The Induced Decomposition of t-Butyl Peroxide in Solution. Part I. Benzyl Methyl Ethers as Solvents[1]

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Decomposition of t-butyl peroxide in the benzyl methyl ethers $\text{ArCH}_2\cdot\text{OMe}$ (Ar = Ph, $p\text{-ClC}_6\text{H}_4$, $m\text{-ClC}_6\text{H}_4$, $p\text{-NO}_2\cdot\text{C}_6\text{H}_4$, $3,4\text{-Cl}_2\text{C}_6\text{H}_3$, $p\text{-PhC}_6\text{H}_4$, $p\text{-MeO}\cdot\text{C}_6\text{H}_4$, and $p\text{-Bu}^t\text{C}_6\text{H}_4$) at 110° gave, besides small quantities (3—13%, except for $3,4\text{-Cl}_2\text{C}_6\text{H}_3$) of the aldehyde ArCHO and varying amounts of the dimer $(\text{Ar}\overset{|}{\text{C}}\text{HOMe})_2$, the acetals $\text{ArCH(OMe)(OBu}^t)$ in yields of 2·8, 36, 17, 85, 62, 0, 0, and 8·5% respectively. The acetal is considered to be formed through an S_H2 attack by the ether radical $\text{Ar}\dot{\text{C}}\text{H}\cdot\text{OMe}$ on the peroxidic O–O bond rather than coupling between the ether and t-butoxy-radicals, and evidence is presented to support this contention. From the acetal-to-dimer ratios found for the substituted ethers, namely, 0·07, 1·2, 0·5, ∞, ∞, 0, 0, and 0·2 respectively, it is concluded that the reaction is facilitated by increased electrophilicity in the ether radical.

THE thermal decomposition of t-butyl peroxide both in the gas phase and in solution has received intensive study,[2] from which it has been concluded that, in contrast to acyl peroxides, the peroxide has little tendency to undergo induced decomposition.[3] In the few instances where induced decomposition has been detected this occurs largely by hydrogen transfer.[2,4] We have now found evidence to show that, contrary to these earlier observations, t-butyl peroxide does undergo, in a variety of solvents, induced decomposition involving attack at the peroxidic O–O bond, in some cases to a considerable extent. We report the occurrence of the phenomenon in substituted benzyl methyl ethers, and present evidence

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[1] Preliminary communication, R. L. Huang, Tong-Wai Lee, and S. H. Ong, *Chem. Comm.*, 1968, 1251.

[2] W. A. Pryor, *J. Phys. Chem.*, 1963, **67**, 519, and references therein.

[3] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 469.

[4] E. R. Bell, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1950, **72**, 337; C. McMillan and M. H. J. Wijnen, *Canad. J. Chem.*, 1958, **36**, 1227; L. Batt and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 895; W. A. Pryor, A. Lee, and C. E. Witt, *J. Amer. Chem. Soc.*, 1964, **86**, 4229; E. S. Huyser and C. J. Bredeweg, *ibid.*, p. 2401; E. S. Huyser, C. J. Bredeweg, and R. M. VanScoy, *ibid.*, p. 4148.

to show that this induced decomposition is facilitated by increased electrophilicity in the attacking radical.

Decomposition of t-butyl peroxide in benzyl methyl ether is known[5] to give the dimer $(\mathrm{Ph\overset{|}{C}H{\cdot}OMe})_2$ and traces of benzaldehyde, formed through dimerisation and fragmentation, respectively, of the radical $\mathrm{Ph{\cdot}\dot{C}H{\cdot}OMe}$ derived from the ether by the action of t-butoxy-radicals [reactions (1)—(3)]. With a number of nuclear substituted benzyl methyl ethers $\mathrm{ArCH_2{\cdot}OMe}$ (Ar = m-$\mathrm{ClC_6H_4}$, p-$\mathrm{ClC_6H_4}$, 3,4-$\mathrm{Cl_2C_6H_3}$, and p-$\mathrm{NO_2{\cdot}C_6H_4}$), however, the products included, in addition to the corresponding dimer and aldehyde, varying quantities of the mixed acetal $\mathrm{ArCH(OMe)(OBu^t)}$, in certain cases in very high yields (up to 85%). The results obtained from eight such ethers are shown in Table 1, in which are also included results from a re-examination of the unsubstituted ether, which in effect gives a low yield (2·8%) of the acetal, undetected in earlier experiments.[5]

TABLE 1

Decomposition of t-butyl peroxide in benzyl ethers $\mathrm{ArCH_2{\cdot}OMe}$ *

Ar	Ether	$\mathrm{Bu^t{}_2O_2}$	Recovered ether	Recovered peroxide	$\mathrm{Bu^tOH}$	$\mathrm{Me_2CO}$	ArCHO	$(\mathrm{Ar\overset{|}{C}HOMe})_2$	$\mathrm{ArCH{<}^{OMe}_{OBu^t}}$	Acetal : dimer
Ph †	200	20	172		27·4 (69%)	3·1	2·8 (10%)	12·2	0·8 (2·8%)	0·07
p-$\mathrm{ClC_6H_4}$	200	20	180		25 (63%)	3·4	2·1 (11%)	6·1	7·2 (36%)	1·2
m-$\mathrm{ClC_6H_4}$	150	15	130		17 (57%)	2·5	2·0 (10%)	6·3	3·4 (17%)	0·5
p-$\mathrm{NO_2{\cdot}C_6H_4}$	50	5	41·8		4·2 (42%)	Trace	1·1 (13%)	Nil	4·0 (49%) ‡	V. large
3,4-$\mathrm{Cl_2C_6H_3}$	100	9·5	90		13·5 (71%)	1·6	3·5 (44%)	Trace	3·1 (39%) §	V. large
p-$\mathrm{PhC_6H_4}$	40	4	33·8	0·8	5·6 (88%)	0·3	0·3 (4·9%)	2·7	Nil	0
p-$\mathrm{MeO{\cdot}C_6H_4}$	100	10	88	2·8	13 (90%)	Trace	0·4 (3%)	5·4	Nil	0
p-$\mathrm{Bu^tC_6H_4}$	50	5·0	44·2	1·5	5·3 (76%)	Trace	0·3 (5·2%)	2·5	0·5 (8·5%)	0·2

* Reactants and products are given in mmoles; experiments carried out in sealed tubes at 110° for 96 hr. † See ref. 10. ‡ Also isolated, methyl p-nitrobenzoate (3·0 mmoles, 36%). § Also isolated, methyl 3,4-dichlorobenzoate (3·1 mmoles, 31%).

Formation of the mixed acetal could be the result of either or both of the following processes: (i) coupling of the ether and the t-butoxy-radicals [reaction (4)] and (ii) a bimolecular substitution reaction by the ether radical on the peroxidic oxygen in the peroxide [reaction (5)]. The latter would represent a hitherto unknown induced decomposition of t-butyl peroxide, and that it not only occurs, but is in all probability the more important process by which the acetal is formed, is evident from the following evidence.

$$\mathrm{PhCH_2{\cdot}OMe + Bu^tO{\cdot} \longrightarrow Ph\dot{C}H{\cdot}OMe} \qquad (1)$$

$$\mathrm{Ph\dot{C}H{\cdot}OMe \longrightarrow PhCHO + Me{\cdot}} \qquad (2)$$

$$\mathrm{2Ph\dot{C}H{\cdot}OMe \longrightarrow (Ph\overset{|}{C}H{\cdot}OMe)_2} \qquad (3)$$

$$\mathrm{Ar\dot{C}H{\cdot}OMe + Bu^tO{\cdot} \longrightarrow ArCH(OMe)(OBu^t)} \qquad (4)$$

$$\mathrm{Ar\dot{C}H{\cdot}OMe + Bu_2{}^tO_2 \longrightarrow ArCH(OMe)(OBu^t) + Bu^tO{\cdot}} \qquad (5)$$

(a) Wherever the yield of the mixed acetal becomes appreciable (>17%) the consumption of the peroxide is also extensive (⩾80%).

(b) The high yield of butanol (in all cases except where Ar = p-$\mathrm{NO_2{\cdot}C_6H_4}$) and the high butanol–acetone ratio, indicate that the hydrogen abstraction step is easy and hence it can be reasonably assumed that the concentration of the t-butoxy-radicals could not have reached a high enough level to render the coupling reaction important.

(c) The half-life of the peroxide (at 127°), as measured on the one hand in t-butylbenzene in which the peroxide has been shown to undergo strictly unimolecular decomposition,[6] and on the other in p-chlorobenzyl methyl ether, showed significant differences. In t-butylbenzene the decomposition took place unimolecularly as reported ($t_{\frac{1}{2}}$ 490 min.). In the latter solvent, however, the rate of decomposition of the peroxide was found to depend on its concentration, the half-lives being 250 and 200 min. for concentrations 0·63 and 1·23M respectively. Where this reduction of the half-life by a factor of 2—2·5 occurred, much acetal was formed, suggesting that induced decomposition had taken place. If the mixed acetal were formed largely through coupling, the half-life of the peroxide would not have been appreciably affected.

(d) By using t-butyl hyponitrite as the source of t-butoxy-radicals it was possible to carry out experiments at a temperature at which the peroxide was thermally stable (60°), but open to attack by the ether radical. The decomposition of the hyponitrite (1 mmole) in p-chlorobenzyl methyl ether (10 mmoles) in the presence of t-butyl peroxide (2 mmoles) at 60° for 280 min. (expt. 1, Table 2) resulted in a 25% consumption of the peroxide and production of 20% (based on hyponitrite) of the mixed acetal. Since the stability of the peroxide under these conditions was confirmed by a blank experiment (100% recovery of the peroxide after heating in the ether under identical conditions), part of the peroxide which was consumed in the above experiment must have been converted by the ether radical into the acetal. Furthermore, when the experiment was carried out without addition of the peroxide, very little acetal could be found (expt. 2, Table 2).

These findings leave little doubt that the $S_{\mathrm{H}}2$ attack by the ether radical on the peroxide in all probability accounts for most of the acetal formed. The coupling reaction probably occurs also to a small extent and,

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[5] R. L. Huang and S. S. Si-Hoe, 'Vistas in Free-radical Chemistry,' ed. W. A. Waters, Pergamon, London, 1959, p. 242; *Proc. Chem. Soc.*, 1957, 354.

[6] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

TABLE 2

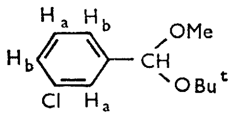
Decomposition of t-butyl hyponitrite in *p*-chlorobenzyl methyl ether *

	Expt. 1	Expt. 2
Ether	10	6·3
$Bu^tON{=}NOBu^t$	1	0·61
$Bu^t_2O_2$	2	
Recovered ether	8·0	5·4
Recovered $Bu^t_2O_2$	1·5	
Bu^tOH	2·6	1·1
Me_2CO	Trace	
ArCHO	0·3	0·09
$(Ar\overset{\vert}{C}H{\cdot}OMe)_2$	0·5	0·35
$ArCH{<}^{OMe}_{OBu^t}$	0·4	0·04

* Reactants and products are given in mmoles.

together with the dimerisation process, constitutes the chain termination mechanism.

The identity of the mixed acetals was established beyond doubt in two cases, with *p*- and *m*-chloro-substituted compounds. The structure of the product in the former case was proved by elemental analysis, and by comparison (i.r. and g.l.c.) with an authentic sample synthesised from α-chloro-*p*-chlorobenzyl methyl ether and sodium t-butoxide in dimethyl sulphoxide and isolated through preparative g.l.c. The structure of the latter acetal was established by elemental analysis and by n.m.r. ($CDCl_3$): τ 8·68 (9H, s, Me_3C), 6·87 (3H, s, OMe), 4·32 (1H, s, PhC*H*), 2·72 ($3H_b$), and 2·45 (H_a).



The effect of nuclear substituents on the formation of the acetal was next studied. Since break-down of the ether radical to aldehyde was relatively slight, and since the coupling reaction is also insignificant, the ratio of the molar yield of acetal to that of dimer could be taken as a rough guide as to the facility with which acetal formation takes place. The acetal–dimer ratio (Table 1) indicates that, whereas ether radicals $Ar\dot{C}H{\cdot}OMe$ which are more electron-releasing than the unsubstituted radical ($Ar = p\text{-}Bu^tC_6H_4$, $p\text{-}MeO{\cdot}C_6H_4$, and $p\text{-}Ph{\cdot}C_6H_4$) gave hardly any acetal, the more electrophilic ones ($Ar = m\text{-}ClC_6H_4$, $p\text{-}ClC_6H_4$, $3,4\text{-}Cl_2C_6H_3$, and $p\text{-}NO_2{\cdot}C_6H_4$) brought about very appreciable induced decomposition, the extent of which, as reflected by the acetal-to-dimer ratio, appears to increase with the electrophilicity of the substituent. In the extreme cases of *p*-nitro- and 3,4-dichloro-benzyl methyl ether no dimer was formed at all, and furthermore it seems certain that the yields of acetals in these cases were in fact much higher than those found (49 and 31% respectively), since the methyl esters produced in these cases (36 and 31% respectively) could only have arisen from the acetals through hydrogen abstraction followed by disproportionation of the radicals so formed, as described later. That induced decomposition here became the predominant reaction (85 and 62% respectively) could, however, be due partly to the disinclination of the ether radicals to dimerise as a result of the polar character of the benzylic carbon atoms induced by the *p*-nitro- and 3,4-dichloro-substituents.

To confirm the postulated precursors of the esters mentioned above, t-butyl peroxide was decomposed, under similar conditions, in the *p*-nitro-acetal itself, and found indeed to give no less than a 75% yield of the corresponding ester. The fragmentation of the radical derived from benzaldehyde dimethyl acetal to give methyl benzoate has been reported earlier,[7] but in the case of the mixed acetal $ArCH(OMe)(OBu^t)$ the radical generated could disproportionate in two possible ways [reaction (6)]: and the fact that the methyl, rather than

$$ArCH(OMe)(OBu^t) \xrightarrow{Bu^tO\cdot} Ar\dot{C}(OMe)(OBu^t) \begin{array}{l} \xrightarrow{(a)} ArCO_2Me + Bu^t\cdot \\ \xrightarrow{(b)} ArCO_2Bu^t + Me\cdot \end{array} \qquad (6)$$

the t-butyl ester, is formed [route (a)] is to be expected since by this process the more stable t-butyl radical, rather than free methyl, is generated. This inclination to release the more stable radical is reminiscent of the behaviour of radicals generated from benzyl alkyl ethers,[5] and of t-alkoxy-radicals derived from the hypochlorites,[8] and might render the mixed acetal as a system through which the stabilities of radicals could be compared.

With the unsubstituted and the *p*-phenyl-substituted ($\sigma = -0{\cdot}01 \pm 0{\cdot}5$) [9] ether radicals, the yields of mixed acetals are very low (2·8 and 0% respectively), indicating little or no induced decomposition. In the case of radicals with electron-releasing substituents (*p*-OMe and *p*-Bu^t), where it might be expected that polar factors might well slow down dimerisation, the extent of induced decomposition was nevertheless insignificant, the acetal-to-dimer ratios being 0 and 0·2 respectively. In each of these cases also, a significant portion (20—30%) of the peroxide was recovered, a finding explicable only in terms of the inability of the ether radicals to attack the peroxide. We therefore conclude that the reactivity of the ether radical in inducing decomposition of the peroxide increases with increasing electrophilicity.

In an earlier report [10] the behaviour in diphenyl ether of the ether radical $Ph\dot{C}H{\cdot}OMe$ led us to postulate its ability to complex with the solvent. In t-butyl peroxide the presence of four pairs of non-bonding electrons on the peroxide oxygen atoms, coupled with the presence of the t-butyl groups, would be expected to result in enhanced nucleophilic character, and hence the greater tendency to complex with the ether radical than in the case of diphenyl ether or, indeed, the cases of hydrogen peroxide and t-butyl hydroperoxide, which themselves

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[7] R. L. Huang and K. H. Lee, *J. Chem. Soc.*, 1964, 5957.

[8] F. D. Greene, M. L. Savits, F. D. Osterholts, H. H. Lau, W. N. Smith, and P. N. Zanet, *J. Org. Chem.*, 1963, **28**, 55.

[9] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1968, **23**, 420.

[10] R. L. Huang, Tong-Wai Lee, and S. H. Ong, *J. Chem. Soc.* (*C*), 1969.

are well known nucleophilic reagents in heterolytic reactions.[11] It might be envisaged therefore that the first step in the induction of decomposition involves complexing of the electrophilic ether radical with the nucleophilic peroxide, followed by the displacement of t-butoxy-radical by an S_H2 mechanism.

EXPERIMENTAL

M.p.s were taken with a Kofler micro-hot-stage apparatus. Unless otherwise stated, i.r. spectra were recorded for solutions in carbon tetrachloride with a Hilger and Watts Infrascan. Analytical gas chromatography was performed with an Aerograph instrument (Modulin model 1520), with a thermal conductivity detector; the relationship between the quantity of each material and the peak area it produced was established by the analysis of synthetic mixtures. Three columns were used: (*a*) 10 ft. × 1/8 in. and (*b*) 5 ft. × ¼ in. columns packed with SE-30 Silicon Gum Rubber on HMDS Chromosorb W, and (*c*) 25 ft. × ⅛ in. dinonyl phthalate column packed with 20% dinonyl phthalate on Celite 545.

Materials.—Di-t-butyl peroxide was distilled before use. Methyl 3,4-dichlorobenzoate, m.p. 46—47° (lit.,[12] 46·5—47·5°), and methyl *p*-nitrobenzoate, m.p. 95—96° (lit.,[13] m.p. 96°) were prepared from the corresponding acids. t-Butyl hyponitrile [14] was synthesised as described in the literature.

Preparation of Ethers.—The following ethers were synthesised; their physical constants were in agreement with those previously reported: benzyl methyl ether,[5] *p*-chlorobenzyl methyl ether,[7] *m*-chlorobenzyl methyl ether,[7] *p*-t-butylbenzyl methyl ether,[7] 3,4-dichlorobenzyl methyl ether,[15] *p*-nitrobenzyl methyl ether,[15] and *p*-methoxybenzyl methyl ether.[15] p-*Phenylbenzyl methyl ether* was prepared from *p*-phenylbenzyl bromide and sodium methoxide; b.p. 144—145°/1·5 mm., n_D^{23} 1·5981 (Found: C, 85·3; H, 7·45. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%).

All the ethers were purified by treatment with Brady's reagent to ensure complete removal of any aldehydes, followed by fractional distillation.

p-*Chloro-α-t-butoxybenzyl Methyl Ether.*—α,*p*-Dichlorobenzyl methyl ether, b.p. 73—74°/0·4 mm., n_D^{25} 1·5442, was prepared (75%) by the method described for α-chlorobenzyl methyl ether.[16] The chloro-ether thus obtained was then added to a stirred solution of sodium butoxide in dimethyl sulphoxide and heated at 60° for 2 days. The solution was poured into water and the organic layer was extracted with ether, dried ($CaCl_2$), and distilled to give the mixed acetal, b.p. 94°/1·5 mm., n_D^{24} 1·4993. A pure fraction was isolated by preparative g.l.c. (25 ft. × ⅜ in. SE-30 column); $\nu_{max.}$ (film) 2980s, 2825w, 1600m, 1490s, 1370s, 1340m, 1198s, 1112s, 1092vs, 1053vs, 1017vs, 930m, and 812s cm.$^{-1}$ (Found: C, 62·7; H, 7·5; Cl, 15·8. $C_{12}H_{17}ClO_2$ requires C, 63·0; H, 7·5; Cl, 15·5%).

p-*Nitro-α-t-butoxybenzyl Methyl Ether.*—α-Chloro-*p*-nitrobenzyl methyl ether was prepared like α,*p*-dichlorobenzyl methyl ether. The chloro-ether was then added to a stirred solution of sodium butoxide in *NN*-dimethylformamide and the mixture was heated at 55° for 10 hr. After removal of sodium chloride and the volatile fraction, the crude product was obtained by fractionation; b.p. 112—116°/0·15 mm. Further purification by chromatography on alumina with light petroleum (b.p. 60—80°) as eluant gave the pure *product*, n_D^{23} 1·5147, $\nu_{max.}$ (film) 2970s, 2830m, 1608s, 1523vs, 1345vs, 1195s, 1100vs, 1056vs, 1016m, 915m, 855s, 830s, 745m, and 710m cm.$^{-1}$ (Found: C, 59·8; H, 7·0. $C_{12}H_{17}NO_4$ requires C, 60·2; H, 7·15%).

Reaction of Ethers with Di-t-butyl Peroxide.—General procedure. A mixture of the ether and di-t-butyl peroxide (molar ratio 10 : 1) was sealed in a Carius tube under nitrogen and heated at 110° for 96 hr. It was then made up to a suitable volume and analysed. Acetone, t-butyl alcohol, unchanged peroxide, and ether were estimated by g.l.c.; aldehydes, dimers, and esters (if any) were estimated by i.r. spectroscopy or g.l.c. Mixed acetals (if any) were converted into the corresponding aldehydes by treatment with 2N-sulphuric acid and the resultant increase in the amounts of aldehydes was estimated by i.r. spectroscopy. Dimers used for calibration in the i.r. and g.l.c. instruments were isolated from the reaction mixtures and their authenticity was established by elemental analysis and n.m.r. spectroscopy (in some cases).

p-*Chlorobenzyl methyl ether.* The ether (31·3 g., 200 mmoles) and di-t-butyl peroxide (2·92 g., 20 mmoles) gave *p-chlorobenzaldehyde* (2·1 mmoles), $\nu_{max.}$ ($CHCl_3$) 1708 cm.$^{-1}$. After treatment with dilute sulphuric acid the amount of aldehyde had increased to 9·3 mmoles. G.l.c. analysis gave the following results: (*a*) acetone and t-butyl alcohol 3·4 and 25·0 mmoles respectively (25 ft. × ⅛ in. dinonyl phthalate column at 62°; standard carbon tetrachloride); (*b*) unchanged ether 180 mmoles (10 ft. × ⅛ in. SE-30 column at 175°; standard benzyl methyl ether); (*c*) 4,4′-dichloro-αα′-dimethoxybibenzyl 6·1 mmoles (10 ft. × ⅛ in. SE-30 column at 280°; standard benzyl benzoate).

Distillation of the reaction mixture under reduced pressure gave unchanged ether, b.p. 114°/34 mm., and then a colourless liquid, *p*-chloro-α-t-butoxybenzyl methyl ether, b.p. 72°/0·25 mm., n_D^{25} 1·4961, i.r. and g.l.c. behaviour identical with that of authentic sample (Found: C, 62·6; H, 7·3; Cl, 15·3).

The residue was chromatographed on alumina and eluted with light petroleum to give meso-*4,4′-dichloro-αα′-dimethoxybibenzyl*, m.p. 144—145° (Found: C, 61·8; H, 5·4; Cl, 22·3. $C_{16}H_{16}Cl_2O_2$ requires C, 61·7; H, 5·2; Cl, 22·8%), and racemic *4,4′-dichloro-αα′-dimethoxybibenzyl*, b.p. 98—98·5° (Found: C, 61·7; H, 5·5; Cl, 22·7%).

m-*Chlorobenzyl methyl ether.* The ether (25 g., 150 mmoles) and di-t-butyl peroxide (2·24 g., 15 mmoles) gave *m*-chlorobenzaldehyde (2 mmoles), $\nu_{max.}$ 1705 cm.$^{-1}$. On treatment with dilute sulphuric acid, the quantity of aldehyde increased to 5·4 mmoles. G.l.c. analysis (columns and standards as for *p*-chloro-system): (*a*) acetone and butanol 2·5 and 17·0 mmoles respectively; (*b*) unchanged ether (column at 185°); (*c*) 3,3′-dichloro-αα′-dimethoxybibenzyl 6·3 mmoles (column at 270°).

Distillation under reduced pressure gave the unchanged ether, b.p. 62°/2 mm. and *m*-chloro-α-t-butoxybenzyl methyl ether, b.p. 86—88°/2 mm., n_D^{24} 1·4939, $\nu_{max.}$ (film)

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[11] J. O. Edwards, 'Peroxide Reaction Mechanisms,' Interscience, New York, 1962, p. 11.

[12] I. Heilbron and H. M. Burnbury, 'Dictionary of Organic Compounds,' 4th edn., Eyre and Spottiswoode, London, 1964.

[13] A. I. Vogel, 'A Text-book of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1957, p. 788.

[14] H. Kiefler and T. G. Traylor, *Tetrahedron Letters*, 1966, 6164.

[15] D. B. Sharp and T. M. Patrick, *J. Org. Chem.*, 1961, **26**, 1389.

[16] F. Strauss and H. Heinze, *Annalen*, 1932, **493**, 203.

1475m, 1371s, 1340m, 1196vs, 1110vs, 1078s, 1055vs, 1027vs, and 790s, n.m.r. spectrum as reported earlier in the text.

Chromatography of the residue on alumina with light petroleum (b.p. 60—80°) as eluant gave meso-*3,3′-dichloro-αα′-dimethoxybibenzyl*, m.p. 87·5—88·5, τ ($CDCl_3$) 6·86 (6H, s, 2 × MeO), 5·80 (2H, s, 2 × Ar*CH*), and 2·9 (8H, m, aromatic) (Found: C, 62·2; H, 5·3; Cl, 22·65. $C_{16}H_{16}Cl_2O_2$ requires C, 61·7; H, 5·2; Cl, 22·8%) and the *racemic modification*, m.p. 73·5—74·5°, τ ($CDCl_3$) 6·72 (6H, s, 2 × MeO), 5·74 (2H, s, 2 × Ar*CH*), and 2·85 (8H, m, aromatic) (Found: C, 62·2; H, 5·35; Cl, 22·7%).

p-*t-Butylbenzyl methyl ether*. The ether (8·9 g., 50 mmoles) and di-t-butyl peroxide (0·73 g., 5 mmoles) gave *p*-t-butylbenzaldehyde (0·3 mmole), $\nu_{\text{max.}}$ 1703 cm.$^{-1}$. On treatment with dilute sulphuric acid, the amount of aldehyde increased to 0·8 mmoles. G.l.c. analysis: (*a*) acetone and t-butyl alcohol, trace amount and 5·3 mmoles respectively (column 5 ft. × $\frac{1}{4}$ in. SE-30 at 30°; standard chloroform); (*b*) unchanged peroxide 1·5 mmoles (column 5 ft. × $\frac{1}{4}$ in. SE-30 at 85°; standard n-octane); (*c*) unchanged ether 44·2 mmoles (column 5 ft. × $\frac{1}{8}$ in. SE-30 at 172°; standard ethyl benzoate); (*d*) αα′-dimethoxy-4,4′-di-t-butylbibenzyl 2·5 mmoles (column 5 ft. × $\frac{1}{4}$ in. SE-30 at 240°; standard benzyl benzoate).

Distillation under reduced pressure gave the ether, b.p. 134°/32 mm., but the mixed acetal could not be isolated. Chromatography on alumina gave first the *meso*-modification of the *dimer*, m.p. 173—174°, τ ($CDCl_3$) 8·68 (18H, s, 2 × Bu^t), 6·90 (6H, s, 2 × MeO), 5·78 (2H, s, 2 × Ar*CH*), and 2·83 (8H, m, aromatic) (Found: C, 81·2; H, 9·85. $C_{24}H_{34}O_2$ requires C, 81·3; H, 9·7%) and then the *racemic modification*, m.p. 118—119°, τ ($CDCl_3$) 8·74 (18H, s, 2 × Bu^t), 6·75 (6H, s, 2 × MeO), 5·77 (2H, s, 2 × Ar*CH*), and 2·99 (8H, m, aromatic) (Found: C, 81·3; H, 9·7%).

p-*Methoxybenzyl methyl ether*. The ether (15·2 g., 100 mmoles) and di-t-butyl peroxide (1·46 g., 10 mmoles) gave anisaldehyde (0·4 mmoles), $\nu_{\text{max.}}$ 1703 cm.$^{-1}$. Treatment with dilute sulphuric acid did not result in an increase of the amount of aldehyde. G.l.c. analysis (columns and standards as for *p*-t-butyl system): (*a*) acetone and t-butyl alcohol, trace amount and 13 mmoles respectively; (*b*) unchanged peroxide 2·8 mmoles (column at 30°); (*c*) unchanged ether 88 mmoles (column at 165°); (*d*) αα′,4,4′-tetramethoxybibenzyl (column at 220°).

The residue, after removal of volatile material and unchanged ether under reduced pressure, was chromatographed on alumina with light petroleum (b.p. 60—80°) as eluant to give first meso-*αα′,4,4′-tetramethoxybibenzyl*, m.p. 139—140° (Found: C, 71·4; H, 7·3. $C_{18}H_{22}O_4$ requires C, 71·5; H, 7·3%), then the *racemic form* of the dimer, m.p. 118—119°, τ ($CDCl_3$) 6·80 (6H, s, 2 × MeO), 6·28 (6H, s, 2 × ArO*Me*), 5·80 (2H, s, 2 × Ar*CH*), and 3·22 (8H, m, aromatic) (Found: C, 71·25; H, 7·3%).

p-*Phenylbenzyl methyl ether*. The ether (7·92 g., 40 mmoles) and di-t-butyl peroxide (0·58 g., 4 mmoles) gave *p*-phenylbenzaldehyde (0·3 mmole), $\nu_{\text{max.}}$ 1701 cm.$^{-1}$. On treatment with dilute sulphuric acid, no increase in the quantity of aldehyde was observed. G.l.c. analysis (5 ft. × $\frac{1}{4}$ in. SE-30): (*a*) acetone and t-butyl alcohol 0·3 and 5·6 mmoles, respectively (column at 30°; standard carbon tetrachloride); (*b*) unchanged peroxide 0·8 mmole (column at 85°; standard n-octane); (*c*) unchanged ether 33·8 mmoles (column at 220°; standard phenyl ether).

To estimate the total dimer formed, the reaction mixture (2 ml. of a total volume of 25 ml.) was distilled under reduced pressure until all the ether had been removed (checked by g.l.c.). The residue was made up to 5 ml. with chloroform. I.r. analysis showed αα′-dimethoxy-4,4′-diphenylbibenzyl (2·7 mmoles), $\nu_{\text{max.}}$ 1101 and 1111 cm.$^{-1}$ (calibration with an equimolar mixture of *meso* and racemic dimers).

To isolate the dimers, the residue, after removal of volatile material and unchanged ether, was chromatographed on alumina and eluted with light petroleum (b.p. 60—80°). The *meso*-modification of the *dimer* was first collected; m.p. 222—223° (from light petroleum) (Found: C, 85·2; H, 6·6. $C_{28}H_{26}O_2$ requires C, 85·3; H, 6·6%), followed by the *racemic form*, m.p. 135—136° (from light petroleum) (Found: C, 85·0; H, 6·8%).

3,4-*Dichlorobenzyl methyl ether*. The ether (19·1 g., 100 mmoles) and di-t-butyl peroxide (1·40 g., 9·5 mmoles) gave 3,4-dichlorobenzaldehyde (3·5 mmoles), $\nu_{\text{max.}}$ 1706 cm.$^{-1}$, which increased to 6·6 mmoles after treatment with dilute sulphuric acid. G.l.c. analysis: (*a*) acetone and t-butyl alcohol 1·6 and 13·5 mmoles respectively (column 25 ft. × $\frac{1}{8}$ in. dinonyl phthalate at 62°; standard carbon tetrachloride) (*b*) unchangedether 90 mmoles (column 10 ft. × $\frac{1}{8}$ in. SE-30 at 182°; standard *p*-chlorobenzyl methyl ether); (*c*) methyl 3,4-dichlorobenzoate 3·1 mmoles (column 5 ft. × $\frac{1}{4}$ in. SE-30 at 138°; standard nitrobenzene).

The reaction mixture was distilled under vacuum to remove volatile material and unchanged ether, and the residue was then chromatographed on alumina with light petroleum (b.p. 60—80°) as eluant. 3,4-Dichloro-α-t-butoxybenzyl methyl ether was isolated; $\nu_{\text{max.}}$ (liquid) 2980m, 2938s, 2830m, 1595w, 1471vs, 1400s, 1370s, 1198vs, 1105vs, 1056vs, 1033vs, and 821s cm.$^{-1}$, τ ($CDCl_3$) 8·69 (9H, s, Bu^{t}O), 6·90 (3H, s, MeO), 4·35 (1H, s, Ar*CH*), and 2·72 (3H, m, aromatic).

p-*Nitrobenzyl methyl ether*. The ether (8·35 g., 50 mmoles) and di-t-butyl peroxide (0·73 g., 5 mmoles) gave methyl *p*-nitrobenzoate (3·0 mmoles), $\nu_{\text{max.}}$ ($CHCl_3$) 1729 cm.$^{-1}$. G.l.c. analysis (5 ft × $\frac{1}{4}$ in. SE-30): (*a*) acetone and t-butyl alcohol, trace amount and 4·2 mmoles respectively (column at 30°; standard carbon tetrachloride) (*b*) unchanged ether 41·8 mmoles (column at 180°; standard *p*-chlorobenzyl methyl ether); (*c*) *p*-nitrobenzaldehyde 1·1 mmoles (180°; standard *m*-chlorobenzyl methyl ether); (*d*) *p*-nitrobenzaldehyde after treatment with dilute sulphuric acid, 5·1 mmoles.

p-*Nitro-α-t-butoxybenzyl methyl ether*. The ether (0·310 g., 1·3 mmole) and di-t-butyl peroxide (0·037 g., 0·25 mmole) were heated in a sealed tube for 88 hr. at 110°. The mixture was then diluted to 10 ml. with chloroform. Methyl *p*-nitrobenzoate was identified by comparison with an authentic sample by g.l.c. and was estimated by i.r. spectroscopy (0·15 mmole; $\nu_{\text{max.}}$ 1729 and 1286 cm.$^{-1}$). The i.r. spectrum of the mixture indicated the presence of unchanged mixed acetal (1·1 mmole) and some *p*-nitrobenzaldehyde.

Reaction of p-*Chlorobenzyl Methyl Ether with t-Butyl Peroxide and t-Butyl Hyponitrite*.—A mixture of *p*-chlorobenzyl methyl ether (10 mmoles), t-butyl peroxide (2 mmoles), and t-butyl hyponitrite (1 mmole) was sealed under nitrogen in a test-tube (150 × 15 mm.) and heated at 62 ± 1° for 280 min. The mixture was then made up to 5 ml. with carbon tetrachloride. I.r. analysis indicated the presence of *p*-chlorobenzaldehyde (0·3 mmole), $\nu_{\text{max.}}$ 1708 cm.$^{-1}$, and t-butyl alcohol (2·6 mmoles), $\nu_{\text{max.}}$ 911 cm.$^{-1}$.

After treatment with dilute sulphuric acid the amount of *p*-chlorobenzaldehyde had increased to 0·7 mmole. G.l.c. analysis: (*a*) unchanged peroxide 1·5 mmole (column 5 ft. × $\frac{1}{4}$ in. SE-30 at 30°; standard n-octane); (*b*) unchanged ether (8·0 mmoles) (10 ft. × $\frac{1}{8}$ in. SE-30 column at 175°; standard benzyl methyl ether); (c) 4,4′-dichloro-αα′-dimethoxybibenzyl 0·5 mmole (10 ft. × $\frac{1}{8}$ in. SE-30 column at 280°; standard benzyl benzoate).

In a blank experiment under identical conditions with *p*-chlorobenzyl methyl ether (10 mmoles) and t-butyl peroxide (2 mmoles) but without t-butyl hyponitrite, g.l.c. analysis indicated 100% recovery of the peroxide.

Decomposition of t-Butyl Hyponitrite in p-*Chlorobenzyl Methyl Ether.*—*p*-Chlorobenzyl methyl ether (0·97 g., 6·3 mmoles) and t-butyl hyponitrite (0·107 g., 0·61 mmole) were heated under nitrogen in a Carius tube at 62° for 280 min. The mixture was then made up to 5 ml. with carbon tetrachloride. I.r. analysis indicated the presence of t-butyl alcohol (1·1 mmole), $\nu_{max.}$ 911 cm.$^{-1}$, and *p*-chlorobenzaldehyde (0·09 mmole), $\nu_{max.}$ 1708 cm.$^{-1}$. After treatment with dilute sulphuric acid, the amount of *p*-chlorobenzaldehyde had increased to 0·13 mmole. G.l.c. analysis indicated the presence of unchanged ether (5·4 mmoles; column 10 ft. × $\frac{1}{8}$ in. SE-30 at 175°; standard ethyl benzoate) and 4,4′-dichloro-αα′-dimethoxybibenzyl (0·35 mmole; column 10 ft. × $\frac{1}{8}$ in. SE-30 at 280°; standard benzyl benzoate).

Determination of the Half-life of Di-t-butyl Peroxide in Various Solvents.—(a) *In t-butylbenzene.* Di-t-butyl peroxide (2·52 g., 17·3 mmoles) was made up to 25 ml. with t-butylbenzene. From this stock solution (0·69M) portions (2 ml.) were pipetted into test-tubes (16 × 150 mm.) which were then sealed under nitrogen. The tubes were then immersed in a bath at 127 ± 0·5° and taken out at different times for estimation of the peroxide content by g.l.c. (column of dinonyl phthalate at 80°; standard carbon tetrachloride). Time zero was taken as the time when the first was taken out.

Time (min.	0	70	172	234	294	364	546	601
Concn. (M)	0·56	0·54	0·48	0·42	0·42	0·36	0·26	0·23

A plot of log conc. against time gives a straight line; the half-life of the peroxide was 496 min.

(b) *In* p-*chlorobenzyl methyl ether.* The half-lives of the peroxide (initial concentrations 0·69 and 1·23M) in *p*-chlorobenzyl methyl ether, similarly determined by plotting log concn. against time, were 250 and 200 min. respectively.

Concn. 0·69M

Time (min.)	0	45	90	120	165	220	230	310	370
Concn. (M)	0·63	0·52	0·50	0·44	0·38	0·32	0·32	0·29	0·22

Concn. 1·23M

Time (min.)	0	30	90	120	135	150	180	240	300
Concn. (M)	1·23	1·07	0·75	0·64	0·71	0·71	0·61	0·60	0·46

The half-life of the peroxide in t-butylbenzene is thus 2—2·5 times greater than that in *p*-chlorobenzyl methyl ether.

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