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THE DECOMPOSITION OF DIACYL PEROXIDE—III

THE PHOTOCHEMICAL DECOMPOSITION OF β-PHENYLISOBUTYRYL PEROXIDE[1]

T. KASHIWAGI, K. FUJIMORI, S. KOZUKA and S. OAE*
Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sumiyoshi-ku, Osaka, Japan

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Abstract— The direct photodecomposition of the title peroxide was performed by irradiation in isooctane solution with a low pressure mercury lamp at room temperature. The rate constant of the decomposition was $8 \cdot 5 \times 10^{-6}$ sec^{-1} (at 0·0162 M/l of initial concentration, at 25°). Main products were carbon dioxide, 1-phenyl-2-propyl β-phenylisobutyrate, 1,4-diphenyl-2,3-dimethylbutane, n-propylbenzene, β-phenylisobutyric acid, 1-phenyl-2-propyl alcohol and 3-phenyl-2-propanone. All these products are apparently formed by the homolytic decomposition of the peroxide in contrast to the thermal decomposition of the peroxide which was found to proceed mainly through heterolysis. The alkyl dimer, a main product in the decomposition of the optically active peroxide, is optically inactive and an equimolar mixture of meso and (±)-compounds. The alcohol moiety of the resulting ester retained the original configuration by 68% while the carbonyl oxygen kept the original ^{18}O-label by 85%. These observations are interpreted in terms of two competing reactions i.e., a 4-membered cyclic process and a radical recombination in solvent cage. The acetophenone-photosensitized decomposition proceeded more smoothly. Since the products are similar to those in the direct photolysis of the peroxide, the mechanism may be similar to that of direct photolysis. In this case, however, the acid was the main product.

WALDER and Wild[2] reported that acetyl peroxide decomposes photochemically in cyclohexane and alcohol. Later, Luner and Szwarc[3] investigated the photochemical decomposition of a dilute solution of acetyl peroxide in benzene with 2537A-light and in isooctane containing a small amount of anthracene or naphthacene with 3650A-light. Fichter *et al.* reported that benzyl peroxide[4] and acetyl benzoyl peroxides[5] decompose under UV light irradiation. Recently the photochemical decomposition of benzoyl peroxide has been investigated in detail.[6-8]

The photochemical decomposition of only a few simple diacyl peroxides such as acetyl and benzoyl peroxides have been investigated in detail. Since these decompositions were carried out in light absorbing solvents, where one cannot separate direct photolysis from sensitized photolysis, only a limited understanding of the mechanism of the photodecomposition can be obtained.

The photochemical decomposition of an aliphatic secondary diacyl peroxide, namely β-phenylisobutyryl peroxide was carried out both in a light-transparent solvent, isooctane, and in the same solvent in which a photosensitizer, acetophenone, was dissolved and the results were compared with those of the thermal decomposition of the peroxide.[9] This paper describes details of the investigation.

RESULTS AND DISCUSSION

Direct photolysis. The isooctane solution of β-phenylisobutyryl peroxide (about 0·02 M/l) was irradiated with 10-W low-pressure mercury lamp at room temperature under nitrogen until complete decomposition (ca. 96 hr).

Since over 95% of light emission from the lamp is 2537 A, the peroxide (λ_{max} 2460 A) can absorb the light, but isooctane is transparent to light.

Carbon dioxide, 1-phenyl-2-propyl β-phenylisobutyrate, 1,4-diphenyl-2,3-dimethylbutane, n-propylbenzene, β-phenylisobutyric acid, 1-phenyl-2-propyl alcohol and 3-phenyl-2-propane were obtained as main products. In addition, there were a few unidentified products (gas chromatographic analysis) but none of these corresponded to compounds such as α-, β-, and *p*-methylstyrene, phenyl isopropyl ether and 3-phenyl-2-methylpropanol.

The conditions of the photolysis and the yields of these products are summarized in Table 1. Since these yields were estimated after the first rough fractional distillation and subsequent gas chromatography, the material balance of all these products was not very good. As all major products derived from the peroxide were detected, the discussion on the mechanism of the photolysis based mainly on the product analysis is legitimate and not meaningless.

TABLE 1. DIRECT PHOTOLYSIS OF β-PHENYLISOBUTYRYL PEROXIDE ($(RCO_2-)_2$)

	Run 1	Run 2[a]	Run 3[b]	Run 4[a]
Condition				
Peroxide (mmole)	35·0	41·4	30·6	35·6
Isooctane (l)	1·70	1·94	1·85	1·85
Temp	17–21°	21–24°	23–25°	24–26°
Irradiation time (hr)	97	113	96	95
Yield[c] (mole %)				
CO_2	127·1	126·4	132·0	118·0
RCO_2R	21·3	25·5	28·3	28·1
RR	33·6 + α[e]	40·5	31·7 + α	36·5
RH	11·9	7	*f*	12·3
RCO_2H	*f*	trace	trace	trace
ROH $PhCH_2COOCH_3$ Unknown [d]	1·0 (g)	1·6 (g)	1·0 (g)	0·9 (g)

[a] Carbonyl-^{18}O-labeled β-phenylisobutyryl peroxide was used.

[b] Optically active (−)-β-phenylisobutyryl peroxide was used.

[c] Total yields based on the alkyl groups are accounted for 61, 70, 60 and 71% for run 1, 2, 3 and 4 respectively. Total yield of the carboxyl compounds plus carbon dioxide are 91, 89, 94 and 87% in run 1, 2, 3 and 4 respectively.

[d] Estimation of each of fraction was impossible.

[e] represents RR which was contained in d.

[f] Failed to estimate.

The formation of 1,4-diphenyl-2,3-dimethylbutane and n-propylbenzene etc indicates that the peroxide decomposed homolytically. Therefore, the decomposition and the formation of some of the resulting products may be formulated in Eqs 1–8.

$$(RCOO-)_2 + h\nu \rightarrow (RCOO-)_2^* \quad (1)$$

$$(RCOO-)_2^* \rightarrow 2RCOO\cdot \quad (2)$$

$$RCOO\cdot \rightarrow R\cdot + CO_2 \quad (3)$$

$$\mathrm{RCOO\cdot + R\cdot \rightarrow RCOOR} \tag{4}$$

$$\mathrm{RCOO\cdot + SH \rightarrow RCOOH} \tag{5}$$

$$\mathrm{R\cdot + R\cdot \rightarrow R - R} \tag{6}$$

$$\mathrm{R\cdot + SH \rightarrow RH} \tag{7}$$

$$\mathrm{(RCOO—)_2^* \rightarrow RCOOR + CO_2} \tag{8}$$

Although most of these mechanistic paths are well-known for the thermal decomposition of a few other diacyl peroxides, the intramolecular decomposition reaction of excited peroxide for the ester formation (Eq. 8) should be noted as a unique path only for the photolysis, the mechanism of which together with that of the dimer formation will be discussed in detail later.

Although the apparent rate constant for the photolysis of β-phenylisobutyryl peroxide (0·0162 M/l) in isooctane at 25° under nitrogen tends to increase very gradually, the first order rate constant, $k_{h\nu_{25}} = 8{\cdot}52 \times 10^{-6}$ sec^{-1}, was estimated from the kinetic data between 33–46% of the reaction.

As the photolysis at room temperature required prolonged irradiation (Table 1), it is possible that the thermal decomposition could occur partially during the irradiation. To check this, 1-phenyl-2-propyl β-phenylisobutyryl carbonate (0·0201 M/l), presumed to be an intermediate in the thermal decomposition of β-phenylisobutyryl peroxide,[9] was irradiated in isooctane for 54 hr under the conditions and in the photolysis of β-phenylisobutyryl peroxide. The carbonate did not decompose. In addition irradiation of the carbonate solution in the presence of a small amount of β-phenylisobutyric acid, produced no change in the carbonate. These facts indicate that photolysis of the peroxide, does not proceed via the carbonate, and even though the thermal decomposition of the peroxide competed with the photolysis, the carbonate would not be involved in the decomposition by light. Therefore, the contribution of the thermal decomposition in the photolysis of the peroxide if any is very small.

The results of the thermal decomposition of β-phenylisobutyryl peroxide[9, 12] show that the alkyl dimer which is the most abundant product in the photolysis was not produced during thermal decomposition, and the yield of the ester in the photolysis (25–28%) was smaller than that in the thermal decomposition (60–64%). These differences suggest a different mechanism for photolysis and thermal decompositions. Namely, contrary to the rearrangement process via carboxy-inversion for the thermal decomposition,[9] the photolysis may proceed through the radical process as formulated in Eqs. (1) ~ (8).

1,4-Diphenyl-2,3-dimethylbutane is only formed during photolysis. The dimer formed in the photolysis of both (+)- and or (−)-peroxide consists of nearly equal amounts of the meso- and (±)-product (gas chromatographic analysis). When the photolysis was carried out with an optically active (−)-peroxide (Run 3), the resulting mixed dimers were optically inactive.

Both thermal and photochemical decompositions of acetyl[3, 13] and benzoyl[6, 14] peroxides give dimerized hydrocarbons by the radical recombination in solvent cage but the yield of the recombination product is higher in the photochemical decomposition which occurs at lower temperatures than the thermal decomposition.

Although we cannot prove that the dimer, 1,4-diphenyl-2,3-dimethylbutane, obtained in the photolysis of β-phenylisobutyryl peroxide is a cage product, the mechanism of formation is probably analogous to the photochemical decomposition of acetyl[3] and benzoyl[6] peroxides, since if 1-phenyl-2-propyl radicals leaked out of the solvent cage they would abstract hydrogen from the solvent to form 1-phenylpropane rather than recombine with each other to form the dimer owing to the very low concentration of the radicals. The formation of nearly equal amounts of the meso- and (±)-dimers, suggests that the alkyl group in the dimer does not retain the original configuration in the decomposition of the peroxide and the subsequent recombination. Namely, the dimerization in this case is also apparently a non-stereospecific reaction as in other "free" radical recombination reactions.[15]

If the dimerization is stereoselective as in the photolysis of meso- azo-bis-3-methyl-3-phenylbutane in frozen benzene (−90°),[16] the optically active diasteromer would be formed in greater amount than the (±) and meso diastereomer and this was not found to be the case.

The ester resulting from the thermal decomposition of β-phenylisobutyryl peroxide in carbon tetrachloride was obtained through the rearrangement process via carboxy-inversion in 60% yield, the photolysis of the peroxide in isooctane gave the ester in a lower yield (25–28%). In order to investigate the mechanism of the ester formation, the ^{18}O-tracer and stereochemical experiments were carried out using carbonyl-^{18}O-labelled and optically active (−)-β-phenylisobutyryl peroxides. The resulting ester was hydrolyzed with methanolic potassium hydroxide to obtain 1-phenyl-2-propanol. Under the same condition for hydrolysis, there was no ^{18}O-exchange between the alcohol and potassium hydroxide. The analytical results for ^{18}O together with the stereochemical outcome are shown in Table 2.

Table 2. The direct photolysis of β-phenylisobutyryl peroxide, $(RCOO-)_2$, in isooctane

Compound	(+)-Peroxide (Run 2)	(−)-Peroxide (Run 3)	
	^{18}O-content (excess %)	Optical rotation $[\alpha]_D$ (degree)	Optical purity[c] (%)
RCOCl[a]	1·03	−20·9	
$(RCO_2-)_2$		−71·0[d]	53·2[e]
RCO_2H[b]		−11·8	53·2
RCO_2R	0·53	−20·0	
ROH	0·16[f]	−6·7	36·2[g]

[a] This acyl chloride was used for the preparation of the peroxide.

[b] This acid is a product obtained by reduction of the peroxide with potassium iodide.

[c] Optical purities of (−)-β-phenylisobutyric acid and (−)-1-phenyl-2-propyl alcohol was determined on the basis of the stereochemical data by DeTar *et al.*[12]

[d] Taking the impurity of the peroxide (the purity; 77%) into account, the true optical rotation of the peroxide was $[\alpha]_D$ −92·2°.

[e] Optical purity of the peroxide was calculated based upon the optical purity of the acid obtained by the reduction of the peroxide.

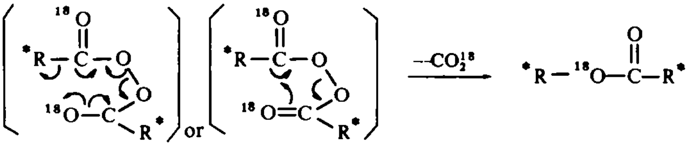
[f] The ^{18}O-concentration correspondents to ca. 15% incorporation of ^{18}O from the original label in the carbonyl oxygens of the peroxide.

[g] It was calculated from the maximum rotation of the alcohol $[\alpha]_D^{24}$ + 18·5° (in EtOH)[17] and the value corresponds to 68% (36·2/53·2) retention of configuration.

From the ^{18}O-tracer experiment (Table 2), the percentage incorporation of ^{18}O in the etheral oxygen (ca. 15%) of the resulting ester agrees with the value of the ester obtained in the thermal decomposition of the peroxide (11–21%).[9] However, the stereochemical outcome indicates that the alcohol portion of the resulting ester retained by 68% the configuration of the alkyl groups of the original peroxide, and this differs from the percentage retention of configuration (92%)[9] of the alkyl group of the resulting ester in the thermal decomposition of the peroxide.

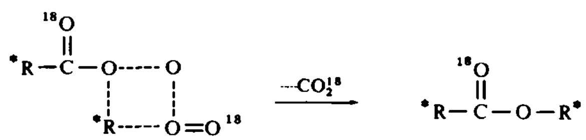
It is unlikely that the ester is the result of a rearrangement process through carboxy-inversion. If the ester is formed only by radical recombination in solvent cage, both O atoms would be completely scrambled,[9] and the alcohol portion of the ester would not retain the configuration since the cage product, 1,4-diphenyl-2,3-dimethylbutane was optically inactive. The induced attack of alkyl radicals on the O—O bond of the original peroxide should produce the ester with ^{18}O incorporation in the etheral oxygen and with the alcohol portion completely racemic. Moreover, the induced decomposition of the peroxide would be difficult in such a low concentration of the peroxide as in this photolysis. Therefore, retention of configuration for the alcohol part of the ester cannot be interpreted by either of these two mechanisms.

An alternative process through a 6-membered cyclic transition state[9] (Eq 9) can give the ester in which the alcohol portion retains the original configuration but the ethereal oxygen would contain all the excess ^{18}O, which is contrary to our observation.



(9)

The following cyclic mechanism through a 4-membered transition state (Eq. 10) would agree with the observed facts.



(10)

At present, our tentative interpretation of our experimental observations is that the ester is formed by two major competing routes, i.e., the one involving the 4-membered cyclic process (at least ca. 70%) and the other, radical recombination in solvent cage (at most ca. 30%). This ratio was estimated, neglecting the possible oxygen scrambling of the original peroxide during the decomposition. Unfortunately the experiment of the ^{18}O-scrambling, $(RCOO)_2 \rightleftharpoons (2RCOO\cdot)$ has not been successful due to the technical difficulty of recovering the peroxide, however, the scrambling would not be very large, since the incorporation of ^{18}O in the etheral oxygen of the resulting ester (15%) agrees with the percentage retention of the alkyl group, when the radical cage mechanism contributes 30% of the ester forming process. The 4-membered cyclic process is reasonable in view of the higher energy state of the reaction and the nature of the electronic excitation which would make the peroxide O atoms more nucleophilic.

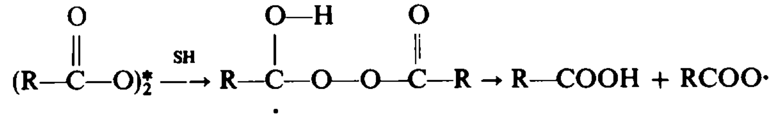
The formation of 1-phenyl-2-propanol and 3-phenyl-2-propanone is probably due to the secondary photolysis of the ester produced in the photolysis of the peroxide. It is known that the photolyses of lower aliphatic esters such as ethyl formate[19] and n-propyl formate[20] produce alkyl-carbonyl carbon and carbonyl carbon-etheral oxygen cleavages.

Photosensitized decomposition. β-Phenylisobutyryl peroxide in isooctane was irradiated in the presence of acetophenone for about 49 hr at room temperature under nitrogen.

The decomposition was found to proceed by energy transfer from excited acetophenone at an excited triplet state to the peroxide. The main products were carbon dioxide (144 mole %), 1-phenyl-2-propyl β-phenylisobutyrate (16 mole %), 1,4-diphenyl-2,3-dimethylbutane (20 mole %), n-propylbenzene (22 mole %) and β-phenylisobutyric acid (42 mole %).

Comparing the yields with those of the direct photolysis (Table 1) one finds that the yields of the dimer and the ester decreased, while those of the acid and n-propylbenzene increased.

Although all these products may be formed by the same mechanistic routes as shown in Eqs 1–8, the formation of substantial portions of the acid and n-propylbenzene may be due to the hydrogen abstraction of triplet peroxide, formed by the energy transfer from the photo-excited sensitizer as formulated in Eq (11) and Eq (12). The induced attack of 1-phenyl-1-hydroxyethyl radicals, which result in the hydrogen abstraction from the solvent is also considerable.



$$(R-\overset{O}{\overset{\|}{C}}-O)_2^{*} \xrightarrow{SH} R-\underset{\bullet}{\overset{O-H}{\overset{|}{C}}}-O-O-\overset{O}{\overset{\|}{C}}-R \rightarrow R-COOH + RCOO\cdot \qquad (11)$$

$$R-COO\cdot \rightarrow RH \text{ or } RCOOH \qquad (12)$$

The dimer obtained in the photosensitized decomposition of the (+)-peroxide also consisted of equal amounts of the (±)- and the meso-forms as in the direct photolysis.

The photosensitized decomposition of the carbonyl-^{18}O-labelled peroxide gave the ester which contained about 12% of ^{18}O in the etheral oxygen.

The ester is considered to be formed in a manner similar to the direct photolysis. Although we have no stereochemical evidence for the ester formation, the results of ^{18}O-tracer experiments indicate that the ester probably results from the two competing reactions of the 4-membered cyclic process and the radical recombination in solvent cage.

EXPERIMENTAL

Optically active (−)- and carbonyl-^{18}O-labelled β-phenylisobutyryl peroxide. These peroxides were prepared according to the previous procedures.[9,12]

Direct photolysis of the peroxide. β-Phenylisobutyryl peroxide in isooctane was irradiated with a low-pressure mercury lamp (Rikosha UVL-2000 Q, 10-W. inner-irradiation type) with stirring at room temp under N_2. The conditions were shown in Table 1.

Isolation and confirmation of products. CO_2 evolved during irradiation was trapped by bubbling through an $Ba(OH)_2$ aq. While the liquid products was isolated and identified by a combustion of fractional distillation, gas chromatography and elemental and IR analyses, for the gas chromatography two kinds of columns were used; column A: liquid phase; PEG # 6000, 2% absorbent; Fire Brick 60–80 mesh, siliconized, 4 m; column B: liquid phase; high vacuum silicone grease, 5% absorbent; siliconized Fire Brick 40–60 mesh, 3 m.

When the peroxide was completely decomposed, the isooctane soln was concentrated to about 40–50 ml by distillation. The residue was washed with 10% Na_2CO_3 aq. A detectable amount of β-phenylisobutyric acid was obtained from the alkaline soln. It was confirmed by comparing the IR spectrum and the gas chromatographic retention time with that of the authentic sample. After the organic layer was washed with water and then dried over Na_2SO_4, it was divided into three parts by fractional distillation; fraction 1; 53°/19 mmHg, fraction 2; 67·5°/2·9 mmHg – 129/1 mmHg and the residue. Although the fraction 1 has two gas chromatographic peaks (column A: 98·5°, H_2 51 cc/min), the main peak (retention time 12·5 min) was confirmed as n-propylbenzene by comparing the retention time of gas chromatography and the IR spectrum with those of the authentic sample. (Found: C, 89·66; H, 9·36. Calc. for C_9H_{12}: C, 89·93; H, 10·6%). Another detectable peak was not identified but it was not α-, β- and p-methylstyrene. Fraction 2 was divided into four parts by further distillation; Fraction 2–1: 74°/5·5 mmHg; fraction 2–2: 66–67°/1 mmHg; fraction 2–3: 99–125°/1 mmHg; fraction 2–4: 125–129°/1 mmHg. The first fraction consisted mainly of one component, but was not purified. By comparison, it was not α-, β-, and *p*-methylstyrene. The second fraction has an IR spectrum characteristic of both ketones (1695 cm^{-1}) and alcohol (3280 cm^{-1}), and the fraction consisted of three components by gas chromatographic analyses (Column A: 70°C, H_2 47 cc/min). The first peak (retention time: 8·6 min) could not be confirmed. The second (8·6 min) and the third (16·3 min) peaks were 1-phenyl-2-propanone and 1-phenyl-2-propyl alcohol respectively. The fraction 2–3 had 4–5 peaks in the gas chromatography (column B: 160°, H_2 55 cc/min). These peaks corresponded to the components in fraction 2–2, two unknown materials, and 1,4-diphenyl-2,3-dimethylbutane. The unknown peaks were not phenylisopropyl ether and 3-phenyl-2-methylpropanol. Fraction 2–4 was a doublet peak and it was 1,4-diphenyl-2,3-dimethylbutane, which also gave the same doublet peak (meso and (±) in gas chromatography). The fraction was purified by column chromatography (15 × 400 mm, carrier: active alumina, eluent: hexane) and fractional distillation (b.p. 120–122°/0·8 mmHg); (Found for mixture of meso- and (±): C, 90·51; H, 9·3. Calc. for $C_{18}H_{22}$: C, 90·69; H, 9·33%). The residue had two peaks (14·2 min and 19·5 min) in the gas chromatography (column B: 217°, H_2 51 cc/min), and they were 1,4-diphenyl-2,3-dimethylbutane and 1-phenyl-2-propyl β-phenylisobutyrate respectively. Both compounds were purified by column chromatography (carrier: active alumina, eluent: hexane) and fractional distillation, and identified by comparing the IR spectra with those of the authentic samples.

Stereochemical experiment. Optically active (−)-β-phenylisobutyryl peroxide was decomposed photochemically under the conditions of run 3 in Table 1, and the products, 1,4-diphenyl-2,3-dimethylbutane and 1-phenyl-2-propyl β-phenylisobutyrate were isolated and purified. The latter was further hydrolyzed with methanolic potassium hydroxide according to the procedure reported.[9] Optical rotation of each compound was measured under the condition of Table 3.

TABLE 3. MEASUREMENT OF OPTICAL ROTATION[a]

Compound[b]	Opt. rotation, $[\alpha]_D$	Temp	Concn. (%)
$(RCO_2—)_2$	− 71·0°	24·5	9·05
RCO_2H[c]	− 11·8	25·0	8·35
Product			
R—R	0·06	18·8	8·60
RCO_2R	− 20·0	25·5	10·70
ROH[d]	− 6·7	24·0	6·55

[a] l=1, in ethyl alcohol.

[b] Where R represents the 1-phenyl-2-propyl group.

[c] The acid was obtained by the reduction of the peroxide with potassium iodide.

[d] The alcohol was obtained by the hydrolysis of the ester.

^{18}O-Tracer experiment. The photochemical decomposition of carbonyl-^{18}O-labeled β-phenylisobutyryl peroxide was performed under the conditions of run 2, and 4 in Table 1. The resulting ester was hydrolyzed to 1-phenyl-2-propyl alcohol. The analytical results for ^{18}O are shown in Table 2.

Kinetic run of photochemical decomposition. A Pyrex reaction container was filled with β-phenylisobutyryl peroxide in isooctane soln (0·0162 M/l) and was kept at 25°, and irradiated under N_2. From time to time, 5 ml of the soln was pipetted out, and the unreacted peroxide titrated with 0·05N $Na_2S_2O_3$ by the procedure reported previously.[9]

Irradiation of 1-phenyl-2-propyl β-phenylisobutytyl carbonate. The carbonate (11·5 g) in isooctane (1750 ml) was irradiated with a low pressure mercury lamp at 17–19°, for about 54 hr under N_2. Isooctane was removed under reduced press (4 mmHg). No change of the carbonate to any other material was found in the IR and UV spectra of the residue. The same irradiation of a system containing β-phenylisobutyric acid (0·521 g) also led to no change.

The carbonate was synthesized by the procedure reported elsewhere;[21] UV spectra: λ_{max} 254 mμ, $\varepsilon_{max} = 900$.

Sensitized photochemical decomposition of β-phenylisobutyryl peroxide. The peroxide (11 g) in isooctane (1·9 l) soln containing acetophenone (1 g) was irradiated with a high pressure mercury lamp (ca. 190 W) at 27·5–29° for 48·7 hr under N_2.

The product analysis was performed by the same techniques as in the direct photolysis.

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