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CONCERTED FRAGMENTATION CONCURRENT WITH A STEPWISE-DIRADICAL FISSION IN THE OXETANE THERMOLYSIS; IMPORTANCE OF STERIC STRAIN

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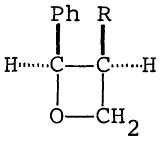
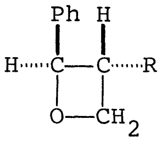
Thermolytic behavior of 3-alkyl-2-phenyloxetanes, in particular that of trans isomers, is best explained by concurrent concerted fragmentation and stepwise diradical fission. Proportion of the concerted process should be small in the cis isomers because of destabilization of the transition state by steric strain. The argument is supported by the thermal behavior of 3-alkyl-4-phenyl-2-oxetanones.

Thermolysis of oxetanes is known to proceed in a stepwise fashion *via* a diradical intermediate.1) We, however, noted that the thermal behavior of geometrically isomeric 3-alkyl-2-phenyloxetanes is hardly explained by such a mechanism. Our results can be interpreted only by an assumption that a concerted fragmentation occurs concurrently with a stepwise-diradical fission in the thermolysis.

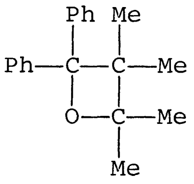
Some time ago, we communicated the distinctive thermal behavior of isomeric 2-phenyl-3-propyloxetanes.2) We were not, however, aware of an extremely acid-sensitive nature of these compounds;3) regioselectivity as well as rates of the fragmentation is disturbed by acidic impurities. We, therefore, re-examined the reaction with oxetanes **1**-**7** as shown below.



1c: R = Me
2c: R = isoPr
3c: R = tert-Bu



1t: R = Me
2t: R = isoPr
3t: R = tert-Bu



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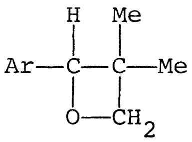
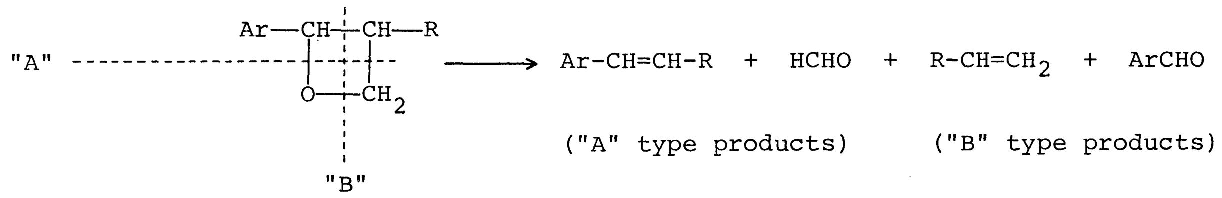


5: Ar = Ph
6: Ar = *p*-Tol
7: Ar = *p*-An

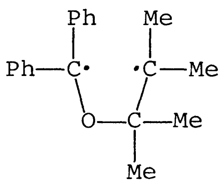
As reported by Jones and his coworkers,4) the oxetane thermolysis was very sensitive to acidic impurities. Indeed, we observed that heatings of **4** in diphenylmethane with no precaution resulted in the formation of 2-methyl-1,1-diphenylpropene ("A" type fragmentation product) in an amount much larger than that of benzophenone ("B" type; A:B = 81:19), but the use of base treated solvent reversed the regioselectivity of the fragmentation dramatically (A:B = 2:98).3) Moreover, we noted that an addition of tertiary amines, such as N,N,N',N'-tetramethylethylenediamine (TMEDA) or N,N-dimethylaniline, resulted in further reduction in the proportion of the type A. After extensive investigations, we finally found that the thermolysis in degassed TMEDA5,6) gave the least amount of the styrene derivative (A:B = 0.4:99.6). The A:B ratio thus



obtained coincides with a ratio (A:B = 0.6:99.4) deduced from the difference in bond dissociation energy for two presumed diradicals 8 and 9.7) Therefore, we concluded that 4 decomposed by the diradical mechanism under such conditions and hence the disturbance caused by the acidic impurities may be eliminated in degassed TMED.

The fragmentation was not stereospecific, even for the trans isomers (Table I). This is, in part, due to the isomerization of the produced styrene. Epimerization of oxetanes prior to the thermolysis was also observed, but it took place only to a minor extent, except for 3c (see footnote c of Table I). We shall thus focus our attention to the regioselectivity of the reaction and the results are summarized in Table II. We interrupted the reaction at a relatively early stage, because the type B product (aromatic aldehydes) was unstable under the thermolysis conditions. We also carried out control experiments for all the aldehydes and the figures given in Table II are corrected for the slow consumption of the aldehyde.

From the results summarized in Table II, we can point out some features of the thermolysis. (i) The type B fragmentation predominates throughout for the cis isomers whereas the reverse is the case for the trans isomers. (ii) The type A fragmentation is more important in the thermolysis at lower temperature with no exception. (iii) The A:B ratio is dramatically influenced by the para substituent in 5, 6, and 7. All these features can hardly be explained by the diradical mechanism. Thus, for (i), consideration of the relative stabilities of two presumed diradical (10 and 11) cannot account for the predominance of the type A fragmentation in the trans isomers.



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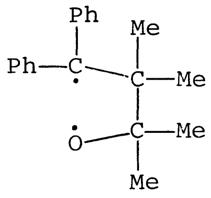

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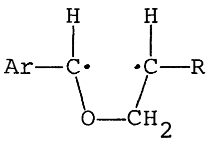

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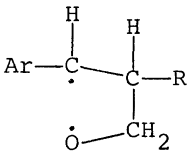

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Table I. Stereochemical Results of the Type A Fragmentation[a]

	% Retention of Configuration		
Oxetane	Methyl (1)	Isopropyl (2)	tert-Butyl (3)
cis-3-Alkyl-2-phenyl	69 (83)[b]	83 (87)[b]	42 (ca. 50)[c]
trans-3-alkyl-2-phenyl	96	99	99.9

[a] In degassed TMEDA at 310 °C for 3 h. [b] Only after 1.5 h at 310 °C. [c] A figure corrected for both isomerization of the styrene and epimerization of the oxetane. The recovered oxetane contained 15% of 3t. In other oxetanes, the epimerization occurred only to a minor extent; the contamination of the epimer in the recovered oxetane was 2.2% for 1c, 2.7% for 2c, 1.4% for 1t, 0.7% for 2t, and none for 3t.

Table II. Regioselectivity in the Thermolysis of 2-Aryloxetanes[a]

Oxetane	Thermolysis					
	270 °C, 16 h		310 °C, 3 h		350 °C, 0.5 h	
	% Conv.	A:B	% Conv.	A:B	% Conv.	A:B
cis-3-Methyl-2-phenyl (**1c**)	7.5	36:64	21	21:79	44	12:88
cis-3-Isopropyl-2-phenyl (**2c**)			25	21:79		
cis-3-*tert*-Butyl-2-phenyl (**3c**)			62	2:98		
trans-3-Methyl-2-phenyl (**1t**)	25	91: 9	29	72:28	43	55:45
trans-3-Isopropyl-2-phenyl (**2t**)			14	71:29		
trans-3-*tert*-Butyl-2-phenyl (**3t**)			14	70:30		
2,2,3,3-Tetramethyl-4,4-diphenyl (**4**)			72	0.4:99.6		
3,3-Dimethyl-2-phenyl (**5**)	13	7:93	41	3:97	85	2:98
3,3-Dimethyl-2-*p*-tolyl (**6**)	16	37:63	44	14:84		
3,3-Dimethyl-2-*p*-anisyl (**7**)	50	92:8	54	61:39		

[a] In degassed TMEDA. Under the thermolysis conditions, the aromatic aldehyde decreased its amount by time. Therefore, control experiments were carried out for all aldehydes and the figures given were corrected. The products were analyzed by GC, except for **7**. Since **7** decomposed under GC conditions, the products of **7** were analyzed by HPLC using N,N-diethylaniline as an internal standard.

As to (ii), if it were the diradicals **10** and **11** which determine the A:B ratio, the type A fragmentation should be more important at higher temperature, not at lower temperature, since **11**, which gives the type A product, is less stable than **10** and hence the type A fragmentation should have higher energy of activation than the type B. Finally, the diradical mechanism would not explain the effect of *p*-methyl and *p*-methoxy group on the A:B ratio as pointed out in the feature (iii).

On the other hand, if we accepted an assumption that concerted fragmentation, which is important particularly for the type A fragmentation, occurred concurrently with the stepwise diradical process, (i)-(iii) will be explained reasonably. The concerted fragmentation could have lower energy of activation than does the diradical process and hence the observation (ii) is not unexpected. The reason why the concerted fragmentation is especially important for the type A fragmentation may be answered by the HOMO-LUMO interactions: styrene-formaldehyde *vs* alkene-aromatic aldehyde.[8] Such interactions will provide an explanation for the feature (iii) as well. In order to account for (i), we must assume increase in the steric strain at the activated complex of the concerted fragmentation. In the activated complex, a development of a partial double bond between C-2 and C-3 will force the two groups in the cis relationship come closer together. Such a destabilization of the transition state should be much more pronounced in the cis isomers. If this argument is true, similar effects of the substituents must be observed in the concerted fragmentation of related four-membered heterocycles. Thus, we examined the thermolysis of 3-alkyl-4-phenyl-2-oxetanones.[9]

The fragmentation reactions of *cis*- and *trans*-3-methyl-4-phenyl- (**12c**, **12t**), *cis*- and *trans*-3-isopropyl-4-phenyl- (**13c**, **13t**), and *cis*- and *trans*-3-*tert*-butyl-4-phenyl-2-oxetanones (**14c**, **14t**) proceeded stereospecifically, which suggested the concerted nature of the reaction.$^{9)}$ Notable observations in the relative reactivities (Table III) were (a) the trans isomer reacted more rapidly than the corresponding cis isomer and (b) the bulkier the alkyl group, the slower the fragmentation. These results are strong supports for the arguments given above. In addition, it should be noted that the plot of log k_1(cis) *vs* $E_S$$^{10)}$ gave a straight line suggesting the effect being steric in origin.

It is thus concluded that the fragmentation of certain oxetanes may proceed in the two concurrent reactions, the concerted fragmentation and stepwise-diradical splitting. Such a duality in the process was observed particularly in the *trans*-3-alkyl-2-phenyl derivatives. This may be because the two processes will be similar in energy especially in those oxetanes of possessing this substitution pattern. It is natural, therefore, that the fragmentation of more highly substituted oxetanes, such as 4, certainly takes the diradical process, because the steric strain will be too high to make the concerted process observable.

Table III. Kinetic Data for the Thermolysis of 3-Alkyl-4-phenyl-2-oxetanones ^{a,b}

2-Oxetanone	$10^5 k_1 (s^{-1})$	Rel. Rate	2-Oxetanone	$10^5 k_1 (s^{-1})$	Rel. Rate
12c	6.29	36	12t	68.1^{c}	390
13c	1.96	11	13t	27.1	150
14c	0.175^{c}	1.0*	14t	13.0	74

^{a} In decane at 150 °C in the presence of TMEDA.$^{9)}$ ^{b} Ref. 7. ^{c} Extrapolated.

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3) Acidic impurities include metallic compounds. In our previous experiments, we used decane as the solvent. We now found that the thermolysis of 4 in simply distilled decane gave A:B = 4:96, whereas the reaction in base treated decane resulted in A:B = 2:98. Since the disturbance observed in decane was in such a degree, our previous results may be qualitatively valid.
4) G. Jones, II, and H. H. Cleinman, Tetrahedron Lett., 2103 (1974).
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6) Degassed conditions obtained by repeated freeze-thaw cycles under high vacuum were necessary to result in the reproducible results.
7) Details will be reported in near future.
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