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SYNTHESIS OF THE THIENOTROPYLIUM CATION

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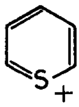
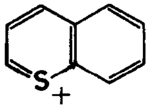
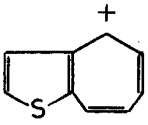
SALTS of the thiapyrylium cation, (I), have recently been prepared in these laboratories by means of a reaction sequence involving ring expansion of thiophene with diazoacetic ester.[1] With the possibility in mind that this route might provide an alternant synthesis of the benzthiapyrylium cation, II, recently reported by Luttringhaus and Engelhard,[2] we have carried out the same sequence of reactions with thianaphthene.



I



II



III

Stable salts of an organic cation are afforded by this series of reactions but their properties do not correspond to those reported for II and it has been shown that the compounds are in fact salts of the thienotropylium cation, III, a novel aromatic system, isoelectronic with the benztropylium cation.

Apparently the course of the first step involves addition of diazoacetic ester to the homocyclic ring of thianaphthene and the

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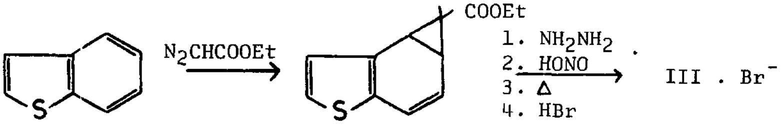
[1] R. Pettit, *Tetrahedron Letters* No. 23, 11 (1960).

[2] A. Luttringhaus and N. Engelhard, *Chem. Ber.* **93**, 1525 (1960).

formation of the cation then results from the transformation indicated below.[3]



If this be so, the isolation of salts of III by this route is all the more surprising since the same reaction sequence fails to yield benztropylium salts when naphthalene is used as the starting material.[4]

Proof of the structure of the new cation has been obtained by treatment of the perchlorate salt of III with $NaBH_4$ followed by reductive desulfurization of the covalent hydride of III thus formed with Raney nickel. The resulting product displays an infrared spectrum, mass spectral cracking pattern and v.p.c. retention time, identical with that of an authentic specimen of ethylcycloheptane prepared from the reaction of suberone with EtMgBr followed by dehydration and reduction.

Thienotropylium perchlorate, formed by addition of $HClO_4$ to aqueous solutions of the bromide, crystallizes in yellow plates from hot water. (Found: C, 43.79; H, 2.86; Cl, 14.21; S, 12.68. $C_9H_7O_4ClS$ requires: C, 43.81; H, 2.93; Cl, 14.37; S, 13.0). The U.V. spectrum, taken in water, displays maxima at 284, 323, 340 and 408 mu, with log E values of 4.7, 3.6, 3.5 and 3.3 respectively.

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[3] The crude product of the addition of the diazoacetic ester is obviously a fairly complex mixture. Only one of the possible isomers is shown in the scheme.

[4] W. von E. Doering and M. J. Goldstein, Tetrahedron 5, 53 (1959). M. J. S. Dewar and R. Pettit. Unpublished observations.

The most striking property of the cation III is its resistance to nucleophilic attack. Whereas the benztropylium cation is decomposed by water,[5] salts of III on the other hand can be readily recrystallized from hot water. As seen from the following equilibrium constants of the hydrolysis of the perchlorate salts in water, the cation III is even more stable in this sense than the tropylium cation. The K_a values for the tropylium,[6] thienotropylium and thiapyrylium cations are found to be 1.8×10^{-5}, 8.7×10^{-7} and 1.8×10^{-9} respectively.

In agreement with this order of stability we find that tropylium perchlorate reacts with the heterocycle obtained from the reaction of III with $NaBH_4$, to produce thienotropylium perchlorate and cycloheptatriene. This hydride abstraction by the less stable carbonium ion is analogous to the reaction of the triphenylmethyl carbonium ion with cycloheptatriene to form triphenylmethane and the tropylium cation.[7]

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[5] H. H. Rennhard, G. Modica, W. Simon, E. Heilbronner and A. Eschenmoser, Helv. Chim. Acta **40**, 957 (1957).

[6] W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc. **76**, 3203 (1954).

[7] H. J. Dauben Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, J. Amer. Chem. Soc. **79**, 4557 (1957).