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. 


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_{2}OH)),\(^{1}\) 9-hydroxymethylthioxanthene (I, X = O)\(^{3}\) and 9-hydroxymethylthioxanthene (I, X = S)\(^{3}\).

In the present study, the transformation of 9-hydroxymethylcarbamide (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 orthoquinoid 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: \(\nu_{\text{SH}}\) stretching.\(^{6}\) II, X = NH: 262 mp (4.47); 310 mp (3.35; inflection); 360 mp (2.90; inflection); 2-amino-cis-stilbene: 245 mp (3.25; inflection); 2.80 mp (3.05), and its nonidentity with 9-methylene-9,10-dihydroacridine (IV).\(^{7}\) This can be assumed from analogy to 9-methylene-9,10-dihydroanthracene.\(^{8}\) However, Decker, \(\textit{Ber.}\), \textbf{38}, 2493 (1905), has described some derivatives of V.

\(9\)-Hydroxymethyl-9,10-dihydroacridine (I, X = NH). In an atmosphere of nitrogen and at the temperature of an iced 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)\(^{9}\) in ether. The mixture was gently refluxed for 3 hr. and decomposed by the successive addition of acetone and water. The ether 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.

\(9\)-Hydroxymethyl-9,10-dihydroacridine (I, 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 to a few drops. The residue was 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, \(\nu_{\text{NH}}\) stretching), 3030, 1587, 1481 (str.) (ortho-disubst. benzene), 1316 (CN stretching), 1266, 1163, 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 to a few drops. The residue was 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, \(\nu_{\text{NH}}\) stretching), 3030, 1587, 1481 (str.) (ortho-disubst. benzene), 1316 (C=N stretching), 1266, 1163, 11, 11, 939, 810, 746 (broad, strong) (ortho-disubst. benzene), 700 cm. \(^{-1}\).
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 Loudon, Sloan, and Summers. This compound would be isoster with 1,2,5,6-dibenzo-1,3,5,7-cyclooctatetraene (II) which has olefinic character. Compounds of the dibenz[bf]oxepin series have been described by Anet and Bavin. The synthesis of I followed the method developed by the Canadian authors. Thioxanthene (III) was metalted by means of butyl lithium and condensed with formaldehyde to give 9-hydroxy-methylthioxanthene (IV). The p-toluenesulfonate of this alcohol, on treatment with boiling 95% formic acid, lost toluenesulfonic acid and rearranged permanganate in acetone gave diphenylsulfide-2,2'-thesize and study dibenzo[bf]thiepin by Loudon, Sloan, and Summers. This compound condensed with formaldehyde to give 9-hydroxy-tives of which have been described recently by 34,991 (1956); 35,1084 (1957).

That the product was not the theoretically experimental. 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. region, in which the cis-disubstituted olefins absorb and two peaks at 1180 and 1307 cm. which represent the asymmetric and symmetric stretching vibrations of the sulfur-oxygen bond.

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

Experimental

Thioxanthene (III) was prepared from thioxanthone essentially by the method of Graebe and Schultz; 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 33.8 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 was added.