Anal. Calcd. for $C_{14}H_{11}N$: C, 87.0; H, 5.7; N, 7.3. Found: C, 86.8; H, 6.1; N, 7.0.

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Dibenzo[bf]thiepin

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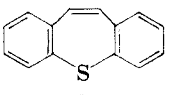
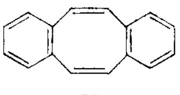
Studies on the correlation of structure with aromatic properties made it appear desirable to synthesize and study dibenzo[bf]thiepin (I), derivatives of which have been described recently by by Loudon, Sloan, and Summers.[1] This compound would be isoster with 1,2,5,6-dibenzo-1,3,5,7-cyclooctatetraene (II) which has olefinic character.[2–4] Compounds of the dibenz[bf]oxepin series have been described by Anet and Bavin.[5]

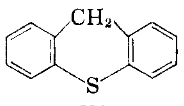
The synthesis of I followed the method developed by the Canadian authors. Thioxanthene (III) was metalated by means of butyl lithium[6] and condensed with formaldehyde to give 9-hydroxymethylthioxanthene (IV). The *p*-toluenesulfonate of this alcohol, on treatment with boiling 95% formic acid, lost toluenesulfonic acid and rearranged to I. That the product was not the theoretically possible 9-methylenethioxanthene (V) follows from its nonidentity with the compound described by Decker[7] and from its properties. The spectrum resembled that of *cis*-stilbene[8] and oxidation with permanganate in acetone gave diphenylsulfide-2,2′-dicarboxylic acid (VI). The ultraviolet spectrum of I shows bands at 227 mμ (4.36); 262 mμ (4.47); 295 mμ (3.70); *cis*-stilbene has bands at 274 mμ (4.04); 294 mμ (3.94).



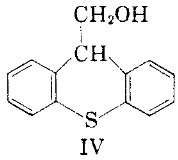
I



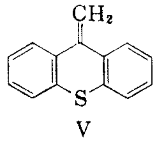
II



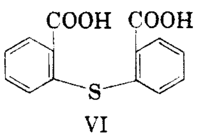
III



IV

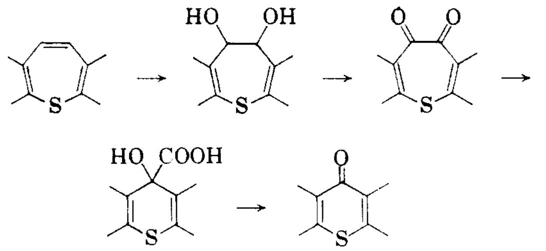


V



VI

Two reactions of I may be mentioned. When the oxidation was carried out in water, instead of acetone, thioxanthone was formed. A similar observation has been made by Manske and Ledingham[9] in the case of dibenz[bf]oxepin and can be explained as resulting from the benzilic rearrangement of the diketone formed by hydroxylation of the double bond in I and dehydrogenation of the di-secondary alcohol so formed:



Performic acid, on the other hand, did not attack the double bond in I, but transformed the compound into the corresponding sulfone, which has approximately the same *cis*-stilbene-type spectrum as I. Its infrared spectrum shows a number of bands in the 700–850 cm.$^{-1}$ region, in which the *cis*-disubstituted olefins absorb and two peaks at 1180 and 1307 cm.$^{-1}$ which represent the asymmetric and symmetric stretching vibrations of the sulfur-oxygen bond.[10]

It appears that the double bond in I is less "olefinic" than in II; this recalls the observation that 9-arylidenexanthenes and -thioxanthenes are more "heptafulvenic" in nature than the dibenzoheptafulvenes themselves.[11]

EXPERIMENTAL

Thioxanthene (III) was prepared from thioxanthone[12] essentially by the method of Graebe and Schultess[13]; the reduction was not carried out in a sealed tube, but under reflux during 20 hr. Care must be taken that the subliming thioxanthene does not block the reflux condenser.

9-Hydroxymethyl-thioxanthene (IV). In a 1 l. flask, mounted with stirrer and reflux condenser, 300 ml. of anhydrous ether and 4.3 g. of lithium metal was introduced and a current of dry nitrogen passed through the flask. By slow addition of a solution of 33.5 g. of butyl bromide in 100 ml. of ether, butyl lithium was obtained. After 1 hr. the solution was cooled in an ice-salt bath and 35 g. of solid thioxanthene was added, which caused an orange-red color to appear. After 15 min. at 0° and 30 min. at reflux temperature, the reaction mixture was again cooled to 0° and 20 g. paraformaldehyde

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[1] J. D. Loudon, A. D. B. Sloan, and L. A. Summers, *J. Chem. Soc.*, 3814 (1957).

[2] L. F. Fieser and M. M. Pechet, *J. Am. Chem. Soc.*, **68,** 2577 (1946).

[3] A. C. Cope and S. W. Fenton, *J. Am. Chem. Soc.*, **73,** 1668 (1950).

[4] G. Wittig, H. Tenhaeff, W. Schoch and G. Koenig, *Ann.*, **572,** 1 (1951).

[5] F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **34,** 991 (1956); **35,** 1084 (1957).

[6] *Cf.* R. R. Burtner and J. W. Cusic, *J. Am. Chem. Soc.*, **65,** 1582 (1943).

[7] H. Decker, *Ber.*, **38,** 2493, 2511 (1905); see also Experimental.

[8] *Org. Syntheses*, **33,** 88 (1953).

[9] R. H. F. Manske and A. E. Ledingham, *J. Am. Chem. Soc.*, **72,** 4797 (1950).

[10] T. Momose and Y. Ohkura, *Chem. Abstr.*, **53,** 9159 (1959). *Cf.* M. Tamres and S. Searles, *J. Am. Chem. Soc.*, **81,** 2100 (1959).

[11] E. D. Bergmann *et al.*, *Bull. Soc. chim. France*, **19,** 262 (1952). *Cf.* H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45,** 173 (1949).

[12] E. G. Davis and S. Smiles, *J. Chem. Soc.*, **97,** 1290 (1910).

[13] C. Graebe and O. Schultess, *Ann.*, **263,** 1 (1891).

(dried over concentrated sulfuric acid for 24 hr.) added. At reflux temperature, the reaction was complete after 20 min.—as indicated by the discharge of the color—and a grayish precipitate had formed. The heating was continued for another 15 min. and the product decomposed with ice and 25% sulfuric acid. The aqueous layer was extracted with ether and chloroform, and the combined organic solutions were washed with sodium bicarbonate solution, dried and concentrated to a volume of 30 ml. Then 100 ml. of cyclohexane was added and the mixture heated to the boiling point and filtered. From the solution crystallized 30 g. of the product (75%); by concentration of the mother liquor a little more product could be obtained. Recrystallization from cyclohexane gave colorless needles, m.p. 110–111°.

Anal. Calcd. for $C_{14}H_{12}OS$: C, 73.7; H, 5.3. Found: C, 73.9; H, 5.6.

p-Toluenesulfonate. To a solution of 11 g. of the foregoing substance in 30 ml. of pyridine, 10 g. of *p*-toluenesulfochloride was added slowly at 0 to −5°. After 18 hr. at 0°, the product was poured into a mixture of ice and 30% hydrochloric acid. The oil which precipitated solidified upon standing or trituration with alcohol, and the product was recrystallized from methanol. It melted at 95°; yield, 15 g. (78%).

Anal. Calcd. for $C_{21}H_{18}O_3S_2$: C, 66.0; H, 4.7. Found: C, 65.8; H, 4.6.

Dibenzo[bf]thiepin (I). The following conditions have been found the most advantageous for the rearrangement: A solution of 9.5 g. of the *p*-toluenesulfonate in 75 ml. of 95% formic acid was refluxed for 30 min. and slowly poured into an excess of sodium carbonate solution, so that the reaction was alkaline all the time. The product was extracted three times with benzene and the benzene extract washed with dilute hydrochloric acid and 5% sodium bicarbonate solution, dried, and concentrated to a volume of 15 ml. After a first chromatography on alumina, 4 g. (77%) of a product was obtained which melted at 73–75° after recrystallization from cyclohexane. For the final purification, 2 g. of product in petroleum ether–benzene (5:1) was chromatographed on 35 g. of alumina. Of the 50-ml. fractions of eluate, the second fraction contained the pure compound, which was recrystallized from methanol and formed yellowish needles, m.p. 89–90°, yield, 1.2 g. (44%). The infrared spectrum showed the absence of a hydroxyl or ester group. The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ (log ϵ): 227 mμ (4.36); 262 mμ (4.47); 295 mμ (3.70).

Anal. Calcd. for $C_{14}H_{10}S$: C, 80.0; H, 4.8. Found: C, 80.2; H, 4.9.

Dibenzo[bf]thiepin-sulfone. A mixture of 1 g. of the foregoing compound in 18 ml. of 95% formic acid and 2.1 g. of 30% hydrogen peroxide, was heated at 40° for 30 min. with magnetic stirring, whereupon a clear solution resulted, and at 98° for 4 hr., and poured into water. The product crystallized from ethanol and melted at 171–172°. It was not affected by alkali or periodic acid and showed no hydroxyl absorption in the infrared. The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ (log ϵ): 229 mμ (4.54); 264 mμ (3.85); 300 mμ (4.08).

The infrared spectrum showed $\tilde{\nu}_{max}^{KBr}$: 1600, 1562, 1481, 1440, 1307 (s), 1260, 1180 (s), 1126, 1087, 1064, 818, 813 (s), 784, 763 (s), 725, 700 cm.$^{-1}$

Anal. Calcd. for $C_{14}H_{10}SO_2$: C, 69.4; H, 4.1. Found: C, 69.2; H, 4.1.

Diphenylsulfide-o,o′-dicarboxylic acid (VI). To a solution of 1 g. of the dibenzothiepin in 25 ml. of acetone (and a few drops of water), powdered potassium permanganate was added in small portions; after each addition, we waited until the color disappeared. When the permanganate color did not change for 3 hr., the solution was filtered and the solid phase washed with 2 ml. of acetone. The residue was then extracted twice with 10 ml. of boiling water and the combined extracts were acidified with dilute hydrochloric acid. The product was reprecipitated from dilute potassium hydroxide solution and finally recrystallized from aqueous alcohol. It melted at 230° (lit.,[14] m.p. 229°) and was identified by mixed melting point with a sample prepared according to Rosenmund and Harms.[14] The ultraviolet spectrum showed $\lambda_{max}^{ethanol}$ (log ϵ): 226 mμ (4.51); 255 mμ (3.98); 322 mμ (3.70).[15]

The infrared spectrum showed $\tilde{\nu}_{max}^{KBr}$: 2940, 1700 (s), 1600 (*o*-disubstituted benzene), 1568, 1475, 1418 (carboxyl), 1307 (s), 1283 (s) (carboxyl), 1266 (s), 1136, 1064, 1047, 939, 810 (s), 755 (s) (superposition of C—S—C and *o*-disubstituted benzene), 724, 714 cm.$^{-1}$

Anal. Calcd. for $C_{14}H_{10}O_4S$: C, 61.3; H, 3.7. Found: C, 60.9; H, 4.1.

Thioxanthone. To a well stirred mixture of 1.4 g. of dibenzothiepin and 60 ml. of boiling water, a mixture of 5 g. of potassium permanganate and 3 g. of sodium carbonate was added slowly. When the color was no longer discharged, the product was acidified with 25% sulfuric acid and decolorized by addition of sodium sulfite. The yellow precipitate was dissolved in benzene and chromatographed on alumina. Thus, 0.6 g. (43%) of thioxanthone was obtained which melted alone and upon admixture of authentic material at 209°.

Reaction of thioxanthone with methylmagnesium iodide. A repetition of the experiment of Decker[7] led to somewhat different results. The whole sequence of operations was carried out in a nitrogen atmosphere.

A solution of methylmagnesium iodide prepared from 6 g. of magnesium and 33 g. of methyl iodide in anhydrous ether, was added to a suspension of 16 g. of thioxanthone in warm benzene. During 4 hr. the ether was distilled off and the resulting product refluxed. It was decomposed with ice and ammonium chloride.[16] From the benzene layer, some thioxanthone crystallized which was removed by filtration. The benzene solution was then washed with water, dried, and evaporated *in vacuo* at a temperature not exceeding 40°. The remaining reddish oil was chromatographed on alumina and eluted with a mixture of benzene and petroleum ether (1:1). Thus, a yellow oil was obtained which crystallized upon trituration with cyclohexane. 9-Methylthioxanthydrol melted at 82–83°.

Anal. Calcd. for $C_{14}H_{12}OS$: C, 73.7; H, 5.3. Found: C, 74.0; H, 5.8.

On standing in a vacuum desiccator (or on heating with a mixture of acetic acid and acetic anhydride) the crystals liquefied through dehydration. 9-Methylenethioxanthene is a liquid which could not be obtained in pure form, as it quickly began to autoxidize and deposit thioxanthone, m.p. 205° and mixed m.p. 207°. The product described by Decker[7] as a semisolid of undefined melting point was, therefore, undoubtedly not 9-methylenethioxanthene.

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(14) K. W. Rosenmund and H. Harms, *Ber.*, **53**, 2226 (1920).

(15) For diphenylsulfide, 2 maxima (at 252 and 278 mμ) have been observed.

(16) Dehydration proceeds with great ease, if the decomposition is carried out with acid. Decker did not isolate the tertiary alcohol.

Dimer of 2-Pyridyl Isothiocyanate

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The synthesis of 2-pyridyl isothiocyanate, described as a brick-red solid, m.p. 110–111°, was