# **238.** *Homolytic Reactions of Aromatic Side Chains. Part I. Reactions of t-Butyl Peroxide with Aromatic Compounds.*

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The reactions of t-butyl peroxide with aromatic compounds containing alkyl side chains give good yields of the corresponding dehydrogeno-dimers. Toluene, ethylbenzene, isopropylbenzene, *p*-cymene, diphenylmethane, 4-methylbiphenyl, *o*-, *m*-, and *p*-chloro-, *p*-bromo-, and *p*-iodo-toluene, β- and γ-picoline, and *p*-methylanisole react in this way. Smaller amounts of higher-boiling products, consisting mainly of dehydrogeno-trimers, are also formed with some substrates. No dimeric product is, however, formed in the reaction of t-butyl peroxide with anisole.

THE thermal decomposition of t-butyl peroxide in aromatic solvents (RH) has been shown [1-3] to yield t-butoxy- and methyl radicals, which react further with the solvent by abstraction of hydrogen atoms to give the radicals R·. If the solvent RH contains a simple alkyl side chain, abstraction takes place mainly from the α-carbon atom, giving stabilised benzyl-type radicals which react further by dimerisation. Raley, Rust, and Vaughan [1] thus isolated 2,3-dimethyl-2,3-diphenylbutane on reaction of t-butyl peroxide with isopropylbenzene, and Farmer and Moore [4] obtained analogous products after similar reactions with ethylbenzene and toluene in sealed vessels at 140°. As well as the simple dimers, unidentified high-boiling residues were obtained, which may well have consisted of the products of reactions of the radicals derived from the decomposition of the peroxide with the primary dimeric products, since the decomposition is rapid at the relatively high temperature at which the reactions were conducted. Moreover, the concentration of t-butyl peroxide used was very high, and hence subsequent reactions of the primary products would be expected to take place under these conditions. Thus, in the reactions with these compounds at lower temperatures with much lower concentrations of t-butyl peroxide, which are reported in the present communication, no high-boiling residue was obtained with ethylbenzene, and only a small amount with toluene.

Apart from these reactions of t-butyl peroxide with alkylbenzenes, the only other reaction with t-butyl peroxide likely to yield a simple product of radical dimerisation which has been investigated previously is that of the peroxide with *p*-chlorotoluene from which Beckwith and Waters [5] isolated 4,4′-dichlorobibenzyl. This result has also been confirmed in the present work.

The reactions of t-butyl peroxide with the following substrates, from which dimeric products were obtained, are now reported: toluene, ethylbenzene, isopropylbenzene, *p*-cymene, diphenylmethane, 4-methylbiphenyl, *o*-, *m*-, and *p*-chloro-, *p*-bromo-, and *p*-iodo-toluene, β- and γ-picoline, and *p*-methylanisole.[6] It has been shown that the reaction proceeds smoothly at considerably lower temperatures than have previously been employed, although with some substrates higher yields of the dimeric products have been obtained at higher temperatures, probably because, at the lower temperatures, insufficient time was allowed for the complete decomposition of the peroxide. The dimeric product of the reaction with ethylbenzene was a mixture of the racemic and the *meso*-form of 2,3-diphenylbutane, which were separated by crystallisation from methanol. This is in accord with the findings of Hey, Pengilly, and Williams,[7] who isolated both forms of this compound from the reaction of ethylbenzene with benzoyl peroxide. The reaction of

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[1] Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88.
[2] Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 95.
[3] Murawski, Roberts, and Szwarc, *J. Chem. Phys.*, 1951, **19**, 698.
[4] Farmer and Moore, *J.*, 1951, 131.
[5] Beckwith and Waters, *J.*, 1957, 1001.
[6] Cf. Johnston and Williams, *Chem. and Ind.*, 1958, 328.
[7] Hey, Pengilly, and Williams, *J.*, 1956, 1463.

t-butyl peroxide with *p*-cymene yielded only one dimer, namely, 2,3-dimethyl-2,3-di-*p*-tolylbutane. The other possible product, 4,4′-di-isopropylbibenzyl, was not isolated and could, therefore, have been formed only in very small amount. No dimer was obtained on decomposition of t-butyl peroxide in anisole, the only product being a dark, involatile residue: this is not unexpected, since the radicals which would be formed from anisole by hydrogen-abstraction from the methoxy-group are not resonance-stabilised, and hence would not be expected to behave in the same way as the radicals derived from the other compounds investigated. On the other hand, the dimeric product, 4,4′-dimethoxybibenzyl, was obtained from the reaction of t-butyl peroxide with *p*-methylanisole, although in rather low yield; this is obviously formed by dimerisation of the *p*-methoxybenzyl radicals arising by hydrogen-abstraction from the methyl group, and the low yield may well be due to the fact that an alternative primary reaction of the t-butoxy-radicals also takes place, namely, that with the methoxy-group. This reaction would, by analogy with that of anisole, be expected to yield only intractable high-boiling material.

## EXPERIMENTAL

t-Butyl peroxide (Light and Co.) was used without further purification, since its purity had been established by Brook,[8] who analysed it by vapour-phase chromatography. Ethylbenzene and isopropylbenzene were purified by the procedure described by Hey, Pengilly, and Williams.[7] Toluene and *p*-chlorotoluene were purified by the same method. Wheeler and Smithey's method [9] was used for the purification of *p*-cymene. Diphenylmethane was purified by fractional distillation *in vacuo* through a helix-packed column (b. p. 140°/18 mm.). *p*-Bromo- and *p*-iodo-toluene (m. p.s 28° and 35° respectively) were crystallised from ethanol. Gomberg and Pernert's method [10] was used for the preparation of 4-methylbiphenyl (m. p. 47°). Anisole, *p*-methylanisole, and *o*- and *m*-chlorotoluene were fractionally distilled through a helix-packed column (b. p.s 155°, 176°, 158°, and 161°/760 mm. respectively). β-Picoline (b. p. 143°/760 mm.) and γ-picoline (b. p. 143°/760 mm., $n_D^{22}$ 1·5043) were fractionally distilled from sodium hydroxide. 4,4′-Dichloro-, -dibromo-, and -di-iodo-bibenzyl were prepared by means of the Sandmeyer reaction from 4,4′-diaminobibenzyl. Details of these preparations will be reported later.

*Decomposition of t-Butyl Peroxide in Pure Solvents.*—The reactions were allowed to proceed for the required time at temperatures between 100° and 140° under an atmosphere of oxygen-free nitrogen; the low-boiling products (acetone and/or t-butyl alcohol), together with any unchanged t-butyl peroxide and the excess of solvent, were then removed through a helix-packed column. The remaining material was transferred to a small distillation flask with the minimum quantity of dry benzene and fractionally distilled *in vacuo*. Details of the reactions with various solvents are summarised below. The Table shows the reaction conditions and the products are described separately.

| Substrate (g.) | $Bu^t{}_2O_2$ (g.) | Temp. | Time (hr.) | Substrate (g.) | $Bu^t{}_2O_2$ (g.) | Temp. | Time (hr.) |
|---|---|---|---|---|---|---|---|
| Toluene (92·1) | 4·0 | 110° | 72 | *p*-Chlorotoluene (100) | 3·75 | 130° | 48 |
| Ethylbenzene (106) | 4·0 | 110 | 72 | *p*-Bromotoluene (170) | 4·0 | 100 | 120 |
| Isopropylbenzene (218) | 10 | 140 | 48 | *p*-Iodotoluene (73) | 1·6 | 100 | 168 |
| *p*-Cymene (218) | 8 | 140 | 48 | Anisole (108) | 4·0 | 110 | 72 |
| Diphenylmethane (84) | 3·75 | 140 | 48 | *p*-Methylanisole (100) | 3·2 | 105 | 120 |
| 4-Methylbiphenyl (56) | 2 | 110 | 72 | γ-Picoline (100) | 3·75 | 127 | 48 |
| *o*-Chlorotoluene (100) | 4 | 110 | 168 | β-Picoline (100) | 3·75 | 127 | 48 |
| *m*- „ (100) | 4 | 110 | 72 | | | | |

*Toluene.* This gave bibenzyl (1·563 g.), m. p. and mixed m. p. 51°, b. p. 85—90°/0·2 mm., and a residue (0·187 g.), b. p. >150°/0·2 mm.

*Ethylbenzene.* A semi-solid mixture of the racemic and the *meso*-form of 2,3-diphenylbutane

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[8] Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.

[9] Wheeler and Smithey, *J. Amer. Chem. Soc.*, 1921, **43**, 2611.

[10] Gomberg and Pernert, *J. Amer. Chem. Soc.*, 1926, **48**, 1372.

(3·02 g.) was obtained, but no higher-boiling material. The *meso*-form is almost insoluble in methanol. After filtration, the methanolic solution was distilled, giving racemic 2,3-diphenylbutane, b. p. 124—125°/2·5 mm., $n_D^{20}$ 1·5510 (Hey, Pengilly, and Williams [7] reported b. p. 116°/2 mm., $n_D^{23}$ 1·5495). *meso*-2,3-Diphenylbutane, crystallised from nitromethane, had m. p. 126° (lit.,[7] 128°).

*Isopropylbenzene.* 2,3-Dimethyl-2,3-diphenylbutane (10·0 g.), m. p. 115°, was characterised by its mixed m. p. No high-boiling residue was formed.

p-*Cymene.* 2,3-Dimethyl-2,3-di-*p*-tolylbutane (9·3 g.), m. p. 154°, (lit.,[11] 157°), was crystallised from ethanol. No high-boiling residue was formed.

*Diphenylmethane.* This gave 1,1,2,2-tetraphenylethane (5·3 g.), m. p. 210° (lit.,[12] 209°), and no high-boiling residue.

4-*Methylbiphenyl.* This gave 4,4′-diphenylbibenzyl (2·3 g.), m. p. 202° (lit.,[13] 205°) (from ethanol), and a residue (0·1 g.), b. p. >180°/0·05 mm.

o-*Chlorotoluene.* The products were 2,2′-dichlorobibenzyl (3·01 g.), m. p. 62° (from ethanol) (lit.,[14] 65°), and a fraction (0·56 g.), b. p. 180—200°/0·01 mm., probably mainly 1,2,3-tri-*o*-chlorophenylpropane, together with some dechlorinated material (Found: C, 68·0; H, 5·1; Cl, 25·7. Calc. for $C_{21}H_{17}Cl_3$: C, 67·1; H, 4·6; Cl, 28·3%). A high-boiling residue (0·41 g.), b. p. >200°/0·01 mm., was also formed.

m-*Chlorotoluene.* This gave 3,3′-*dichlorobibenzyl* (0·585 g.), m. p. 52° (from ethanol) (Found: C, 67·0; H, 4·8; Cl, 27%; *M*, 239. $C_{14}H_{12}Cl_2$ requires C, 67·0; H, 4·2; Cl, 28·2%; *M*, 251·2), which had all the infrared absorption maxima of 1,3-disubstituted derivatives of benzene.[15] A higher-boiling fraction (0·24 g.), b. p. 182—198°/0·01 mm., was almost certainly chiefly the dehydrogeno-trimer, 1,2,3-tri-*m*-chlorophenylpropane, together with some dechlorinated material (Found: C, 70·5; H, 5·4; Cl, 25·0. Calc. for $C_{21}H_{17}Cl_3$: C, 67·1; H, 4·6; Cl, 28·3%). A high-boiling residue (0·46 g.), b. p. >200°/0·1 mm., was also formed.

p-*Chlorotoluene.* Products were: 4,4′-dichlorobibenzyl (2·3 g.) (from ethanol), m. p. and mixed m. p. 101° (Found: Cl, 28·5%; *M*, 237. Calc. for $C_{14}H_{12}Cl_2$; Cl, 28·2%; *M*, 251·2); a fraction (0·35 g.), b. p. 180—200°/0·01 mm., probably mainly 1,2,3-tri-*p*-chlorophenylpropane; and a residue (0·63 g.), b. p. >200°/0·01 mm.

p-*Bromotoluene.* This gave 4,4′-dibromobibenzyl (1·16 g.) (from ethanol), m. p. and mixed m. p. 114°, and a residue (0·34 g.), b. p. >150°/0·5 mm. A similar experiment with t-butyl peroxide (3·75 g.) and *p*-bromotoluene (78 g.) at 130° for 48 hr. gave 4,4′-dibromobibenzyl (3·0 g.).

p-*Iodotoluene.*—4,4′-Di-iodobibenzyl (1·64 g.), m. p. and mixed m. p. 152°, a fraction (0·22 g.), which sublimed at 320° (bath-temp./0·5 mm.), m. p. 230—232°, probably 4,4′-di-iodostilbene,[16] and a residue (0·380 g.), b. p. >300°/0·5 mm., were formed.

*Anisole.* Only low-boiling products, and a residue (0·38 g.), b. p. >250°/1 mm., were obtained.

p-*Methylanisole.*—Distillation gave 4,4′-dimethoxylbibenzyl (0·452 g.), m. p. 125° (lit.,[17] 125°), a fraction (0·370 g.), b. p. 185—200°/0·03 mm., and a residue (0·385 g.), b. p. >220°/0·03 mm.

γ-*Picoline.*—This gave 1,2-di-4′-pyridylethane (2·0 g.), m. p. 111° (lit.,[18] 110—111°) (from cyclohexane–benzene) [dimethiodide, m. p. 322° (lit.,[18] 322°) (Found: C, 36·1; H, 4·0; N, 6·3; I, 54·2. Calc. for $C_{14}H_{18}N_2I_2$: C, 35·9; H, 3·9; N, 6·0; I, 54·2%); *dipicrate*, m. p. 278° (Found: C, 45·4; H, 2·7; N, 17·0. $C_{24}H_{18}O_{14}N_8$ requires C, 44·9; H, 2·8; N, 17·4%)]. The ultraviolet absorption spectrum of the dipyridylethane showed it to be free from 1,2-di-4′-pyridylethylene, since there was no appreciable absorption in the region of 295 mμ, where the C=C absorption maximum of this compound occurs. A high-boiling residue (1·31 g.) was also formed in the reaction.

β-*Picoline.* Distillation gave 1,2-*di*-3′-*pyridylethane* (2·2 g.), b. p. 110—112°/1 mm., m. p. 34—36° (from ether at −40°) (Found: C, 78·2; H, 6·6; N, 15·3%; *M*, 180. $C_{12}H_{12}N_2$ requires

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[11] Boedter and Hierlar, *Compt. rend.*, 1929, **188**, 1681.

[12] Biltz, *Annalen*, 1897, **296**, 221.

[13] Hopff and Koulen, *Chem. Ber.*, 1952, **85**, 897.

[14] Thiele and Holzinger, *Annalen*, 1899, **305**, 100.

[15] Randle and Whiffen, "The Characteristic Vibration Frequencies of Substituted Benzenes: Molecular Spectroscopy," Institute of Petroleum, London, 1955, p. 111.

[16] Meyer and Hofmann, *Monatsh.*, 1917, **38**, 151.

[17] Buck and Jenkins, *J. Amer. Chem. Soc.*, 1929, **51**, 2166.

[18] Bergmann, Crane, and Fuoss, *J. Amer. Chem. Soc.*, 1952, **74**, 5979.

C, 78·2; H, 6·6; N, 15·2%; *M*, 184) [*dipicrate*, m. p. 244—245° (Found: C, 44·7; H, 2·8; N, 17·2. $C_{24}H_{18}O_{14}N_8$ requires C, 44·9; H, 2·8; N, 17·4%)].

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