[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Color of Sulfuric Acid Solutions of Di- and Triphenylmethanes

BY LEIGH C. ANDERSON

A yellow color develops when sulfuric acid solutions of di- and triphenylmethanes are allowed to stand. The causes of the color of these solutions have been discussed by several investigators, most of whom suppose it to be due to the presence of impurities in the original materials. Baeyer and Villiger[1] assumed at first that the color was due to an acid salt of triphenylmethane but after Ullmann[2] had shown that triphenylmethane contained impurities which were removed by treatment with 75–80% sulfuric acid, they ascribed the production of the color of their solutions to the presence of anthracene. Baker,[3] Massol and Faucon,[4] and McVicker, Marsh and Stewart[5] have presented spectroscopic evidence for the presence of anthracene in samples of triphenylmethane, while Orndorff, Gibbs, McNulty and Shapiro[6] found similar evidence of the presence of anthracene in some of their samples of diphenylmethane. On the other hand, Zelinsky and Gawerdowskaja[7] claim that the stable form of triphenylmethane (m. p. 92°) dissolves in sulfuric acid without color and that it then changes over to the metastable form (m. p. 82°) to which they ascribe the yellow color. They were unable to detect the presence of anthracene in their samples. Evidence has been obtained in this Laboratory that color is produced when pure samples of these methanes are dissolved in sulfuric acid and that this production of color is a result of chemical reaction between solute and solvent.

Triphenylmethane is very slightly soluble in sulfuric acid.[8] The solution is colorless at first but it slowly acquires a yellow color upon standing or more quickly upon being warmed or exposed to sunlight. The absorption spectrum of one sample of the yellow solution is shown by curve 1, together with the curve 2 for pure triphenylcarbinol sulfate. It is apparent that the two curves are produced by the same substance. The curves indicate that only a portion of the triphenylmethane is converted to the carbinol sulfate; for example, in the particular experiment for which the absorption curve of the solution is given, the data indicate the formation of 0.0006 g. of triphenylcarbinol sulfate from 0.00247 g. of triphenylmethane. At-

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(1) Baeyer and Villiger, *Ber.*, **35**, 1194, 1754 (1902).

(2) Ullmann, *ibid.*, **35**, 1811 (1902).

(3) Baker, *J. Chem. Soc.*, **91**, 1490 (1907).

(4) Massol and Faucon, *Compt. rend.*, **166**, 819 (1918).

(5) McVicker, Marsh and Stewart, *J. Chem. Soc.*, **127**, 999 (1925).

(6) Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, **49**, 1541 (1927).

(7) Zelinsky and Gawerdowskaja, *Ber.*, **61**, 1049 (1928).

(8) A mixture of dimethyl sulfate and sulfuric acid constitutes a much better solvent than sulfuric acid for these hydrocarbons. It has been found that the spectra of the solutions in this mixture of solvents, at least in those cases where the concentration of dimethyl sulfate is less than 30% by volume, are identical with the spectra obtained for corresponding solutions in concentrated sulfuric acid alone. The mixture of solvents has therefore been used for nearly all of the solutions discussed in this paper.

tempts were made to produce sufficient sulfate in the solution to allow the isolation of some pure carbinol. The passage of either air or oxygen through a suspension of several grams of finely powdered triphenylmethane in sulfuric acid (4 volumes) and dimethyl sulfate (1 volume) produced only slightly more color after several days than was obtained by shaking a sealed tube containing the same mixture. Only a few tenths of a gram could be recovered from four grams of triphenylmethane which went into solution. The recovered material, which was obtained by distillation of the diluted acid solution in a current of steam, melted at 81–82° and was impure triphenylmethane, as was proved by the melting point of mixtures of this material with pure triphenylmethane. It was not the metastable form of triphenylmethane since its melting point was not changed by seeding the supercooled molten mass with crystals of the 92° form. Schaum[9] has shown that the rate of change of the metastable form to the

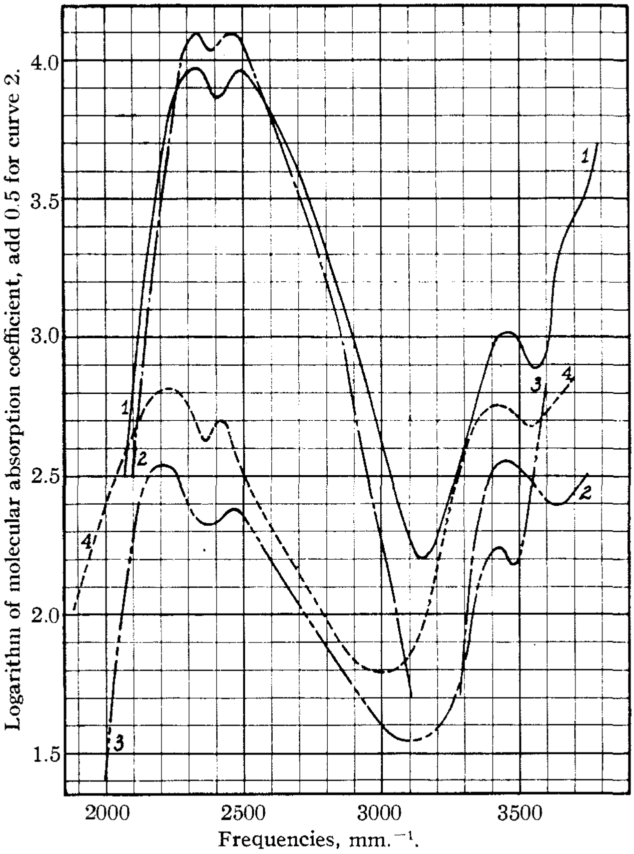

Fig. 1.

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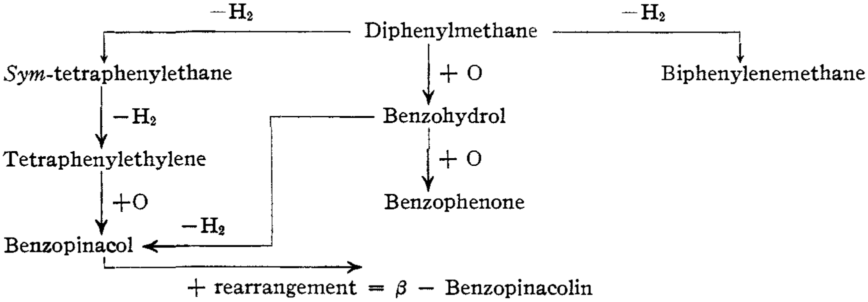
(9) Schaum, *Ann.*, **462**, 194 (1928).

stable is extremely rapid at 90°. The balance of the triphenylmethane which dissolves in sulfuric acid is probably sulfonated, as has been suggested by Ullmann.[2] Attempts to isolate the sulfonic acid have thus far been unsuccessful.

As a result of the spectroscopic data, we conclude that the color of a sulfuric acid solution of triphenylmethane is due to the presence of the sulfate of triphenylcarbinol which has been produced by the oxidation of a portion of the hydrocarbon.

The causes of the color produced in solutions of diphenylmethane in sulfuric acid are not so apparent. The following chart illustrates the more obvious ways in which oxidation of diphenylmethane might be expected to take place



The absorption spectra of sulfuric acid solutions of each of the above compounds, as well as of anthracene and anthraquinone, have been determined. These curves have been compared and it has been found that with the exception of the curve for tetraphenylethane there is no similarity between the absorption spectrum of a sulfuric acid solution of any of these compounds and that shown by the diphenylmethane solutions.

Curve 3 was obtained from a 1-cm. layer of a solution of 0.00826 g. of diphenylmethane in 25 cc. of sulfuric acid (4:1) and curve 4 from a solution of 0.00058 g. of tetraphenylethane in 25 cc. of the same solvent. The similarity of the curves leads one to believe that very similar solutions are produced when either diphenylmethane or *sym*-tetraphenylethane is dissolved in sulfuric acid. Only very dilute solutions can be obtained and it has thus far been impossible to isolate any of the products. The close relationship between derivatives of diphenylmethane and tetraphenylethane has been noted also by other investigators.[10]

The absorption curves were obtained by methods which have been described.[11] The crystalline compounds were recrystallized from anhydrous ether or optically clear petroleum ether and in every case melted sharply at temperatures close to those recorded for them. The diphenyl-

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(10) (a) Willstätter and Goldmann, *Ber.*, **39**, 3765 (1906); (b) Madelung and Oberwegner, *ibid.*, **60**, 2469 (1927); (c) Gilman and Leermakers, *Rec. trav. chim.*, **49**, 532 (1930).

(11) Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928).

methane was purified by treatment for thirty minutes with 85% sulfuric acid and was then distilled in a current of steam. The product gave no color with concentrated sulfuric acid until the mixture was warmed or allowed to stand for several hours.

Summary

1. Curves are presented for the absorption spectra of diphenylmethane, tetraphenylethane and triphenylmethane in solution in a mixture of sulfuric acid and dimethyl sulfate.

2. It has been shown that the color produced when triphenylmethane is dissolved in sulfuric acid is caused by the formation of triphenylcarbinol sulfate due to the oxidation of some of the triphenylmethane to triphenylcarbinol.

3. Sulfuric acid solutions of diphenylmethane give absorption spectra which are very similar to the spectra of sulfuric acid solutions of *sym*-tetraphenylethane. Whether this is due to the oxidation of diphenylmethane to a derivative of tetraphenylethane or to a cleavage of the tetraphenylethane to a diphenylmethane derivative cannot be demonstrated at present.

ANN ARBOR, MICHIGAN

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Tertiary Aliphatic Alcohols Containing an Adjacent Tertiary Hydrogen, the Related Chlorides and Dehydration Products

BY FRANK C. WHITMORE AND W. L. EVERS[1]

The need for more knowledge about tertiary alcohols in connection with studies on rearrangements prompted this work.[2] The group of alcohols selected may be represented by the formula, $R(CH_3)(iso\text{-}C_3H_7)COH$, in which R is ethyl, *n*-propyl, *n*-butyl and *n*-amyl. Two adjacent carbons hold tertiary hydroxyl and tertiary hydrogen. These are readily removed to give a tetrasubstituted olefin. That the dehydration does not follow this course alone has been shown repeatedly with the first member of the series in which R is methyl.[3] The dimethylisopropylcarbinol gave the expected tetramethylethylene and amounts of 2,3-dimethylbutene-1 varying with the conditions of dehydration. The second member of the

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[1] Submitted in partial fulfilment of the requirements for the Ph.D. degree.

[2] (a) Whitmore, THIS JOURNAL, **55**, 3274 (1932); (b) Whitmore and Woodburn, *ibid.*, **55**, 361 (1933); (c) Whitmore and Williams, *ibid.*, **55**, 406 (1933).

[3] Henry, *Compt. rend.*, **144**, 552 (1907); Couturier, *Bull. soc. chim.*, [4] **9**, 898 (1911); Lindner, *Monatsh.*, **32**, 403 (1911); Kishner and Chonin, *Chem. Zentr.*, I, 1496 (1914); *J. Russ. Phys.-Chem. Soc.*, **45**, 1770 (1913).