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MOLECULAR REARRANGEMENT UPON ELECTRON IMPACT III.[1] MASS SPECTROMETRY OF ORGANIC OXALATES

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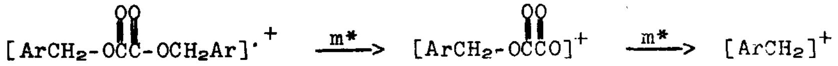
The investigation of group migrations and neighboring group participations in gas phase carbonium ions is currently an active and exciting area of research (3). The expulsion of an atom or a group of atoms from the interior portions of a molecule with concurrent rebonding of the termini constitute the most often encountered type of rearrangement. Organic oxalate esters possess the structural prerequisites for possible rearrangements involving (a) the loss of one molecule of carbon monoxide, (b) the loss of one molecule of carbon dioxide, (c) the loss of one molecule each of carbon monoxide and carbon dioxide or (d) the loss of two molecules of carbon dioxide. We wish to report here on the behavior of representative oxalates and closely related compounds in which the relative importance of these fragmentation types are evaluated.

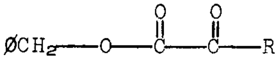
Dialkyl oxalates are very unstable upon ionization but we found that when one or both of the esters was a benzyl type, sufficient stability was imparted to the molecular ion to provide strong molecular ions and controlled fragmentations. A series of symmetrical and unsymmetrical benzyl and aryl oxalates were prepared (4) and subjected to mass spectrometric investigation (5).

Simple single bond cleavage produces intense ions of the following type:



$$[ArCH_2\text{-}O\overset{O}{C}\overset{O}{C}\text{-}OCH_2Ar]^{\cdot +} \xrightarrow{m^*} [ArCH_2\text{-}O\overset{O}{C}\overset{O}{C}O]^{+} \xrightarrow{m^*} [ArCH_2]^{+}$$

In the spectrum of 2 intense fragment ions for both Ar=Ø and Ar=Ø-p-F are present, but for the more electronically unsymmetrical oxalates 3, 5, 7 and 8 only the analogous ion containing the most electron supplying aryl group is present. This attests to a surprisingly pronounced dependence of the fragmentation of oxalates on electronic effects which is discussed later for the rearrangement reactions (6).



$$\phi CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R$$

1 $R=OCH_2\phi$

2 $R=OCH_2\phi$-p-F

3 $R=OCH_2\phi$-p-OCH_3

4 R=O-α-naphthyl

5 R=O-cinammyl

6 R=O-9-fluorenyl

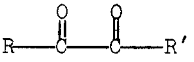
7 R=O-benzyhydryl[a]

8 $R=OCH_2\phi$-p-NO_2

9 $R=NH_2$

10 $R=NH\phi$[a]

11 $R=N\phi_2$[a]



$$R-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R'$$

12 $R=R'=O\phi$

13 $R=R'=O\phi$-p-OCH_3

14 $R=R'=O\phi$-p-F

15 $R=OCH_2\phi$; $R'=O\phi$-p-OCH_3

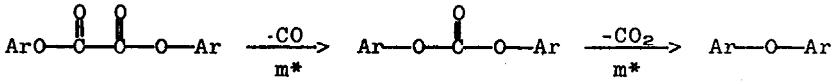
16 $R=R'=NH\phi$[a]

[a] Intense ions necessitating prior phenyl migration were found. Discussion is deferred until the full paper.

Of the rearrangement processes, the loss of carbon monoxide (path a) is not an observed fragmentation in the spectrum of open chain dibenzyl or dibenzyl-like oxalates 2-8. However the expulsion of carbon monoxide is an important process in the fragmentation of cyclic oxalates such as catechol oxalate (17, 44% rel. int.), meso-hydrobenzoin oxalate 18 (10%), the oxanilides 9 and 10 (25% and 2%) and diaryl oxalates 12-14 (70%, 68% and 100%, respectively).

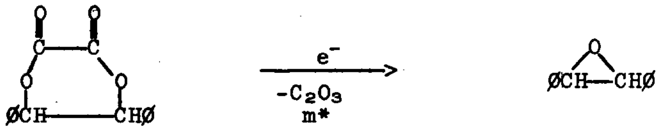
The loss of carbon dioxide (pathway b) from the molecule ion is apparently a much less favorable process. Of the compounds mentioned in this report only 6 exhibited an M-44 ion of greater than trace intensity (7).

A most interesting result of this study is that pathway (c) can be an important fragmentation process, and that furthermore, depending on the substituents on the dicarbonyl grouping, the carbon monoxide and carbon dioxide can be lost in one or two separate steps. Again a sensitivity to the electronic nature of a para substituent in the dibenzyl oxalates was noticed. Electron donating substituents caused single bond cleavages to predominate and no M-CO, M-CO_2 or M-C_2O_3 ions were observed. Electron withdrawing substituents (e.g., 8) produced a molecule ion of appropriate lifetime to reach the field free region of the mass spectrometer before fragmenting with simultaneous (8) expulsion of carbon monoxide and carbon dioxide (M-72 ion is 60% int. of M^+, 10% int. of largest fragment). Benzyl aryl oxalates behave similarly to give an M-72 ion with no ions at M-28 or M-44; e.g., 15 has an M-72 ion of 10% rel. int. with a m* at 160.3 (8). In contrast the diaryl oxalates 12-14 and catechol oxalate fragment <u>only</u> by stepwise losses of CO and CO_2 (9). The strength of the Ar-O bond combined



$$ArO-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-O-Ar \xrightarrow[m^*]{-CO} Ar-O-\overset{O}{\overset{\|}{C}}-O-Ar \xrightarrow[m^*]{-CO_2} Ar-O-Ar$$

with the stability of the carbonate ester is possibly responsible for this change in behavior. Cyclic oxalates such as hydrobenzoin oxalate (18) can form M-C_2O_3 by <u>both</u> stepwise and synchronous processes (8). The lowest energy fragmentation in 18 is the one step formation of stilbene oxide (11).



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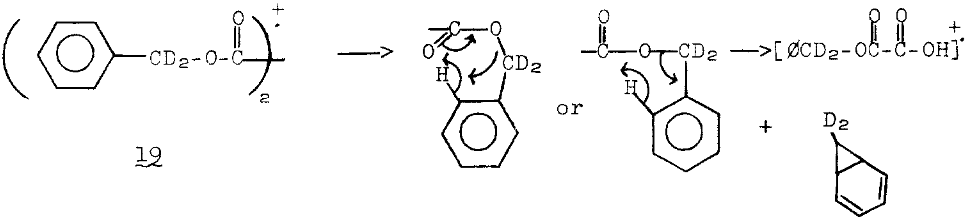
Fragmentation process (d), the loss of two molecules of carbon dioxide, is observed to a minor extent only in the spectrum of dibenzhydryl oxalate. This process, which parallels the thermal process in mass but probably not in mechanism (12), is rendered unimportant by the restrictive nature of the transition state as well as by the susceptibility of the product ion to undergo further bond cleavage. The homologous dibenzhydryl ester of succinic acid was also observed to produce small amounts of tetraphenylethane cation formed by losses of two molecules of CO_2 and one molecule of C_2H_4 (12).

A final observation relating the extreme sensitivity of the mass spectral behavior of oxalates to the nature of the substituent concerns a rearrangement fragmentation to produce a half-ester of oxalic acid. This process produces intense ions (~10% rel. int.) in the spectrum of oxalates with electronically similar aryl groups (i.e., 1, 2, 5), but with oxalates of very disimilar aryl groupings (as in 3, 5, 7, and 8) this rearrangement is not observed. By a study of the deuterated derivative 19 it was shown that the source of the rearranged hydrogen atom was the benzene ring.



The results cited in this communication indicate that these oxalates will be useful substrates for more detailed mechanistic studies of mass spectral fragmentations due to the variety of fragmentations which are sensitive to the electronic nature of a remote substituent. Furthermore these oxalates provide ideal substrates for studies of metastable processes. Particularly useful for this work are the fragmentations which result in the $M-C_2O_3$. A question to be answered is the requirements necessary, either timing or structural, by which two distinct fragmentations can appear to be a single mass loss fragmentation based on the observation of a metastable ion peak (13). Studies on both these points are continuing.

REFERENCES

1. For Paper II, see J. Am. Chem. Soc., (in press).
2. National Science Foundation Undergraduate Research Participant, Summer, 1966 to present.
3. C. Djerassi, Angew. Chemie, (in press).
4. Correct micro-analyses have been obtained on all new compounds cited herein.
5. An Atlas CH_4 Mass Spectrometer operated with a direct molecular beam inlet system and a room temperature source was used in this study. We thank the National Science Foundation for a Research Instruments Grant which partially supported the purchase of this instrument.
6. See M. M. Bursey and F. W. McLafferty, J. Am. Chem. Soc., 89, 1 (1967) for a discussion of substituent effects. The effects which we find in this work are more effective over longer distances than those noted in the above reference.
7. Bowie, et. al., Chem. Comm., 403 (1965) have reported several instances of carbon dioxide loss from esters. The lack of this ion in our spectra may reflect the propensity of the product ester ion to fragment further.
8. A strong, but broad and distorted metastable ion peak was observed. This distortion is undoubtedly due to energy transfer (10) in the fragmentation and may be due to two non-simultaneous fragmentations.
9. D. Brown and C. Djerassi, J. Am. Chem. Soc., 88, 2469 (1966) have reported the loss of carbon dioxide from carbonates.
10. T. W. Shannon, F. W. McLafferty and C. R. McKinney, Chem. Comm., 478 (1966) and references cited therein.
11. Subsequent fragmentation parallels that reported by Audier, et. al., Tet. Letters, 2077 (1966) for stilbene oxide.
12. Private communication from W. S. Trahanovsky, Iowa State University. A paper comparing the thermal and mass spectral behavior of oxalates will be submitted shortly.
13. Similar phenomena have been encountered by D. C. DeJongh, S. C. Perricone and W. Korytonyk, J. Am. Chem. Soc., 88, 1233 (1966), and W. D. Crow, J. H. Hodgkins and J. S. Shannon, Aust. J. Chem., 18, 1433 (1965); Added in proof: J. Seibl, Helv. Chim. Acta, 50, 263 (1967).