DECOMPOSITION OF DIACYL PEROXIDE—V

A NEW MODE OF OXYGEN SCRAMBLING IN BENZOYL 1-APOCAMPHYL CARBONATE

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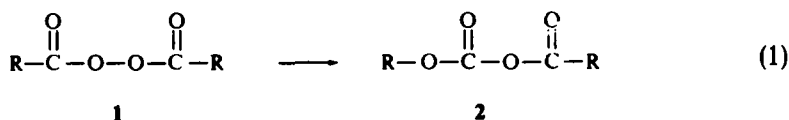
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Abstract. Specifically ^{18}O-labeled benzoyl 1-apocamphyl carbonate which corresponds to the carboxy-inversion product of 1-apocamphoryl benzoyl peroxide was synthesized and heated in CCl_4. The two carbonyl oxygen atoms and an etheral oxygen atom sandwiched between two carbonyl carbon atoms in benzoyl 1-apocamphyl carbonate were completely scrambled. Heating of ^{18}O-labeled benzoyl 1-apocamphyl carbonate with an equimolar amount of benzoic acid in CCl_4 gave quantitatively 1-apocamphanol, CO_2 and benzoic anhydride. Based on ^{18}O-analysis of these products and other data, an intramolecular mechanism was suggested for the oxygen scrambling in benzoyl 1-apocamphyl carbonate.

INTRODUCTION

EARLIER Denney *et al.* discussed carboxy-inversion reaction (1) on the basis of the ^{18}O-distribution in the inversion product **2** obtained from carbonyl-^{18}O-labeled peroxide **1**.[1a] Meanwhile it was known that thermal decomposition of *sec.* alkaneformyl peroxide often gives an anomalously high yield of the ester. In a previous paper we reported that on the basis of the examination of ^{18}O-distribution in the ester obtained from the decomposition of carbonyl ^{18}O-labeled peroxide, the ester is the secondary product formed from acyl alkyl carbonate (**2**), **2** being the primary product formed through the carboxy-inversion process from peroxide **1**.[1b]

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \quad \longrightarrow \quad R-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R \qquad (1)$$

$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$

In order to discuss fully the mechanism of decomposition of diacyl peroxide on the basis of ^{18}O-tracer results, however, all the possible oxygen scramblings after the primary process must be thoroughly examined. The purpose of this work is to examine the possible ^{18}O-scrambling in benzoyl 1-apocamphyl carbonate (**3**) which would be the inversion product of the thermal decomposition of 1-apocamphoryl benzoyl peroxide.

RESULTS AND DISCUSSION

Oxygen scrambling in benzoyl 1-apocamphyl carbonate

Specifically ^{18}O-labeled benzoyl 1-apocamphyl carbonate **3a** in c- and d-oxygen atoms was synthesized by reaction (2).

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$$ \text{(2)} $$
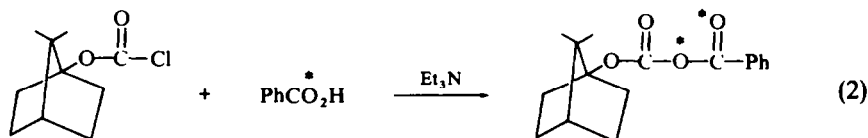
A solution of **3a** in CCl_4 was heated in an evacuated tube at 70°. After heating the solution for 40·5 or 60 hr. starting material (**3a**) was quantitatively recovered. Since a primary amine preferentially attacks acyl carbonyl carbon atom of acyl alkyl carbonate, the ^{18}O-distribution of **3** can be examined by the analysis of the products formed by the cleavage of **3** in reaction (3).[2] The results are in Table 1.
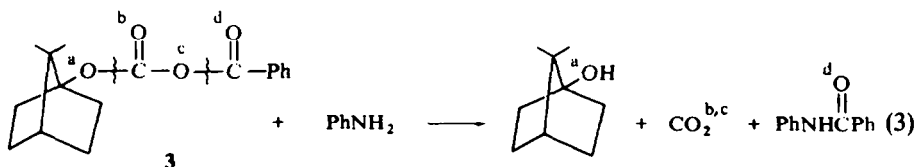

$$ \text{(3)} $$

TABLE 1. OXYGEN SCRAMBLING IN BENZOYL 1-APOCAMPHYL CARBONATE (3a) AT 70° IN CCl_4, ANALYSED BY THE REACTION (3)

Compound	^{18}O-Content (excess atom %)	
	Obs	Calc[a]
$PhCO_2H$[b]	2·70	
Derived from original **3a**		
1-Apocamphanol	0·00	0·00
CO_2	0·71	0·68
Benzanilide	1·28	1·35
Derived from recovered **3a** *after heating for* 40·5 *hr*		
1-Apocamphanol	0·00	0·00
CO_2	0·95	0·90
Benzanilide	0·88	0·90
Derived from recovered **3a** *after heating for* 68 *hr*		
1-Apocamphanol	0·00	0·00
CO_2	0·95	0·90
Benzanilide	0·87	0·90

[a] Calculated on the basis of the postulation that the original ^{18}O-label in **3a** is completely scrambled into b-, c- and d-oxygen atoms, reaction (4).
[b] Starting material for the preparation of **3a**.

Since the ^{18}O-content of the benzanilide obtained in the reaction of freshly prepared **3a** with aniline was slightly smaller than that of benzoic acid which is the starting material for the preparation of **3a**, a small portion of ^{18}O-label of d-oxygen in the freshly prepared **3a** was found to be scrambled already into b- or c-oxygen atoms. Data in Table 1 show that ^{18}O-distribution is not changed upon prolonged heating and the observed values of ^{18}O-distribution in **3** recovered after heating are in accordance with the values calculated on the basis of the postulation that the ori-

ginal ^{18}O-label in **3a** is completely scrambled among b-, c- and d-oxygen atoms in **3**, as shown in (4).


$$(4)$$
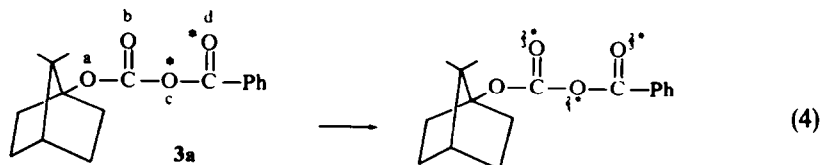
Therefore oxygen scrambling among b-, c- and d-oxygen atoms in **3a** reaches equilibrium within 40 hr by heating at 70°. Consequently, when the decomposition mechanism of diacyl peroxide is discussed on the basis of the ^{18}O-tracer results, this mode of oxygen scrambling has to be considered.

Mechanism of oxygen scrambling in 3

There are two possible mechanistic pathways, i.e. intermolecular and intramolecular for the oxygen scrambling in **3**.

Earlier Rittenberg showed that there is an intermolecular ^{18}O-exchange between ^{18}O-labeled benzoic acid and Ac$_2$O.[3] In view of the fact that **3** is the acid anhydride of a carbonic acid and a carboxylic acid, the oxygen scrambling in **3** could take place through intermolecular chain reactions initiated by a trace of benzoic acid and 1-apocamphylcarbonic acid **4**, formed by the reaction between **3** and water absorbed on the surface of reaction vessel.

$$(5)$$

$$(6)$$

$$(7)$$

$$(8)$$

.... etc.
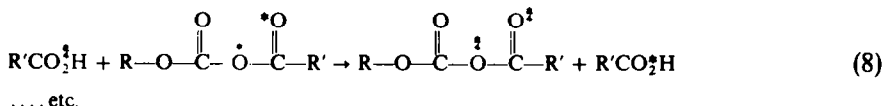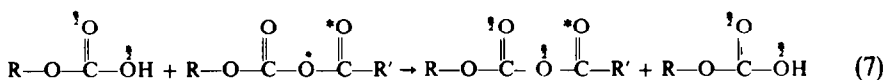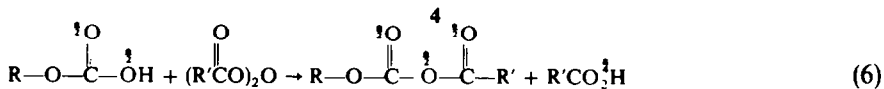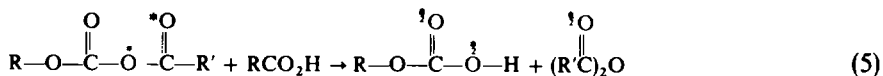
Tarbell's observation that thermal decomposition of acyl alkyl carbonate gives carboxylic anhydride and diaklyl carbonate appears to support this intermolecular mechanism.[4]

However, if oxygen scrambling in **3** proceeds through such intermolecular chain reactions, ^{18}O-label in **3a** should be scrambled into benzoic acid upon heating a mixture of **3a** and benzoic acid. **3a** was heated with an equimolar amount of unlabeled benzoic acid at 70° in CCl$_4$ for 38 hr, but the following reaction (9) was found to take place quantitatively.

The occurence of reaction (9) seems to imply no contribution of the intermolecular chain reactions to the oxygen scrambling in **3**. This has been further confirmed by ^{18}O-analysis of the benzoic anhydride formed *via* reaction (9). Since benzoic
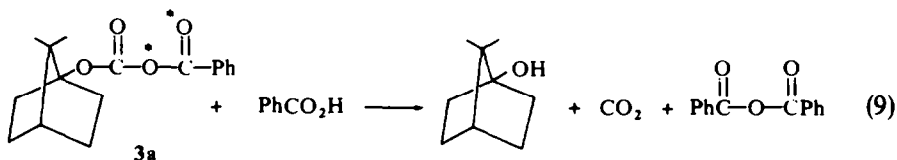
anhydride is not a suitable form for the ^{18}O-analysis because of difficulty in isolation and purification, the anhydride obtained by reaction (9) was treated with aniline, to yield benzanilide and benzoic acid which were subjected to the routine ^{18}O-analysis, Table 2.

TABLE 2. ^{18}O-TRACER STUDY OF REACTION (9)

Compound	^{18}O-content (excess atom %)		
	Observed	Calc[a]	Calc[b]
PhCO$_2$H[c]	1·35		
PhCONHPh[d]	1·28		
PhCONHPh[e]	0·42	0·43	0·54
PhCO$_2$H[e]	0·42	0·43	0·54

[a] The value is based on the postulation that benzoyloxy anion attacks carboxylic carbonyl carbon atom in 3a prior to oxygen scrambling reaction (4) and oxygen scrambling takes place in the resulting benzoic anhydride.

[b] The value is based on the postulation that ^{18}O-scrambling in 3a takes place via the intermolecular chain reactions (5–8).

[c] Starting material for the preparation of 3a.

[d] Obtained by the cleavage reaction (3) from original 3a.

[e] Derived from benzoic anhydride obtained by reaction (9).

If the ^{18}O-scrambling in 3 takes place by such an intermolecular process, reaction (8) must be faster than reaction (9), and also reactions (6) and (7) must be faster than the decarboxylation reaction of 1-apocamphyl-carbonic acid 4. As a result, if such intermolecular chain reactions would operate, the original ^{18}O-label in 3a should be completely scrambled into the b-, c- and d-oxygen atoms in 3a and two oxygen atoms in benzoic acid during reaction (9). However, the results in Table 2 show that no such oxygen scrambling takes place but the ^{18}O-label in d-oxygen atom in 3a is eventually transfered into benzoic anhydride through attack of the benzoyloxy anion at carbon atom of 3a prior to the oxygen scrambling in 3a and then oxygen atoms in benzoic anhydride are equilibrated.† Thus, the intermolecular chain reaction mechanism can be ruled out, and our ^{18}O-experimental results must be explained by an intramolecular mechanism.

Two intramolecular mechanisms are conceivable for the oxygen scrambling reaction (4), e.g., zwitterion mechanism (10) and ion pair mechanism (11).

† Control experiment showed that scrambling of ^{18}O-label between benzoic anhydride and ^{18}O-labeled benzoic acid readily takes place. Oxygen scrambling in benzoic anhydride would take place in this intermolecular reaction and/or in a manner of intramolecular reaction as shown in eq. 10 or eq. 11.

Zwitterion mechanism

$$R{-}O{-}\overset{O}{\underset{}{C}}{-}O{-}\overset{\overset{\bullet}{O}}{\underset{}{C}}{-}R' \longrightarrow \left[\cdots \rightleftharpoons \cdots \rightleftharpoons \cdots \right] \rightleftharpoons R{-}O{-}\overset{O}{\underset{}{C}}{-}O{-}\overset{O}{\underset{}{C}}{-}R' \quad (10)$$

Ion pair mechanism

$$R{-}O{-}\overset{O}{\underset{}{C}}{-}O{-}\overset{\overset{\bullet}{O}}{\underset{}{C}}{-}R' \longrightarrow \left[\cdots \rightleftharpoons \cdots \right] \rightleftharpoons R{-}O{-}\overset{O}{\underset{}{C}}{-}O{-}\overset{O}{\underset{}{C}}{-}R' \quad (11)$$

Of the two, the zwitterion mechanism seems to be more plausible than the ion pair mechanism in view of the observations that the carbonium ion centre is remarkably stabilized by the resonance participation of the adjacent oxygen atoms[5] and that in the pyrolysis. of the acyl alkylcarbonate derivatives the carbonyl oxygen atom attacks another carbonyl carbon atom by an intramolecular bicyclic mechanism.[6]

A study on the effect of substituent will clarify the nature of the transition state of the oxygen scrambling and is being investigated in these laboratories.

EXPERIMENTAL

Preparation of 1-apocamphyl chlorocarbonate. To a solution of 7 g of phosgene in 25 ml of benzene cooled to 0°, a mixture of 0·96 g of 1-apccamphanol, 1 g of pyridine and 25 ml of benzene was added with stirring and ice cooling. The mixture was allowed to stand overnight at room temp and poured onto crushed ice. Organic layer was washed with cold sat. $NaHCO_3$ aq and water, dried ($MgSO_4$), and evaporated to dryness to give crude crystals, purified by recrystallization from n-hexane, followed by sublimation under reduced pressure. Clear prisms, m.p. 65°, were obtained. $\nu_{max}(CCl_4)$ 1779 cm^{-1} (C=O); (calc. for $C_{10}H_{14}O_2Cl$: C, 59·26; H, 7·46. Found: C, 58·80; H, 7·24%).

Preparation of ^{18}O-labeled benzoyl 1-apocamphyl carbonate **3a**. To a solution of 0·73 g of 1-apocamphyl chlorocarbonate in 10 ml of dried ether cooled to 0°, a mixture of 0·44 g of ^{18}O-labeled benzoic acid, 0·36 g of Et_3N, and dry ether (10 ml) was added with stirring and cooling in an ice bath. After 1 h the mix was poured onto 50 g of crushed ice, the organic layer washed twice with cold dil. HCl, cold $NaHCO_3$ solution, then water, dried ($MgSO_4$) and evaporated to dryness at room temp under reduced pressure.

The residue obtained was crystallized by addition of 1 ml of hexane followed by trituration and decantation after cooling. Recrystallization was performed by dissolving the residue in 5 ml of hexane without heating, follwed by cooling. Thrice recrystallizations of the product yielded white prisms m.p. 44° ν_{max} 1753 and 1808 cm^{-1}. (C=O) (calc. for $C_{17}H_{20}O_4$: C, 70·81; H, 6·99. Found: C, 70·96; H, 6·99%).

Cleavage reaction (3). 3 (100 mg) was disolved in 3 ml of abs. ether and placed in a two necked reaction flask with one neck equipped with a bent tube charged with 0·3 g of aniline. The reaction flask was connected to a vacuum line, evacuated under dry ice–acetone cooling, and warmed to room temp. The tube

was turned (180°), so as to mix aniline and carboxy-inversion product solution. Formation of white crystals of benzanilide and evolution of CO_2 take place. After 10 min the flask was cooled with dry ice–acetone and then CO_2 was transfered to the tube cooled with liq. N_2. In this way CO_2 was distilled four times in the vacuum line, and subjected to mass spectral analysis. Benzanilide was filtered and recrystallized from $CHCl_3$-hexane to give white needles m.p. 162°, undepressed by admixture with an authentic sample, m.p. 163°. This was submitted to ^{18}O-analysis. The mother liquor was washed with $NaHCO_3$ aq followed by water, dried and passed through 5 g activated alumina. The ether was carefully distilled and the residue thrice sublimed to yield clear needles of 1-apocamphanol m.p. 163°, IR showed no amide absorption, the compound was subjected to [18]-O-analysis.

[18]O-*Scrambling in benzoyl 1-apocamphyl carbonate* (3). A solution of 200 mg of 3a in 35 ml of CCl_4 was placed in 70 ml glass tube, evacuated, sealed and heated for 40·5 hr or 68 hr at 70°. The tube was opened and evaporated *in vacuo* at room temp to give crystals of starting material. Recovered 3 was cleaved by reaction (3) and the products formed were subjected to ^{18}O-analysis.

[18]O-*Tracer study of reaction* (9). A solution of 200 mg 3a and 85 mg of benzoic acid in 40 ml of CCl_4 was heated in an evacuated tube at 70° for 38 hr. After reaction the tube was opened and the mixture was analysed by IR, the spectrum of which was identical to that of an equimolar mixture of 1-apocamphanol and benzoic anhydride except a sharp absorption at 2300 cm^{-1} due to CO_2. The reaction mixture was evaporated *in vacuo* at room temp. The residue was dissolved in abs. ether and mixed with aniline. After 6 hr the mixture was dissolved in 50 ml of ether, washed with cold dil. HCl and water, and extracted with $NaHCO_3$ aq. The ether solution was dried, condensed and crystals formed were filtered. Recrystallization of benzanilide gave white leaflets, m.p. 162-3° which were subjected for ^{18}O-analysis. From the mother liquor 1-apocamphanol, m.p. 163°, was separated by sublimation. The $NaHCO_3$ extract was acidified and extracted with ether to give 81 mg of benzoic acid which was recrystallized from hexane to give plates m.p. 121°, undepressed by admixture with authentic sample. This was subjected for ^{18}O-analysis.

[18]O-*Analysis*. The samples for ^{18}O-analysis were converted to CO_2 according to the modified method of Rittenberg and Ponticorvo.[7] The CO_2 was purified and subjected to mass spectrometric analysis. ^{18}O-Content was calculated from the mass peak heights of 44 and 46.

REFERENCES

[1] [a] D. B. Denney, *J. Am. Chem. Soc.* **78**, 590 (1956); D. B. Denney and D. Z. Denney, *Ibid.* **78**, 4296 (1956); [b] T. Kashiwagi, S. Kozuka and S. Oae, *Tetrahedron* **26**, 3619 (1970)

[2] J. R. Vaughan Jr. and R. L. Osato, *J. Am. Chem. Soc.* **73**, 5553 (1951), **74**, 676 (1952); D. S. Tarbell and J. A. Price, *J. Org. Chem.* **22**, 245 (1959); O. S. Tarbell and N. A. Leister, *Ibid.* **23**, 1149 (1958)

[3] L. Ponticorvo and D. Rittenberg, *J. Am. Chem. Soc.* **76**, 1705 (1954)

[4] C. J. Michejda and D. S. Tarbell, *J. Org. Chem.* **29**, 1168 (1964); R. C. Chow and D. S. Tarbell, *Ibid.* **32**, 2188 (1968)

[5] M. Murakami and S. Oae, *Prc. Japan Acad.***25**, 11, 12 (1949); Mem. of Inst. Sci. Ind. Research, Osaka Univ. **8**, 173 (1951); H. Bohme, H. Fiser and R. Frank, *Ann.* **563**, 54 (1949); H. Meerwein, V. Hederick, H. Morshel and K. Wunderlich, *Ibid.* **635**, 1 (1960); H. Meerwein, K. Bondenbenner, P. Borner, K. Kunert and K. Wunderlich, *Ibid.* **632**, 38 (1960); G. A. Olah, A. M. White and D. H. O'Brien, *Chem. Rev.* **70**, 561 (1970)

[6] M. S. Newman and S. S. Gupte, *J. Org. Chem.* **35**, 4176 (1970); M. S. Newman and S. Malandenovic, *J. Am. Chem. Soc.* **88**, 4253 (1966); M. S. Newman, S. Maladenvoic and L. K. Lala, *Ibid.* **90**, 747 (1968)

[7] M. Halman and S. Pichas, *J. Chem. Soc.* 3264 (1958); D. Rittenberg and L. Ponticorvo, *Int. J. Appl. Radiat. Isotopes* **1**, 208 (1956)