Thioxanthylium Perbromide

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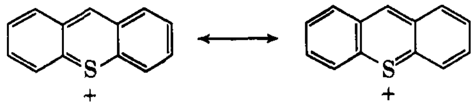
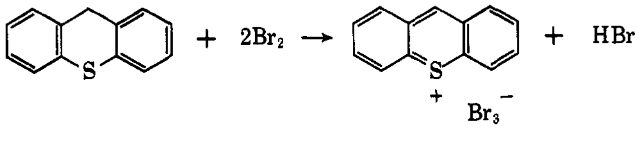
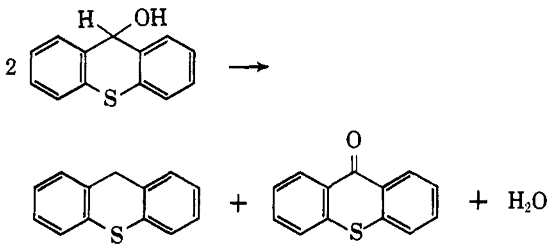
The most abundant ion in the mass spectrum of thioxanthene arises by loss of one hydrogen atom from the ionized molecule.[1] This species can be formulated as the thioxanthylium ion, stabilized by the following resonance hybrids. We have found a similar strong tendency for thioxanthene to go over to thioxanthylium ion in solution chemistry. Bromination of thioxanthene in carbon tetrachloride, even in total absence of light, resulted in the quantitative precipitation of thioxanthylium perbromide. This is the first example of the direct conversion of thioxanthene to a thioxanthylium salt. The perbromide has been prepared previously by the action of hydrogen bromide and bromine vapor on thioxanthydrol,[2] but no yield or properties were reported.

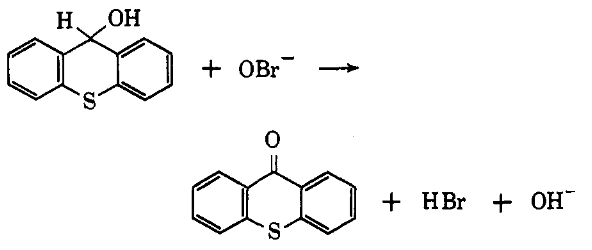




The thioxanthylium perbromide slowly hydrolyzed in aqueous sodium hydroxide to a mixture of thioxanthene and thioxanthone, in the ratio 1:3. Stoichiometrically the hydrolysis should give thioxanthydrol; the thioxanthone was probably formed partly by the disproportionation shown in eq. 1 and partly by oxidation of the thioxanthydrol by hypobromite as shown by eq. 2.

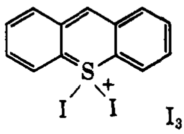


(1)



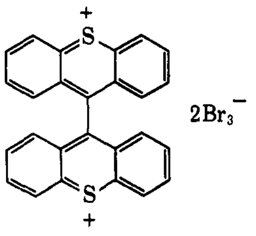
(2)

With excess periodide ion, the perbromide gave quantitatively a black periodide melting at 148° and containing five atoms of iodine, presumably 1.



1

Dithioxanthyl[3] similarly brominated in the dark to dithioxanthylium perbromide (2). So great is the tendency for thioxanthene derivatives to convert to thioxanthylium ions that even thioxanthone, with hydrogen bromide and bromine, went readily to the slightly soluble 9-hydroxythioxanthylium perbromide.



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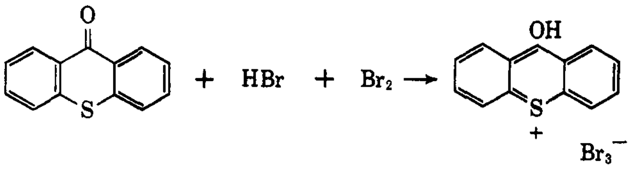

This however, proved less stable than thioxanthylium perbromide, and, in air, slowly evolved bromine and hydrogen bromide. There was no evidence for the formation of 9-bromothioxanthylium perbromide.

Experimental

Thioxanthylium Perbromide.—A solution of 20.5 ml. (0.4 mole) of bromine in 100 ml. of carbon tetrachloride was added with stirring at 25° over 1 hr. to a solution of 39.6 g. (0.2 mole) of thioxanthene in 650 ml. of carbon tetrachloride. The mixture was stirred for 2 hr. more; the red solid was washed with carbon tetrachloride and dried. It weighed 89 g. (97%) and melted with decomposition at 169°.

Anal. Calcd. for $C_{13}H_9Br_3S$: C, 35.7; H, 2.1; Br, 55.8; S, 7.4. Found: C, 35.4; H, 2.2; Br, 55.8; S, 7.7.

The perbromide was hydrolyzed by being vigorously stirred with excess 5% aqueous sodium hydroxide at 20° for 16 hr. The white solid was isolated and analyzed by mass spectrometry. The 197 peak (parent − 1) for thioxanthene was one-third the height of the 212 peak (parent) for thioxanthone.

Thioxanthylium Periodide.—A mixture of aqueous potassium periodide solution, from 49.8 g. (0.3 mole) of potassium iodide and 50.8 g. (0.2 mole) of iodine, and 17.48 g. (0.04 mole) of thioxanthylium perbromide was stirred 1 hr. at 30°. The black solid was collected on a filter and washed thoroughly with carbon tetrachloride, giving 33.8 g. of thioxanthylium periodide melting at 148°.

Anal. Calcd. for $C_{13}H_9I_5S$: C, 18.8; H, 1.1; I, 76.3; S, 3.9. Found: C, 18.5; H, 1.3; I, 76.5; S, 4.1.

Dithioxanthylium Perbromide.—A suspension of 0.985 g. (0.0025 mole) of dithioxanthyl in 100 ml. of carbon tetrachloride

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[1] Intensity at m/e = 197 is approximately twice that at m/e 198 in the mass spectrum measured with 70-v. electrons on a Consolidated Model 21-103 instrument with the inlet system at 250°. Mass spectra of thioxanthene, thioxanthone, and thioxanthydrol, and some labeled thioxanthene derivatives will be published.

[2] A. Werner, *Ber.*, **34**, 3311, (1901).

[3] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

was stirred with 7.5 moles of bromine at 20° for 70 hr., giving 2.0 g. (92%) of dithioxanthylium perbromide.

Anal. Calcd. for $C_{26}H_{16}Br_6S_2$: Br, 55.8; S, 8.4. Found: Br, 55.6; S, 8.1.

9-Hydroxythioxanthylium Perbromide.—A filtered solution of 3.28 g. (0.02 mole) of thioxanthone in 1250 ml. of carbon tetrachloride was saturated with dry hydrogen bromide at 25°. The yellow solution became hazy orange, but nothing precipitated. A solution of 20 moles of bromine in carbon tetrachloride was added at one time; after 40 hr., the red solid was collected on a filter and washed with carbon tetrachloride, giving 4.7 g. (58% yield).

Anal. Calcd. for $C_9H_9Br_3OS$: C, 26.7; H, 2.2; Br, 59.2; S. 7.9. Found: C, 27.0; H, 2.4; Br, 57.8; S, 8.2.

The Synthesis of Some Bicyclo[3.3.0]octane Derivatives[1]

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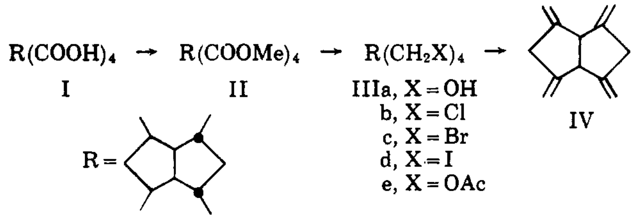
In an earlier communication,[2] the synthesis and characterization of *cis*-bicyclo[3.3.0]octane-*cis,cis*-2,4-*trans,trans*-6,8-tetracarboxylic acid (I) was reported and the suggestion was made that this acid might serve as a readily obtainable intermediate for an attempted synthesis of pentalene. We wish to report the results of some of the work directed along these lines.



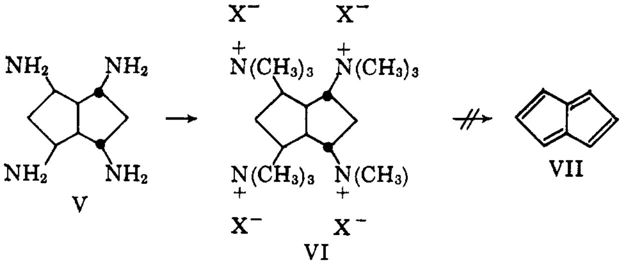
The preparation of tetramethyl *cis*-bicyclo[3.3.0]-octane-*cis,cis*-2,4-*trans,trans*-6,8-tetracarboxylate (II) can be accomplished from the tetraacid chloride of I or by the direct methylation of I. The reduction of II with lithium aluminum hydride gave the tetraalcohol IIIa.[3]

The tetrabromide IIIc was prepared in a 26% yield by the reaction of IIIa with phosphorus tribromide. The reaction of IIIa with potassium iodide in 95% phosphoric acid afforded *cis,cis*-2,4-*trans,trans*-6,8-tetra(iodomethyl)-*cis*-bicyclo[3.3.0]octane (IIId). The n.m.r. spectra of the tetraalcohol IIIa, the tetrabromide IIIc, and the tetraiodide IIId all show the $-CH_2X$ protons as multiplets in the region τ 6.2–7.0, centered near 6.6 (relative to tetramethylsilane). The ratio of these protons to the remainder of the ring protons (from τ 7.4 upfield) exhibited the correct 8:6 ratio. Since the structure of the tetraalcohol IIIa is unambiguous, the halides isolated from the reaction of this alcohol with the halogenating agents must possess the unrearranged skeleton R. Although the corresponding tetrachloride IIIb[3] was allowed to react with sodium iodide in acetone for 1 hr. at the reflux temperature, the starting materials were recovered in quantitative yields.

Dehydrohalogenation of the tetrabromide IIIc or the tetraiodide IIId to obtain 2,4,6,8-tetramethylene-*cis*-bicyclo[3.3.0]octane (IV) was accomplished by warming the halide in an alcoholic solution of potassium hydroxide. The product IV could be recrystallized from methanol to give long colorless needles, but prolonged exposure to light even in the solid state caused a change in the compound. The compound was assigned the *exo*-methylene structure on the basis of the nature of the reaction which produced it, the elemental analysis, the infrared, ultraviolet, and n.m.r. spectrum. The n.m.r. spectrum exhibited two different vinyl protons centered at τ 4.70 and 4.93 (ratio 4:4) with the remainder of the ring protons above 7.5 (ratio 6).

The pyrolysis of *cis,cis*-2,4-*trans,trans*-6,8-tetra(acetoxymethyl)-*cis*-bicyclo[3.3.0]octane afforded a mixture of olefins whose spectrum indicated that both *endo*- and *exo*-methylene unsaturation were present. The vapor phase chromatography of the mixture indicated at least seven different olefins were present.

The thermal decomposition of both the quaternary ammonium hydroxide VI (X = OH) and the corresponding tertiary amine oxide have been shown to be ineffective for the preparation of pentalene.[3] Although pentalene may be formed under these circumstances, it is questionable whether or not it would survive the rough treatment encountered in these reactions. In addition, the stereochemistry of the compound is such that three of four of the amine functions are situated to provide either facile *trans* or *cis* elimination, respectively, while the fourth amine function would be forced into an elimination which is not generally associated with that function. Mixtures of *cis* and *trans* isomers of cyclooctene have been obtained, however, from cyclooctane trimethylammonium bromide with the reagents potassium amide in liquid ammonia (−33°) and phenyl lithium in ether (20°).[4] Because the quaternary salt VI requires that both *cis* and *trans* eliminations occur in the formation of pentalene and the conditions of temperature are mild, these modifications of the Hofmann elimination seemed to be especially inviting.



Treatment of *cis*-bicyclo[3.3.0]octane-*cis,cis*-2,4-*trans,trans*-6,8-tetra(trimethylammonium bromide) (VI, X = Br) with phenyl lithium in ether or with potassium amide in liquid ammonia gave red viscous residues. The infrared spectra showed the presence of *cis* double bonds, but no hydrocarbons could be isolated by gas chromatography or by column chromatography.

The tetraacetamide and tetrabenzamide of V were prepared. Treatment of these amides with thionyl

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[1] This research was supported by a grant (NSF G-10472) from the National Science Foundation whose assistance is gratefully acknowledged.

[2] J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **81**, 4273 (1959).

[3] E. R. Hanna, K. T. Finley, W. H. Saunders, Jr., and V. Boekelheide, *ibid.*, **82**, 6342 (1960).

[4] G. Wittig and R. Polster, *Ann.*, **612**, 102 (1958).