Communications to the Editor

Cyclic Peroxyesters. III.[1] Kinetics and Products of the Rearrangement of Thermally Generated Oxygen Diradicals[2]

Sir:

The thermal decomposition of β-methyl-β-phenyl-β-peroxypropiolactone has been shown to lead to propiophenone and phenylacetone as the principal products.[3] Control experiments showed that α-methylstyrene oxide and α-methoxystyrene are not precursors to the above ketones. The fact that propiophenone product predominated over phenylacetone by a factor of about five was taken as evidence that the thermal decomposition of this cyclic peroxyester proceeded *via* a free-radical 1,2 migration of the β-methyl group (propiophenone product) and β-phenyl group (phenylacetone product). Preferential 1,2-alkyl migrations over phenyl migrations of thermally generated free radicals are unknown in the literature.[4] On the other hand, recently the photolysis of α,β-epoxy ketones has been shown to undergo preferential alkyl over phenyl 1,2 migration.[5] In this communication we present evidence that the thermolysis of a series of β-alkyl-β-phenyl-β-peroxypropiolactones involves first the generation of a transient oxygen diradical which subsequently undergoes preferential 1,2 shift of the β-alkyl substituent over the phenyl group.

In Table I are listed the quantitative data for the rearrangement ketones $C_6H_5COCH_2R$ and $C_6H_5CH_2COR$. The product studies were carried out by means of vapor phase chromatography employing the internal standard technique. As the ratios of alkyl to phenyl rearrangements indicate, in all cases the alkyl 1,2 shift predominates over phenyl, the order being isopropyl > benzyl > ethyl > methyl > phenyl.

Table I. Product Data of the Thermal Decomposition of β-Alkyl-β-phenyl-β-peroxypropiolactones

	Yield,[a] %		
Alkyl group	$C_6H_5COCH_2R$	$C_6H_5CH_2COR$	Ratio
Methyl	77.4 ± 1.0	13.9 ± 0.10	5.56
Ethyl	89.7 ± 1.3	6.18 ± 0.13	14.5
Benzyl	77.5 ± 0.7	2.12 ± 0.06	36.5
Isopropyl	79.6 ± 0.6	1.45 ± 0.01	55.0

[a] The remainder of the products are $C_6H_5COCH_3$ and C_6H_5COR, making a total balance of 98–100% in all cases.

The kinetic data are collected in Table II, listing the unimolecular rate constants and the activation enthalpies and entropies. An error analysis of the activation parameters according to the procedure of Petersen and coworkers[6] showed that $\Delta H^{\ddagger}$ varied by 0.6 kcal/mol and $\Delta S^{\ddagger}$ by 1.9 eu. Therefore, within the experimental error the activation parameters are independent of the β-alkyl group structure.

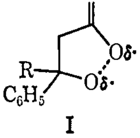
Table II. Kinetic Data of the Thermal Decomposition of β-Alkyl-β-phenyl-β-peroxypropiolactones[a]

Alkyl group	Temp, °K	$k \times 10^5$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
Methyl	397.6	3.18 ± 0.03	31.7	+0.1
	373.2	0.216 ± 0.01		
Ethyl	397.6	6.81 ± 0.10	31.2	+0.3
	373.2	0.483 ± 0.01		
Isopropyl	397.6	13.8 ± 0.2	31.1	−1.0
	373.2	1.08 ± 0.01		
Benzyl	397.6	17.5 ± 0.1	31.0	−0.8
	373.2	1.26 ± 0.01		

[a] In carbon tetrachloride, following the rate of disappearance of the characteristic 1810 cm^{-1} carbonyl band of the peroxylactone on the Infracord 237B.

Bartlett and Hiatt in their classical work on the thermal decomposition of acyclic peroxyesters have shown that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are a funtion of the structure of the alkyl group bonded to the acyl carbon.[7] The more stable the alkyl radical formed, the lower the activation enthalpy and the more negative the activation entropy. Clearly, decarboxylation has proceeded more significantly in the activated complex of the benzyl compound, for example, compared to the methyl compound. This implies a transition state with a large degree of multiple bond fragmentation for the benzyl group. Similarly, the thermal decomposition of acyl peroxides[8] and the solvolysis of *p*-nitroperbenzoates[9] reveal as well a pronounced interplay between alkyl group structure and reactivity.

The relative rate constants of the above systems and of the β-peroxylactones are summarized in Table III. From this table it is immediately apparent that the rupture of the peroxide bond in the cyclic peroxyester is not assisted in the transition state by the fragmentation of the incipient alkoxy radical site or by decarboxylation at the carboxylate radical site. On the basis of this kinetic evidence the thermolysis of β-peroxylactones is proposed to involve unassisted breakage of the peroxide bond leading to an oxygen diradical *via* transition-state I before any gross structural changes have taken place. Concerted transposition of the β-alkyl group as the peroxide bond is stretched apart *via* transition-state II is unlikely. The relatively large



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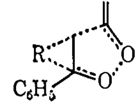

II

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Table III. Relative Rates as a Function of Alkyl Structure

Alkyl group	RCO_3-*t*-Bu[a]	$ArCO_3$-CR<[b]	$(RCO_2)_2$[c]	β-Peroxylactones
Methyl	1	1	1	1
Ethyl		45	2	2.1
Isopropyl	50	2940	1490	4.3
Benzyl	300	1630	1695	5.5

[a] Reference 7. [b] Reference 9. [c] Reference 8.

Table IV. Migration Aptitudes as a Function of Substituent Structure

Substituent (R)	$ArCO_3CR<$[a]	C_6H_5COR[b] and CH_3CO_3H	$>CRCH_2OTs$[c]	C_6H_5COR[d] and CH_2N_2	$>CROCl$[e]	β-Peroxylactones
Phenyl	1	1	1	1	1	1
Methyl	9.1×10^{-6}	Very small	3×10^{-3}	6.2×10^{-2}	1.2×10^{2}	5.56
Ethyl	4.1×10^{-4}	7×10^{-2}		6.5×10^{-2}	8.0×10^{4}	14.5
Benzyl	1.5×10^{-2}	1.3	4.5×10^{-4}	3.9×10^{-2}	1.1×10^{5}	36.5
Isopropyl	2.6×10^{-2}	1.9	1.6×10^{-2}	3.3×10^{-2}	4.0×10^{6}	55.0

[a] Reference 9. [b] Reference 10. [c] Reference 11. [d] Reference 12. [e] Reference 13.

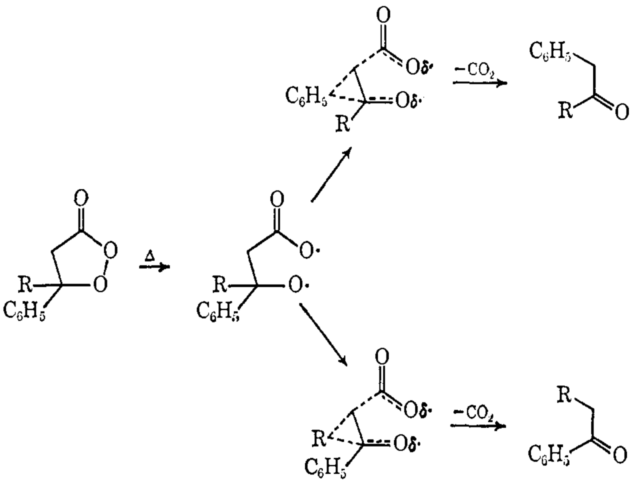
and more significantly constant activation enthalpies ($\Delta H^{\ddagger}$ = 31.0–31.7 kcal/mol) and the effectively zero entropies of activation ($\Delta S^{\ddagger}$ = −1.0 to +0.3 eu) seem more reasonable for transition-state I in which the activated complex resembles structurally the reactant state rather than transition-state II in which the activated complex resembles structurally the product state. Unfortunately, no thermokinetic data are available on related systems to defend this argument on quantitative grounds.

Of considerable mechanistic value are the ratios of alkyl to phenyl rearrangement in Table I. For comparison we have summarized in Table IV the migration aptitudes of a number of reactions. In the solvolysis of *p*-nitroperbenzoates[9] (column 2 in Table IV) and in the Baeyer–Villiger oxidation of aryl alkyl ketones[10] (column 3 in Table IV) the rearranging group migrates to a positive oxygen terminus, while in the solvolysis of neopentyl tosylates[11] (column 4 in Table IV) and in the reaction of diazomethane with aryl alkyl ketones[12] (column 5 in Table IV) the group migrates to a positive carbon center. The relative ordering of the β substituents in the peroxylactones (column 7 in Table IV) is clearly distinct from the above-cited rearrangements. Therefore, the rupture of the peroxide bond is homolytic in character, leading to an oxygen diradical, rather than heterolytic, leading to a dipolar ion.

In fact, the only data which reproduce the migration sequence of the peroxylactones is the relative ease of β scission of alkoxy radicals derived from hypochlorites[13] (column 6 in Table IV). Consequently, in the oxygen diradical produced from the cyclic peroxy ester the principal driving force for the transposition of the β substituent stems from the fragmentation at the alkoxy center. However, there is one important difference. In the oxygen diradical the discrimination among the β substituents is several orders of magnitude less than in the simple alkoxy radicals derived from the hypochlorites. Therefore, the β substituent in the oxygen diradical derives considerable help from the incipient radical site developing at the α carbon due to concurrent decarboxylation at the carboxylate radical center. This novel free-radical "push–pull" transposition of the β substituent, that is, a pushing action due to β scission at the alkoxy site and pulling action due to simultaneous decarboxylation at the carboxylate site, appears to be the most efficient mode of energy dissipation of thermally generated oxygen diradicals.

On the basis of the kinetic and product data presented here, the mechanism of the thermal decomposition of β-peroxylactones is proposed to involve first the formation of an oxygen diradical with no major structural reorganization in the transition state. Subsequently, the oxygen diradical undergoes a "push–pull" triggered migration of the β substituent (Scheme I). In the following communication[14] we describe stereochemical evidence in support of this interpretation.

Scheme I. Mechanism of the Thermal Decomposition of β-Alkyl-β-phenyl-β-peroxypropiolactones



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