

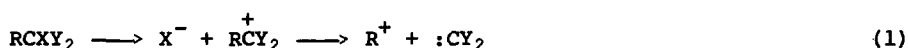
### THE FATE OF 7-CYCLOHEPTATRIENYL CATIONS

S. Kohen and S. J. Weininger

Department of Chemistry, Worcester Polytechnic  
Institute, Worcester, Massachusetts, 01609, U.S.A.

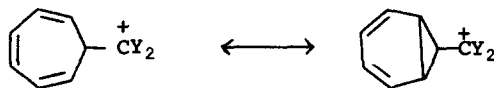
(Received in USA 21 August 1972; received in UK for publication 22 September 1972)

As part of a study on the relationship between the origin and the reactivity of carbenes, we have been seeking to generate carbenes from carbonium ion precursors (equation 1). We have studied some compounds in which



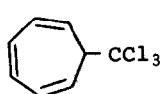
R = 7-cycloheptatrienyl, and wish to report some of our observations on the behavior of the intermediate carbonium ions.

Sargent and coworkers have shown that the 7-cycloheptatrienyl group is very effective at stabilizing neighboring cationic carbon atoms, presumably by way of its norcardienyl valence tautomer (since this tautomer incorporates the

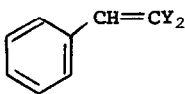


cyclopropylcarbinyl structure).<sup>1</sup> Much of their discussion centers on the relative carbonium ion-stabilizing power of the 7-cycloheptatrienyl ring, compared with that of other such groups. They conclude that 7-cycloheptatrienyl is very effective in this role, while our results suggest that its efficacy, and possibly mechanism of action, depends upon the nature of the other substituents at the reacting center.

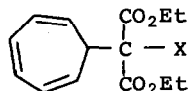
We have solvolyzed 7-trichloromethylcycloheptatriene (I) in 50% aqueous acetone,<sup>2</sup> and we find it to be roughly one-third as reactive as trichloromethylbenzene.<sup>3</sup> The sole organic product of this solvolysis is  $\beta,\beta$ -dichlorostyrene (II); cycloheptatrienylmethyl cations characteristically and readily rearrange



I



II: Y = Cl

VI: Y = CO<sub>2</sub>Et

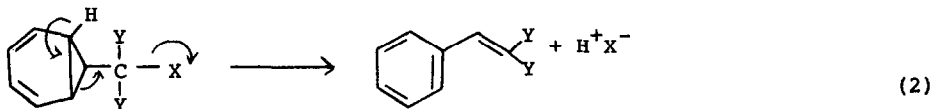
III: X = Br

IV: X = Cl

V: X = NH<sub>2</sub>

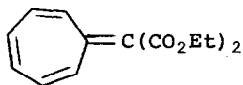
to styrene derivatives.<sup>1,4</sup> In this case the phenyl and cycloheptatrienyl groups seem to be about equally effective in promoting carbonium ion formation.

The bromomalonate III<sup>5</sup> is also a fairly reactive compound, despite the presence of the electron-withdrawing ester groups. It completely rearranges to diethyl benzalmalonate (VI) in the course of 24 hr at room temperature in acetonitrile; the rearrangement is even faster in pyridine. The chloro compound IV is rather more sluggish, but it may be rearranged to the benzalmalonate by treatment with one equivalent of silver nitrate for 1.5 hr in refluxing acetonitrile. By contrast, the phenyl analogues of III and IV are very unreactive; they are unaffected by exposure to silver nitrate in boiling acetonitrile for one day. These observations suggest that carbonium ions cannot be generated in this system; the cycloheptatrienyl compounds are nonetheless able to undergo rearrangement to styrene derivatives, possibly by way of an E2-type mechanism.

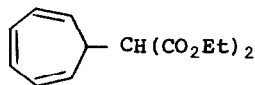


Our most striking results were obtained by diazotization of the amine V<sup>6</sup> under a variety of conditions. When treated with an equivalent of nitrosonium fluoborate in acetonitrile at room temperature V yielded two organic products, approximate ratio 2:1 (glc). The minor product proved to be VI, while the major one was shown to be the heptafulvene VII. To our knowledge this is the first

recorded instance of a cycloheptatrienylmethyl cation decomposing to a heptafulvene, a route presumably available only to "hot" carbonium ions.



VII



VIII

Diazotization of V in a two-phase aqueous organic medium (water-cyclohexane) at 5° results in the formation of VI, VII and diethyl cycloheptatrienylmalonate (VIII) as the major products. When the same medium was employed at reflux no VI was found; the major product was diethyl diazomalonate, accompanied by some VIII! The intermediate diazonium ion apparently preferred to eject tropylium ion. Finally, diazotization of V with NOBF<sub>4</sub> in refluxing benzene yielded VII, VI, VIII and a substantial quantity of diethyl malonate.

In none of these reactions was there any evidence of the formation of :C(CO<sub>2</sub>Et)<sub>2</sub>. Further attempts at generating carbenes by this route, as well as investigations of cycloheptatrienylmethyl cation chemistry, are in progress.<sup>7</sup>

#### Footnotes and References

1. G. D. Sargent, N. Lowry, and S. D. Reich, J. Amer. Chem. Soc., 89, 5985 (1967).
2. M. Sharpe, unpublished results. We are in the process of obtaining accurate rate data. The compound was synthesized by allowing trichloromethyl lithium to react with tropylium fluoborate at -105° (J. Holmes).
3. J. Hine and D. E. Lee, J. Amer. Chem. Soc., 73, 22 (1951); B. Bensley and G. Kohnstam, J. Chem. Soc., 287 (1956).
4. W. A. Bonner, E. K. Raunio, and D. M. Bowen, J. Org. Chem., 31, 912 (1966).
5. Compound III was prepared by allowing the sodium salt of diethyl 7-cycloheptatrienylmalonate to react with bromine in glyme at 0°. Compound IV was a

product of the reaction of diethyl chloromalonate with tropylium fluoroborate in pyridine at 25°. Both III and IV had spectral properties completely in accord with the proposed structures.

6. We have synthesized this amine by two different routes. The preferred route involves dissolving diethyl aminomalonate hydrochloride in pyridine containing two equivalents of sodium hydride, followed by one equivalent of tropylium fluoborate.
7. We are grateful to the Society of the Sigma Xi, Worcester Polytechnic Institute Chapter, for partial support of our work.