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THE DECOMPOSITION OF DIACYL PEROXIDES—I

THE THERMAL DECOMPOSITION OF PRIMARY AND SECONDARY DIACYL PEROXIDE*

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Abstract—The mechanism of ester formation in the thermal decomposition of a few primary and secondary diacyl peroxides has been investigated by the analysis of both the ^{18}O-distributions and the stereochemical configurations of the resulting esters, using ^{18}O-labelled and/or optically active diacyl peroxides.

The decomposition of primary diacyl peroxides is mainly homolytic. Acetyl peroxide, the lowest member of the primary diacyl peroxide series, was found to decompose only homolytically. The decomposition of δ-phenylvaleryl peroxide, a higher primary homologue, was mainly by homolytic cleavage of the O—O bond, however 30% of the ester formed was a product of heterolysis involving carboxy inversion. Ester formation from secondary diacyl peroxides, such as β-phenylisobutyryl and α-methylbutyryl peroxides, was found to proceed mainly through the heterolytic carboxy-inversion process.

Carboxy-inversion is discussed in the light of other similar rearrangements.

THE MECHANISM of thermal decomposition of diacyl peroxides has been extensively investigated.

Szwarc *et al.*[1] have shown that the thermal decomposition of acetyl peroxide produces various radical decomposition products including ethane, and methyl acetate formed by the recombination of methyl and acetoxy radicals in a solvent cage. A cyclic transition state for ester formation was suggested by Bartlett and Leffler[2] and Hart and Wyman.[3]

While Leffler[4] proposed that *p*-methoxy-*p'*-nitrobenzoyl peroxide decomposes homolytically in non-polar solvents but heterolytically in polar solvents, Denney *et al.*[5] presented the first concrete evidence to support a mechanism involving carboxy inversion for the decomposition of this peroxide in thionyl chloride.

We have used the same approach for the investigation of the mechanisms of the thermal decompositions of aliphatic diacyl peroxides, focusing our main attention on the ^{18}O-distributions and the stereochemical configurations of the resulting esters.

This paper describes in detail our investigations of the thermal decompositions of acetyl, δ-phenylvaleryl, β-phenylisobutyryl and α-methylbutyryl peroxides.

RESULTS AND DISCUSSION

A *The thermal decomposition of primary symmetrical diacyl peroxides*

1 *Thermal decomposition of acetyl peroxide* (APO). In applying the ^{18}O-tracer technique to the investigation of the decomposition mechanism of a diacyl peroxide,

* Taken from the doctoral thesis of T. Kashiwagi, Osaka City University (1968).

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it is assumed that both oxygens of an acyloxy radical are equivalent ($R-\overset{\overset{^{18}O}{\|}}{C}-O\cdot \leftrightarrow R-\overset{\overset{^{18}\dot{O}}{|}}{C}=O$), before recombination with an alkyl radical to form an ester in the solvent cage. Therefore, it is to be expected that both carbonyl and etheral oxygens of the ester formed will contain an identical concentration of ^{18}O, when an acyl peroxide, labeled with an excess of ^{18}O at its two carbonyl groups, is decomposed. This hypothesis is quite reliable since the resonance in an acyloxy radical should be much faster than the rate of recombination of two radicals in a solvent cage. Such a hypothesis has served as a strong argument in the postulation of the mechanisms of the reactions of 2-picoline,[6a] quinaldine[6b] and N,N-dimethylaniline N-oxides[6c] with acylating agents.

In order to substantiate this hypothesis, the thermal decomposition of carbonyl-^{18}O-labeled APO was carried out in a large amount of toluene. Since many workers[1,7] have suggested that methyl acetate is produced by the recombination of methyl and acetoxy radicals in a solvent cage, the ^{18}O-concentrations of both oxygens of the methyl acetate produced must be a half that of the carbonyl groups of the original APO.

A toluene solution of carbonyl-^{18}O-labeled APO (0·67 excess atom % below 0·012 M/l) was heated at 65 ± 1° for 27 hours under a nitrogen stream. After the decomposition was completed, methyl acetate was isolated by careful fractionations. The ^{18}O-content of carbonyl oxygen for the purified methyl acetate was determined by converting it into acetyl phenylhydrazide (0·65 excess atom %) with phenylhydrazine.

Although the ^{18}O-content of methyl acetate was not measured, its ^{18}O-content is considered to be 0·67 excess atom % of ^{18}O, identical to that of the original APO. The ^{18}O-content of the alcoholic oxygen in the ester, i.e., 0·69 excess atom %, was estimated from the ^{18}O-content of the APO and the acetyl phenylhydrazine. The ^{18}O-incorporations of the carbonyl and alcoholic oxygens in methyl acetate are estimated to be 48·5 and 51·5% respectively.

When our ^{18}O-tracer work with acetyl peroxide was completed, Taylor and Martin published an identical but more complete set of data on this decomposition.[8] In place of toluene they used isooctane and showed that the incorporations of ^{18}O in the carbonyl and etheral oxygens were found to be 49·8 and 50·0% respectively, in good agreement with our results. They also found that there is a slow preequilibration of ^{18}O in the starting material due to the recombination of two acyloxy radicals during the reaction.

Since the two oxygen atoms are shown to be equivalent even in the least stable, short-lived acetoxy radical before recombination, it can be considered to be so for more stable acyloxy radicals. However, the solvent cage recombination of radicals is not the only route for the formation of esters in the decompositions of diacyl peroxides, as will be seen from the following section.

2. *Thermal decomposition of δ-phenylvaleryl peroxide.* It has been suggested that

primary diacyl peroxides decompose homolytically in non-polar solvents, however, only in a very few cases, such as in the decomposition of acetyl and benzoyl peroxide,[9] has it been demonstrated that an ester is formed only by a radical recombination in solvent cage. It is not legitimate, though, to assume that the ester always results as a cage product just because the yield of the ester does not change by the addition of radical scavengers or by the variation of peroxide concentration and temperature. Other processes, such as an intramolecular cyclic route[10] and a rearrangement via carboxy-inversion[10] will also not be effected by the presence of radical scavengers.

The thermal decomposition of δ-phenylvaleryl peroxide in both carbon tetrachloride and benzene has been studied in detail by DeTar *et al.*[11] Although they have suggested that 4-phenylbutyl δ-phenylvalerate, is a geminate product formed mainly by the recombination of radicals in the solvent cage, there is no conclusive evidence to support this argument.

We have analysed the ^{18}O-distribution of the ester formed in the thermal decomposition of δ-phenylvaleryl peroxide labelled with ^{18}O at the two carbonyl groups.

A carbon tetrachloride solution containing the carbonyl-^{18}O-labeled δ-phenylvaleryl peroxide (0·62 excess atom % 0·032 M/l) was refluxed for 59 h under a nitrogen stream. Among many products,[11a] 4-phenylbutyl δ-phenylvalerate (0·62 excess atom %) was isolated by fractional distillation. The ester was also hydrolysed with methanolic potassium hydroxide to obtain δ-phenylbutyl alcohol (0·43 excess atom %). Under the hydrolysis conditions, there was no ^{18}O-exchange between the alcohol and potassium hydroxide. The excess atom % of ^{18}O (0·43%) in the etheral oxygen of the ester corresponds to approx 35% incorporation of ^{18}O from the original label in the carbonyl oxygens of the peroxide. If the ester is only formed by radical recombination in a solvent cage, its etheral oxygen would be expected to include 50% incorporation of ^{18}O from the original label, while the cyclic mechanism and the rearrangement process demand the etheral oxygen to contain 100% and 0% of ^{18}O respectively. The results actually obtained cannot be explained with any one of the three mechanisms alone. Therefore it may be that two or possibly three pathways are competing together in the formation of the ester. There remains a possibility of ^{18}O equilibration in the original peroxide however, less ^{18}O equilibration in the ester itself manifests less ^{18}O equilibration in the original peroxide.

It is known that the thermal decomposition of this peroxide in carbon tetrachloride affords 4-phenyl-1-chlorobutane in 41% yield[11a] and the addition of iodine and water into the system can trap δ-phenylvaleryloxy and other radicals derived from it.[12] These observations indicate that the decomposition does form both 4-phenyl-n-butyl and δ-phenylvaleryloxy radicals. Accordingly, the radical recombination is quite an important route for the ester formation.

Induced decomposition by 4-phenyl-n-butyl radicals can also give the ester. In this case the ^{18}O-distribution of the resulting ester will be the same as in the rearrangement involving carboxy-inversion. However, it is known that induced decomposition of the peroxide is insignificant at concentrations below 0·02 M/l and of only very minor importance even at about 0·6 M/l.[11b] The cyclic process also cannot be accepted because it requires the alcohol to contain all the excess ^{18}O and the actually observed value of ^{18}O-concentration of the alcohol is lower than that of the ester itself.

The most plausible interpretation of the ^{18}O-data may be that the major path (approx. 70%) of the ester formation is the recombination of two radicals in a solvent

cage while the rearrangement process is responsible for the rest (30%) of the ester formation.

Taylor and Martin found 38% of cage recombination of two acetoxy radicals in the thermal decomposition of APO.[8] However, we were unfortunate in that we could not recover peroxides in a pure state from the reaction mixture, and hence could not examine the possibility of ^{18}O-equilibration in the original labelled peroxide. Therefore, the value of 30% estimated for the carboxy-inversion process is the minimum value while that of 70% estimated for the radical process is the maximum value.

B Mechanism of thermal decomposition of secondary symmetrical diacyl peroxides

When optically active secondary diacyl peroxides, i.e., α-methylbutyl,[13] α-phenylpropionyl[14] and β-phenylisobutyryl[15] peroxides were decomposed thermally in a large amount of solvent, the alcohol moieties of the resulting esters were found to retain practically the configuration of the corresponding acyl groups of the original diacyl peroxides, and a mechanism involving a very fast radical recombination in the solvent cage has been suggested for the ester formation by Green[14] and DeTar *et al.*[15]

These reactions have been considered as novel examples of retention of configuration in carbon radicals.

These stereochemical results can also be explained by assuming the two other mechanisms—the rearrangement process involving carboxy-inversion and the concerted cyclic process—for the ester formation, since both these mechanisms are expected to give stereospecific products.

The thermal decompositions of both carbonyl-^{18}O-labelled (+)- and (±)-β-phenylisobutyryl peroxides (0·021–0·025 M/l) in carbon tetrachloride were carried out by refluxing the solution for about 14 h under a nitrogen stream. While DeTar and Weis[15] found carbon dioxide, 2-chloro-1-phenylpropane, 1-phenyl-2-propyl β-phenylisobutyrate, 1,1,1-trichloro-2-methyl-3-phenylpropane and β-phenylisobutyric acid as the main products under identical reaction conditions, in our experiment, only the resulting ester, i.e., 1-phenyl-2-propyl β-phenylisobutyrate, obtained in about 60% yield, was isolated and purified through a combination of fractional distillation and column chromatography.

Stereospecificities and ^{18}O-incorporations of both β-phenylisobutyric acid and 3-phenyl-1-propanol obtained by the hydrolysis of the resulting ester were examined, and the results are summarized in Table 1.

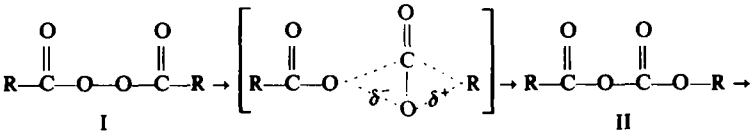
As we have suggested earlier,[10] the most plausible interpretation of these data is that the major path for the ester formation is the heterolytic carboxy-inversion process while the formations of β-phenylisobutyric acid, 2-chloro-1-phenylpropane and 1,1,1-trichloro-2-methyl-3-phenylpropane in this decomposition indicate clearly that a portion of the peroxide decomposes homolytically to form both β-phenylisobutyryloxy and 1-phenyl-2-propyl radicals as DeTar and Weis[15] have suggested. Therefore, while a major portion[16] of the ester may be formed by the ionic route, the remaining portion probably arises from the recombination of β-phenylisobutyryloxy with 1-phenyl-2-propyl radicals in the solvent cage.

Evidence to support the rearrangement process for the ester formation has been obtained as described below. The intermediate, the carbonate (II), presumed to be

TABLE 1. ^{18}O-ANALYSES AND STEREOCHEMISTRY OF THE ESTERS OBTAINED IN THE THERMAL DECOMPOSITION OF β-PHENYLISOBUTYRYL PEROXIDE

$R-C(=^{18}O)-O^{18}-R$		Found %	Calc % cage	Calc % cyclic	Calc % rearr
Retention of configuration (%)	Acid part	(100)[a]	100	100	100
	Alcohol part	92 (approx 75[b])	?[c]	100	100
Incorporation of ^{18}O (%)	Carbonyl-^{18}O	79–89	50	0	100
	Ethereal-^{18}O	11–21	50	100	0

[a] see experimental section; [b] lit[10]; [c] probably partial retention of configuration.



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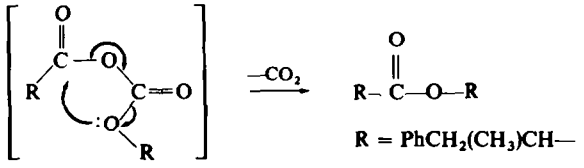


III (1)

obtained by carboxy-inversion of β-phenylisobutyryl peroxide, was identified by infrared analysis during the thermal decomposition of the peroxide. After refluxing the carbon tetrachloride solution of the peroxide for about 10 h, carbon tetrachloride was carefully distilled off at room temperature under reduced pressure. Then, on observing the IR spectrum of the residue, we found that a doublet carbonyl absorption (1805, 1775 cm^{-1}) of the peroxide disappeared completely while that of the carbonate (II, 1815, 1750 cm^{-1}) appeared together with those of the ester (1725 cm^{-1}) and the acid (1705 cm^{-1}).

We have also synthesized 1-phenyl-2-propyl β-phenylisobutyryl carbonate, the key intermediate in the rearrangement process,[17] and subjected it to decomposition in carbon tetrachloride at 77°. Decomposition was very slow under these conditions however, in the presence of β-phenylisobutyric acid (4·5 mole % for the carbonate), it was found to decompose quite smoothly. This indicates that in the thermal decomposition of the peroxide, β-phenylisobutyric acid, a product of the thermal decomposition of the peroxide, may catalyze the decomposition of the carbonate (II).

The kinetic experiments on the thermal decomposition of the β-phenylisobutyryl peroxide (0·1 M/l) in isooctane were carried out in degassed sealed tubes in the temperature range between 30° and 40° ($k_{30} = 2{\cdot}04.\ 10^{-5}\ sec^{-1}$; $k_{35} = 4{\cdot}13.\ 10^{-5}\ sec^{-1}$; and $k_{40} = 7{\cdot}49.\ 10^{-5}\ sec^{-1}$). Hence the activation energy for the decomposition, E_a, was calculated as 25·7 Kcal/mole.

Recently Lamb *et al.*[18] have suggested the rearrangement process via carboxy-inversion for the thermal decomposition of secondary diacyl peroxides such as

cyclohexaneformyl and isobutyryl peroxides in various solvents. The activation energies for the thermal decompositions of these peroxides in carbon tetrachloride were shown to be 23·8 ± 0·4, and 26 ± 0·3 Kcal/mole, respectively.

On the other hand, acetyl and propionyl peroxides and other similar peroxides known to decompose homolytically, usually require 30–32 Kcal/mole of activation energy for their thermal decompositions.[1b]

It is interesting to note that these secondary peroxides require relatively smaller activation energies for decomposition in comparison with those of primary diacyl peroxides. This may be related to the fact that secondary diacyl peroxides decompose mainly by heterolytic rearrangement processes.

Kharasch and his co-workers have reported that the decomposition of an optically active α-methylbutyryl peroxide in benzotrichloride gave, among other products, 2-butyl-α-methylbutyrate in which the 2-butyl group retained 80% of the original configuration.[13]

The thermal decomposition of carbonyl-^{18}O-labeled α-methylbutyryl peroxide, as reported previously,[10] gave 2-butyl α-methylbutyrate the etheral oxygen of which contains ^{18}O corresponding to approx. 8% incorporation of ^{18}O from the original label in the carbonyl oxygens of the peroxide.

We have suggested previously, based on both the ^{18}O-analytical data and the stereochemical results, that the major route (approx. 85%) of the ester formation is the rearrangement process.

Recently, a few reports have appeared to claim that secondary diacyl peroxides such as isobutyryl,[18] cyclohexaneformyl[18] and 4-t-butylcyclohexaneformyl[19] peroxides yield from their decompositions the corresponding carbonates, by carboxy-inversion, which eventually rearranged to afford the corresponding esters.

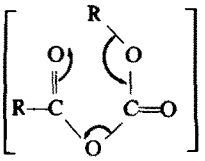
All these observations seem to indicate that the ester formation in the thermal decompositions of most secondary aliphatic diacyl peroxides proceed predominantly through the rearrangement path via carboxy-inversion, leading to retention of configuration in the alcohol moiety of the resulting ester.

C Rearrangement process via carboxy-inversion

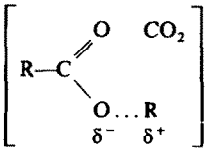
In the preceding section, we have presented evidence to support the decomposition of β-phenylisobutyryl peroxide to the ester by the rearrangement process, as indicated in equation (1).

Since the alcohol part of the resulting ester retains the original configuration by 92% while the carbonyl group also hold the ^{18}O by the same extent in the decomposition, the main path for the decomposition of the carbonate (II) to the ester should involve the acyl-oxygen cleavage shown at (III) of (1), the cyclic path shown at (IV) being completely ruled out. As for the remaining portion of decomposition (approx. 8%) there are two possibilities. One is a path involving alkyl-oxygen cleavage to form an intimate ion pair (V), resulting in partial racemization and ^{18}O-equilibration like other similar ion-pair processes.[20] Another possibility is competing homolytic cleavage, resulting in ester formation in the solvent cage.

At present, there is no good way to make a choice between these two pathways for the competing reaction which is responsible for both the partial racemization and ^{18}O-equilibration. However, the formation of various products, such as 2-chloro-1-phenylpropane, 1,1,1-trichloro-2-methyl-3-phenylpropane, which can be produced



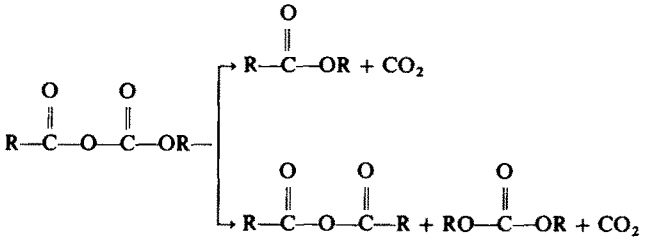
(IV)



(V)

only by the free radical process, seems to favour the competing homolysis for the formation of a partially racemized and ^{18}O-equilibrated ester. The major path of thermal decomposition of II was found to be accelerated in the presence of β-phenylisobutyric acid, just as most ionic reactions involving acyl-oxygen cleavage are affected by general acid catalysis.

Tarbell *et al.*[21] have recently suggested on the basis of ^{18}O-tracer experiments and stereochemical data that the following two different pathways are conceivable for the thermal decomposition of alkyl acyl carbonates.



(2)

(3)

where R = primary or secondary alkyl group.

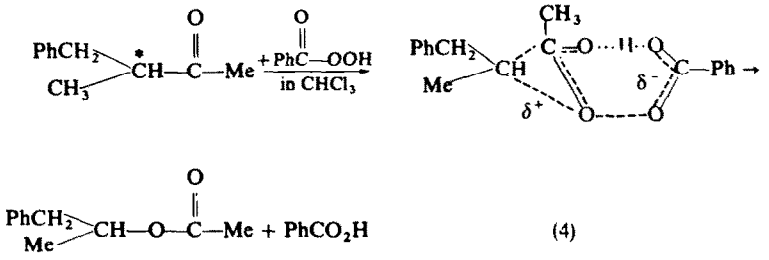
However, in our experiments on the thermal decompositions of both β-phenylisobutyryl peroxide and 1-phenyl-2-propyl β-phenylisobutyryl carbonate (II) in carbon tetrachloride, no formation of products corresponding to (3) was observed from the careful infrared analyses during and after the reaction; just the ester and carbon dioxide were obtained. If these possible intermediates were present in sufficient concentrations in the solution, they could be readily detected from their characteristic carbonyl absorptions in the IR.

The most interesting and still unresolved problem concerning the rearrangement process is the stereochemical fate of the migrating alkyl group of I in reaction (1). Unfortunately, it is very difficult to investigate the stereochemistry of the intermediate, the carbonate (II), in the rearrangement, since the carbonate cannot be isolated during the decomposition of the initial peroxide.

The first step of the decomposition of I undoubtedly involves a concerted 1,2-shift of the 1-phenyl-2-propyl group from carbonyl carbon to peroxide oxygen together with carboxy-inversion. This rearrangement of alkyl group from carbon to oxygen atom resembles those of the Criegee reaction[22] and the Baeyer-Villiger oxidation,[22] and hence knowledge of the stereochemistry of these similar rearrangements helps to strengthen the case.

In order to examine whether or not the same migrating alkyl group retains its

configuration during the Bayer-Villiger rearrangement, an optically active (+)-1-phenyl-2-propyl methyl ketone was subjected to the reaction conditions shown in (4). A full account of this work will be the subject of a subsequent paper[23] in this series. We found that the alcohol moiety of the resulting ester retained its original configuration nearly completely.



(4)

Since the transition state of this reaction resembles that of the decomposition of the peroxide and in both reactions the 1-phenyl-2-propyl group migrates from the carbonyl carbon to the peroxide oxygen and while the leaving groups are similar acylates, this stereochemical trend can be taken as a general pattern for this type of rearrangement. Therefore, the rearrangement of the alkyl group of the peroxide to the carbonate (II) can be assumed as stereospecific, in a way similar to the Baeyer-Villiger reaction of the ketone.

EXPERIMENTAL

Carbonyl-^{18}O-labelled acetyl peroxide (^{18}O—APO). Carbonyl-^{18}O-labelled acetyl chloride (b.p. 51–52°, 1·60 atom %), 5 g, synthesized by the procedure described elsewhere,[6a] in 30 ml of dry ether was kept at 0° and 3 g of sodium peroxide was added. After stirring the mixture at 0–2°, for 30 min 3·2 g of ice water was slowly added into the stirred mixture over a period of 45 min, and the mixture stirred further for 45 min. The ether layer separated from the reaction mixture, was washed with cold 10% Na_2CO_3 soln and cold water and then dried over Na_2SO_4. This was condensed to half volume, the residual solution giving crystals at dry-ice acetone temp. ^{18}O—APO (0·87 atom %) 2·1 g was obtained by recrystallizing 3 from ether following the procedure of Martin and Drew.[24] The purity of the peroxide was found to be >95% according to the method of Price and Morita.[25]

Thermal decomposition of ^{18}O—APO in toluene. The thermal decomposition of 13·5 g of ^{18}O—APO (0·87 atom %) was performed in 450 ml of toluene at 65 ± 1° in a nitrogen atmosphere. The APO was added in 5 or 6 portions over 27 hr, keeping the concentration below 0·012 M/l. The time and the weight of ^{18}O—APO added at intervals were calculated from the decomposition rate, $k = 1{\cdot}14 \cdot 10^{-5}$ sec^{-1} which was obtained for the thermal decomposition of APO (at 0·00685 M/s) in toluene at 64·9° by Levy et al.[1a]

The apparatus consisted of a 500 ml flask with an air-cooled condenser, a sealed-in gas inlet tube and a dropping funnel. Attached to the upper end of the condenser was a cold trap maintained at −60° to −50°.

Isolation of methyl acetate. During the heating of the peroxide solution, all of the decomposition products, methane, ethane and methyl acetate, together with a small amount of the solvents, toluene and ether, originally present in ^{18}O—APO, were collected in the cold trap. Of these only methyl acetate was isolated in pure form by fractional distillation of the trapped materials. Identification of the ester was performed by comparison with an authentic sample in gas chromatography and IR analyses. The ^{18}O-content of the ester thus obtained was found to be 0·394 atom %. The smaller figure is due to the crude ester that contained ether used in the synthesis of ^{18}O-APO.

Reaction of methyl acetate with phenylhydrazine. The mixture of the ester (0·1 g) containing ether thus

obtained by fractionation and phenylhydrazine (0·2 g) was placed in a sealed tube and heated in an oil bath at 130–125° for 2 h. Acetyl phenylhydrazine (m.p. 128–129°), 0·85 atom% of ^{18}O, 30 mg, was obtained by recrystallizing the reaction mixture from benzene and hexane.

δ-Phenylvaleryl chloride. δ-Phenylvaleryl chloride was obtained from δ-phenylvaleric acid and thionyl chloride according to the method of DeTar and Weis.[11a]

δ-Phenylvaleric acid was prepared from cinnamaldehyde and ethyl malonate by the procedure reported by Aspinall and Backer.[26]

Carbonyl-^{18}O-labelled δ-phenylvaleryl chloride. This was obtained from ^{18}O-labelled δ-phenylvaleric acid and thionyl chloride by the same procedure as for the unlabelled compound.

^{18}O-labelled δ-phenylvaleric acid was obtained by hydrolylzing δ-phenylvaleryl chloride with an equimolar amount of ^{18}O-enriched water (approx 3·4 atm %) at 130–140°. ^{18}O-Labelled δ-phenylvaleric acid (m.p. 60°) was obtained in 95% yield by recrystallizing the reaction mixture from hexane.

Carbonyl-^{18}O-labelled δ-phenylvaleryl peroxide. This was prepared by the same procedure as reported the unlabelled peroxide by DeTar and Weis.[11a]

Thermal decomposition of carbonyl-^{18}O-labelled δ-phenylvaleryl peroxide in carbon tetrachloride. Carbonyl-^{18}O-labelled δ-phenylvaleryl peroxide (m.p. 33–34°), 24·5 g, in about 2 l of CCl_4 was refluxed for 59 h under N_2. Apparatus and remaining procedure were described in detail by DeTar and Weis.[11a]

Isolation of 4-phenylbutyl-δ-phenylvalerate. The bulk of the solvent was removed by distillation. The residue was washed with 10% Na_2CO_3 and then water. The organic layer was dried over Na_2SO_4 and then the fraction of b.p. 175–193°/1 mm Hg was collected by fractional distillation. From the IR spectra the fraction (0·82 atom% of ^{18}O) was identical to that of the authentic 4-phenylbutyl-δ-phenylvalerate. Though it could contain trace amounts other decomposition products, 1,8-diphenyloctane and 1,1,1,3-tetrachloro-5-phenylpentane, they could not be distinguished by the IR analysis alone. However, these impurities do not interfere with the ^{18}O-analysis of the ester.

Hydrolysis of 4-phenylbutyl δ-phenylvalerate. A mixture of the ester (1 g) obtained above, MeOH (6 ml), KOH (0·36 g) and water (0·17 ml) was kept at room temp for about 2 h. After MeOH was removed under reduced pressure, water and ether were added to the solid residue, and then the mixture was fractionated. The ether layer was washed with water and then dried over Na_2SO_4. 4-Phenyl-1-butanol (b.p. 133–134°/12 mm Hg, 0·63 atom % of ^{18}O) was obtained from the ether layer by fractional distillation.

^{18}O-Exchange reaction of the ester with ^{18}O-enriched water. A mixture of 4-phenylbutyl-δ-phenylvalerate (0·5 g), MeOH (3 ml), KOH (0·17 g) and ^{18}O-enriched water (0·08 g, 1·5 atom %) was heated at 40° for about 2 h. 4-Phenyl-1-butanol isolated revealed no excess incorporation of ^{18}O, i.e., 0·203 atom %).

Optically active (+)-β-phenylisobutyric acid. β-Phenylisobutyric acid (b.p. 126°/1·3 mm Hg) was prepared from ethyl malonate, benzyl chloride and MeI by the commonly used procedure for ordinary malonic syntheses. The resolution of the acid with quinine was carried out by the technique of DeTar and Weis;[15] $[\alpha]_D^{13}$ +22·1° (C; 9·7, EtOH), 100% of optical purity. Maximum rotation obtained in this series; $[\alpha]_D^{13}$ +22·2° (C; 2·60, EtOH), reported $[\alpha]_D^{21}$ +17·87° (C; 5·034, EtOH).[27]

Carbonyl-^{18}O-labelled (+)-β-phenylisobutyryl chloride. A mixture of (+)-β-phenylisobutyric acid (20 g, $[\alpha]_D^{13}$ +22·1°) and thionyl chloride (33 g) was heated at 55° for 1 h and (+)-β-phenylisobutyryl chloride (b.p. 76°/2 mm Hg) 24·1 g, was obtained by fractional distillation (below 97° bath temperature).

A mixture of the acid chloride (23 g), ^{18}O-enriched water (2·3 g, 3·05 atom % ^{18}O) and dioxane (50 ml) was warmed, with shaking, on a water bath (50°) for 30 min. ^{18}O-Labelled (+)-β-phenylisobutyric acid [b.p. 130°/1·5 mm Hg; $[\alpha]_D^{14·5}$ +13·4° (C = 5·35, EtOH, 64·6% optical purity)] 18 g, was obtained by distillation.

^{18}O-Carbonyl labelled (+)-β-phenylisobutyryl chloride 17 g, was obtained from 17 g of the ^{18}O-labelled (+)-acid and 22·6 g of thionyl chloride. ^{18}O-Content was 1·31 atom %.

Carbonyl-^{18}O-Labelled (+)-β-Phenylisobutyryl Peroxide. Into a stirred mixture of carbonyl-^{18}O-labelled (+)-β-phenylisobutyryl chloride (16 g, 1·31 atom %) and ether (96 ml) at 2°, sodium peroxide (4 g) was added for 10 min and then stirred at 1–2° for 15 min. After cooling the slurry to $-5° \sim -7°$ chopped ice (20 g) was slowly fed into the stirred mixture over a period of 55 min. The emulsion was broken by adding ice-water (20 g) and after stirring at 1–2° for 30 min, the ether layer was separated, washed with 10% Na_2CO_3 and ice-water, and then dried over Na_2SO_4. A highly viscous oily material {$[\alpha]_D^{13}$ +65·5° (C; 6·31, EtOH) 0·78 atom % of ^{18}O}, 13·5 g, was obtained by removing ether under reduced pressure. It showed IR bands at 1805 and 1775 cm^{-1} characteristic of carbonyl absorption in diacyl peroxides. No band corresponding to the peracid, the ester or the acid was observed in the spectrum and ether was the only impurity in it. Its purity was over 84% based upon the method of Price and Morita.[25] Taking the im-

purity into account, the true optical rotation of the peroxide was $[\alpha]_D^{13}$ +78·0°. The optical purity of the peroxide was determined as follows; the oily peroxide was reduced to the acid with KIaq in acetone according to the procedure of DeTar and Weis.[15] β-Phenylisobutyric acid obtained thus showed $[\alpha]_D^{17.5}$ +10·8° (C; 6·55, EtOH).

The optical purity of the acid obtained by the reduction of peroxide is somewhat lower than that of the starting material. So was also the alcohol moiety of the ester which formed by the decomposition of the peroxide. This fact suggests that the optical purity of the acid, is apparently reduced during work-up procedure and hence the calculation of the stereospecificity of the ester formation was estimated on the basis of the optical purity of the starting material.

Thermal decomposition of carbonyl-^{18}O-labelled (+)-β-phenylisobutyryl peroxide in carbon tetrachloride. The carbonyl-^{18}O-labelled-(+)-peroxide ($[\alpha]_D^{13}$ +78·0 atom %) 9·6 g in 1·41 of CCl_4 was refluxed for 14 h under N_2. The decomposition was performed according to the method of DeTar and Weis.[15]

Isolation of 1-phenyl-2-propyl β-phenylisobutyrate. 1-Phenyl-2-propyl β-phenylisobutyrate (b.p. 139°/0·5 mm Hg) was purified by fractional distillation and column chromatography (carrier: 80–100 mesh of active alumina for chromatography, eluent: hexane). The ester was identified by comparing its IR spectrum with that of the authentic sample and also by gas chromatography. The pure ester had $[\alpha]_D^{13}$ +20·7° (C; 4·26, EtOH) and 0·78 atom % of ^{18}O.

^{18}O-Exchange reaction of the ester during the chromatography of the ester. ^{18}O-Labelled 1-phenyl-2-propyl β-phenylisobutyrate (0·67 atom %, its etheral oxygen was 0·30 atom % of ^{18}O) was passed through a 15 × 400 mm column of active alumina using hexane as eluent. The ester eluted from the column revealed no variation of incorporation of ^{18}O, i.e., 0·68 atom %.

Hydrolysis of the ester. A mixture of the resulting ester (1·8 g, $[\alpha]_D^{13}$ +20·7°, 0·78 atom % of ^{18}O), MeOH (17 ml), KOH (0·7 g), and water (0·25 ml) was kept at room temperature for about 3 h. After removing MeOH under reduced pressure, water and ether were added and the mixture fractionated.

The ether layer was washed with water, and dried over Na_2SO_4, and then fractionally distilled. 1-Phenyl-2-propyl alcohol obtained had $[\alpha]_D^{17}$ +10·3° (C; 5·0, EtOH) or 55·7% optical purity (based on the maximum rotation of $[\alpha]_D^{24}$ 18·5 in EtOH)[23] and 0·44 atom % of ^{18}O.

After the water layer was neutralized with conc H_2SO_4, ether extraction was performed, and the extract was washed with water, and then dried over Na_2SO_4. β-Phenylisobutyric acid obtained had $[\alpha]_D^{17.5}$ +9·2° (C; 5·98, EtOH, 41·4% optical purity) and 0·67 atom % of ^{18}O. The optical purity of the acid was also lower than that of the alcohol part of the ester. This may be due to the technical loss during the isolation as in the case of the reduction of the peroxide.

^{18}O-Exchange reaction of the ester with ^{18}O-enriched water. A mixture of 1-phenyl-2-propyl β-phenylisobutyrate (1·45 g), MeOH (14 ml), KOH (0·58 g) and ^{18}O-enriched water (0·2 g, 1·5 atom %) was refluxed for 3·4 h. 1-Phenyl-2-propyl alcohol obtained revealed no incorporation of ^{18}O, 0·210 atom %.

Thermal decomposition of 1-phenyl-2-propyl β-phenylisobutyryl carbonate (II) in carbon tetrachloride. II (0·9 g) in CCl_4 (100 ml) was refluxed for 20 h. After the solvent was removed under reduced pressure, the spectrum of the residue revealed the formation of a small amount of 1-phenyl-2-propyl-β-phenylisobutyrate in addition to unreacted II.

On the other hand, in the presence of β-phenylisobutyric acid (0·020 g) under the same conditions, the reaction proceeded smoothly with evolution of CO_2; the carbonate disappeared completely by refluxing for 7 h. The ester and 2-chloro-1-phenylpropane were identified by comparison with authentic samples by gas chromatography. The synthesis of the carbonate will be described in the following paper.[17]

Kinetic runs in the thermal decomposition of β-phenylisobutyryl peroxide in isooctane. Each of the 17 ml Pyrex reaction tubes was filled with 2 ml of the peroxide-isooctane solution (0·100 M/l) kept at 0°C, then frozen in a dry ice-methanol bath, evacuated and sealed. The tubes were then immersed in a constant temperature water bath. After desired time intervals, tubes were taken out, placed in a dry ice-methanol bath, the seal broken, and the contents titrated for peroxide concentration by the following procedure: isopropyanol, 7–8 ml, was added into the reaction mixture in a reaction tube, and shaken until the contents become homogeneous. It was then poured into a prepared soln of isopropanol (30 ml), glacial AcOH (1 ml), sat KIaq (1 ml) and dry ice (5·8 g). The mixture was heated until it began to boil and then titrated with 0·05 N $Na_2S_2O_3$. A good first order kinetic behaviour was observed in each case.

α-Methylbutyryl chloride. This chloride (b.p. 58°/98 mm Hg) was prepared by treatment of α-methylbutyric acid with thionyl chloride following the same procedure as Kharasch *et al.*[13]

Carbonyl-^{18}O-labelled α-methylbutyryl chloride. A mixture of α-methylbutyryl chloride (39·8 g) and ^{18}O-enriched water (6 g, 2·8 atom %) was heated on an oil bath at 120–130° for about 3 h. ^{18}O-Labelled

α-methylbutyric acid (31 g, b.p. 74–75°/12 mm Hg) was obtained by the fractional distillation of the reaction mixture containing 30 ml of benzene.

Carbonyl-^{18}O-labelled α-methylbutyryl chloride (b.p. 115°, 0·67 atom % of ^{18}O) was obtained by treatment of the ^{18}O-labelled acid and thionyl chloride.

Thermal decomposition of carbonyl-^{18}O-labelled α-methylbutyryl peroxide in benzotrichloride. The preparation and the thermal decomposition of the carbonyl-^{18}O-labelled peroxide were worked up according to the method of Kharasch *et al.*[13]

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