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THE STABILITY OF 2,2′-DIHYDROXYDIPHENYLMETHANE

C. A. BUEHLER, DOUGLAS E. COOPER, AND EUGENE O. SCRUDDER

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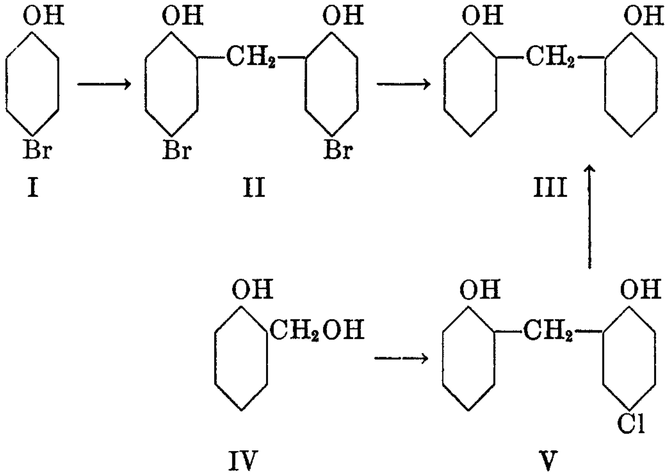
The literature contains several references (1) to the ease with which 2,2′-dihydroxydiphenylmethane loses water to form xanthene. In fact, Megson (2) makes the positive statement that xanthene "is the only form in which 2,2′-dihydroxydiphenylmethane exists."

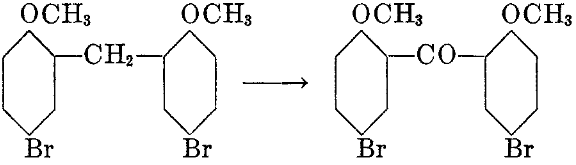
Our interest in this particular dihydroxydiphenylmethane arose in the search for a simple method to identify its derivatives which were to be expected in the condensation of formaldehyde with various *p*-substituted phenols. When the first attempts to prepare the corresponding xanthenes from what were thought to be 2,2′-dihydroxy-5,5′-dichloro- and 2,2′-dihydroxy-3,3′,5,5′-tetrachlorodiphenylmethanes, by the use of ordinary dehydrating agents, were unsuccessful, it was decided to re-examine the stability of 2,2′-dihydroxydiphenylmethane. This substituted diphenylmethane was synthesized by two methods, as shown in Formulas I–V.



p-Bromophenol, I, gave, with formaldehyde and sulfuric acid, 2,2′-dihydroxy-5,5′-dibromodiphenylmethane, II, which on reduction with sodium and amyl alcohol (3) produced 2,2′-dihydroxydiphenylmethane, III, a stable white solid, m.p. 119–120°. The latter is soluble in alkali, gives no color with ferric chloride, and forms a dibenzoate.

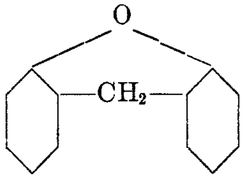
Since large amounts of resinous materials were produced in the synthesis described above, purification of the dihydroxydibromodiphenylmethane proved to be extremely troublesome. To obviate this difficulty a second synthesis (4) was devised. Saligenin, IV, gave, on treatment with *p*-chlorophenol in the presence of hydrochloric acid, 2,2′-dihydroxy-5-chlorodiphenylmethane, V, which on reduction as before produced the desired 2,2′-dihydroxydiphenylmethane, III.

Since II is an unknown compound[1] it was necessary to establish its structure as a means for proving the structure of III. That II is 2,2′-dihydroxy-5,5′-dibromodiphenylmethane was shown by its methylation with dimethyl sulfate to give the known methoxy derivative, VI, and this on oxidation with chromium trioxide in acetic acid produced the known keto derivative, VII.



VI VII

Additional proof of the structure of III was shown by its conversion into the known xanthene, VIII,



VIII

by distillation at ordinary pressure. This dehydration was not successful with several ordinary dehydrating agents which were tried. In fact, our experience with the more readily available homolog, 2,2′-dihydroxy 5,5′-dimethyldiphenylmethane (5) was similar in that satisfactory dehydration was accomplished only by distilling at ordinary pressure.

EXPERIMENTAL PART

Synthesis of 2,2′-dihydroxydiphenylmethane

2,2′-Dihydroxy-5,5′-dibromodiphenylmethane. A solution of 296 cc. of concentrated sulfuric acid and 520 cc. of water in a three-liter, three-necked flask in a water-bath at 80–90° was refluxed and stirred while a mixture of 184 g. of *p*-bromophenol, m.p. 61–63°, and 12 cc. of U.S.P. 40% formaldehyde was introduced. Each four hours 4 cc. more of formaldehyde was added until a total of 12 additional cc. had been utilized. After four more hours of stirring and heating, the viscous red mass, 220 g., which had formed, was removed and washed with cold water. Further purification was accomplished by stirring the crude condensation product vigorously in boiling water for several hours. To remove the resins present the crude 2,2′-dihydroxy-5,5′-dibromodiphenylmethane was dissolved in 600 cc. of hot methanol and the solution was poured, with vigorous stirring, into six

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[1] 2,2′-Dihydroxy-5,5′-dibromodiphenylmethane is described in Swiss Patent 137,927 (to I.G. Farbenindustrie Akt-Ges.) although there is no evidence of its structure other than the fact that it was produced from *p*-bromophenol.

times its volume of boiling water. The dirty white emulsion which formed coagulated on standing cold to give an upper layer of fluffy, almost white needles and a lower layer of a reddish brown resin. By reworking the resin and recrystallizing the needles from methanol-water (1/6), using Norit, 16.7 g. of product, m.p. 180–182°, was obtained. A final crystallization gave crystals, m.p. 183–184°.

Anal. Calc'd for $C_{13}H_{10}Br_2O_2$: Br, 44.64.
Found: Br, 44.55, 44.77.

The *dibenzoate* prepared in the usual manner melted at 192°.

Anal. Calc'd for $C_{27}H_{18}Br_2O_4$: Br, 28.23.
Found: Br, 28.01, 28.03.

2,2'-Dihydroxydiphenylmethane. The method of preparation employed was that suggested by Auwers (3). Sodium was added in small pieces through the top of the condenser to a refluxing solution of 7 g. of 2,2'-dihydroxy-5,5'-dibromodiphenylmethane in 100 cc. of *n*-amyl alcohol in an oil-bath at 160–170°. After the mass in the flask became almost solid, 25 cc. more of amyl alcohol was added and refluxing was continued for half an hour longer. Upon cooling, the excess of sodium was taken up in methanol and then sufficient water was added to dissolve the cake of sodium bromide which had separated. After acidification with glacial acetic acid, which changed the color from red to yellow, the solution was distilled to remove most of the methanol. Water was then added until an amyl alcohol layer separated and the solution was freed from amyl alcohol by distillation with steam. The liquid remaining was filtered and upon cooling, long brown needles, 3.9 g., m.p. 114–116°, separated. One crystallization from water gave white needles, m.p. 119–120°, which were soluble in alkali but produced no color with ferric chloride.

Anal. Calc'd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04.
Found: C, 77.22, 77.49; H, 6.05, 6.15.

The *dibenzoate* was prepared by dissolving 0.2 g. in 20 cc. of benzene and adding 0.5 cc. of benzoyl chloride. After two hours refluxing the benzene was evaporated and an oil remained. Upon stirring the oil with 5% sodium hydroxide solution, a solid was obtained. Three crystallizations from ethanol-water (3:1) gave white needles, 0.06 g., m.p. 76–77°.

Anal. Calc'd for $C_{27}H_{20}O_4$: C, 79.39; H, 4.94.
Found: C, 79.24, 79.22; H, 4.99, 5.04.

2,2'-Dihydroxy-5-chlorodiphenylmethane. This method was an adaptation of one (4) already published. Saligenin, 10 g., was dissolved by warming in 200 g. of *p*-chlorophenol (b.p. 213–214°) and to the rotated solution cooled to 30°, 0.5 cc. of concentrated hydrochloric acid was added dropwise. After cooling again to 30°, 25 cc. more of the acid was added in a single portion and the mixture was stirred for forty minutes. Distillation at reduced pressure in an all-glass apparatus gave 5.7 g. of the dihydroxychlorodiphenylmethane, b.p. 220–222° (6 mm.). The solid formed on cooling was crystallized first from a ligroin-benzene mixture and then from water to give white crystals, m.p. 128–129°.

Anal. Calc'd for $C_{13}H_{11}ClO_2$: Cl, 15.11; mol. wt., 235.
Found: Cl, 14.91, 14.98; mol. wt. (cryoscopic, benzene), 235, 239.

The *dibenzoate* prepared in the usual manner and crystallized from methanol melted at 80–81°.

Anal. Calc'd for $C_{27}H_{19}ClO_4$: Cl, 8.01.
Found: Cl, 7.99, 7.97.

2,2'-Dihydroxydiphenylmethane. 2,2'-Dihydroxy-5-chlorodiphenylmethane, 5.7 g., was reduced with sodium and amyl alcohol as described previously to give 2.7 g. of the crude dihydroxydiphenylmethane. One crystallization from water produced 2 g., m.p. 114–116°, while another crystallization elevated the m.p. to 119–120°.

Anal. Calc'd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04.
Found: C, 77.74, 77.97; H, 6.35, 6.20.

Derivatives for structural proof

2,2'-Dimethoxy-5,5'-dibromodiphenylmethane. This procedure is an adaptation of that used by Mosettig and Stuart (6): To 1.9 g. of 2,2'-dihydroxy-5,5'-dibromodiphenylmethane dissolved in a mixture of 10 cc. of acetone and 10 cc. of an aqueous solution of 6.6 g. of potassium hydroxide, 16 cc. of dimethyl sulfate was added in small portions with vigorous shaking. During this process most of the acetone was permitted to escape in vapor form and some solid appeared. Complete separation was effected by pouring the mixture over cracked ice. Four crystallizations from 95% ethanol gave 1.4 g., m.p. 107.5° [Diels and Rosenmund (7) give 108°].

Anal. Calc'd for $C_{15}H_{14}Br_2O_2$: Br, 41.40.
Found: Br, 41.24, 41.29.

2,2′-Dimethoxy-5,5′-dibromodiphenylketone. This oxidation was accomplished essentially by the method of Diels and Rosenmund (7): To 1 g. of the dimethoxydibromodiphenylmethane dissolved in 10 cc. of hot glacial acetic acid was added in small portions 1.5 g. of chromium trioxide in 20 cc. of glacial acetic acid. This mixture was refluxed for five minutes, diluted with several volumes of water, and extracted with ether. The residue from evaporation of the ether was crystallized three times from ethanol-water (1/1) and once from glacial acetic acid to give 0.06 g. of a tan solid, m.p. 123–124° (Diels and Rosenmund give 123°).

Anal. Calc'd for $C_{15}H_{12}Br_2O_3$: Br, 39.95.
Found: Br, 39.47, 39.41.

Xanthene. 2,2′-Dihydroxydiphenylmethane, 1.1 g., was heated for two hours in a phosphoric acid bath at 150–160° and then it was distilled from a fused zinc chloride bath. The distillate, most of which came over from 140–180°, was cooled and treated with 2% sodium hydroxide solution to remove any phenolic material. Crystallization of the residue from ethanol gave 0.02 g., m.p. 99.5–100.5° [Graebe (8) gives 100.5°]. The product in warm concentrated sulfuric acid gives the characteristic green-yellow fluorescence shown by xanthene.

Anal. Calc'd for $C_{13}H_{10}O$: C, 85.69; H, 5.53.
Found: C, 85.10, 85.00; H, 5.44, 5.44.

SUMMARY

2,2′-Dihydroxydiphenylmethane has been synthesized by two methods and, contrary to literature statements, it has been shown to be quite stable.

Characterization of the compound was accomplished by conversion into several known derivatives.

Knoxville, Tenn.

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