

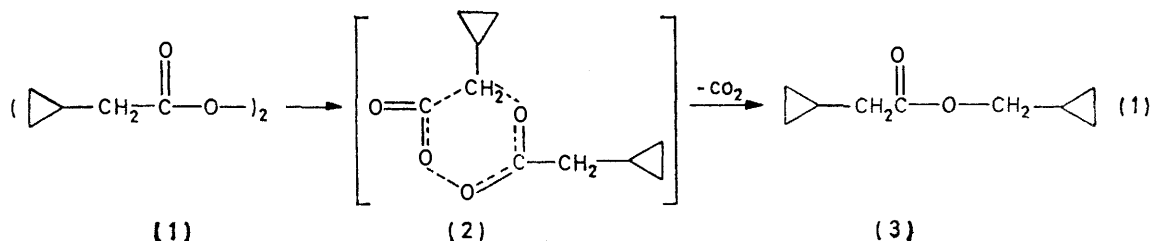
Decomposition of Diacyl Peroxides. Part VIII.¹ Mechanism of Thermal Decomposition of Cyclopropaneacetyl Peroxide

By Shigeru Oae, Kenji Fujimori, and Seizi Kozuka,* Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi, Osaka 558, Japan
Yuzuru Uchida, Department of Applied Chemistry, Osaka Institute of Technology, Asahi-ku, Osaka 535, Japan

The thermal decomposition of cyclopropaneacetyl peroxide in CCl_4 has been studied in detail. Major products of the decomposition at 55° were cyclopropylmethyl cyclopropaneacetate, cyclopropylmethyl cyclopropaneacetyl carbonate, 1,1,1,3,5-pentachloropentane, and carbon dioxide. A tracer study with [^{18}O]carbonyl labelled peroxide indicated that there was no oxygen scrambling in the original peroxide while there was oxygen scrambling both in the resulting carbonate formed *via* carboxy-inversion and in the ester. The carbonate did not give the ester under the conditions employed for the decomposition of the peroxide. On the basis of the ^{18}O and other studies, radical cage recombination is suggested for the formation of the ester and a cyclic mechanism is ruled out. The distribution of ^{18}O in the carbonate is explained by the assumption of transient formation of a common intermediate prior to both the radical and carboxy-inversion processes. Thermal decomposition of the carbonate to give the ester was also studied and this proceeds by acyl-oxygen bond fission.

HART *et al.* studied the thermal decomposition of several cycloalkaneacetyl peroxides and reported that decomposition of cyclopropaneacetyl peroxide (1) gives cyclopropylmethyl cyclopropaneacetate (3) in anomalously high yield (56%) compared with the decomposition of

via both radical and carboxy-inversion processes.⁴ The carboxy-inversion process is favoured in polar media⁵ and by the presence of an alkyl group to stabilize the positive charge which develops on the oxygen in the transition state.⁴ Thus, a cyclopropylmethyl group, as



other peroxides.² The rate of decomposition of the peroxide in CCl_4 is 55 times faster than that of cyclohexaneacetyl peroxide.³ On the basis of these observations, a six-membered cyclic intermediate (2) was suggested in the decomposition of cyclopropaneacetyl peroxide [equation (1)].²

The thermal decomposition of diacyl peroxide proceeds

¹ Part VII, K. Fujimori, and S. Oae, *Tetrahedron*, 1973, **29**, 65.

² H. Hart and D. P. Wyman, *J. Amer. Chem. Soc.*, 1959, **81**, 4891.

³ H. Hart and R. A. Cipriani, *J. Amer. Chem. Soc.*, 1962, **84**, 3697.

expected, promotes the carboxy-inversion process. The high yield of ester formation in the thermal decomposition can be explained on the basis of carboxy-inversion rather than a cyclic process since the ester is readily formed by decarboxylation of the inversion product, *i.e.*, the acyl alkyl carbonate.^{4,6} However, there is also a possibility of the ester formation by radical recombination.

⁴ (a) T. Kashiwagi, S. Kozuka, and S. Oae, *Tetrahedron*, 1970, **26**, 3169; (b) F. D. Green, H. P. Stein, C. C. Chu, and F. M. Vans, *J. Amer. Chem. Soc.*, 1964, **86**, 2081.

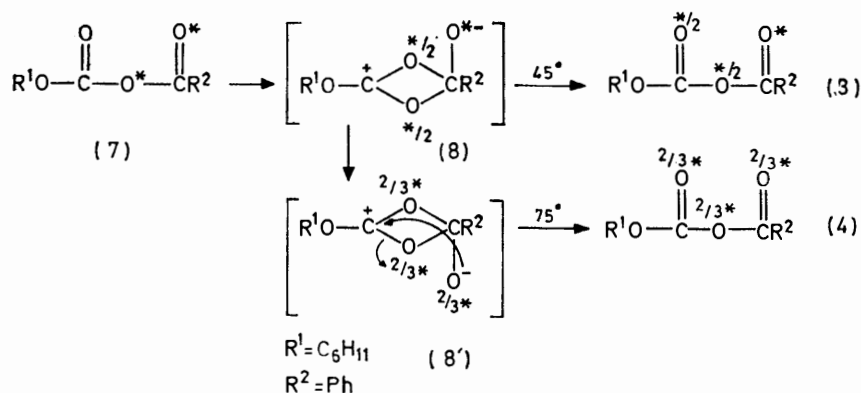
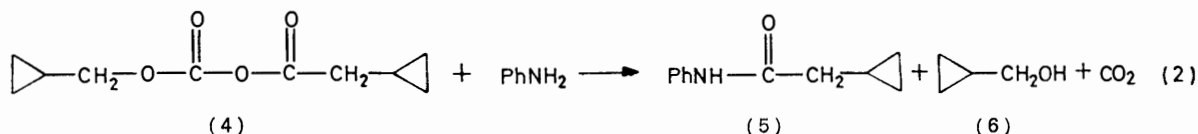
⁵ J. E. Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 67.

⁶ C. L. Michejda, D. S. Tarbell, and W. H. Saunders, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 4113.

These different modes of decomposition can be distinguished by careful product analysis, inspection of changes in the i.r. spectra in the carbonyl region during decomposition, and by ^{18}O tracer experiments. Thus, we reinvestigated the thermal decomposition of cyclopropaneacetyl peroxide by all these methods.

RESULTS AND DISCUSSION

Decomposition of peroxide (1) was carried out in dilute CCl_4 solution ($<0.03\text{M}$) in an evacuated sealed tube at 55° . Under these conditions, the rate follows first-order kinetics ($k\ 3.2 \times 10^{-4}\ \text{s}^{-1}$). I.r. analysis of the solution during the reaction was performed at appropriate intervals. New bands at 1790 and $1810\ \text{cm}^{-1}$ were observed



together with a decrease in the peroxide carbonyl absorption. The absorptions at 1790 and $1810\ \text{cm}^{-1}$ were evidently due to the carboxy-inversion product, *i.e.*, cyclopropaneacetyl cyclopropylmethyl carbonate (4).^{1,7b} Decarboxylation of the carbonate (4) to the ester (3) was not detected by i.r. analysis even after prolonged heating of the solution at 55° . However, at higher temperatures ($>80^\circ$), the carbonate was found to decompose giving the ester and carbon dioxide.

The extent of ester formation was substantially lower than that reported by Hart *et al.*³ The amount previously found may have included some carbonate in view of the experimental procedure adopted. Another possibility is that the thermal or acid-catalysed decomposition of carbonate resulted in ester being formed during work-up.

The i.r. observations clearly suggest that there are at least two competing processes in the thermal decomposition of the peroxide, one giving the carbonate (4) and the other leading to the ester (3) direct from the peroxide, presumably by radical recombination.

Several attempts to isolate the carbonate were unsuccessful. However it was easily trapped by the addition

⁷ (a) S. Oae, Y. Uchida, K. Fukimori, and S. Kozuka, *Bull. Chem. Soc. Japan*, 1973, **46**, 1741; (b) S. Oae, K. Fujimori, and Y. Uchida, *Tetrahedron*, 1972, **28**, 5321.

of aniline at room temperature to the residue of the solution to give cyclopropaneacetanilide (5), cyclopropane-methanol (6), and carbon dioxide [equation (2)]. Under these conditions the ester was unaffected. This procedure is beneficial not only in determining the yields of ester and carbonate but also for ^{18}O tracer experiments (see later).

Another new product, 1,1,1,3,5-pentachloropentane, which was not reported earlier,^{2,3} was obtained in our experiments. This compound is probably derived from radical decomposition of the peroxide followed by the rearrangement of the cyclopropylmethyl group by analogy with the mode of decomposition of other diacyl peroxides in CCl_4 .²

The product analysis is given in Table I and accounts for 94% of the carboxy and 85% of the alkyl portions of the original peroxide.

TABLE I
Products of the thermal decomposition of cyclopropaneacetyl peroxide (0.025M) in CCl_4 at 55°

Products ^a	Yield (%) ^b
$\text{C}_4\text{H}_7\text{CO}_2\text{C}_4\text{H}_7$	18 ^c
$\text{C}_4\text{H}_7\text{OCO}_2\text{COC}_4\text{H}_7$	37 ^d
CO_2	96 ^e
$\text{CCl}_3\text{CH}_2\text{CHClCH}_2\text{CH}_2\text{Cl}$	60 ^e

^a C_4H_7 = Cyclopropylmethyl. ^b Mole % from one mole of peroxide. ^c Determined by g.l.c. ^d Estimated from the reaction with aniline. ^e By titration.

Examination of the [^{18}O]carbonyl labelled peroxide indicated that there was no ^{18}O scrambling in the original peroxide, *i.e.* peroxide recovered at about the half-way point of the reaction showed no excess ^{18}O in the peroxide oxygen upon analysis by Goldstein's procedure.⁸

¹⁸O Distribution in the Carbonate.—Recently we found a novel, stepwise, scrambling reaction of the oxygen atoms in benzoyl cyclohexyl carbonate (7).⁷ Two oxygen atoms of the carbonate (7) were found to scramble upon heating at 45° and three oxygen 75° [equations (3) and (4)].

⁸ M. J. Goldstein and H. A. Judson, *J. Amer. Chem. Soc.*, 1970, **92**, 4119.

In order to examine this mode of reaction in carbonate (4) and also to clarify the mechanism of decomposition of peroxide (1), the ^{18}O content of the carbonate was examined.

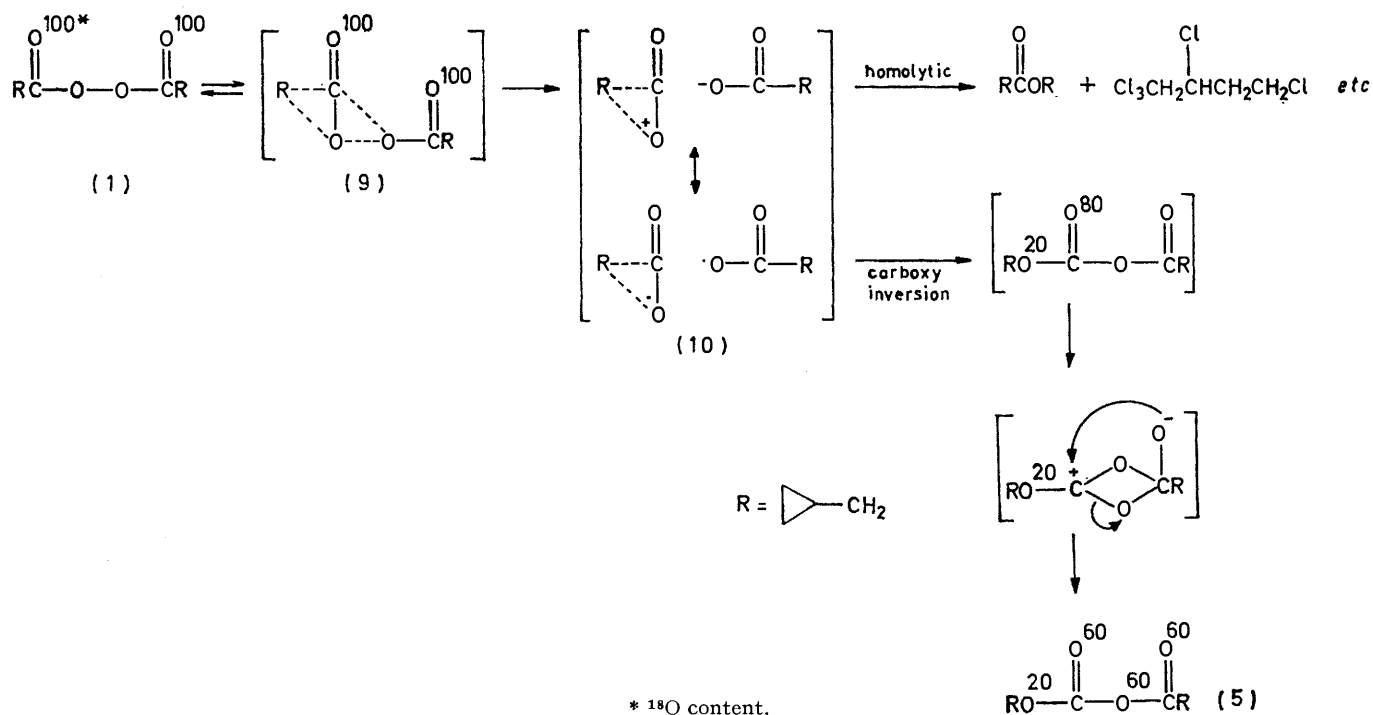
Aniline was added to the reaction mixture after decomposition of the peroxide (55° ; 6 h) and the solvent was evaporated at room temperature. Cyclopropaneacetanilide (5) was isolated, the residue was subjected to reaction with phenyl isocyanate after removal of the ester, and the alcohol (6) was isolated as the carbamate. To examine possible oxygen scrambling in carbonate (4),

TABLE 2
Results of ^{18}O analysis for cyclopropylmethyl
cyclopropaneacetyl carbonate formed at 55°

Compound ^a	^{18}O Excess (atom %)		
	6 h	9 h	15 h
$\text{C}_4\text{H}_7\text{COCl}$ ^b	1.62	1.62	1.62
$\text{C}_4\text{H}_7\text{CONHPh}$	1.00	1.00	0.96
$\text{C}_4\text{H}_7\text{OCONHPh}$ ^c	0.16	0.16	0.16

^a C_4H_7 = Cyclopropylmethyl. ^b Analysed after conversion to anilide. ^c Derived from the alcohol, ^{18}O content of the alcohol should be multiplied by two.

heating of the solution at 55° was continued for an additional 3 and 9 h. The anilide and carbamate were



* ^{18}O content.

obtained each time. The analytical results of ^{18}O content for these compounds are given in Table 2 together with that of the acyl chloride used for the preparation of the ^{18}O -labelled peroxide.

As shown in Table 2, the alcohol contains ca. 20% of

⁹ (a) D. B. Denny and D. G. Denny, *J. Amer. Chem. Soc.*, 1957, **79**, 4806; (b) D. B. Denny, *ibid.*, 1956, **78**, 590.

¹⁰ S. Oae, K. Fujimori, and S. Kozuka, *Tetrahedron*, 1972, **28**, 5327.

the original label in the peroxide. This pattern is considerably different from those we observed previously with other peroxides.^{9,10} The incorporation of ^{18}O into the alcohol oxygen was apparently not due to any scrambling of oxygen in the carbonate after its formation because prolonged heating produced no variation in the distribution of ^{18}O . The ^{18}O content of the anilide remained essentially the same irrespective of the heating period and was in good agreement with the calculated value based on complete scrambling of the three oxygen atoms of the carbonate except for the alcohol oxygen (0.97%). These data suggest that a small amount of ^{18}O was incorporated into the alcohol oxygen during the initial step leading to the carbonate and the remaining three oxygens were scrambled immediately after formation of the carbonate. This pattern of oxygen scrambling was also different from cases we previously encountered in the decomposition of apocamphoryl peroxide¹⁰ and benzoyl cyclohexanecarbonyl peroxide.¹¹ The cycloalkyl groups migrated to the peroxide oxygen with very little scrambling of ^{18}O and the scrambling of the three other oxygens in the resulting carbonates required higher temperatures than those for the decomposition of the peroxides.^{7a}

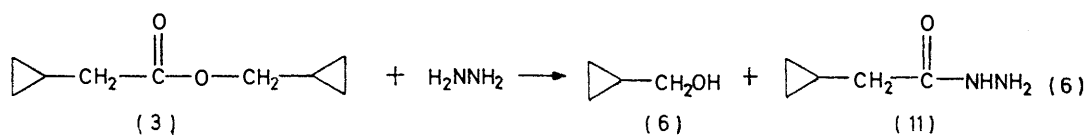
A common intermediate which includes contributions

from both radical and ion pairs was suggested recently by Walling *et al.*¹² to account for both radical and ionic processes in the decomposition of peroxides. A similar intermediate has also been postulated by us to explain the rate of decomposition of apocamphoryl peroxide and

¹¹ S. Oae, K. Fujimori, S. Kozuka, and Y. Uchida, unpublished results.

¹² C. Walling, H. P. Waits, J. Milovanovic, and C. G. Rapiannou, *J. Amer. Chem. Soc.*, 1970, **92**, 4927.

the extent of radical, polar, and oxygen scrambling processes in various solvents.¹³ The partially separated structure (10) is presumed to arise from a common intermediate. No oxygen scrambling reaction is expected when the peroxide decomposes *via* (9) when both bonds form and break concurrently¹⁰ as in the Criegee reaction where no oxygen scrambling was found in the migrating carboxylate group.¹⁴ The reaction pathway through (10), on the other hand, results in a substantial scrambling in the carboxylate half and subsequently simultaneously gives rise to at least partial scrambling in the other half, resulting in the partial incorporation of ¹⁸O in the alcohol oxygen in the carbonate. The different



pattern of ¹⁸O incorporation in the alcohol oxygen in carbonate (4) from that of apocamphoryl benzoyl peroxide¹⁰ and benzoyl cyclohexanecarbonyl peroxide¹¹ can be explained in terms of the stabilizing of intermediate (10) by the cyclopropylmethyl group that induces ready separation of intermediate (9) into (10). The ready decomposition of phenylacetyl peroxide,¹⁵ reported earlier by Bartlett *et al.*, can also be explained in terms of the carboxy-inversion process facilitated by the stabilization of the incipient intermediate by the migrating benzyl group.

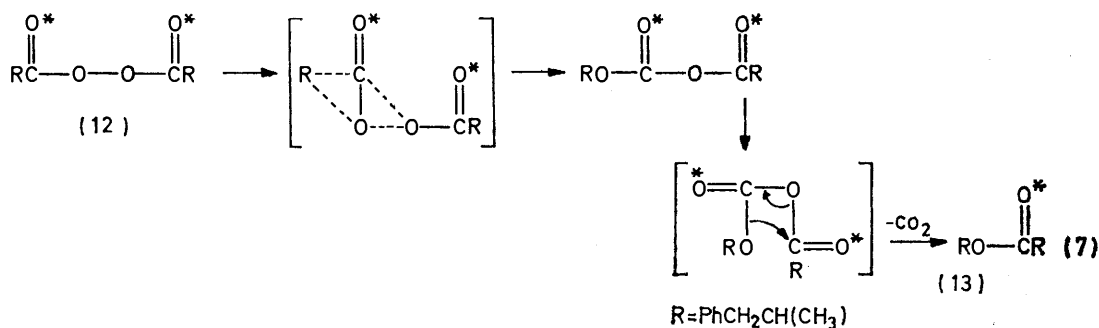
¹⁸O Distribution in the Ester.—The ester, formed directly by thermal decomposition of ¹⁸O-labelled

scrambled in the resulting ester. Since there was no oxygen scrambling in the starting material, this result indicates clearly that the ester is formed not by the cyclic process² but by radical cage recombination as in the cases of acetyl¹⁶ and other primary alkyl peroxides.⁴

Thermal Decomposition of the Carbonate.—On the basis of stereochemical and ¹⁸O tracer experiments, we reported earlier that carboxy-inversion is the predominant route to ester (13) in the thermal decomposition of (+)-β-phenylisobutyryl peroxide (12).^{4a} A small amount of racemization and ¹⁸O scrambling was explained in terms of the competing radical recombination process on the assumption that the inversion process produces the

stereospecific and unscrambled product [equation (7)]. In the present study, however, carbonate (4) was found not only to be stable at the temperature for decomposition of the peroxide but also to decompose at a slightly higher temperature. Therefore, the mechanism of the decarboxylation of the carbonate may be diagnosed from the analysis of content and distribution of ¹⁸O in the resulting ester.

The carbonate formed in the reaction mixture was allowed to decompose at 80° for 150 h. After decomposition was complete the ester was obtained in 37% yield (suggesting 51% ester was derived from the carbonate since the yield of directly formed ester was 18%).



peroxide (1), can be isolated free from any impurity derived from thermal decomposition of carbonate (4). After trapping the carbonate with aniline, the ester was isolated by column chromatography and was then subjected to treatment with hydrazine in liquid ammonia [equation (6)]. The alcohol (6) was converted into the carbamate as before. The hydrazine (11) and the carbamate were subjected to ¹⁸O analysis and the isotope distribution in the ester was obtained with an estimated error of <±2%. The original label is nearly completely

The ¹⁸O content and distribution in the ester were analysed as described above and the amount of ¹⁸O due to the ester formed by the radical cage recombination was proportionally subtracted from the observed value. The ¹⁸O content of the ester, formed by decarboxylation of carbonate (4) was found to be 75–76% that of the original isotope content. The ¹⁸O distribution in the ester was 44–50 and 23–32% in the carbonyl and alcohol oxygens respectively. These results support acyl-oxygen bond fission during decarboxylation as

¹³ S. Oae, K. Fujimori, S. Kozuka, and Y. Uchida, unpublished results.

¹⁴ D. B. Denny and D. G. Denny, *J. Amer. Chem. Soc.*, 1956, **78**, 4296.

¹⁵ P. D. Bartlett and J. E. Leffler, *J. Amer. Chem. Soc.*, 1950, **72**, 3030.

¹⁶ J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, 1967, **89**, 6904.

shown in equation (7), though some experimental error due to the method of analysis was unavoidable.

EXPERIMENTAL

Materials.—Cyclopropaneacetic acid, b.p. 105° at 37 mmHg, was obtained by alkaline hydrolysis of methyl cyclopropaneacetate which was prepared by photolysis of cyclopropyl diazomethyl ketone in methanol.¹⁷ The ¹⁸O labelled acid was obtained by adding ¹⁸O enriched water (3.1 g) to cyclopropaneacetyl chloride (12 g) in an ice-bath, and then heating at 80° for 2 h. The labelled acid was converted to the acyl chloride by treating it with thionyl chloride (15 g) at room temperature, b.p. 133—135° (88%). Cyclopropaneacetyl peroxide (8.8 g) was prepared as by Hart *et al.*² from the acyl chloride (12 g) and Na₂O₂ (4.5 g).

Oxygen Scrambling in Peroxide (1).—The ¹⁸O labelled peroxide (1) was recovered when decomposition was about half complete in CCl₄ at 55° and was converted into molecular oxygen by alkaline hydrolysis to H₂O₂ followed by oxidation with Ce(SO₄)₂.^{8,10} The oxygen contained no excess ¹⁸O.

Thermal Decomposition of Cyclopropaneacetyl Peroxide.—A typical run for product isolation was as follows. The peroxide (7.32 g) solution in CCl₄ (1.5 l) was sealed in four evacuated 500 ml glass tubes in a constant temperature bath and were left at 55° for 6 h. After decomposition was complete the solvent was removed at room temperature, aniline (2.23 g) was added to the residue, and was left overnight at room temperature. The mixture was separated by chromatography through silica gel (35 g) using CCl₄ as eluant to obtain the ester. This was rechromatographed through silica gel (30 g) and distilled under reduced pressure giving the ester (0.33 g), b.p. 95—96° at 25 mmHg. Cyclopropaneacetanilide and cyclopropanemethanol were obtained by elution with ether. The *anilide* (0.32 g) was collected by filtration after removal of ether and washed with n-hexane (30 ml), m.p. 99.0—99.5° (from n-hexane-chloroform) (Found: C, 75.2; H, 7.5; N, 8.0. C₁₁H₁₃NO requires C, 75.4; H, 7.5; N, 8.0%). The alcohol was characterized by distilling the filtrate and allowing the distillate to react with phenyl isocyanate to give *cyclopropylmethyl N-phenyl-carbamate*, m.p. 76.5—77.0° (from n-hexane) (Found: C, 68.95; H, 6.85; N, 7.35. C₁₁H₁₃NO₂ requires C, 69.1; H, 6.85; N, 7.35%).

I.r. Analyses and Kinetic Experiments of Decomposition.—I.r. spectra of the decomposition solution were examined for CCl₄ solutions with a JASCO SG-25 spectrometer. Kinetic measurements were taken at 55° in degassed sealed tubes and the rate was followed by estimating the remaining peroxide by iodometry.¹⁰

¹⁷ R. G. Bergman, *J. Amer. Chem. Soc.*, 1969, **91**, 7405.

Hydrazine Cleavage of Ester (3).—Dry hydrazine hydrochloride (1 g) was dissolved in liquid NH₃ (60 ml). Cyclopropylmethyl cyclopropaneacetate (0.30 g) was added and the mixture was stirred for 12 h in Dry Ice-acetone bath. The residue was extracted with ether after evaporation of NH₃ and gave *cyclopropaneacetohydrazide* (11) (0.15 g), m.p. 92.0—92.5° (from CCl₄-CHCl₃) Found: C, 52.9; H, 8.75; N, 24.8. C₅H₁₀N₂O requires C, 52.6; H, 8.85; N, 24.55%. Cyclopropanemethanol was obtained from the filtrate and converted into the carbamate. The ¹⁸O content of these compounds is listed in Table 3. Another experiment using [¹⁸O]carbonyl labelled ester (1.56 excess atom %) gave hydrazide (11) with the same ¹⁸O content within experimental error suggesting no oxygen exchange during hydrazine cleavage.

TABLE 3

¹⁸O Content and distribution in ester (3) formed by decomposition of (1)

Compound ^a	¹⁸ O Excess (atom %)
C ₄ H ₇ COCl ^b	1.47
C ₄ H ₇ CO ₂ C ₄ H ₇	0.74
C ₄ H ₇ CONHNH ₂	0.69
C ₄ H ₇ CONHPh ^c	0.40

^a C₄H₇ = Cyclopropylmethyl. ^b Used for preparation of (1), analysed in the form of anilide (5). ^c ¹⁸O Content of the alcohol should be multiplied by two.

Decomposition of Carbonate (4).—After complete decomposition of peroxide (1) at 55°, the solution was kept at 80° for 150 h to decompose carbonate (4). After removal of the solvent by distillation, the ester was isolated as above. The ¹⁸O analytical results are given in Table 4.

TABLE 4

¹⁸O Analyses of the combined ester fractions (3) ^a

Compound ^b	¹⁸ O Excess (atom %)	
	Run 1	Run 2
RCOCl ^c	1.70	1.58
RCO ₂ R	0.75	0.69
RCONHNH ₂	0.81	0.79
ROH	0.69 ^d	0.59 ^d

^a 49% Formed by radical cage process and 51% from decarboxylation of carbonate (4). ^b R = Cyclopropylmethyl. ^c Used for synthesis of (1), analysed after conversion into anilide (5). ^d Calculated value obtained from the ¹⁸O content of ester (3) and hydrazide (11).

¹⁸O Analyses were performed as reported previously.^{8b} Mass spectra were recorded on a Hitachi RMU-6E mass spectrometer.

[4/815 Received, 22nd April, 1974]