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# THE DECOMPOSITION OF DIACYL PEROXIDES—II

## LEWIS ACID-CATALYSED DECOMPOSITION OF β-PHENYLISOBUTRYL PEROXIDE*

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**Abstract**—Optically active (+)- and carbonyl-$^{18}O$-labelled β phenylisobutyryl peroxides were decomposed in the presence of antimony pentachloride in light petroleum. Optically active (+)-1-phenyl-2-propyl β-phenylisobutyrate, (+)-β-phenylisobutyric acid, 2-chloro-1-phenylpropane, n-propylbenzene and carbon dioxide were obtained as main products. The carbonyl oxygen of the peroxide was retained as much as 83 ~ 89% in the carbonyl group of the resulting ester while the alcohol portion of the ester showed 91% retention of configuration. It was possible to observe through an infrared spectroscopic analysis the intermediate, 1-phenyl-2-propyl β-phenylisobutyryl carbonate, which resulted from the decomposition of the peroxide. These data were interpreted in terms of an ionic mechanism.

The mechanism of the ester formation is discussed in a detailed comparison with that of the thermal decomposition of β phenylisobutyryl peroxide. Here too, the rearrangement process via carboxy-inversion is considered as the main path for ester formation.

EARLIER, Leffler[1] suggested that *p*-methoxy-*p'*-nitrobenzoyl peroxide decomposes both homolytically and heterolytically. While it appeared to decompose via a radical path-way in a nonpolar solvent, it decomposed by an ionic route either in polar solvents or in nonpolar solvents containing organic acids. When the reaction was carried out in a highly polar solvent, such as thionyl chloride, *p*-methoxyphenyl-*p*-nitrobenzoyl carbonate was obtained in 38% yield. A mechanism was proposed for the decomposition of the peroxide in polar conditions which involved heterolytic cleavage of the peroxide to give incipient *p*-nitrobenzoate anion and *p*-methoxybenzoyloxinium ion. The latter rearranges to anisyloxycarbonylium ion and the product arises from recombination of the rearranged carbonium ion with the anion.

Denney *et al.*[2] rejected this mechanism and, using $^{18}O$-tracer studies, suggested that the carbonate was obtained by a concerted process in which *p*-methoxyphenyl group migrates from carbonyl carbon to peroxide oxygen during the cleavage of the oxygen–oxygen bond.

The decomposition of bisphenylacetyl peroxide has been studied similarly by Bartlett and Leffler,[3] who suggested that the peroxide decomposed concurrently via both homolytic and heterolytic processes.

It has been known for some time that the decomposition of benzoyl peroxide is catalyzed by Lewis acids, such as aluminum chloride[4] and antimony pentachloride. Denney *et al.*[5] found that phenyl benzoate was obtained in 90% yield in the $SbCl_5$ catalyzed decomposition of benzoyl peroxide, and suggested a rearrangement process via carboxy-inversion for the reaction from an $^{18}O$-tracer experiment.

Most of these investigations of acid catalyzed decompositions were made on aromatic diacyl peroxides whose decomposition may be anchimerically assisted

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

by the participation of phenyl group forming an incipient phenonium ion type intermediate in the 1,2-shift of the rearrangement. The one avilable study with aliphatic diacyl peroxides is that of bisphenylacetyl peroxide which is also considered to readily undergo acid-catalyzed decomposition due to the facile cleavage of benzyl group in both ionic and radical reactions. The acid catalyzed decomposition of less reactive aliphatic diacyl peroxides is interesting in this connection, since the stereochemistry of the reaction may be different from that of anchimerically assisted cleavage.

Thus the decomposition of β-phenylisobutyryl peroxide in the presence of antimony pentachloride has been studied, and this paper gives a detailed account of the decomposition mechanism based on the stereochemical and $^{18}$O-tracer experimental results.

## RESULTS

β-Phenylisobutyryl peroxide (34·6 mmole) was allowed to decompose in the presence of antimonyl pentachloride in light petroleum at room temperature under nitrogen atmosphere. 1-Phenyl-2-propyl β-phenylisobutyrate (25·7 mol %), β-phenylisobutyric acid (72·2 mol %), n-propyl-benzene (17·2 mol %), 2-phenyl-1-chloropropane (51·4 mol %), and carbon dioxide (72·2 mol %) were obtained as major products.

In run 1, a vigorous evolution of carbon dioxide was observed about 10 min after the addition of 10 mole % (1 g) of antimony pentachloride into the peroxide solution, but stopped completely after about 16 h. The carbonyl absorptions of the acid (1705 $cm^{-1}$) and the ester (1725 $cm^{-1}$) together with those for the unreacted peroxide (1805 and 1775 $cm^{-1}$) were then observed in the IR spectra of the reaction mixture. An evolution of carbon dioxide was again observed when 16 mole % of antimony pentachloride was added into the solution, but stopped again after 38 h. Then, on observing the IR spectra of the mixture, we found no longer the doublet carbonyl absorption of the peroxide, but that of 1-phenyl-2-propyl β-phenylisobutyryl carbonate (1815 and 1750 $cm^{-1}$) appeared together with those of the ester and the acid. The third addition of 4 mole % of antimony pentachloride led to a slow evolution of carbon dioxide, and after 88 h the IR absorption band of the carbonate disappeared while only those of the acid and the ester were observed in the IR spectra of the reaction mixture.

In run 3, 30 mole % of antimony pentachloride was added initially and the evolution of a large amount of carbon dioxide was observed for 4 h. When 4·8 mole % of antimony pentachloride was added to the reaction mixture after 8 h, the evolution carbon dioxide was no longer observed. After 16 h, strong IR bands of only the acid and the ester and a very weak doublet peak of the carbonate were observed, suggesting that the reaction was nearly complete.

It is difficult to distinguish the infrared carbonyl absorption band of the carbonate from that of β-phenylisobutyric anhydride (1810 and 1740 $cm^{-1}$), but these two compounds can be discriminated by the difference in their thermostabilities. Thus, although the doublet carbonyl absorption of the carbonate readily disappears from the IR spectrum of the reaction mixture by heating an aliquot from run 1 (38 h) in an oil bath at 130–140°C the authentic β-phenylisobutyric anhydride was stable at this temperature. The authentic sample of 1-phenyl-2-propyl β-phenylisobutyryl carbonate freshly prepared was also found to decompose readily at 120–130°C to give carbon dioxide and 1-phenyl-2-propyl β-phenylisobutyrate.

The carbonate decomposed smoothly also under the same conditions as for the peroxide decomposition. In this case, carbon dioxide, 1-phenyl-2-propyl β-phenylisobutyrate, β-phenylisobutyric acid and a few other compounds were obtained.

The ester resulting from $SbCl_5$-catalyzed decomposition of the peroxide was hydrolyzed with methanolic potassium hydroxide to obtain 1-phenyl-2-propyl alcohol. Under the hydrolysis conditions there was no $^{18}O$-exchange between the alcohol and the potassium hydroxide. The analytical results from the $^{18}O$-studies together with the stereochemical outcome of the reaction are shown in Table 1.

TABLE 1. $SbCl_5$-CATALYZED DECOMPOSITION OF β-PHENYLISOBUTYRYL PEROXIDE. $(RCO_2\ )_2$

| | (±)-peroxide | | (+)-peroxide (run 3) | |
|---|---|---|---|---|
| Compound | $^{18}O$-content (excess %) | | optical rot. | optical purity |
| | run 1 | run 2 | $[\alpha]_D$° | (%) |
| RCOCl[a] | 1·47 | 1·65 | | |
| $(RCO_2—)_2$ | | | +120 | 70·7[d] |
| $RCO_2H$[b] | | | +15·7 | 70·7 |
| Product | | | | |
| $RCO_2R$ | 0·67 | 0·80 | +24·2 | |
| $RCO_2H$ | | | +15·1 | 68·0 |
| ROH[c] | 0·23[e] | 0·18[f] | +11·8 | 64·5[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] The alcohol was obtained by hydrolysis of the resulting ester.

[d] Optical purity of the peroxide was calculated from the optical purity of the acid obtained by the reduction of the peroxide.

[e, f] These $^{18}O$-concentrations correspond to approx. 17% and 11% incorporation of $^{18}O$ respectively from the original label in the carbonyl oxygens of the peroxide.

[g] It was calculated from the maximum rotation of alcohol $[\alpha]_D^{24}$ + 18·5 EtOH[9] that this value corresponds to 91·2% retention (64·5/70·7).

## DISCUSSION

The decomposition of β-phenylisobutyryl peroxide was found to be markedly catalyzed by antimony pentachloride and various products resulted. This reaction is not as simple as the antimony pentachloride-catalyzed decomposition of benzoyl peroxide which gave only phenyl benzoate and carbon dioxide.[5]

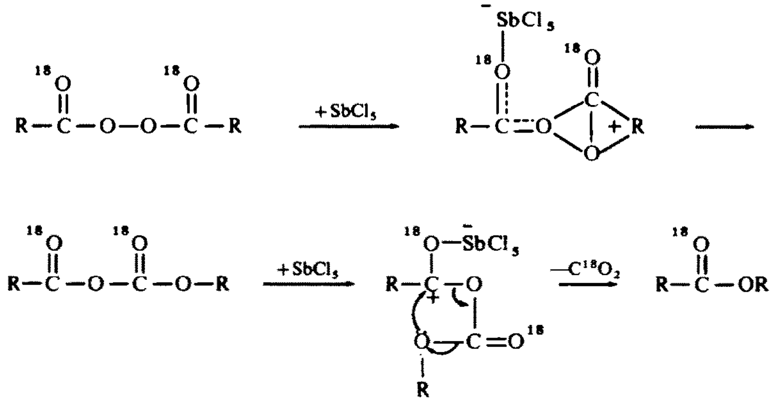
The formation of 2-chloro-1-phenylpropane in the decomposition of β-phenylisobutyryl peroxide, seems to suggest that antimony pentachloride acts not only as catalyst for the decomposition of the peroxide but also participates in the reaction as a reagent. This is in keeping with the fact that the complete decomposition of the peroxide required about 30 mole % of antimony pentachloride; 20 mole % of antimony pentachloride was not enough to lead to complete decomposition of the peroxide.

The IR spectroscopic analysis of the reaction mixture indicates that the decomposition of the peroxide gave an intermediate, 1-phenyl-2-propyl β-phenylisobutyryl carbonate, suggesting that the carbonate was formed through a carboxy-inversion of the peroxide similar to the initial process of the thermal decomposition of the peroxide.[6] Probably the coordination of antimony pentachloride to one of the carbonyl oxygens of the peroxide leads to the carboxy-inversion (equation 1) as in the case of benzoyl peroxide suggested by Denney *et al.*[5]

Although 1-phenyl-2-propyl β-phenylisobutyryl carbonate was relatively stable at room temperature, it was rapidly decomposed by antimony pentachloride in light petroleum to give mainly 1-phenyl-2-propyl β-phenylisobutyrate. In this case, the formation of β-phenylisobutyric acid anhydride, a possible product in the thermal decomposition of the other carbonates,[7] was not observed.

Therefore, it appears that the major portion of the ester resulted from the rearrangement process via initial carboxy-inversion as shown below.

I

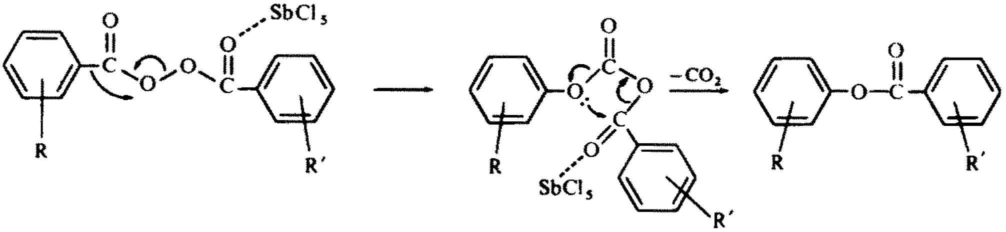


(1)

From the $^{18}$O-tracer results, the etheral oxygen of the resulting ester in this reaction contained 11 ~ 17% of $^{18}$O from the original label in the carbonyl oxygen of the peroxide and the alcohol portion of the resulting ester was found to have retained its configuration by as much as 91%. These $^{18}$O and stereochemical results are similar to those from the thermal decomposition in boiling carbon tetrachloride, i.e., 11–21% and 92% respectively.

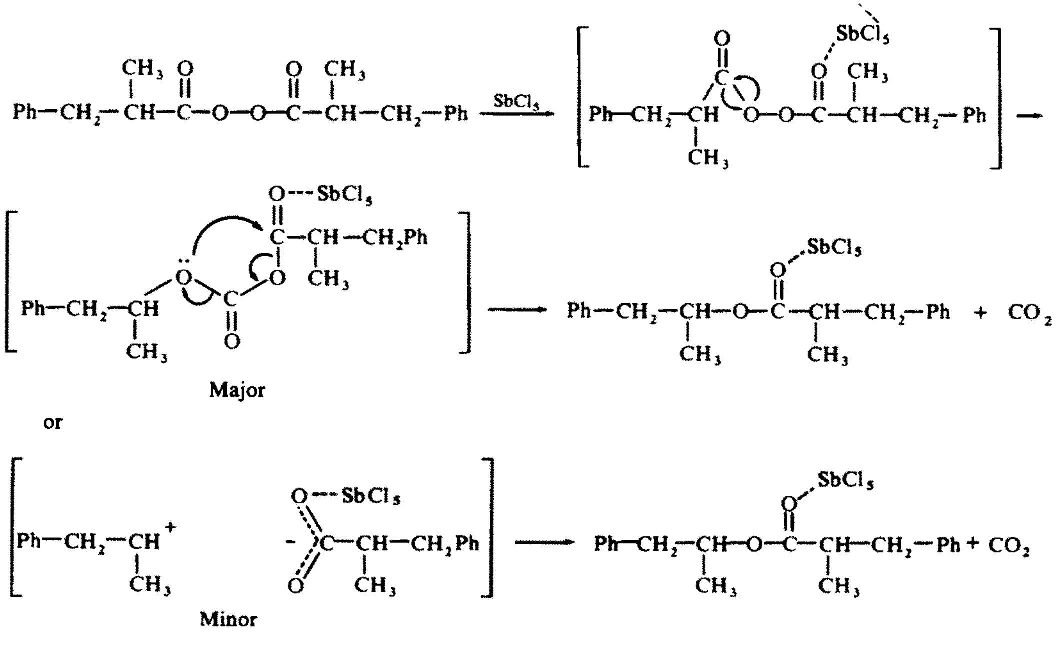
If the ester resulted only from the rearrangement process as shown by equation 1 both acyl and alcohol moieties of the resulting ester would completely retain their configurations, while its etheral oxygen would contain no excess $^{18}$O. Therefore, it is difficult to explain the formation of the ester only by a mechanism involving rearrangement via a concerted initial carboxy-inversion (equation 1). The amount of partial racemization of the alcohol portion and the incorporation of $^{18}$O in the etheral oxygen of the resulting ester are in good agreement. The partial racemization is very probably caused by partial dissociation of alkyl and acyloxy groups during the reaction. The similar racemization and $^{18}$O-equilibration observed in the thermal decomposition of the peroxide could be interpreted in terms of the competing radical reaction. However, it is quite unlikely that any free radical reaction is competing in this acid-catalyzed reaction in view of the lack of possible products resulting from a free radical process. The reaction is undoubtedly of ionic character, a partial dissociation of the intimate ion pair between 1-phenyl-2-propyl cation and 2-phenyl-butyrate anion taking place during the reaction. This is quite reasonable since the reaction is markedly catalyzed by antimony pentachloride, a strong Lewis acid and the formation of all the products isolated can be explained on the basis of an ionic cleavage process.

In the Lewis acid-catalyzed decomposition of diaryl peroxides, the migrating phenyl group may perhaps enhance the reactivity by anchimeric assistance while keeping $^{18}$O-label in the carbonyl group equilibrated all through the carboxy-inversion and the succeeding decarboxylative ester formation, as shown below.



R = R' = H[5] R = OCH$_3$ R' = NO$_2$[3]

In the case of β-phenylisobutyryl peroxides, too, the first step, namely, the carboxy-inversion rearrangement, would be a stereospecific reaction; however, the second step, the decomposition of 1-phenyl-2-propyl β-phenylisobutyryl carbonate may also be stereospecific, only a small portion undergoing racemization. A partial alkyl-oxygen cleavage may participate in this Lewis acid-catalyzed decarboxylation in addition to the normal route involving acyl-oxygen cleavage, thus resulting in the partial formation of carbonium ion, to give such a partially racemized and $^{18}$O-equilibrated ester as shown below,



The resulting 1-phenyl-2-propyl cation reacts with $SbCl_5$ yielding 2-chloro-1-phenylpropane and n-propylbenzene. β-Phenylisobutyric acid would also result from this reaction. The other possible route to 2-chloro-1-phenylpropane is the reaction of the ester with $SbCl_5$ giving the chloride and β-phenylisobutyryl hypochlorite which may decompose to the halide and carbon dioxide.

## EXPERIMENTAL

*Materials.* Optically active (+)- and carbonyl-$^{18}O$-labelled β-phenylisobutyryl peroxide were prepared by the procedure reported previously.[5] Light petroleum b.p. below 60°C was used.

*Antimony pentachloride-catalyzed decomposition of β-phenylisobutyryl peroxide.* To stirred mixture of β-phenylisobutyryl peroxide (11·2 g) and light petroleum (145 ml), $SbCl_5$ (3·1 g) was added under cooling with ice-water, and then the solution was kept stirring at room temperature under $N_2$ until both the peroxide and the intermediate carbonate disappeared. The disappearance of these compounds was checked by examining the IR spectrum of the reaction mixture as mentioned above.

*Product Analyses.* Carbon dioxide evolved during the reaction was trapped quantitatively by bubbling it through a sat $Ba(OH)_2$ soln. Then the reaction mixture was washed thoroughly with water, and the light petroleum layer was washed with 10% $NaHCO_3$, then with water, while the aqueous layer was extracted with light petroleum. The petroleum layers were all combined and dried over anhyd $Na_2SO_4$. After removing light petroleum, the organic layer was fractionated into the following four portions by distillation; 1: 59°/23 mm Hg, 2: 95–100·5°/23 mm Hg, 3: 143–150°/0·5 mm Hg and 4: residue. Fraction 1 was pure n-propylbenzene which was identified by comparing its NMR, UV and IR spectra together with the gas chromatographic pattern with those of an authentic sample. The fraction of b.p. 100°/27·5 mm Hg was obtained by redistillation of fraction 2. This was found to be gas-chromatographically pure, and identical to 1-phenyl-2-chloropropane from the NMR and IR spectra and elementary analysis. (Found: C, 70·21; H, 7·35. Calc for $C_9H_{11}Cl$: C, 69·90; H, 7·71%) (60 MC. NMR ($CCl_4$): multiplet at 1·22, 2·77 and 4·04 ppm and singlet at 7·19. Peak areas are in the ratio 3:2:1:5. 1-phenyl-2-propyl β-phenylisobutyrate was obtained by redistillation of fraction 3 (b.p. 138–139°/0·3 mm Hg). The ester (carbonyl absorption: 1725 $cm^{-1}$) was identified by comparing its IR spectrum with that of an authentic sample. The residue was mainly 1-phenyl-2-propyl β-phenylisobutyrate from its IR analysis (carbonyl absorption was 1725 $cm^{-1}$).

TABLE 2. MEASUREMENTS OF OPTICAL PURITY

| Compound[a] | Optical rotation $[\alpha]_D$ (°) | Temp (°C) | Concentration |
|---|---|---|---|
| RCOOH[b] | +15·4 | 25 | 6·15 |
| RCOCl[c] | +30·2 | 27 | 6·95 |
| $(RCO_2—)_2$ | +88·0[e] | 26 | 3·85 |
| RCOOH[d] | +15·7 | 25 | 9·45 |
| Product | | | |
| RCOOH | +15·1 | 25 | 5·02 |
| RCOOR | +24·2 | 25 | 6·30 |
| Hydrolyzed | | | |
| ROH | +11·8 | 30 | 4·60 |

[a] Where R represents the 1-phenyl-2-propyl group.
[b] used for the preparation of RCOCl.
[c] used for the preparation of $(RCO_2—)_2$.
[d] was obtained by reduction of $(RCO_2—)_2$ with KI.
[e] The optical rotation of the pure peroxide is +120°, hence, purity of this peroxide is 73%, determined by iodometry.

*Preparation of* 1-*phenyl*-2-*propyl β-phenylisobutyryl carbonate.* To purified phosgene (about 25 g) cooled down below its boiling point (8°C) with an ice–salt water bath, 1-phenyl-2-propyl alcohol[8] (7 g) was added with stirring, and then was kept standing for 2–3 h in the cold bath and then for 14 h at room temp. After dry air was passed through the reaction mixture to remove an excess phosgene, 1-phenyl-2-propyl chlorocarbonate (b.p. 83°/8 mm Hg, IR carbonyl absorption: 1768 $cm^{-1}$) was obtained by fractional distillation of the residue.

To the mixture of β-phenylisobutyric acid[6] (1·6 g), triethylamine (1 g) and dry ether (20 ml), the chlorocarbonate (2 g) was added with stirring for 15 min, keeping the temp of the soln at 4–6°. The soln was then stirred for 1 h and kept for 13 h at room temp. The reaction mixture was filtered. The filtrate was washed with dil HCl, sat $Na_2CO_3$ soln and water, then dried over $Na_2SO_4$. An oily material was obtained by removing ether from the dried soln under reduced pressure. Although this material could not be purified any further because of its thermo-instability, it was identified as 1-phenyl-2-propyl β-phenylisobutyryl carbonate since the IR and UV spectra resemble those of other similar carbonates;[8] IR: 1815 and 1750 $cm^{-1}$; UV (in isooctane); $\lambda_{max}$ 254·3 mμ, $\lambda_{max}$ 901.

*Antimony pentachloride-catalyzed decomposition of* 1-*phenyl*-2-*propyl β-phenylisobutyryl carbonate.* To a light petroleum soln (20 ml) of the carbonate (1·5 g), 0·5 g of $SbCl_5$ (36·3 mole % for the carbonate) was added, and then stirred at room temp under $N_2$. After 5 min, vigorous evolution of $CO_2$ was confirmed by bubbling of the $N_2$ stream into a sat $Ba(OH)_2$ soln. Evolution of $CO_2$ stopped completely after about 1 h and the reaction mixture was then washed thoroughly with water, dried over $Na_2SO_4$, and then light petroleum was removed under reduced pressure. The carbonyl absorptions of 1-phenyl-2-propyl β-phenylisobutyrate (1725 $cm^{-1}$) and β-phenylisobutyric acid (1705 $cm^{-1}$) were observed in the IR spectrum of the residue. The formation of 2-chloro-1-phenylpropane was also confirmed from its gas chromatographic pattern.

*Thermo-instability of the carbonate.* When the carbonate was heated in an oil bath at 120–130°, it decomposed completely within about 1 h with evolution of $CO_2$ to give only 1-phenyl-2-propyl β-phenylisobutyrate. Formation of a small amount of the ester (1725 $cm^{-1}$) was observed from the IR spectra after keeping the carbonate at room temp (27°) for 2 days.

*Preparation of β-phenylisobutyric acid anhydride.* A mixture of β-phenylisobutyric acid (1·6 g), β-phenylisobutyryl chloride (1·8 g) and pyridine (0·8 g) was kept standing overnight, and then heated at 140–150° for about 5 min. The reaction mixture diluted with ether was washed with water and dried over $Na_2SO_4$. β-Phenylisobutyric acid anhydride (b.p. 171–173°/0·8 mm Hg) was then obtained by fractional distillation (IR: 1810 and 1740 $cm^{-1}$).

## REFERENCES

[1] J. E. Leffler, *J. Am. Chem. Soc.* **72**, 67 (1950)
[2] [a] J. E. Denney, *Ibid.* **78**, 590 (1956);
[b] D. B. Denney and D. G. Denney, *Ibid.* **79**, 4806 (1957)
[3] P. D. Bartlett and J. E. Leffer, *Ibid.* **72**, 3032 (1950)
[4] H. Gelissen and P. H. Hermans, *Ber. Dtsch. Chem. Ges.* **58**, 479 (1925)
[5] [a] D. Z. Denney, T. M. Valega and D. B. Denney, *J. Am. Chem. Soc.* **84**, 2455 (1962);
[b] D. B. Denny and D. Z. Denney, *ibid.* **84**, 2455 (1962)
[6] T. Kashiwagi, S. Kozuka and S. Oae, *Tetrahedron* **26**, 3619 (1970)
[7] D. S. Tarbell and E. J. Longosz, *J. Org. Chem.* **24**, 774 (1959)
[8] M. S. Newman, *J. Am. Chem. Soc.* **62**, 2298 (1964)
[9] T. Kashiwagi, K. Fujimori, S. Kozuka and S. Oae, Part IV of this series