The Mechanism of the Liquid-Phase Thermal Decomposition of Some Dialkyl Oxalates[1]

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Abstract: The liquid-phase thermal decomposition of bis(*cis*-1,2-dimethylcyclopentyl) oxalate at 135° gave a 92% yield of a hydrocarbon mixture, whose composition was 85% 1,2-dimethylcyclopentene and 15% 2,3-dimethylcyclopentene; that of the *trans* isomer gave an 83% yield, whose composition was 22% 1,2-dimethylcyclopentene, 75% 2,3-dimethylcyclopentene, and 3% 1-methylene-2-methylcyclopentane. The decompositions of bis(2,3,3-trimethyl-2-butyl-1,1,1-d_3) and bis(1-*t*-butylcyclohexyl) oxalates proceeded with 1,2-methyl migrations as evidenced by the formation of 14% 2,3,3-trimethyl-1-butene-4,4,4-d_3 and 6% isopropenyl-1-methylcyclohexane, respectively. The k_H/k_D isotope effect for the formation of isobutenes from the decomposition at 170° of bis(2-methyl-2-propyl-1,1,1,3,3,3-d_6) oxalate and for the formation of trimethylbutenes from the decomposition at 160° of the bis(2,3,3-trimethyl-2-butyl-1,1,1-d_3) oxalate was 1.8. The isotope effect for the formation of 2-methyl-2-butenes from the decomposition of bis(2-methyl-2-pentyl-3-*d*) oxalate at 145° was 1.6. All oxalates with deuterium atoms at the α-carbons decomposed more slowly than the corresponding unlabeled analogs. Bis(*erythro*-1,2-diphenylethyl-2-*d*) oxalate gave a 56% mixture of 95% *trans*-stilbene and 5% *cis*-stilbene. The *trans*-stilbene was about 90% d_1 and 10% d_0. The *trans*-stilbene from the corresponding *threo* compound was about 10% d_1 and 90% d_0. No 1,2-diphenylethanes were detected. Bis(*exo*-2-norboryl) oxalate decomposed at 250° to give a hydrocarbon mixture whose composition was 95% norbornene and 5% nortricyclene. The composition of the corresponding mixture from the decomposition at 280° of the *endo* compound was 33% norbornene and 67% nortricyclene. Bis[2-(Δ^3-cyclopentenyl)ethyl] oxalate decomposed at 320–350° to give a hydrocarbon mixture of 3% norbornene, 70% nortricyclene, and 27% Δ^3-cyclopentenylethene. No norbornane was detected from any of the three decompositions. The above data have been interpreted in terms of an ion-pair intermediate, whose collapse to give olefins is about five to ten times faster than its internal reorientation in terms of the spacial relationship of the anion with respect to the cation. The thermal decomposition of bis(cyclopentylcarbinyl) oxalate at 360° yielded a 30% mixture of hydrocarbons, whose composition was 52.5% methylenecyclopentane, 17.5% 1-methylcyclopentene, 5.3% cyclohexene, and 24.7% methylcyclopentane. Several other dialkyl oxalates of primary and secondary acyclic alcohols were found to decompose slowly at temperatures above 350°.

The liquid-phase thermal decomposition of dialkyl oxalates of tertiary alcohols containing β-hydrogens to give 80–100% yields of olefins was interpreted[2] in terms of an ion-pair mechanism, eq 1, on the basis of

$$\mathrm{R_1R_2CHC(R_3R_4)Ox} \xrightarrow{140°} \mathrm{R_1R_2CH\overset{+}{C}R_3R_4Ox^-} \longrightarrow \mathrm{R_1R_2C{=}CR_3R_4 + (CO_2H)_2} \quad (1)$$

the following. (1) The decomposition occurred at relatively low temperatures, 140–170°, with oxalic acid being the other product at temperatures below 160°. (2) The kinetically controlled isomeric olefin distribution resembled those obtained from reactions known to proceed through ion-pair mechanisms, such as the dehydration of alcohols in dimethyl sulfoxide,[3] the thermal decomposition of borate esters,[4] and the acid-catalyzed dehydration of alcohols, rather than those obtained from the thermal decomposition of xanthates, amine oxides, halides, and related compounds that proceed through cyclic transition states.[5] (3) The olefin distribution was unaffected by decomposing the esters in 1 equiv of oxalic acid, or by carrying out the reaction in quinoline. (4) The dialkyl oxalates of primary and secondary acyclic alcohols did not decompose upon heating to 325° for 1 hr.

It was shown[2] that the oxalates of secondary alicyclic alcohols decompose upon heating to 250–300° to yield the expected alkenes, in yields of about 50%, and the corresponding formate esters. Generally, whenever the decomposition temperature exceeded 210° the olefins were accompanied by the formation of formates. Recently, Trahanovsky and his coworkers[6] and Warkentin and Singleton[7] have established that the thermal decomposition of benzhydryl oxalates at 225° proceeds through a free-radical mechanism involving the stretching of two bonds in the transition state.

The research described in this paper was undertaken with the following objectives in mind: (1) to establish more firmly the ionic mechanism suggested for the thermal decomposition of the oxalates of tertiary alcohols; (2) to see if the ion pair collapses to products prior to ion-pair reorientation, especially in view of the fact that the decomposition is carried out in a medium (neat ester) of low dielectic constant with poor solvating ability; and (3) to examine systems where the ionic and free-radical paths might compete with each other.

As criteria to evaluate the mechanism under the experimental conditions we have used primarily product distributions and deuterium isotope effects.

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[1] Taken from the Ph.D. Thesis of K. L. Krumel, Michigan State University, 1965.

[2] G. J. Karabatsos, J. M. Corbett, and K. L. Krumel, *J. Org. Chem.*, 30, 689 (1965).

[3] V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *ibid.*, 27, 2377 (1962).

[4] O. L. Chapman and G. W. Borden, *ibid.*, 26, 4193 (1961).

[5] For a review, see C. H. DePuy and R. W. King, *Chem. Rev.*, 60, 431 (1960).

[6] W. S. Trahanovsky, C. C. Ong, and J. A. Lawson, *J. Am. Chem. Soc.*, 90, 2839 (1968); W. S. Trahanovsky, J. A. Lawson, and D. E. Zabel, *J. Org. Chem.*, 32, 2287 (1967).

[7] J. Warkentin and D. M. Singleton, *Can. J. Chem.*, 45, 3035, 3045 (1967).

Results

In Table I are summarized the results of the liquid-phase thermal decomposition of several dialkyl oxalates. Product analyses were done by gas chromatography and nuclear magnetic resonance spectroscopy. The nmr analyses were facilitated by the differences in the chemical shifts of the olefinic protons: terminal at τ 5.4, nonterminal at τ 4.8–4.9, and endocyclic at τ 4.65 (cyclohexenes) and τ 4.75 (cyclopentenes).

In all cases the oxalates of the tertiary alcohols decomposed smoothly at about 140–170° yielding olefins (over 80%) as the only organic products. Once started, the reactions proceeded vigorously (catalyzed by oxalic acid) and were complete within 5 min. Whenever the temperature required for decomposition exceeded 220°, the olefin yields decreased to 30–50%, with the remaining product being formate esters and high-boiling compounds whose identity was not established. It was originally reported[2] that oxalates of primary and secondary acyclic alcohols resisted decomposition up to 325°. Such oxalates decompose upon prolonged heating (3–4 hr) at 330–370° (see **15**, **17**, and **18** in Table I).

All oxalates containing deuterium atoms at the α-carbons decomposed more slowly (higher temperatures) than the corresponding unlabeled analogs. For example, whereas **1** decomposed at 170°, its unlabeled analog decomposed[2] at 150°; whereas **2** decomposed at 160°, its unlabeled analog decomposed at 150°. Also, compare **4** and **5**.

1, **2**, and **4** were designed to measure the k_H/k_D effect in the formation of olefins. From the relative concentration of the relevant products, k_H/k_D for **1** and **2** is calculated to be 1.8. We were unable to measure accurately by nmr the relative amounts of I, II, and III, and, therefore, we have calculated the k_H/k_D for the formation of II and III by comparing the relative

$CH_3CH_2CHDC(CH_3){=}CH_2$ I

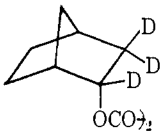
$CH_3CH_2CD{=}C(CH_3)_2$ II

$CH_3CH_2CH{=}C(CH_3)_2$ III

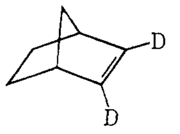
ratios of terminal/nonterminal olefins obtained from **4** and **5**. If the ratio I/II were to be twice the ratio of terminal/nonterminal olefin from **5**, *i.e.*, if the secondary deuterium isotope effect accompanying the formation of II were negligible, then k_H/k_D for the formation of II/III would be about 1.6. **3** is included to give the corresponding deuterium isotope effect, 1.5, from the gas-phase decomposition of the acetate.

2 and **6** how that 14% and 6% product, respectively, has arisen subsequent to methyl migration. Bis(cyclopentylcarbinyl) oxalate (**16**) shows not only product arising subsequent to a 1,2-hydrogen shift (17.5% 1-methylcyclopentene), but 5.3% product (cyclohexene) having arisen after ring expansion. The thermal decomposition of bis(cyclohexylcarbinyl) oxalate at 330–360° gave no detectable amount of cycloheptene.

7 and **8**, **10** and **11**, and **12–14** are striking examples of the effect that the stereochemistry of the starting oxalate has on the olefin composition.[8] Furthermore, bis-(*endo*-2-norbornyl-2,3,3-d_3) oxalate (IV) decomposed at 290–310° to give norbornene and nortricyclene. The nmr of the norbornene product showed strong



IV



V

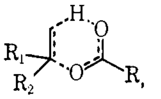
absorption at the vinyl region, thus, establishing that the norbornene isotope position labeled species is not exclusively V.

Discussion

The present results reinforce the conclusion previously drawn[2] that the liquid-phase thermal decomposition of the dialkyl oxalates of tertiary alcohols proceeds through an ionic mechanism. As evidence may be cited the deuterium isotope effects and the skeletal rearrrangements that acccompnay some of the reactions.

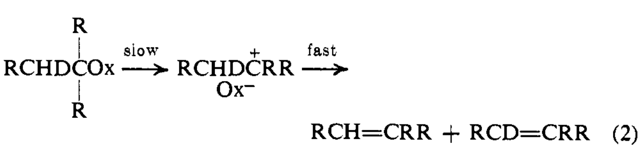
Deuterium Isotope Effects

The small k_H/k_D effects, 1.6–1.8, observed in the formation of olefins from the thermal decompositions, at 140–170°, of **1**, **2**, and **4**, argue against any extensive carbon–β-hydrogen bond breakage at the transition state. A cyclic concerted mechanism, with a transition state such as VI, would have given rise to appreciably



VI

higher isotope effects, as a k_H/k_D of about 4 is expected at such decomposition temperature for the loss of one carbon–hydrogen stretching vibration.[9] The gas-phase decomposition of acetates that go through a cyclic transition state such as VI, have isotope effects[10,11] of 1.6–1.9 at 400° and 1.5 (**3**, Table I) at 500°. At these high temperatures, the calculated k_H/k_D effect is indeed about 2. The isotope effects observed in this study are, therefore, best interpreted as arising according to (2), *i.e.*, after the rate-determining formation of the



$$\mathrm{RCHD}\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{C}}}\mathrm{Ox} \xrightarrow{\text{slow}} \mathrm{RCHD}\overset{+}{\mathrm{C}}\underset{\mathrm{Ox}^-}{\mathrm{RR}} \xrightarrow{\text{fast}} \mathrm{RCH{=}CRR} + \mathrm{RCD{=}CRR} \qquad (2)$$

ion pair.[12] The slower rates of decomposition of the dialkyl oxalates containing deuterium atoms at the α-carbons, than those of the unlabeled analog, probably

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[8] The decompositions of the bis(1,2-diphenylethyl) oxalates were carried out in refluxing quinoline, at 237°, so as to avoid any adverse reactions of the oxalic acid with the stilbenes. The ratios of norbornene to nortricyclene, especially those obtained at the higher decomposition temperatures, might not be truly representative of the kinetically controlled ratios of these two compounds as norbornene decomposes to cyclopentadiene and ethylene at temperatures above 300° [see W. C. Hendron, W. B. Cooper, Jr., and M. J. Chambers, *J. Phys. Chem.*, **68**, 2016 (1964)]. The rate of this decomposition, however, at these temperatures is sufficiently slow, $k_1 = 3.8 \times 10^{-3}$ sec^{-1} at 304°, that our results should not be appreciably affected by this side reaction.

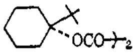
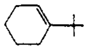
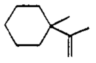
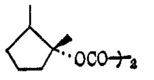
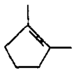
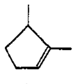
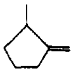
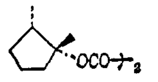
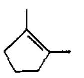
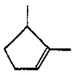
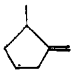
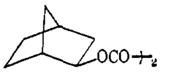
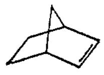
(9) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(10) C. H. DePuy, R. W. King, and D. H. Froensdorf, *Tetrahedron*, **7**, 123 (1959).

(11) P. S. Skell and W. L. Hall, *J. Am. Chem. Soc.*, **86**, 1557 (1964).

(12) In view of the catalysis of the reaction by the oxalic acid, or its half-ester, formed during the decomposition, the ion-pair picture is—strictly speaking—incorrect. The Ox⁻ might be better represented as HOx. We will continue throughout the text to use the term ion pair.

Table I. Hydrocarbon Products from the Thermal Decomposition of Dialkyl Oxalates

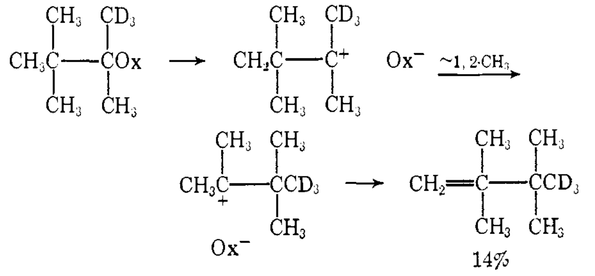
No.	Oxalate	Dec temp, °C	Olefin yield, %	Olefin	Olefin compn, mol % Vpc	Nmr
1	$(CD_3)_2CCH_3OCO\text{–)}_2$	170	80	$(CD_3)_2C{=}CH_2$		47
				$CD_3(CH_3)C{=}CD_2$		53
2	$(CH_3)_3CCCD_3CH_3OCO\text{–)}_2$	160–165	75	$(CH_3)_3CC(CD_3){=}CH_2$		55
				$(CH_3)_3CC(CH_3){=}CD_2$		31
				$(CH_3)_2C(CD_3)C(CH_3){=}CH_2$		14
3	$(CH_3)_3CCCD_3CH_3OCOCH_3$[a]	500	>80	$(CH_3)_3CC(CD_3){=}CH_2$		60
				$(CH_3)_3CC(CH_3){=}CD_2$		40
4	$CH_3CH_2CHDC(CH_3)_2OCO\text{–)}_2$[b]	143	90	$CH_3CH_2CHDC(CH_3){=}CH_2$	45	
				$CH_3CH_2CD{=}C(CH_3)_2$ $CH_3CH_2CH{=}C(CH_3)_2$	55	
5	$CH_3CH_2CH_2C(CH_3)_2OCO\text{–)}_2$	140	90	$CH_3CH_2CH_2C(CH_3){=}CH_2$	40	
				$CH_3CH_2CH{=}C(CH_3)_2$	60	
6		150–160	85		94	94
					6	6
7		135–140	92		85	
					15	
					0	
8		140–145	83		22	
					75	
					3	
9	$C_6H_5CH_2CC_6H_5HOCO\text{–)}_2$	*c*	51	$C_6H_5CH{=}CHC_6H_5$ (*trans*)		95
				$C_6H_5CH{=}CHC_6H_5$ (*cis*)		5
10	$C_6H_5CHDCC_6H_5HOCO\text{–)}_2$ *erythro*	*c*	56	$C_6H_5CD{=}CHC_6H_5$ (*trans*)[d]		90
				$C_6H_5CH{=}CHC_6H_5$ (*trans*)[d]		10
11	$C_6H_5CHDCC_6H_5HOCO\text{–)}_2$ *threo*	*c*	48	$C_6H_5CD{=}CHC_6H_5$ (*trans*)[d]		10
				$C_6H_5CH{=}CHC_6H_5$ (*trans*)[d]		90
12		245–255	*e*		94	95
					6	5

[a] These results were obtained by Dr. R. A. Taller. [b] These results were obtained by Dr. N. Hsi. [c] These compounds were decomposed in refluxing quinoline (bp 237°). [d] The *trans*-stilbene product was recrystallized from ethanol and analyzed by integrating the vinyl signal *vs.*

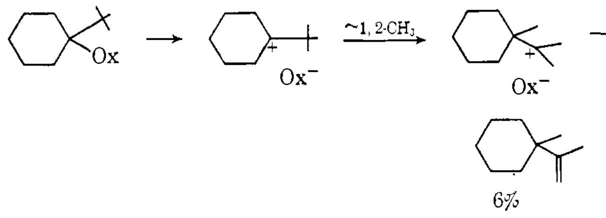
result from secondary β-deuterium isotope effects on the rate-determining step (formation of ion pair).

Rearrangements

Both bis(2,3,3-trimethyl-2-butyl-1,1,1-d_3) oxalate (**2** in Table I) and bis(1-*t*-butylcyclohexyl) oxalate (**6**) undergo 1,2-methyl migrations as evidenced by the formation of 14% 2,3,3-trimethyl-1-butene-4,4,4-d_3 and 6% 1-isopropenyl-1-methylcyclohexane, respectively (eq 3 and 4). The 14% rearrangement of the trimethyl-2-butyl system is comparable to the 11% rearrangement observed[13] in the reaction of 2,3,3-trimethyl-2-butanol-1-^{14}C with hydrochloric acid. Similar rearrangements involving 1,2-hydride shifts were observed[12] in the thermal decomposition of bis(2-cyclohexyl-2-propyl)



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}\!\!-\!\!\overset{CD_3}{\underset{CH_3}{C}}Ox \longrightarrow CH_3\overset{CH_3}{\underset{CH_3}{C}}\!\!-\!\!\overset{CD_3}{\underset{CH_3}{C^+}}\;\; Ox^- \xrightarrow{\sim 1,2\text{-}CH_3} \underset{Ox^-}{CH_3\overset{CH_3}{\underset{+}{C}}\!\!-\!\!\overset{CH_3}{\underset{CH_3}{C}}CD_3} \longrightarrow \underset{14\%}{CH_2{=}\overset{CH_3}{C}\!\!-\!\!\overset{CH_3}{\underset{CH_3}{C}}CD_3}} \qquad (3)$$



(4)

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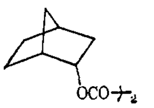
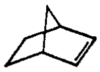
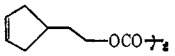
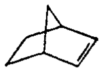
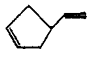
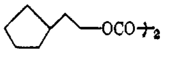
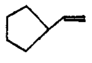
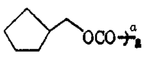
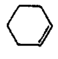
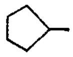
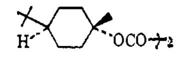
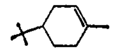
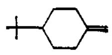
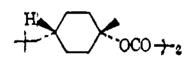
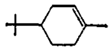
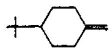
(13) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, **77**, 5558 (1955).

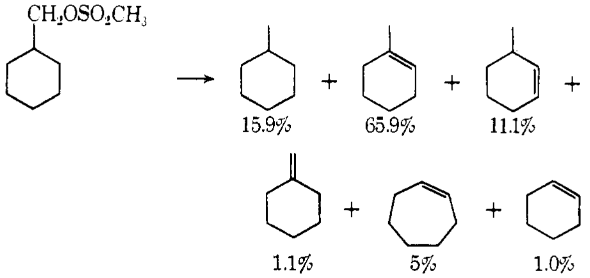
No.	Oxalate	Dec temp, °C	Olefin yield, %	Olefin	Olefin compn, mol % Vpc	Nmr
13		275–285			33	
					67	
14		320–350	*e*		3	
					70	
					27	
15		350–360	*e*		100	
16		360–370	30		52.5	
					17.5	
					5.3	
					24.7	
17	$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OCO})_2$	350–360	*e*	$\text{CH}_3(\text{CH}_2)_5\text{CH}{=}\text{CH}_2$	98	
				$\text{CH}_3(\text{CH}_2)_4\text{CH}{=}\text{CHCH}_3$	2	
18	$\text{CH}_3(\text{CH}_2)_5\text{CCH}_3\text{HOCO})_2$	320–350	*e*	$\text{CH}_3(\text{CH}_2)_5\text{CH}{=}\text{CH}_2$	44	35
				$\text{CH}_3(\text{CH}_2)_4\text{CH}{=}\text{CHCH}_3$	56	65
19		140–145	80		91	
					9	
20		175–180	60		88	90
					12	10
21	$\text{C}_6\text{H}_5\text{CCH}_3\text{HOCO})_2$	150–170	67	$\text{C}_6\text{H}_5\text{CH}{=}\text{CH}_2$	100	

the phenyl signal. The vinyl signal of the *trans*-stilbene obtained from the *threo* compound was a singlet at τ 2.88; that of the product from the *erythro* compound was a triplet at τ 2.91. [e] Exact yields from these compounds were not determined.

and bis(2-cyclopentyl-2-propyl) oxalates. We consider these results as good evidence supporting an ion-pair mechanism over a mechanism involving a cyclic transition state. The absence of any product (saturated hydrocarbons, esters) that would be associated with a free-radical mechanism is good evidence against such a mechanism under the experimental conditions. Furthermore, no 1,2-methyl rearrangements of free radicals have been reported.

Dialkyl Oxalates of Secondary and Primary Alcohols

The results do not permit an unambiguous decision to be made regarding the mechanism of the thermal decomposition of the dialkyl oxalates of all the secondary and primary alcohols that were studied. The methylcyclopentane formed in the decomposition of the bis(cyclopentylcarbinyl) oxalate (**16**) implicates a free-radical path. On the other hand, the product composition of most reactions is atypical of free-radical reactions. For example, the thermolysis of cyclohexylcarbinyl methylsulfonate, that is reportedly occurring through a free-radical mechanism, gives the products[14] given in eq 5. Yet, the thermal decomposition at 330–360°



(5)

of bis(cyclohexylcarbinyl) oxalate gives a hydrocarbon mixture whose composition is mainly methylenecyclohexane (88%) and 1-methylcyclohexene (12%).

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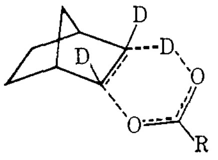
(14) R. Kotani, *Bull. Chem. Soc. Japan*, **39**, 1767 (1966).

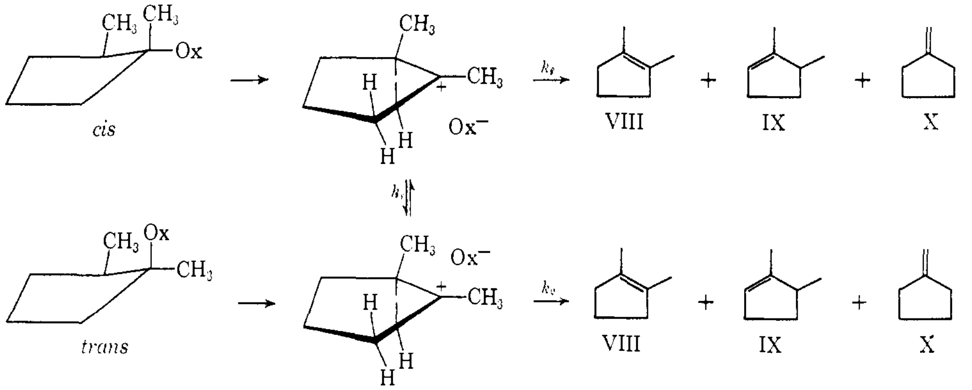
Neither cycloheptene nor any of the other products given in eq 4 were detected. The 48–56% yield of stilbenes as the only hydrocarbon product—no 1,2-diphenylethane—from the thermal decomposition of bis(1,2-diphenylethyl) oxalates, **9–11**, is not consistent with a free-radical mechanism. Nor are the products from the thermal decomposition of the oxalates of the norborneols, as the hydrocarbon product from the thermal decomposition of the peresters of the *exo*- and *endo*-norbornanecarboxylic acids is norbornane,[15] not norbornene or nortricyclene. The mechanistic path responsible for these products must, therefore, be ionic. Furthermore, the fact that the norbornene obtained from the thermal decomposition of IV is not exclusively V, argues against a cyclic transition-state mechanism involving VII as the path leading to norbornene.



VII

Ion-Pair Reorientation *vs.* Olefin Formation

Inspection of the product distributions in **7** and **8**, **10** and **11**, and **12–14** leads to the conclusion that the pyrolysis of these compounds proceeds with a high degree of product stereospecificity. In view of the evidence presented against a cyclic transition-state mechanism, a reasonable way to look at these results is in terms of the relative rates of ion-pair reorientation and olefin formation.

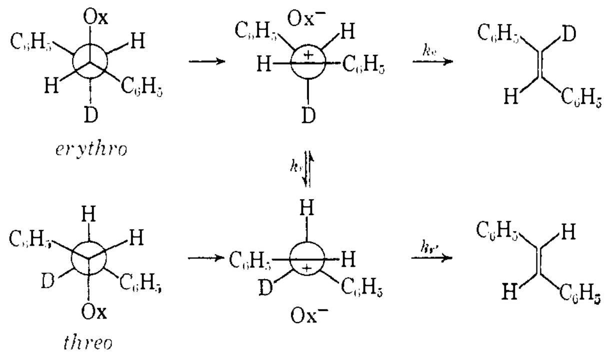


(6)

(7)

The differences in the composition of the olefins obtained from the pyrolysis of *cis*- and *trans*-bis(1,2-dimethylcyclopentyl) oxalates can be rationalized by considering (6) and (7). The *cis* compound can readily lead to all three olefins, VIII, IX, and X; the *trans* can only lead to IX and X with relative ease. The transition state leading to VIII from the *trans* compound prior to ion-pair reorientation would be quite strained. The fact that X was not detected in the reaction of the *cis* oxalate is not surprising, as the elimination of a primary hydrogen to introduce a double bond exocyclic to a five-membered ring should compete poorly with the elimination of a tertiary and a secondary hydrogen to introduce an endocyclic double bond.[16] For example, in the thermal decomposition of bis(1-methylcyclopentyl) oxalate[2] the ratio methylenecyclopentane/1-methylcyclopentene is only 7/93. The 22% yield of VIII from the reaction of the *trans* compound cannot all arise through the first ion pair of this compound. For example, the pyrolysis of the corresponding acetate,[16] which proceeds through a cyclic transition state, gives about 5–10% of VIII. Thus, about 10–15% of VIII formed from the thermal decomposition of the *trans* compound probably arises after ion-pair equilibration. Although the results do not permit an exact evaluation of k_e/k_r, they suggest that the ion-pair collapses to give olefins about five to ten times faster than it reorients itself.

The ion-pair mechanism adequately accommodates the results obtained from the thermal decomposition of *erythro*- and *threo*-bis(1,2-diphenylethyl-2-*d*) oxalates (**10** and **11**, Table I); it requires that the rate of ion-pair collapse to give *trans*-stilbene, k_e, be about nine times times faster than the rate of ion-pair reorientation, k_r (eq 8 and 9). Our experimental technique, integration of the vinyl *vs.* the phenyl regions of the product *trans*-stilbenes, was not accurate enough to determine any isotope effects in the elimination step.[17] The product distributions obtained from bis(*exo*-2-norbornyl) (**12**), bis(*endo*-2-norbornyl) oxalate (**13**), and bis[2-(Δ^3-cyclopentenyl)ethyl] oxalate (**14**) are consistent with the ion-pair mechanism. For example, the anion in the ion pair from the *exo* compound is in a position favorable for removal of a proton from C-3 or C-7 to give norbornene, but unfavorable for removal of a



(8)

(9)

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[15] M. M. Martin and D. C. DeJohgh, *J. Am. Chem. Soc.*, **84**, 3526 (1962); P. D. Bartlett and R. E. Pincock, *ibid.*, **84**, 2445 (1962).

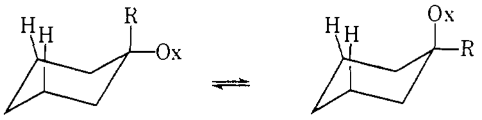
[16] It is worth pointing out that the pyrolysis of the corresponding acetate, which proceeds through a cyclic transition state, yields 20–30% of X, according to D. H. Froensdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

[17] D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953) observed such an isotope effect in the gas phase pyrolysis of the corresponding acetates. The *trans*-stilbene from the *erythro*-acetate contained 95.6% d_1 and 4.4% d_0; that from the *threo*-acetate contained 73.6% d_0 and 26.4% d_1.

proton from C-6 to form nortricyclene. In the ion pair from the *endo* compound, it is in a position favorable for removal of a proton from C-6 and C-3 to give nortricyclene and norbornene, respectively; and in the ion pair from the Δ^3-cyclopentenylethyl compound, in a position favorable for removal of a proton from C-6 to give nortricyclene. Furthermore, the ion-pair mechanism, as contrasted to a mechanism involving a cyclic transition state, also rationalizes the formation of norbornene with vinylic protons from the decomposition of IV. However, in view of the uncertainties regarding the extent to which norbornene and nortricyclene have equilibrated at these temperatures under the reaction conditions, any conclusion regarding the relative rates of ion-pair reorientation and ion-pair collapse to products would be premature and unwarranted by the results.[18]

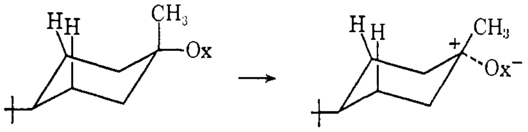
Conformational Effects of Cyclohexyl Ring Systems

It was shown[2] that the rates of decomposition of bis(1-methylcyclohexyl) and bis(1-ethylcyclohexyl) oxalates were faster than that of bis(1-isopropylcyclohexyl) oxalate. This fact could be attributed to the effect of R on the relative populations of XI and XII. For example, since XI would ionize faster than

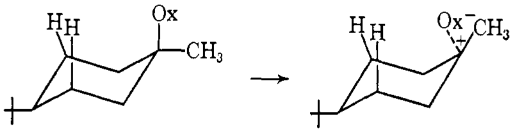


XI XII

XII by relieving the two 1,3-alkyl-hydrogen interactions, the isopropyl compound should decompose more slowly than the other two on account of the ratio XI/XII being smaller when R is isopropyl than when it is methyl or ethyl. The correctness of this interpretation is supported by the relative rates of decomposition of the bis(*cis*-1-methyl-4-*t*-butyl) and bis(*trans*-1-methyl-4-*t*-butyl) oxalates (**19** and **20**). The *cis* compound, XIII, indeed decomposes faster than the *trans*, XIV.



XIII



XIV

Experimental Section

Preparation of alcohols used in this study was carried out by well established procedures. The *erythro*- and *threo*-1,2-diphenylethanols-2-*d* were prepared by lithium aluminum deuteride reduction of *trans*-stilbene and *cis*-stilbene oxides, respectively.[17]

Dialkyl oxalates reported in this study were prepared in 50–85% yields according to the procedure described in ref 2. Most of them were oils or low-melting solids. The only oxalate melting above 75° was bis(2,3,3-trimethyl-2-butyl-1,1,1-d_3) oxalate, whose melting point was 143–144°.

Thermal decomposition of the oxalates was done according to method A described in ref 2. Those derived from tertiary and benzylic alcohols decomposed easily at 140–170° requiring about 5 min to complete the reaction. Those derived from secondary alicyclic alcohols required heating at 250–300° for about 60 min; and those derived from primary aliphatic alcohols required prolonged heating, about 4 hr, at temperatures of 330–370°, in order to obtain enough distillate for analysis.

Product analysis of the alkene mixtures was done by gas chromatography, nuclear magnetic resonance, and infrared spectroscopy. Gas chromatographic analyses of the alkene mixtures were obtained by using an Aerograph A-90 vapor phase chromatography unit with a 6-ft Apiezon L on Chromosorb W column. All nmr spectra reported were taken with a Varian A-60 nmr spectrometer.

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[18] The details of the ion-pair mechanism, including internal return, are under investigation with suitable deuterium and oxygen-18 labeling experiments.