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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—XXXVII.[1]

TROPONE AND TROPOLONE DERIVATIVES[2,3]

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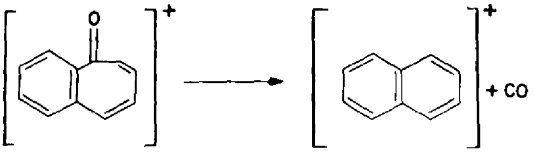
Abstract—The general observation is made that on electron impact the molecular ions of tropone derivatives eliminate carbon monoxide as a neutral molecule and the resultant ions behave as benzene derivatives. Exceptions from this rule can be explained in terms of the presence of specific structural features.

THE observation[4] that aromatic compounds exhibit in their mass spectra intense peaks formed by loss of carbon monoxide or of a formyl radical has prompted the examination of a series of substituted anthraquinones[5] and diaryl ethers.[6] No further studies have been carried out on troponoid compounds and this article is a report of observations of the behavior on electron impact of a wide variety of derivatives of tropone.

Beynon *et al.* found[4] that the most intense peak in the spectrum of benztropone had the formula $C_{10}H_8^+$ and that at lower mass numbers the spectrum was very similar to that of naphthalene. Thus the suggested process was as follows:



Ring contractions and expansions[7] have been suggested several times to explain the mass spectra of aromatic compounds and it is of interest to note that similar behavior has been confirmed for some neutral molecules and radicals under pyrolytic conditions.[8]

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[1] For paper XXXVI see: M. Ohashi, H. Budzikiewicz, J. M. Wilson, C. Djerassi, J. Lévy, J. Gosset, J. LeMen and M. -M. Janot, *Tetrahedron* **19**, (1963) (previous paper).

[2] We wish to thank our colleagues of Tohoku University for the generous supply of many samples discussed in this paper. The work at Stanford University was supported by grant No. A-4257 from the National Institutes of Health of the U.S. Public Health Service.

[3] For reviews of the chemistry of tropone derivatives see: (*a*) P. L. Pauson, *Chem. Rev.* **55**, 9 (1955); (*b*) T. Nozoe, *Fortschrifte der Chemie Organischer Naturstoffe* (Edited by L. Zechmeister) Vol. 13. 232 ff. Springer Verlag, (1956).

[4] J. H. Beynon, G. R. Lester and A. E. Williams, *J. Phys. Chem.* **63**, 1861 (1959).

[5] J. H. Beynon and A. E. Williams, *Appl. Spectroscopy* **14**, 156 (1960).

[6] J. M. Wilson, *Experientia* **16**, 403 (1960); R. I. Reed and J. M. Wilson, *Chem. & Ind.* 1428 (1960).

[7] S. Meyerson, P. N. Rylander and H. M. Grubb, *J. Amer. Chem. Soc.* **79**, 842 (1957).

[8] S. R. F. Pottie and F. P. Lossing, *J. Amer. Chem. Soc.* **85**, 41 (1963).

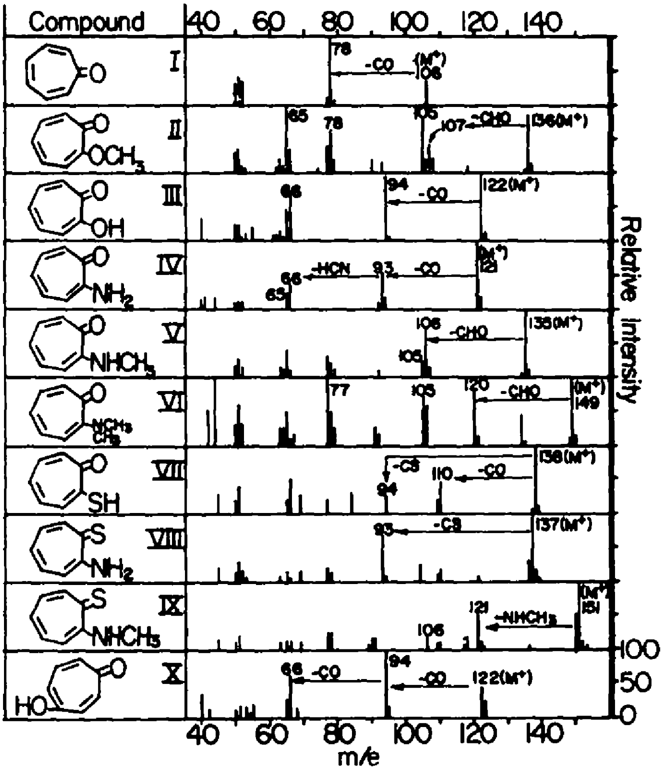

Fig. 1. Mass spectra of tropone, tropolone and some simple analogs.

The mass spectrum of tropone (I, Fig.1) shows that its behavior is similar to that of benztropone. Below m/c 78, the similarity to the spectrum of benzene[9] is obvious. The other spectra shown in Fig. are of derivatives of tropolone and its nitrogen and sulfur analogs.

The mass spectrum of tropolone (III) exhibits a much more abundant molecular ion than is found in the spectrum of the parent compound I. This is a reflection of the greater ability of the two oxygen atoms to bear the positive charge. The less abundant molecular ion of 4-hydroxytropone (X) suggests that hydrogen bonding may contribute to the stability of the ion in tropolone (III). Both hydroxytropones (III and X) show a further loss of carbon monoxide as well as of a formyl radical from the M-28 ion (*m/e* 94). This is analogous to the behavior of the molecular ion of phenol.[4] In the case of 2-aminotropone (IV) the M-28 ion (which should in this case have the structure of aniline) decomposes by losing the elements of HCN and H_2CN. The ions produced (*m/e* 65 and 66) will have the same structure as those formed from tropolone (III), i.e. cyclopentadiene and cyclopentadienyl.

Tropolone methyl ether (II) exhibits striking differences in behavior. Loss of CHO (M-29) becomes more prominent than loss of CO, as was observed in the spectra of the colchicine alkaloids.[10] There is also an intense M-31 peak (*m/e* 105) formed by loss of the methoxyl group. Such fission is observed in the fragmentation of some aryl

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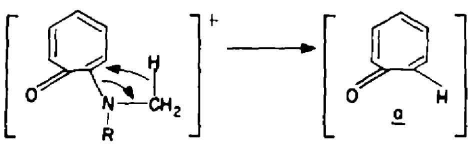
[9] Taken from A.P.I. catalog of Mass Spectral Data, Spectrum No. 417.

[10] J. M. Wilson, M. Ohashi, H. Budzikiewicz, F. Santavy and C. Djerassi, *Tetrahedron* **9**, 2225 (1963).

methyl ethers,[11,12] although not generally to the extent observed here. Similar behavior can be noted in the mass spectra of some nitrogen and sulfur analogs.

Thus 2-amino-tropone (IV) exhibits an intense M-28 peak (*m*/*e* 93) but in the spectrum of 2-methyl aminotropone (V) the most abundant fragment ion appears at *m*/*e* 106 (M-29). An intense M-29 peak also occurs in the spectrum of 2-dimethylaminotropone (VI), so in both of these cases the 29 mass units must represent a formyl radical or carbon monoxide and a hydrogen atom.

In both V and VI, fission of the aromatic C–N bond takes place with production of ions of *m*/*e* 105. This is probably not a simple cleavage, but involves rearrangement to form the intermediate *a* followed by loss of a hydrogen atom. Such a process is suggested since there is no C–N fission observed in the spectrum of the unmethylated compound IV, and an analogy can be made to the behavior of aromatic methyl ethers.[12]



2-Mercaptotropone (VII) exhibits peak formed by loss of carbon monoxide (*m*/*e* 110) and by loss of carbon monosulfide (*m*/*e* 94). It is interesting that 2-aminothiotropone (VIII) and 2-methylaminothiotropone (IX) behave analogously to tropolone (III) and its methyl ether (II). Thus, in VIII, the most intense fragment (*m*/*e* 93) is formed by elimination of CS from the molecular ion, while in the spectrum of IX loss of the elements of $NHCH_3$ (*m*/*e* 121) and of CHS (*m*/*e* 106) rather than CS, become prominent.

In Fig. 2 are shown the mass spectra of a number of brominated tropones and tropolones. In most cases, the pattern observed in the spectra of the simpler

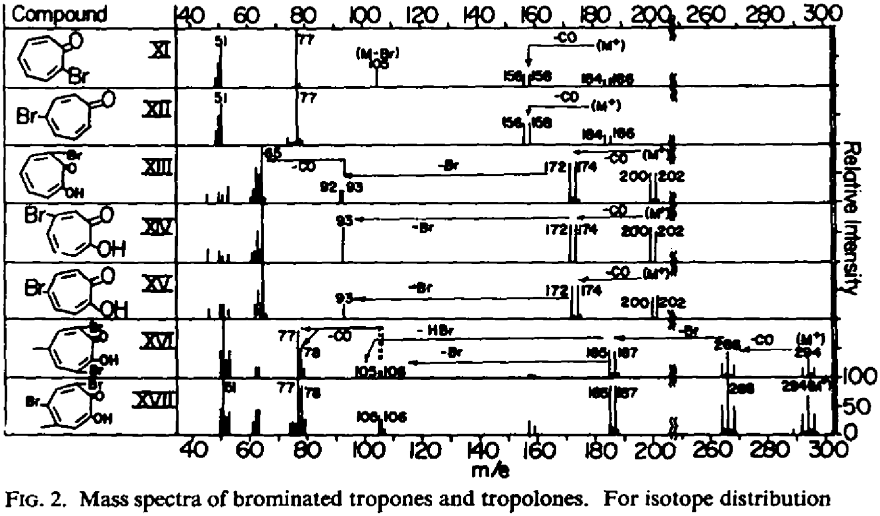
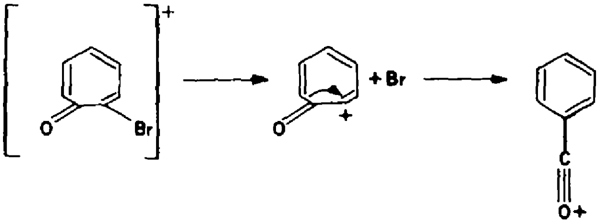


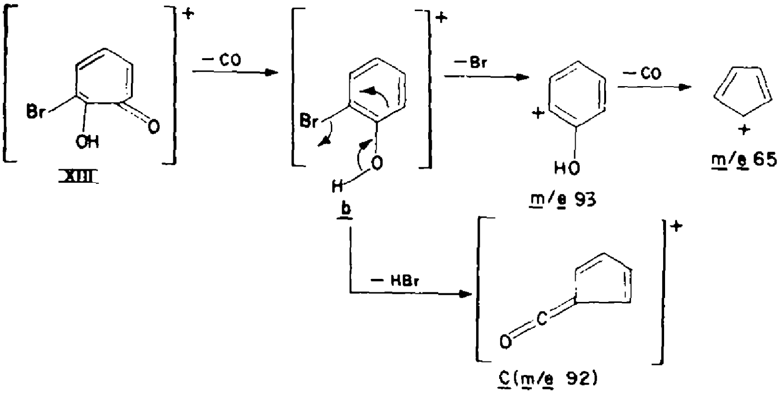
FIG. 2. Mass spectra of brominated tropones and tropolones. For isotope distribution in brominated compounds, see J. H. Beynon, "Mass Spectrometry and its applications to organic chemistry," Elsevier Publishing Co., Amsterdam, 1960.

[11] Z. Pelah, J. M. Wilson, M. Ohashi, H. Budzikiewicz and C. Djerassi, *Tetrahedron* **19**, 2233 (1963).
[12] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.* **16**, 219 (1963).

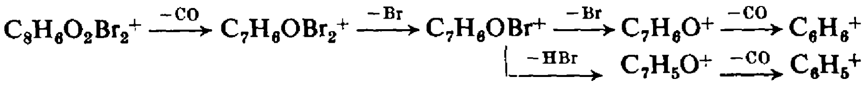
derivatives is obeyed, i.e. elimination of carbon monoxide is followed by decomposition of the resulting ion in the manner of a benzene derivative. 2- (XI) and 4- (XII) Bromotropone both exhibit peaks at *m/e* 77 ($C_6H_5^+$) and 51 ($C_4H_3^+$) as does bromobenzene.[13] The only important difference between the two spectra is the presence of an M-Br ion (*m/e* 105) in the spectrum of XI, which can rearrange to a benzoyl ion whereas the 4- isomer cannot do so without a more extensive rearrangement.



3- (XIII), 4- (XIV) and 5- (XV) isomers of bromotropolone exhibit decomposition by loss of carbon monoxide, followed by expulsion of the bromine atom. The resulting $C_6H_5O^+$ ion (*m/e* 93) loses a further molecule of carbon monoxide with the formation of the stable cyclopentadienyl ion (*m/e* 65). The intermediate *b*, formed from the 3-bromo compound XIII can also eliminate a molecule of hydrogen bromide (*m/e* 92). Such a stereospecific reaction will probably involve the hydroxyl hydrogen and the ion formed may have the configuration *c*. Such a mechanism cannot operate in the 4- (XIV) and 5-bromo (XV) isomers and these substances do not exhibit the loss of hydrogen bromide.



The spectra of the methyldibromotropolones (XVI and XVII) show no specific difference between the two isomers, since in both cases there is a bromine atom in an α-position. In these spectra loss of carbon monoxide (*m/e* 266) and a bromine atom is followed by elimination of a further atom of bromine (*m/e* 106) or a molecule of hydrogen bromide (*m/e* 105). The resultant ions have the formulae $C_7H_6O^+$ and $C_7H_5O^+$ and may be tropone or benzyl ions. These fragments decompose further in the expected fashion with elimination of carbon monoxide (*m/e* 77 and 78).



$$C_8H_6O_2Br_2^+ \xrightarrow{-CO} C_7H_6OBr_2^+ \xrightarrow{-Br} C_7H_6OBr^+ \xrightarrow{-Br} C_7H_6O^+ \xrightarrow{-CO} C_6H_6^+$$
$$C_7H_6OBr^+ \xrightarrow{-HBr} C_7H_5O^+ \xrightarrow{-CO} C_6H_5^+$$

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[13] Reference 9, Spectrum No. 1296.

In Fig. 3 are shown the mass spectra of some alkylated tropones and tropolones. Methylated tropones behave in a predictable manner, i.e. the ion formed by loss of carbon monoxide decomposes by the same path observed for the corresponding benzene derivative. Typical examples are 3- (XIX), 4- (XX) and 5- (XXI) methyltropolone in which the M-28 ion (*m/e* 108) readily loses a hydrogen with formation of the fragment of mass 107. In these cases the M-28 ions will be cresol ions which have been shown[14] to lose readily a hydrogen atom. Similarly in the spectrum of 2,3-dimethyltropone (XVIII) there are peaks at *m/e* 105 and 91, which correspond to the loss of a hydrogen atom and a methyl group respectively from the M-CO ion (*m/e* 106). This is the same behavior which is observed in the mass spectra of the xylenes.[7] 3,4-Dimethyltropolone (XXVII) and 3,5,7-trimethyltropolone (XXVIII) exhibit analogous decomposition patterns: in both cases there are major peaks formed by loss of a methyl group or a hydrogen atom from the M-CO ion.

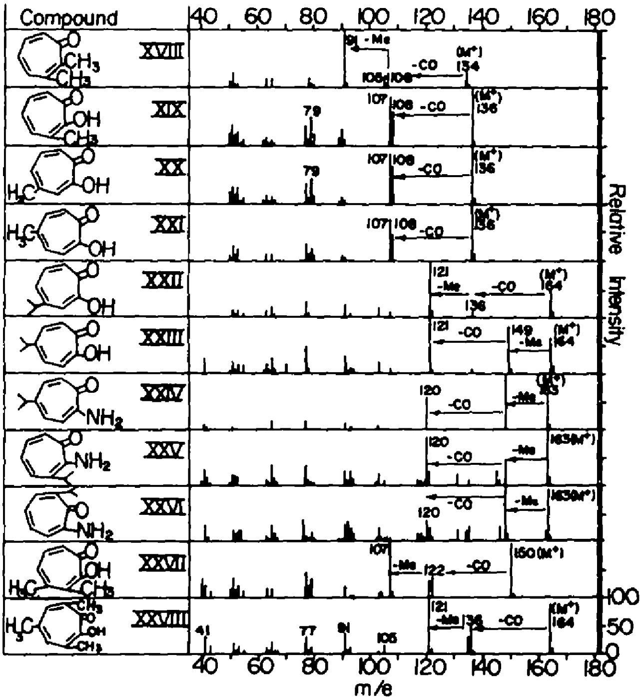

Fig. 3. Mass spectra of alkylated tropones and tropolones.

Exceptions to this general rule are some isopropyl tropones which lose a methyl group directly from the molecular ion. Examples are 5-isopropyltropolone (XXIII), 2-amino-5-isopropyltropone (XXIV), 2-amino-3-isopropyltropone (XXV) and 2-amino-7-isopropyltropone (XXVI). Such a fission is not observed in the spectrum of 4-isopropyltropolone (XXII), so the intensity of the M-CH_3 peaks in the spectra of the other compounds can be ascribed to stabilization of the positive charge on one of

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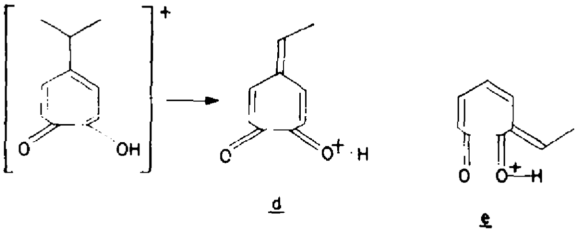
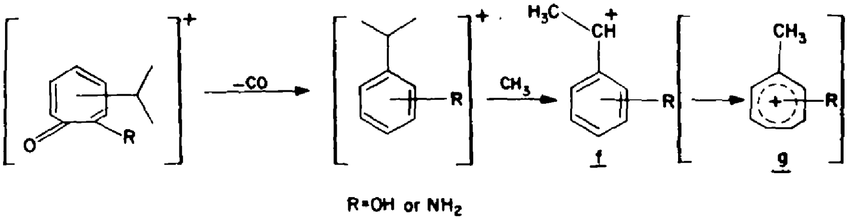
[14] T. Aczel and H. E. Lumpkin, *Analyt. Chem.* 32, 1819 (1960).

the oxygen or nitrogen atoms in a structure of type *d* or *e*. Such stabilization is not possible in an ion derived from a 4-substituted tropolone.



All the isopropyltropones exhibited ions formed by loss of 43 mass units (carbon monoxide and methyl) from the molecular ion. By elimination of carbon monoxide a benzenoid ring can be formed, which can then lose a methyl group to give an entity which may be a benzyl or tropylium ion (*f* or *g*). Stabilization of this type is available to all isomers.



An interesting phenomenon is observed in the mass spectra of some phenyltropones (Fig. 4). In those of 2-phenyltropone (XXIX), 3-phenyltropolone (XXX) and 2-amino-7-phenyltropone (XXXIII), the base peak is formed by loss of a hydrogen atom from the molecular ion. In the spectra of 4- (XXXII) and 5- (XXXI) phenyltropolone, however, the M-1 peak is extremely small. This difference can be explained by postulating a cyclic structure (*h*) for this fragment, which can only be formed if

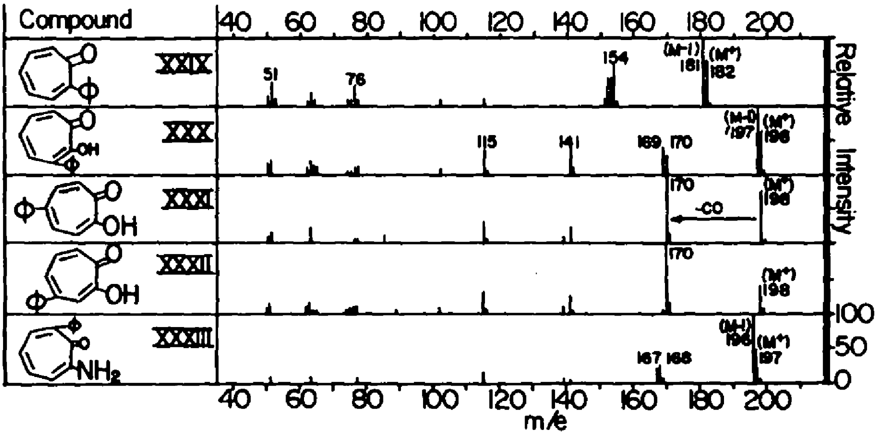
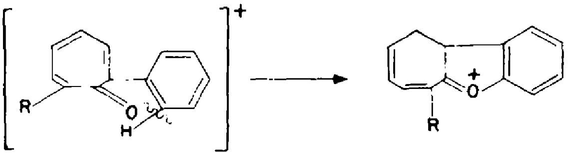


FIG. 4. Mass spectra of phenyltropone and derivatives.

there is a suitable substituent on a carbon atom adjacent to one bearing a hetero atom.



(R = H, OH, or NH_2)

h

A similar M-1 peak is observed in the spectrum of *o*-hydroxybiphenyl[15] but with reduced intensity in that of the *para* isomer.[15] The remainder of the spectrum reflects the previously discussed fragmentation pattern of the parent substances.

All spectra were measured with a CEC 21-103C mass spectrometer equipped with a heated (200°) all glass inlet system. The ionizing current was maintained at 50 μA, and the ionizing energy at 70 eV.

[15] Ref. 9, Spectra Nos. 634 and 635.