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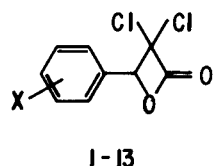
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The electron impact mass spectrometric fragmentation pathways for a series of 4-aryl-3,3-dichlorooxetan-2-ones were investigated. It was found that cleavage to radical cations of dichloroketene and/or the substituted benzaldehyde is preferred by a large measure to cleavage to radical cations of carbon dioxide and/or the substituted β,β -dichlorostyrene. Furthermore, it was demonstrated that the nature of the substituent has a significant influence on the localization of charge in the preferred direction of cleavage.

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The thermal decomposition of oxetan-2-ones (β -lactones) to provide an alkene and carbon dioxide is a widely known and synthetically useful reaction (1,2). In a previous report from this laboratory, the thermally induced decarboxylations of 4-aryl-3,3-dichlorooxetan-2-ones **1-13** were described (3). Briefly, it was discovered that the de-



- | | |
|----------------------------------|-----------------------------------|
| 1, X = H | 5, X = <u>m</u> -OCH ₃ |
| 2, X = <u>o</u> -CH ₃ | 6, X = <u>p</u> -OCH ₃ |
| 3, X = <u>m</u> -CH ₃ | 7, X = <u>o</u> -Cl |
| 4, X = <u>p</u> -CH ₃ | 8, X = <u>m</u> -Cl |
| | 9, X = <u>p</u> -Cl |
| | 10, X = <u>o</u> -NO ₂ |
| | 11, X = <u>m</u> -NO ₂ |
| | 12, X = <u>p</u> -NO ₂ |
| | 13, X = <u>p</u> -CN |

carboxylation process is remarkably sensitive to the nature of the substituent attached to the phenyl ring: electron-donating substituents greatly facilitate the extrusion of carbon dioxide, whereas electron-withdrawing groups severely retard the reaction. With this background it was considered to be of importance to ascertain whether or

not such substituent effects would also be manifested by the strained heterocycles **1-13** upon external activation by photochemical irradiation or by electron impactation. In this report the latter method is dealt with and the principal mass spectrometric fragmentation patterns of **1-13** are described. Somewhat surprisingly, although the mass spectrometry of the structurally related oxetane and β -lactam frameworks has been extensively investigated (4,5), the mass spectrometry of the β -lactone skeleton has received only limited attention (6).

Results and Discussion.

After electron bombardment of the β -lactone to provide the molecular ion (**a**) fragmentation can proceed in two directions: (i) to give the radical cations corresponding to the molecular ions of a substituted β,β -dichlorostyrene (**b**) and/or carbon dioxide (**f**) as indicated in Equation 1, and (ii) to generate the radical cations analogous to the parent ions of dichloroketene (**g**) and/or a substituted benzaldehyde (**h**) as illustrated in Equation 2. In fact, besides the relatively small amounts of β -lactone molecular ion (**a**), the mass spectra consist principally of signals due to **b**, **g**, and **h**, and their respective daughter ions. Scheme I summarizes these fragmentation sequences, while Table I collects the corresponding relative intensity

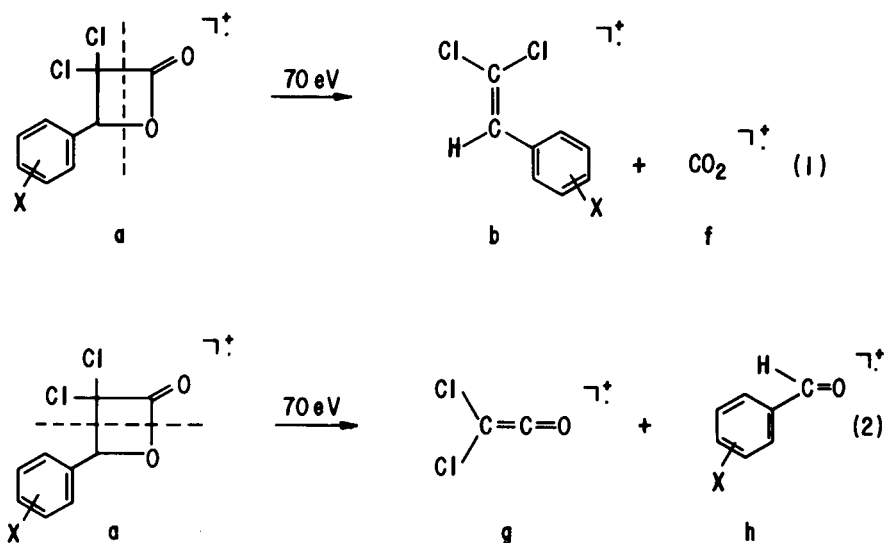


Table I
Relative Intensity Data for Scheme I (a)

CMPD	a	b	c	d	e	f	g	h	i	j
1(b,c)	13	19 (100)	8 (38)	12 (45)	7 (25)	12	100	4 (90)	21 (92)	19 (100)
2(b,c)	20	7 (75)	13 (57)	12 (26)	56 (100)	4	100	89 (78)	93 (77)	62 (100)
3(b,c)	14	32 (100)	13 (25)	14 (29)	47 (84)	5	100	58 (78)	85 (85)	50 (100)
5(c)	17	8 (100)	2 (15)	0 (0)	0 (0)	1	10	100 (100)	36 (94)	9 (35)
7(c)	6	17 (100)	12 (60)	19 (68)	9 (30)	2	100	15 (73)	61 (100)	13 (43)
8(c)	9	18 (100)	7 (39)	15 (76)	5 (25)	<1	100	8 (78)	22 (100)	16 (54)
9(c)	11	17 (100)	7 (25)	14 (34)	5 (13)	1	100	9 (70)	20 (100)	15 (55)
10(c,d)	0	0 (5)	8 (35)	0 (3)	3 (8)	6	100	<1 (<1)	<1 (1)	(e) (e)
11(c)	2	21 (92)	2 (2)	0 (0)	0 (0)	7	100	2 (100)	6 (81)	0 (f)
12(c)	2	9 (100)	0 (0)	0 (0)	0 (0)	1	100	<1 (100)	1 (f)	0 (f)
13	7	28 (100)	13 (28)	12 (34)	6 (16)	<1	100	1 (71)	5 (100)	12 (68)

(a) Values in parentheses are for the corresponding β,β -dichlorostyrenes and benzaldehydes; unless stated otherwise the values were determined in the present investigation. (b) Values for h-j taken from T. Aczel and H. E. Lumpkin, *Anal. Chem.*, **33**, 386 (1961). (c) Values for h-j taken from "Eight Peak Mass Spectra", 2nd Ed., Mass Spectrometry Data Centre, AWRE, Aldermaster, Reading RG7 4PR, UK, 1974. (d) J. Harley-Mason, T. P. Toubé, and D. H. Williams, *J. Chem. Soc. (B)*, 396 (1966). (e) Value obscured by P + 1 signal of the m/e 121 ion. (f) Not reported.

data (7).

Upon careful inspection of the data assembled in Table I (which also includes independently determined information for the mass spectrometry of the appropriate mono-substituted β,β -dichlorostyrenes and benzaldehydes), it is clearly evident that the substituents exert significant influence on the fragmentation pathway. First of all, it is immediately apparent that the initial fragmentation of β -lactone molecular ions occur preferentially by way of Equation 2 rather than Equation 1. Therefore, the electron-impact induced cleavage of the β -lactone system is in marked contrast to the fragmentation initiated by thermolysis. Furthermore, within the confines of Equation 1, it is seen that the radical cation of carbon dioxide along with its substantially less abundant decomposition ions (8) are formed to a very minor extent relative to intensities of the radical cation of β,β -dichlorostyrene and its major daughter ions. However, examination of the ions (and their daughter ions) shown in Equation 2 reveals important substituent effects. Thus, although the base ion

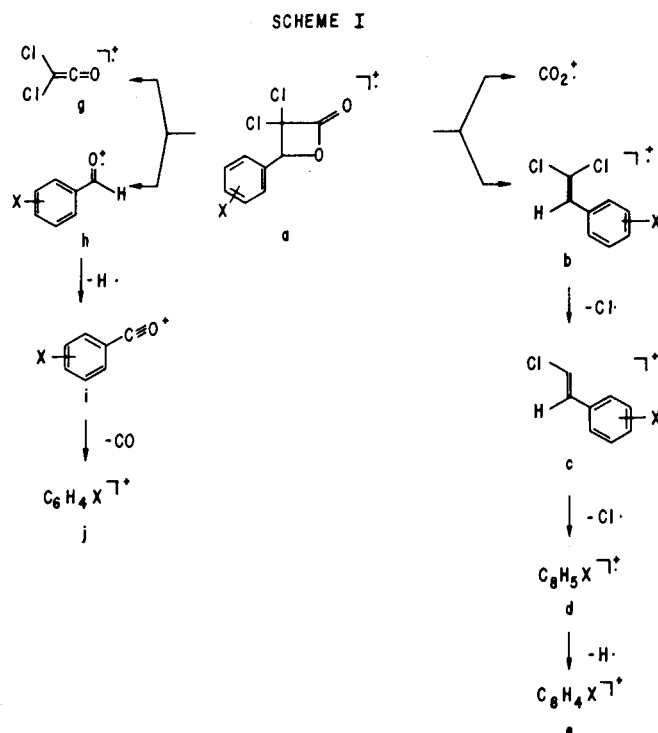


Table II

Relative Intensity Data for Scheme II (a)

CMPD	b	k	1	m	n	o
10	0 (5)	0 (3)	36 (100)	0 (3)	13 (63)	8 (43)
11	21 (92)	<1 (2)	5 (14)	12 (58)	30 (100)	26 (42)
12	9 (100)	7 (47)	3 (35)	2 (17)	14 (96)	9 (48)

(a) Values in parentheses are for the corresponding β,β -dichlorostyrenes.

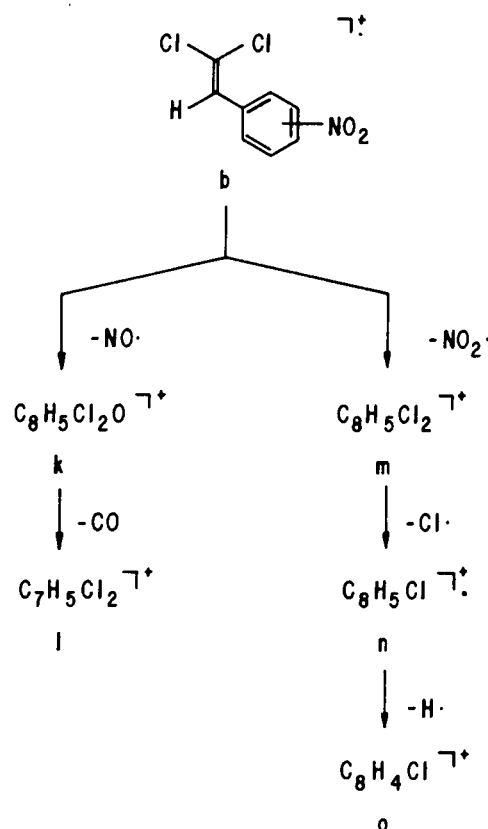
in all instances except one (the *m*-methoxy derivative 5) is due to radical cation of dichloroketene (g), the summation of the relative intensities of the cations due to the substituted benzaldehyde (h) and its major daughter ions (i and j) yields a composite relative intensity which is greater (in some cases) than that of the base ion due to g (9).

Specifically, while the parent phenyl β -lactone 1 prefers to localize the positive charge on g, the tolyl β -lactones 2 and 3 actually prefer to form h (which goes on to i and j). This result can be attributed to the fact that the methyl groups of h and i (and the tropylium ion in the case of j) can stabilize the positive charge by induction (10). At the other extreme are the results for the nitrophenyl (10-12) and the *p*-cyanophenyl (13) β -lactones. These substrates give rise to virtually only trace amounts of ions derived from the corresponding benzaldehyde; such an occurrence is attributable to the fact that the strongly electron-withdrawing nitro and cyano substituents destabilize the ions h-j. For the chlorophenyl β -lactones 7-9 the combined intensities of h-j are similar in magnitude to that of the parent β -lactones 1, which indicates that the electron-withdrawing ability (via induction) is effectively counteracted by the electron-donating ability (via resonance). The *m*-anisyl β -lactone 5 responds to electron bombardment by producing only a relatively small amount of g and a relatively large amount of h. Apparently, the methoxy group is able to donate electrons by resonance to the cationic sight of the fragment ion h (7).

Finally, for the nitrophenyl β -lactones 10-12, it should be pointed out that the "major" fragmentation paths (besides the generation of g) involve the losses of NO and NO₂ from the β,β -dichlorostyrene system (b), as shown in Scheme II. Table II collects the relative intensity data for the fragmentations shown in Scheme II. These processes were substantiated by measuring the spectra of the various nitro substituted β,β -dichlorostyrenes themselves.

In conclusion, it has been shown that (i) the electron-impact induced cleavage of the β -lactones 1-13 is, for the most part, in the alternative direction compared to the

SCHEME II



thermally promoted fragmentation, and (ii) electron-donating substituents attached to the phenyl ring tend to favor charge localization on the benzaldehyde fragment ion, whereas electron-withdrawing groups lead to preferential generation of the dichloroketene radical cation.

EXPERIMENTAL

The β -lactones 1-13 were prepared, purified, and characterized as described previously (3). Mass spectra were determined with a DuPont CEC 21104 mass spectrometer operated at 70eV and ambient source temperatures (<30°).

Acknowledgement.

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(6) L. Friedman and F. A. Long, *J. Am. Chem. Soc.*, **75**, 2832 (1953); F. A. Long and L. Friedman, *ibid.*, **75**, 2837 (1953).

(7) The actual structures shown in the schemes have not been rigorously established, but represent reasonable and convenient vehicles for discussion; see for example the discussion in H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, Inc., San Francisco, CA, 1967, p. 162.

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(9) The two "major" fragments of dichloroketene arise from the losses of chlorine or carbon monoxide (**6**); however, the combined relative intensities are only about 25% of that of **g**.

(10) Unfortunately, it was not possible to measure the mass spectra of the *p*-tolyl and *p*-anisyl β -lactones on account of the extreme ease with which they undergo thermal decarboxylation (**3**); these spectra would have been especially desirable since they might have been able to reveal additional stabilization of **h** and its daughter ions by hyperconjugation with **4** or by resonance with **6**.