Steric Influences in Radical Reactions. Part II.[1] The Abstraction of Benzylic Hydrogen Atoms from 1-Phenylphthalan, 1,3-Diphenylphthalan, and 2-Formyl-2′-methylbiphenyl by t-Butoxy Radicals

By R. L. Huang and H. H. Lee

Hydrogen-abstraction from 1-phenylphthalan by t-butoxy radicals at 120° liberates both of the radicals in which the free electron is at either of the benzylic carbon atoms C_3 and C_1, as evidenced by isolation of products resulting from rearrangement of the former radical and from dimerisation of the latter. Abstraction occurs from the methyl group of *o*-benzoyltoluene to give a radical which dimerises at 30°, but at 125° cyclises, to give ultimately anthraquinone and dianthrone. 1,3-Diphenylphthalan gives mainly 1,2-dibenzoylbenzene, the same product as when the phthalan is heated alone.

Abstraction from 2-formyl-2′-methylbiphenyl, at both 30 and 120°, occurs mainly at the aldehyde group; the benzoyl radical so formed then cyclises to 4-methylfluorenone in 60—67% yield. The intramolecular acylation of the radical is believed to be facilitated by steric effects.

THE phthalanyl radical (I), generated from phthalan by dehydrogenation with t-butoxy radicals at 120—125°,[1] has been found to dimerise, rather than rearrange to free 2-formylbenzyl (II) as would be expected by analogy with the radical derived from dibenzyl ether. This has been attributed [1] to diminished stability in (II), relative to free benzyl, due to steric suppression of resonance by the *ortho*-substituent. If this hypothesis were correct the substituted phthalanyl radicals (III) and (IV) would be expected to rearrange, at least appreciably, to (V) and (VI), respectively, since in each of these latter radicals the additional benzene ring adjacent to the radical centre would restore the stability of a true benzyl radical. We have, therefore, extended our study of the dehydrogenation of cyclic homologues of dibenzyl ether to 1-phenylphthalan and 1,3-diphenylphthalan.

Attack on 1-phenylphthalen by t-butoxy radicals at 120—125° appears to generate both of the radicals (III) and (VII), yielding a mixture of products from which were isolated in small yields the dimer (VIII) and a monoaldehyde, tentatively assigned the structure (IX). Traces of a dialdehyde, probably (X), and anthraquinone were also obtained. That the dimer was (VIII), rather than (XI) or (XII), is supported by its n.m.r. spectrum which shows, besides aromatic protons, a typical AB quartet at τ_A 5·18 and τ_B 4·91 with $J_{AB} = 12{\cdot}0$ c./sec. The radical (VII) thus appears to favour dimerisation over rearrangement to the 2-benzoylbenzyl radical (XIII), and this is confirmed by the absence, among the products, of the dimers (XIV) and (XV), which are the main products when (XIII) itself is generated from *o*-benzyltoluene by the action of t-butoxy radicals (see below). The monoaldehyde (IX), which forms a 2,4-dinitrophenylhydrazone and was shown by infrared absorption to contain an aldehyde but not a ketone group, and the dialdehyde (X), obtained as the bis-2,4-dinitrophenylhydrazone, must both have originated from the radical (V), in turn derived from the radical (III) through rearrangement. The indications are therefore that, while (III) rearranges to (V), at least to a certain extent, (VII) hardly does so.

The generation of (XIII) from *o*-benzoyltoluene was effected both at 30—45° with t-butyl peroxyoxalate [2] and at 120—125° using t-butyl peroxide. At the lower temperature the radical dimerised, giving (XIV) whose

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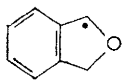
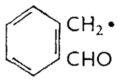
[1] Part I, R. L. Huang and H. H. Lee, *J. Chem. Soc.*, 1964, 2500.
[2] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, 1960, **82**, 1762.

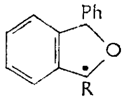
structure is confirmed by the presence in the n.m.r. spectrum of a singlet at τ 7·07 due to four identical methylene protons; at the higher temperature the radical apparently underwent intramolecular alkylation to give anthrone, which suffered dehydrogenation to give anthraquinone and dianthrone (XV),[3] the latter compound being identified by an independent synthesis. Generation of the 2-benzoylbenzyl radical (XIII) was undertaken also to ascertain whether intramolecular addition of the benzyl radical to the carbonyl group, *i.e.*, a reversal of the rearrangement process, to give the 1-phenylphthalanyl radical (VII), could occur. None of the dimer (VIII), however, could be found.



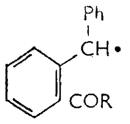
(I)



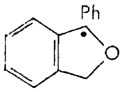
(II)



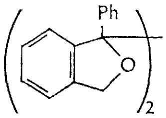
(III: R = H)
(IV: R = Ph)



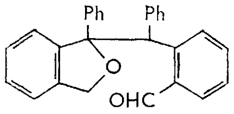
(V: R = H)
(VI: R = Ph)



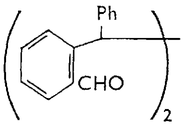
(VII)



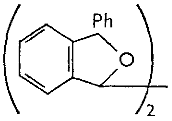
(VIII)



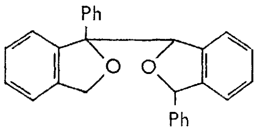
(IX)



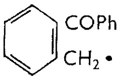
(X)



(XI)



(XII)



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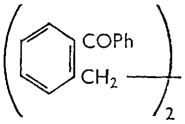

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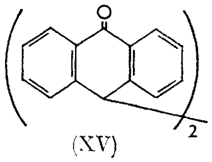

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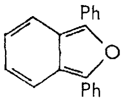
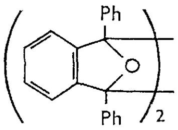
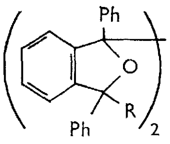


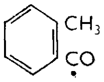
(XVI)



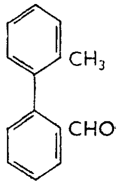
(XVII)



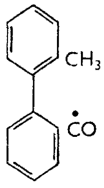
(XVIII: R = OH
or O·OH)



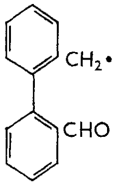
(XIX)



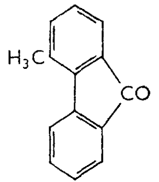
(XX)



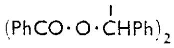
(XXI)



(XXII)

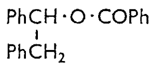


(XXIII)



$(\mathrm{PhCO{\cdot}O{\cdot}\overset{|}{C}HPh})_2$

(XXIV)



$\mathrm{PhCH{\cdot}O{\cdot}COPh}$
$\mathrm{\overset{|}{P}hCH_2}$

(XXV)

The reaction of t-butoxy radicals with 1,3-diphenylphthalan gave chiefly *o*-dibenzoylbenzene accompanied by a small quantity (~3%) of a dimer. Since heating of the phthalan itself also gives *o*-dibenzoylbenzene, probably by way of the *o*-quinonoid compound (XVI),[4] no inference as to the reaction path(s) can be drawn here. That the dimer obtained is not (XVII), derived from (XVI) through a self-addition of the type postulated by Adams and Gold,[5] is shown by a singlet for benzylic protons at τ 4·3 and aromatic protons at τ 2·6—3·0 in the n.m.r. spectrum. [The integrated areas for aromatic protons and benzylic protons are, however, in the ratio of 20—21 : 1, instead of the expected 14 : 1, and may be due to partial autoxidation of the dimer to (XVIII).] The mass spectrum of the dimer shows a parent-ion peak at *m/e* 271.

In Part I[1] it was reported that abstraction of hydrogen atoms by the t-butoxy radical from *o*-tolualdehyde generates the benzoyl radical (XIX), rather than the 2-formylbenzyl radical (II). This study has been extended to the biphenyl (XX) from which would be produced the radical (XXI) and/or (XXII), " vinylogues " of (XIX) and (II), respectively, in which steric interference due to the *ortho*-substituents would be less pronounced. Dehydrogenation was carried out at 30 and at 120° as described earlier, and in each case the main product, obtained in no less than 60—67% yield, was 4-methylfluorenone (XXIII), probably formed from the benzoyl radical (XXI) through intramolecular acylation. It appears therefore that, as in *o*-tolualdehyde, hydrogen-abstraction from (XX) occurs predominantly at the aldehyde carbon atom. Although the possibility cannot be excluded of abstraction first taking place at the methyl group, followed by an exchange reaction (intra- or inter-molecular) to give the benzoyl radical, this reaction, if it occurs, is probably slight. An experiment in which benzyl radicals are generated, by thermolysis of dibenzylmercury, in benzaldehyde gives a mixture of bibenzyl, *meso* and racemic (XXIV), and the ester (XXV), all derived from the benzyl and benzoyl radicals,[6] in such yields as to indicate that, even at 180° in a large excess of aldehyde, the exchange reaction does not proceed beyond 14%. The preference exhibited by the benzoyl radical (XXI) to acylate the neighbouring benzene ring, rather than add to an aldehyde group as does the free benzoyl radical liberated from benzaldehyde,[6] seems best attributed to the favourable spatial disposition of the reaction centres in (XXI).

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[3] J. S. Meek, W. B. Evans, V. Godefroi, W. R. Benson, M. F. Wilcox, W. G. Clark, and T. Tiedeman, *J. Org. Chem.*, 1961, **26**, 4281.

[4] A. Guyot and J. Catel, *Bull Soc. chim. France*, 1906, [3], **35**, 1124.

[5] R. Adams and M. H. Gold, *J. Amer. Chem. Soc.*, 1940, **62**, 2038.

[6] F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258.

[7] A. Pernot and A. Willemart, *Bull. Soc. chim. France*, 1953, 321.

EXPERIMENTAL

1-*Phenylphthalan.*—The reaction mixture from 1-phenylphthalan[7] (23 g., 118 mmoles) and di-t-butyl peroxide (2·10 g., 15 mmoles) after 22 hr. at 120—125° (see General Procedure in Part I[1]) was distilled to remove unreacted 1-phenylphthalan (b. p. 98°/0·3 mm., m. p. 38°; 13·2 g.), and a portion (6·0 g.) of the residue (8·4 g.) was chromatographed on alumina (180 g.). Elution with petroleum (b. p. 60—80°) gave a semi-solid mixture (4·2 g.) consisting of 1-phenylphthalan and the dimer (VIII). Trituration with methanol gave the pure *dimer* (0·38 g.) which crystallised from light petroleum as prisms, m. p. 208—209° (decomp.) (Found: C, 86·2; H, 6·0. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%). Further elution with petroleum–benzene (5—25%) gave the *monoaldehyde* (IX) (0·76 g.), m. p. 204—207° (from aqueous methanol), $\nu_{max.}$ ($CHCl_3$) 2850, 2730, 1694, 1050, and 1017 cm.$^{-1}$ (Found: C, 86·3; H, 5·8. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%); 2,4-*dinitrophenylhydrazone*, m. p. 249—251° (decomp.) (Found: C, 72·0; H, 5·0; N, 10·6. $C_{34}H_{26}N_4O_5$ requires C, 71·6; H, 4·6; N, 9·8%). Reduction of (IX) with sodium borohydride afforded the corresponding *alcohol*, m. p. 193—195° (benzene–petroleum) (Found: C, 85·9; H, 6·6. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·2%). Elution with petroleum–benzene (1 : 1) and with benzene gave small amounts of (i) the dialdehyde (X), $\nu_{max.}$ 2840, 2740, and 1691 cm.$^{-1}$, converted readily into the *bis*-2,4-*dinitrophenylhydrazone*, m. p. 308—310° (Found: C, 64·3; H, 4·5. $C_{40}H_{30}N_8O_8$ requires C, 64·0; H, 4·0%), and (ii) 3-phenylphthalide,[8] $\nu_{max.}$ ($CHCl_3$) 1770 cm.$^{-1}$, m. p. and mixed m. p. 115—118°. Further elution with ether gave a yellow gum (0·3 g.) which showed strong absorption at 1775 and 1680 cm.$^{-1}$. Trituration of the gum with chloroform gave traces of anthraquinone (mixed m. p. and infrared spectrum).

1-Phenylphthalan after being heated alone under identical conditions to the above was recovered unchanged (m. p. and infrared).

o-*Benzoyltoluene.*—(a) *Reaction with di-t-butyl peroxyoxalate.* A solution of di-t-butyl peroxyoxalate[2] (2·52 g., 11 mmoles) in *o*-benzoyltoluene (40 g., 204 mmoles) was kept under nitrogen at 30° for 1 hr. and then at 45° for 20 hr. The volatile products were distilled at 30—50°(bath)/3 mm. into two receivers connected in series and cooled at −80° (acetone–solid carbon dioxide). Quantitative infrared analysis of the distillate indicated the presence of di-t-butyl peroxide (3·5 mmoles) and t-butyl alcohol (13 mmoles), but no acetone. The reaction mixture was further distilled to remove unreacted ketone (b. p. 98—100°/0·2 mm.; 36 g.), and the residue (3·7 g.) was chromatographed on alumina (160 g.). Elution with petroleum–benzene (1 : 1) and benzene gave more ketone (1·8 g.). Elution with benzene containing ether (2—10%) gave (i) anthraquinone (48 mg.), m. p. and mixed m. p. 288—290°, and (ii) 2,2′-*dibenzoylbibenzyl* (XIV) (1·2 g.) which crystallised from methanol as rhombic prisms, m. p. 109—110°, $\nu_{max.}$ (CCl_4) 1665 cm.$^{-1}$ (Found: C, 85·7; H, 5·8. $C_{28}H_{22}O_2$ requires C, 86·1; H, 5·7%). Elution with ether containing methanol (1—5%) gave a red-brown resinous material (0·6 g.) having infrared absorption similar to that of the bibenzyl (XIV).

(b) *Reaction with di-t-butyl peroxide.* The reaction mixture from *o*-benzoyltoluene (29 g., 148 mmoles) and di-t-butyl peroxide (1·5 g., 10 mmoles) was distilled to remove unreacted ketone (b. p. 98—100°/0·2 mm.; 25 g.), and the residue (2·7 g.) on extraction with boiling light petroleum left a solid (0·12 g.) which crystallised from benzene–petroleum in needles, m. p. 260—262° (decomp.), identified as dianthrone (XV) by elemental analysis (Found: C, 86·9; H, 4·8. Calc. for $C_{28}H_{18}O_2$: C, 87·0; H, 4·7%) and by mixed m. p. and comparison of infrared spectrum with that of an authentic sample prepared from anthrone as described below. The combined petroleum extracts were percolated through alumina (100 g.). Elution with light petroleum–benzene (1 : 1) gave more unreacted ketone (1·9 g.), and with benzene and benzene–ether (50 : 1) gave anthraquinone, m. p. and mixed m. p. 288—291° (0·1 g.). Further elution with ether and ether containing methanol (1—5%) gave intractable material (0·25 g.).

Dianthrone.—A solution of anthrone (19·4 g., 100 mmoles) and di-t-butyl peroxide (2·2 g., 15 mmoles) in chlorobenzene (100 ml.) was refluxed under nitrogen for 50 hr. and cooled. The solid product (4·5 g.) was filtered off and after one recrystallisation from benzene–petroleum had m. p. 260—262° (decomp.) (lit.,[9] 275°).

1,3-*Diphenylphthalan.*—The reaction mixture from 1,3-diphenylphthalan[4] (12 g., 44 mmoles) and di-t-butyl peroxide (1·50 g., 10 mmoles) was extracted with boiling carbon tetrachloride (3 × 20 ml.), and the insoluble material (0·15 g.) filtered off. Recrystallisation from benzene gave bis-diphenylphthalan as prisms, m. p. 205—206° (Found: C, 88·6; H, 5·9. $C_{40}H_{30}O_2$ requires C, 88·5; H, 5·6%). The carbon tetrachloride solution on evaporation gave a yellow solid, m. p. 85—120° (12 g.), from which was isolated *o*-dibenzoylbenzene (8 g.), m. p. 148—150° (lit.,[5] 145—146°), $\nu_{max.}$ ($CHCl_3$) 1660 cm.$^{-1}$, by fractional recrystallisation from ethanol.

1,3-Diphenylphthalan, after being heated alone for 22 hr. at 122—125° under nitrogen in a Carius tube, turned yellow and showed absorption at 1665 cm.$^{-1}$.

2-*Formyl*-2′-*methylbiphenyl.*—(a) *Preparation.* αα′-Dibromo-2,2′-bitolyl[10] (22 g.) was added with stirring to a suspension of the sodium salt of 2-nitropropane (from 2·3 g. of sodium and 9·2 g. of nitropropane) in absolute ethanol (100 ml.). After 16 hr., the mixture was filtered, the filtrate concentrated, and the residue redissolved in ether (200 ml.). The ethereal solution was washed with aqueous sodium hydroxide (10%) and water, and dried ($MgSO_4$). The *product* was obtained as a colourless liquid, b. p. 86—87°/0·1 mm. (12·5 g.), n_D^{23} 1·5995, $\nu_{max.}$ (CCl_4) 2840, 2740, and 1695 cm.$^{-1}$ (Found: C, 85·3; H, 5·85. $C_{14}H_{12}O$ requires C, 85·7; H, 6·2%); *semicarbazone*, m. p. 212—214° (Found: C, 71·2; H, 5·8; N, 16·8. $C_{15}H_{15}N_3O$ requires C, 71·1; H, 6·0; N, 16·6%). Reduction of the aldehyde with sodium borohydride afforded the corresponding *alcohol*, m. p. 86—88° (Found: C, 85·0; H, 7·1. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%). Oxidation with silver oxide afforded 2-carboxy-2′-methylbiphenyl, m. p. 105—107° (lit.,[11] 104·4—105·6°).

(b) *Reaction with di-t-butyl peroxyoxalate.* Di-t-butyl peroxyoxalate (1·2 g., 5·1 mmoles) was allowed to decompose at 30° under nitrogen in 2-formyl-2′-methylbiphenyl (10 g., 51 mmoles) for 80 hr. Quantitative infrared analysis of the volatile distillate indicated the presence of t-butyl alcohol (4·8 mmoles) and di-t-butyl peroxide (0·8 mmole). The

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[8] M. S. Newman, *J. Org. Chem.*, 1961, **26**, 2630.

[9] E. de B. Barnett and M. A. Matthews, *J. Chem. Soc.*, 1923, **23**, 380.

[10] G. Wittig, G. Koenig, and K. Clauss, *Annalen*, 1955, **593**, 127.

[11] M. Orchin and E. O. Woolfolk, *J. Amer. Chem. Soc.*, 1945, **67**, 122.

residue from the distillation (11 g.) was dissolved in ether and extracted with aqueous sodium hydrogen carbonate. The extracts on acidification yielded 2-carboxy-2′-methylbiphenyl (0·4 g.), m. p. 104—106°. After removal of ether, a portion (5·0 g.) of the residue was chromatographed on alumina (160 g.). Elution with petroleum gave (i) unreacted aldehyde (4·6 g.), and (ii) a yellow solid, m. p. 93—93·5° (0·18 g.), identified as 4-methylfluorenone by mixed m. p. and comparison of infrared spectrum with a sample prepared as described by Haworth and Tinker.[12] Further elution with benzene and ether gave only intractable gum (0·2 g.), $\nu_{max.}$ 1720 cm.$^{-1}$.

In another experiment, the perester (0·7 g., 3 mmoles) was allowed to decompose at 30° in a benzene (30 ml.) solution of the aldehyde (5·5 g., 28 mmoles), and the mixture chromatographed on alumina (160 g.) after removal of volatile material. The products obtained were (i) unreacted aldehyde (4·9 g.), (ii) 4-methylfluorenone (0·37 g.), and (iii) intractable gum (0·1 g.).

(c) *Reaction with di-t-butyl peroxide*. The reaction mixture from 2-formyl-2′-methylbiphenyl (9·7 g., 50 mmoles) and di-t-butyl peroxide (3·0 g., 23 mmoles) was dissolved in ether and extracted with saturated aqueous sodium hydrogen carbonate. Acidification of the extracts gave 2-carboxy-2′-methylbiphenyl, m. p. 105—107° (0·3 g.). After removal of ether a portion (4·4 g.) of the residue (9·5 g.) was chromatographed on alumina (150 g.). Elution with petroleum gave (i) unreacted aldehyde (3·2 g.), and (ii) 4-methylfluorenone, m. p. and mixed m. p. 93—94° (0·8 g., 66%). Elution with more polar solvents gave only intractable gum (0·2 g.), $\nu_{max.}$ 1720 cm.$^{-1}$.

Decomposition of Dibenzylmercury in Benzaldehyde.—A solution of dibenzylmercury (19·5 g., 51 mmoles) in benzaldehyde (72 g.) was refluxed under nitrogen for 16 hr. (Estimated half-life of dibenzylmercury at 179° is *ca.* 3 min.)[13] The solution was decanted from precipitated mercury (10·1 g.) and fractionally distilled through a 4-in. Vigreux column under nitrogen, giving (i) a forerun, b. p. 28—92°/35 mm. (5·6 g.), and (ii) unreacted benzaldehyde, b. p. 92°/35 mm. (62 g.). The forerun was treated with alkaline silver oxide, and the unoxidised material isolated with pentane, giving toluene (0·2 g.), identified by its infrared spectrum.

A portion (4 g.) of the distillation residue (11·6 g.) was chromatographed on alumina (150 g.). Elution with petroleum gave bibenzyl, m. p. and mixed m. p. 52—53° (2·3 g.). Elution with petroleum containing benzene (10—50%) gave (i) a solid, m. p. 69—71° (0·8 g.), $\nu_{max.}$ 1720 and 1265 cm.$^{-1}$ (Found: C, 83·4; H, 6·2. Calc. for $C_{21}H_{18}O_2$: C, 83·4; H, 6·0%), identified as α-benzoyloxybibenzyl (lit.,[14] m. p. 70°) by mixed m. p. and comparison of infrared spectrum with an authentic sample prepared by benzoylation of benzylphenylmethanol, and (ii) a mixture of racemic and *meso*-αβ-dibenzoyloxybibenzyl (0·43 g.) separated by boiling ethanol into the pure components, m. p. 126—129° (lit.,[15] 128—131°) and 246—248° (lit.,[15] 245—246°). Elution with ether gave resinous material (0·2 g.), $\nu_{max.}$ 1725 cm.$^{-1}$, which was not investigated.

The products are thus bibenzyl (37 mmoles), α-benzoyloxybibenzyl (8 mmoles), and *meso*- and racemic αβ-dibenzoyloxybibenzyl (3 mmoles).

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