Tetrahedron Letters No. 47, pp 4577 - 4579, 1971. Pergamon Press. Printed in Great Britain.

MASS SPECTROMETRY OF 2-SUBSTITUTED ADAMANTANES

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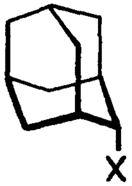
(Received in USA 23 August 1971; received in UK for publication 26 October 1971)

The recent communication of Karpenko and co-workers[3] prompts us to disclose our related results[4] on a much wider variety of compounds. We have found that under standard mass spectrometric conditions[5], the molecular ions derived from a variety of 2-substituted adamantanes (I) undergo primary loss of X • or HX depending on the relative C-X bond strength (or X • radical stability).

Relative Ease of Loss of HX and X • from the Molecular Ion[a]

I



Substituent (X)	Loss of HX/ Loss of X •
OH	~∞
NH_2	290.
F	86.
$OCOCH_3$	44.
$OCOCF_3$	8.0
Cl	6.5
Br	.016
I	.004

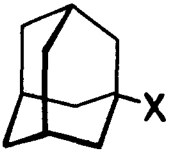
[a] Calculated from the m/e 134 and 135 peaks after correcting the latter for isotopic contributions of the former.

In all cases, either the m/e 134 (loss of HX) or the 135 (loss of X •) peak is prominent, if not the base peak. In those cases in which loss of HX is dominant, the presence of appropriate "*metastables*" is consistent with the fragmentation occuring in a concerted fashion. Deuterium labeling studies eliminate H-2 as an important source of hydrogen for HX.

We have also examined several derivatives of adamantane 2-carboxylic acid (*e.g.* I, X= COOH; $COOCH_3$; $CONH_2$). In these cases, loss of HX by a two-step process (confirmed by "*metastables*") effectively competes with *but does not exclude* the analogous concerted fragmentation. The related carbinol (I, X= CH_2OH) shows important loss of X • rather than HX.

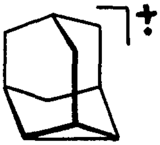
This behavior should be compared with that of the isomeric 1-substituted derivatives (II).[6] The molecular ions derived from the tertiary 1-alcohol and 1-amine (II, X= OH; NH_2) undergo predominant primary loss of alkene fragments with retention of oxygen or nitrogen in the principal ionic species. The related halides (Cl, Br, I) and similar compounds lose the 1-substituent (as a neutral species) with concomitant formation of the relatively stable tertiary 1-adamantyl cation in the dominant primary fragmentation pathway. No important loss of HX was detected.

II



The frequent occurrence of important loss of HX from 2-substituted adamantanes (I) is quite likely due to the rigid, axial disposition of the substituent. A likely primary fragmentation product is the dehydroadamantane[7] radical cation (III).[8]

III



A complete discussion of the various fragmentations observed is deferred to the full paper.

REFERENCES

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2. Author to whom inquiries should be addressed.
3. N. F. Karpenko, O. S. Chizhov, S. S. Novikov, A. G. Yurchenko, and G. I. Danilenko *Zh. Org. Khim.*, 7, 416 (1971); *Chem. Abstr.*, 74, 140375d (1971).
4. Presented at the Southeast-Southwest Regional Meeting, American Chemical Society, New Orleans, La., December 1970, Abstract No. 371.
5. All spectra were obtained using an AEI MS-1201 mass spectrometer operated at 70eV. Samples were introduced using the direct insertion probe with a source temperature of 50-100° C.
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8. An excellent discussion of the factors involved in the fragmentation of substituted cyclohexanes is found in: M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, *J. Amer. Chem. Soc.*, 92, 3076 (1970).