Tetrahedron. Vol. 26, pp. 1163 to 1168. Pergamon Press 1970. Printed in Great Britain

ELECTRON IMPACT STUDIES—XLII[1]

PERI-EFFECTS IN THE MASS SPECTRA OF ALKOXYQUINONES

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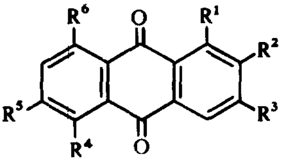
(*Received in the UK* 2 *June* 1969; *Accepted for publication* 3 *July* 1969)

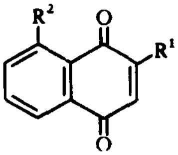
Abstract—The mass spectra of certain 1-alkoxyanthraquinones, 5-alkoxynaphthaquinones and 1,8-dialkoxyanthraquinones exhibit diagnostic fragmentations which are absent in the spectra of other alkoxyquinones. These fragmentations are characteristic of the *peri*-alkoxyquinone moiety, and may be used as useful aids to structure determinations.

THE basic fragmentations in the mass spectra of benzoquinones,[2,3] naphthaquinones,[2,4–7] anthraquinones[2] and certain higher quinones[2,8,9] have been described. *Ortho*-effects[10] have been noted in the spectra of naphthaquinones[11,12] and anthraquinones.[11–13]

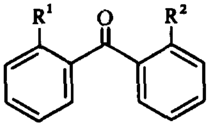
In connection with our studies[11,12] of the *ortho*-effects which occur in the mass spectra of aromatic carbonyl compounds containing adjacent alkoxyl groups, we observed large differences between the spectra of 1- and 2-ethoxyanthraquinone. As it seemed that mass spectrometry may usefully complement the use of IR[14] and UV[15] spectroscopy for the determination of the oxygenation pattern of an hydroxyquinone, we examined the mass spectra of I–XXI. This paper describes the diagnostic *peri*-effects which are observed in many of these spectra.



	R^1	R^2	R^3	R^4	R^5	R^6
I	CD_3O	H	H	H	H	H
II	EtO	H	H	H	H	H
III	CD_3CH_2O	H	H	H	H	H
IV	H	EtO	H	H	H	H
V	H	CD_3CH_2O	H	H	H	H
VI	*n*PrO	H	H	H	H	H
VII	H	*n*PrO	H	H	H	H
VIII	*iso*PrO	H	H	H	H	H
IX	Me_2CDO	H	H	H	H	H
X	MeO	MeO	H	H	H	H
XI	MeO	H	MeO	H	H	H
XII	MeO	H	H	MeO	H	H
XIII	MeO	H	H	H	H	MeO
XIV	CD_3O	H	H	H	H	CD_3O
XV	H	MeO	H	H	MeO	H
XVI	EtO	H	H	EtO	H	H
XVII	EtO	H	H	H	H	EtO

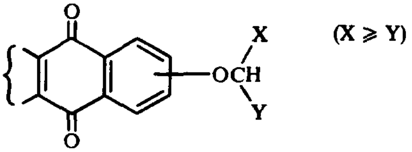


	R^1	R^2
XVIII	EtO	H
XIX	H	EtO

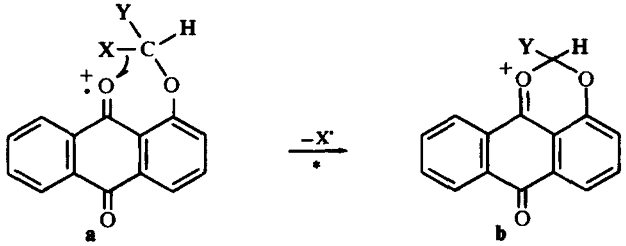


	R^1	R^2
XX	EtO	H
XXI	MeO	MeO

Table 1. Relative abundances of $M^{+\cdot}-X^{\cdot}$ ions in the spectra of compounds of the type



Compound	$M^{+\cdot}$	$M^{+\cdot}-X^{\cdot}$	Compound	$M^{+\cdot}$	$M^{+\cdot}-X^{\cdot}$
I	100	6	VIII	15	12
II	98	100	IX	13	10
III	88	87	XVI	100	31
IV	93	—	XVII	1	—
V	94	—	XVIII	100	75
VI	18	9	XIX	88	—
VII	10	—			



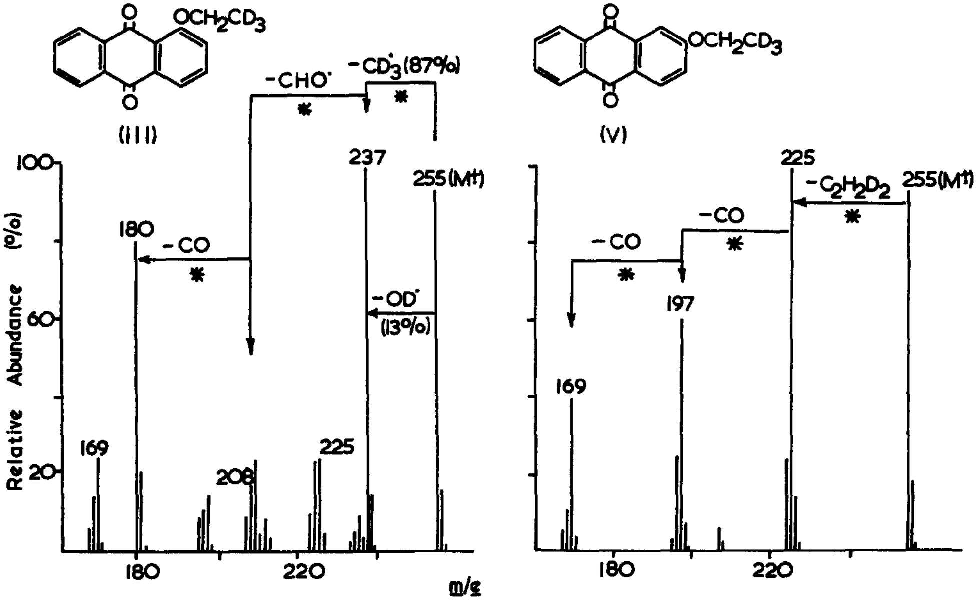


Fig. 1

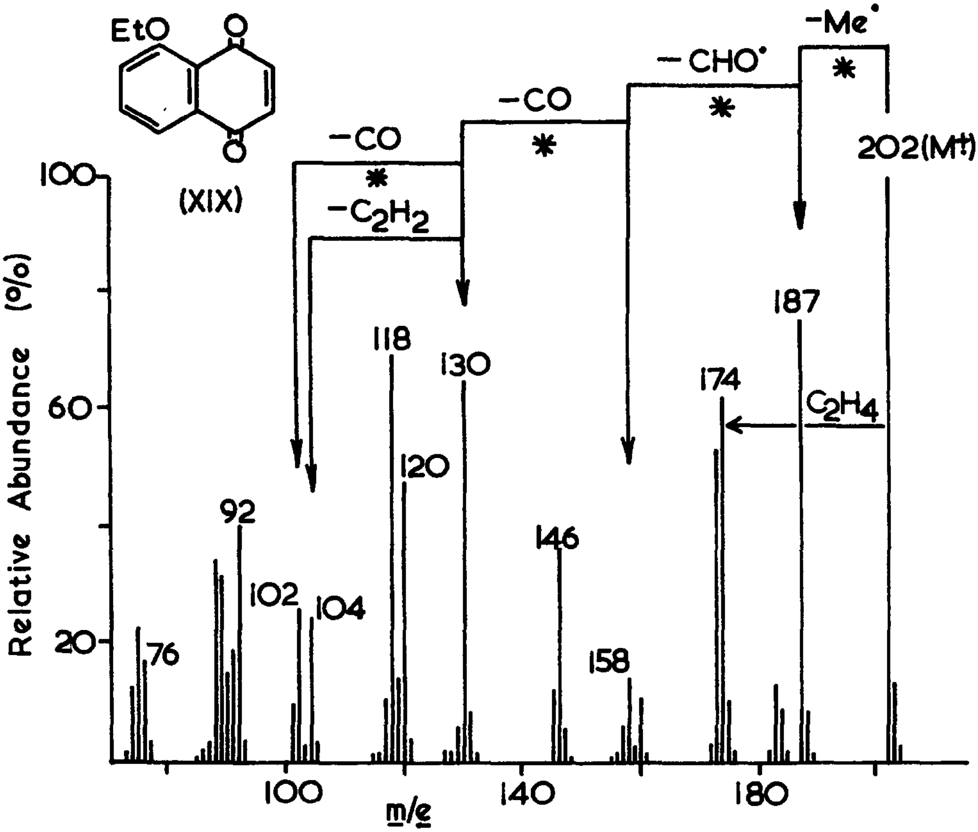
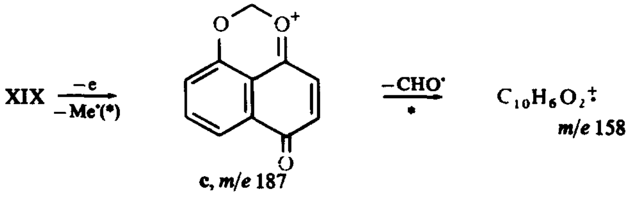


FIG. 2

The mass spectra of 1- and 2-alkoxyanthraquinones are very different. The major differences are summarised in Table 1, and are illustrated [for the cases of 1- and 2-(2,2,2-d_3-ethoxy)anthraquinone (III and V)] in Fig. 1. The pronounced loss of $CD_3^{\bullet}$ from the molecular ion of III is absent in the spectrum of V. This effect is characteristic of the spectra of 1-alkoxyanthraquinones (when X $\geqslant$ Me, see *a*), and is most pronounced for 1-ethoxyanthraquinone. The *peri*-effect may be rationalised by the formation of the stabilised oxonium species **b** and its formation is always substantiated by a metastable peak (represented by an asterisk in a Figure or the text). It is of interest to note that this effect is minor in the spectrum of *o*-ethoxybenzophenone ($M^+ - Me^{\bullet}$ = 100 and 12% in the spectra of I and XX respectively).



The spectrum (Fig. 2) of 5-ethoxynaphthaquinone also shows a pronounced $M^{+\cdot} - Me^{\cdot}$ ion. In marked contrast, 2-ethoxynaphthaquinone does not eliminate a Me radical upon electron impact. The fragmentation of the oxonium species **c** is indicated in Fig. 2. Loss of a formyl radical from **c** produces a species which fragments in the same way as the 1,4-naphthaquinone molecular ion.[4] However, this species may not correspond to the 1,4-naphthaquinone radical ion because of the large differences between the abundance ratios of *m/e* 158 and its daughter ions in the spectra of 1,4-naphthaquinone[2] and XIX. The same situation occurs for III (Fig. 1) where the process $M^{+\cdot}$—$CD_3^{\cdot}$—$CHO^{\cdot}$ produces a species which may not correspond to the anthraquinone molecular ion. The spectra of the labelled derivatives III, IV and IX show that no hydrogen randomisation in the alkoxyl groups precedes the $M^{+\cdot} - X^{\cdot}$ process at 70 eV.

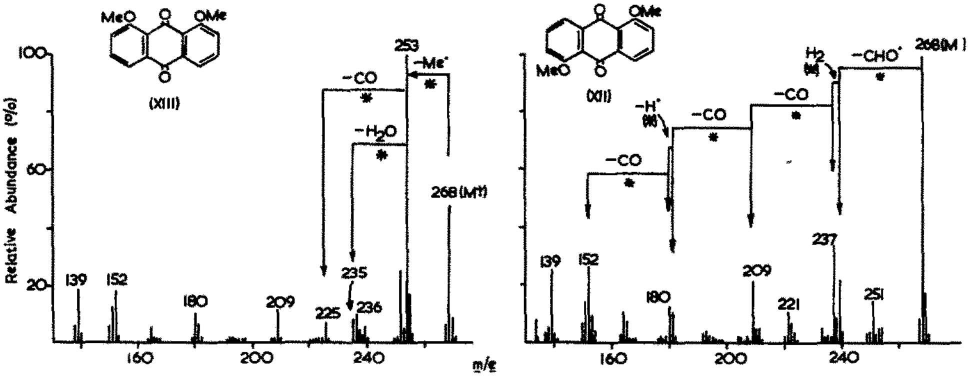


FIG. 3

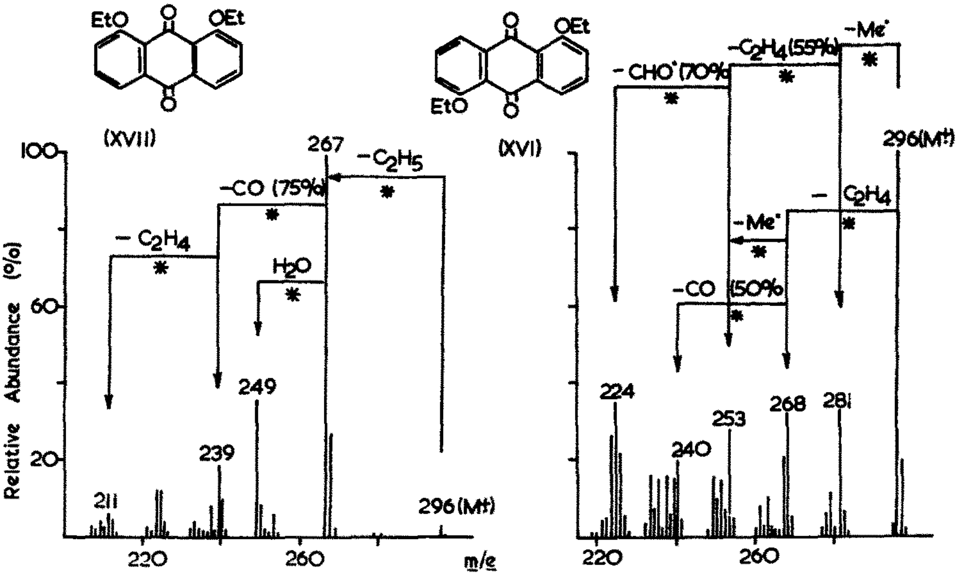


FIG. 4

The mass spectra of the isomeric dimethoxyanthraquinones (X–XII and XV) are reasonably similar and are typified by that (Fig. 3) of 1,5-dimethoxyanthraquinone (XII). The spectrum (Fig. 3) of 1,8-dimethoxyanthraquinone (XIII) is easily distinguishable from that of XII in that the process $M^{+\cdot}-Me^{\cdot}$ produces the base peak for XIII but only a peak of 5% relative abundance in the spectrum of XII. This distinction is even more apparent in the spectra (Fig. 4) of the isomeric diethoxyanthraquinones (XVI and XVII). Although these spectra are complex, they can be easily differentiated, because the base peak in the spectrum of 1,8-diethoxyanthraquinone is an $M^{+\cdot}-Et^{\cdot}$ ion, whereas the corresponding peak in that of 1,5-diethoxyanthraquinone is only 19% of the base peak. It is of interest to note that a major fragmentation in the spectrum of XVI proceeds through the $M^{+\cdot}-Me^{\cdot}$ ion, and that this *peri*-effect is completely absent in the spectrum of XVII which is dominated by the second *peri*-effect discussed above.

Although mass spectrometry can be used to determine the presence of 1,8-dialkoxyl substitution in an anthraquinone, it is not obvious why this *peri*-effect occurs. The tricyclic aromatic system is a prerequisite for the elimination, as the spectrum of *o,o'*-dimethoxybenzophenone (XXI) does not contain an $M^{+\cdot}-Me^{\cdot}$ ion. There seems to be no obvious reason why the M-15 ion in the spectrum of XIII should be any more stable than a similar species which could be produced from other isomeric dimethoxyanthraquinones unless a cyclic structure is involved. Whatever the structure of the $M^{+\cdot}-R^{\cdot}$(R = Me or Et) ion is, it is unusual, in that it decomposes by loss of water (see Figs 3 and 4). The process $M^{+\cdot}-Me^{\cdot}-H_2O$ in the spectrum (Fig. 3) of 1,8-dimethoxyanthraquinone becomes $M^{+\cdot}-CD_3^{\cdot}-D_2O$ in that of 1,8-di(d_3-methoxy)anthraquinone (XIV).

In summary, mass spectrometry will allow the determination of the 1-hydroxyl and 1,8-dihydroxyl substitution pattern in an anthraquinone and a 5-OH group in a naphthaquinone if the OH groups are first converted into ethoxyl substituents. In this way mass spectrometry complements the use of other spectroscopic methods for the structure determination of hydroxyquinones.

EXPERIMENTAL

All spectra were determined with an Hitachi Perkin–Elmer RMU 6D double focusing mass spectrometer operating at 70 eV. Samples were introduced through an all glass heated inlet system at 200°. The compositions of species indicated by schematic arrows in a Figure were determined by exact mass measurements at a resolution of 10,000 (40% valley definition) using heptacosafluorotributylamine to provide reference masses.

All unlabelled compounds were available from previous studies.[11, 12] The labelled ethers were prepared by alkylation of the appropriate hydroxyquinone with the required labelled alkyl iodide.

Acknowledgement—The Hitachi Perkin–Elmer RMU 6D mass spectrometer was purchased with the aid of a grant from the Australian Research Grants Committee.

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