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MASS SPECTROMETRY IN STRUCTURAL AND STEREOCHEMICAL PROBLEMS—CXLVIII[1]

ELECTRON IMPACT INDUCED FRAGMENTATIONS OF SOME CYCLIC SULFITES AND CARBONATES*

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Abstract The low and high resolution mass spectra of a series of cyclic sulfite and carbonate esters of acyclic and cyclic 1,2-diols have been examined, and the principal fragmentation pathways described. With the aid of deuterium labeling and the new technique of "metastable ion characteristic" comparison, it has been possible to demonstrate "ketone-like" and "epoxide-like" M-XO_2 ions. Two routes for M-HXO_2 processes were uncovered, and another important decomposition mode involves loss of $C_nH_{2n}O$ fragments from the parent ion. Attempts were also made to compare the electron impact induced reactions of the cyclic esters with those reported in the literature for pyrolysis of the same compounds particularly where the latter showed a stereochemical preference. Attention is drawn in the experimental section to the use of a direct inlet technique for measuring the mass spectra of thermally labile, volatile liquids.

IN CONTINUATION of our earlier work on carbonate esters of monohydric alcohols and phenols,[2] we now report a study of the mass spectrometric behavior of cyclic sulfite and carbonate esters of some simple 1,2-diols. The systems investigated previously (dialkyl, aryl alkyl and diaryl carbonates)[2] supplied cogent examples of the increasingly widely recognized phenomenon of skeletal rearrangement under electron impact,[3] and migratory aptitudes of competing aryl groups were determined[2b] for the decarboxylation reaction of diaryl carbonates. It was anticipated that cyclic esters such as sulfites and carbonates might also undergo interesting rearrangements on electron bombardment.‡

In order that the full potential of mass spectrometry as an analytical tool can be realized, it is essential to recognize and document as many instances as possible of skeletal reorganization. No less important is the study of mechanistic requirements for such processes, that they may be better understood and eventually predicted, and also to shed further light on the reactions of gaseous ions in general.

In order that comparisons may be made between the reactions of such ions in the mass spectrometer, and processes induced by vibrational (thermal)[5] and electronic (photo-chemical)[6] excitation, both in solution and in the vapor phase, it is desirable

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‡ Kunstmann *et al.*[4] has recently reported the occurrence of a cyclic carbonate ester in the macrolide antibiotic aldgarose.

to subject the same chemical systems to each kind of initiation. Some pyrolytic studies of cyclic sulfites are already in the literature,[7,8] and it seemed opportune to compare their behavior on electron impact. In particular, the cyclic sulfites (and carbonates) of *cis*- and *trans*-cyclohexane-1,2-diol were examined, to investigate the possibility of an electron impact induced analogy to the dramatic difference found[8] on their pyrolysis. In this connection, it has already been reported[11] that the mass spectral fragmentation modes of DL- and *meso*-hydrobenzoin cyclic sulfites (XII) are very similar, whereas on pyrolytic elimination of SO_2 quite different products are obtained.[8,9] Some correlation between the electron impact and thermally initiated processes occurring in *o*-phenylene cyclic sulfite have recently been noted.[5b]

Since inadvertent pyrolysis of a sample in the inlet system or source of a mass spectrometer is not entirely unknown, extremely mild thermal conditions (direct sample insertion into room temperature source) were employed in an effort to overcome this pitfall.

(1) *Cyclic esters of acyclic* 1,2-*diols*

The principal peaks of interest in the mass spectra* of the cyclic esters are summarized in Table 1. In general, the molecular ions of the cyclic carbonates are more stable than those of the corresponding cyclic sulfites. Four major fragmentation modes appear to operate: (a) loss of $C_nH_{2n}O$ units; (b) a pinacol-type rearrangement resulting in expulsion of XO_2 and formation of a ketone or aldehyde rearrangement radical ion; (c) a second process also affording M-XO_2 ions, but in which the daughter ions are relation to the corresponding epoxide parent ions; (d) formation of M-HXO_2 species by two pathways. These processes are discussed further below. Peaks at *m/e* 48, 50, 64 and 65 in the spectra are due to SO, H_2SO, SO_2 and HSO_2 ion respectively.*

(a) *Formation of* M-$C_nH_{2n}O$ *ions*. This reaction is of significance only in the simpler cyclic esters (Table 1, column 3), and is more prevalent in the sulfites than the carbonates. Possible fragmentation sequences are depicted in Scheme 1 for propane-1,2-diol cyclic sulfite (III). (In all Schemes, presence of a metastable peak is indicated by an asterisk over the appropriate arrow). From the per cent total ionization figures (Σ_{25}) in Table 1, and the mass spectrum of III (Fig. 3), it can be seen that loss of the smaller $C_nH_{2n}O$ entity (*aa*, M-CH_2O) is preferred over the larger (*ab*, M-CH_3CHO). This difference becomes even more pronounced at low electron energies (10–15 eV nominally), *aa* accounting for 54·9% Σ_{25} and *ab* 3·3% Σ_{25} at approximately 10 eV. The contribution of the M-$C_nH_{2n}O$ process in all the other cyclic sulfites (I, III, V and VII) increases at low electron energies, but the reverse is true for the carbonates (II, IV and VI). With XVI, (Table 1) *aa* remains at *m/e* 92, while *ab* moves from *m/e* 78 to *m/e* 80.

(b) *Pinacol rearrangement to* M-XO_2 *ions*. The pinacol-type rearrangement† is invoked to explain the occurrence of 1,2-Me and Ph group migrations in compounds V, VI, VII, VIII, XI, XII and XIII, where the compositions of certain rearrangement

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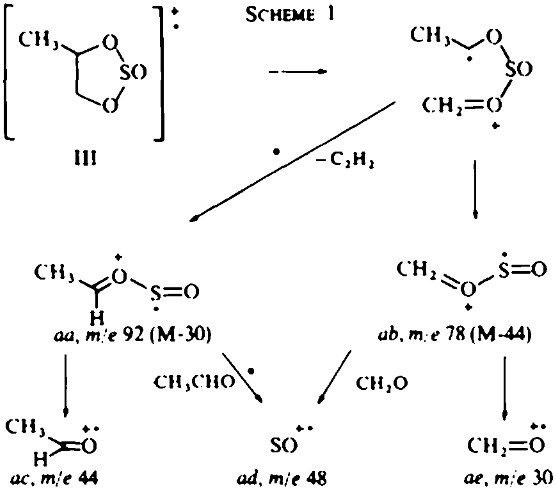
* The elemental compositions of ions contributing to all peaks discussed or tabulated have been determined by precise mass measurements (Experimental Section).

† It has been claimed[10] that an electron impact induced pinacol rearrangement occurs in pinacol itself (and related 1,2-diols), but the rearrangement peaks reported are of low abundance and unknown composition.

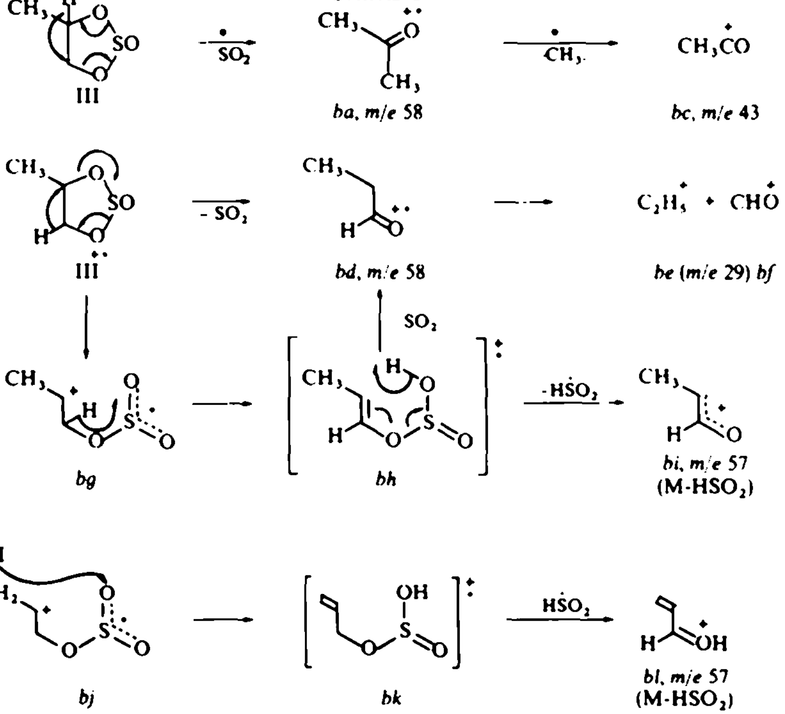
SCHEME 1



peaks (Table 1, last column) clearly suggest an ionized aldehyde or ketone M-XO_2 species. Possible decomposition pathways are set out in Scheme 2 (III → *ba* → *bc*; III → *bd* → *be* + *bf*), and in Scheme 3 for 2,3-dimethylbutane-2,3-diol (pinacol) cyclic sulfite (VII) and carbonate (VIII).

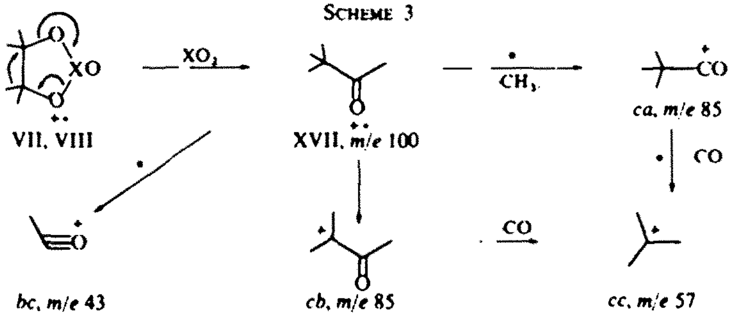
In the case of III → *bd* (Scheme 2, hydrogen migration), an alternative and indistinguishable mechanism (III → *bg* → *bh* → *bd*) is conceivable, involving overall reciprocal transfer of the same hydrogen. This route appears to operate to some

SCHEME 2



extent, since in the deuterium labeled analog (XVI, Table 1) of III, the M-HSO_2 process comprises two components. First, 57% remains as M-HSO_2 (Scheme 2, *bj* → *bk* → *bl*, *m/e* 59 in XVI), and second, 43% moves to *m/e* 58 in XVI as M-DSO_2 (*bg* → *bh* → *bi*). Thus the rearranged parent ion *bh* can also easily be imagined to expel SO_2, and produce the same ionized propionaldehyde (*bd*) that would arise from the pinacol process. A metastable peak for the loss of SO_2 from III was observed, but which process (III → *ba*, III → *bd*, *bh* → *bd*, or others) or processes are responsible is not known.

SCHEME 3



With VII, VIII → XVII (Scheme 3), pinacol-type 1,2-Me migration is envisaged, producing ionized 3,3-dimethylbutan-2-one (XVII, Fig. 12; pinacolone),† at mass 100, and its characteristic further decomposition peaks at *m/e* 85 (*ca*, *cb*), 57 (*cc*) and 43 (*bc*) (Table 1). Comparison of the relative abundances of the mass spectral peaks of authentic pinacolone with those of VII (Fig. 6) over the range 12–70 eV, and also comparison of their respective metastable peak characteristics*,[12] permit (but do not demand) the assignment of XVII radical ion as the main M-SO_2 species derived from VII. Similar comparison using tetramethylethylene oxide (XVIII, Fig. 13), on the other hand, seems to exclude its molecular ion as another (major) possible formal representation of an M-SO_2 species, since two metastable peaks [*m/e* 24·4 (69 → 41), *m/e* 28·6 (59 → 41)] are present in the spectrum of the epoxide (XVIII), but not in that of VII (Table 2). This finding is of some interest, since pyrolysis of 2,3-dimethylbutane-2,3-diol cyclic sulfite (VII) has been reported[13] to give tetramenthylethylene epoxide (XVIII).

An important decomposition mode of tetramethylethylene epoxide (XVIII) to the same rearrangement ions as VII (and VIII) (mass 43, C_2H_3O; mass 57, C_4H_9) has already been described.[14] Comparison of the mass spectra of XVIII with that of pinacolone at various electron energies, and of their metastable ion characteristics* allows the possibility of XVII as a rearranged molecular ion of XVIII, as previously proposed.[14] Thus it seems probable that the cyclic sulfite VII and the epoxide XVIII both fragment to some extent *via* ionized pinacolone XVII, but the parent ion of XVIII does not arise from ionized VII. However, use of metastable ion characteristics*,[12] and the "external standard method"[15] to rule out a particular structure for an ion derived by two separate routes is dependent on the assumption that both ions are

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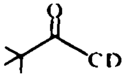
* Shannon and McLafferty[11] call attention to the useful fact that ions identical in structure and energy should exhibit identical decomposition reactions and, therefore, the spectra should also show the same metastable peaks, with identical peak shapes and intensities relative to the parent ion.

† See footnote † p. 2950.

produced in the same energy state.* This assumption, in the absence of any definite evidence, would seem to be most in doubt when one ion is a molecular ion, and the other a daughter ion. Therefore the conclusions reached here are presented in the light of these reservations.

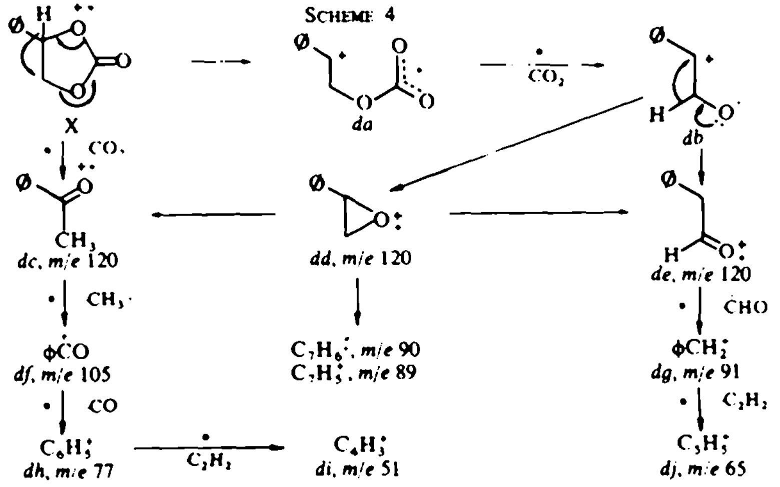
In Scheme 3, loss of a methyl group from XVII is shown both as α-cleavage to the ketone (XVII → *ca*) and as β-cleavage in the t-butyl group (XVII → *cb*). This interesting situation was betrayed by the presence of both M-15 (61%) and M-18 (39%) peaks in the 70 eV mass spectrum of d_3-3,3-dimethylbutan-2-one (XIX).† At lower electron energies (10–15 eV), the contribution of M-18 eventually overcomes that of M-15.



XIX

In those cyclic esters containing a phenyl substituent (IX–XIII), peaks at *m/e* 105 (Scheme 4, *dc* → *df*, C_7H_5O) and at *m/e* 91 (*de* → *dg*, C_7H_7) (IX, Fig. 7; X, Fig. 8; XIII, Fig. 9) are considered diagnostic of the pinacol-type rearrangement (see Table 1). In compounds with 1,2-diphenyl substitution (XII, XIII, Fig. 9), further analogous rearrangement peaks at *m/e* 167 ($\phi-\overset{+}{C}H-\phi$) are present (Table 1), and with XI 35% of *m/e* 105 corresponds to $\phi-\overset{+}{C}H-CH_3$. Appearance of peaks at *m/e* 89 (C_7H_5) anc *m/e* 90 (C_7H_6), on the other hand, suggest operation of an epoxide-type mechanism,[16] (Scheme 4, *db* → *dd*), discussed further below.

SCHEME 4



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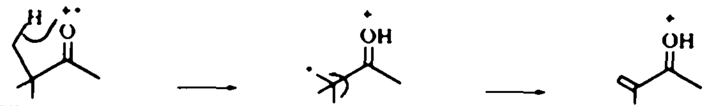
* See footnote * p. 2952.

† This cleavage, written as XVII → *cb* in Scheme 3, would be expected at first glance to be unfavorable, in that a positive charge is generated adjacent to the carbonyl moiety (see K. Biemann, *Mass Spectrometry*, McGraw-Hill Book Co., Inc., New York, N.Y., 1962, p. 133). However, other instances of this behavior are on record [for example M-15 in androstan-1-one arises 50% from the loss of C-19: M. Powell, D. H. Williams, H. Budzikiewicz and C. Djerassi, *J. Am. Chem. Soc.* **86**, 2623 (1964)]. An equally plausible mechanism for M-15 in XVII at this time is shown below:



(c) *Formation of epoxide intermediates by* XO_2 *elimination.* In compounds X (Fig. 8), XI and XIII (Fig. 9) intense peaks due to hydrocarbon ions occur at *m/e* 89 and 90 (Table 1), and to a lesser extent in IX and XII also. This behavior is characteristic of phenyl substituted epoxides,[16] and completely atypical for the isomeric aldehydes and ketones.[17] In Scheme 4, the three possible decarboxylation product ions (*dc*, *dd*, *de*) are depicted, together with their characteristic decomposition products, for phenylethane-1,2-diol cyclic carbonate (X). The simplest interpretation of the mass spectra of the phenyl substituted compounds (IX–XIII) is that most of the major peaks can be accounted for by varying proportions of ionized aldehyde (e.g. *de*), ketone (e.g. *dc*) and epoxide (e.g. *dd*) M-XO_2 intermediates.

To put this suggestion to the test, *meso*-hydrobenzoin cyclic carbonate (XIII) was selected, as its mass spectrum (Fig. 9, Table 1) contains the largest ratio of *m/e* 89/90 peaks to *m/e* 91/105 in this series. Comparison of the low resolution spectrum of *trans*-stilbene epoxide[*] with that of XIII below *m/e* 196 (M-CO_2) at various electron energies showed that every peak in the former is accounted for in that of the latter, relative to *m/e* 196. More dramatically, every metastable peak position,[†] shape and relative intensity[‡] in the spectrum of the epoxide is prominently reproduced in that of the cyclic ester (XIII) (Table 3). In contrast, the spectrum[9] of benzyl phenyl ketone is dominated by the peak at *m/e* 105 (C_7H_5O, 62% Σ_{40}), and therefore its parent ion can only be a minor contributor to the M-CO_2 species from XIII (Fig. 9).

The mass spectrum (see Table 1) of *meso*-hydrobenzoin cyclic sulfite (XII) on the other hand, has its base peak (18·2% Σ_{40}) at *m/e* 105, and *m/e* 89/90 are quite small (2·6 and 2·0% Σ_{40} respectively), indicating that pinacol-type loss of SO_2 predominates in this instance. Other rearrangement processes also operate in the sulfite (XII)[9] that are apparently absent in the corresponding carbonate (XIII). Thus an ion of mass 154 ($C_7H_6O_2S$) is formed[9] by the loss of the elements of benzaldehyde from XII, which can further eliminate either CO (to give *m/e* 126, C_6H_6OS) or SO (to give *m/e* 106, C_7H_6O). No peaks at either *m/e* 154 or 126 were detected in XIII, although the mass spectrum of XII obtained under our conditions (see Experimental) was qualitatively similar to that previously published.[9]

On pyrolysis, *meso*-hydrobenzoin cyclic sulfite (*cis*-XII) affords[8,9] benzyl phenyl ketone and SO_2, whereas *dl*-hydrobenzoin cyclic sulfite (*trans*-XII) yields diphenylacetaldehyde as the main product. However, the mass spectra of the two isomers are very similar,[9] and both contain ions of mass 91 and 105 (derived from benzyl phenyl ketone radical ion) and of mass 167 (derived from stilbene epoxide or diphenylacetaldehyde radical ions), of which mass 105 is by far the most abundant.

The trend observed for pinacol-type *vs* epoxide-type M-XO_2 processes in XII and XIII seems to be general for the rather limited range of compounds employed. Thus in the carbonates X (Fig. 8), XI and XIII (Fig. 9) the *m/e* 89/90 peak group is more important than the *m/e* 91/105 (and 167 in XIII), whereas in the sulfites IX (Fig. 7) and XII, the reverse is true.

(d) M-HXO_2 *processes.* In the mass spectra of certain of the cyclic esters there are peaks present at one mass unit less than the M-XO_2 peak (Table 1) which are of

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[*] The mass spectra of *cis/trans* pairs of alkyl[14] and aryl[16] substituted epoxides are identical.

[†] These appear at *m/e* 163 (broad) ($165^2/167$); *m/e* 161 (broad) ($178^2/196$); *m/e* 142·5 ($167^2/196$); *m/e* 138·8 ($165^2/196$); *m/e* 88·1 ($89^2/90$); *m/e* 56·5 ($77^2/105$); *m/e* 46·5 ($65^2/91$); *m/e* 44·7 ($63^2/89$).

[‡] See footnote * on page 4.

greater abundance than expected for simple loss of a hydrogen atom from the M-XO_2 species. For example, loss of a hydrogen atom from propionaldehyde is insufficient to explain the intensity of the peak at *m/e* 57 in III (Fig. 3). At least two mechanisms appear to operate, and these are revealed by deuterium labeling.

As previously mentioned, the M-HSO_2 peak (*m/e* 57) in III (Fig. 3) splits in XVI to 57% M-HSO_2 and 43% M-DSO_2, and this observation is conveniently interpreted in terms of ring-opened molecular ions *bj* (Scheme 2) → *bk* → M-HSO_2 (in XVI), and *bg* → *bh* → M-DSO_2 (in XVI). Similarly, the M-HSO_2 peak (*m/e* 97) in XIV (Figs 10, 11) splits in XX to 15% M-HSO_2 and 85% M-DSO_2, and this situation can be explained by analogous ring-opened molecular ions *fa* (Scheme 5) → *fc* → *fc*–HSO_2, and *fa* → *fb* → *fl*. Clearly only one of these pathways can operate in compounds I, II, X and XIII.

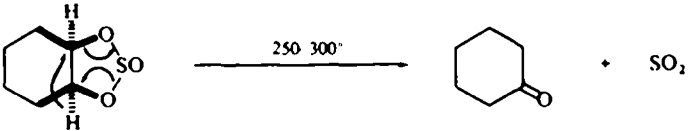
(e) *Other fragmentation routes.* With the higher cyclic esters (VII–XIII), small peaks ($\Sigma_{40} \not> 2\%$) may be discerned in their spectra corresponding formally to ionized olefin species, generated by loss of XO_3. Thus in IX (Fig. 7) there are metastable peaks at *m/e* 56·5 ($104^2/184$) and at *m/e* 58·5,* in support of the following sequence:

IX *ea m/e* 104 *eb m/e* 78

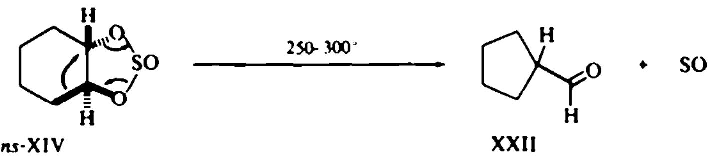
The first stage of this transformation survives at low electron energies, (12–15 eV), but the second is eliminated at the lower end of the range.

(2) *Cyclic esters of cyclic* 1,2-*diols*

The mass spectra of the cyclic sulfites of *cis*-cyclohexane-1,2-diol (*cis*-XIV, Fig. 10) and *trans*-cyclohexane-1,2-diol (*trans*-XIV, Fig. 11) and the corresponding cyclic carbonates (*cis*-XV and *trans*-XV) were obtained in order to assess any electron impact induced parallel to the sterochemical dependence of the pyrolytic reaction products reported by Price and Berti.[8]



cis-XIV XXI



trans-XIV XXII

Thermolysis[8] of *cis*-XIV at 250–300° yields cyclohexanone (XXI) as the principal product, the formation of which can be rationalized by 1,2-migration of a tertiary

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* The mass spectrum[18] of styrene shows a significant peak (32% relative abundance) at *m/e* 78, and observation of a metastable peak for its formation from the parent ion has been reported.[19]

hydrogen atom *trans* to the breaking ester C—O bond. In *trans*-XIV, elimination of SO_2 is accompanied by ring contraction to afford cyclopentane carboxaldehyde (XXII), again by migration of the bond (C—C) *trans* to the leaving group.

The 70 eV mass spectrum of *cis*-XIV, obtained on an Atlas CH-4 instrument with gas inlet system reservoir at 100°, inlet line at 145° and ion source (TO-4) at 180°, had the base peak (14·0% Σ_{40}) at *m/e* 55 (70% C_3H_3O) (cf. cyclohexanone)[20] and prominently displayed all other peaks characteristic of cyclohexanone[20] [*m/e* 42, 69 (C_4H_5O), 70, 80, 83, 98]. Under identical conditions, the 70 eV spectrum of *trans*-XIV displayed the base peak (16·8% Σ_{40}) at *m/e* 69 (95% C_5H_9) (cyclopentyl cation), while *m/e* 55 now accounted for only 5·4% Σ_{40}, and other "cyclohexanone peaks" (e.g. *m/e* 42) were similarly reduced in intensity. Although both spectra contained peaks at the same *m/e* values, the relative intensities of most of the peaks were quite different.

The mass spectra of *cis*-XIV (Fig. 10) and *trans*-XIV (Fig. 11) were also run under much milder conditions. These were direct insertion of the sample adsorbed on charcoal into the ion source (TO-4) of the Atlas CH-4 mass spectrometer at room temperature.* Obtained in this way, the spectra of the *cis/trans* isomers are much more similar, although some relative intensity differences still remain. It is considered unlikely that selectivity of rearrangement will increase with increasing vibronic excitation of the gaseous molecules immediately prior to ionization, and therefore the spectra obtained under the more severe thermal conditions undoubtedly contain peaks due to pyrolysis products such as XXI and XXII.

Comparison of the low temperature spectra (Figs. 10 and 11) of *cis*-XIV and *trans*-XIV revealed that the same metastable peaks (Table 4) were present in each case, and in the same abundances relative to the molecular ion, within experimental error. This fact strongly suggests† that a large proportion of the molecular ions of *cis*-XIV and *trans*-XIV undergo ring-opening (e.g. to *fa*, Scheme 5) and loss of stereochemical identity prior to decomposition, or that the respective bicyclic molecular ions are sufficiently flexible that the stereochemistry of the ring junction plays no major role in the course of fragmentation, or that simply no stereospecific processes are involved at all. Quite small differences in relative abundance of peaks and of fragment ion appearance potentials for *cis/trans*-stereoisomeric pairs such as decalins[21] and 1,2-dialkyl-cycloalkanes[22] have been explained by Franck-Condon translation of ground state energy differences into the molecular ions.

The precise mass measurements available for the *cis/trans* isomers XIV (Table 1) could only be obtained under highly pyrolytic conditions (see Experimental), and cannot be extrapolated to the low resolution spectra (Figs 10, 11) obtained at a much more benign temperature. Therefore any stereospecific processes that may operate in *cis/trans* XIV to produce different proportions of isobaric components to a spectral peak (e.g. *m/e* 69, C_4H_5O/C_5H_9) would remain undetected under our conditions.

An overall fragmentation flowsheet offering rationalizations for the principal decomposition pathways of the cyclic sulfites XIV is shown in Scheme 5. M-SO_2 (*m/e* 98) species are plausibly formed as follows:

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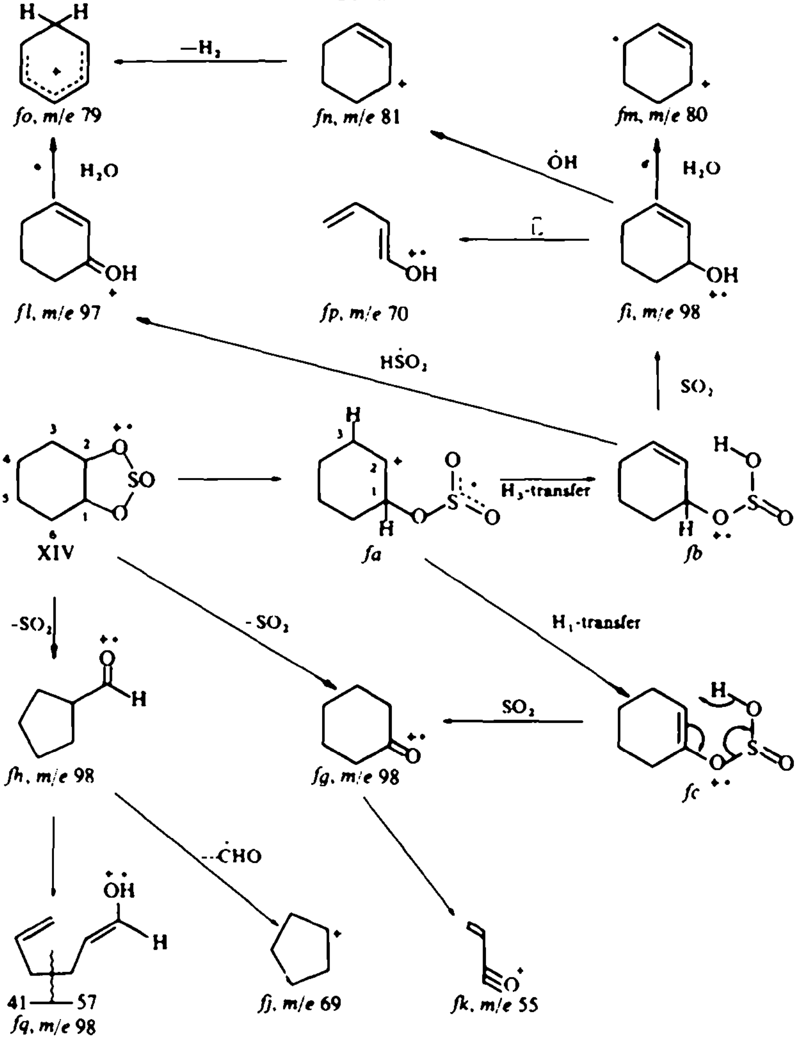
* See Experimental Section.

† See footnote * on p. 2952

SCHEME 5



(i) Pinacol-type hydrogen migration, giving cyclohexanone radical ion *fg* ($C_6H_{10}O$), which characteristically fragments[20] to ion *fk* of mass 55 (70% C_3H_3O). In the d_4-*trans*-cyclic sulfite (XX), the majority of *m/e* 98 is shifted to *m/e* 102 (10% relative abundance) and *m/e* 55 splits equally between *m/e* 56 and 57. At low electron energies (12–15 eV) the peak at *m/e* 98 (in XIV) persists, whereas *m/e* 55 is much reduced in intensity. These data, therefore, are consistant with visualizing this process as the electron impact induced analog of the pyrolytic reaction *cis* – XIV → XXI + SO_2.

(ii) Pinacol-type ring contraction, giving cyclopentane carboxaldehyde radical ion (*fh*), which in turn affords *fj* of mass 69 (95% C_5H_9). In the labeled compound XX, *fj* now appears at *m/e* 73. At low electron energies, the peak at *m/e* 69 (in XIV) becomes less significant, but survives longer than *fk* at *m/e* 55. This process is the electron impact induced parallel of the pyrolytic reaction *trans*-XIV → XXII + SO_2.

If *fh* can undergo a McLafferty rearrangement to produce *fq*, then important peaks at *m/e* 41 (C_3H_5) (*m/e* 43 in XX) and *m/e* 57 (95% C_3H_5O) (*m/e* 59 in XX) are accounted for. Both of these peaks are suppressed at low electron energies.

(iii) Hydrogen transfer from the tertiary position (C-1) in *fa* furnishing *fc*, which may then back transfer the same hydrogen in a McLafferty process (to C-2), giving *fg* once again. This route is indistinguishable from XIV going directly to *fg* by (i). Its operation is revealed, however, by the appearance of a peak at *m/e* 101 (15% relative abundance) corresponding to M-HSO_2 (rather than M-DSO_2) in XX (Table 1), which can be derived by simple cleavage of HSO_2 in *fc*.

(iv) Hydrogen transfer from the secondary position (C-3) in *fa* affording *fb*, which may then back-transfer the same hydrogen to oxygen, producing *fi*. In XX (Table 1), 85% of the M-HSO_2 peak in XIV (*fl*, *m/e* 97) moves to *m/e* 100 (M-DSO_2), and this is conveniently visualized as arising by cleavage in *fb* furnishing a species such as *fl*. It is noteworthy that most (85%) of the hydrogen lost as HSO_2 in XIV originates from the secondary (C-3 and C-6) positions (labeled in XX), whereas a maximum of 57% arises from the equivalent position (methyl group) in III.*

Thus the ions contributing to mass 98 (M-SO_2) in the cyclic sulfites (XIV) probably have at least four structures (*fg*, *fh*, *fi*, *fq*), in that this seems to be the minimum number required to account for the major characteristics (i.e. peak positions, compositions and abundances of fragment ions at different electron energies, metastable peaks, and isotope shifts) of the mass spectra. Comparison of metastable peak shapes, positions and relative abundances† of XIV with those of cyclohexanone and cyclohex-3-enol (XXIII, Fig. 14) showed that these molecular ions could be possible M-SO_2 species, but by the same criteria, the parent ion of cyclohexene oxide[23] can be excluded. The mass spectrum of the epoxide contained a prominent additional metastable peak at *m/e* 28·1.

The behavior of the related carbonates (XV) was completely analogous to that of the sulfites (XIV), and does not warrant separate discussion.

Summary

The M-XO_2 ions derived from the cyclic sulfite and carbonate esters are most simply represented as ionized aldehydes or ketones resulting from pinacol-type rearrangement (common to all compounds studied), or as ionized epoxides (or their immediate product ions) when phenyl substituents are present (compounds IX-XIII). Specifically, epoxide-type intermediates could be ruled out for compounds VII and XIV.

Pyrolytic studies of *meso*- and DL-hydrobenzoin cyclic sulfites[8, 9] (*cis*- and *trans*-XII) and *cis*- and *trans*-cyclohexane-1,2-diol cyclic sulfites (*cis*- and *trans*-XIV)[8] showed marked stereoselectivity. Hydrogen migration occurred in the *cis*-compounds (affording ketone products), and carbon migration in the *trans*-series (yielding aldehydes), together with SO_2. Electron impact investigations of the *cis*/*trans*-isomers of XII[9] and of those of XIV showed, on the other hand, that very little difference is observable in the respective mass spectra (see Figs 10 and 11), taken under the mildest thermal conditions available.

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* Strictly, the peak shifts observed in XVI do not rule out transfer of the tertiary hydrogen, although this seems mechanistically unlikely in the most stable open form of the molecular ion (*bg*, *bj*, Scheme 2).

† See footnote * on p. 2952.

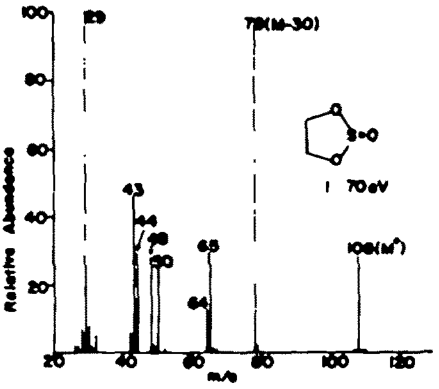


FIG. 1 Mass spectrum of ethane-1,2-diol cyclic sulfite (I).

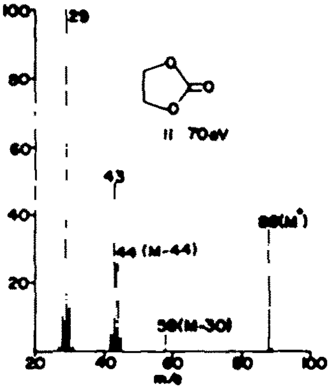


FIG. 2 Mass spectrum of ethane-1,2-diol cyclic carbonate (II).

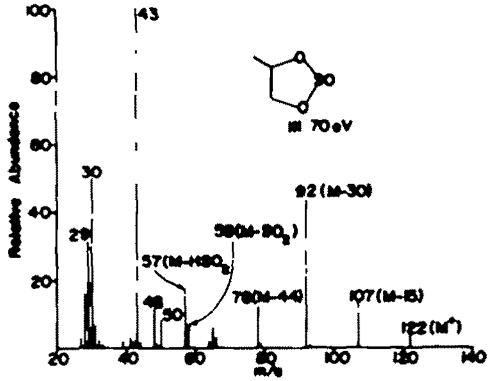


FIG. 3 Mass spectrum of propane-1,2-diol cyclic sulfite (III).

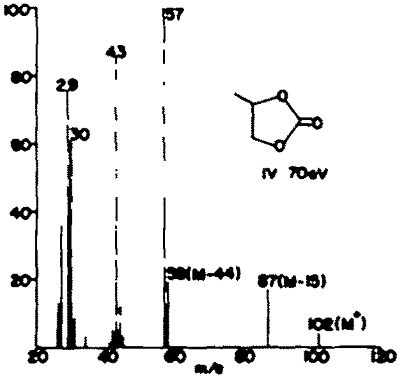


FIG. 4 Mass spectrum of propane-1,2-diol cyclic carbonate (IV).

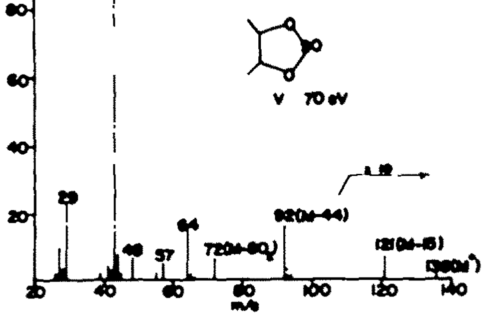


FIG. 5 Mass spectrum of *cis*/*trans*-butane-2,3-diol cyclic sulfite (V).

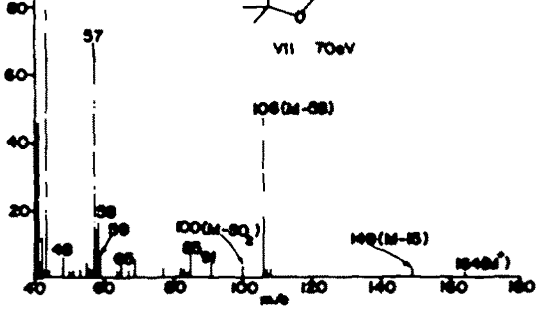


FIG. 6 Mass spectrum of 2,3-dimethylbutane-2,3-diol cyclic sulfite (VII).

Fig. 7 Mass spectrum of phenylethane-1,2-diol cyclic sulfite (IX).

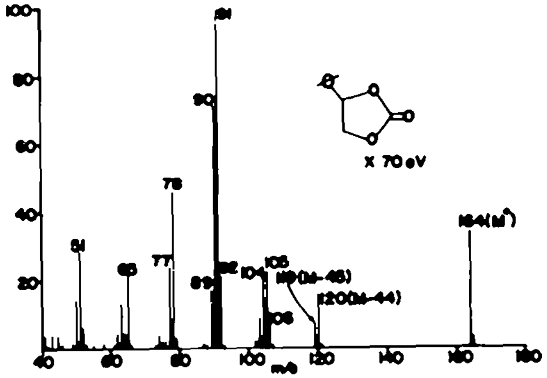


Fig. 8 Mass spectrum of phenylethane-1,2-diol cyclic carbonate (X).

Fig. 9 Mass spectrum of *meso*-hydrobenzoin cyclic carbonate (*cis*-XIII).

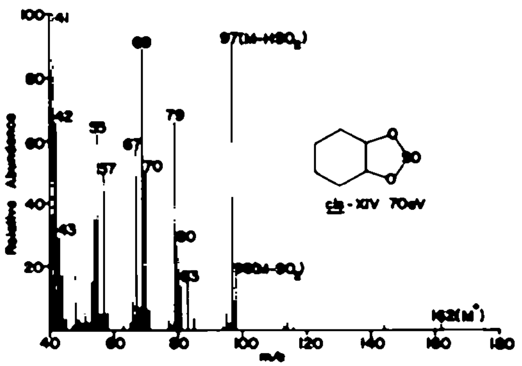


FIG. 10 Mass spectrum of *cis*-cyclohexane-1,2-diol sulfite (*cis*-XIV).

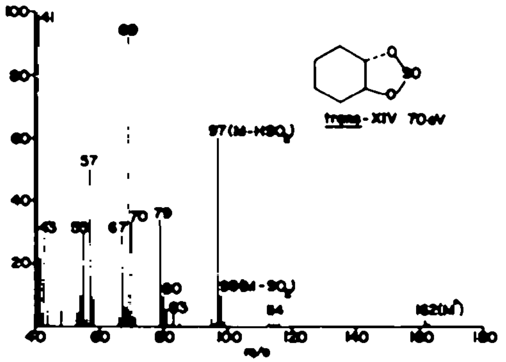


FIG. 11 Mass spectrum of *trans*-cyclohexane-1,2-diol cyclic sulfite (*trans*-XIV).

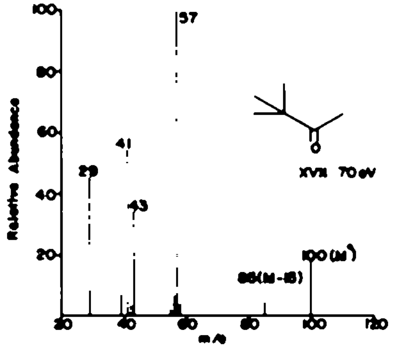


FIG. 12 Mass spectrum of pinacolone (XVII).

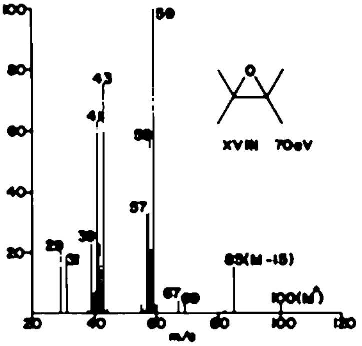


FIG. 13 Mass spectrum of tetramethylethylene epoxide (XVIII).

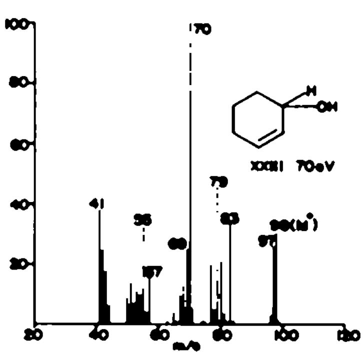
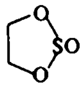
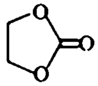
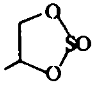
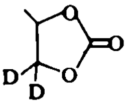
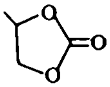
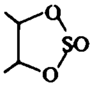
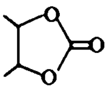
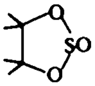
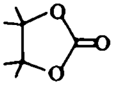
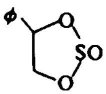
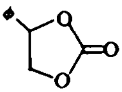
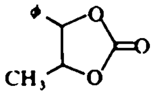
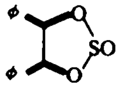
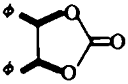
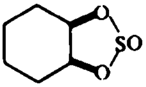
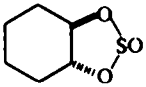
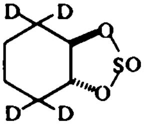
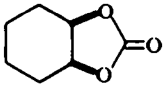
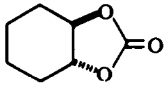


FIG. 14 Mass spectrum of cyclohex-3-enol (XXIII).

TABLE 1. PRINCIPAL PEAKS IN THE MASS SPECTRA OF CYCLIC SULFITE AND CARBONATE ESTERS*

Compound	$M^{\cdot +}$	M-$C_nH_{2n}O$	M-XO_2	M-HXO_2	Rearrangement peaks
 I (Fig. 1)	108: 6·4	78: (M-30): 21·7	44: 5·1	43: 10·5	29 (CHO) : 22·8
 II (Fig. 2)	88: 14·3	58 (M-30): 2·0	44: 7·2	43: 19·5	29 (CHO) : 39·8
 III (Fig. 3)	122: 1·0	92 (M-30): 12·3 78 (M-44): 3·4	58: 2·0	57: 4·8	43 (C_2H_3O) : 28·6 29 (C_2H_5) : 5·3 29 (CHO) : 3·6
 XVI	124^b: 1·0	92 (M-32): 10·7 80 (M-44): 3·9	60: 2·9	58: 2·4 58: 3·4	43 (C_2H_3O) : 24·4 45 (C_2HD_2O): 11·7
 IV (Fig. 4)	102: 0·9	72 (M-30): · 58 (M-44): 7·5	58: 7·5	57: 22·8	43 (C_2H_3O) : 19·4 29 (C_2H_5) : 9·5 29 (CHO) : 7·8
 V (Fig. 5) (*cis*/*trans*)	136: 0·5	92 (M-44): 8·0	72: 3·0	71:	57 (C_3H_5O) : 2·5 43 (C_2H_3O) : 45·0 43 (C_3H_7) : 5·0 29 (CHO) : 4·0 29 (C_2H_5) : 7·5
 VI (*cis*/*trans*)	116: 3·2	72 (M-44): 0·4	72: 0·4	71- 2·4	57 (C_3H_5O) : 2·4 43 (C_2H_3O) : 30·0 43 (C_3H_7) : 10·0 29 (CHO) : 5·7 29 (C_2H_5) : 10·7
 VII (Fig. 6)	164: 0·3	106 (M-58): 11·8	100: 0·8	99:	85 (C_5H_9O) : 2·0 57 (C_4H_9): : 19·3 43 (C_2H_3O) : 28·0
 VIII	144: 5·7	86 (M-58): —	100: 1·2	99: ··	85 (C_5H_9O) : 4·2 57 (C_4H_9) : 12·5 43 (C_2H_3O) : 23·6
 IX (Fig. 7)	184: 0·1	154 (M-30): 1·1 78 (M-106): ·	120: 6·6	119: –	105 (C_7H_5O) : 1·8 92 (C_7H_8) : 8·8 91 (C_7H_7) : 36·8 90 (C_7H_6) : 1·5
 X (Fig. 8)	164: 6·4	134 (M-30): 58 (M-106): —	120: 3·0	119: 1·3	106 (C_7H_6O) : 1·2 105 (C_7H_5O) : 4·2 92 (C_7H_8) : 4·0 91 (C_7H_7) : 19·0 90 (C_7H_6) : 13·5

Compound	M·[a]	M-$C_nH_{2n}O$	M-XO_2	M-HXO_2	Rearrangement peaks
 XI (*cis*/*trans*)	178: 7·0	134 (M-44): -- 72 (M-106): ·	134: 0·9	133: 4·3	105 (C_7H_5O) 7·3 105 (C_8H_9) : 4·0 91 (C_7H_7) : 7·0 90 (C_7H_6) : 22·7 43 (C_2H_3O) : 2·7
 XII (*cis*)	260: 0·2	154 (M-106):	196: --	195:	167 ($C_{13}H_{11}$) : 0·7 106 (C_7H_6O) : 2·6 106 (C_7H_5O) : 18·2 91 (C_7H_8) : 1·3 90 (C_7H_7) : 2·0
 XIII (Fig. 9) (*cis*)	240: 8·7	134 (M-106):	196: 1·5	195: 3·8	167 ($C_{13}H_{11}$) : 7·5 106 (C_7H_6O) : 1·6 105 (C_7H_5O) : 4·0 91 (C_7H_7) : 3·5 90 (C_7H_6) : 14·6
 *cis*- XIV (Fig. 10)	162: 0·2	—	98: 2·0	97: 11·0	69 (C_5H_9) : 8·6 55 (C_3H_3O) : 5·2
 *trans*- XIV (Fig. 11)	162: 0·3		98: 1·7	97: 10·4	69 (C_5H_9) : 15·2 55 (C_3H_3O) : 3·5
 XX	166[c]: 0·4		102: 1·2	100: 10·3 101: 1·9	73 ($C_5H_5D_4$) : 12·4 56 (C_3H_2DO): 3·1 57 (C_3HD_2O): 2·5
 *cis*-XV	142: 0·2		98: 0·7	97: 0·7	69 (C_5H_9) - 5·8 55 (C_3H_3O) : 7·3
 *trans*-XV	142: 0·5	--	97: 0·5	97: 0·3	69 (C_5H_9) : 26·6 55 (C_3H_3O) : 2·5

[a] The first figure in each column refers to nominal *m/e* value, and the second to % Σ_{25}^{M} (I–VI) and % Σ_{40}^{M} (VII–XX).

[b] Isotopic composition: 80% d_2; 20% d_1.

[c] Isotopic composition: 95% d_4; 4% d_2; 1% d_1.

TABLE 2. METASTABLE PEAKS IN THE MASS SPECTRUM OF 2,3-DIMETHYLBUTANE-2,3-DIOL CYCLIC SULFITE (VII)

m^*_{obs}	m^*_{calc}	Δ^*_m	Parent	Daughter	Neutral
72·3	72·25	0·05	100	85	15
54·8	54·74	0·06	82	67	15
52·9	52·81	0·09	85	67	18
38·4	38·64	−0·24	106	64	42
	38·22	0·18	85	57	28
37·1	37·10	0	41	39	2
36·5	36·21	0·29	42	39	3
31·8	31·74	0·06	106	58	48
	31·88	−0·08	58	43	15
29·5	29·49	0·01	57	41	16
28·1	28·17	−0·07	54	39	15
25·1	24·98	0·12	164	64	100
	25·14	−0·04	29	27	2
21·8	21·81	−0·01	149	57	92
	21·74	0·06	106	48	58
	21·75	0·05	85	43	42
16·3	16·29	0·01	59	31	28

EXPERIMENTAL

Mass Spectra

The low resolution mass spectra of the cyclic esters were obtained by Dr. A. M. Duffield and one of the authors, using an Atlas CH-4 instrument. At first, standard heated inlet conditions were employed, viz. TO4 ion source at 180° and gas inlet reservoir at 100°. In view of the known thermal lability of these compounds, spectra were also obtained by direct insertion of the sample into the ion source at ambient temperature. Liquid samples (I–VI, IX–XI, XIV and *cis*-XV) were adsorbed directly onto charcoal (and hence treated as solids), and solid samples (VII, VIII, XII, XIII and *trans*-XV) were ground intimately with charcoal before loading into the Atlas direct insertion cartridge charcoal crucibles. This technique, developed by Dr. A. M. Duffield of our laboratories at Stanford University, is particularly useful for thermally labile liquid samples of moderate volatility. Relatively slow diffusion of the sample out of the charcoal adsorbent in the ion source gives quite stable ion currents, by assuming the role of the source leak in the heated inlet system. It was found that for the simple low molecular weight esters, there was little difference between the spectra obtained by each method, but for the more complex compounds (see text) there were considerable differences in peak relative intensities and peaks observed. Figs 1–4 and 12–14 were obtained with the heated inlet, and Figs 5–11 by the direct insertion method. For example, molecular ions were relatively less abundant by the heated inlet method, and compound VII exhibited a large peak (23 % relative abundance) at *m/e* 82, due to loss of H_2SO_3, and almost absent when the spectrum was taken by direct insertion (Fig. 6). Mass spectra were taken routinely at 70, 15 and 12 eV, but in special cases at other nominal values.

TABLE 3. METASTABLE PEAKS IN THE MASS SPECTRUM OF *meso*-HYDROBENZOIN CYCLIC CARBONATE (XIII)

m^*_{obs}	m^*_{calc}	Δ^*_m	Parent	Daughter	Neutral
162 (broad)	163·47	-	196	179	17
	163·02	—	167	165	2
161 (broad)	161·65		196	178	18
142·5	142·29	0·21	196	167	29
139·0	138·90	0·10	196	165	31
88·1	88·01	0·09	90	89	1
58·4	58·41	−0·01	196	107	89
	58·33	0·07	107	79	28
56·5	56·47	0·03	105	77	28
54·5	54·48	0·02	152	91	61
46·5	46·43	0·07	91	65	26
	46·52	−0·02	178	91	87
44·6	44·59	0·01	89	63	26
	44·50	0·10	178	89	89
33·9	33·78	0·12	77	51	26

High resolution mass measurements were secured by Mr. R. G. Ross, with an A.E.I. MS-9 double focussing mass spectrometer, of apparent resolution 1 part in 15,000, and fitted with an all glass heated inlet system at 200°, and ion source temp of 250°. It is appreciated that the precise mass measurements were taken under very different conditions from the low resolution spectra.

The recorded metastable peaks were assigned to the transitions shown in Tables 2, 3 and 4 by computer. In a Fortran IV program devised by Mr. S. H. Brown of these laboratories for I.B.M. 7090 use, the input data comprises the mass spectral peak positions, metastable peak positions, and fractional mass tolerance between observed and calculated metastable values ($\pm 0{\cdot}3$ for Tables 2–4).[24] Output consists of the list of observed metastable peak positions, and for each, all possible transitions (parent), daughter, neutral) among the integral peaks are given (neutrals such as 13, 21, etc. are "forbidden" in the program), as well as the calculated metastable peak position and the mass difference Δ^*_m.

Preparation of cyclic esters

All the unlabeled 1,2-diols were commercial samples of reasonable purity, as were the cyclic esters I–IV. All the cyclic esters had satisfactory C, H (and S in the sulfites) analyses.

(a) *Cyclic sulfites.* These were prepared essentially according to Price and Berti,[8] except that $CHCl_3$ was used as solvent. In a typical preparation, the diol (1 mole) and dry pyridine (1·5–2 moles) were stirred at 0°, in ethanol-free $CHCl_3$, and thionyl chloride (1 mole) added dropwise over 30 mins. The solution was stirred at room temp for 1·5–2 hr, and then poured into water in a separatory funnel. The organic phase was washed to neutrality and dried over anhydrous $CaSO_4$ (Drierite). The solvent was removed under reduced pressure, and the crude cyclic sulfite purified by GLC or crystallization. In the former case, 10% SE30 on Chromosorb W or 5% Apiezon L proved effective columns. Characteristic IR absorptions were observed at 900–960 and 1200–1220 cm^{-1}. The solid sulfites VII and *cis*-XII melted at 41–42° and 126–128° (lit. 126–128°)[8] respectively. Yields were typically 50–70% on a 200 mg scale.

TABLE 4. METASTABLE PEAKS IN THE MASS SPECTRA OF *cis*- AND *trans*-CYCLOHEXANE-1,2-DIOL CYCLIC SULFITES (*cis*- AND *trans*-XIV)

m^*_{obs}	m^*_{calc}	Δ^*_m	Parent	Daughter	Neutral
77·10	77·11	−0·01	83	80	3
70·20	70·30	−0·10	98	83	15
65·30	65·31	−0·01	98	80	18
	65·06	0·24	69	67	2
64·40	64·34	0·06	97	79	18
48·90	49·08	−0·18	97	69	28
46·30	46·28	0·02	97	67	30
43·20	42·98	0·22	114	70	44
	43·21	−0·01	70	55	15
37·10	37·10	0·00	41	39	2
31·20	31·19	0·01	97	55	42
	30·95	0·25	57	42	15
29·50	29·39	0·11	162	69	93
	29·76	−0·26	98	54	44
	29·49	0·01	57	41	16
25·20	25·28	−0·08	162	64	98
	25·20	0·00	70	42	28
24·20	24·01	0·19	70	41	29
	24·36	−0·16	69	41	28

(b) *Cyclic carbonates.* The diol (1 mole) and dry pyridine (1·5–2 moles) were stirred in EtOH-free $CHCl_3$ at 0°, and phosgene bubbled through the soln slowly for 1 hr. The soln was stirred at 0° for a further hr., then at room temp for 1–2 hr. The workup, methods of purification and yields were as in (a) above. Characteristic IR absorptions were observed at 1050–1070, 1260–1300 and 1770–1800 cm^{-1}. The solid carbonates melted as follows: VIII, 180–181°; XIII, 116–117°; *trans*-XV, 46–47°.

(c) 1,1-d_2-*Propane*-1,2-*diol cyclic sulfite* (XVI) Ethyl lactate (900 mg) was reduced with LAD (300 mg) in dry ether for 2 days at reflux temp. The reaction was worked up with sat. Na_2SO_4 aq, the solvent removed under vacuum, and the crude product isolated by continuous extraction with CH_2Cl_2. GLC purification on 10% Apiezon L/Chrom. W column was effected, using authentic propane-1,2-diol as a standard. Yield of 1,1-d_2-propane-1,2-diol was 310 mg, and a low resolution mass spectrum indicated an isotopic purity of about 80% d_2.

The labeled diol was converted to XVI in the usual way (see (a) above), and the isotopic purity was determined as 80% d_2, 20% d_1 from its spectrum.

(d) 3,3,6,6-d_4-*Cyclohexane*-1,2-*diol cyclic sulfite* (XX). 3,3,6,6-d_4-Cyclohexene* (500 mg) was converted to the epoxide by published procedures.[14] The epoxide (500 mg) was dissolved in 50% aq acetone (25 ml) and a few drops of 60% $HClO_4$ aq added. The solution was stirred at room temp overnight, then neutralized with solid $NaHCO_3$, the acetone stripped off, and the aqueous phase continuously extracted with CH_2Cl_2

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* Supplied by Merck, Sharp and Dohme, Montreal, Canada.

for 2 days. The crude diol (450 mg) was not purified at this stage, but converted directly to the cyclic sulfite, which was then rigorously purified by GLC. Using a 10 ft 10% Apiezon L/Chrom. W column at 150° with Helium flow 80 ml min^{-1}, the retention time of *cis*-XIV is 21 mins and *trans*-XIV 17 mins. The labeled sulfite XX had retention time identical to that of *trans*-XIV. The mass spectrum showed the d_4-cyclic sulfite to be 95% d_4, 4% d_3 and 1% d_2.

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