

mass spectrometric analysis, and the system again evacuated. The first trap was cooled by a Dry Ice-acetone mixture and the second by liquid nitrogen. The flask was allowed to warm to room temperature, the solvent distilled to the first trap and the gases condensable in liquid nitrogen were caught in the second trap. After closing the stopcock between the traps, the condensable gas was allowed to warm to room temperature and its pressure measured. Samples of the gas were then taken for infrared and mass spectral analysis. The carbon dioxide formed was absorbed on Ascarite and weighed. Any residual gas was analyzed by its infrared and mass spectra. From the pressure of the gases and the known volumes of the system, the number of moles formed was calculated.

The solvent caught in the Dry Ice cooled trap was viewed in the infrared against pure solvent and the spectrum was compared with spectra of authentic samples of possible products in the same

solvent. The amount of *tert*-butyl alcohol and acetone formed was found by measurement of their absorption at 2.8 and 5.83 μ , respectively, and calibrating against known solutions. The quantitative analysis of any other volatile products found in the solvent was made by infrared or gas chromatographic methods.

The non-distilled residue left in the decomposition flask was chromatographed on silica gel and the fractions identified usually by their infrared spectra.

The gases obtained were analyzed using a Consolidated-Nier mass spectrometer, model 21-103C. A Reco Distillograph model D-2000 and a Perkin-Elmer vapor fractometer model 154-C were used for the gas chromatographic analyses.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Peresters. XI. Di-*tert*-butylperoxy Diphenylmalonate. α -Lactone Intermediates in Free Radical Reactions

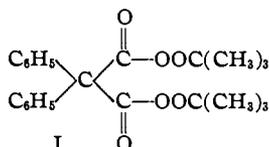
BY PAUL D. BARTLETT AND LEON B. GORTLER

RECEIVED DECEMBER 14, 1962

The chief decomposition product of di-*tert*-butylperoxy diphenylmalonate (I) in cumene is a polyester (II) of benzoic acid. The same polyester can be prepared by Staudinger's procedure of oxygenating diphenyl ketene, and in low yield by the thermal decomposition of *tert*-butylperoxy diphenylacetate without solvent. Mechanisms are proposed for the formation of diphenylacetolactone in all three reactions and the occurrence of this α -lactone is supported by controlled trapping experiments with methanol. The same mechanism is applied to the polyester obtained by Milas and Golubović from *tert*-butylperoxy isobutyrate (V). Rate and product studies are reported for I, *tert*-butylperoxy diphenylacetate and V, whose half-lives at 60° in cumene are 15, 37 and 10,000 minutes, respectively.

Introduction

In one of the extensions of our study of the concerted decomposition of peresters,¹ it was of interest to examine the behavior of double peresters which might, as a result of concerted or successive bond fissions, yield carbenes. It was with this in mind that di-*tert*-butylperoxy diphenylmalonate (I) was first



prepared. Although it soon appeared that diphenyl carbene was not formed in the course of the decomposition of this perester, other interesting and novel phenomena were observed.

Preparation and Properties of Di-*tert*-butylperoxy Diphenylmalonate.—The perester was synthesized by the dropwise addition of a solution of diphenylmalonyl chloride in ether-pentane to a cooled solution of *tert*-butyl hydroperoxide and pyridine in the same solvent. The perester, obtained in 17–25% yield, was a white crystalline solid easily recrystallized from pentane and ether. The perester melted at 66.4–67.6° with decomposition. The rate of decomposition in cumene solution was determined by following the disappearance of the perester carbonyl peak at 5.63 μ as has been done with other compounds in this series. The results yielded good first-order rate constants with no more than a 10% increase in value for a 10-fold increase in perester concentration. Table I shows the results of the kinetic studies at all three temperatures and lists the activation parameters.

A preliminary product study of the decomposition in cyclohexene gave no indication of the presence of cyclopropanes. The principal products showed absorption in the 5.6–6.1 μ region indicating the presence of car-

TABLE I

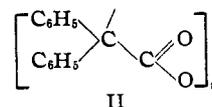
RATE CONSTANTS FOR THE DECOMPOSITION OF DI-*tert*-BUTYLPEROXY DIPHENYLMALONATE IN CUMENE

T, °C.	Concn., mole/l.	$k \times 10^4$, sec. ⁻¹	Half-life, min.
69.8	0.175	28.8	4.0
69.8	.0175	26.3	4.4
58.9	.175	7.90	14.6
58.9	.0175	7.83	14.7
50.2	.175	2.63	43.9
50.2	.0175	2.56	45.0

$$\Delta H^\ddagger = 25.8 \text{ kcal./mole}; \Delta S^\ddagger = 4.8 \text{ cal./deg.-mole}$$

bonyl groups and the incomplete loss of carbon dioxide. Product studies were then carried out with cumene as solvent where it was observed that approximately 50% of the maximum amount of carbon dioxide was evolved and an amount of *tert*-butyl alcohol and acetone was found which accounted for 90% of the *tert*-butoxy groups originally present. The residue could be separated into two fractions by trituration with low-boiling petroleum ether. The insoluble fraction included the carbonyl-containing material. It did not separate into clean fractions on chromatography with silica gel or alumina. It appeared to be polymeric in character. When a benzene solution of it was evaporated, the residue was a hard lacquer which yielded a white solid on solution in ether and evaporation. The solid, which melted over a 20° range depending upon its form, evolved gas from the melt at about 200° and turned red. After refluxing for several hours with methanolic potassium hydroxide, about 20% of α -methoxydiphenylacetic acid could be obtained.

This material proved to be identical with the polyester of benzoic acid (II) prepared by Staudinger and



co-workers in 1925 by the oxygenation of diphenyl ketene.² The infrared spectrum of our product was

(1) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958), and later papers in this series

identical with that of the product prepared by Staudinger's directions, having strong bands at 5.62, 5.69, 6.70, 6.90, 7.98, 8.58, 9.25 and 9.8 μ in chloroform.

Table II lists the products obtained from the decomposition of the perester.

TABLE II

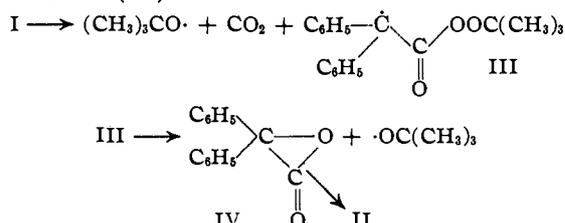
PRODUCTS OF DECOMPOSITION OF DI-*tert*-BUTYLPEROXY DIPHENYLMALONATE IN CUMENE AT 70°

1.0124 g. (run 1) and 1.0233 g. (run 2) in 10 ml. of cumene

Product	—Moles/mole of perester—	
	Run 1	Run 2
Carbon dioxide	1.00–1.18 ^a	1.08
<i>tert</i> -Butyl alcohol	1.68	1.67
Acetone	0.07	0.08
Dicumyl	0.42	0.42
Hydrocarbon		[33 mg.]
Benzophenone	0.17	0.15
<i>tert</i> -Butyl α,α -dimethylbenzyl ether ^b	.06	.08
Polyester	.85 ^c	.96 ^c

^a Limits of error caused by leak in run 1. ^b Identification incomplete. ^c Based upon molecular weight of monomer unit, 210.

Mechanism of Decomposition.—The concerted decomposition which is responsible for the evolution of one mole of carbon dioxide per mole of perester must result in the radical III which is of the benzhydryl type and will not rapidly dimerize nor abstract hydrogen from the solvent cumene. Indeed, the easiest thing for such a radical to do is to perform an internal displacement on its carboxyl oxygen with the ejection of a *tert*-butoxy radical and the formation of diphenylacetolactone (IV).

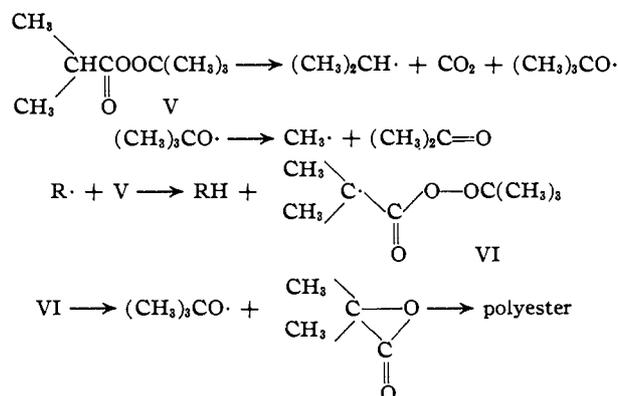


Despite the instability of α -lactones, this reaction may well be exothermic, replacing as it does an O–O bond with a C–O bond.

The α -lactone is a familiar hypothetical intermediate in the field of ionic reactions, having been implicated in displacement reactions of α -bromoacids in alkaline medium. In the literature, there has been discussion as to whether the intermediate should actually be called an α -lactone or a dipolar ion.^{3–6} The large amount of ionic character, on which all workers in the field are agreed,^{7,8} might be expected to render an α -lactone readily polymerizable even in a non-polar medium such as cumene where the merest trace of water should be sufficient to convert it into polymer, as in the case of adipic anhydride.⁹

There is another observation in the recent literature which seems best interpreted by the intervention of an α -lactone. Milas and Golubović¹⁰ decomposed *tert*-butylperoxy isobutyrate (V) without solvent and obtained as the principal product a white, sharply melting

solid which was interpreted as a cyclic polyester of α -hydroxyisobutyric acid with degree of polymerization 18. We have verified that the use of chlorobenzene or cumene as solvent greatly lowers the yield of this polyester. This fact makes the following mechanism appear probable for the formation of the polyester.



The essential conditions are the presence of hydrogen-abstracting radicals in a medium¹¹ where the most available hydrogen atom is that in the α -position of the perester. The radical VI, generated by attack of the R \cdot on the perester, is a complete analog of the radical II produced from di-*tert*-butylperoxy diphenylmalonate. From this point on, then, the formation of the polyester of Milas and Golubović is entirely parallel to the formation of polybenzilic acid from the permaltonate.

Two questions then arise, namely, whether the perester of Milas and Golubović could be produced from di-*tert*-butylperoxy dimethylmalonate, and whether the polyester of Staudinger could be correspondingly produced by the decomposition of *tert*-butylperoxy diphenylacetate. In the course of a study of the rate and products of decomposition of the latter, we have found no polyester when the decomposition was conducted in dilute solution, but when the perester was decomposed in the pure state, the polyester was isolated in the amount of 12–16% of that theoretically possible.

Attempts to Trap the α -Lactone.—An ideal trapping reagent for the α -lactone might be a nucleophile incapable of reacting with the carbonyl group of an ester or polyester but reacting rapidly at the alkyl carbon of a lactone. Such a trapping agent must also be soluble in non-ionizing solvents. We were not successful in finding such an ideal reagent. Aniline reacted directly with the perester. No way was found to attain high concentrations of sodium halides¹² in the non-polar system. Decomposition of the perester in methanol at 60° for 2.5 hours yielded approximately 65% of acidic product, most of which was α -methoxydiphenylacetic acid. No precipitate appeared during the decomposition, even though the polyester is quite insoluble in methanol, and no polyester was obtained. Thus it was no problem to find a reagent which would react exclusively at the α -carbon atom. The difficulty is that benzoic acid polyester also reacts at the α -carbon atom even with methanol, and the problem is to prove that our scavenger is reacting directly with the α -lactonic intermediate and not with the already-formed polyester. This conclusion was only made probable by the demonstration that much

(11) From the products (methane, acetone and less *tert*-butyl alcohol) of Milas and Golubović it appears that most of the hydrogen abstracting was done by methyl radicals.

(12) T. L. Gresham, J. E. Jansen, F. W. Shaver and J. T. Gregory, *J. Am. Chem. Soc.*, **70**, 999 (1948), found sodium halides to be good nucleophiles for β -propiolactone.

(2) H. Staudinger, K. Dyckerhoff, H. W. Klever and L. Ruzicka, *Ber.*, **58**, 1079 (1925).

(3) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 841 (1948).

(4) W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

(5) E. D. Hughes, *Trans. Faraday Soc.*, **34**, 202 (1938).

(6) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca N. Y., 1953, p. 383ff.

(7) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. H. Taher, *J. Chem. Soc.*, 1011 (1940).

(8) S. Winstein and R. B. Henderson, *J. Am. Chem. Soc.*, **65**, 2196 (1943).

(9) J. W. Hill, *ibid.*, **52**, 4111 (1930).

(10) N. A. Milas and A. Golubović, *ibid.*, **80**, 5994 (1958).

more α -methoxyacid results when methanol is present during the perester decomposition than when it reacts under similar conditions with polyester.

Despite its insolubility, when solid polyester of low molecular weight, obtained from the oxygenation of diphenyl ketene, was heated with methanol at 60° for 2.5 hours, there was approximately a 10% conversion into α -methoxydiphenylacetic acid. Approximately 20% conversion into the α -methoxy acid was observed when the solid polyester had been heated under reflux in 0.1 *N* methanolic potassium hydroxide for eight hours.

In order to learn how methanol attacks the polyester under homogeneous conditions, a solution of the polyester in a mixture of benzene and methanol in the ratio of 1.5:1 was heated for 2.75 hours at 60°. This reaction afforded about 20% of α -methoxydiphenylacetic acid. When di-*tert*-butylperoxy diphenylmalonate was decomposed under identical conditions, there was at least a 50% conversion to α -methoxydiphenylacetic acid. Finally, we adopted as a solvent for a complete product study a 50-50 mixture by volume of methanol and cumene. Table III shows the product analysis from a decomposition of the perester in this medium and Table IV shows the results of identical treatment of a specimen of polyester isolated from a decomposition in pure cumene. The results show that, from the decomposition of the permalonate, α -methoxydiphenylacetic acid is isolated in 54% yield, its formation being consistent with the α -lactone mechanism. The control experiment on polyester shows that the product of Table III was not obtained by reaction of fully formed polyester since the reaction of polyester with methanol in this medium is 3-4 times slower than would be required for this course of events.

TABLE III

PRODUCTS OF DECOMPOSITION OF DI-*tert*-BUTYLPEROXY DI-PHENYLMALONATE IN METHANOL-CUMENE

Perester: 1.017 g., 2540 mmoles; solvent: 10 ml. of 50:50 methanol-cumene; temperature 50° for 8.5 hours

Products	mg.	mmoles	Moles/mole of perester
Non-condensable gas		0.13	0.05
Carbon dioxide	113.3	2.57	1.01
		2.59	1.02
<i>tert</i> -Butyl alcohol	327	4.42	1.74 ^a
Acetone	32	0.55	0.22 ^a
Dicumyl	87	.37	.14
Benzophenone	36	.20	.08
Diphenylacetic acid	115	.54	.21
α -Methoxydiphenylacetic acid	330	1.36	.54
Unidentified acid	75		
Unidentified hydrocarbons and esters	85		

^a By vapor phase chromatography.

TABLE IV

COMPARISON OF PRODUCTS FROM HOMOGENEOUS REACTION OF METHANOL WITH PERESTER I AND WITH POLYESTER II

Temperature: 50°; time: 8.5 hours

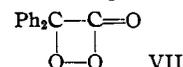
Compound recovered	—Basal moles per basal mole of starting material—		
	From I I: 1.017 g. Methanol: 5 ml. Cumene: 5 ml.	From II— Run 1 II: 140 mg. Methanol: 4 ml. Cumene: 5 ml.	Run 2 II: 142.6 mg. Methanol: 2.2 ml. Cumene: 3.5 ml.
Polyester II	None	0.82	0.87
α -Methyldiphenylacetic acid	0.54	0.12 ^a	0.20 ^a

^a Crude product.

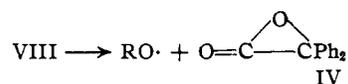
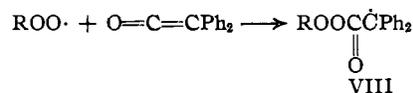
The "unidentified acid" of Table III melted at 152-154° after recrystallization from ethanol-water. Its non-identity with benzoic acid was shown by a mixture

melting point (benzoic acid m.p. 147-149°, mixture 138-141°).

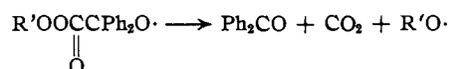
Autoxidation Mechanism of Diphenyl Ketene.—Staudinger and co-workers proposed that the α -lactone precursor of polybenzoic acid arose by conversion of monomeric diphenylketene peroxide (VII) by an



unknown mechanism. In the meantime, the work of Mayo and Miller^{13,14} has clarified the manner in which styrene oxide and other epoxides can be formed during the autoxidation of an olefinic substance. Such epoxides are formed in greatest amount at certain intermediate oxygen pressures where the lifetime of a copolymer radical such as VIII is long enough to make internal attack on the peroxy group an important reaction. This mechanism is directly applicable to the autoxidation of diphenyl ketene. The relatively high



yield of polyester may be related to the stabilization of the radical by the two phenyl groups which will prolong its lifetime and increase the likelihood of the lactone-forming step which now appears analogous to the step postulated in the decomposition of the peroxy malonate. The radical RO· in the above scheme is an oxygen-diphenyl ketene copolymer radical which now yields benzophenone and carbon dioxide by successive fragmentation



Other analogous situations among free radical reactions are the occurrence of isobutylene oxide in the decomposition of di-*tert*-butyl peroxide without solvent¹⁵ and the proposal of Walling and Savas¹⁶ for the formation of substituted benzoic acids in the decomposition of benzoyl peroxide.

Experiments with *tert*-Butylperoxy Isobutyrate.—

When *tert*-butylperoxy isobutyrate was decomposed in the absence of solvent, Milas and Golubović¹¹ isolated a solid product, melting at 170-171°, which represented 39.9% of the total decomposition products. This solid, identified as the cyclic polyester, accounts for 74% of the isobutyroxy group. The liquid products from this experiment, representing 39.4% of the total, consisted chiefly of acetone with about 3% *tert*-butyl alcohol. By varying the conditions of the decomposition, they also obtained polymer melting at 148-149°. From a similar experiment, we isolated a compound, m.p. 97-102°, whose infrared spectrum corresponded exactly to that of the polyester reported by Milas and Golubović.

To establish with certainty the importance of concentration in the formation of polyester, the products of decomposition of *tert*-butylperoxy isobutyrate in cumene and chlorobenzene at 90 and 100° were studied. The results of these experiments are presented in Table V. It is notable that the polyester declines to 14-18% of the product in chlorobenzene and 6 to 7% in cumene. These results are consistent with the product originat-

(13) F. R. Mayo, *J. Am. Chem. Soc.*, **80**, 2465 (1958).

(14) F. R. Mayo and A. A. Miller, *ibid.*, **80**, 2480 (1958).

(15) E. R. Bell, F. F. Rust and W. E. Vaughan, *ibid.*, **72**, 337 (1950).

(16) C. Walling and E. S. Savas, *ibid.*, **82**, 1738 (1960).

TABLE V

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY ISOBUTYRATE IN CUMENE AND IN CHLOROBENZENE

A, 0.8095 g. of perester in 10 ml. of cumene, 90°; B, 0.7664 g. of perester in 10 ml. of cumene, 100°; C, 0.8026 g. of perester in 10 ml. of chlorobenzene, 90°; D, 0.8450 g. of perester in 10 ml. of chlorobenzene, 100°.

Product	Moles per mole of perester			
	A	B	C	D
Carbon dioxide	0.79, ^a 0.82 ^b	<i>d</i>	0.82, ^a 0.80 ^b	<i>d</i>
Methane	...	<i>d</i>	0.04	0.06
Propane	0.55 ^c	<i>d</i>	0.23 ^b	<i>d</i>
Other alkanes	.04 ^c	<i>d</i>		
<i>tert</i> -Butyl alcohol	.75	<i>d</i>	0.38 ^d	0.46 ^e
Acetone	.06	<i>d</i>	0.47 ^d	0.35 ^e
Isobutyric acid	<i>d</i>	0 ^e	<i>d</i>	0 ^e
Dicumyl	0.44	0.48
Polyester ^f	0.07	0.06	0.14	0.18
Non-ester residue, mg.	34	34	165	190
Total condensable gases	0.78		1.03	1.23 ^b

^a Absorbed on Ascarite. ^b By volume. ^c From mass spectral fragmentation pattern. ^d Not determined. ^e By vapor phase chromatography. ^f Basal moles. ^g By infrared.

ing from attack of *tert*-butoxy radical on the original perester. The remaining products are those which are normal for concerted or unconcerted decomposition of a perester.

The sharp melting points of Milas's polyesters suggest a uniform molecular weight as might be expected for the cyclic structure suggested by the previous authors.¹¹ However, the variability of melting point and molecular weight from one experiment to another would be consistent with a linear polymerization mechanism of the α -lactone initiated by adventitious water.¹⁰

We took the occasion to measure the rate of decomposition of *tert*-butylperoxy isobutyrate in cumene solution. The calculated half-life at 60° is 10,000 minutes. This perester accordingly decomposes 50 times as fast as *tert*-butyl peracetate, roughly one-thirtieth as fast as *tert*-butyl trimethylperacetate, and one-three hundredth as fast as *tert*-butyl diphenylperacetate. The activation parameters are ΔH^\ddagger 31.8 kcal. and ΔS^\ddagger 9.1 cal./deg. There is no significant difference between the rate constant at concentrations of 0.03 and 0.3 *M*. This is consistent with the conclusion from the product studies that induced decomposition assumes little importance in a solvent. Table VI lists the rate constants at several temperatures in both cumene and chlorobenzene.

TABLE VI

RATE CONSTANTS FOR DECOMPOSITION OF *tert*-BUTYLPEROXY ISOBUTYRATE IN CUMENE AND IN CHLOROBENZENE

<i>T</i> , °C.	—In cumene—		—In chlorobenzene—	
	Concn., <i>M</i>	<i>k</i> × 10 ⁴ , sec. ⁻¹	Concn., <i>M</i>	<i>k</i> × 10 ⁴ , sec. ⁻¹
90.6	0.309	6.67	0.308	8.73
90.6	.312	6.72		
90.6	.0312	6.90	0.0308	8.13
100.7	.317	23.2	.322	33.2
100.7	.0317	23.5	.0322	27.5
110.0	.322	66.0	.327	87.3
110.0	.0322	65.7	.0327	89.2
	$\Delta H^\ddagger = 31.8$ kcal./mole		$\Delta H^\ddagger = 33.6$ kcal./mole	
	$\Delta S^\ddagger = 9.4$ cal./deg. mole		$\Delta S^\ddagger = 14.6$ cal./deg. mole	

Experiments with *tert*-Butylperoxy Diphenylacetate.—*tert*-Butylperoxy diphenylacetate, prepared in the usual way and recrystallized from petroleum ether,

melts at 58.2–60.0° and appears pure by analysis and infrared examination although, as with many peresters, its iodometric peroxide titer is low, being only 76%. Table VII lists the rate constants for decomposition of this perester in cumene at four temperatures. In three out of four cases, the rate constant increased by about 10% for a tenfold increase in concentration. The activation parameters were ΔH^\ddagger 25.0 kcal., ΔS^\ddagger 0.5 cal./deg. Table VIII shows the decomposition products of this perester in cumene at 40° and in toluene at 40 and 60°. The first point of interest is the absence of isolable polyester previously commented upon. The products contain the usual quite high ratio of *tert*-butyl alcohol to acetone (more than 55:1 at 40° in cumene), 84–91% of the theoretical carbon dioxide and all three of the possible coupling products of solvent and benzhydryl radicals. In addition there is benzhydryl *tert*-butyl ether, which might be a product of coupling of free *tert*-butoxy and benzhydryl radicals or it might be produced by a cage effect, or might possibly be present as a contaminant in the perester (it has no infrared absorption by which it could be sensitively detected in perester). The missing 15% of carbon dioxide might be explained by such an impurity, which would not affect the first-order rate constants.

TABLE VII

RATE CONSTANTS FOR THE DECOMPOSITION OF *tert*-BUTYLPEROXY DIPHENYLACETATE IN CUMENE

Temp., °C.	Concn., mole/l.	<i>k</i> × 10 ⁴ , sec. ⁻¹	Temp., °C.	Concn., mole/l.	<i>k</i> × 10 ⁴ , sec. ⁻¹
70.4	0.398	117	49.6	0.375	9.93
70.4	.384	114	49.6	.0375	9.81
70.4	.0398	103	40.3	.381	3.02
70.4	.0384	105	40.3	.0381	2.75
59.9	.388	33.7	$\Delta H^\ddagger = 25.0$ kcal./mole;		
59.9	.0388	31.0	$\Delta S^\ddagger = 0.5$ cal./deg.		

TABLE VIII

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY DIPHENYLACETATE IN CUMENE AND IN TOLUENE

Product	—Moles per mole of perester—		
	In cumene, 40°	In toluene, 40°	In toluene, 60°
Carbon dioxide	{ 0.85 ^a .84 ^b	{ 0.85 ^a .75 ^b	{ 0.89 ^a .91 ^b
<i>tert</i> -Butyl alcohol	.55	.55	.66
Acetone	<.01	<.01	.03
Dicumyl	.07		
Dibenzyl		0.10	.14
1,1,2-Triphenyl-2-methylpropane	0.20		
1,1,2-Triphenylethane		0.19	0.20
<i>sym</i> -Tetraphenylethane	0.16	.21	.25
Benzhydryl <i>tert</i> -butyl ether	0.34	.31	.22
Other hydrocarbons, mg.	85	70	60
Carbonyl compounds, mg.	30	55	40
Init. perester taken in 10 ml. solvent, g.	1.036	0.7643	0.938

Absorbed in Ascarite. ^b By volume.

Table IX lists the products of decomposition of *tert*-butylperoxy diphenylacetate in the pure state. Here the amount of carbon dioxide found is down to 60%, there is 12 to 16% of polyester and the amount of benzhydryl *tert*-butyl ether is up to 47 and 65% in the two experiments. Here there is a large discrepancy between the shortage of carbon dioxide and the polyester isolated, again indicating some undetected fate for perester which becomes involved in induced decomposition. *tert*-Butyl alcohol and acetone were present in

TABLE IX

PRODUCTS OF DECOMPOSITION OF *tert*-BUTYLPEROXY DIPHENYL-
ACETATE WITHOUT SOLVENT AT 60°

Product	Weight, mg.		Mole/mole of perester	
	Run 1	Run 2	Run 1	Run 2
Carbon dioxide	92.7	84.9	0.61 ^a	0.60 ^b
			.61 ^b	.58 ^b
Methane14
Benzhydryl <i>tert</i> -butyl ether	390	503	0.47	.65
<i>sym</i> -Tetraphenylethane	93	47	.08	.04
Benzophenone	38	27	.06	.05
Polyester	86	106	.12	.16
Hydrocarbon 1	25	9		
Hydrocarbon 2	75	45		
Initial perester taken	974.6	909.7		

^a Absorbed on Ascarite. ^b By volume.

these products, but were not determined quantitatively.

Experimental

Materials.—*tert*-Butyl hydroperoxide, pyridine, pentane, ether and chlorobenzene were purified as described in reference 1; toluene¹⁷ and cumene¹⁸ as described in earlier papers of this series. Reagent grade methanol from the Fisher Scientific Co. was used without purification.

Spectra and Analyses.—The infrared spectra were determined on a Perkin-Elmer model 21 spectrophotometer and a Perkin-Elmer Infracord model 137 spectrophotometer. The model 21 was used for all rate determinations in which the disappearance of the perester carbonyl was followed.

Gases, other than carbon dioxide, were analyzed using a Consolidated Engineering Corporation mass spectrometer, model 21-103C.

The carbon-hydrogen analyses were done by S. M. Nagy, M. I. T. Microchemical Laboratory.

Preparations of Peresters.—Diphenyl ketene was prepared using the procedure of Smith and Hoehn.¹⁹ Two small modifications were necessary to obtain acceptable yields. First, several drops of methanolic potassium hydroxide was added to the reaction mixture to initiate the oxidation of the benzil monohydrazone. Second, since the pyrolysis and rearrangement of the diazo compound, accomplished by dropping a benzene solution of this compound into a heated flask, takes 8–10 hours, it is desirable to remove rearranged material from the flask every hour or hour and a half, or very little of the desired product is obtained.

Diphenylmalonyl chloride was prepared by a modification of the procedure of Staudinger, Göhring and Schöller.²⁰ In one arm of a Y-flask was placed 4.8 g., 25 mmoles, of diphenyl ketene and in the other arm 3.9 g., 31 mmoles, of oxalyl chloride (Eastman Kodak Co. White Label). After degassing the reactants two or three times, the flask was filled with carbon dioxide and sealed. The reactants were warmed to room temperature and mixed. The mixture was allowed to stand at room temperature for 1 hour and then heated in a steam-bath for 1 hour, after which the flask was opened and the contents distilled. The major fraction, collected at 146–160° (1–2 mm.), crystallized on cooling or seeding. The yield of crude product was 80–85%. Pure, colorless acid chloride, m. p. 51–52°, was obtained by several recrystallizations of the crude product from petroleum ether.

Di-*tert*-butylperoxy Diphenylmalonate.—A solution of 3.88 g. (13.2 mmoles) of diphenylmalonyl chloride in 5 ml. of ether and 10 ml. of pentane was added dropwise to a continuously stirred solution of 2.37 g., 30 mmoles, of pyridine and 2.70 g., 30 mmoles, of *tert*-butyl hydroperoxide in 4 ml. of ether and 15 ml. of pentane. The temperature of the reaction solution was maintained at –15 to –25° with a Dry Ice-carbon tetrachloride bath. The addition of acid chloride took 15–20 minutes, during which time pyridinium chloride slowly precipitated from solution. After addition was complete, the reaction mixture was stirred for another 20 minutes at –20°, and then stored overnight in a –25° freezer. The solution was then filtered and the collected hydrochloride washed with pentane and small quantities of ether. The ether-pentane filtrate was washed once with cold water, three times with cold 10% sulfuric acid, three times with cold 10% sodium carbonate, and three times with cold water. The organic solution was dried over magnesium sulfate, filtered and most of the solvent removed. On cooling, colorless crystals formed and were

collected. The yield was 1.6 g. (30%) (two crops). The yields were usually 15–25%. The perester could be recrystallized by dissolving it in a small quantity of ether at room temperature, adding pentane, and cooling; m. p. 66.4–67.6° dec. The peroxide content of unrecrystallized perester by iodometric titration was 88%. In the preparation, only the minimum amount of ether necessary to dissolve and keep the acid chloride in solution should be used. When ether was used as the only solvent, almost no perester was obtained.

Anal. Calcd. for C₂₃H₂₈O₆: C, 68.98; H, 7.05. Found: C, 68.59; H, 7.29.

***tert*-Butylperoxy Isobutyrate.**—Isobutyryl chloride was initially prepared from isobutyric acid (Eastman Kodak Co.) using the method of Brown.²¹ Later preparations of the perester were carried out using commercial acid chloride (Eastman Kodak Co.) as received.

A solution of 5 g. (46.7 mmoles) of isobutyryl chloride in 20 ml. of pentane was added dropwise over 25 minutes to a continuously stirred solution of 6.3 g. (70 mmoles) of *tert*-butyl hydroperoxide and 5.5 g. (70 mmoles) of pyridine in 25 ml. of pentane that had been cooled to –5 to 0°. After addition of the acid chloride was completed the solution, now containing a considerable amount of white precipitate, was stirred at 0° for an additional 20–30 minutes. The reaction mixture was poured over crushed ice and as the ice melted the pyridinium chloride dissolved. The pentane solution was separated from the water layer, washed three times with cold 10% sulfuric acid, three times with cold 10% sodium carbonate, and three times with cold water. After drying the pentane solution over magnesium sulfate, the pentane was removed under vacuum at or below room temperature. The residue remaining was a light yellow oil weighing 5.5 g.

The perester was dissolved in pentane and passed over a short column packed with Florisil. It was also recrystallized from petroleum ether at low temperatures. The peroxide content by iodometric titration was 90–93.5%.

Anal. Calcd. for C₈H₁₆O₃: C, 59.97; H, 10.07. Found: C, 60.40; H, 10.07.

***tert*-Butylperoxy Diphenylacetate.**—Diphenylacetyl chloride was prepared from diphenylacetic acid (Eastman Kodak Co.) using the method described by Staudinger.²² The acid chloride was recrystallized from petroleum ether several times before use; m. p. 53.5–54.5°.

A solution of 5.21 g. (25.2 mmoles) of diphenylacetyl chloride in 20 ml. of ether was added dropwise to a stirred solution of 2.84 g. (36 mmoles) of pyridine and 3.25 g. (36 mmoles) of *t*-butyl hydroperoxide in 15 ml. of pentane and 5 ml. of ether kept at –5 to 0°. The addition was completed in 25 minutes after which the reaction mixture was stirred for another 25 minutes. If the precipitate in the flask became too heavy for stirring, more pentane and ether were added. The entire reaction mixture was poured on crushed ice and more ether was added if necessary to dissolve precipitated perester. When the ice melted the organic layer was separated from the water, washed with cold 10% sulfuric acid, cold 10% sodium carbonate and cold water, and finally dried over magnesium sulfate. The perester solution was decanted from the magnesium sulfate, some of the solvent evaporated, and the solution cooled to –25°. The crystals formed were collected and the last traces of solvent removed under vacuum. The first crop of crystals yielded 2.97 g. (41.5%) of perester. Second and third crops increased the yield to approximately 60%. Iodometric titration of the first crop yielded a peroxide titer of 76%. The perester was easily recrystallized from petroleum ether; m. p. 58.2–60.0°.

Anal. Calcd. for C₁₈H₂₀O₃: C, 76.03; H, 7.09. Found: C, 76.18; H, 7.21.

Once prepared and purified the peresters were stored at –25°. Even at this low temperature there was some decomposition of the peresters after long periods of time. This was particularly true of the peroxy malonate which would turn yellow after only a few hours at room temperature or after a few months at –25°.

The kinetic procedure was that described by Bartlett, Benzing and Pincock.¹⁸ Calibration curves showed the validity of Beer's law for the infrared absorption used. Plots of log (*P*)/(*P*)₀ against time were straight lines in all cases.

Product Studies.—The general technique used for analysis of the products of decomposition was that described by Bartlett, Benzing and Pincock.¹⁸

The polyester of benzoic acid, isolated from decomposition of di-*tert*-butylperoxy diphenylmalonate, was partially purified by dissolving it in benzene and then precipitating by adding the benzene solution dropwise to petroleum ether.

Anal. Calcd. for C₁₄H₁₀O₂: C, 79.98; H, 4.79. Found: C, 79.86; H, 5.18.

Polyester of Benzoic Acid.—The procedure of Staudinger, *et al.*,² was followed. Oxygen was bubbled through a solution of

(17) P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1761 (1960).

(18) P. D. Bartlett, E. P. Benzing and R. E. Pincock, *ibid.*, **82**, 1766 (1960).

(19) L. I. Smith and H. H. Hoehn, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 356.

(20) H. Staudinger, O. Göhring and M. Schöller, *Ber.*, **47**, 43 (1914).

(21) H. C. Brown, *J. Am. Chem. Soc.*, **60**, 1325 (1938).

(22) H. Staudinger, *Ber.*, **44**, 1620 (1911).

8 g. of diphenyl ketene in 110 ml. of pentane at 0° for 4.5 hours. The solution was filtered and the collected solid washed with petroleum ether. This solid, weighing 5 g., was triturated with a solution of 12 ml. of acetone and 20 ml. of ether. The undissolved solid was dissolved in benzene and the resulting solution extracted with 10% sodium carbonate. The benzene solution was washed with water, dried over magnesium sulfate, and the benzene evaporated. The residual solid was Staudinger's "high molecular weight" polyester of benzoic acid. The "low molecular weight" polyester was obtained from the ether-acetone wash. The infrared spectra of the "high" and "low" polymers were identical with the spectrum of the polymer from the decomposition of permalunate. The gross physical properties of all these polymers, e.g., the wide melting point range, the change in form on trituration with various solvents and the solubility in various solvents, were quite similar. No molecular weight measurements were made, but the average molecular weight of the polymer obtained from perester is probably between the molecular weights of the "high" and "low" polymers from the oxygenation of diphenyl ketene.

Reaction with Methanol.—Di-*tert*-butylperoxy diphenylmalonate (102 mg., 0.255 mmole) was dissolved in 2 ml. of methanol, and the resulting solution degassed, sealed under vacuum, and heated for 2.5 hours at 60°

When decomposition was complete the solvent and volatile products were distilled from the reaction solution, leaving a residue of 41.9 mg. The infrared spectrum was almost identical with that of α -methoxydiphenylacetic acid. The only difference was a weak band at 6.01 μ which can be attributed to a trace of benzophenone. Chromatographing the residue on silica gel neither changed the spectrum nor yielded any new compounds. Assuming that 40 mg. of the residue was the α -methoxy acid, this would correspond to a 65% conversion from perester.

α -Methoxydiphenylacetic acid for comparison purposes was prepared using the method described by Klosa.²³ Recrystallization from benzene-petroleum ether yielded white crystals melting at 105–106.5° (reported m.p. 104–106°).

The 1,1,2-triphenyl-2-methylpropane, previously unknown, was identified by its infrared spectrum and its analysis. This compound was recrystallized from ethanol-water; m.p. 70.2–70.8°.

Anal. Calcd. for C₂₂H₂₂: C, 92.26; H, 7.74. Found: C, 92.10; H, 7.87.

Acknowledgment.—We thank the National Institutes of Health for support of this work.

(23) J. Klosa, *Archiv. Pharm.*, **288**, 42 (1955).

COMMUNICATIONS TO THE EDITOR

Resolution of an Asymmetric Organogermanium Compound, Methyl- α -naphthylphenylgermane

Sir:

To the best of our knowledge the resolution of an organogermanium compound asymmetric at germanium has not been reported, although Schwarz and Lewinsohn¹ have reported attempts to resolve isopropylphenylethylbromogermane through the α -bromo- π -camphor sulfonate ester. We therefore wish to report the first resolution of an asymmetric germanium compound into its enantiomers, namely, the compound methyl- α -naphthylphenylgermane (I).^{1a} This compound is of particular interest since it is isostructural with methyl- α -naphthylphenylsilane, the absolute configuration of which has recently been reported.² In addition, considerable knowledge regarding the stereochemistry of displacements at silicon has been derived from the study of the reactions of this compound and its derivatives.^{3–6}

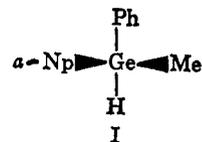
The synthesis and resolution of methyl- α -naphthylphenylgermane was best accomplished by the route shown in Fig. 1. This route, utilizing the ready cleavage of phenyl groups from germanium by bromine,^{1,7} was far superior to that using germanium tetrachloride and successive couplings with the appropriate Grignard reagents.

Several details of this synthetic route warrant comment. The methyl- α -naphthylphenylbromogermane derived from coupling of α -naphthyl Grignard reagent with methylphenyldibromogermane was not isolated, but the entire reaction mixture was reduced to the germane in order to facilitate purification at this stage. The subsequent bromination was best accomplished using N-bromosuccinimide since bromine

was found to lead to considerable cleavage of the naphthyl group from germanium.

The resolution was achieved by converting the bromogermane to the methoxygermane, which was not isolated because of its anticipated instability⁸ but was instead immediately converted to the menthoxygermane by exchange with (–)menthol. This compound in pentane yielded a crystalline diastereomer, $[\alpha]^{22D} - 49.3^\circ$, which on treatment with lithium aluminum hydride gave crystalline methyl- α -naphthylphenylgermane, $[\alpha]^{26D} + 26.7^\circ$. Following removal of several crops of this diastereomer, the residual oil, $[\alpha]^{20D} - 59.4^\circ$, was similarly reduced to give the other enantiomer, $[\alpha]^{26D} - 25.5^\circ$.

It was of interest to compare the relative configurations of these compounds with their silicon analogs. Using the Fregda method of quasi-racemates^{6,9,10} it was found as expected that mixtures of (+)Ge*H¹¹ and (+)Si*H behave as a solid solution having at most a 1.0° melting point range over a range of concentrations, whereas mixtures of (+)Ge*H and (–)Si*H or (–)Ge*H and (+)Si*H gave melting point ranges from 10 to 25°, as shown in Fig. 2. Since the absolute configuration of (+)Si*H has been shown to be R,¹² it follows that the absolute configuration of (+)Ge*H is also R (I).



It is perhaps worthy of note that the (+) rotatory germane was obtained from the less levorotatory ether, whereas in the silicon case the (+) silane was obtained from the *more* levorotatory menthoxy ether.¹³ Since the relative polarizabilities of groups should remain

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(1a) NOTE ADDED IN PROOF.—Since the submission of this communication the resolution of ethyl- α -naphthylphenylgermane has been reported: R. W. Bott, C. Eaborn and I. D. Varna, *Chem. Ind. (London)*, 614 (1963).

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(5) C. Eaborn and O. W. Steward, *Proc. Chem. Soc.*, 59 (1963).

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(8) A. G. Brook, *ibid.*, **77**, 4827 (1955).

(9) A. Fregda, *Tetrahedron*, **8**, 126 (1960).

(10) K. Mislow and M. Heffer, *J. Am. Chem. Soc.*, **74**, 3668 (1952).

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(12) R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 8 (1956).

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