A New Type of Induced Decomposition. III.[1] Induced Decomposition of Cinnamoyl Peroxide, *t*-Butyl Peroxycinnamate and *t*-Butyl 2,3-Diphenylperoxypropionate in Solution

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(Received March 8, 1976)

Phenyl and benzyl radicals were found to induce decomposition of cinnamoyl peroxide or *t*-butylperoxycinnamate to give stilbene and 1,3-diphenylpropene, respectively. Similarly, *t*-butoxyl radicals caused *t*-butyl 2,3-diphenylperoxypropionate to decompose affording stilbene. A mechanism is proposed which involves a radical attack on a substrate peroxide producing a radical carrying an odd electron on the carbon atom β to the carboxyl group and its subsequent collapse to final products by way of β-scission.

In previous papers we showed that phenylpropioloyl peroxide and *t*-butyl phenylperoxypropiolate decompose *via* a new type of induced path involving a radical attack on the triple bond of the peroxides and a subsequent β-scission.[1] We now extended the study to cinnamoyl peroxide[2] and *t*-butyl peroxycinnamate,[3] and *t*-butyl 2,3-diphenylperoxypropionate.

Results and Discussion

trans-Cinnamoyl peroxide or *t*-butyl peroxycinnamate was heated in toluene at 35 °C for 15 h under a nitrogen atmosphere in the presence of di-*t*-butyl diperoxyoxalate, a generator of *t*-butoxyl radicals.[4] Significant part of these peroxides, which are both stable at this temperature in the absence of decomposing di-*t*-butyl diperoxyoxalate, was decomposed, the characteristic product being 1,3-diphenylpropene (see Table 1), which resulted from the reaction with benzyl radicals generated by the action of *t*-butoxyl radicals on toluene.

Similarly phenyl radicals, generated from *N*-nitrosoacetanilide,[5] caused the decomposition of *cis*- and *trans*-cinnamoyl peroxides and *t*-butyl peroxycinnamate to give stilbene (Table 2).

These results are satisfactorily explained by assuming the following reaction sequence (1)—(2) in keeping with the reaction sequence with the acetylenic peroxide set forth in previous papers.[1] Benzyl or phenyl radicals add to the double bond of the peroxides (I and II) to give intermediate radicals (III), which then decompose into 1,3-diphenylpropene or stilbene (Reactions 1 and 2).

Table 1. Decomposition of *trans*-cinnamoyl peroxide and *t*-butyl peroxycinnamate in the presence of di-*t*-butyl diperoxyoxalate at 35 °C for 15 h under nitrogen[a]

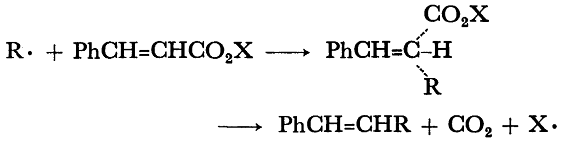
	Cinnamoyl peroxide	*t*-Butyl peroxycinnamate
Peroxide taken, mmol	1.39	2.49
Peroxide decomposed, mmol	1.15	1.63
($(t\text{-BuOOCO})_2$), mmol	2.15	2.77
Products, mmol		
CO_2	5.16	7.04
$PhCH{=}CHCH_2Ph$	0.63 (0.55)[b]	1.45 (0.89)[b]
$PhCH_2CH_2Ph$	0.73	0.40

a) In 8 ml of toluene. b) Yields in mol per mol of peroxide decomposed.

$$PhCH{=}CHCO_2X + R\cdot \longrightarrow Ph\dot{C}H{-}CHRCO_2X \qquad (1)$$

I: $X = PhCH{=}CHCO_2$ III
II: $X = t\text{-BuO}$

$$Ph\dot{C}H{-}CHRCO_2X \longrightarrow PhCH{=}CHR + CO_2 + X\cdot \qquad (2)$$



$$R\cdot + PhCH{=}CHCO_2X \longrightarrow PhCH{=}\overset{CO_2X}{\underset{R}{C}}{-}H \longrightarrow PhCH{=}CHR + CO_2 + X\cdot \qquad (3)$$

$R\cdot = PhCH_2\cdot$ or $Ph\cdot$

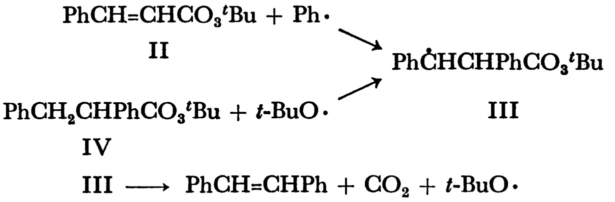
Table 2. Decomposition of *cis*- and *trans*-cinnamoyl peroxides and *t*-butyl peroxycinnamate induced by phenyl radicals at room temperature under nitrogen

	cis-Cinnamoyl peroxide		*trans*-Cinnamoyl peroxide		*t*-Butyl peroxycinnamate	
Peroxide taken, mmol	1.28	0.162	1.33	1.31	2.05	1.97
PhN(NO)Ac, mmol	1.92	1.19	2.39	6.20	2.90	2.75
Solvent (ml)	PhH (8)	PhCl (4)	PhCl (8)	PhCl (8)	Hexane (8)	Me_2CO (8)
Time, h	20	50	47	47	16	16
Peroxide decomposed, mmol	0.78	0.162	0.63	0.97	0.94	1.06
Products,[a] mmol						
cis-Stilbene	0.008 (0.01)	nil	nil	nil	nil	nil
trans-Stilbene	0.34 (0.43)	0.032 (0.20)	0.069 (0.11)	0.22 (0.23)	0.41 (0.44)	0.19 (0.18)
CO_2					0.51	1.14

a) Yields in moles per mole of peroxides decomposed are given in parentheses.

A possible alternative mechanism may be a direct bimolecular homolytic displacement reaction, in which benzyl or phenyl radicals directly displace the CO_2X group on the α-carbon atom of *t*-butyl peroxycinnamate (II) or cinnamoyl peroxide (I) (Reaction 3). This mechanism, however, can safely be ruled out because both *cis*- and *trans*-cinnamoyl peroxides afforded with phenyl radicals a considerable amount of *trans*-stilbene together with traces of the *cis*-isomer (Table 2). *cis*- and *trans*-Cinnamoyl peroxides would have given stilbene in different isomer rations, if the direct displacement by phenyl radicals had taken place.

In the foregoing scheme, the decomposition of *t*-butyl peroxycinnamate induced by the phenyl radical involves the 2-(*t*-butylperioxycarbonyl)-1,2-diphenylethyl radical (III) (reaction 2), which then decomposes into stilbene, carbon dioxide, and the *t*-butoxyl radical. The same intermediate radical (III) may be generated by abstraction of a β-hydrogen atom from *t*-butyl 2,3-diphenylperoxypropionate (IV), which, accordingly, is expected to undergo a similar type of induced decomposition.



$$PhCH{=}CHCO_3{}^tBu + Ph\cdot \ (\text{II}) \longrightarrow Ph\dot{C}HCHPhCO_3{}^tBu \ (\text{III})$$

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

$$\text{III} \longrightarrow PhCH{=}CHPh + CO_2 + t\text{-}BuO\cdot$$

Table 3. Decomposition of *t*-butyl 2,3-diphenylperoxypropionate in the presence of di-*t*-butyl diperoxyoxalate[a)]

Peroxypropionate taken, mmol	0.300	0.299
$(t\text{-}BuOOCO)_2$, mmol	none	0.302
Peroxypropionate decomposed, mmol	0.0615 (20.5)[b)]	0.0936 (31.3)
Products, mmol		
$(PhCH_2)_2$	0.0018 (0.6)	0.0021 (0.7)
$PhCH_2CH(Ph)O^tBu$	0.0072 (2.4)	0.0062 (2.1)
PhCH=CHPh	0.0121 (4.0)	0.0348 (11.6)

a) The peroxypropionate was decomposed in 3.0 ml of chlorobenzene in degassed ampoules at 35 °C for 12 h. b) Yields in percent based upon the starting peroxypropionate are given in parentheses. Yields given are the averages of results from three in dependent decompositions.

This expectation proved to be true in the following experiments. *t*-Butyl 2,3-diphenylperoxypropionate was heated in chlorobenzene at 35 °C for 12 h in the presence or absence of di-*t*-butyl diperoxyoxalate as radical generator (Table 3). The presence of the diperoxyoxalate increased the decomposition of the peroxypropionate (IV) to 31.3%, while the decomposition took place only to an extent of 20.5% in its absence. The diperoxyoxalate increased the yield of stilbene from 4.0% to 11.6%, but did not affect the yields of bibenzyl 0.6%) and *t*-butyl 1,2-diphenylethyl ether (2%). *t*-Butyl 2,3-diphenylperoxypropionate belongs to a class of peroxy-esters such as *t*-butyl 2-phenylperoxyacetate and 2-methyl-2-phenylperoxypropionate which are rather labile even at relatively low temperature.[3)] It is highly probable, therefore, that the initial homolysis takes place generating a 1,2-diphenylethyl and a *t*-butoxyl radical and a molecule of carbon dioxide in a cage of solvent. Among the products identified, *t*-butyl 1,2-diphenylethyl ether is obviously a cage combination product between a 1,2-diphenylethyl and a *t*-butoxyl radical, since its yield was not changed when more *t*-butoxyl radicals were produced by adding di-*t*-butyl diperoxyoxalate. Bibenzyl was probably formed by disproportionation of 1,2-diphenylethyl radical together with the corresponding amount of stilbene. The stilbene formed in excess of this amount must have been provided by the action of the *t*-butoxyl radical on the starting peroxypropionate, abstraction of a hydrogen atom giving the intermediate radical (III) postulated above and this radical in turn decomposing to give stilbene. In the presence of di-*t*-butyl diperoxyoxalate, the concentration of *t*-butoxyl radicals available in solution will be increased resulting in efficient abstraction of a hydrogen atom, and the amount of stilbene is thus increased.

Experimental

Materials. Chlorobenzene, toluene, and hexane were washed with concentrated sulphuric acid and then with water, dried with calcium chloride, and distilled, and middle fractions were used. *trans*- and *cis*-Cinnamoyl peroxides,[2)] *t*-butyl peroxycinnamate,[3)] di-*t*-butyl diperoxyoxalate,[4)] and *N*-nitrosoacetanilide[5)] were prepared by the published procedures.

t-Butyl 2,3-Diphenylperoxypropionate. 2,3-Diphenylpropionic acid, prepared by the published procedure,[6)] mp 87.5—88.0 °C (lit,[6)] mp 88—89 °C), was heated with thionyl chloride under reflux for 7 h and the resulting 2,3-diphenylpropionyl chloride was distilled under reduced pressure, bp 132—134 °C/1.5 mmHg. A solution of this chloride (4.83 g) in 20 ml of anhydrous pentane was added slowly (1.3 h) to a stirred solution of 2.77 g of *t*-butyl hydroperoxide in 2.42 g of pyridine and 60 ml of anhydrous pentane cooled in an ice-water bath. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. A small amount of water was added, followed by pentane until all the precipitate was dissolved. The organic layer was washed with 10% aqueous sodium carbonate, dried over anhydrous sodium sulphate, and cooled in a bath of acetone and solid carbon dioxide, to give a crystaline precipitate, which was filtered off and recrystallized from pentane several times. The yield was 3 g (51%), mp 74.5—76.1 °C (Found: C, 76.48; H, 7.37%. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43%. Purity, 100.8% by iodometric titration[7)]); IR (Nujol) 1775 cm^{-1} ($\nu_{C=O}$); NMR ($CDCl_3$) τ 8.95 (s, 9H, *t*-Bu), 6.0—7.2 (m, 3H, CH_2CH), 2.81 (broad s, 5H, phenyl), and 2.70 (broad s, 5H, phenyl).

Decomposition of trans-*Cinnamoyl Peroxide and* t-*Butyl Peroxycinnamate in the Presence of Di*-t-*butyl Diperoxyoxalates.* A typical run was as follows. A solution of the peroxide (1.39 mmol) in 8 ml of toluene was placed in a two-necked reaction flask equipped with a gas inlet tube and a reflux condenser which was connected to a trap cooled with acetone and solid carbon dioxide. The other end of the trap was attached to a tube containing Ascarite-magnesium perchlorate. Nitrogen was bubbled through the solution vigorously for a while to remove dissolved oxygen, and di-*t*-butyl diperoxyoxalate (2.15 mmol) was added to the solution. The flask was placed in a bath kept at 35 °C and the peroxides were allowed to decompose, a very slow stream of nitrogen being passed through the solution during the course of the reaction. After 15 h (5 half-life periods of di-*t*-butyl diperoxyoxalate⁴⁾), the reaction mixture was diluted to 10.0 ml with toluene. A 1.0 ml portion of this solution was pipetted out to analyze for undecomposed peroxy-ester by iodometric titration.⁷⁾ The remainder of the solution was treated with 10% sodium carbonate solution. The aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. The ether was removed under reduced pressure and the acidic residue was weighed. The organic layer was treated with 5 ml of acetic acid containing very small quantity of iron(III) chloride and 1 g of sodium iodide, and the mixture was allowed to stand for 20 min at room temperature in order to decompose the remaining peroxide. The iodine liberated was reduced with sodium thiosulphate solution. The organic layer was washed with 10% aqueous sodium carbonate solution, dried over anhydrous sodium sulphate, and analyzed by VPC (Table I).

Decompositions of cis- *and* trans-*Cinnamoyl Peroxides and* t-*Butyl Peroxycinnamate in the Presence of* N-*Nitrosoacetanilide.* A typical run was as follows. A solution of the peroxy-ester (II, 2.05 mmol) and *N*-nitrosoacetanilide (2.90 mmol) in 8 ml of hexane was allowed to decompose for 16 h at room temperature under a nitrogen atmosphere. The reaction mixture was diluted to 10 ml with hexane and a 1.0 ml portion of the mixture was taken to determine undecomposed peroxy-ester by iodometric titration.⁷⁾ The remaining solution was treated and analyzed in the same way as described above (Table 2).

Decomposition of t-*Butyl 2,3-Diphenylperoxypropionate in Chlorobenzene.* A solution (3 ml) of the 2,3-diphenylperoxypropionate in chlorobenzene (0.10 M) was degassed (three freeze-thaw cycles) and allowed to decompose in a bath kept at 35 °C for 12 h. One millilitre aliquot of the reaction mixture was dissolved in 10 ml of chloroform. A small piece of solid carbon dioxide, 0.5 g of sodium iodide, and a little Iron(III) chloride solution in glacial acetic acid (*ca.* 0.002%) were added successively. The resulting mixture was kept at about 60 °C under nitrogen for 15 min and the iodine liberated was titrated with standard sodium thiosulphate solution (0.0316M). The aqueous layer was extracted with chloroform. The extracts were combined with the organic layer, washed with 10% aqueous sodium carbonate, and dried over anhydrous sodium sulphate. The solution was concentrated to 5.0 ml by distillation through a helix-packed column, a weighed amount of diphenylmethane was added as an internal standard, and the whole was subjected to VPC analysis (Table 3).

Decomposition of t-*Butyl 2,3-Diphenylperoxypropionate in the Presence of Di*-t-*butyl Diperoxyoxalate in Chlorobenzene.* A solution (3 ml) of the 2,3-diphenylperoxypropionate (0.1 M) and diperoxyoxalate (0.1 M) in chlorobenzene was degassed and heated at 35 °C for 12 h. The reaction mixture was treated and analyzed in the same way as described above (Table 3).

Product Analysis. Analysis of the products was carried out by vapor phase chromatography on a Hitachi Gas Chromatograph Model K-53 FID or a Perkin Elmer Vapor Fractometer Model 154-D. Most of the products were identified by comparing their VPC retention times on Apiezon grease L (5%) at 190 °C or SE 30 (15%) at 199 °C with those of commercial samples. Stilbene was further identified by comparing its UV spectrum with that of an authentic sample. Carbon dioxide was absorbed on Ascarite–magnesium perchlorate and weighed. *t*-Butyl 1,2-diphenylethyl ether was isolated from the reaction mixture by preparative thin layer chromatography and was identified by elemental analysis and IR and NMR spectra (Found: C, 84.70; H, 8.50%. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72%), IR (neat) 1200 cm^{-1} characteristic of *t*-BuO;⁸⁾ NMR (CCl_4) τ 9.12 (s, 9H, *t*-Bu), 7.30 (d, 2H, J=6.1 Hz, CH_2), 2.95 (broad s, 5H, phenyl).

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