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SYNTHESIS OF THE THIAPYRYLIUM CATION

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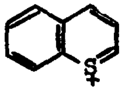
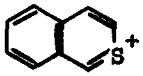
According to current concepts the tropylium, pyridinium, pyrylium and thiapyrylium cations (I, X = CH = CH, NH, O and S respectively) should all possess enhanced stability because of the presence of a sextet of delocalised π electrons occupying low energy molecular orbitals associated with the cationic system. Of these ions, only salts of the thiapyrylium cation remain to be isolated. The stability of this cation can, however, be anticipated following the isolation of salts of various alkyl and aryl substituted thiapyrylium cation,[1] from mass spectral studies of alkylated thiophenes[2] and, more recently, from the isolation of salts of the two possible benz-derivatives (II) and (III).[3]

I



II



III

We now wish to report the isolation of several salts of the parent, unsubstituted cation (I, X = S). The synthetic route we have used is similar to that employed by Dewar and Pettit for the synthesis of tropylium salts[4] and is outlined in the following scheme.

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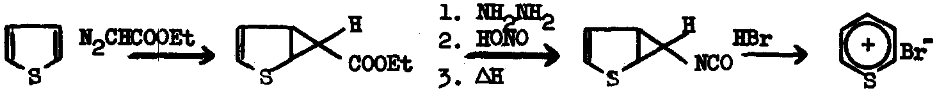
[1] R. Wizinger and P. Ulrich, Helv. Chim. Acta 39, 207 (1956).

[2] V. Hanus and V. Cermak, Coll. Czech. Chem. Comm. 24, 1602 (1959).

[3] A. Lüttringhaus and N. Engelhard, Chem. Ber. 93, 1525 (1960).

[4] M. J. S. Dewar and R. Pettit, J. Chem. Soc. 2021 (1956).



IV V

The product (IV) of the reaction between thiophene and diazoacetic ester was converted to the isocyanate (V) in the manner indicated above. Treatment of the isocyanate in nitromethane with hydrogen chloride followed by addition of ether afforded cyanuric acid and thiapyrylium chloride. Thiapyrylium bromide was prepared in a similar manner using hydrogen bromide. The chloride and bromide salts are solids, insoluble in nonpolar solvents but readily soluble in polar solvents, especially water. Thiapyrylium iodide was obtained as a crystalline solid following addition of sodium iodide to an aqueous solution of thiapyrylium bromide. The perchlorate, and chloroplatinate salts were obtained in the same manner.

It is interesting that the chloride, bromide and iodide salts of thiapyrylium are white, yellow and orange respectively. This same type of charge transfer spectra is also shown with the corresponding salts of the tropylium cation.

It is also interesting to note that whereas pyrylium perchlorate apparently is readily decomposed in water,[5] thiapyrylium iodide on the other hand is best recrystallised from hot water, indicating a greater stability of the latter cation. Of course, the thiapyrylium cation is attacked by stronger nucleophiles such as OH$^-$ and CN$^-$; the products of these reactions are being studied further and will be reported at a later date.

Preparation of thiapyrylium iodide. The ester (II)[6] (10 g) was heated with hydrazine (35 cc of 85 g) and alcohol (60 cc) for four hours. The alcohol was removed under reduced pressure and, on cooling the residue,

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[5] F. Klages and H. Träger, *Chem. Ber.* *86*, 1327 (1953).

[6] Prepared through a modified procedure of W. Steinkopf and H. Augestad - Jensen. *Leibigs Ann.* *428*, 154 (1922).

the hydrazide was obtained as white needles (6.0 g) m.p. 166°. (Found: C, 46.13; H, 5.11; N, 17.70; S, 20.53. $C_6H_8N_2OS$ requires: C, 46.13; H, 5.16; N, 17.94; S, 20.53).

At 0° a solution of sodium nitrite (1.0 g) was added with stirring to a solution of the hydrazide (2.0 g) in acetic acid (25 cc), water (10 cc) and benzene (10 cc). After fifteen minutes more benzene (40 cc) was added, the mixture then filtered and the benzene layer separated, washed with sodium carbonate and dried over sodium sulfate. The benzene solution was heated at reflux for 1 1/4 hours and the solvent then carefully removed under reduced pressure. The residue of isocyanate V was immediately dissolved in dry nitromethane (20 cc) and, while kept cold, the solution was saturated with hydrogen bromide. Anhydrous ether was added to the mixture and the yellow precipitate then collected and dissolved in water (20 cc). The aqueous solution was filtered and the filtrate added to a saturated aqueous solution of sodium iodide. Thiapyrylium iodide separated as orange-red needles (0.9 g), m.p. 209° (dec.). (Found: C, 26.65; H, 2.13; S, 14.04; I, 56.35. C_5H_5SI requires: C, 26.80; H, 2.25; S, 14.31; I, 56.63).

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