The Decomposition of *t*-Butyl *erythro*- and *threo*-2,3-Diphenylperoxybutyrate in Solution. The Product Analysis and the Cage Effect

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Decomposition of *t*-butyl *erythro*- and *threo*-2,3-diphenylperoxybutyrate was examined in solution at 60 °C; there was no indication of induced decomposition taking place as is the case with *t*-butyl 2,3-diphenylperoxypropionate. Various hydrocarbons resulting from the reaction of the 1,2-diphenylpropyl radical in a variety of ways were identified in the product, and *t*-butyl 1,2-diphenylpropyl ether was found to be formed as cage recombination product in the *threo*/*erythro* isomeric ratio which depended on the stereochemistry of the starting peroxybutyrate.

In a previous paper[1] we have demonstrated that *t*-butyl 2,3-diphenylperoxypropionate undergoes decomposition involving a pathway induced by radicals and gives stilbene as product characteristic of this pathway.

$$PhCH_2CHPhCO_3{}^tBu \longrightarrow PhCH_2\dot{C}HPh + CO_2 + t\text{-}BuO\cdot \quad (1)$$

$$PhCH_2CHPhCO_3{}^tBu + t\text{-}BuO\cdot \longrightarrow Ph\dot{C}HCHPhCO_3{}^tBu + t\text{-}BuOH \quad (2)$$

$$Ph\dot{C}HCHPhCO_3{}^tBu \longrightarrow PhCH{=}CHPh + CO_2 + t\text{-}BuO\cdot \quad (3)$$

In order to study the stereochemistry of a β-scission reaction of the type shown in reaction 3, we examined the decomposition of *t*-butyl *erythro*- and *threo*-2,3-diphenylperoxybutyrate (I) in the expectation that they might afford α-methylstilbene (Reaction 6) in different *cis* to *trans* ratios, thus giving some clue to elucidation of the stereochemical course.

$$MePhCHCHPhCO_3{}^tBu \longrightarrow MePhCH\dot{C}HPh + CO_2 + t\text{-}BuO\cdot \quad (4)$$

$$MePhCHCHPhCO_3{}^tBu + t\text{-}BuO\cdot \longrightarrow MePh\dot{C}CHPhCO_3{}^tBu + t\text{-}BuOH \quad (5)$$

$$MePh\dot{C}CHPhCO_3{}^tBu \longrightarrow MePhC{=}CHPh + CO_2 + t\text{-}BuO\cdot \quad (6)$$

Results and Discussion

t-Butyl *erythro*-2,3-diphenylperoxybutyrate, mp 96.5—98 °C (dec), and the *threo*-isomer, mp 56.5—57 °C (dec), were prepared from the corresponding acid chloriods and *t*-butyl hydroperoxide according to the usual method and decomposed in chlorobenzene and toluene at 60 °C. The results are summarized in Table 1.

The yield of α-methylstilbene, a product expected from the induced decomposition (Reactions 5 and 6) was relatively low, and the *cis-trans* ratios did not differ appreciably. The decomposition of *t*-butyl *erythro*-2,3-diphenylperoxybutyrate in chlorobenzene was not accelerated in the presence of di-*t*-butyl diperoxyoxalate, a generator of the *t*-butoxyl radical,[2] contrary to the case with *t*-butyl 2,3-diphenylperoxypropionate,[1] and furthermore, kinetic measurements showed that the peroxybutyrate decomposes according to a strict first order rate law without any indication of induced decomposition ($k=6.29\times10^{-5}$ s^{-1} at 60 °C in toluene);[3] accordingly, it may safely be said that with the diphenylperoxybutyrate the hydrogen abstraction of the type shown in Eq. 5 is operative only to a very limited extent, if at all. Thus, the purpose of examining the stereochemistry of Reaction 6 envisaged in the beginning was defeated.

TABLE 1. PRODUCTS FROM DECOMPOSITION OF *erythro*- AND *threo*-2,3-DIPHENYLPEROXYBUTYRATE[a]

Peroxybutyrate Solvent	*erythro* PhCl	*threo* PhCl	*erythro* $PhCH_3$	*threo* $PhCH_3$
Products[b]				
1,2-Diphenylpropane	7.1	8.2	1.6	1.3
dl-2,3-Diphenylbutane	1.0	1.2		
meso-2,3-Diphenylbutane	1.0	1.2		
cis-α-Methylstilbene	1.6	2.3	2.4	2.5
trans-α-Methylstilbene	1.8	2.4	1.7	0.7
erythro-Ether (II)	6.3	2.9	4.7	2.4
threo-Ether (II)	5.5	8.7	4.5	6.9
1,2,3-Triphenylbutane			39	25
Bibenzyl			7.3	8.1

a) The peroxybutyrate (0.30 mmol) in 3.0 ml of solvent was decomposed at 60 °C for 36 h in degassed and sealed ampoules. b) Yields in per cent based upon the starting peroxybutyrate are estimated by VPC and average values from two independent decompositions are given.

The precursor of 1,2-diphenylpropane, one of the major products is obviously the 1,2-diphenylpropyl radical produced in Reaction 4. It either abstracts a hydrogen atom from some hydrogen donors including acetone formed from the *t*-butoxyl radical or disproportionates giving 1,2-diphenylpropane and α-methylstilbene. The fact that the yield of 1,2-diphenylpropane is much lower in toluene than in chlorobenzene is explained by the combination reaction of the 1,2-diphenylpropyl radical with the benzyl radical generated from toluene by hydrogen abstraction by the *t*-butoxyl radical furnished by Reaction 4, giving 1,2,3-triphenylbutane. Thus, Table 1 shows that the 1,2-diphenylpropyl group is better accounted for in the decomposition in toluene than in chlorobenzene. In the absence of the benzyl radical much of the 1,2-diphenylpropyl radical certainly combined with itself to give the dimeric product, which it was not attempted to detect in the present analysis.

2,3-Diphenylbutanes were formed in chlorobenzene solvent in the same *dl*/*meso* ratio of 1.0 from both diastereomeric peroxybutyrates, whereas in toluene none of the butanes was produced at all. Obviously, the butanes are formed by combination of the free 1,2-

diphenylpropyl with the methyl radical generated by decomposition of the *t*-butoxyl radical outside the solvent cage; in toluene the concentration of the methyl radical is too low to give the butanes since the methyl radical or the *t*-butoxyl radical for that matter reacts efficiently with toluene by abstruction of hydrogen.

t-Butyl 1,2-diphenylpropyl ether (II) was isolated by preparative thin-layer chromatography on silica gel, and the structure was established on the basis of the NMR and IR spectra and analytical data. The NMR spectrum showed the ether isolated to be a mixture of the diastereomers. Thus, one set of signals consisting of a sharp singlet at τ 9.15 (9H) and two doublets at τ 8.94 (3H) and 5.56 (1H) corresponding to *t*-butyl, methyl, and methine protons, respectively, is assigned to the *erythro*-diastereomer, and the other set of signals at τ 9.03 (singlet 9H), 8.70 (doublet 3H), and 5.48 (doublet 1H) quite similar in appearance to those of the first set and all shifted to lower field regions is assigned to the *threo*-isomer, because of the fact that *t*-butyl *erythro*-2,3-diphenylperoxybutyrate and *erythro*-2,3-diphenylbutyric acid show the proton signals due to *t*-butyl and methyl groups all at higher field regions than the corresponding peaks shown by the *threo*-peroxybutyrate and *threo*-acid.

A similar ether, namely *t*-butyl 1,2-diphenylethyl ether, is formed in the thermolysis of *t*-butyl 2,3-diphenylperoxypropionate in chlorobenzene, and this has been shown to be the cage recombination product between the *t*-butoxyl and the 1,2-diphenylethyl radical.[1] *t*-Butyl 1,2-diphenylpropyl ether was therefore thought, by analogy, also to be a cage product, and experiments with scavenger confirmed this view. Thus, the amount and isomer ratio of the ether produced did not change appreciably (Table 2) in the presence of 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl,[4] which is known to capture radicals generated in the autoxidation of diphenylmethane very efficiently, that is, almost at the same rate as molecular oxygen does.[5]

Table 2. *t*-Butyl 1,2-diphenylpropyl ether from decomposition of *t*-butyl *erythro*-2,3-diphenylperoxybutyrate in toluene in the presence of 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl[a]

Nitroxyl, M	*t*-Butyl Ether	
	erythro + *threo*[b]	*threo*/*erythro*
0.00	9.2	0.96
0.14	8.8	0.92
0.40	8.7	0.89
0.80	8.3	0.89

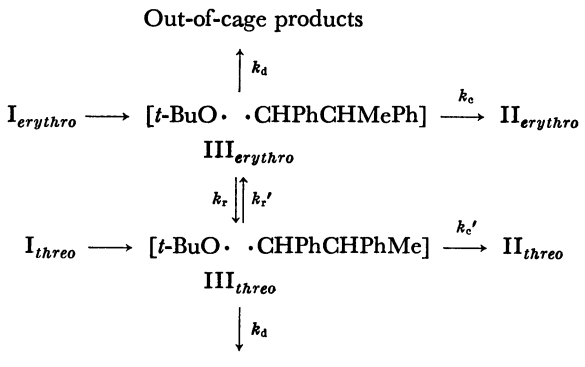
a) The peroxybutyrate (0.10 M) was decomposed at 60 °C for 36 h in degassed and sealed ampoules. b) Yields in per cent based upon the starting peroxybutyrate.

The formation of 1,2,3-triphenylbutane (25—39%) in the decomposition in toluene shows that 1,2-diphenylpropyl radicals from the peroxybutyrate combined outside the solvent cage with free benzyl radicals generated from toluene by hydrogen abstraction by the *t*-butoxyl radical, while absence of even traces of benzyl *t*-butyl ether from the product indicates that all *t*-butoxyl radicals have been consumed before they combine with benzyl radicals; accordingly, the *t*-butoxyl radical does not have any chance to react with free 1,2-diphenylpropyl radicals to yield *t*-butyl 1,2-diphenylpropyl ether outside the cage.

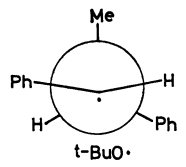
A change in solvent from toluene to chlorobenzene caused a slight increase in the yield of the *t*-butyl ether (II); this effect may be attributed to solvent viscosity effect (chlorobenzene, 0.51 cP; toluene, 0.39 cP at 60 °C).[6]

All these observations considered above support that almost all of the *t*-butyl ether (II) is formed in the solvent cage.

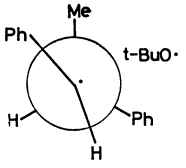
Obviously, the *threo* to *erythro* ratio in which *t*-butyl 1,2-diphenylpropyl ether (II) was produced depends on the stereochemistry of the starting peroxybutyrate (I). The decomposition of the isomeric peroxybutyrates, with special regard to the cage effect, may be formulated as shown in the annexed scheme, in which the solvent cage is denoted by brackets. These peroxybutyrates undergo most likely a two-bond scission[7] giving rise to a 1,2-diphenylpropyl and a *t*-butoxyl radical and carbon dioxide, the last of which is omitted from the scheme for the sake of simplicity. It is assumed that, at the moment of generation, a radical pair (III) of 1,2-diphenylpropyl and *t*-butoxyl as a whole retains the stereochemistry of the parent peroxybutyrate and that the stereoisomeric radical pairs interconvert in the cage with rate constants k_r and k_r'. Thus, the diffusion of radicals from the cage with rate constant k_d results in the formation of out-of-cage products and the recombination of radicals give isomeric *t*-butyl 1,2-diphenylpropyl ethers $II_{erythro}$ and II_{threo} with rate constants k_c and k_c', respectively. The usual steady state treatment of this reaction scheme using the yields of the respective ethers in toluene gives the relative values of the reaction constants as follows: $k_c=1$, as standard; $k_c'=1.1$; $k_d=10$; $k_r=21$; $k_r'=12$.



Although it is natural to suppose that the radical pair in the cage (III) consisting of a 1,2-diphenylpropyl and a *t*-butoxyl radical resembles the parent peroxybutyrate in stereochemistry and, therefore, that such structures as shown below are probable for the diastereomeric radical pairs in the cage, further discussion in terms of steric effects of substituents would seem



$III_{erythro}$



III_{threo}

meaningless, because, in the first place, such steric effects are not known accurately enough and secondly, the difference between the interconversion rates $k_r=21$ and $k_r'=12$ corresponds to an energy difference between the two conformations of only 370 cal/mol at 60 °C.

Greene and his coworkers studied the cage effect in the thermolysis of *S*-(+)-*t*-butyl 2-phenylperoxypropionate using butanethiol as a scavenger and determined the relative rates of the processes occurring in the cage.[8]

We attempted experiments with 1-propanethiol as possible scavenger in the decomposition of *t*-butyl *erythro*-2,3-diphenylperoxybutyrate in toluene at 60 °C, but copious precipitation of 2,3-diphenylbutyric acid took place, which was not observed in the absence of the thiol. The acid was evidently produced by the direct bimolecular reaction of the thiol and the peroxybutyrate, since the normal mode of the decomposition of the peroxybutyrate is thought to be a two-bond scission expelling a molecule of carbon dioxide.[7] In view of this finding the use of thiols seems to be inadequate for scavenging experiments.

Experimental

Materials. Di-*t*-butyl diperoxyoxalate,[2] 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl,[4] 2,3-diphenylbutane,[9] benzyl *t*-butyl ether,[10] and *trans*-[11] and *cis*-α-methylstilbene[12] were prepared by published procedures.

The following compounds were also prepared for comparison with reaction products in VPC analysis.

erythro-*1,2,3-Triphenylbutane.* *erythro*-1,2,3-Triphenyl-1-butanone[13] (2.0 g) was hydrogenated in 60 ml of ethanol containing 10 drops of concentrated hydrochloric acid over 290 mg of 10% palladium on carbon catalyst at room temperature under atmospheric pressure. The catalyst and the solvent were removed, and the product was chromatographed on silica gel using benzene as eluent and recrystallized from ethanol to give 0.6 g (31%) of *erythro*-1,2,3-triphenylbutane (Found: C, 92.60; H, 7.72%. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74%), mp 88.0—88.5 °C; *m/e* 286 (M^+); NMR ($CDCl_3$) τ 9.0 (d, 3H, J= 6.0 Hz, CH_3), 7.7—6.8 (m, 4H, $-CH\dot{C}H\dot{C}H_2-$), and 3.5—2.6 (m, 15H, phenyls).

1,2-Diphenylpropane. *trans*-α-Methylstilbene (1.7 g) in 50 ml of ethanol was hydrogenated over 10% palladium on carbon (91 mg) under atmospheric pressure at room temperature. Hydrogenation was stopped when the hydrogen uptake corresponded to one mole of hydrogen per mole of the compound. Removal of the catalyst and solvent left a colourless liquid, which was gas-chromatographically pure, yield 1.5 g (88%).

t-*Butyl* erythro-*2,3-Diphenylperoxybutyrate.* *erythro*-2,3-Diphenylbutyric acid[14] was allowed to react with thionyl chloride at room temperature for 7 h. The resulting *erythro*-2,3-diphenylbutyryl chloride (1.77 g), without further purification, was added to a stirred solution of 1.0 g of *t*-butyl hydroperoxide in 0.9 g of pyridine and 60 ml of pentane cooled in an ice–water bath. The addition required 15 min and stirring was continued for four more hours. Cold 10% aqueous sulphuric acid was added, and the product was extracted with ether. The ethereal layer was washed with cold 10% aqueous sodium carbonate solution and then with water, and dried with anhydrous sodium sulphate at 0 °C. After removal of the solvent under reduced pressure, the residue was recrystallized from ether to give 1.4 g (67%) of *t*-butyl *erythro*-2,3-diphenylperoxybutyrate (Found: C, 77.04; H, 7.90%. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.94 %. Purity, 99% by iodometric titration[15]), mp 96.5—98.0 °C (dec); IR (Nujol) 1760 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) τ 9.08 (s, 9H, *t*-Bu), 8.99 (d, J=5.9 Hz, 3H, CH_3), 6.8—6.1 (m, 2H, $-\dot{C}H\dot{C}H-$), and 3.0—2.4 (m, 10H, phenyls).

t-*Butyl* threo-*2,3-Diphenylperoxybutyrate.* *threo-2,3*-Diphenylbutyronitrile (mp 31.5—32.5 °C; lit,[14] mp 35—36 °C), prepared from benzyl cyanide and α-chloroethylbenzene according to the procedure of Hauser and Brasen[14] with the modification that the anion derived from benzyl cyanide and sodium amide was added to α-chloroethylbenzene, was hydrolyzed by heating in a mixture of 50% aqueous sulfuric acid and glacial acetic acid under reflux for 80 h. The resulting crude *threo*-acid was dissolved in acetone and the solution allowed to evaporate slowly to dryness at room temperature until a mixture of crystalline *threo*- and *erythro*-2,3-diphenylbutyric acids formed. Well developed larger crystals of the *threo*-acid were sorted out manually, mp 135.3—136.0 °C (lit,[14] mp 130—133 °C). The *threo*-acid (3.0 g) was treated with thionyl chloride at room temperature for 20 h. The resulting acid chloride, without purification, was dissolved in 25 ml of anhydrous pentane, and the solution added very slowly (40 min) to a solution of *t*-butyl hydroperoxide (1.56 g) and pyridine (1.17 g) in 25 ml of anhydrous pentane cooled in an ice–water bath. The reaction mixture was stirred for 2 h at 2 °C, while a pasty mass formed. Ice–water (20 ml) was added to the reaction mixture and the organic layer was washed successively with 10% sulphuric acid, water, 10% sodium carbonate, and water, and dried with anhydrous sodium sulphate at 0 °C overnight. The dried solution was chilled in a Dry Ice bath, and the crystals which separated were filtered off and recrystallized from pentane–dichloromethane (1: 1) to give 1.5 g (37%) of *t*-butyl *threo*-2,3-diphenylperoxybutyrate (Found: C, 77.01; H, 7.53%. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74%. Purity, 98% by iodometric titration[15]), mp 56.5—57.0 °C (dec); IR (Nujol) 1760 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) τ 8.80 (s, 9H, *t*-Bu), 8.59 (d, 3H, J=5.9 Hz, CH_3), 6.8—6.1 (m, 2H, $-\dot{C}H\dot{C}H-$), and 3.2—2.7 (m, 10H, phenyls).

Decomposition of t-*Butyl* erythro- *or* threo-2,3-*Diphenylperoxybutyrate in Solution.* A solution of either peroxybutyrate in chlorobenzene (3.0 ml, 0.100 M) was placed in an ampoule, degassed (three freeze-thaw cycles), and, the ampoule having been sealed, allowed to decompose in a constant-temperature bath at 60 °C for 36 h. A weighed amount of diphenylmethane was then added as an internal standard to the reaction mixture and it was subjected to VPC (Hitachi Gas Chromatograph Model K-53 FID). The following three columns were used: a 2 m column packed with Apiezon L grease (5%) to analyze for *meso*- and *dl*-2,3-diphenylbutanes, *t*-butyl 1,2-diphenylpropyl ether, and *trans*-α-methylstilbene at 190 °C; a 2 m column packed with Ucon oil LB-550-X (5%) plus a 1 m column packed with Silicone grease (5%) to analyze for *cis*-α-methylstilbene and 1,2-diphenylpropane at 175 °C; and a 300 ft. capillary column coated with Apiezone L grease to separate *erythro*- and *threo*-*t*-butyl 1,2-diphenylpropyl ethers.

The decomposition in toluene was carried out in a similar manner as described above.

Decomposition of the *erythro*-peroxybutyrate in the presence of 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl was similarly

carried out in toluene (Table 2).

Decomposition of t-*Butyl* erythro-*2,3-Diphenylperoxybutyrate in Chlorobenzene in the Presence of Di-*t*-butyl Diperoxyoxalate.* A solution of *t*-butyl *erythro*-2,3-diphenylperoxybutyrate (1.02 mmol) and di-*t*-butyl diperoxyoxalate (1.45 mmol) in chlorobenzene (3.0 ml) was heated at 35 °C for 14.5 h under a nitrogen atmosphere, and the remaining peroxybutyrate was determined by iodometric titration[15] (0.75 mmol, 74% of the peroxybutyrate used). A control experiment without di-*t*-butyl diperoxyoxalate showed the same result, demonstrating that the peroxyoxalate caused no induced decomposition.

Separation and Purification of t-*Butyl 1,2-Diphenylpropyl Ether and 1,2,3-Triphenylbutane.* *t*-Butyl *erythro*-2,3-diphenylperoxybutyrate (1.2 g) in 50 ml of toluene was heated at 61 °C for 70 h under nitrogen. After removal of most of the solvent by distillation under atmospheric pressure, the mixture was distilled under reduced pressure (0.1—0.5 mmHg), while the temperature of the heating bath was maintained below 160 °C. The distillate was subjected to purification by thin-layer chromatography on silica gel using chloroform–petroleum ether (1: 1) as eluent. A band of R_f 0.6 was extracted with diethyl ether, the extract condensed, and the residue purified by trap-to-trap distillation to give *t*-butyl 1,2-diphenylpropyl ether (Found: C, 85.11; H, 8.91%. Calcd for $C_{19}H_{24}O$: C, 85.02; H, 9.01 %), IR (neat) 1195 cm^{-1} characteristic of *t*-BuO.[16]

The residue from the vacuum distillation was chromatographed on silica gel. The faster-moving component was purified by molecular distillation to give an oil, which was gas chromatographically pure, *m/e* 286 (M^+) (Found: C, 92.56; H, 8.01%. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74%). Comparison of its IR and NMR spectra with those of authentic *erythro*-1,2,3-triphenylbutane led to the conclusion that the oil was a mixture of *erythro*- and *threo*-1,2,3-triphenylbutanes in equal amounts.

Kinetics of Decomposition of t-*Butyl erythro-2,3-Diphenylperoxybutyrate.* A solution of the peroxybutyrate (*ca.* 0.1 M) in toluene was decomposed in sealed tubes at 60 °C. The tubes were removed from the bath at intervals and chilled at −78 °C to quench the reaction. The peroxybutyrate was determined by titration according to Swern's method,[15] and plots of the logarithms of the concentration of the peroxybutyrate *vs.* time gave a straight line up to 85% decomposition.

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