was recrystallized from methanol, it melted at 166–168°, showed no absorption in the ultraviolet region, and had a weak, well-defined absorption at 2685 cm.$^{-1}$ characteristic of SH stretching.[5]

Anal. Calcd. for $C_{31}H_{54}S_4$: C, 67.11; H, 9.81; S, 23.07. Found: C, 67.02, 66.79; H, 9.56, 9.83; S, 23.20.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF TENNESSEE
KNOXVILLE, TENNESSEE

---

[5] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley & Sons, New York, N. Y., 1958, p. 351.

5-Dibenzo[b,f]azepine

ERNST D. BERGMANN AND MORDECAI RABINOVITZ

Received October 27, 1959

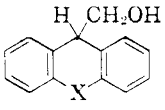
Six-membered ring systems of the general type I have been shown to undergo dehydration on solvolysis with ring enlargement to seven-membered systems (II), *i.e.* 9,10-di(hydroxymethyl)-9,10-dihydroanthracene (I, X = CH(CH_2OH)),[1,2] 9-hydroxymethylxanthene (I, X = O)[3] and 9-hydroxymethylthioxanthene (I, X = S).[4]

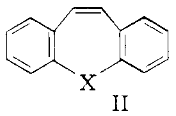
In the present study, the transformation of 9-hydroxymethylacridane (I, X = NH) into 5-dibenzo[b,f]azepine (II, X = NH) is described.

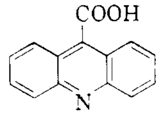
The primary alcohol (I, X = NH) was obtained by reduction of acridine-9-carboxylic acid (III) with lithium aluminum hydride. This reagent reduced not only the carboxyl group, but also the *ortho*-quinoid C = N system. Analogous observations have been made in other acridine derivatives.[5] Treatment of the alcohol with polyphosphoric acid at 160° caused the desired dehydration. Structure II, X = NH for the product, m.p. 189–191°, follows from the similarity of its spectrum with that of 2-amino-*cis*-stilbene:[6] II, X = NH: 262 mμ (4.60); 310 mμ (3.35; inflection); 360 mμ (2.90; inflection); 2-amino-*cis*-stilbene: 245 mμ (3.25; inflection); 2.80 mμ (3.05), and its nonidentity with 9-methylacridine (IV), m.p. 114°,[7] which would probably have formed spontaneously from 9-methylene-9,10-dihydroacridine (V).[8] The spectrum of II, X = NH is also very similar to that of II, X = O,[3] II, X = S[4] and II, X = CH_2.[2]

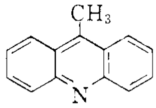
II,X = O: 230 mμ (4.35); 290 mμ (3.95)
II,X = S: 227 mμ (4.36); 262 mμ (4.47); 295 mμ (3.70)
II,X = CH_2: 288 mμ (4.19)

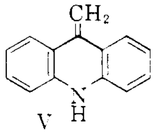
10,11 - Dihydro - 5 - dibenzo[b,f]azepine ("*o*-iminodibenzyl") has been described by Thiele and Holzinger,[9] but no derivatives of II, X = NH carrying a double bond in the 10,11- position appear to have been prepared.


I


II


III


IV


V

EXPERIMENTAL

9-Hydroxymethyl-9,10-dihydroacridine (I, X = NH). In an atmosphere of nitrogen and at the temperature of an ice-salt mixture, 13 g. of lithium aluminum hydride was added in small portions to a suspension of 40 g. of acridine-9-carboxylic acid (III)[10] in ether. The mixture was gently refluxed for 3 hr. and decomposed by the successive addition of acetone and water. The ethereal solution was then decanted from the solid and the latter extracted several times with ether and benzene. When the solvents were evaporated (at a temperature not exceeding 40°), a colorless solid remained which was triturated with petroleum ether and recrystallized from benzene-petroleum ether or methanol. The compound formed white needles, m.p. 135–136°, and was very sensitive to oxygen, which caused quick discoloration to brown. The yield was 30 g. (80%). That the acridine system had been reduced, followed from the absence of the typical green fluorescence of the acridine derivatives in concentrated sulphuric acid solution.

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.6; H, 6.2. Found: C, 79.6; H, 6.6.

5-Dibenzo[b,f]azepine (II, X = NH). A mixture of 2.5 g. of the foregoing substance and 150 ml. of polyphosphoric acid was heated at 160° for 3 hr. with vigorous agitation. Water was added and the product extracted with ether and benzene. The organic layer was washed with sodium bicarbonate solution, dried, and evaporated *in vacuo* and the ethereal solution of the residue chromatographed twice on activated alumina. The product contained in the yellow fraction (50-ml. fractions) was dissolved in petroleum ether and chromatographed again. The third fraction gave yellow leaflets which melted at 189–191°; the melting point did not change upon recrystallization from cyclohexane. The infrared spectrum (in potassium bromide pellet) showed 3333 cm.$^{-1}$ (strong, N—H stretching), 3030, 1587, 1481 (str.) (*ortho*-disubst. benzene), 1316 (C—N stretching), 1266, 1163, 1117, 939, 810, 746 (broad, strong) (*ortho*-disubst. benzene), 700 cm.$^{-1}$

---

[1] J. Rigaudy and P. Tardieu, *Compt. Rend.*, **248**, 1538 (1959).

[2] E. D. Bergmann and M. Rabinovitz, *Bull. Res. Counc. Israel*, in press (1960).

[3] F. A. L. Anet and P. M. G. Bavin, *Can. J. Chem.*, **35**, 1084 (1957).

[4] E. D. Bergmann and M. Rabinovitz, *J. Org. Chem.*, in press (1960).

[5] F. Bohlmann, *Ber.*, **85**, 390 (1952); G. M. Badger, J. H. Seidler, and B. Thomson, *J. Chem. Soc.*, 3207 (1951).

[6] D. L. F. De Tar and L. A. Caprino, *J. Amer. Chem. Soc.*, **78**, 475 (1956).

[7] H. Jensen and F. Rethwisch, *J. Amer. Chem. Soc.*, **50**, 1144 (1928).

[8] This can be assumed from analogy to 9-methylene-9,10-dihydroanthracene.[2] However, Decker, *Ber.*, **38**, 2493 (1905), has described some derivatives of V.

[9] J. Thiele and O. Holzinger, *Ann.*, **305**, 100 (1899).

[10] K. Lehmstedt and F. Dostal, *Ber.*, **72**, 804, 1071 (1939). G. I. Braz and T. V. Gortinskaya, *J. Gen. Chem. (U.S.S.R.)*, **10**, 1751 (1940); *Chem. Abstr.*, **35**, 4025 (1941).

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.

Department of Organic Chemistry
Hebrew University
Jerusalem, Israel

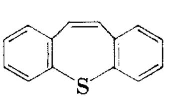
Dibenzo[bf]thiepin

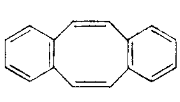
Ernst D. Bergmann and Mordecai Rabinovitz

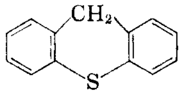
Received September 18, 1959

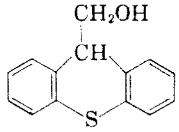
Studies on the correlation of structure with aromatic properties made it appear desirable to synthesize and study dibenzo[bf]thiepin (I), derivatives of which have been described recently by by Loudon, Sloan, and Summers.[1] This compound would be isoster with 1,2,5,6-dibenzo-1,3,5,7-cyclooctatetraene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

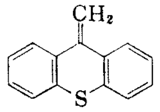
The synthesis of I followed the method developed by the Canadian authors. Thioxanthene (III) was metalated by means of butyl lithium[6] and condensed with formaldehyde to give 9-hydroxymethylthioxanthene (IV). The *p*-toluenesulfonate of this alcohol, on treatment with boiling 95% formic acid, lost toluenesulfonic 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).

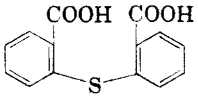

I


II

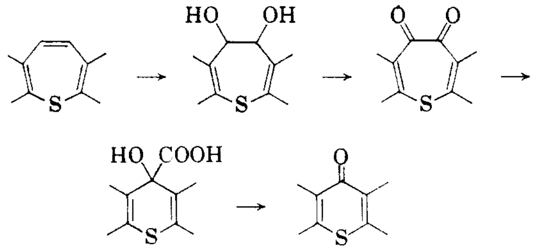

III


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

---

[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).