239. *The Oxidation of Ethers and Related Compounds. Part II.*[1] *Reactions of t-Butyl Methyl Ether with t-Butyl Peroxide and Benzoyl Peroxide.*

By H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling.

Decomposition of t-butyl peroxide in t-butyl methyl ether at 140° yielded a mixture of compounds in which neopentyl alcohol was identified. This product is considered to arise from t-butoxymethyl radicals by way of migration of t-butyl groups from oxygen to carbon. The photochemical reaction at 40° gave 1,2-di-t-butoxyethane dimer and trimer, t-butoxymethyl radicals being more stable at the lower temperature.

Decomposition of benzoyl peroxide in t-butyl methyl ether yielded benzoic acid and t-butoxymethyl benzoate.

In Part I,[1] the reactions of anisole with t-butoxy-radicals, produced both thermally and photochemically from t-butyl peroxide, were discussed. The reactions were complicated by the occurrence of nuclear substitution in anisole by phenoxymethyl and methyl radicals derived, respectively, from the solvent and subsequent decomposition of t-butoxy-radicals. In the present Paper, reactions of the aliphatic ether, $Me_3C{\cdot}OMe$, with radicals derived from decomposition of t-butyl and benzoyl peroxide are reported.

t-Butyl Peroxide Reactions.—Thermal dissociation of t-butyl peroxide with formation of t-butoxy-radicals is well known,[2] and photolysis[3] gives the same radicals although an alternative mode of scission, giving butyl radicals and oxygen, has been reported.[4] t-Butoxy-radicals are capable of abstracting hydrogen atoms from a wide range of compounds, and, when an oxygen function is present, the carbon–hydrogen bond adjacent to the oxygen atom is preferentially attacked. Peroxide-initiated addition of alcohols to olefins yields[5] products resulting from α-hydrogen abstraction, and the products obtained from the thermal reactions of t-butyl peroxide with esters,[6] tetrahydropyrans,[7] acetals,[8] and benzyl ethers[9] have been accounted for in similar terms. An explanation for this behaviour has been presented in Part I and will be developed further in Part III.

We have investigated the decomposition of t-butyl peroxide (1 mol.) in t-butyl methyl ether (10 mol.), induced thermally at 140° and photochemically at 40°. The thermal reaction, which was allowed to go to completion, gave a complex mixture which contained t-butyl alcohol (93%) and acetone (2%) (yields based on peroxide) and neopentyl alcohol (18%, based on peroxide and the equation below).

The photochemical reaction at 40°, carried out by irradiation with a mercury-arc lamp (principal wavelength 2570 Å), was allowed to go to completion. The main product (45%, based on peroxide) was 1,2-di-t-butoxyethane (I), which was absent in the mixture from the thermal reaction. A higher-boiling compound had properties consistent with those expected of 1,2,3-tri-t-butoxypropane (II). Only a trace of neopentyl alcohol was detected.

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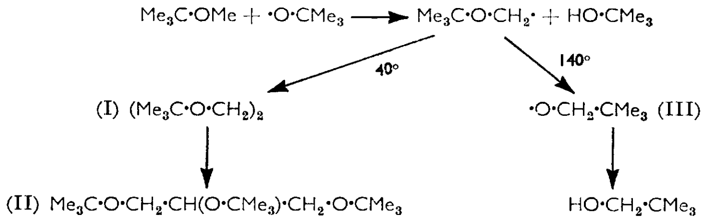
[1] Part I, Henbest, Reid, and Stirling, *J.*, 1961, 5239.
[2] Gray and Williams, *Chem. Rev.*, 1959, **59**, 239.
[3] McMillen, *J. Amer. Chem. Soc.*, 1960, **82**, 2422.
[4] Frey, *Proc. Chem. Soc.*, 1959, 385.
[5] Urry, Stacey, Huyser, and Juveland, *J. Amer. Chem. Soc.*, 1954, **76**, 450.
[6] Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258.
[7] Huyser, *J. Org. Chem.*, 1960, **25**, 1820; Wallace and Gritter, *ibid.*, 1961, **26**, 5256.
[8] Kuhn and Wellman, *J. Org. Chem.*, 1957, **22**, 774.
[9] Huang, " Vistas in Free-radical Chemistry," ed. Waters, Pergamon, Oxford, 1959, p. 242.

These facts are accommodated by the following scheme:



The formation of neopentyl alcohol at the higher temperature may be accounted for by rearrangement of t-butoxymethyl radicals to oxy-radicals (III) followed by hydrogen abstraction by this species. Isomerisations of radicals in which the migrating groups are aryl or halogen are well authenticated,[10] but rearrangement involving movement of an alkyl group appears as yet to be restricted to the 2-bornyl system.[11]

If the isomerisation $Me_3C{\cdot}O{\cdot}CH_2{\cdot} \longrightarrow {\cdot}O{\cdot}CH_2{\cdot}CMe_3$ is occurring in the formation of neopentyl alcohol from t-butyl methyl ether, it appears to be the first reported example of a radical migration involving movement of a group from oxygen to carbon. In the isomerisation, a C–C bond becomes replaced by a C–O bond; differences in bond strengths alone would suggest that such a change might be endothermic.[2] Of more relevance perhaps is the observation that alcohols, not ethers, are produced in reactions in which alkyl radicals add to carbonyl bonds ($R{\cdot} + {>}C{=}O$ gives $R\overset{|}{\underset{|}{C}}{-}O{\cdot}$ not ${>}C{\cdot}{-}OR$).[12]

Alternative reaction pathways are, of course, available to the t-butoxymethyl radical; the low yield of neopentyl alcohol shows that these compete effectively with isomerisation. One alternative is the fragmentation of the radical into formaldehyde and a t-butyl radical. Di-t-butyl ether, a product that could be derived by combination of t-butyl and t-butoxy radicals, was not detected in the products of the thermal reaction.

In the photochemical reaction at 40°, rearrangement of the t-butoxymethyl radical is less favoured, and dimerisation [to (I)] consequently becomes the predominant reaction. Formation of trimer (II) results from hydrogen abstraction from the dimer, and coupling of the resultant radical with a t-butoxymethyl radical. In support of this suggestion, photochemical decomposition of t-butyl peroxide in t-butyl methyl ether in the presence of added dimer increased the yield of trimer by 50%.

The different reaction courses in the thermal and photochemical reactions with t-butyl methyl ether followed closely parallel those found in the corresponding reactions with anisole.[1] In the latter reactions, dimer was detected only in reactions at low temperatures while alternative reactions of the phenoxymethyl radical, in particular nuclear substitution, predominated in the thermal reaction.

Benzoyl Peroxide Reactions.—Kinetics of the decomposition of benzoyl peroxide in ethers have been studied by Bartlett and Nozaki[13] and by Cass[14] who found that the rates of decomposition were very much greater than in " inert " solvents such as benzene. This increase in rate was ascribed to an induced decomposition caused by attack on the peroxide by radicals derived from the solvent, and the isolation[14] of α-benzoyloxy-ethers in *ca.* 90% yields confirmed this conclusion.

Kinetics of the t-butyl methyl ether–benzoyl peroxide reaction have been studied previously[13] but the reaction products were not examined. We found, using an ether : peroxide ratio of 10 : 1 at 55°, that this reaction gave benzoic acid (50%) and

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[10] Freidlina, Kost, and Khorlina, *Uspekhi Khim.*, 1962, **31**, 3 (*Russ. Chem. Rev.*, 1962, **31**, 1).

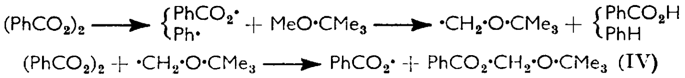
[11] Berson, Olsen, and Walia, *J. Amer. Chem. Soc.*, 1962, **84**, 3337.

[12] Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 4253; Fuller and Rust, *ibid.*, 1958, **80**, 6148.

[13] Bartlett and Nozaki, *J. Amer. Chem. Soc.*, 1947, **69**, 2299.

[14] Cass, *J. Amer. Chem. Soc.*, 1947, **69**, 500.

t-butoxymethyl benzoate (IV) (23%), together with small amounts of benzene, t-butanol, and, unexpectedly, di-t-butoxymethane. The main products can be accounted for by the following sequence, analogous to that proposed by Cass[14] for other ether–peroxide reactions:



$$(PhCO_2)_2 \longrightarrow \left\{\begin{matrix}PhCO_2\cdot\\ Ph\cdot\end{matrix}\right. + MeO\cdot CMe_3 \longrightarrow \cdot CH_2\cdot O\cdot CMe_3 + \left\{\begin{matrix}PhCO_2H\\ PhH\end{matrix}\right.$$

$$(PhCO_2)_2 + \cdot CH_2\cdot O\cdot CMe_3 \longrightarrow PhCO_2\cdot + PhCO_2\cdot CH_2\cdot O\cdot CMe_3 \text{ (IV)}$$

EXPERIMENTAL

t-Butyl methyl ether (dried over sodium) was homogeneous [gas chromatography (silicone at 18°)].

Thermal Decomposition of t-Butyl Peroxide in t-Butyl Methyl Ether.—The peroxide (4 g., 1 mol.) and the ether (24·1 g., 10 mol.) were heated in a sealed tube under nitrogen at 140° for 60 hr. The product contained t-butyl alcohol (93%; gas chromatography on trixylyl phosphate at 18°). Slow distillation of the total reaction mixture gave a fraction, b. p. 40—60°, from which acetone 2,4-dinitrophenylhydrazone (0·13 g., 2%), m. p. and mixed m. p. 125° was obtained. The fraction (1·14 g.), b. p. 100—144°, showed hydroxyl and carbonyl absorption in the infrared region and gave seven gas-chromatographic peaks (silicone at 50°), one of which corresponded to 2,2-dimethylpropan-1-ol. Treatment of this fraction with phenyl isocyanate (1·3 ml.) gave the phenylurethane (0·99 g.) of 2,2-dimethylpropan-1-ol, m. p. and mixed m. p. 114°. Oxidation (CrO_3) of another sample of this fraction followed by steam distillation gave trimethylacetaldehyde, isolated as its 2,4-dinitrophenylhydrazone, m. p. 210° (from ethanol). The weight of reaction product, b. p. >140°, was 1·61 g.; no gas-chromatographic peak corresponding to 1,2-di-t-butoxyethane was detected.

A separate experiment showed that t-butyl methyl ether was stable at 140° in the absence of peroxide.

Photochemical Decomposition of t-Butyl Peroxide in t-Butyl Methyl Ether.—The peroxide (48·1 g., 10 mol.) and the ether (8 g., 1 mol.) were irradiated in a quartz flask for 95 hr., as in the anisole experiment.[1] Gas chromatography of a sample of the product revealed the presence of t-butyl alcohol and the absence of acetone and t-butyl peroxide. t-Butyl alcohol and unreacted ether were distilled off; the following fractions were then collected (leaving a residue of 0·42 g.): (1) 0·32 g., b. p. 100—140°, n_D^{18} 1·4073; (2) 4·42 g., b. p. 160—168°, n_D^{19} 1·4110; (3) 1·595 g., D. p. 100—105°/10 mm., n_D^{19} 1·4222. Fraction (1) gave six gas-chromatographic peaks, one of which had the same retention time as neopentyl alcohol. Oxidation (CrO_3) and distillation gave material from which trimethylacetaldehyde 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 210°, was isolated. Fraction (2) consisted mainly of 1,2-di-t-butoxyethane (gas chromatography showed traces of three other compounds). Redistillation gave the diether (I), b. p. 168—169°, n_D^{18} 1·4098 (Found: C, 68·6; H, 12·5. Calc. for $C_{10}H_{22}O_2$: C, 68·9; H, 12·7%), whose infrared spectrum was identical with that of an authentic sample made from isobutene and ethanediol by the general method of Beyerman and Bontekoe[15] (lit. values:[16] b. p. 171°; n_D^{19} 1·4111). The yield of diether was 45%, estimated by gas chromatographic (silicone at 91°) on a sample of the original reaction mixture, thioanisole being used as internal standard. Fraction (3), found to be mainly one compound by gas chromatography (trixylyl phosphate at 120°), was redistilled to give 1,2,3-tri-t-butoxypropane (II), b. p. 111—113°/10 mm., n_D^{18} 1·4230 (Found: C, 68·9; H, 12·3. $C_{15}H_{32}O_3$ requires C, 69·2; H, 12·4%). Its infrared spectrum was generally similar to that given by the dibutoxyethane, and its n.m.r. spectrum was consistent with the structure assigned.

The triether was obtained in higher yield (1·17 g., 33%) from the product of irradiation of a mixture of t-butyl methyl ether (24·1 g., 10 mol.), t-butyl peroxide (4 g.), and 1,2-di-t-butoxyethane (2·65 g.) for 95 hr.

Benzoyl Peroxide and t-Butyl Methyl Ether.—A mixture of the peroxide (12·1 g., 1 mol.) and the ether (44 g., 10 mol.) was kept at 55° for seven days; a test for the peroxide was then negative. As one of the products (t-butoxymethyl benzoate) is easily hydrolysed, the free benzoic acid was removed by stirring the reaction mixture with calcium hydroxide (5 g.) and magnesium sulphate (5 g.) for 36 hr. Filtration left a solid which was treated with aqueous

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[15] Beyerman and Bontekoe, *Rec. Trav. chim.*, 1962, **81**, 691.

[16] Evans and Edlund, *Ind. Eng. Chem.*, 1936, **28**, 1186.

hydrochloric acid; extraction with dichloromethane gave benzoic acid (3·1 g., 50%). The filtrate from the calcium and magnesium salts contained unchanged ether and traces of benzene and t-butyl alcohol (gas chromatography on silicone at 18°). Apart from lower-boiling material, distillation gave di-t-butoxymethane (0·32 g., 4%), b. p. 42°/11 mm., n_D^{21} 1·4004 (Found: C, 67·6; H, 12·6. Calc. for $C_9H_{20}O_2$: C, 67·45; H, 12·6%) (9 : 1 ratio of primary : secondary hydrogens in the n.m.r. spectrum) (lit. values:[17] b. p. 50—52°/18 mm.; n_D^{20} 1·3990), and *t-butoxymethyl benzoate* (IV) (2·52 g., 23%), b. p. 96—97°/1 mm., n_D^{19} 1·4980 (Found: C, 68·9; H, 7·55. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). The infrared spectrum of this compound showed strong bands in the 1000—1200 cm.$^{-1}$ region, typical of a C–O–C–O–C structure. A sample was hydrolysed (methanol : N-hydrochloric acid, 1 : 9) for 12 hr. at 20°, to give benzoic acid and formaldehyde, the latter being isolated as its dimethone derivative, m. p. and mixed m. p. 194°.

The authors thank Monsanto Chemicals Ltd. for financial assistance (to J. A. W. R.) and Dr. R. J. Abraham for nuclear magnetic resonance spectra.

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[*Received, July 9th*, 1963.]

[17] Leimu, *Suomen Kem.*, 1946, **19**, 66.