Induced Decomposition of t-Butyl Peroxide in Solution

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THE thermal decomposition of t-butyl peroxide has been studied extensively.[1] Earlier work has shown that the peroxide has little tendency to undergo induced decomposition and that its rate of decomposition is solvent independent.[2] In the few instances where induced decomposition has been detected this occurs largely by hydrogen-abstraction.[1,3] In contrast, we now show that t-butyl peroxide undergoes considerable induced decomposition in substituted benzyl methyl ethers, $\mathrm{ArCH_2OMe}$, which probably involves attack by the solvent radical ArCHOMe on the O–O bond in the peroxide.

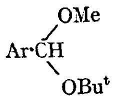
Decomposition of t-butyl peroxide in *p*-chlorobenzyl methyl ether at 110° gave α-t-butoxy-*p*-chlorobenzyl methyl ether (I) (36%), among other products (see Table) known to be derived from the solvent radical $\mathrm{Ar\dot{C}HOMe}$.[4] The structure of (I) was determined by elemental analysis, and by comparison (i.r. and v.p.c.) with an authentic sample prepared from α-chloro-*p*-chlorobenzyl methyl ether and sodium t-butoxide in dimethyl sulphoxide and isolated through preparative v.p.c. Similarly, decomposition of the peroxide in *m*-chlorobenzyl methyl ether yielded the acetal (II) (17%). The structure of (II) was determined by

Decomposition of t-butyl peroxide in benzyl ethers $\mathrm{ArCH_2OMe}$*

Ar	Ether	$\mathrm{Bu^t{}_2O_2}$	Recovered ether	$\mathrm{Bu^tOH}$	MeCOMe	ArCHO	$[\mathrm{Ar\overset{|}{C}HOMe}]_2$	$\mathrm{ArCH(OMe)OBu^t}$
p-$\mathrm{Cl{\cdot}C_6H_4}$	200	20	180	25	3·4	2·1	6·1	7·2
m-$\mathrm{Cl{\cdot}C_6H_4}$	150	15	130	17	2·5	2·0	6·3	3·4

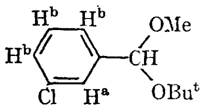
* Reactants and products are given in moles; the experiments were carried out in sealed tubes at 110° for 96 hours.

elemental analysis and by n.m.r. in deuteriochloroform (see IIa): τ 8·68 (9 H, s, $\mathrm{Bu^tO}$), 6·68 (3 H, s, MeO), 4·32 (1 H, s, PhC*H*), and signals centred at 2·72 ($3\mathrm{H^b}$) and at 2·45 ($1\ \mathrm{H^a}$).



$$\mathrm{Ar{\cdot}CH(OMe)(OBu^t)}$$

(I) Ar = p-$\mathrm{Cl{\cdot}C_6H_4}$
(II) Ar = m-$\mathrm{Cl{\cdot}C_6H_4}$



(IIa)

To show that induced decomposition of the peroxide had taken place, measurement was made of the half-life of the peroxide (a) in t-butylbenzene, in which the peroxide had been shown to undergo strictly unimolecular decomposition, and (b) in p-chlorobenzyl methyl ether (at 127°). It was found that the half-life in (b) was reduced by a factor of 2·5, indicating that induced decomposition had taken place. This fact, together with the formation of the acetals (I) and (II) constitutes strong evidence for the mechanism suggested. An alternative route to the formation of these acetals is coupling of the solvent radical $\mathrm{Ar\dot{C}HOMe}$ with a t-butoxy-radical $\mathrm{Bu^tO\cdot}$, although this could not have occurred to any large extent.

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