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AN ICR STUDY OF SOME 7-SUBSTITUTED CYCLOHEPTATRIENES

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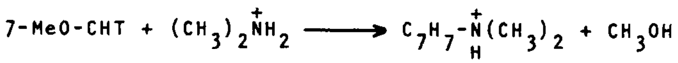
In some previous papers it has been shown that 7-methyl- and 7-cyanocycloheptatriene partly collapse to a six-membered ring upon electron impact[1]. Metastable studies in 7-methoxycycloheptatriene have suggested a similar ring collapse[2]. From a comparative investigation in our laboratory of the latter compound, benzyl methyl ether and their CD_3O analogues, using a conventional double-focusing mass spectrometer, no conclusive information about the ring contraction could be obtained[3].

Recently, a mixture of benzyl methyl ether and dimethyl amine or dimethyl ether has been found to give some interesting ion-molecule reactions in an ICR cell[4]. Evidence has been presented for a benzyl cation transfer in the collision complex in which the two different molecules are held together by a proton. In addition it has turned out that the $C_7H_7^+$- ion from benzyl methyl ether condenses with dimethyl amine, a reaction also observed in gas-phase radiolyses experiments[5]. These results prompted us to investigate the ion-molecule reactions of 7-substituted cycloheptatrienes with dimethyl amine.

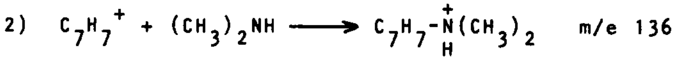
Like in the case of benzyl methyl ether[4] a reaction product at m/e 136 is observed for 7-methoxycycloheptatriene (7-MeO-CHT) (see reaction 1, proved by ICDR).

1) 

$$\text{7-MeO-CHT} + (CH_3)_2\overset{+}{N}H_2 \longrightarrow C_7H_7\text{-}\underset{H}{\overset{+}{N}}(CH_3)_2 + CH_3OH$$

m/e 136

The same reaction product m/e 136 is found starting with 7-CD_3O-CHT, indicating a C_7H_7 transfer to the amine in the collision complex under expulsion of methanol. It is not known whether the C_7H_7 group in the ion m/e 136 (reaction 1) has a tropylium or a benzyl structure. A striking difference however is found in the reactivity of $C_7H_7^+$ from ØCH_2OCH_3 and 7-Meo-CHT towards neutral dimethyl amine[6]. Within the limitations of observation the $C_7H_7^+$- ion from 7-MeO-CHT <u>does not</u> react with amine (reaction 2), whereas that from ØCH_2OCH_3 does[7].



$$2)\quad C_7H_7^+ + (CH_3)_2NH \longrightarrow C_7H_7-\overset{+}{\underset{H}{N}}(CH_3)_2 \qquad m/e\ 136$$

In view of the original structure it seems reasonable that this *nonreactive* $C_7H_7^+$ species has the *tropylium* structure, thus excluding ring collapse in the molecular ion of 7-MeO-CHT prior to the formation of $C_7H_7^+$, at least under the present experimental conditions[8]. The $C_7H_7^+$- ions generated from 7-Me-CHT however appear to react with dimethyl amine, so that, at least part of them, cannot have a tropylium structure. This agrees with the previous reported ring collapse of the molecular ion of 7-Me-CHT[1a] and with the results of a collisional activation study on this compound[9].

It is interesting to note that ICR photodissociation experiments on toluene have shown the existence of two $C_7H_7^+$ species, one being reactive and the other non-reactive towards neutral toluene[10].

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REFERENCES.

1a. A. Venema, N.M.M. Nibbering and Th.J. de Boer, *Tetrahedron Lett.*, 2141 (1971).

1b. A. Venema, N.M.M. Nibbering and Th.J. de Boer, *Org.Mass Spectrom.*, **6**, 675 (1972).

2. R.G. Cooks, J.H. Beynon, M. Bertrand and M.K. Hoffman, *Org.Mass Specrom.*, **7** 1303 (1973).

3. A. Venema and N.M.M. Nibbering, unpublished results.

4. A.P. Bruins and N.M.M. Nibbering, *Tetrahedron Lett.* in press.

5. S. Takamuku, N. Sagi, K.Nagaoka and H. Sakurai, *J.Amer.Chem.Soc.*, **94**, 6217 (1972);
   S. Takamuku, K. Nakamura, K. Nagaoka and H. Sakurai, *Chem.Lett.*, 1303 (1973).

6. The $C_7H_7^+$- ions are generated both from EI induced decompositions of the molecular ions and from an interaction of protonated dimethyl amine and neutral 7-MeO-CHT.

7. In case of $ØCH_2OCH_3$ a signal to noise ratio of 20 was obtained for the relevant ICDR signal.

8. A Varian V5903 ICR spectrometer equipped with a standard flat cell was used. The measurements were performed at 20 eV and a total pressure of $9x10^{-5}$ torr (ion pump reading). To each investigated compound $ØCD_2OCD_3$ was added as internal standard to be sure in observing the relevant ICDR under the same conditions.

9. F.W. McLafferty and J. Winkler, *J.Amer.Chem.Soc.* in press. We are greatly indebted to Prof. F.W. McLafferty for communicating these results in advance of publication.

10. R.C. Dunbar, presented at the 22th annual conference on Mass Spectrometry and allied topics, May 19-24 (1974), Philadelphia.