

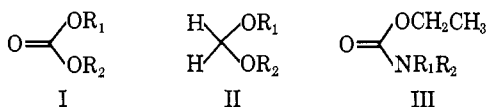
Mass Spectrometry in Structural and Stereochemical Problems. CVI.¹ Occurrence of Alkyl and Aryl Rearrangements in the Fragmentation of Some Organic Carbonates²

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Contribution from the Department of Chemistry, Stanford University, Stanford, California. Received January 17, 1966

Abstract: The mass spectra of a series of dialkyl, alkyl phenyl, and aryl phenyl carbonates have been studied. By a combination of isotope labeling and high-resolution mass spectrometry, the electron impact induced migration of groups other than hydrogen has been uncovered in each class of compound. In the rearrangement step, in each instance, elimination of carbon dioxide occurs with concomitant alkyl or aryl migration.

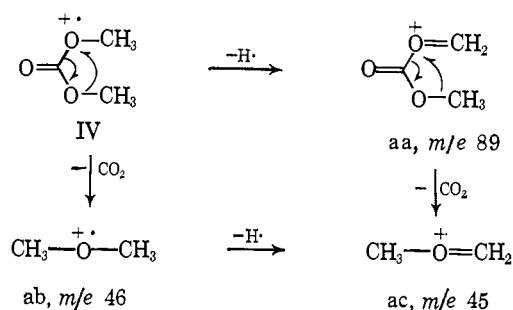
In continuation of our studies on the incidence of electron impact induced skeletal rearrangements,⁴ the fragmentation of some dialkyl, alkyl phenyl, and aryl phenyl carbonates (I) has been examined. Although these esters are not especially important compounds chemically, they were selected for mass spectral investigation for several reasons. For example, formaldehyde acetals (II) had been found⁵ to rearrange upon



electron impact in the mass spectrometer, eliminating a neutral formaldehyde molecule in the process. It was surmised that the corresponding carbonates (I) might conceivably rearrange by an analogous elimination of carbon dioxide. Our suspicions concerning this point were appreciably heightened by the appearance of two papers⁶ in which skeletal reorganization, with accompanying loss of carbon dioxide, was encountered in the closely related ethyl carbamates (III). Similar alkyl-aryl rearrangements involve expulsion of carbon dioxide from phenyl pivalate and *t*-butyl benzoate,^{4b} from neopentyl benzoate⁷ and other esters⁸ including trimethylsilyl derivatives;⁹ of formaldehyde from butyl propionate¹⁰ and neopentyl esters;¹¹ of hydrogen cyanide and acetonitrile from amidines;¹² and of nitrogen from azobenzene.¹³ Inspection of published

spectra¹⁴ of dimethyl, diethyl, and di-*n*-propyl carbonates disclosed rearrangement peaks at m/e 45 [$M - (1 + 44)$, 58%, m/e 59 [$M - (15 + 44)$, 3%], and m/e 73 [$M - (29 + 44)$, 0.5% relative intensity], respectively. In view of the important bearing of such rearrangement reactions on the scope and limitation of the "element mapping" technique,¹⁵ a detailed study of organic carbonates was undertaken in order to determine the structural prerequisites for the occurrence and extent of such skeletal rearrangements.

Dialkyl Carbonates. The rearrangement peak in the mass spectrum (Figure 1) of dimethyl carbonate (IV) at m/e 45 was resolved by high-resolution mass spectrometry into a doublet, comprising 85% C_2H_5O and 15% CHO_2 . Two obvious stepwise mechanisms can be written to explain the origin of the principal component. The first proceeds *via* an $M - 1$ α -cleavage



species aa, followed by methyl migration and loss of carbon dioxide, and the second through the intermediacy of ionized dimethyl ether (ab), which could then lose a hydrogen atom by α cleavage. The mass spectrum¹⁶ of dimethyl ether, however, shows the intensity of the molecular ion (m/e 46) as about half that of the $M - 1$ peak (m/e 45). Complete absence of such a peak at m/e 46 in the spectrum (Figure 1) of IV renders the second rearrangement mechanism improbable. It can be concluded, then, that loss of a hydrogen atom and carbon dioxide probably occurs sequentially (through aa), or concertedly. No con-

- (1) Paper CV: J. Karliner and C. Djerassi, *J. Org. Chem.*, in press.
- (2) Financial assistance (Grants No. CA-07195 and AM-04257) from the National Institutes of Health of the U. S. Public Health Service is gratefully acknowledged. The purchase of the Atlas CH-4 mass spectrometer was made possible through NASA Grant Nsg 81-60.
- (3) Postdoctoral Research Fellow, 1964-1966.
- (4) (a) F. Komitsky, J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965); (b) M. Fischer and C. Djerassi, *Chem. Ber.*, in press; (c) C. Djerassi, A. M. Duffield, F. Komitsky, and L. Tökes, *J. Am. Chem. Soc.*, **88**, 860 (1966).
- (5) P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S.-O. Lawesson, *ibid.*, **87**, 4559 (1965).
- (6) C. P. Lewis, *Anal. Chem.*, **36**, 176, 1582 (1964).
- (7) W. H. McFadden, K. L. Stevens, S. Meyerson, A. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, **69**, 1742 (1965).
- (8) J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Commun.*, 403 (1965).
- (9) R. M. Teeter, 10th Annual Conference on Mass Spectrometry, American Society of Testing Materials, Committee E-14, New Orleans, La., 1962, p 51.
- (10) C. Djerassi and C. Fenselau, *J. Am. Chem. Soc.*, **87**, 5756 (1965).
- (11) D. R. Black, W. H. McFadden, and J. W. Corse, *J. Phys. Chem.*, **68**, 1237 (1964).
- (12) A. K. Bose, I. Kugajevsky, P. T. Funke, and K. G. Das, *Tetrahedron Letters*, 3065 (1965).

- (13) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2935 (1965).
- (14) "Catalog of Mass Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., spectra no. 769, 812, and 829, respectively.
- (15) (a) K. Biemann, *Pure Appl. Chem.*, **9**, 95 (1964); (b) K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).
- (16) See ref 14, spectrum no. 761.

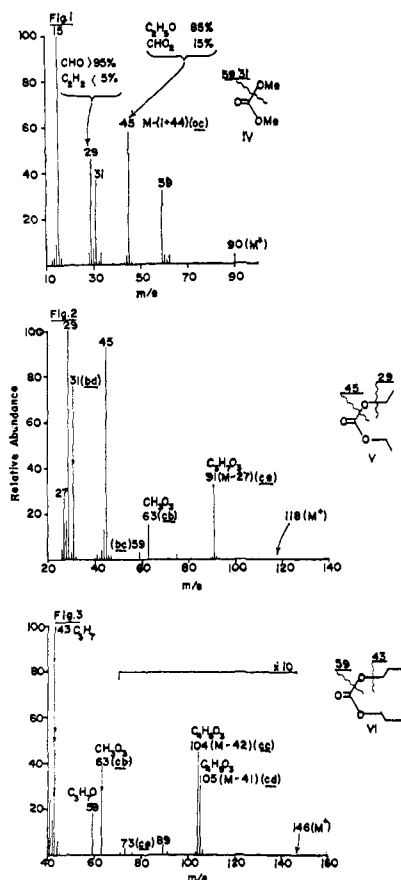
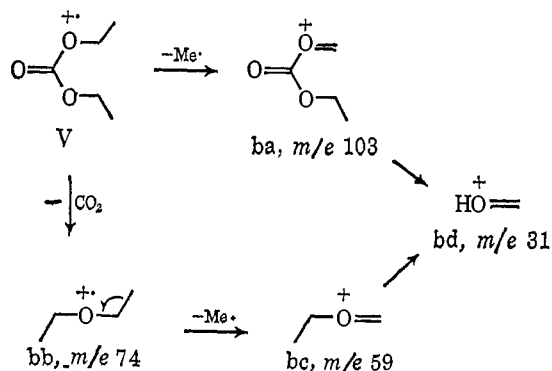


Figure 1. Mass spectrum of dimethyl carbonate (IV).
 Figure 2. Mass spectrum of diethyl carbonate (V).
 Figure 3. Mass spectrum of di-*n*-propyl carbonate (VI).

firmatory metastable peaks¹⁷ for either alternative could be detected. The hydrocarbon ion formed by C-O bond cleavage (e.g., CH₃⁺ in this case) is responsible for the base peak in all dialkyl carbonates studied.

The mass spectrum (Figure 2) of diethyl carbonate (IV) displays a much reduced rearrangement peak [M - (15 + 44)] at *m/e* 59. Again two alternative



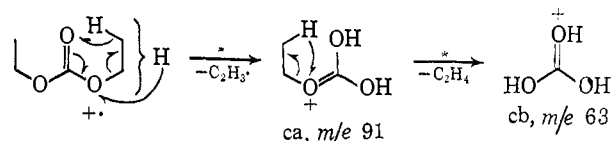
stepwise paths can be envisaged. In the absence of any relevant metastable peaks, no strong preference for either route can be expressed, but the spectrum¹⁸ of diethyl ether does show a molecular ion (*m/e* 74) of approximately two-thirds the relative intensity of the

(17) A logarithmic transfer recorder was employed, in conjunction with an Atlas CH-4 mass spectrometer; see R. T. Aplin, H. Budzikiewicz, H. S. Horn, and J. Lederberg, *Anal. Chem.*, **37**, 776 (1965).

(18) See ref 14, spectrum no. 321.

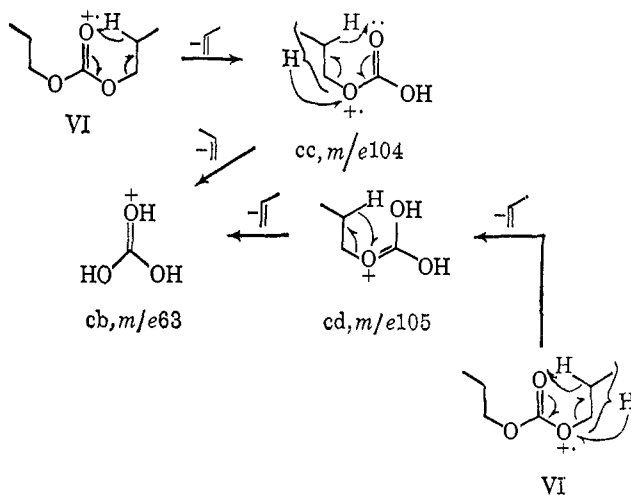
M - 15 species (*m/e* 59). No corresponding peak is apparent in the spectrum of V (Figure 2).

Two other significant peaks occur at *m/e* 91 (M - 27) and *m/e* 63. High-resolution mass determinations revealed the compositions as C₃H₇O₃⁺ and CH₃O₃⁺, respectively. The latter is characteristic of all the dialkyl carbonates scrutinized, except for the dimethyl compound IV. The first step (V → ca) is formally a



single hydrogen transfer superimposed on a normal McLafferty rearrangement.^{19,20} The second step (ca → cb) could then be represented as a typical ether oxonium ion type of fragmentation.^{21,22} This type of stepwise hydrogen rearrangement to oxygen is commonly encountered¹⁹ in the spectra of ethyl (and higher alkyl groups) acetals²² and esters, e.g., acetates,²³ orthoformates,²⁴ orthoacetates,²⁴ and orthocarbonates.²⁴ Metastable peaks at *m/e* 70.3 (91²/118 = 70.2) and *m/e* 43.6 (63²/91 = 43.6) substantiate the operation of this pathway. (The presence of metastable ions in a reaction scheme will be depicted by the symbol (*) over the arrow.) The ion of mass 31 (bd) could reasonably be formed from either ba⁵ or bc.²¹

Di-*n*-propyl carbonate (VI, Figure 3) exhibits rather similar behavior, except that the additional hydrogen atom transferred en route to *m/e* 63 (cb) can now apparently move either in the first elimination (VI → cd → cb), or during the second (VI → cc → cb). The corresponding oxonium ion rearrangement peak [M - (29 + 44)] is present at *m/e* 73 (ce, Figure 3).



The mass spectrum (Figure 4) of diisopropyl carbonate (VII) shows the expected peaks at *m/e* 105 (M - 41), *m/e* 104 (M - 42), and *m/e* 63 (cb), whose compositions were routinely checked by high resolution.

(19) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).

(20) C. Djerassi, G. von Mutzenbecher, J. Fajkos, D. H. Williams, and H. Budzikiewicz, *J. Am. Chem. Soc.*, **87**, 817 (1965), and references cited therein.

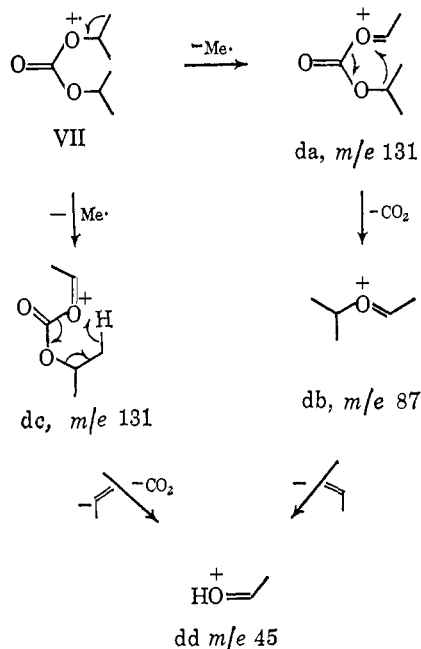
(21) C. Djerassi and C. Fenselau, *ibid.*, **87**, 5747 (1965).

(22) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day Inc., San Francisco, Calif., 1964, Chapter 3.

(23) See for example ref 10, and references cited therein.

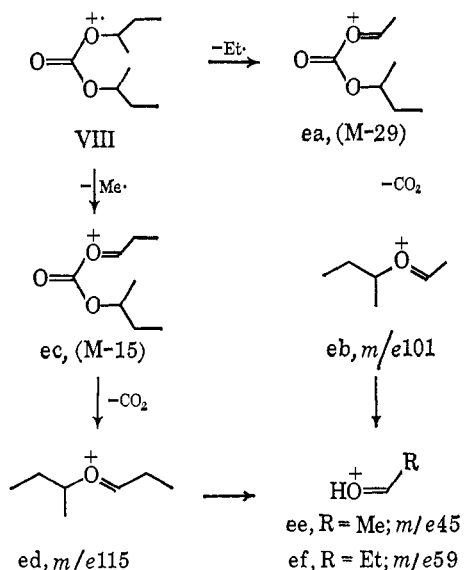
(24) Unpublished results with Dr. S.-O. Lawesson.

The alkyl migration process is described in this case as VII \rightarrow da \rightarrow db (compare the analogous formaldehyde acetal⁵), due to the presence of an appreciable m/e 131



peak ($M - 15$, Figure 4), although the alternative mechanism (prior loss of carbon dioxide from VII affording diisopropyl ether, which then loses a methyl group²⁵ by α cleavage) cannot be ruled out. Although α -cleavage ion $[(CH_3)_2CH \cdot O=C=O]^+$ would also have a nominal mass of 87, high-resolution measurements showed only a single component of composition $C_5H_{11}O$. Species dd (m/e 45) can be expected to originate from either dc⁵ ($M - 15$), or from the rearrangement ion db²¹ (m/e 87).

Di-*sec*-butyl carbonate (VIII) exhibits in its mass spectrum (Figure 5) by now predictable peaks at m/e 119 ($M - 55$), m/e 118 ($M - 56$), and m/e 63 (cb), the compositions of which were again confirmed by high resolution. No peak corresponding to $M - 15$,



$M - 29$, or $M - 44$ is large enough to appear in the plotted spectrum (Figure 5), but rearrangement peaks

(25) See ref 14, spectra no. 322 and 372.

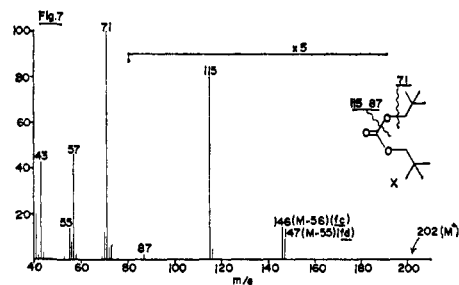
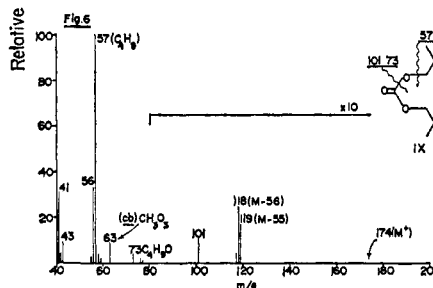
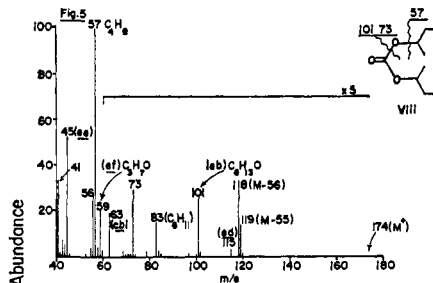
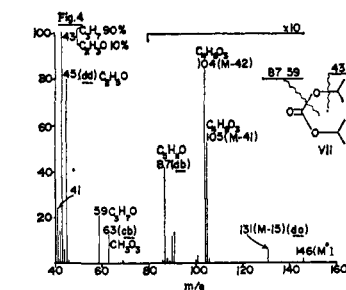


Figure 4. Mass spectrum of diisopropyl carbonate (VII).
Figure 5. Mass spectrum of di-*sec*-butyl carbonate (VIII).
Figure 6. Mass spectrum of diisobutyl carbonate (IX).
Figure 7. Mass spectrum of di-*n*opentyl carbonate (X).

at m/e 115 (ed) [$M - (15 + 44)$] and m/e 101 (eb) [$M - (29 + 44)$] are present. High-resolution determinations demonstrated that m/e 101 comprised solely $C_6H_{13}O$ (eb), no $C_5H_9O_2$ ($CH_3CH_2(CH_3)CHO=C=O$) being detected. Again, in the absence of any relevant metastable ions, either rearrangement sequence would seem equally feasible. Peaks at m/e 45 (ee) and m/e 59 (ef) are exactly analogous to db and dc \rightarrow dd (m/e 45) in diisopropyl carbonate (VII), except that in the di-*sec*-butyl compound (VIII) there are two α -cleavage ions [$M - 15$ (ec) and $M - 29$ (ea)] and two rearrangement ions [$M - 59$ (ed) and $M - 73$ (eb)]. The fragment of m/e 83 was shown to have the composition C_6H_{11} , and a metastable peak at m/e 68.2 ($83^2/101 = 68.2$) suggests its genesis from rearrangement ion eb (m/e 101), by formal loss of water. High resolution also demonstrated that the base peak species m/e 57 is entirely C_4H_9 .

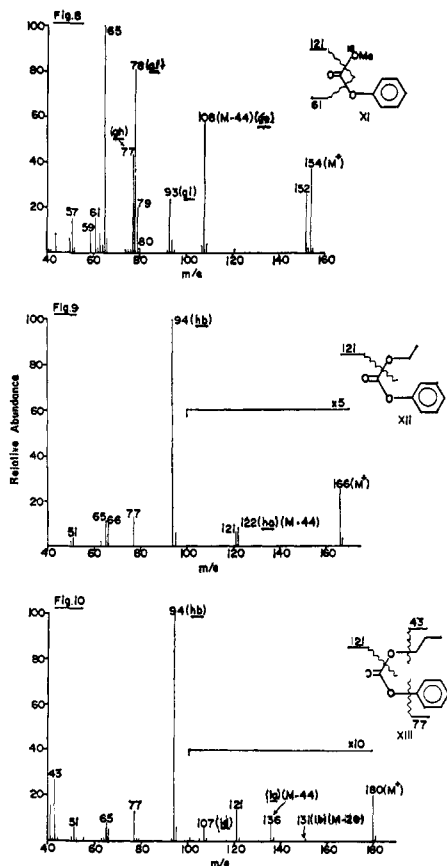
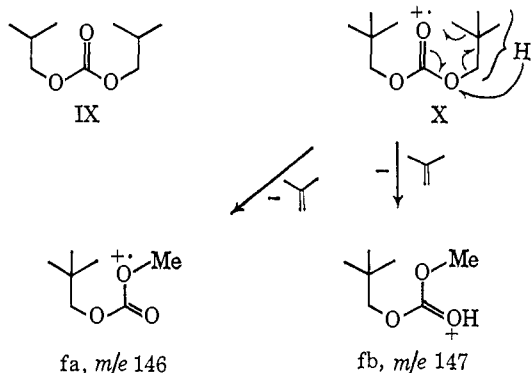


Figure 8. Mass spectrum of methyl phenyl carbonate-¹⁸O (XI).
 Figure 9. Mass spectrum of ethyl phenyl carbonate (XII).
 Figure 10. Mass spectrum of *n*-propyl phenyl carbonate (XIII).

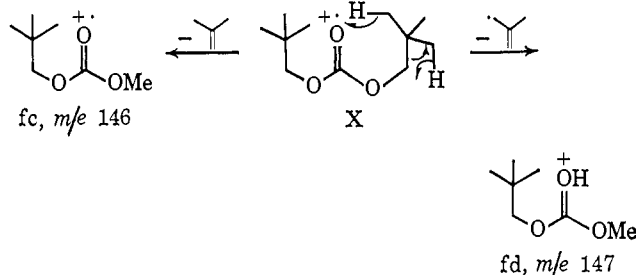
The mass spectrum (Figure 6) of diisobutyl carbonate (IX) is extremely simple, and poses no unexpected interpretation problems. No rearrangement ion at m/e 87 [(CH₃)₂CHCH₂O=CH₂]⁺ can be discerned.

At first sight, the spectrum (Figure 7) of dineopentyl carbonate (X) seems equally unremarkable, with no $M - (57 + 44)$ rearrangement peak (m/e 101) visible. However, $M - 56$ (m/e 146) and $M - 55$ (m/e 147) peaks are in evidence, as observed with di-*sec*-butyl (VIII) and diisobutyl (IX) carbonates, but in this instance no β -hydrogen atoms are available for six-center transfer in the usual way. One possible explanation for this observation could be that a methyl group is migrating 1,5 on to the carbonyl oxygen (X \rightarrow fa, fb).



However, although this type of alkyl rearrangement has been implied²⁶ in the fragmentation of neopentyl

esters, subsequent labeling experiments showed⁷ that the α -carbon atom of the neopentyl group is retained in the ion. Similarly, neopentyl ketones do not undergo "methyl-McLafferty" rearrangement,²⁷ and neither do a variety of other systems where the γ position is fully substituted with methyl groups.^{4b} To elucidate the situation obtaining in carbonate esters, neopentyl phenyl carbonate labeled with two deuterium atoms in the α position was synthesized (XVII, R = D), and its mass spectrum was compared with that of the unlabeled compound (XVII, R = H, Figure 14). Shifts of m/e 152 ($M - 56$) to m/e 154 and of m/e 153 ($M - 55$) to m/e 155 were observed, and the mechanism can therefore be represented as the following (for X).



Alkyl Phenyl Carbonates. The mass spectrum of methyl phenyl carbonate displays a major peak (58% of the base peak, $\Sigma^M_{40} = 11.81$) at m/e 108, corresponding to the loss of 44 mass units (carbon dioxide) from the molecular ion. The operation of this process is confirmed by the recognition of a metastable peak at m/e 76.7 ($108^2/152 = 76.7$). In order to clarify the mechanism of this important rearrangement, and to determine the subsequent fate of the rearrangement ion, methyl phenyl carbonate-¹⁸O (XI) was prepared from phenyl chloroformate and methanol-¹⁸O,²⁸ containing 55.5% ¹⁸O. Comparison of the spectra of labeled (XI, Figure 8) and unlabeled materials demonstrates that formation of the $M - 44$ species involves exclusive loss of CO¹⁸O. This observation can be accommodated by either a six-center (A) or a four-center (B) alkyl migration mechanism.

The six-center pathway (A) leads to the radical ion of the keto tautomer of *o*-cresol (ga, m/e 108). This species would then be expected to lose carbon monoxide,²⁹ affording a radical ion which could³⁰ be formulated as gb (m/e 80); further cleavage of gb by loss of a methyl radical and a hydrogen atom, respectively, would then furnish ions gd (m/e 65) and gc (m/e 79). However, it is known³¹ that the $M - 1$ peak in the mass spectrum of methylcyclopentadiene³² is more intense than $M - 15$, while the reverse situation obtains in methyl phenyl carbonate (Figure 8, m/e 65 is base peak). Also, the spectrum of *o*-cresol³³ does not have

(26) H. O. Colomb, B. D. Fulks, and V. A. Yarborough, 10th Annual Conference on Mass Spectrometry, ASTM Committee E-14, New Orleans, La., 1962, p 41.

(27) R. R. Arndt and C. Djerassi, *Chem. Commun.*, 578 (1965).

(28) Supplied by Yeda Research and Development Co. Ltd., Rehovoth, Israel.

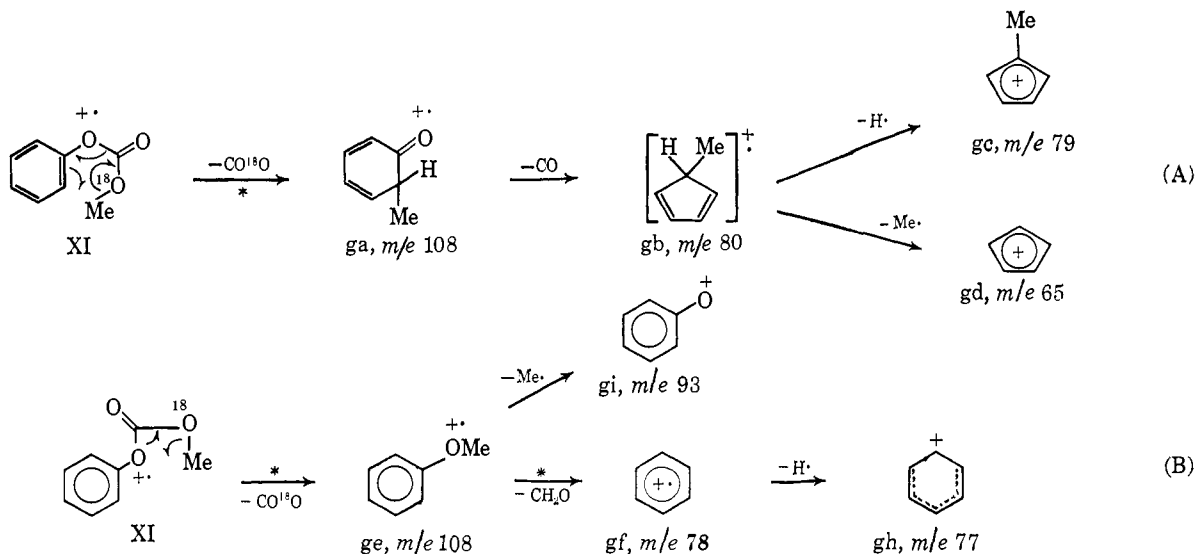
(29) J. H. Benyon, G. R. Lester, and A. E. Williams, *J. Chem. Phys.*, **63**, 1861 (1959).

(30) See, however, W. H. Pirkle, *J. Am. Chem. Soc.*, **87**, 3023 (1965).

(31) A. G. Harrison, P. Haynes, S. McLean, and F. Meyer, *ibid.*, **87**, 5099 (1965).

(32) 5-Methylcyclopentadiene rearranges rapidly at room temperature to isomeric methylcyclopentadienes: see S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

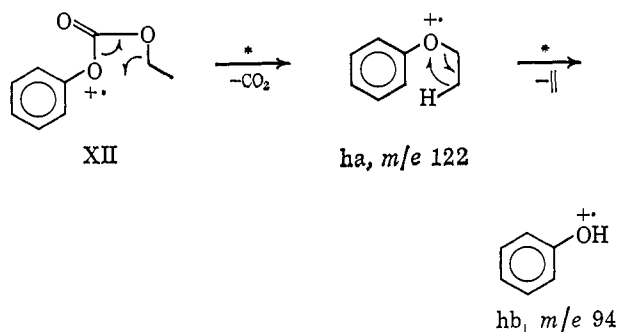
(33) T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **32**, 1819 (1960).



peaks at m/e 93 or 78, m/e 65 is only 4% of the base peak (m/e 108), and m/e 107 is 75% of the base peak. The fragment of m/e 93 in the carbonate spectrum (XI, Figure 8) cannot be attributed to simple C-O bond cleavage (*i.e.*, PhO), since it is not observed in the spectra of other alkylphenyl carbonates; also m/e 107 (Figure 8) is only 2% of the base peak.

The four-center mechanism (B) predicts the intermediacy of anisole radical ion *ge* (m/e 108). The mass spectrum of anisole itself³⁴ has peaks at m/e 108 (100%), m/e 93 (14%), m/e 80 (2%), m/e 79 (13%), m/e 78 (63%), m/e 77 (17%), and m/e 65 (67%), and thus bears a marked resemblance to the spectrum of methyl phenyl carbonate (Figure 8) below m/e 108 (except for α -cleavage species MeOCO at m/e 59). Additional support for this route is provided by the observation of a metastable peak at m/e 56.4 ($78^2/108 = 56.3$) in the carbonate spectrum, corresponding to the genesis of ionized benzene (*gf*) from anisole ion radical (*ge*) by the loss of formaldehyde.³⁵ The 1,3-alkyl migration mechanism (XI \rightarrow *ge*) is therefore to be preferred in this instance.

In the mass spectrum (Figure 9) of ethyl phenyl carbonate (XII), it is evident that the $M - 44$ rear-

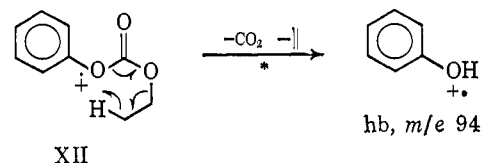


angement peak (m/e 122) is now much less prominent ($\Sigma M_{40}^M = 0.51$). The four-center mechanism is again favored (XII \rightarrow *ha*), due to the very close similarity between the spectrum of phenetole and that of XII

(34) C. S. Barnes and J. L. Occolowitz, *Australian J. Chem.*, **16**, 219 (1963). As a more precise check, the mass spectrum of vpc-purified anisole was run under exactly the same conditions as the carbonate.

(35) See ref 22, p 175.

(Figure 9) below m/e 122 (except for the α -cleavage species PhOCO at m/e 121), run under identical conditions. The rearrangement ion *ha* can now lose ethylene,³⁶ affording species *hb* at m/e 94, which is responsible for the base peak in all the alkyl phenyl carbonates investigated (except the methyl compound XI). The occurrence of metastable peaks at m/e 89.6 ($122^2/166 = 89.8$) and m/e 72.4 ($94^2/122 = 72.4$) confirms the sequential loss of carbon dioxide and ethylene, but in addition, a metastable peak at m/e 53.3 ($94^2/166 = 53.3$) betrays the simultaneous operation of a concerted process, reminiscent of the suggested³⁷ pyrolysis mechanism for ethyl aryl carbonates. Although no deuterium labeling was effected in this particular case, other alkyl phenyl carbonates with larger alkyl groups than ethyl were labeled. With the



exception of the d_8 -isopropylphenyl compound (where deuterium transfer is heavily favored statistically) (XIV, R = CD₃), the origin of the transferred hydrogen is revealed (Table I) as surprisingly nonspecific, con-

Table I. Origin of Hydrogen Transfer in the Formation of *hb* (m/e 94) in Alkyl Phenyl Carbonates RO·CO·OPh^a

R	C _{α}	C _{β}	% transfer
<i>n</i> -Propyl	d_2	...	26
	...	d_2	16
Isopropyl	...	d_6	>97
<i>n</i> -Butyl	d_2	...	16
	...	d_2	20
<i>sec</i> -Butyl	d_1	...	14
Isobutyl	d_2	...	29
Neopentyl	d_2	...	32

^a All deuterium-labeled compounds contained at least 97% of the isotope at the positions indicated.

(36) Unpublished work in these laboratories (J. K. McLeod and C. Djerassi) has indicated that *n*-butylphenyl ether is transformed into ionized phenol (*hb*) by nonspecific hydrogen transfer from the alkyl chain to oxygen, rather than to the aromatic ring.

(37) G. G. Smith and B. Kösters, *Chem. Ber.*, **93**, 2400 (1960). The temperature range employed in these pyrolysis studies was 500–525°, and the principal products were ethylene, carbon dioxide, and the phenol.

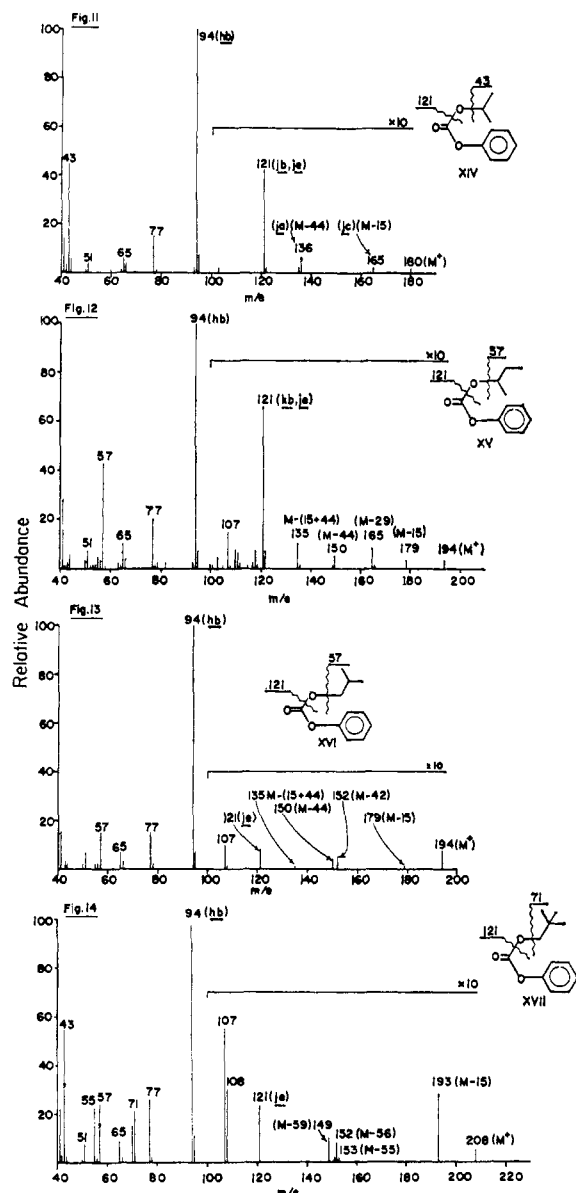


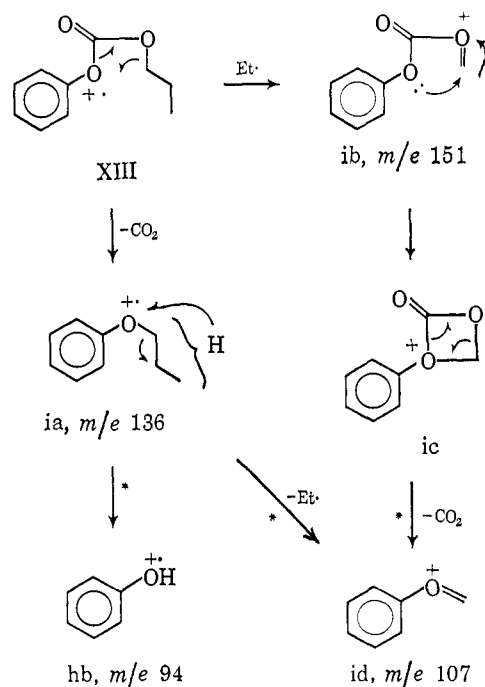
Figure 11. Mass spectrum of isopropyl phenyl carbonate (XIV).
 Figure 12. Mass spectrum of *sec*-butyl phenyl carbonate (XV).
 Figure 13. Mass spectrum of isobutyl phenyl carbonate (XVI).
 Figure 14. Mass spectrum of neopentyl phenyl carbonate (XVII).

sidering the formal mechanistic and structural similarities between this process ($\text{XII} \rightarrow \text{hb}$) and the (specific) McLafferty rearrangement.^{19, 20} Alkyl phenyl formaldehyde acetals behave in a precisely similar manner.⁵

The known³⁶ nonspecificity of hydrogen migration in the formation of ionized phenol (hb, m/e 94) from *n*-butyl phenyl ether provides a means of resolving the anomaly, provided that the corresponding ether ($M - 44$ species) is the intermediate in the major fragmentation pathway of alkyl phenyl carbonates to phenol (e.g., $\text{XII} \rightarrow \text{ha} \rightarrow \text{hb}$ (m/e 94)). None of the alkyl phenyl carbonates show peaks corresponding to $M - \text{olefin}$ (m/e 138) or $M - (\text{olefin}-1)$ (m/e 139), although this type of fragmentation is prominent in dialkyl carbonates.

In the mass spectrum (Figure 10) of *n*-propyl phenyl carbonate (XIII) the $M - 44$ rearrangement peak (ia, m/e 136) is again reduced in intensity ($\Sigma^M_{40} = 0.36$). This trend cannot be expected to reflect the

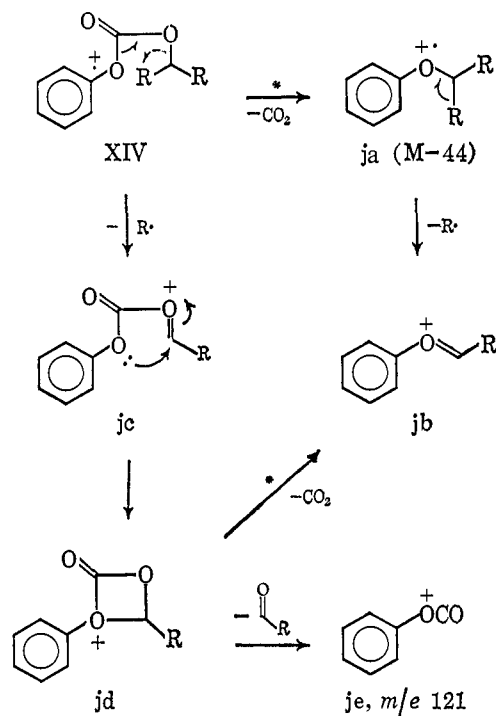
relative migratory aptitudes^{5, 38} of the various alkyl groups, due to different rates and routes for subsequent decomposition of the $M - 44$ species. A small peak



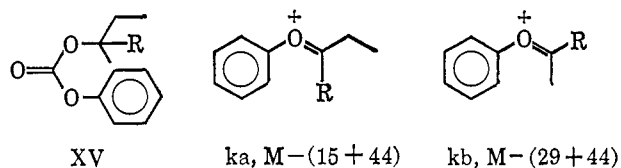
at m/e 107 (*id*) is now apparent (also in the spectrum of *n*-propyl phenyl ether), which was not present in the case of ethyl phenyl carbonate (XII) or ether. The dual origin of this fragment (*id*) is revealed by the presence of metastable peaks at m/e 84.2 ($107^2/136 = 84.1$) (ether α cleavage $\text{ia} \rightarrow \text{id}$), and at m/e 75.8 ($107^2/151 = 75.8$) ($\text{ib} \rightarrow \text{ic} \rightarrow \text{id}$). The latter process is visualized as passing through a cyclic intermediate *ic*; no metastable ion corresponding to the alternate collapse of *ic* (loss of formaldehyde to provide α cleavage ion Ph^+OCO) was detected. Deuterium labeling of the *n*-propyl group confirmed that the α -carbon atom is retained in *id*, and the β carbon lost. Metastable peaks at m/e 65.0 ($94^2/136 = 64.9$) and 49.0 ($94^2/180 = 49.0$) showed that the formation of *hb* (m/e 94) is again both stepwise ($\text{XIII} \rightarrow \text{ia} \rightarrow \text{hb}$) and concerted (analogous to $\text{XII} \rightarrow \text{hb}$). *n*-Butyl phenyl carbonate fragmented in exactly the same way, and the intensity of the $M - 44$ rearrangement ion was once more reduced ($\Sigma^M_{40} = 0.12$).

The mass spectrum (Figure 11) of isopropyl phenyl carbonate (XIV, $R = \text{Me}$) contains a small $M - 15$ peak *jc* ($R = \text{Me}$, m/e 165), and the usual $M - 44$ peak (*ja*, $R = \text{Me}$, m/e 136, $\Sigma^M_{40} = 0.37$). Sequential loss of carbon dioxide ($\text{XIV} \rightarrow \text{ja}$) and subsequent decay of the resulting ether ion ($\text{ja} \rightarrow \text{hb}$) to phenol (m/e 94) are once again evidenced by the appropriate metastable peaks. The α -cleavage species (*je*) of the carbonate (XIV, $R = \text{Me}$) and the α -cleavage fragment (*jb*, $R = \text{Me}$) of isopropyl ether (*ja*, $R = \text{Me}$) both appear at m/e 121. The spectrum of *d*₆-isopropyl phenyl carbonate (XIV, $R = \text{CD}_3$) demonstrates that 40% of m/e 121 is unaffected by the isotope substitution (*je*), and 60% moves up to m/e 124 (*jb*, $R = \text{CD}_3$).

(38) For a discussion of alkyl group migratory aptitudes in the (thermal) pinacol rearrangement, see M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959).



The situation is somewhat similar with *sec*-butyl phenyl carbonate (XV, R = H, Figure 12), except that two α -cleavage ions are now displayed (M - 15 at m/e 179 and M - 29 at m/e 165) in the expected intensity ratio.^{5,39,40} Cyclization of these species as before, followed by elimination of carbon dioxide, furnishes analogous oxonium ions at m/e 135 (ka, R = H) and m/e 121 (kb, R = H), respectively. The resolution of m/e 121 was carried out with the aid of



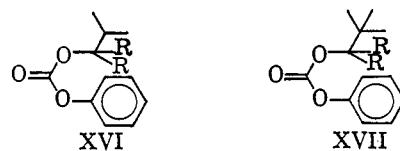
the d_1 -labeled carbonate (XV, R = D), 55% moving up to m/e 122 (kb, R = D) and the remainder staying unshifted at m/e 121 (je). The usual M - 44 (*sec*-butyl phenyl ether) peak (XV, R = H) at m/e 150 appeared at m/e 151 in XV (R = D) ($\Sigma^M_{40} = 0.19$).

Besides the expected peaks at m/e 150 (M - 44), m/e 121 (je), and m/e 107 (id), the mass spectrum (Figure 13) of isobutyl phenyl carbonate (XVI, R = H) also contained unexpected peaks at m/e 179 (M - 15), m/e 152 (M - 42), and m/e 135 [M - (15 + 44)]. The M - 15 species (m/e 193) is even more important in the spectrum of neopentyl phenyl carbonate (XVII, R = H, Figure 14), as are m/e 153 (M - 55), m/e 152 (M - 56), and m/e 149 [M - (15 + 44)]. In addition, a peak at m/e 108 is now in evidence. Both XVI (R = D) and XVII (R = D) clearly retain the isotope in their respective M - 59 species.

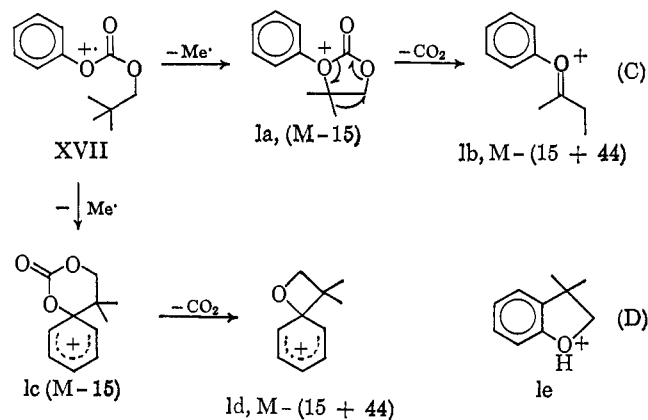
Loss of a methyl group from XVI (R = H) and XVII (R = H), where the site of cleavage is remote from any reasonable charge localization center, can best be

(39) See ref 22, Chapter 1.

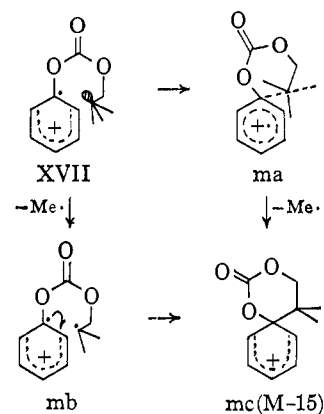
(40) For interesting comparisons to α -cleavage in alkoxy radicals, see J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962); C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963); F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).



accounted for in terms of cyclic stabilization of the resulting ion. A variety of tentative mechanisms can be written for this process, two of which are presented here. Mechanism C ascribes no critical role to the



aromatic ring, which seems unlikely since the two symmetrical diisobutyl (IX) and dineopentyl (X) carbonates do not show an M - 15 ion (Figures 6 and 7). Also, loss of carbon dioxide by a similar methyl migration mechanism from pinacol cyclic carbonate⁴¹ (admittedly a radical ion process) to give pinacolone does not seem to operate. Mechanism D implies phenyl participation (widely accepted⁴² in certain thermal reactions of phenyl-substituted compounds), with lc then losing carbon dioxide to ld or perhaps le. However, the question of whether loss of the methyl radical and cyclization are sequential steps, or concerted, must remain at least partly conjectural. Molecular models of XVII show that progression to an array ma is likely to be accompanied by severe crowding, but the "inside" lobe of the sp^3 C_β -Me σ bond to be broken is geometri-



cally in a good position for overlap with the electron deficient π orbital at C_1 of the ring, although well shielded by the *t*-butyl group as a whole. The alternative route *via* mb implies no fragmentation direction in the first step by the electron-deficient nature of the molecular ion, a situation to be deplored in a compound containing so many possible charge localization loci.

(41) P. Brown and C. Djerassi, unpublished results.

(42) See, for example, D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964).

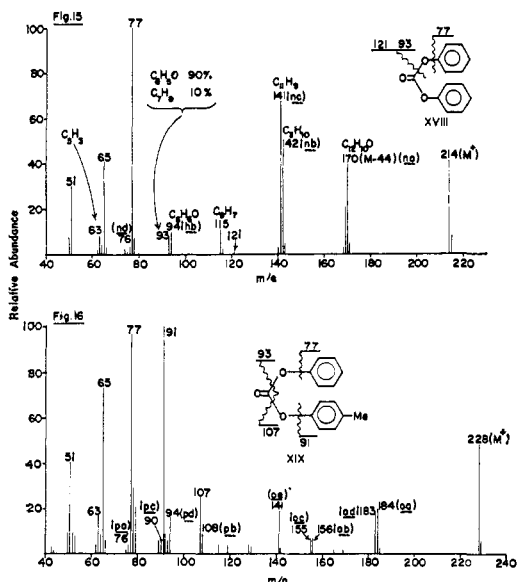


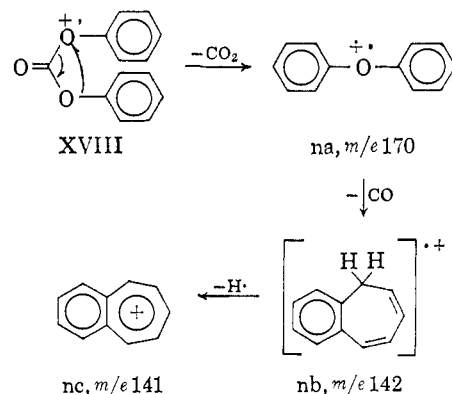
Figure 15. Mass spectrum of diphenyl carbonate (XVIII).
Figure 16. Mass spectrum of phenyl *p*-tolyl carbonate (XIX).

The $M - 55$ (m/e 153) and $M - 56$ (m/e 152) peaks in the spectrum (Figure 14) of neopentyl phenyl carbonate (XVII, $R = H$) were discussed in the previous section (see dialkyl carbonates). It is of interest to note that although diisobutyl carbonate (IX, Figure 6) exhibits the expected $M - 55$ (m/e 119) and $M - 56$ (m/e 118) peaks, isobutyl phenyl carbonate (XVI, $R = H$, Figure 13) has an $M - 42$ (m/e 152) peak, analogous to $M - 56$ (m/e 152) in neopentyl phenyl carbonate (XVII, Figure 14). The peaks at m/e 107 and 108 displayed by carbonate XVII ($R =$ (Figure 14)) are worthy of mention. High-resolution mass measurements showed that m/e 107 comprises 95% C_7H_7O , 5% C_8H_{11} , whereas m/e 108 is 85% C_7H_8O and 15% C_8H_{12} . In the labeled compound (XVII, $R = D$), these peaks split into four components from m/e 107 to 110 (relative intensities approximately 2:4:3:3), and it is immediately clear that the m/e 107 species is not solely id in this case. Some of the oxygen-containing portion of m/e 108 in XVII ($R = H$) is readily explained as arising by rearrangement with loss of carbon dioxide from the methyl phenyl carbonate (m/e 152) produced by the neopentyl ester rearrangement (e.g., $X \rightarrow fc$) of the molecular ion. In the labeled compound (XVII, $R = D$) this should all move up to m/e 110 (α -carbon atom retained), but a quantitative shift could not be substantiated due to the complexity of the spectrum in this region.

Aryl Phenyl Carbonates. The mass spectrum (Figure 15) of diphenyl carbonate⁴³ (XVIII) contains a large peak (40% of base peak) at m/e 170, corresponding to the elimination of carbon dioxide.⁴⁴ High-resolution mass spectrometry determined the composition of this ion (na) as $C_{12}H_{10}O$. The mechanism envisaged involves

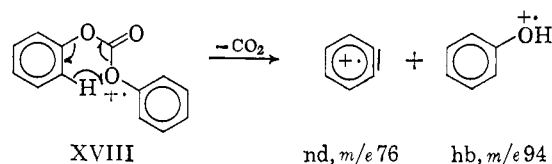
(43) Since completion of this work, the spectrum of diphenyl carbonate has been reported by Natalis and Franklin.¹³

(44) (a) Diphenyl monothiocarbonate ($PhS \cdot CO \cdot OPh$) rearranges with loss of CO rather than CO_2 or COS. An extensive study of the effect different heteroatoms have on this type of skeletal rearrangement is in progress; (b) the pyrolytic analog of this process has been reported by P. D. Ritchie, *J. Chem. Soc.*, 1054 (1935), who observed that at 640–670° diphenyl carbonate is transformed into diphenyl ether by loss of carbon dioxide.



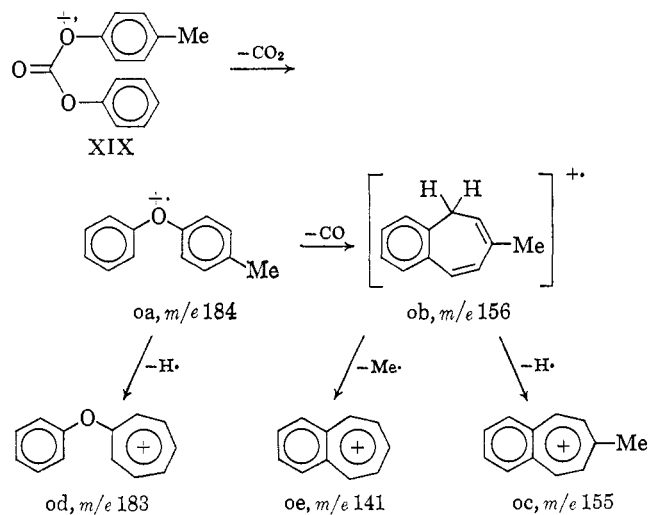
1,3-phenyl migration⁴⁵ (XVIII \rightarrow na) to oxygen, affording diphenyl ether radical ion. Some evidence³⁰ that at least a portion of this rearrangement ion may be identical with the molecular ion of diphenyl ether is provided by the characteristic^{13,29} loss of 28 mass units [CO, na \rightarrow nb (m/e 142)], followed by further loss of one hydrogen atom [nb \rightarrow nc (m/e 141)].

An interesting peak occurs at m/e 94 (Figure 15). High resolution demonstrated the composition to be C_6H_6O , and a cyclic 1,5-hydrogen transfer is proposed to account for it, by analogy with ethyl phenyl carbonate (XII). The alternative ion (benzyne⁴⁶ radical ion, nd)



may also be observed at m/e 76 (Figure 15). High-resolution mass measurements showed that m/e 63 is C_5H_3 and not CH_3O_3 in this instance.

Phenyl *p*-tolyl carbonate (XIX, Figure 16) fragments similarly; predictably,⁴⁷ m/e 91 now becomes the base peak, and $M - (44 + 1)$ (od, m/e 183) is now almost as intense as $M - 44$ (oa, m/e 184). Peaks at m/e 94 and 108 are analogous to hb (m/e 94) in the spectrum of diphenyl carbonate (XVIII). High resolution con-

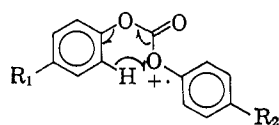


(45) In ref 13, no corresponding rearrangement is reported for phenyl benzoate.

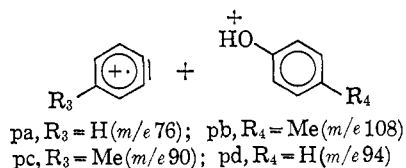
(46) For an example of the intervention of benzyne in mass spectrometry, see E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965).

(47) See ref 22, Chapter 9.

firmed the compositions of all ions assigned, and showed that m/e 63 is again C_5H_3 .

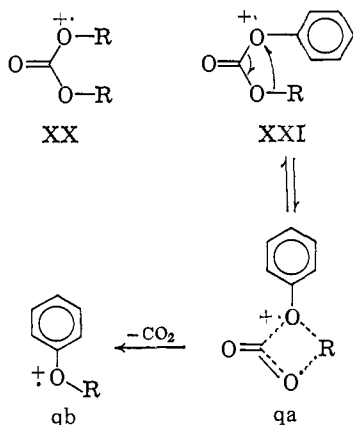


XIX i, $R_1 = H$; $R_2 = Me$
ii, $R_1 = Me$; $R_2 = H$



Conclusions

From the results obtained, the following generalizations can be made. The dialkyl carbonates (IV \rightarrow VIII) very probably rearrange predominantly by initial α cleavage (e.g., IV \rightarrow aa), followed by alkyl migration to a positively charged oxygen atom and accompanying loss of carbon dioxide (aa \rightarrow ac). The alkyl phenyl (XI–XVII) and aryl phenyl (XVIII, XIX) carbonates, on the other hand, suffer direct loss of carbon dioxide from the molecular ion (e.g., XI \rightarrow ge, XVIII \rightarrow na). Alkyl and aryl migration, respectively, occurs in these instances to an oxygen atom that is part of a delocalized radical ion system. One rationale that might be offered for these observations is that the migrations in question tend toward carbonium ion rearrangements. In the



dialkyl carbonate radical ion (XX), the charge on oxygen is delocalized by the electron-donating alkyl group R_1 , and is insufficient to induce migration of R_2 , until α cleavage in R_1 provides a full positive charge. With the alkyl phenyl (XXI, $R =$ alkyl) and aryl phenyl (XXI, $R =$ aryl) carbonate radical ion, the electron deficiency on oxygen is now relatively enhanced, due to the charge-withdrawing character of the phenyl substituent, and migration of R is facilitated. Detailed work is in progress to examine these mechanistic proposals further.

Experimental Section

All low-resolution mass spectra were obtained by Dr. A. M. Duffield, using an Atlas CH-4 mass spectrometer, operating under

the following conditions: ionizing voltage 70 ev, trap current 10 μ a, inlet temperature 70°, ion source temperature 180°. High-resolution mass measurements were secured by Mr. R. G. Ross, with the aid of an AEI MS9 double-focusing machine (apparent resolution 1 part in 15,000). Nmr spectra were recorded by Mr. A. Pandell with a Varian A-60 spectrometer, employing carbon tetrachloride as solvent and tetramethylsilane as internal reference.

Dialkyl Carbonates⁴⁸ (IV–X). **A. Preparation of Alkyl Chloroformate.** Phosgene (1 mole) is introduced into a dry reaction vessel equipped with drying tubes, magnetic stirring bar, and dropping funnel, and cooled to -40° . The requisite dry alcohol (0.8 mole) is then added, and the reaction mixture is stirred for about 3 hr.⁴⁹ After this time, excess phosgene and hydrogen chloride are removed under reduced pressure, and the crude alkyl chloroformate remains.

B. Conversion to Dialkyl Carbonate. The required alcohol (1.2 moles) dissolved in ethanol-free chloroform (3–5 moles) is then added, and stirring is continued for a further 15 min at -40° . Dry pyridine (1.5 moles) in chloroform (3–5 moles) is now added cautiously with stirring over a period of at least 1 hr, during which the reaction temperature is allowed to rise to ambient. The pink reaction mixture is then stirred at room temperature for a further 1–2 hr, until it is pale yellow in color. An equal volume of chloroform is added, and the solution is washed well with water (to neutrality) and dried over anhydrous sodium sulfate. Excess solvent is removed under reduced pressure, and the crude product is distilled. Purification was effected by means of gas chromatography, using a Wilkens Aerograph Moduline 202 instrument equipped with a 5 ft \times 0.25 in. 20% SE-30 on 60–80 Chromosorb W column. For example, diisobutyl carbonate (IX) had a retention time of 9.5 min at 130° and 35 ml min^{-1} helium flow rate. Identification of the carbonate fraction was easily accomplished, the infrared spectrum having characteristic⁵⁰ C=O absorption at 1740–1780 cm^{-1} , and C–O at 1250–1280 cm^{-1} . Yields of carbonates of primary alcohols were excellent by this method, whereas secondary alcohols gave slightly poorer yields, and tertiary alcohols furnished no carbonate product at all.

Alkyl Phenyl (XI–XVII) and Aryl Phenyl Carbonates (XVIII, XIX). Phenyl chloroformate (Eastman Kodak) was used, together with the requisite alcohol or phenol, under essentially the same conditions described in B above, except that the reaction mixture could be kept at room temperature (20–25°, but no higher) throughout. Work-up and purification were exactly as before, except for diphenyl carbonate (XVIII) (mp 78–79°)^{44b} and phenyl *p*-tolyl carbonate (XIX) (mp 49–50°), which were recrystallized from petroleum ether (bp 60–68°). At 180° and 40 ml min^{-1} helium flow rate, and on the same SE-30 gas chromatography column, neopentyl phenyl carbonate (XVII) had a retention time of 7.5 min.

Purity was established for each compound by gas chromatographic analysis (thin layer chromatography for compounds XVIII and XIX), the mass spectrum, and especially the highly characteristic nmr spectrum coupled with integrated proton count. As an example of nmr assay, di-*n*-propyl carbonate (VI) had the following spectral data (all chemical shifts are quoted in δ values, TMS = 0): 4.23 (four-proton triplet), 1.75 (four-proton multiplet), and 1.02 (six-proton triplet). *n*-Propyl phenyl carbonate (XIII) absorbed at δ 7.22 (five-proton multiplet), 4.13 (two-proton triplet), 1.76 (two-proton multiplet), and 1.02 (three-proton triplet). The α, α -*d_2*-*n*-propyl phenyl carbonate showed no peak at δ 4.13, the multiplet at 1.76 was reduced to a quartet, and the triplet at 1.02 remained unaltered. In the corresponding β, β -*d_2*-*n*-propyl phenyl carbonate, the resonances at δ 4.13 and 1.02 were both simplified to singlets, while no absorption at 1.76 was detected.

All other compounds prepared in this work gave nmr spectra completely compatible with their expected structures and position of isotope labels. One notable feature of the carbonate nmr spectra is the relatively greater deshielding of protons in attached alkyl groups compared with formaldehyde acetals.⁵

(48) Dimethyl carbonate (IV) was purchased from Eastman Organic Chemicals, Distillation Products Industries, Rochester 3, N. Y.

(49) (a) H. E. Carter, R. L. Frank, and H. W. Johnston, *Org. Syn.*, **23**, 13 (1943); (b) C. E. Slimowicz and E. F. Degering, *J. Am. Chem. Soc.*, **71**, 1043 (1949); (c) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

(50) J. L. Hales, J. I. Jones, and W. Kynaston, *J. Chem. Soc.*, 618 (1957).