

240. *The Oxidation of Ethers and Related Compounds. Part III.¹
Reactions of Sulphides with *t*-Butyl Peroxide and Benzoyl Peroxide.*

By H. B. HENBEST, J. A. W. REID, and C. J. M. STIRLING.

Thioanisole and *t*-butyl peroxide at 140° give 1,2-di(phenylthio)ethane and nuclear methylated products. By contrast, photochemical reactions at 40° yield diphenyl disulphide. At 140°, radicals from *t*-butyl peroxide remove hydrogen from the nuclear group of methyl *p*-tolyl sulphide.

t-Butyl methyl sulphide and *t*-butyl peroxide at 140° yield 1,2-di-(*t*-butylthio)ethane and di-*t*-butyl disulphide; in photochemical reactions at 40°, the yield of the former product is greater and the disulphide is not formed. When benzoyl peroxide is used, *t*-butyl methyl sulphoxide and *t*-butylthiomethyl benzoate are obtained.

IN Parts I² and II¹ we reported on the reactions of radicals derived from *t*-butyl peroxide with aryl methyl and *t*-butyl methyl ethers. The first step of these reactions was considered to involve removal of a hydrogen atom from the carbon atom adjacent to oxygen, and the products could be accounted for in terms of the subsequent reactions of the aryl-oxymethyl or *t*-butoxymethyl radicals thereby produced. Striking differences in the behaviour of these radicals were observed according to whether they were produced in thermal reactions at 140° or in photo-initiated reactions at 40°.

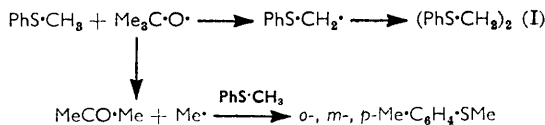
The present Paper describes the reactions of aryl and *t*-butyl methyl sulphides with *t*-butyl peroxide. The courses of the thermal and photochemical reactions are again markedly different and are not analogous to those with the ethers. The reaction between *t*-butyl methyl sulphide and benzoyl peroxide has also been briefly studied.

Aryl Methyl Sulphides.—Thermal reactions were carried out at 140° with *t*-butyl peroxide and the sulphide (10 mol.), and were allowed to go to completion. The products from thioanisole were acetone (40%), *t*-butyl alcohol (7%), 1,2-di(phenylthio)ethane (I) (12%), and isomeric methylthiotoluenes. (Yields in this and subsequent reactions are based on peroxide; cf. Part I².) Water (14%) giving an acid reaction was also obtained; the low yield of *t*-butyl alcohol can therefore be attributed to loss by dehydration. The absence of thiophenol and ethyl phenyl sulphide was established by gas chromatography. Dimer is formed by combination of phenylthiomethyl radicals, and methylthiotoluenes

¹ Part II, Henbest, Reid, and Stirling, preceding paper.

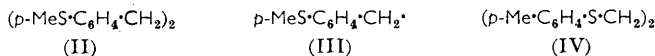
² Henbest, Reid, and Stirling, *J.*, 1961, 5239.

arise from nuclear substitution by methyl radicals derived from fragmentation of *t*-butoxy-radicals.



No dimer is formed in anisole-peroxide reactions at 140°; the phenoxymethyl radical, instead of combining, attacks the nucleus of anisole, yielding phenoxymethylanisoles. These results indicate the lower reactivity of phenylthiomethyl radicals towards aromatic nuclei. Copolymerisation data³ also suggest that α -thioalkyl radicals are less reactive (more stabilised) than their oxygen analogues. Vinyl sulphides are more reactive than vinyl ethers towards radicals from polymerising styrene and methyl acrylate.

The reaction with methyl *p*-tolyl sulphide at 140° gave *t*-butyl alcohol (10%) and acetone (7.5%), together with 4,4'-di(methylthio)bibenzyl (II) (12%). This product clearly arises from combination of 4-methylthiobenzyl radicals (III), and shows that hydrogen is preferentially removed from the nuclear methyl group. Formation of the



dimer (IV) arising from *S*-Me hydrogen abstraction was not detected. In this respect, methyl *p*-tolyl sulphide behaves like *p*-methylanisole⁴ and differs from *NN*-dimethyl-*p*-toluidine⁵ in that abstraction of hydrogen from the nuclear methyl group occurs in both the ether and the sulphide. These observations suggest that reactivities towards hydrogen abstraction are in the sequence: Ar-NMe₂ > Ar-Me > Ar-SMe \approx Ar-OMe.

Photochemical reactions with thioanisole at 40° were very slow, 78% of the peroxide being recovered after 80 hr. No acetone was detected and diphenyl disulphide (22%) was the only product identified. Irradiation of thioanisole alone caused slight decomposition but diphenyl disulphide was not a product. Further, no disulphide was obtained by irradiation of a mixture of thioanisole and 1,2-di(phenylthio)ethane (a possible product). It is probable that abstraction of hydrogen from the methyl group is the first stage as in the thermal reaction. The phenylthiomethyl radical, however, may be produced in an excited state; disruption into thiophenoxy-radicals and subsequent dimerisation can follow. Demethylation of this type has been observed in other reactions; *t*-butyl peroxide with *N*-methyl diphenylamine⁶ and with *NN*-dimethylbenzamide (see Experimental section) yields diphenylamine and *N*-methylbenzamide, respectively.

t-Butyl Methyl Sulphide.—*t*-Butyl methyl sulphide with *t*-butyl peroxide at 140° gave acetone (19%), *t*-butyl alcohol (21%), and a complex mixture containing the dimer [1,2-di(*t*-butylthio)ethane] (8%) and di-*t*-butyl disulphide (trace). The low yield of *t*-butyl alcohol was probably again due to dehydration. The photochemical reaction, on the other hand, gave a higher yield of dimer (34%) and no di-*t*-butyl sulphide. Neither disulphide nor dimer was obtained by irradiation of the sulphide in the absence of peroxide. These results suggest that the *t*-butylthiomethyl radical is unstable at 140° and is fragmented, in contrast with the phenylthiomethyl radical which is more stable at this temperature.

Reactions with benzoyl peroxide were carried out in order to compare the behaviour of the sulphide with that of *t*-butyl methyl ether.¹ Sulphide-benzoyl peroxide reactions

³ Price and Zomlefer, *J. Amer. Chem. Soc.*, 1950, **72**, 14; Lewis, Walling, Cummings, Briggs, and Wenisch, *ibid.*, 1948, **70**, 1527; Mayo, Lewis, and Walling, *ibid.*, p. 1529.

⁴ Johnston and Williams, *J.*, 1960, 1168.

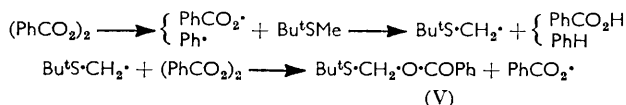
⁵ Henbest and Patton, *Proc. Chem. Soc.*, 1959, 225.

⁶ Henbest and Patton, *J.*, 1960, 3557.

were studied by Horner and Jürgens⁷ who found that the principal products from the sulphide were the sulphoxide and the α -benzoyloxy-sulphide:



t-Butyl methyl sulphide and benzoyl peroxide at 18° gave benzoic acid (48%) and benzoic anhydride, together with t-butyl methyl sulphoxide (7%) and t-butylthiomethyl benzoate (V) (21%). Comparable yields of benzoic acid (50%) and t-butoxymethyl benzoate (23%) were obtained from the t-butyl methyl ether-benzoyl peroxide reaction.¹ Sulphoxide formation is believed to involve nucleophilic attack at peroxidic oxygen⁸ whilst the α -benzoyloxy-sulphide results from the reaction of t-butylthiomethyl radicals with unchanged peroxide (cf. Part II¹).



EXPERIMENTAL

t-Butyl peroxide, thioanisole, methyl *o*-tolyl sulphide,⁹ methyl *p*-tolyl sulphide,¹⁰ and t-butyl methyl sulphide¹¹ were homogeneous by gas chromatography. 1,2-Di(phenylthio)ethane had m. p. 68.5–69° (lit.,¹² 69°).

4-Methylthiobenzyl Phenyl Sulphide.—4-Methylthiobenzyl alcohol¹³ was converted into 4-methylthiobenzyl chloride (77%), b. p. 94–95°/0.4 mm., n_D^{19} 1.6074 (lit.,¹³ b. p. 83°/0.3 mm., n_D^{27} 1.6034) by Newman's¹⁴ method. The chloride (1.8 g.) was refluxed with thiophenol (1.14 g.) in ethanolic sodium ethoxide (1 mol.) for 1 hr. Acidification of the mixture and extraction with chloroform gave the sulphide (2.44 g.), m. p. 93–94° [from benzene-light petroleum (b. p. 40–60°)] (Found: C, 68.2; H, 5.9. $\text{C}_{14}\text{H}_{14}\text{S}_2$ requires C, 68.3; H, 5.7%).

Thermal Reactions of Aryl Methyl Sulphides with t-Butyl Peroxide.—(a) *Thioanisole.* The sulphide (20 g.) and t-butyl peroxide (2.35 g., 0.1 mol.) were kept in a sealed tube under nitrogen for 60 hr. The product contained t-butyl alcohol (7%) and acetone (40%) (gas chromatography on trixylyl phosphate at 18°). An immiscible portion (80 mg.) of the reaction mixture, after being washed with pentane, had m. p. –2° and was acidic. It was neutralised (dry Na_2CO_3) and distilled, to give water, m. p. and mixed m. p. 0°, n_D^{18} 1.3340. The organic product was fractionally distilled. Fraction (i), b. p. 79–90°/10 mm., was chiefly unchanged thioanisole, but gas chromatography (silicone oil; 125°; N_2) showed the presence of two components with retention times identical with those of *o*- and *p*-methylthiotoluenes. Fraction (ii) (0.237 g.), b. p. 66–74°/0.1 mm., was not identified, but addition of light petroleum (b. p. 40–60°) to the final fraction (0.487 g.), b. p. 126–130°/0.1 mm., gave 1,2-di(phenylthio)ethane (12% crude yield), m. p. and mixed m. p. 67–68°. Infrared spectra of the mother-liquors failed to reveal any isomeric methylthiobenzyl phenyl sulphides.

(b) *Methyl p-tolyl sulphide.* The sulphide (27.6 g.) and t-butyl peroxide (2.92 g., 0.1 mole) were kept at 140° as before. t-Butyl alcohol (10%) and acetone (7.5%) were determined by gas chromatography. Excess of methyl *p*-tolyl sulphide was distilled off, and chromatography of the residue (6.8 g.) on alumina in benzene gave 4,4'-di(methylthio)bibenzyl (0.65 g., 12%), m. p. 141–142° (from ethanol) (Found: C, 70.1; H, 6.7. $\text{C}_{16}\text{H}_{18}\text{S}_2$ requires C, 70.1; H, 6.6%). Oxidation of the bis-sulphide with hydrogen peroxide in acetic acid gave the bis-sulphone, m. p. 269–270° (from ethanol) (Found: C, 56.2; H, 5.5. $\text{C}_{16}\text{H}_{18}\text{O}_4\text{S}_2$ requires C, 56.1; H, 5.3%). Subsequent fractions yielded amorphous solids, and 1,2-di(*p*-tolylthio)ethane was not detected by infrared spectroscopic examination of them.

⁷ Horner and Jürgens, *Annalen*, 1957, **602**, 135.

⁸ Cf. Davies, "Organic Peroxides," Butterworths, London, 1961.

⁹ Truce and Vriesen, *J. Amer. Chem. Soc.*, 1953, **75**, 5032.

¹⁰ Gilman and Beaber, *J. Amer. Chem. Soc.*, 1925, **47**, 1449.

¹¹ Vogel and Cowan, *J.*, 1943, 16.

¹² Bell and Bennett, *J.*, 1928, 3189.

¹³ Goldberg and Japolsky, U.S.P. 2,624,738.

¹⁴ Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 2295.

Photochemical Decomposition of t-Butyl Peroxide in Thioanisole.—The sulphide (60 g.) and t-butyl peroxide (7.05 g., 0.1 mole) were irradiated in a quartz flask for 80 hr. at 40–45° with a Hanovia mercury-arc lamp type 590/10 (principal wavelength 2570 Å). Gas chromatography of the mixture showed the absence of acetone and the presence of t-butyl alcohol and unreacted peroxide (78%). Removal of the excess of thioanisole, and chromatography of the residue on alumina in light petroleum (b. p. 40–60°), gave diphenyl disulphide (0.52 g., 22.5%), m. p. 59–60° (from ethanol) (mixed m. p. and identical infrared spectra).

1,2-Di-(t-butylthio)ethane.—The *bis-sulphide* was obtained by treatment of 2-methylpropane-2-thiol (2 mol.) in ethanolic sodium ethoxide (2 mol.) with ethylene dibromide (1 mol.). It had b. p. 114–116°/12 mm., n_D^{18} 1.4910, m. p. 16° (Found: C, 57.9; H, 10.7. $C_{10}H_{22}S_2$ requires C, 58.2; H, 10.7%). Oxidation with hydrogen peroxide in acetic acid gave the bis-sulphone, m. p. 241° (from chloroform–ethanol) (Found: C, 44.4; H, 8.0. Calc. for $C_{10}H_{22}O_4S_2$: C, 44.4; H, 8.1%). Backer, Strating, and Hazenberg¹⁵ give m. p. 230–231°.

t-Oxidation of t-Butyl Methyl Sulphide.—Oxidation of t-butyl methyl sulphide with hydrogen peroxide (1 mol.) in acetic acid at 20° gave the *sulphoxide* (61%), b. p. 82°/18 mm., n_D^{19} 1.4750 (Found: C, 50.1; H, 10.2. $C_5H_{12}OS$ requires C, 50.0; H, 10.1%) (infrared S=O stretching, 1050 cm^{-1}).

Reaction between NN-Dimethylbenzamide and t-Butyl Peroxide (performed by S. A. KHAN).—The amide (29.8 g.) and the peroxide (2.92 g.) were heated in a sealed tube at 140° for 60 hr. Much of the unchanged amide was removed by distillation. The residue (3.27 g.) gave a fraction (1.64 g.), b. p. 110–111°/0.1 mm., leaving non-volatile material (1.61 g.). The fraction (1.64 g.) was separated by chromatography into *NN*-dimethylbenzamide (0.37 g.), m. p. and mixed m. p. 41–42°, and *N*-methylbenzamide (1.17 g.), m. p. and mixed m. p. 75–76°.

Reactions of t-Butyl Methyl Sulphide.—(a) *With t-butyl peroxide at 140°.* Reactions were carried out as before with the sulphide and the peroxide (0.1 mol.). t-Butyl alcohol (21%) and acetone (19%) in the product were determined by gas chromatography. The mixture was carefully distilled, and gas chromatography of the fractions of b. p. 107°/760 mm. to 70°/10 mm. showed the presence of eight components. The presence of di-t-butyl disulphide and the absence of di-t-butyl sulphide were established by comparison of retention times with those of authentic specimens. Oxidation of the fractions of b. p. 140–142°/760 mm. and 60–70°/10 mm. with hydrogen peroxide in acetic acid gave a sulphone (infrared) (31 mg.), m. p. 167–168° (from ethanol) (Found: C, 33.2; H, 6.5. $C_6H_{14}O_4S_2$ requires C, 33.6; H, 6.5%). The fraction of b. p. 90–110°/10 mm. was shown by gas chromatography to consist chiefly of 1,2-di-(t-butylthio)ethane, and oxidation gave the bis-sulphone, m. p. and mixed m. p. 240–241°.

(b) *With t-butyl peroxide at 40°.* The sulphide and peroxide (0.1 mol.) were irradiated for 90 hr. Unchanged peroxide (87%) was still present and was removed by distillation together with t-butyl alcohol and the excess of sulphide. Distillation of the residue gave a fraction b. p. 66–106°/17 mm., in which gas chromatography showed 1,2-di-(t-butylthio)ethane (34%) to be the main component.

(c) *With benzoyl peroxide.* The sulphide and peroxide (0.1 mol.) were kept at 18° for 1 week. The peroxide had completely decomposed and benzoic acid (48%) was isolated from the mixture as described in Part II.¹ Distillation of the remainder under nitrogen gave, first, t-butyl methyl sulphoxide (7%), b. p. 64–66°/10 mm., n_D^{18} 1.4777 (infrared spectrum identical with that of an authentic specimen), and then *t-butylthiomethyl benzoate* (21%), b. p. 152–155°/10 mm., n_D^{21} 1.5318 (Found: C, 64.6; H, 7.2. $C_{12}H_{16}O_2S$ requires C, 64.3; H, 7.1%). Alkaline hydrolysis of the ester gave 2-methylpropane-2-thiol (*S*-2,4-dinitrophenyl derivative,¹⁶ m. p. and mixed m. p. 109–110°), and benzoic acid, m. p. and mixed m. p. 121–122°.

Treatment of a cold benzene solution of the distillation residue with aniline converted benzoic anhydride into benzanilide, m. p. and mixed m. p. 166°.

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THE QUEEN'S UNIVERSITY OF BELFAST.

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¹⁵ Backer, Strating, and Hazenberg, *Rec. Trav. chim.*, 1953, **72**, 833.

¹⁶ Cairns, Larchar, and McKusick, *J. Org. Chem.*, 1953, **18**, 748.