Mass Spectrometry. I. A Novel Elimination of Carbon Dioxide from Ions in the Mass Spectrometer

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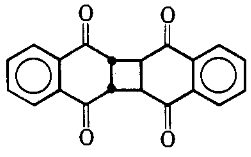
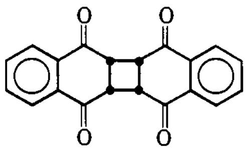
Abstract: The molecular ions of the *syn* and *anti* photodimers of 1,4-naphthoquinone lose carbon dioxide in the mass spectrometer on account of a transannular O rearrangement. Further loss of a hydrogen radical leads to the formation of a tropylium ion derivative. From a study of some related compounds, it has been possible to propose a rule for the electron impact induced decarboxylation of compounds containing a cyclobutane ring, condensed in the 5,6 positions to a cyclohexene-1,4-dione ring.

Much attention has recently been paid to unusual electron impact induced rearrangements in the mass spectrometer, such as the migration of groups other than hydrogen.[1] Skeletal rearrangements involving the loss of carbon dioxide from N-methyl[2a] and N-phenylphthalimide[2b] have been observed.

We have examined the mass spectra (Figures 1 and 2) of the *anti* and *syn* dimers[3] (I and II) of 1,4-naphthoquinone. As one should expect, they are almost identical (apart from small differences in the relative abundance of ions). The mass spectra of the stereoisomers I and II are notable for the fact that both of them display a loss of carbon dioxide, to the same extent, from the molecular ion. This observation is striking, since structures I and II cannot account for the ejection of carbon dioxide. Such a fragmentation may, therefore, be visualized only if interaction between remote functional groups occurs. The composition of ions c and d has been established by exact mass measurements, indicating the following fragmentation pattern[4]

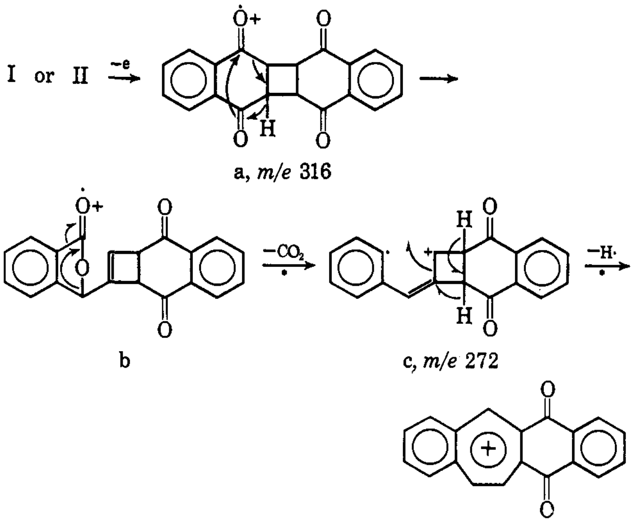

I


II

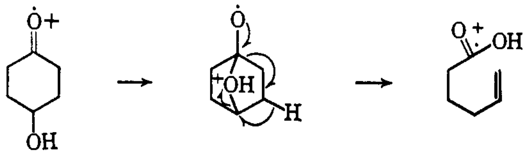
$$\begin{array}{ccccc} [C_{20}H_{12}O_4]\cdot^{+} & \underset{*}{\xrightarrow{-CO_2}} & [C_{19}H_{12}O_2]\cdot^{+} & \underset{*}{\xrightarrow{-H\cdot}} & [C_{19}H_{11}O_2]^{+} \\ \text{a, } m/e \text{ 316} & & \text{c, } m/e \text{ 272} & & \text{d, } m/e \text{ 271} \end{array}$$

A plausible mechanism for the ejection of carbon dioxide from I and II must involve a rather novel electron impact induced rearrangement (Scheme I) of the molecular ion a to the lactone ion b. The lactone ion b eliminates carbon dioxide, leading to c, which, on further elimination of a hydrogen radical, produces the stable tropylium ion derivative d. Ion d does not lose carbon dioxide, as can be expected. In fact, we could find no evidence for further decomposition of d.

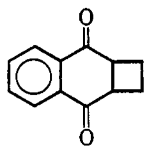
Scheme I



This proposed O rearrangement of a to b is analogous to the O rearrangement of 4-hydroxycyclohexanone.[5]



The process M+ − CO_2 − ·H [a (*m/e* 316) to d (*m/e* 271)] is significant, and we believe such fragmentations to occur in compounds containing the tricyclic structural unit III, which, by consecutive loss of carbon dioxide and a hydrogen radical, will lead to stable tropylium ion derivatives.


III

To confirm the generality of this proposed rule, we extended our investigation to compounds closely related to I and II. The mass spectra of IV and V show that

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[1] For an extensive review, see P. Brown and C. Djerassi, *Angew. Chem.*, 79, 481 (1967).

[2] (a) R. A. W. Johnstone, B. J. Millard, and D. S. Millington, *Chem. Commun.*, 600 (1966); (b) J. L. Cotter and R. A. Dine-Hart, *ibid.*, 809 (1966).

[3] J. Dekker, P. Janse van Vuuren, and D. P. Venter, *J. Org. Chem.*, 33, 464 (1968).

[4] Transitions substantiated by an appropriate metastable peak are indicated by an asterisk.

[5] M. M. Green, D. S. Weinberg, and C. Djerassi, *J. Amer. Chem. Soc.*, 88, 3883 (1966).

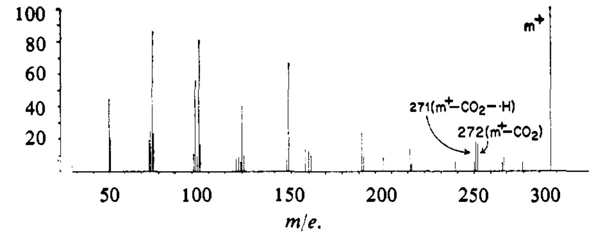


Figure 1. Mass spectrum of the *anti* photodimer (I) of 1,4-naphthoquinone.

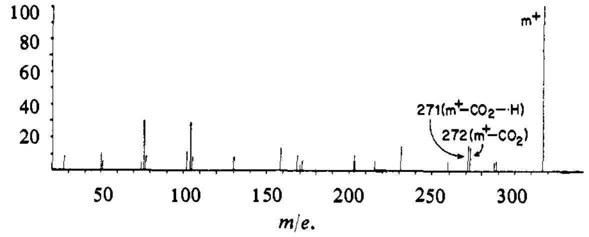


Figure 2. Mass spectrum of the *syn* photodimer (II) of 1,4-naphthoquinone.

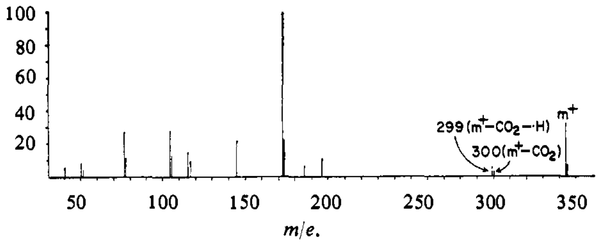


Figure 3. Mass spectrum of the photodimer (IV) of 2-methyl-1,4-naphthoquinone.

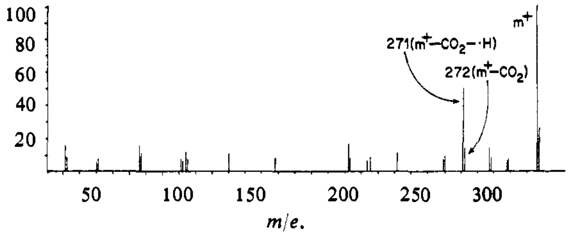
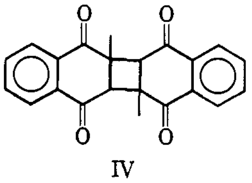
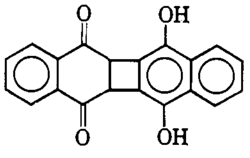


Figure 4. Mass spectrum of V.

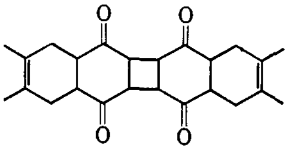
both compounds do indeed undergo a similar O rearrangement, since the consecutive loss of carbon dioxide and a hydrogen radical occurs in both cases. The mass spectrum (Figure 3) of IV, the photodimer[6] of 2-methyl-1,4-naphthoquinone, shows the molecular peak at *m/e* 344 and the base peak at *m/e* 172 (monomer mass). In this case the loss of carbon dioxide is accompanied by the migration of a methyl group (Scheme II). As in the case of I and II, no further decomposition of ion h is observed.



IV

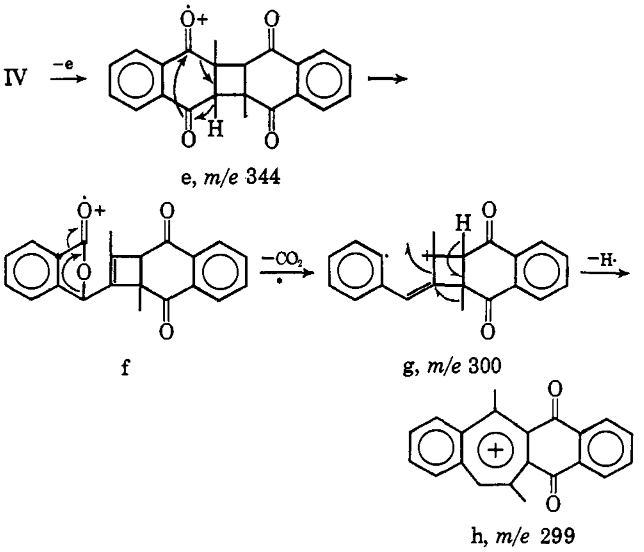


V



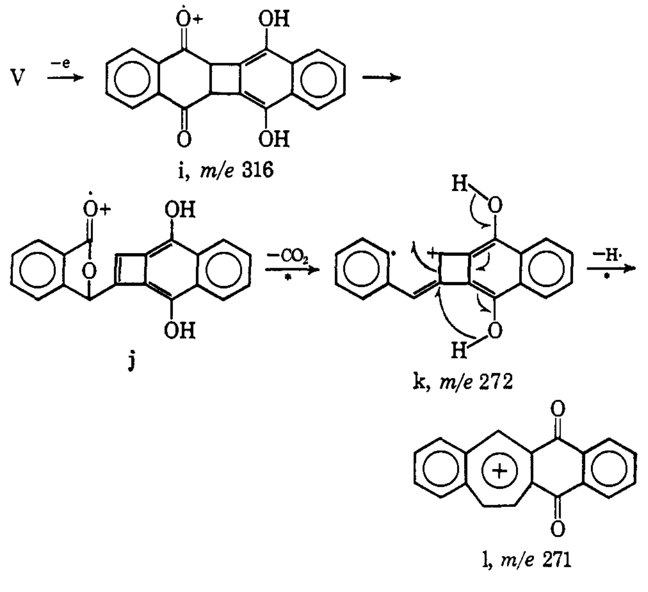
VI

Scheme II



It is noteworthy that the mass spectrum (Figure 4) of V[7] is almost identical with that of I and II, differing mainly in the relative abundance of the ions. The molecular peak (i, *m/e* 316) is also the base peak. The fragmentation may either proceed as illustrated in Scheme III, or, if ketonization should occur prior to ionization, proceed as in Scheme I.

Scheme III



In order to test the validity of the above-mentioned empirical rule for compounds which are closely related, but do not fulfill all the requirements laid down in structural unit III, we examined the mass spectrum of VI, the photodimer of the 2,3-dimethyl-1,3-butadiene–*p*-benzoquinone adduct. The mass spectrum of VI, which displays the molecular ion at *m/e* 380 and the

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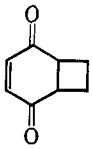
[6] J. Mandinaveitia, *Anales Soc. Españ. Fis. Quim.*, **31**, 750 (1933).

[7] The synthesis of V is to be published shortly in *The Journal of Organic Chemistry*.

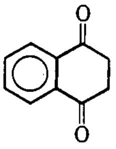
base peak at m/e 190 (monomer mass), does, accordingly, not show a loss of carbon dioxide.

Compounds containing the structural unit VII may, however, initially also undergo an O rearrangement, followed by the consecutive loss of carbon dioxide and a hydrogen radical, leading to stable tropylium ion derivatives. Consequently, we are presently involved in the syntheses of a series of compounds containing either the structural units III or VII, in order to furnish further supporting evidence for the proposed rule.

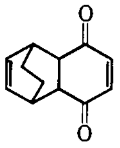


VII

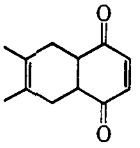
It should finally be mentioned that compounds VIII, IX, X, and XI do not lose carbon dioxide in the mass spectrometer, thereby proving that the presence of the cyclobutane ring, condensed in the 5,6 positions to the cyclohexene-1,4-dione ring (as illustrated in structural units III and VII), is essential.



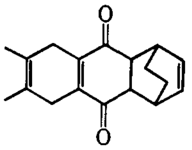
VIII



IX



X



XI

Acknowledgment. The authors are indebted to Dr. S. Eggers for recording the mass spectra. Generous support of this work and a postgraduate grant to D. P. V. by the Council for Scientific and Industrial Research of South Africa is gratefully acknowledged.

Electron Impact Induced Rearrangements of Benztropones. 1,4-Aryl Migrations[1]

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Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. Received February 13, 1967

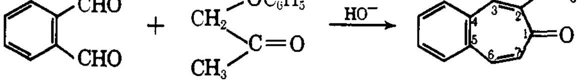
Abstract: A study of the electron impact induced fragmentations of 2-phenoxy-4,5-benztropone, a variety of D-, ^{18}O-, and ^{13}C-labeled derivatives, and certain model compounds has made possible a detailed description of these fragmentations. Two particularly novel fragmentations have been observed: (1) loss of OH, and (2) loss of CO, which involve both the carbonyl oxygen and the ether oxygen. These processes are correlated by demonstration of a 1,4-phenyl migration from one oxygen to the other. A corresponding phenyl migration has been shown to occur from a sulfur to an oxygen atom, but not from nitrogen to oxygen, in the analogous compounds. Loss of carbon monoxide from 2-phenoxy-4,5-benztropone gives 2-phenoxynaphthalene radical cation. Further fragmentation of this radical cation to β-naphthol radical cation and benzyne, to naphthyl cation, to phenyl cation, and to hydrocarbon cation and carbon monoxide is documented by the labeled materials. The origin of almost all fragment ions is determined by an unusually large number of metastable ions.

In the course of investigation of the photochemistry of 2-phenoxy-4,5-benztropone[2] it became necessary to prepare a variety of isotopically labeled derivatives of 2-phenoxy-4,5-benztropone. Mass spectroscopic examination of the labeled derivatives revealed a novel rearrangement induced by electron impact.[1] Prompted by this observation we have undertaken a detailed study of the behavior of 2-phenoxy-4,5-benztropone (I) and its isotopically labeled derivatives.

We have further expanded these investigations to include the study of possible aryl migrations from sulfur to oxygen and from nitrogen to oxygen using corresponding 2-thiophenoxy- and 2-N-methylanilino-4,5-benztropones. We have also evaluated the importance of alkyl group migrations using ^{18}O- and ^{13}C-labeled derivatives of 2-methoxy-4,5-benztropone.

Synthesis

Synthesis of 2-phenoxy-4,5-benztropone (I) is readily achieved by the method of Tarbell, *et al.*[3] This method also proved readily adaptable to the synthesis of isotopically labeled derivatives of 2-phenoxy-4,5-benztropone. Condensation of *o*-phthalaldehyde with phenoxyacetone in basic solution gives crude I. Treatment of phthaloyl chloride with dimethylamine gave the bisamide. Reduction of the bisamide with lithium aluminum deuteride gave *o*-phthalaldehyde with deuterium in each aldehyde group.[4] Condensation with phenoxyacetone gave 2-phenoxy-4,5-benztropone-3,6-d_2 (II).



I

(1) Portions of this work have appeared in a previous communication: O. L. Chapman, T. H. Kinstle, and M. T. Sung, *J. Am. Chem. Soc.*, 88, 2618 (1966).

(2) O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *ibid.*, 85, 2031 (1963).

(3) D. S. Tarbell, G. P. Scott, and A. D. Kemp, *ibid.*, 72, 379 (1950).

(4) H. C. Brown and A. Tsukamoto, *ibid.*, 83, 4549 (1961).