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DECOMPOSITION OF DIACYL PEROXIDE—VI

^{18}O-TRACER STUDY ON THERMAL DECOMPOSITION OF 1-APOCAMPHORYL BENZOYL PEROXIDE

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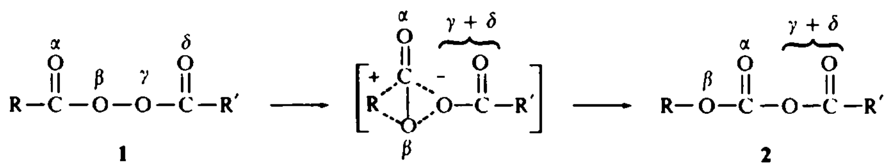
Abstract— When 1-apocamphoryl benzoyl peroxide was heated in CCl_4, both radical and carboxy-inversion reactions occurred concurrently giving benzoyl 1-apocamphyl carbonate (51%), 1-apocamphyl benzoate (20%), 1-apocamphyl chloride (20%), chlorobenzene (17%), hexachloroethane, and carbon dioxide (59%).

In the carboxy-inversion the 1-apocamphyl group was the only migrating group which migrated to oxygen. During the decomposition little or no oxygen scrambling occurred between carbonyl and peroxidic oxygen atoms in the peroxide. The carboxy-inversion mechanism is discussed on the basis of ^{18}O-tracer results.

INTRODUCTION

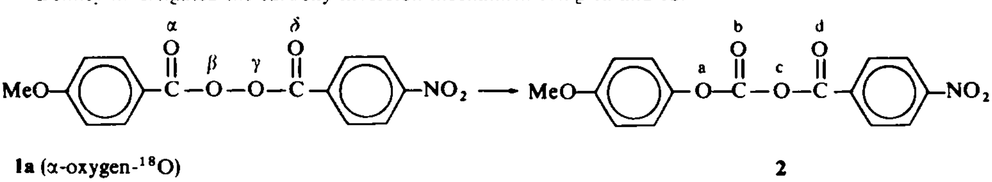
LEFFLER first showed that the thermal decomposition of *p*-methoxy-*p*′-nitrobenzoyl peroxide **1** undergoes not only homolytic cleavage to give radical reaction products but also heterolytic bond cleavage, i.e. carboxy-inversion to afford *p*-nitrobenzoyl-*p*-methoxyphenyl carbonate **2**.[1] Earlier Denney investigated the mechanism of the carboxy-inversion[2] using an ^{18}O-tracer and proposed the following mechanism on the basis of incomplete examination* of the ^{18}O-distribution in **2** obtained from carbonyl ^{18}O-labelled peroxides.



(1)

where R = *p*-methoxyphenyl, R′ = *p*-nitrophenyl

* Denney investigated the carboxy-inversion mechanism using **1a** and **1b**.[2]

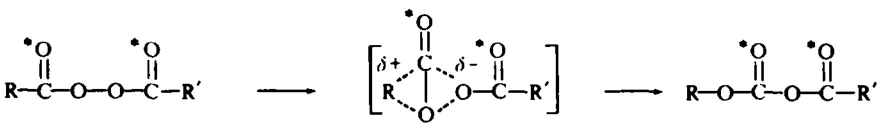


1a (α-oxygen-^{18}O) **2**

1b (δ-oxygen-^{18}O)

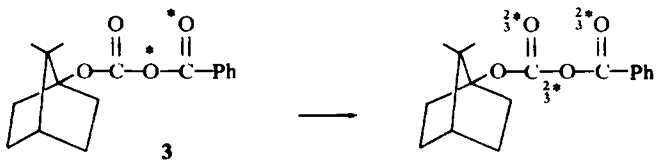
Based on the observation that a-oxygen atom in **2** obtained from **1a** did not contain any excess ^{18}O, all the original ^{18}O in the α-oxygen of **1a** was believed to have migrated to b-oxygen in **2** during the carboxy-inversion without further experimental support.[2a] Since 66% of the original ^{18}O in **1b** was retained in d-oxygen of **2**, it was assumed that the remaining 34% of the original ^{18}O in **1b** resided in the c-oxygen atom of **2**.[2b]

In the previous paper we also discussed the mechanism of the decomposition of diacyl peroxide assuming the complete retention of the specific ^{18}O-label throughout the carboxy-inversion process as shown below.[3]



(2)

Recently we found, however, a new mode of oxygen scrambling in benzoyl 1-apocamphyl carbonate **3** which corresponds to carboxy-inversion product shown in eq. 3.[4]



(3)

Meanwhile, oxygen scrambling between carbonyl and peroxidic oxygen atoms in the peroxide, has been observed for a few diacyl peroxides and different mechanisms have been proposed.[5]

(4)

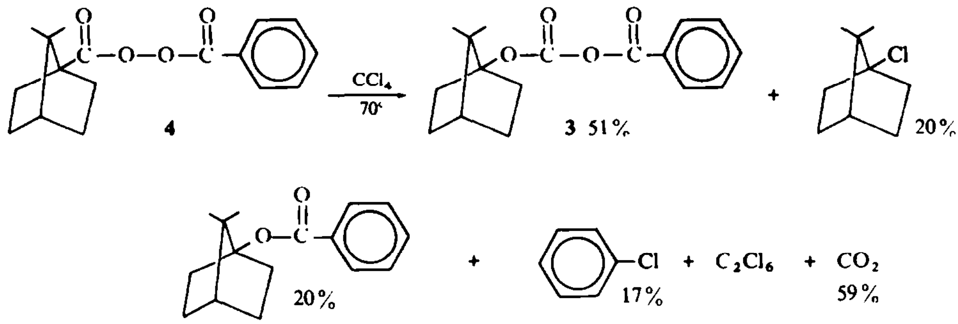
However, the peroxides in which oxygen scrambling (eq. 4) has been examined are all presumed to decompose only through a homolytic reaction path.[5]

In earlier discussions on the carboxy-inversion mechanism neither Denney nor we considered the oxygen scrambling both in the peroxide (eq. 4) and the carboxy-inversion product (eq. 3).[2,3]

The peroxide **4** was found to undergo both homolytic cleavage of the peroxidic bond and carboxy-inversion upon heating. Therefore, one has to consider oxygen scrambling in both the starting peroxide and the inversion product in order to use the ^{18}O-tracer technique to study the mechanism of the decomposition, as this is the first example of oxygen scrambling (eq. 4) in peroxides which decompose concurrently by both homolytic and carboxy-inversion processes. The purpose of this work is to reexamine the mechanism of the carboxy-inversion reaction in consideration of both modes of oxygen scrambling.

RESULTS AND DISCUSSION

Products. Thermal decomposition of 1-apocamphoryl benzoyl peroxide **4** was carried out with a CCl_4 solution of 0·02M initial concentration of peroxide in evacuated tubes. Peroxide decomposition gave the following products:



Meanwhile, it was found through IR analysis that **3** was stable and did not decompose under the same conditions.[4] The analysis of products formed in the reaction indicate that both carboxy-inversion and radical reactions occur concurrently. 1-Apocamphoryl phenyl carbonate **5**, the other possible alternative carboxy-inversion product which would be formed by the migration of phenyl to oxygen was completely absent in the mixture.[6]

In a previous paper we reported that the thermal decomposition of the primary alkaneformyl peroxide proceeds almost exclusively through homolytic cleavage of the peroxidic bond, however carboxy-inversion was the major course of the thermal decomposition of the secondary alkaneformyl peroxide.[3] The facts were rationalized in term of the ability of the migrating alkyl group to stabilize positive charge which would develop on peroxydic oxygen in the transition state of the heterolytic cleavage of the peroxidic bond.[3] In view of the pK_a values of 1-bicyclo[2.2.1.] heptanecarboxylic acid (4·9) and benzoic acid (4·2), the 1-apocamphyl group would be less electronegative than the phenyl group.[7] Therefore, the 1-apocamphyl is expected to migrate preferentially to phenyl. Lack of **5** in the products seems to support the above argument.

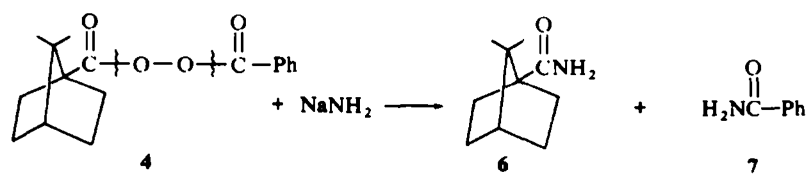
 (5)

TABLE 1. ^{18}O-DISTRIBUTION IN THE PEROXIDE **4a**. ANALYZED BY CLEAVAGE REACTION 5

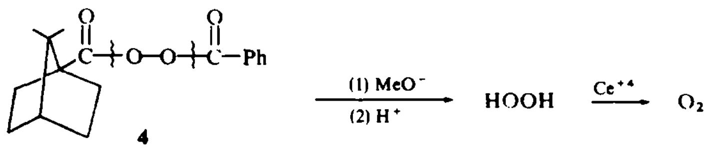
Origin of amide	^{18}O-Content (excess atom %)	
	1-Apocamphoramide (**6**)	Benzamide (**7**)
1-Apocamphyl chloride[a]	2·55	
Freshly prepared **4a**	2·55	0·00
Recovered **4a** after heating for 16 hr at 70° in CCl_4	2·51	0·00

[a] Starting material for the preparation of **4a**.

Oxygen scrambling in peroxide

1-Apocamphoryl carbonyl-^{18}O-labelled 1-apocamphoryl benzoyl peroxide **4a** was prepared from ^{18}O-labelled 1-apocamphoryl chloride and perbenzoic acid. When **4a** was treated with $NaNH_2$ in liq. NH_3, corresponding amides were obtained and these were subjected to ^{18}O-analysis. Results are in Table 1.

Carbonyl ^{18}O-labelled benzoyl peroxide prepared from ^{18}O-labelled benzoyl chloride was converted to carbonyl-^{18}O-labelled perbenzoic acid by the usual procedure.[4] The reaction between 1-apocamphoryl chloride and carbonyl-^{18}O-labelled perbenzoic acid gave benzoyl carbonyl-^{18}O-labelled 1-apocamphoryl benzoyl peroxide **4b**. The two peroxidic oxygen atoms in **4b** were converted into



4 (6)

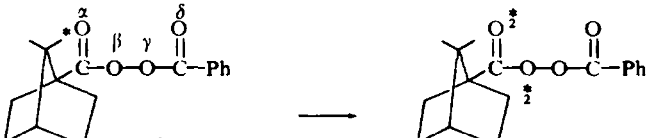
molecular oxygen by hydrolysis of **4b** to H_2O_2 followed by oxidation with Ce^{+4}.[5b,c] Oxygen thus obtained was subjected for mass spectral analysis as in Table 2. No incorporation of ^{18}O into molecular oxygen indicates that the preparation procedure of **4b** is completely free from the equilibration steps which would lead to scrambling excess ^{18}O into the oxygen molecule.

TABLE 2. KINETICS OF OXYGEN SCRAMBLING IN THE PEROXIDE AT 70° IN CCl_4, ANALYSED BY CLEAVAGE REACTION 6

Reaction time (hr)	Completion of decomposition (%)	^{18}O-Content in O_2 (excess atom %) obtained from **4a**[a]	**4b**[b]
0	0	0·00	0·00
7	35	0·00	0·00
14	59	0·00	0·00
27	82	0·04	0·01

[a] The carbonyl oxygen atom in original **4a** contained 2·55 excess atom %.
[b] The carbonyl oxygen atom in original **4b** contained 4·60 excess atom %.

The possibility of the oxygen scrambling reactions shown in eqs. 7 and 8 must be examined prior to the ^{18}O-tracer study of the carboxy-inversion.



4a (7)

4b (8)

Since this mode of oxygen scrambling has been a matter of controversey in recent years,[5] the structural effect of R on the rate of oxygen scrambling in $(\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}})_2$ is an interesting subject.

Thus, **4a** and **4b** were allowed to decompose to various degrees. Undecomposed peroxide recovered was cleaved by the reactions in eqs. 5 or 6 and the products subjected to ^{18}O-analysis. The results are listed in Table 1 and Table 2.

The oxygen scrambling reactions shown in eqs. 7 and 8 were so slow relative to decomposition ($1{\cdot}74 \times 10^{-5}$ sec^{-1} at 70°) that accurate rates could not be obtained. The rates of scrambling reactions shown in eqs. 7 and 8 are estimated as less than 8×10^{-7} sec^{-1} and 10^{-7} sec^{-1} respectively from the data in Table 2.

Thus, the oxygen scrambling in peroxide **4** does not disturb the ^{18}O-tracer study on the carboxy-inversion process in the thermal decomposition of **4**. These slow oxygen scrambling reactions in **4** are interesting in contrast to the rapid scrambling in acetyl peroxide ($4{\cdot}4 \times 10^{-5}$ sec^{-1} at 80°,[5a] $1{\cdot}18 \times 10^{-5}$ sec^{-1} at 55·1°[5c] in isooctane). It has been noted that the substitution of R by Ph in $(\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}O{-}})_2$

TABLE 3. ^{18}O-DISTRIBUTION OF THE CARBOXY-INVERSION PRODUCT 3, ANALYZED BY THE CLEAVAGE REACTION 9

Compound	^{18}O-Content (excess atom %) Obs		Calc.[a]
Reaction time	68 hr	135 hr	
Derived from the inversion product obtained from **4a**			
1-Apocamphoramide[b]	2·55	2·55	
1-Apocamphanol **8**	0·07	0·07	
CO_2	0·84	0·84	0·83
Benzanilide **9**[c]	0·62	0·63	0·83
Derived from the inversion product obtained from **4b**			
Benzamide **7**[d]	1·81	1·81	
1-Apocamphanol **8**	0·00	0·00	
CO_2	0·66	0·66	0·60
Benzanilide **9**	0·60	0·63	0·60

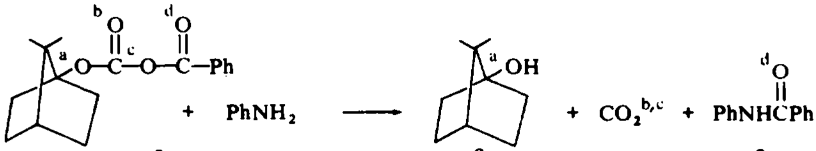
[a] Value calculated on the basis of postulation that the original ^{18}O-label in starting **4** is scrambled into b-, c- and d-oxygen atoms in **3** (except for 0·07 excess atom % when **4a** was used as starting material).

[b] Derived from ^{18}O-labelled 1-apocamphoryl chloride, starting material for the preparation of **4a**.

[c] Benzanilide contaminated with unknown impurity.

[d] Derived from ^{18}O-labelled benzoyl chloride, starting material for the preparation of **4b**.

tend to slow down the oxygen scrambling in the peroxides; the order of oxygen scrambling is acetyl peroxide (Martin *et al.*,[5b] Goldstein *et al.*[5c]) > acetyl benzoyl peroxide (Kobayashi *et al.*[5e]) > benzoyl peroxide (Kobayashi *et al.*,[5d] Martin *et al.*[5b]). This specific effect of Ph group may be responsible for the slow oxygen scrambling in **4** observed in our ^{18}O-tracer studies. The other possibility is the special effect of apocamphyl group in **4**, i.e. steric effect due to bulkiness and/or inductive effect of the t-alkyl group, which may lead to the facile carboxy-inversion in the thermal decomposition of **4** concurrent with homolytic cleavage.



3 **8** **9** (9)

^{18}O-Tracer studies on carboxy-inversion

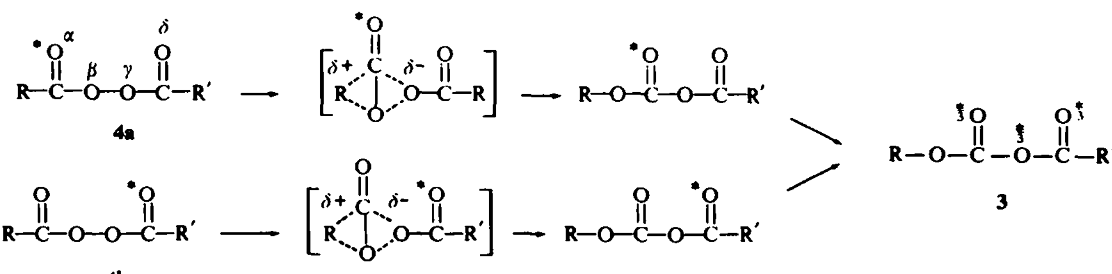
Thermal decomposition of **4a** and **4b** were carried out at 70° under the same conditions used in the product analysis. The ^{18}O-distribution in the inversion product **3** was analysed by the usual procedure as shown in eq. 9[4] and the results are in Table 3.

The following deductions can be made from the data in Table 3.

(i) Since there is no incorporation of ^{18}O-atoms into a-oxygen atom in **3** obtained from both **4a** and **4b**,† the apocamphyl group is shown to migrate exclusively to β-oxygen in peroxide **4**; in keeping with Denney's observation.[2]

(ii) The original label in peroxide **4** is scrambled into inversion product **3** in a manner which cannot be explained by mechanisms in eqs. 1 or 2. According to these mechanisms, carbonyl-^{18}O-label in **4a** should not enter into both c- and d-oxygen in **3** and carbonyl-^{18}O-label in **4a** should not enter into b-oxygen in **3**. However, the observed values in Table 3 are in good accord with the calculated values on the basis of the postulation that the original ^{18}O-labels in **4a** and **4b** are completely scrambled into b-, c- and d-oxygen in inversion product **3**.

Meanwhile, we found that under the decomposition conditions of **4** the oxygen scrambling reaction (eq. 3) takes place. Thus, our ^{18}O results can be explained in that the oxygen scrambling in the inversion product resulted after the carboxy-inversion process in which the original ^{18}O-label in the peroxide is maintained as shown below.



where R = 1-Apocamphyl, R' = Phenyl

SCHEME

† The very slow oxygen scrambling reaction 7 is responsible for the fact that a small amount (0·07 excess atom %) of original ^{18}O-label of **4a** is incorporated into a-oxygen atom of **3** yielded from **4a**.

This is in keeping with earlier ^{18}O-studies on the Criegee reaction of carbonyl-^{18}O-labelled 9-decalyl perbenzoate[2b] in which specificity of ^{18}O-label is completely maintained and also the ^{18}O-study on the solvolytic rearrangement of carbonyl-^{18}O-labelled 1-bicyclo [2.2.0] hexylcarbinyl *p*-nitrobenzonate in which the carbonyl-^{18}O-label is completely retained in the carbonyl oxygen atom of 1-bicyclo [2.2.1] heptyl *p*-nitrobenzoate.[8]

Thus, the carboxy-inversion mechanism shown in eq. 2, suggested in our previous paper[3] has been confirmed.

EXPERIMENTAL

All IR absorption spectra were taken in CCl_4 with a SG-25 instrument, Japan spectroscopic Co. Ltd. The mass spectra were recorded on a Hitachi RMU-6E mass spectrometer. Gas liquid chromatographic data were taken with a K-53 instrument, Hitachi Co. Ltd., using H_2 as a carrier gas. The column used was 4 m × 3 mm column packed with PEG-6000 (30%) supported on celite 545 (80–100 mesh). All m.ps are uncorrected.

Preparation of 1-*apocamphryl benzoyl peroxide* 4. To a solution of 6·52 g 1-apocamphoryl chloride and 2·8 g of pyridine in 40 ml of hexane, 44 ml of 0·78 M-perbenzoic acid chloroform solution was added dropwise with stirring at −20°. The mixture was kept for 1 hr at −20° and then poured onto 50 g crushed ice. The organic layer was washed twice with cold dil. HCl, twice with cold water, dried ($MgSO_4$), and evaporated to yield white crystalline residue to which 30 ml of MeOH was added, filtered, washed with 30 ml of MeOH. The peroxide (9·2 g) m.p. 79° (90%) was recrystallized from Et_2O–MeOH as needles, m.p. 80%. ν_{max} 1768 and 1792 cm^{-1} (C=O): NMR 7·3–8·2 (m, 5, aromatic): 1·2–2·5 (m, 9, aliphatic), 1·2 ppm (s, 6, Me). (Calc. for $C_{17}H_{20}O_4$: C, 70·81, H, 6·99. Found: C, 70·95: H, 7·06%).

1-*Apocamphyl benzoate* was prepared by the reaction of 1-apocamphanol with benzoyl chloride in the presence of pyridine. Sublimation of the crude product gave clear needles m.p. 68·5–69·5°, carbonyl stretching absorption at 1726 cm^{-1}. (Calc. for $C_{16}H_{20}O_2$: C, 78·65; H, 8·25. Found: C, 78·48: H, 8·39%).

Phenyl 1-*apocamphorate* was prepared by the reaction of phenol with 1-apocamphoric acid in the presence of pyridine. Sublimation of the crude product gave white plates m.p. 42–45°, carbonyl stretching absorption at 1745 cm^{-1}. (Calc. for $C_{16}H_{20}O_2$: C, 78·65; H, 8·25. Found: C, 78·54; H, 8·38%).

Quantitative product analysis

1-*Apocamphyl benzoate and* 3. A solution (0·02M) of 4 in CCl_4 was placed in glass tubes, degassed by three freeze–thaw cycles and evacuated under the liq. N_2 cooling. The charged tubes were immersed in a thermoregulated bath at 70° for 68 hr. The yield of 1-apocamphyl benzoate and 3 were analyzed by IR using carbonyl absorption at 1726 and 1808 cm^{-1},[4] respectively.

1-*Apocamphyl chloride and chlorobenzene.* The peroxide 3 144 mg was decomposed in 25 ml of CCl_4 in evacuated tube at 70°. After heating for 68 hr, aniline was added to the mixture at room temp to destroy 4. Under the conditions the ester did not react with aniline. After 30 min 17 mg of dichlobenzene, was added as internal standard to the mixture which was then washed with dil. HCl and water and passed through 5 g of silica gel. The eluent was concentrated by fractional column to about 0·5 ml and then GLC analyzed. Absence of phenyl 1-apocamphorate was confirmed by GLC.

CO_2 was converted to $BaCO_3$ and weighed.

Kinetics of the decomposition was followed by measuring the amount of remaining peroxide by idometiric titration. A good first order rate constant, $1·74 \times 10^{-5}$ sec^{-1} was obtained at 70°.

Carbonyl-^{18}O-labelled 1-*apocamphoryl chloride.* A mixture of 18·7 g of 1-apocamphoryl chloride, 1·8 g of ^{18}O-enriched water, and 30 ml of dioxane was refluxed for 3 hr and then solvent removed. Water, 50 ml was added to the residue and filtered. Crude ^{18}O-labelled 1-apocamphoric acid was recrystallized from MeOH–H_2O to yield 14·5 g of clear prisms m.p. 214–215°. A mixture of 6·4 g of ^{18}O-labelled 1-apocamphoric acid and 10 g of $SOCl_2$ was refluxed for 1 hr. Excess $SOCl_2$ was removed from the mixture and the residue distilled under reduced pressure, b.p. 107°/18 mm, to give 6·5 g of semicrystals. Since the acid chloride did not appear to be suitable for the ^{18}O-analysis, carbonyl-^{18}O-labelled 1-apocamphoryl chloride was converted to 1-apocamphoramide. To a solution of 0·3 g of carbonyl-^{18}O-labelled 1-apocamphoryl chloride, ammonia was bubbled for 10 min, and filtered. The mother liquor was evaporated to dryness to yield white crystalline residue which was thrice recrystallized from hexane to yield needles m.p. 187–188°. IR spectrum (CCl_4) of the amide shows a carbonyl absorption at 1690 cm^{-1}. (Calc. for $C_{10}H_{17}ON$: C, 71·81; H, 10·25. Found: C, 71·69; H, 9·91%).

Carbonyl-^{18}O-labelled benzoyl peroxide. The peroxide was prepared from carbonyl ^{18}O-labelled benzoyl chloride (1·81 excess atp, %)[9] according to the method of Denney.[10] The peroxide was obtained in yield of 78%, m.p. 106–107°.

Carbonyl-^{18}O-labelled perbenzoic acid. The peracid was prepared from carbonyl ^{18}O-labelled benzoyl peroxide similarly according to the method of Braun (80%).[11]

Apocamphoryl carbonyl-^{18}O-labelled peroxide **4a** was prepared by the reaction of ^{18}O-labelled 1-apocamphoramide and benzoyl carbonyl-^{18}O-labelled peroxide **4b** (the latter prepared by reaction of 1-apocamphoryl chloride and carbonyl-^{18}O-labelled perbenzoic acid as for **4**).

Cleavage reaction 3

To 100 ml of liq. NH_3 containing a trace of $FeCl_3$, 200 mg of small pieces of Na was added and stirred until the blue colour of Na disappeared (about 3 hr) under dry ice–acetone cooling. Then to the NH_3 solution a solution of 100 mg of **4** in 2 ml of abs. ether was added and the mixture was stirred for 6 hr at temp near boiling point of NH_3.

The mixture was cooled to $-70°$ and 2 g of NH_4Cl added to destroy excess $NaNH_2$. Ammonia was distilled off. Residue was extracted by CH_2Cl_2, decolourized and condensed to about 2 ml. White crystals separated, were filtered and recrystallized from CCl_4 to give pure benzamide, m.p. 125–126°. The mother liquid was chromatographed through activated alumina. 1-Apocamphoramide **6** was eluted by ether and recrystallized from hexane to afford needles, mp. 187–188°. Benzamide and 1-apocamphoramide gave one spot on TLC and were subjected to ^{18}O-analysis. Control experiment showed no oxygen exchange during alumina chromatography of 1-apocamphoramide.

Cleavage reaction 4

To a solution of 100 mg of **4** in 2 ml of CCl_4 2 ml of 0·5M NaOMe in MeOH was added under dry-ice cooling, then the cooling bath was changed to an ice bath. After 20 min at 0°, 10 ml of ice–water was added to the reaction. Water layer was separated and washed twice with cold CCl_4. The water solution was placed in a three necked flask equipped with two bent tubes charged with 10 ml of 12 M-H_2SO_4 and 200 mg $Ce(SO_4)_2$ powder respectively which can be transferred into the flask by turning the tube 180°. The reaction flask was connected to a vacuum line, degassed by three freeze–thaw cycles, and evacuated by an oil diffusion pump. Then H_2SO_4 was slowly added to the alkaline solution with ice–salt cooling and stirring by a magnetic stirrer. The cooling bath was removed and the mixture was allowed to stir at room temp for 20 min. When $Ce(SO_4)_2$ was added to the mixture, oxygen gas was evolved. After stirring for 20 min, the mixture was cooled with dry ice–acetone. The oxygen gas was transferred to the gas sampler passed through a trap cooled with liquid N_2 and subjected to mass spectral analysis. The oxygen gas contained 8·0% N_2.

Oxygen scrambling in **4**. Peroxide **4a** or **4b** was decomposed as for product analysis at 70°. Each tube was charged with an appropriate amount of 0·02M solution of the peroxide to leave about 200 mg of undecomposed peroxide after heating for various time intervals respectively. After reaction, the tubes were opened and the mixture evaporated to dryness at room temp under reduced pressure. To the residue, 5 ml of MeOH was added and filtered. Crude peroxide recovered was recrystallized from ether–MeOH to yield 130 mg of clear needles m.p. 80°, IR spectrum found identical to that of starting peroxide. Peroxides recovered were cleaved by reactions 3 or 4 and the products were subjected to ^{18}O-analysis.

^{18}O-Analysis of carboxy-inversion product

A solution containing 1·44 g of ^{18}O-labelled 1-apocamphoryl benzoyl peroxide in 240 ml of CCl_4 was placed in 400 ml of glass tube, degassed three freeze–thaw cycles, evacuated and sealed. The filled tube was immersed in a thermoregulated bath at 70°. After reaction, solvent was evaporated *in vacuo* at room temp. ^{18}O-Distribution in the inversion products were analyzed by the cleavage reaction 9; colourless oil residue was treated by 0·5 g of analine in the same manner reported in the previous paper. CO_2 evolved was subjected to mass spectral analysis.[4] The mixture was filtered and washed with ether to give 0·45 g of white crystals of **9** which were recrystallized from $CHCl_3$–hexane to give white needles mp. 158°, underpressed by adimixture with authentic sample m.p. 163°. This was subjected to ^{18}O-analysis. The IR and NMR spectra and the R_f value on TLC were identical to those of the authentic sample, showing no 1-apocamphyl N-phenylcarbamate and 1-apocamphoranilide. The mother liquid was washed with $NaHCO_3$ solution and water, $NaHCO_3$ extract gave 130 mg of benzoic acid whose NMR spectrum showed no 1-apocamphoric acid. The ether solution was dried and the solvent removed. TLC of the residue showed the presence of

1-apocamphyl benzoate, 1-apocamphanol **8**, 1-apocamphyl chloride, benzanilide and 1-apocamphyl N-phenylcarbamate, but no 1-apocamphoranilide. The residue was chromatographed through 20 g of activated alumina. Petrol extracts gave 1-apocamphyl chloride. Ether fraction gave a mixture of **8** and 1-apocamphyl benzonate, which was rechromatographed. 1-Apocamphanol **8** separated by chromatography was thrice sublimed to yield clear needles m.p. 163°, whose IR spectrum showed no ester and amide. Then the compound was subjected to ^{18}O-analysis as usual.[4]

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