Dibenzo[b]thiepin

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Studies on the correlation of structure with aromatic properties made it appear desirable to synthesize and study dibenzo[b]thiepin (I), derivatives of which have been described recently by Loudon, Sloan, and Summers. This compound would be isoster with thiazine and study dibenzo[b]thiepin by Loudon, Sloan, and Summers. This compound

tioned that the product was not the theoretically expected, 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.

It appears that the double bond in I is less “olefinic” than in II; this recalls the observation that 9-arylideneanthoxanes and -thioxanthenes are more “heptafulvenic” in nature than the dibenzoheptafulvenes themselves.

EXPERIMENTAL

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

9-Hydroxymethyl-thioxanthone (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°C and 30 min. at reflux temperature, the reaction mixture was again cooled to 0°C and 20 g of paraformaldehyde

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(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 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 (7570); by concentration of the mother liquor a little more product could be obtained. Recrystallization from cyclohexane gave colorless needles, m.p. 110-111°.

Anal. Caled. for C₁₄H₁₂O₂S: C, 73.7; H, 5.3. Found: C, 73.9; H, 5.6.

Dibenzo[b]thiepin (I). The following conditions have been found the most advantageous for the rearrangements:

A solution of 9.5 g. of the p-toluene sulfonate 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. The oil which precipitated solidified upon standing or trituration with alcohol, and the product was recrystallized from methanol. It melted at 85°; yield, 15 g. (78%).

Anal. Caled. for C₁₄H₁₂O₂S: C, 73.7; H, 5.3. Found: C, 73.9; H, 5.6.

Dibenzo[b]thiepin-sulfone (VI). To a solution of 11 g. of the foregoing compound in 18 ml. of 95% formic acid and 2.1 g. of potassium permanganate was added slowly. When the permanganate color was no longer discharged, it 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 solution of methylmagnesium iodide prepared from 6 g. of magnesium and 35 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. 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-Methylthioxanthonyldiol melted at 82-83°.

Anal. Caled. for C₁₄H₁₂O₂S: 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-Methylthioxanthone is a liquid which could not be obtained in pure form, as it quickly began to autoxidize and deposit thioxanthone, m.p. 252° and mixed m.p. 278°. The product described by Decker7 as a semisolid of undefined melting point was, therefore, undoubtedly not 9-methylthioxanthone.

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(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...