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DECOMPOSITION OF DIACYL PEROXIDE—VII

OXYGEN SCRAMBLING IN l-APOCAMPHORYL PEROXIDE AND RELATED DIACYL PEROXIDES—GENERAL REMARKS ON THE RELATIONSHIP BETWEEN THE STABILITY OF ACYLOXY RADICAL AND AMOUNTS OF CAGE RECOMBINATIONS AND ESTER FORMATION IN THE DECOMPOSITION OF DIACYL PEROXIDE

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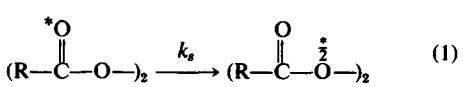
Abstract—Thermal decomposition of 1-apocamphoryl peroxide has been investigated in CCl_4 using the ^{18}O-labelled peroxide. 1-Apocamphoryl peroxide is the first example which undergoes radical decomposition, carboxy-inversion and oxygen scrambling reaction between carbonyl and peroxidic O atoms in the peroxide in comparable rates. The major product of the decomposition was the inversion product, 1-apocamphoryl 1-apocamphyl carbonate (52·5%), and only a minute amount of 1-apocamphyl 1-apocamphorate (2·2%) was formed. The rates of oxygen scrambling were found to be $2{\cdot}70 \pm 0{\cdot}21 \times 10^{-6}$ (55°), $1{\cdot}85 \pm 0{\cdot}12 \times 10^{-5}$ sec^{-1} (70°) and $9{\cdot}33 \pm 0{\cdot}18 \times 10^{-5}$ sec^{-1} (84·3°) (E_a, 27·5 Kcal/mol, $\Delta S\ddagger$, −2·3 e.u.). The cage recombination mechanism was suggested for the oxygen scrambling and the amounts of cage recombination of 1-apocamphoryloxy radical pair were calculated as 65% (55°), 60% (70°) and 52% (84·3°). The yield of the ester and the amount of cage recombination of geminate acyloxy radical pair were rationalized in terms of the stability of acyloxy radicals formed in the cage.

INTRODUCTION

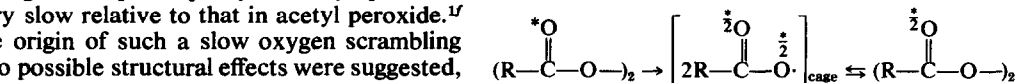
Oxygen scrambling in diacyl peroxides has recently drawn considerable attentions since Martin *et al.* found an oxygen scrambling between carbonyl and peroxidic O atoms in acetyl peroxide (Eq. 1) in 1967.[1]



(1)

In the previous paper we reported that the oxygen scrambling in 1-apocamphoryl benzoyl peroxide **1** is very slow relative to that in acetyl peroxide.[1f] For the origin of such a slow oxygen scrambling in **1**, two possible structural effects were suggested, i.e., (1) specificity of phenyl group, (2) specific feature of the peroxide which undergo decomposition through not only radical process but also carboxy-inversion process.[1f]

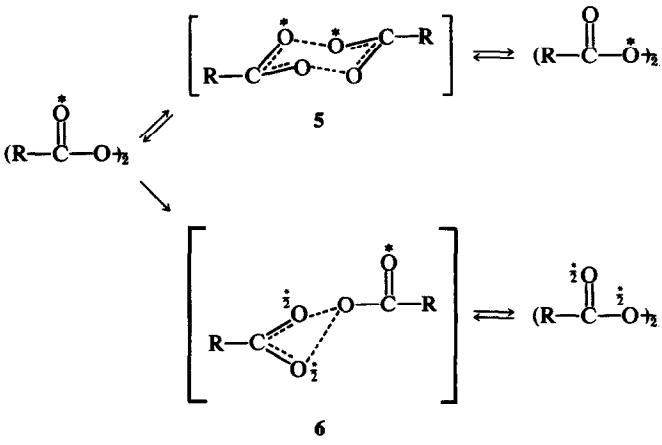
Earlier, Kharasch *et al.* reported that the thermal decomposition of 1-apocamphoryl peroxide **2** give an ester, 1-apocamphyl 1-apocamphorate **3**, in an anomalously high yield, and claimed the radical mechanism.[2] Our early observations also suggested that the high yield of ester formation is usually associated with the carboxy-inversion.[1f,3] Therefore, the peroxide **2** seems to be a good model to clarify these points concerning the oxygen scrambling in the peroxide. Three mechanisms have been suggested for the oxygen scrambling (Eq. 1), i.e., the cage recombination of acyloxy radical pair[1a,c] and the two kinds of sigmatropic rearrangements (Eqs. 3, 4).[1d] Martin *et al.* proposed the radical cage mechanism (Eq. 2) for the oxygen scrambling in both acetyl[1a] and benzoyl peroxide,[1c] based on several experimental observations which include the effect of viscosity illustrate the importance of the cage effect.[4]



(2)

Meanwhile Goldstein *et al.* suggested the importance of the [3, 3] sigmatropy (Eq. 3) and [1, 3] sigmatropy (Eq. 4) in the oxygen scrambling in acetyl peroxide, based on their detailed kinetics of ^{18}O-scrambling.[1d]

The purpose of this work is to discuss the mechanism of the oxygen scrambling (Eq. 1) on the basis of the kinetic observations of the decomposition and the oxygen scrambling in **2**.



(3)

(4)

5

6

RESULTS

A. Products and kinetics of the decomposition

Earlier Kharasch *et al.* reported that the thermal decomposition of **2** in CCl_4 gave the ester **3** (50%), 1-apocampyl chloride (36%), 1-apocamphoric acid (5%) and 1-apocamphyl dimer (9%).[2] We have reinvestigated thermal decomposition of **2** in CCl_4 (0·02 M initial conc) at various temperatures. All the decompositions were carried out in degassed sealed tubes.

From the reaction mixture the inversion product **4**, 1-apocamphoryl 1-apocamphyl carbonate (m.p. 169°), 1-apocamphyl chloride (m.p. 170–171°) and 1-apocamphyl dimer (m.p. 216–217°) were isolated and identified, however, no acidic substance was obtained. The yields of **3** and **4** at various temperatures were measured by following the spectral change after heating the mixture for 7 half lives of **2** and the yield of **3** was found to be very low (2·2%). Temperature of the reaction did effect very little on the yield of **3**. Prolonged reaction time up to 14 half lives of **2** did not change the intensities of the carbonyl absorptions of both **3** and **4**. This means that 1-apocamphoryl-1-apocamphyl carbonate **4** does not decompose to give the ester **3** under the condition.

Kinetics of the decomposition were followed by the iodometric titration of the remaining peroxide. Good first order specific rates (k_d) were obtained over the range up to 80% completion of the decomposition. The apparent rates of the carboxy-inversion (k_i) and the radical (k_r) processes of the decomposition of **2** are calculated from the proportional allotment of k_d to the product ratios of the two paths. These results are summarized in Table 1.

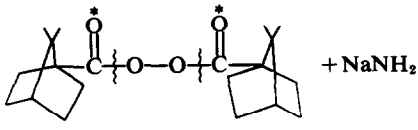
Table 1. Kinetics of Thermal Decomposition of 1-Apocamphoryl peroxide **2**

Temp (deg)	$k_d \times 10^6$ (sec^{-1})	$k_i \times 10^6$ (sec^{-1})	$k_r \times 10^6$ (sec^{-1})	Yield of **4** (%)
55·0	3·38 ± 0·09	1·95[a]	1·43[a]	57·6[a]
65·3	14·3 ± 0·01	7·94	6·36	55·5
70·0	27·6 ± 0·06	15·0	12·6	54·5
75·3	56·0 ± 0·3	30·5	25·5	54·5
80·0	104 ± 0·5	54·1	50·2	52·0
84·3	180 ± 1	94·7	85·6	52·0
90·0	348 ± 6	177	171	50·8
95·0	657 ± 1	329	328	50·0
E_a Kcal/mol		31·0 ± 0·1	30·1 ± 0·1	31·9 ± 0·1
$\Delta S^{\ddagger}$ e.u.		+8·5 ± 0·2	+4·8 ± 0·3	+9·8 ± 0·3

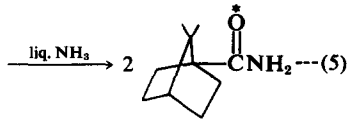
[a]Calculated value from the activation parameters.

B. Kinetics of ^{18}O-scrambling in 2

Specifically carbonyl-^{18}O-labelled 1-apocamphoryl peroxide **2a** was prepared in the usual manner.[3] The specificity of the ^{18}O-labelling in **2a** was examined by the following cleavage reaction.



2a



(5)

5

1-Apocamphoramide **5** obtained from the reaction in eq. 5 was then subjected to the routine ^{18}O-analysis and the results are summarized in Table 2 together with the results of the preliminary test for the ^{18}O-scrambling in **2a**.

A solution containing 0·02 M of **2a** in CCl_4 was heated in a bath (70°) with continuous bubbling of

Table 2. Specific label in **2a** and preliminary test for ^{18}O-scrambling in **2a** at 70°, analyzed by cleavage reaction shown in eq. 5

Origin of 1-apocamphoramide **5**	^{18}O-Content (excess atom %) Run 1	Run 2
1-Apocamphoryl chloride[a]	2·63	2·31
2a, original peroxide	2·65	2·31
2a, recovered after heating for 2 hr	2·60	
2a, recovered after heating for 6 hr	2·31	

[a]Starting material for the preparation of **2a**.

N_2 stream. After heating for 2 and 6 hr, the remaining peroxide was recovered, purified and cleaved by the reaction shown in Eq. 5. The data in Table 2 show that no oxygen scrambling takes place during both processes, i.e., the preparation of **2a** and the cleavage reaction in Eq. 5. However, the ^{18}O-content of the CO group in **2a** is somewhat reduced upon prolonged heating.

Thereupon, the rate of the scrambling of the CO-^{18}O-label to the peroxidic O atom of **2a** was measured under the same condition applied for the kinetics of the decomposition by following the decrease of ^{18}O-content of the carbonyl O atom of the recovered peroxide using the reaction in Eq. 5 at various temperatures. Results are shown in Table 3.

DISCUSSION

As was expected, the major product of decomposition of **2** is the inversion product **4** but not the ester **3**. The data in Tables 1 and 3 reveal that three reactions take place concurrently with comparable rates (k_r, k_i and k_s) during the thermal decomposition of **2**.

We reported previously that decomposition of **1** at 70° in CCl_4 proceeds with the rate of $1{\cdot}74 \times 10^{-5}$ sec^{-1} and gives 51% yield of the inversion product and 20% yield of the ester.[1f] Comparison of the data of the thermal decompositions of **1** and **2**, reveals that the extents of contribution of the carboxy-inversion process are nearly identical and both peroxides decompose in nearly identical rates. However, the rates of the oxygen scrambling and the yields of esters are quite different.

One of the most striking features is that the oxygen scrambling in **2** proceeds 100 times faster than that in **1**. This appears to suggest that the slow oxygen scrambling in **1** relative to that in acetyl peroxide is not due to the apocamphyl group, but phenyl group is responsible for the slow oxygen scrambling in **1**.[1f]

Another striking feature is that decomposition of **1** gives an ester, 1-apocamphyl benzoate, in 20% yield, while that of **2** gives the ester **3** in only 2·2% yield.

Meanwhile, the radical process of the decomposition of the peroxide may be shown by the following Scheme 1.[1a,5]

In the radical decomposition process, since both oxygen scrambling in the peroxide and the ester formation take place in the solvent cage, the reactivity of the geminate acyloxy radical pair **7** formed in the solvent cage should determine both the ease of oxygen scrambling and the yield of ester.

A. Formation of ester

It is well known that ester is often the secondary product formed by the decomposition of inversion product.[3] However, in view of the fact that in the decompositions of both **1** and **2** the corresponding inversion products do not decompose under the reaction condition,[1f] these esters are considered to be formed via the radical cage reaction. Actually the ^{18}O-tracer experiment of the formation of the ester from **1** support this mechanism.[6] Consequently the yields of esters via the radical process are calculated as 40% for **1** and 4·6% for **2**. Application of the steady state theory to **7** and **8** gives Eq. 6.

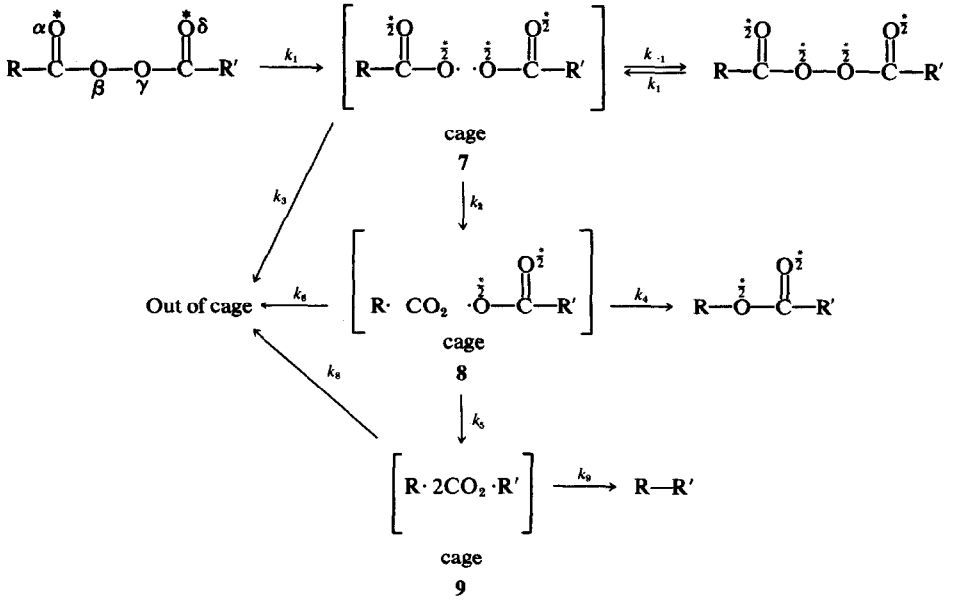
$$\text{Ester yield in radical process} = \frac{k_2 k_4}{(k_4 + k_3)(k_4 + k_5 + k_6)} \qquad (6)$$

Since recombination of R· and R'CO_2· forms a stable covalent bond, this process would require almost no activation energy. Therefore, the struc-

Table 3. Scrambling of the CO-^{18}O-label to the Peroxidic O Atom of **2** in CCl_4

Temp (deg)	$k_s \times 10^6$ (sec^{-1})	n[a]	k_r/k_s	Cage return %[b] of apocamphoryloxy radical pair	Viscosity of solvent (cP)
55·0	2·70 ± 0·12	4	0·53	65·4	0·62
70·0	18·5 ± 1·2	6	0·68	59·5	0·55
84·3	93·3 ± 1·8	6	0·92	52·1	0·45

[a]Number of independent samples subjected to the ^{18}O-analysis.
[b]The value is based on the postulation that the radical cage mechanism is the only process of the ^{18}O-scrambling.



SCHEME 1

tural effect on the process of combination of **8** (k_4) would have little effect on the yield of ester as compared to the structural effect on decarboxylation (k_2, k_5). Since the diffusion process would not be effected much by the structural change in radicals, the yield of the ester is mainly determined by the rates of decarboxylation, namely the stability of acyloxy radicals.

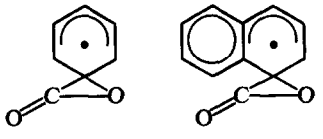
Based on the stabilities of the geminate acyloxy radicals **7**, the peroxide may be classified into the following three cases.

Case 1. Both two acyloxy radicals are unstable. Since the decarboxylation of both acyloxy radicals proceed rapidly, **7** should easily change to **9** and the yield of ester must be low.

Case 2. One of the acyloxy radicals is unstable and another is stable. Since the unstable acyloxy radical readily decarboxylates while the life time of the other stable one is long, **8** should be easily formed and the yield of ester must also be high.

Case 3. Both two acyloxy radicals are stable. Since both acyloxy radicals would diffuse out from the cage prior to decarboxylation, the yield of ester must be low.[7]

Meanwhile, benzoyloxy radical is well known to be a quite stable acyloxy radical, for example, benzoyloxy radical formed by the decomposition of benzoyl peroxide can be quantitatively scavenged by I_2.[8] However, acetoxy radical, a typical aliphatic one, is quite unstable, as illustrated by the fact that none of acetoxy radical can be scavenged with I_2 during the decomposition of acetyl peroxide.[4b] The considerable difference of stability between aroyloxy radical and the aliphatic one is well exemplified in the activation energies of decarboxylation, i.e., benzoyloxy radical (17 Kcal/mol)[9] and acetoxy radical (5–7 Kcal/mol).[4e,10] One attractive explanation of such a remarkable stability of benzoyloxy radical is the participation of phenyl group as shown below.[11] Leffler suggested that α-naphthyl group participate to stabilize α-naphthoyloxy radical as shown in **11** in the course of the decomposition of α-naphthoyl peroxide.[12]



10 **11**

Based on these considerations the relationship between the stability of acyloxy radical and the yield of ester may be summarized in Table 4. The peroxide **2** is a typical example of the case 1 while the peroxide **1** is a typical example of the Case 2. In fact, our experimental results are best explained by the postulation in Table 4. Several typical examples listed in Table 5 actually support our postulation.

B. Oxygen scrambling in peroxide

Our experimental results can be rationalized in terms of the radical cage mechanism as mentioned below.

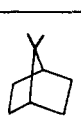
(1) *Viscosity of medium.* The viscosity dependency of decomposition of peroxide has been well documented.[4]

Table 4. Structural effect on ester yield and oxygen scrambling reaction in the thermal decomposition of diacyl peroxide

Case	Structure of substituent[a] in R—C(=Oα)—O—O—C(=Oδ)—R′ : Oα	Oδ	Yield of ester	Rate of[b] oxygen scrambling (k_s)	Cage return % of geminate acyloxy radical pair (C_a)
1	Al	Al	Low	Fast	High
2	Al	Ar	High	Slow	Low
3	Ar	Ar	Low	Slow	Low

[a]Al signifies aliphatic group and Ar signifies aromatic group.
[b]This posturation hold with the peroxides which have k_1 values of nearly similar order.

Table 5. Ester yield in radical process, oxygen scrambling in peroxide and cage return of the acyloxy radical pair 7, in thermal decomposition of diacyl peroxide

Peroxide αO δO R—C—O—O—C—R′		Solv	Temp (deg)	$k_r \times 10^5$[a] (sec^{-1})	$k_s \times 10^5$[b] (sec^{-1})	Cage return % of radical pair 7	Ester yield (%)	Ref
		CCl_4	80	5·40	6·20[c]	55		This work
			70	1·26	1·85	59·5	4·6	This work
	Ph	CCl_4	70	0·86	α: *ca* 0·07 δ: *ca* 0·01	*ca* 7	41	If
Ph	Ph	i-Octane	80	2·7	0·13	4·3	3	1c
		Mineral oil	80	2·9	0·63	17·8		1c
α-Naphthyl	α-Naphthyl	C_6H_6	60	18			10	12
Me	Me	i-Octane	80	7·2	4·4	38	15	1a
$Ph(CH_2)_4$	$Ph(CH_2)_4$	CCl_4	77·1	7·05			12	13
Me	Ph	C_6H_6	78		α: *ca* 1·1 δ: *ca* 0·2	*ca* 14		1e 1e
i-Pr	i-Pr	CCl_4	60	57·5			21	14
i-Pr	Ph	CCl_4	60	118			100[d]	5
$PhCH_2$	$PhCH_2$	C_6H_5Me	0			*ca* 22	15	
$PhCH_2$	*p*-Br-Ph	C_6H_6	30				64	16

[a]Apparent rate of radical process of decomposition.
[b]Rate of oxygen scrambling.
[c]The value is calculated based on the value of activation parameters.
[d]Total yield of the ester (9%) and benzoic acid, since benzoic acid would be produced by the disproportionation of radicals in the cage prior to ester formation.

The data in Table 3 reveal that the amount of cage recombination of geminate 1-apocamphoryloxy radical pair increase with the increase of viscosity of medium* in keeping with Martin's observations[1c] (benzoyl peroxide, see Table 5) and that of Szwarc.[4a]

*The cage mechanism is the dominating process for the oxygen scrambling in **2**, since our data in Table 3 is consistent with the theory of cage reaction R. M. Noyes, *Progress in Chemical Kinetics* Vol. 1, p. 129; Pergamon Press, New York (1961); O. Dobis, J. M. Peason and M. Szwarc, *J. Am. Chem. Soc.* **90**, 278 (1968), i.e., the plots of $1/p$ vs. $T^{1/2}/\eta$ fall on linear line.

(2) *Activation parameters.* From the data in Table 3 the activation parameters of oxygen scrambling in **2** are calculated as E_a; 27·5 ± 0·2 Kcal/mol, $\Delta S\ddagger$; −2·3 ± 0·7 e.u. Our observed $\Delta S\ddagger$ value is well consistent with the radical cage mechanism which requires less $\Delta S\ddagger$ than the radical decomposition process, since the obtained value of −2·3 e.u. is between that of radical decomposition (+9·8 e.u.) and the other typical [3, 3] sigmatropic rearrangements (*ca* − 10 e.u.).[17]

Apparent activation energy of the radical decomposition of **2** is larger than that of oxygen scrambling by 4·4 Kcal/mol which is nearly iden-

tical to the difference in apparent activation energy (4 Kcal/mol) for the decomposition of acetyl peroxide in CCl_4 and in gas phase.[4a]

(3) *Structural effect.* It is expected that phenyl group stabilizes the transition states of sigmatropic rearrangement (**5** and **6**) by resonance participation. However, the data in Table 5 clearly show that the substitution of R group in $(R—\overset{\overset{O}{\|}}{C}—O—)_2$ by phenyl group reduces the k_s. If [3, 3] sigmatropy is the dominating process for the oxygen scrambling in the peroxide, k_s values of oxygen scrambling of both α-oxygen and δ-oxygen must be identical in the case of unsymmetrical peroxides (Table 5).

In the light of above consideration, the radical cage recombination is considered to be the dominating process in the oxygen scrambling in the peroxide. Therefore, the specific nature of phenyl group to reduce the k_s must be rationalized in terms of the geminate acyloxy radical pair **7** in the solvent cage.

The cage return (C_s) of **7** is represented by the Eq. 8.

$$C_s = \frac{k_{-1}}{k_{-1}+k_2+k_3} \qquad (8)$$
$$k_s = k_1 C_s$$

While recombination of **7** gives the highly energetic peroxide bond, recombination of the stabilized aroyloxy radicals would require some energy though small.[18]

In the Case 1 peroxide, since two acyloxy radicals are unstable, energy required for the process would be nearly zero and hence k_{-1} should be very large. Consequently the C_s should become large in spite of the facile decarboxylation of the acyloxy radical. In the Case 3 peroxide, since recombination of two aroyloxy radical (k_{-1}) is slow, the C_s must be small.[19] In the Case 2 peroxide, since k_{-1} is relatively small and k_2 is large, the C_s must also be small. The outcomes of the postulations are summarized in Table 4. These postulations can explain the anomalously large difference between k_s of **1** and that of **2** and all the data of oxygen scrambling listed in Table 5.

EXPERIMENTAL

Preparation of 1-*apocamphoryl peroxide* **2**. The peroxide was prepared by the reaction between 1-apocamphoryl chloride and sodium peroxide in the usual manner.[3] Crude **2** was dissolved in a minium volume of ether, then MeOH was added slowly and the soln cooled with an ice bath. After 1 hr clear prisms separated were filtered and washed with MeOH, m.p. 110° (dec); IR, 1766, 1789 cm^{-1} (C=O); NMR, 1·1 ppm (12 H, s, CH_3), 1·0, 2·5 ppm (18 H, m): (Found: C, 72·07; H, 9·19. Calc. for $C_{20}H_{30}O_4$: C, 71·82; H, 9·04%).

Preparation of 1-*apocamphoryl* 1-*apocamphyl carbonate* **4**. To a soln of 186 mg 1-apocamphoryl chlorocarbonate[21] in 5 ml abs. ether, a mixture of 101 mg Et_3N, 168 mg 1-apocamphoric acid and 10 ml ether was added dropwise with ice-cooling and stirring. The mixture was kept under the same condition for 1 hr and then poured onto 20 g crushed ice. The organic layer was separated, washed with cold dil HCl, cold $NaHCO_3$ aq, and cold water, dried ($MgSO_4$) and then the solvent was evaporated to obtain dry crude crystals. Remaining white crystals were recrystallised from hexane by dissolving at room temp followed by cooling down to −50°. Three recrystallisations yielded white prisms, m.p. 169°; IR, 1756, 1800 cm^{-1} (C=O). (Found: C, 71·92; H, 9·24. Calc. for $C_{20}H_{30}O_4$: C, 71·82; H, 9·04%).

Preparation of 1-*apocamphyl* 1-*apocamphorate* **3**. The ester was prepared by the reaction between 1-apocamphanol and 1-apocamphoryl chloride in the presence of pyridine and purified by sublimation.

White needles m.p. 71–73° were obtained, IR, 1724 cm^{-1} (C=O). (Found: C, 78·52; H, 10·65. Calc. for $C_{19}H_{30}O_2$: C, 78·57, H, 10·41%).

Decomposition of **2**. A soln of 1·34 g of **2** in 200 ml CCl_4 was placed in two 150 ml tubes, evacuated and sealed. The tubes were heated in thermoregulated bath at 70±0·02° for 43 hr which corresponded to 6 half lives of **2**. After heating, the mixture was extracted with sat $NaHCO_3$ aq. No acidic substance was obtained from the $NaHCO_3$ extracts by acidifying and extraction with ether. The soln of CCl_4 was washed with water, dried ($MgSO_4$) and evaporated to dryness under reduced pressure at room temp to yield semicrystals, which were dissolved in 5 ml n-hexane, cooled by dry ice acetone bath and allowed to stand for 1 hr. The crystals which separated were filtered off and recrystallised twice from n-hexane and twice from MeOH by the same procedure to yield 250 mg of white needles of the inversion product **4** m.p. 166–169°, and also identified further by comparing of the IR spectrum with the authentic sample. The mother liquor was evaporated to dryness. To the residue 20ml MeOH and 5 ml 20% NaOH aq were added and the mixture was refluxed for 3 hr to destroy any remaining inversion product and then MeOH was distilled off. The residue was extracted with hexane. The alkaline soln was acidified and extracted with ether. The ether extracts were combined and washed with a small portion of water, dried ($MgSO_4$) and evaporated to yield 1-apocamphoric acid (680 mg) which upon recrystallisation from hexane yielded clear needles m.p. 214–215° which were undepressed by admixture with the authentic sample. The hexane extract was dried, passed through 50 g of alumina and evaporated. The residue was crystallised from MeOH. Sublimation of the crystals yielded 1-apocamphyl chloride (needles) m.p. 170–171°.[2] The residue of the sublimation was recrystallised from MeOH and hexane to yield clear cubes of 1-apocamphyl dimer m.p. 216–217°.[2]

Quantitative analyses of **3** and **4**. A 0·02 M soln of **2** (5 ml) was placed in each of 20 ml tubes, evacuated under liquid N_2 cooling and sealed. Three tubes were heated at various temps respectively. Reaction times were 6 and 12 half lives of **2**. Yields of **3** and **4** were calculated from intensities of absorptions at 1724 and 1800 cm^{-1} respectively.

Cleavage reaction of **2**. A soln of $NaNH_2$ in 100 ml abs liq NH_3 was prepared from 200 mg of Na.[1f] To the NH_3 soln a soln of 100 mg of **2a** in 2 ml abs ether was added and the whole mixture was stirred for 6 hr at a temp near b.p. of NH_3. The mixture was cooled to −70°

and 2 g of NH_4Cl was added to destroy any excess $NaNH_2$. NH_3 was distilled off by removing the cooling bath. Residue was extracted by CH_2Cl_2, decolourized by active charcoal, and condensed to nearly dryness. To the residue 2 ml of hexane was added and cooled. 1-Apocamphoramide (60 mg) obtained was recrystallised from hexane twice to yield needles, m.p. 187–188° which were subjected for ^{18}O-analysis.

Kinetics of ^{18}O*-scrambling in* **2**. Kinetics were followed by the analysis of ^{18}O-content of carbonyl O atom of the remaining peroxide used in the reaction. The peroxide **2a** was decomposed under the same condition applied for kinetics of the decomposition. Each tube was charged with an appropriate amount of 0·02 M soln of **2a** to leave about 200 mg of undecomposed peroxide after heating for various time intervals, respectively. After the reaction, the tubes were opened and the mixture was evaporated to dryness at room temp under reduced pressure. To the residue 5ml MeOH was added and filtered. Crude peroxide recovered and was recrystallized from ether-MeOH to yield about 130 mg needles, the IR of which was found to be identical with that of starting **2a**. Peroxides recovered were cleaved by $NaNH_2$ (Eq. 5) and products were subjected to ^{18}O-analysis. The results are shown in Tables 6–8.

^{18}O-*Analysis* was performed in a same procedure reported in the previous paper.[1f]

Table 6. Kinetics of the scrambling of the carbonyl label of **2a** during thermal decomposition at 55° in CCl_4

Reaction time (sec)	Carbonyl label (excess atom %)	$a-x$	$k_s \times 10^5$ (sec^{-1})
0	2·313	1·157	
73800	2·059	0·902	3·38
165600	1·926	0·769	2·47
205200	1·847	0·690	2·53
328740	1·679	0·522	2·42
		average	2·70 ± 0·21

Table 7. Kinetics of the scrambling of the carbonyl label of **2a** during thermal decomposition at 70° in CCl_4

Reaction time (sec)	Carbonyl label (excess atom %)	$a-x$	$k_s \times 10^5$ (sec^{-1})
0	2·313	1·157	
14880	2·041	0·884	1·81
25820	1·849	0·692	2·11
35820	1·714	0·584	1·91
45060	1·650	0·493	1·89
48480	1·641	0·483	1·80
61500	1·592	0·435	1·59
		average	1·85 ± 0·12

Table 8. Kinetics of the scrambling of the carbonyl label of **2a** during thermal decomposition at 84·3° in CCl_4

Reaction time (sec)	Carbonyl label (excess atom %)	$a-x$	$k_s \times 10^5$ (sec^{-1})
0	5·313	1·157	
3600	1·982	0·825	9·39
4020	1·962	0·805	9·02
5700	1·831	0·674	9·49
5700	1·839	0·682	9·27
7620	1·738	0·581	9·04
7800	1·703	0·546	9·75
		average	9·33 ± 0·18

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REFERENCES

[1a] J. W. Taylor and J. C. Martin, *J. Am. Chem. Soc.* **89**, 6904 (1967);
[b] M. Kobayashi, H. Minato and Y. Ogino, *Bull. Chem. Soc. Japan* **41**, 2822 (1969);
[c] J. C. Martin and J. H. Hargis, *J. Am. Chem. Soc.* **91**, 5399 (1969);
[d] M. J. Goldstein and H. A. Judson, *Ibid.* **92**, 4119 (1970);
[e] M. Kobayashi, H. Minato and R. Hisada, *Bull. Chem. Soc. Japan* **44**, 2271 (1971);
[f] S. Oae, K. Fujimori and S. Kozuka, *Tetrahedron* **28**, 5372 (1972).
[2] M. S. Kharasch, F. Engelmann and W. H. Urry, *J. Am. Chem. Soc.* **65**, 2428 (1943).
[3] T. Kashiwagi, S. Kozuka and S. Oae, *Tetrahedron* **26**, 3619 (1970).
[4a] M. Levy, M. Steinberg and M. Szwarc, *J. Am. Chem. Soc.* **76**, 5978 (1954);
[b] A. Rembaum and M. Szwarc, *Ibid.* **77**, 3486 (1955);
[c] L. Herk, M. Feld and M. Swarc, *Ibid.* **83**, 2998 (1961);
[d] W. Braum, L. Rajhanbach and F. R. Eirich, *J. Phys. Chem.* **66**, 1951 (1962);
[e] R. C. Neuman, Jr. and J. V. Behar, *J. Am. Chem. Soc.* **91**, 6024 (1969).
[5] R. C. Lamb and J. R. Sanderson, *Ibid.* **91**, 5034 (1969).
[6] S. Oae and K. Fujimori, unpublished work.
[7] D. F. DeTar, *J. Am. Chem. Soc.* **89**, 4058 (1967).
[8] G. S. Hammond and L. M. Soffer, *Ibid.* **72**, 4711 (1951).
[9] J. C. Bevington and J. Toole, *J. Polymer Sci.* **28**, 413 (1958).
[10] A. Yamamoto, N. Inamoto, T. Morikawa and O. Simamura; *Abstract of 19th Annual Meeting of Japan Chem. Soc.* III, p. 113 (1966).
[11] W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.* **84**, 1561 (1962).
[12] J. E. Leffler and R. G. Zepp, *Ibid.* **92**, 3713 (1970).
[13a] D. F. DeTar and C. Weis, *Ibid.* **78**, 4296 (1956).
[b] D. F. DeTar and C. Weis, *Ibid.* **79**, 3041 (1957).
[14] R. C. Lamb, J. G. Paciphici and P. W. Ayers, *Ibid.* **87**, 3926 (1965).
[15] P. D. Bartlett and J. E. Leffler, *Ibid.* **72**, 3030 (1950).
[16] F. D. Greene, H. P. Stein and F. M. Vane, *Ibid.* **86**, 2080 (1964).
[17a] S. J. Roads *Molecular Rearrangement* (Edited by P. de Mayo) Chap. 11, Interscience, N.Y. (1963);
[b] W. E. von Doering, V. G. Toscano and G. H. Beasly, *Tetrahedron* **27**, 5299 (1971).
[18] P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.* **84**, 2596 (1962).
[19] R. A. Cooper, R. G. Lawler and H. R. Ward, *Ibid.* **94**, 552 (1972).
[20] S. Oae, K. Fujimori and Y. Uchida, *Tetrahedron* **28**, 5321 (1972).