the S crystals are a racemate, which may be designated *rac.* S. If the crystals prove to be the same as those of *d*-S and *l*-S, the racemate has not been found in the test.

Case 2.—Suppose now that the substance S is tautomeric in addition to being optically active, and assume two tautomers (S_1 and S_2) for simplicity; in this case there are two racemates possible, namely, *rac.* S_1 and *rac.* S_2. The number of possible racemates equals the number of possible tautomers.

Most racemates belong under Case 1; the designation of them as *rac.* S is quite definitive if they belong under this case. The experimental methods for the detection of such as fall under Case 1 are well known and are relatively simple. In the case of racemates which belong under Case 2, the designation *rac.* S is not definitive; obviously it must be determined experimentally whether the particular racemate is *rac.* S_1 or *rac.* S_2. The considerable number of racemic crystalline substances that have been recognized in the sugar group have always been regarded tacitly as under Case 1; it is obvious, however, as will now be shown by an example, that many of them really belong under Case 2 and that for these racemates new experimental study is required in order to classify them according to tautomeric forms. The first racemic crystals of a sugar were recognized by Ruff[1]; from a hot alcoholic solution containing equal quantities of *d*- and *l*-arabinose, well formed crystals separated on cooling; these crystals melted higher than the components and showed a much smaller solubility, which proves that they are a racemate. Ruff designated the substance "*rac.* arabinose," a name which must have appeared definitive at that time because the tautomerism of arabinose and other reducing sugars was not well recognized until later. It is now known that the mutarotation of arabinose definitely proves its tautomeric character and it is necessary to assume in the most general case that it may crystallize, under suitable conditions, as an alpha or beta form of a pyranose or of a furanose modification, or as an *aldehydo* form. There are thus five possible racemates comprised under the name "*rac.* arabinose": namely, *rac.* α-arabinopyranose, *rac.* β-arabinopyranose, *rac.* α-arabinofuranose, *rac.* β-arabinofuranose, *rac.* aldehydo-arabinose. The problem of determining which of these five racemates is represented by Ruff's "*rac.* arabinose" will require the devising of some new experimental procedure because no past observations bear upon it. Similar considerations apply to some other substances of the sugar group which have been reported as forming racemic crystals, for example some hydrazones and osazones; the mutarotation of the optically-active forms of these substances indicates tautomerism. On the other hand, the well-recognized racemate of α-methyl-mannoside[2] belongs under Case 1, since the glycosides are not tautomeric; it is definitely *rac.*-α-methyl-mannopyranoside. Likewise *rac.*-mannitol[3] and *rac.*-perseitol[4] are precise designations. An experimental study of "*rac.* arabinose" for the purpose of learning its real composition is in progress. Although the substance naturally does not exhibit "mutarotation" in the precise derivation of this term, the tautomeric change which it must undergo in solution (a sort of "masked mutarotation") should be observable through physical measurements of change of volume, refraction or solubility, or of heat of reaction, or of change of conductivity of added boric acid, to mention some of the more obvious ways. Acetylation of the racemic sugar at low temperature to yield non-tautomeric tetraacetates, which may be identifiable, seems a promising chemical method for a conclusive determination.

Drs. M. L. Wolfrom and E. F. Evans join me in expressing the opinion that the crystals of *rac.*-perseulose, which they have described recently[5] and for which they have proved the racemic nature, very probably fall under Case 2 for the reason that the *d*- and *l*-forms of perseulose exhibit mutarotation prominently.

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(1) Ruff, *Ber.*, **32**, 550 (1899).

(2) E. Fischer and Beensch, *ibid.*, **29**, 2927 (1896)

(3) E. Fischer, *ibid.*, **23**, 370 (1890).

(4) W. Stanley Smith, *Ann.*, **272**, 182 (1892).

(5) Wolfrom and Brown, This Journal, **65**, 1021 (1943).

Division of Chemistry
National Institute of Health
Bethesda, Maryland

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Model Experiments on the Use of Cyclopentadiene in the Synthesis of Sterol-like Compounds[1]

By C. F. Koelsch and F. J. Lucht

The synthesis of sterol-like compounds involves the fusion of a six-membered ring with a five-membered ring; the latter must contain a functional group, and one of the angular carbon atoms must bear a methyl group. The diene synthesis appears applicable to the formation of such substances, and attempts to use it have been made.[2] In these attempts, the six-membered ring has been formed from a diene, and the five-membered ring from a methylated cyclopentene bearing an activating group.

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(1) This paper is from the incomplete Ph.D. Thesis of Lt. F. J. Lucht. The work is being published in its present form because military duties have necessitated postponement of the investigation by the junior author.

(2) For a discussion and references, see Woodward, This Journal, **62**, 1478 (1940).