

480. *Steric Influences in Radical Reactions. Part I. Benzyl Radicals Derived from Cyclic Homologues of Dibenzyl Ether.*

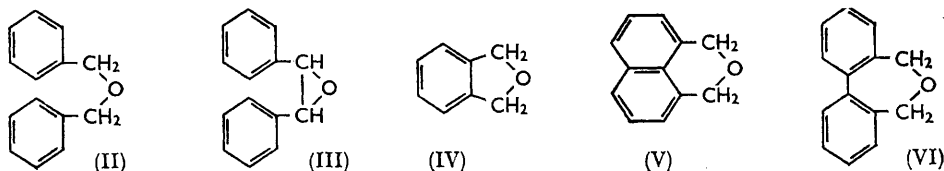
By R. L. HUANG and H. H. LEE.

Hydrogen-abstraction, by *t*-butoxy radicals, from *cis*- and *trans*-stilbene oxide, phthalan, naphthalan, and diphenan generates radicals which behave in various ways. Whilst the radicals from the stilbene oxides disproportionate to the α -benzoylbenzyl radical (VIII), those derived from phthalan and naphthalan dimerise. The failure of the latter radicals to disproportionate is attributed to steric inhibition of resonance in the secondary radicals (XIV) and (XXV) which would be produced by such a process. A study of hydrogen-abstraction from *o*-tolualdehyde substantiates this view. The radical derived from diphenan disproportionates to the benzyl radical (XXIX), which then cyclises, giving ultimately 9,10-dihydro-9-phenanthrol. The cyclisation process, involving intramolecular addition of the benzyl radical to the aldehyde function, is considered to be facilitated by (a) a gain in resonance energy in the system, (b) a favourable polar effect, and (c) steric assistance.

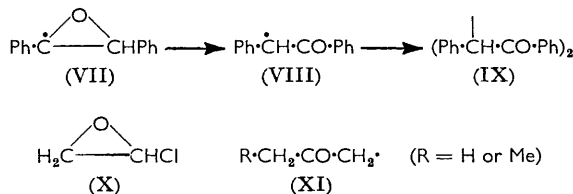
THE α -alkoxybenzyl radicals $\text{Ph}\cdot\dot{\text{C}}\text{H}\cdot\text{OR}$ (I), generated from the benzyl ether $\text{Ph}\cdot\text{CH}_2\cdot\text{OR}$ by dehydrogenation with *t*-butoxy radicals,¹ exhibit a wide range of reactivity with respect to fragmentation into the radical $\text{R}\cdot$ and benzaldehyde. Disproportionation of (I) occurs extensively when the radical $\text{R}\cdot$ so produced is resonance-stabilised, such as benzyl, but

¹ Huang and Si-Hoe, (a) *Proc. Chem. Soc.*, 1957, 354; (b) "Vistas in Free-Radical Chemistry," ed. Waters, Pergamon, London, 1959, p. 242; see also Ang, Huang, and Sim, *J.*, 1963, 4841.

not at all if $R\cdot$ is highly energised such as methyl or phenyl. Thus, whilst dibenzyl ether (II) gives benzaldehyde and products derived from free benzyl radicals, benzyl methyl or benzyl phenyl ether yields only the dimer $(Ph\cdot CH\cdot OR)_2$. Study of a series of benzyl ethers show that, under similar conditions, the readiness with which fragmentation occurs follows the scale: $PhCH_2 > t-Bu > i-Pr > Et > Me$ and Ph, which, as would be expected, is the generally accepted scale of relative stabilities of the radicals. It should be possible, therefore, by observation of the behaviour of the radicals (I) to make inferences as to the



relative stabilities of the radicals $R\cdot$, where these are not already known. With this possibility in view we have extended our work to a number of cyclic ethers containing the dibenzyl ether moiety, namely, *cis*- and *trans*-stilbene oxide (III), phthalan (IV), naphthalan (V), and diphenan (VI), the structures of which lend themselves to a study of steric and strain effects on the chemical properties of the derived free radicals.



cis-Stilbene oxide, on being heated with di-*t*-butyl peroxide (0.1 mole per mole of oxide) at 120–125° for 22 hours, gave a good yield (at least 57%) of $\alpha\alpha'$ -dibenzoylbibenzyl (IX) in the *meso*- and racemic forms, the isomers being obtained in approximately equal quantities. *trans*-Stilbene oxide also gave this dimer, but in much lower yields and in the *meso*-form only, the product being contaminated with a good deal of polymer. The formation of the dimer in either case clearly indicates the transient existence of the radical (VIII), which in turn must have been generated through rearrangement (in effect an intramolecular disproportionation) of the oxiranyl radical (VII), derived from the oxide by abstraction of an α -hydrogen atom. To substantiate the existence of the α -benzoylbibenzyl radical and the behaviour attributed to it, this radical was prepared by an unambiguous route, namely, by treating deoxybenzoin with di-*t*-butyl peroxide under similar conditions. This also yielded $\alpha\alpha'$ -dibenzoylbibenzyl in both forms and in good yield, accompanied by little by-products.

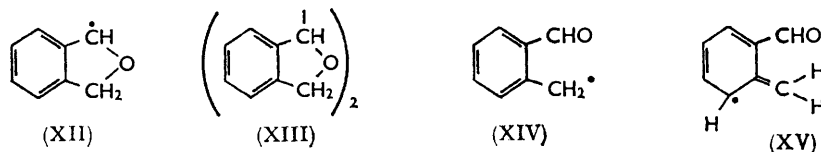
The difference in yields of the dimer from the *cis*- and *trans*-oxides could be explained on steric grounds, if it is assumed that abstraction of hydrogen atoms by the *t*-butoxy-radical occurs more readily with the *cis*- than with the *trans*-isomer. In the case of the *cis*-oxide, abstraction would be directed mainly at the starting material (present in large excess), leaving the dimer untouched. With the *trans*-oxide, however, dehydrogenation of the substrate being less facile, the dimer already formed would also be subject to attack and thereby converted into polymer. The assumption that the *cis*-oxide is more reactive towards the *t*-butoxy-radical than the *trans*-isomer has been substantiated by a measurement² of the *t*-butyl alcohol:acetone ratio in each case. These are 5:1 and 0.8:1, respectively.

Hydrogen-abstraction from epoxides by the *t*-butoxy-radical has been studied with

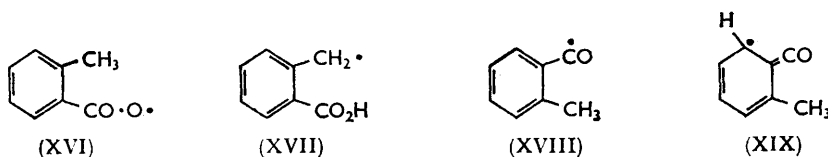
² Brook, *Trans. Faraday Soc.*, 1957, **53**, 327; Williams, Oberright, and Brooks, *J. Amer. Chem. Soc.*, 1956, **78**, 1190.

epoxides such as 1,2-epoxy-ethane, -propane, and -butane, under a variety of conditions,³ and has been found to occur usually with difficulty. With *t*-butyl hypochlorite at 40° the radical derived from epoxyethane retains its structure and abstracts a chlorine atom from the hypochlorite to give (X). The radicals from 1,2-epoxy-propane and -butane, however, disproportionate to the ketonic radicals (XI) when generated by heating with di-*t*-butyl peroxide at 125—200°. In the case of the stilbene oxides (III), which represent dibenzyl ether with the α -carbon atoms bonded in a strained ring, disproportionation of the derived oxiranyl radical (VII), with concomitant release of strain, to generate the resonance-stabilised α -benzoylbenzyl radical, would be entirely expected, and probably took place with greater ease than even with dibenzyl ether itself. As to the rate of hydrogen-abstraction, relative to the aliphatic epoxides mentioned above, it would be expected that for the stilbene oxides, this rate would be enhanced by the presence of the benzene rings. In attack by *t*-butoxy-radicals at 150° this is the case with styrene oxide.^{3b}

The radical (XII) derived from phthalan did not disproportionate, but dimerised to give (XIII) in the normal and iso-forms.* These are easily autoxidisable, leading in good yield to phthalide, which is also the main product if air is not rigidly excluded from the reaction system. Structurally phthalan represents dibenzyl ether with the benzene rings anchored to each other, and the failure of the radical (XII) to disproportionate to the 2-formylbenzyl radical (XIV) seems best explained by the fact that resonance is inhibited



in the latter. It will be noted that resonance hybrids such as (XV), which would have to be planar, are sterically inhibited by the 2-formyl group, and, as a result, delocalisation of the unpaired electron to the 2- and 4-positions in the benzene ring, which in the case of a benzyl radical without 2-substituents contribute to its stability, cannot operate here. An analogous situation has been encountered in the 2-methylbenzoyloxy-radical (XVI), in which intramolecular hydrogen-abstraction to form the 2-carboxybenzyl radical (XVII) occurs to only a small extent,⁴ despite the fact that other factors (*e.g.*, a six-membered-ring transition state) are favourable for such abstraction to occur. The radical (XII) has thus the property of a stable radical, and is to be compared with the radical derived from benzyl methyl or benzyl phenyl ethers, rather than dibenzyl ether. The fact that photolytic oxidation of phthalan gives a hydroperoxide⁵ in good yield is further evidence of the phthalan radical's being able to retain its identity in a chemical reaction, without undergoing disproportionation or rearrangement.



To substantiate the role attributed to steric factors in the situation described above, it seemed worthwhile to investigate the abstraction of benzylic hydrogen atoms from

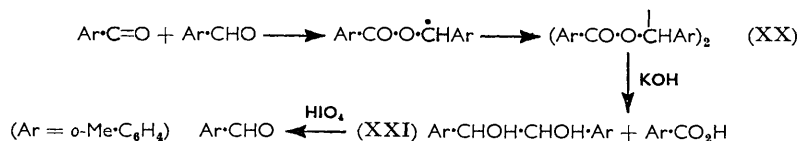
* No attempt was made to assign actual configurations to these isomers. In all cases the higher-melting isomer is designated the normal form and the other isomer the iso-form.

³ (a) Walling and Fredricks, *J. Amer. Chem. Soc.*, 1962, **84**, 3326; (b) Wallace and Gritter, *Tetrahedron*, 1963, **19**, 657.

⁴ Green, Van Norman, Cantrill, and Gilliom, *J. Org. Chem.*, 1960, **25**, 1790.

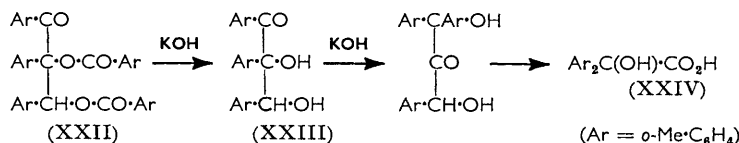
⁵ Rieche and Schulz, Ger. Pat. 1,057,606 (1959) (*Chem. Abs.*, 1961, **55**, 6496).

o-tolualdehyde, from which could be obtained either, or both, of the 2-formylbenzyl (XIV) and the *o*-toluoyl (XVIII) radicals. Since the benzylic α -hydrogen atoms in toluene and in benzaldehyde have much the same bond-dissociation energies (78 and 79 kcal., respectively),⁶ abstraction by *t*-butoxy-radicals should, if considered on energetic grounds alone, occur to much the same extent on both benzylic carbon atoms. This appears to be substantiated by the observation⁷ that free benzyl radicals, when generated from azotoluene in an excess of benzaldehyde, show no tendency to abstract hydrogen atoms from the solvent to generate benzoyl radicals. However, if steric factors are also considered, it would be noted that, unlike the 2-formylbenzyl radical, the *o*-toluoyl radical is capable of being stabilised by resonance with the benzene ring through participation of hybrids such as (XIX), and thus abstraction of α -hydrogen atoms from *o*-tolualdehyde should preferentially occur at the aldehyde group. This expectation has been fulfilled. Treatment of *o*-tolualdehyde with di-*t*-butyl peroxide gave, as the main product, the diester (XX) in both the normal and iso-forms. This diester was undoubtedly formed from the toluoyl radical (XIII) by way of addition of this radical to *o*-tolualdehyde, in a manner analogous to the addition of the free benzoyl radical (from benzaldehyde and di-*t*-butyl peroxide) to benzaldehyde,⁸ followed by dimerisation, as follows:



The identity of the isomeric diesters (XX) was established from elemental analyses and infrared spectra, and from their both being hydrolysed with potassium hydroxide to the substituted hydrobenzoin (XXI) in the normal and iso-forms. These hydrobenzoin were hitherto unknown, and their structures were confirmed through cleavage with periodic acid to *o*-tolualdehyde in each case.

The action of *t*-butoxy-radicals on *o*-tolualdehyde yielded also, as minor products, *o*-toluic acid, *t*-butyl *o*-toluate, and a keto-ester, for which the structure (XXII) is suggested. This structure would be consistent with its analysis and infrared absorption and with the



fact that on hydrolysis with potassium hydroxide it gave *o*-toluic acid and the acid (XXIV). A plausible route by which the latter is produced is as indicated, involving a rearrangement of the intermediate tertiary ketol (XXIII), for which analogies are known.⁹

If steric hindrance in the 2-formylbenzyl radical operates sufficiently strongly to inhibit resonance, the same factor would be expected to assert its control in the radical (XXV) in which the radical centre and the aldehyde group are also in close proximity. This expectation seems well grounded. Thus, the radical (XXVI), obtained by dehydrogenation of naphthalan in the usual way, dimerised to normal and iso-bisnaphthalan, and no product which might have arisen from the radical (XXV) could be isolated.

Diphenan, when acted upon by *t*-butoxy-radicals, yielded 9,10-dihydro-9-phenanthrol

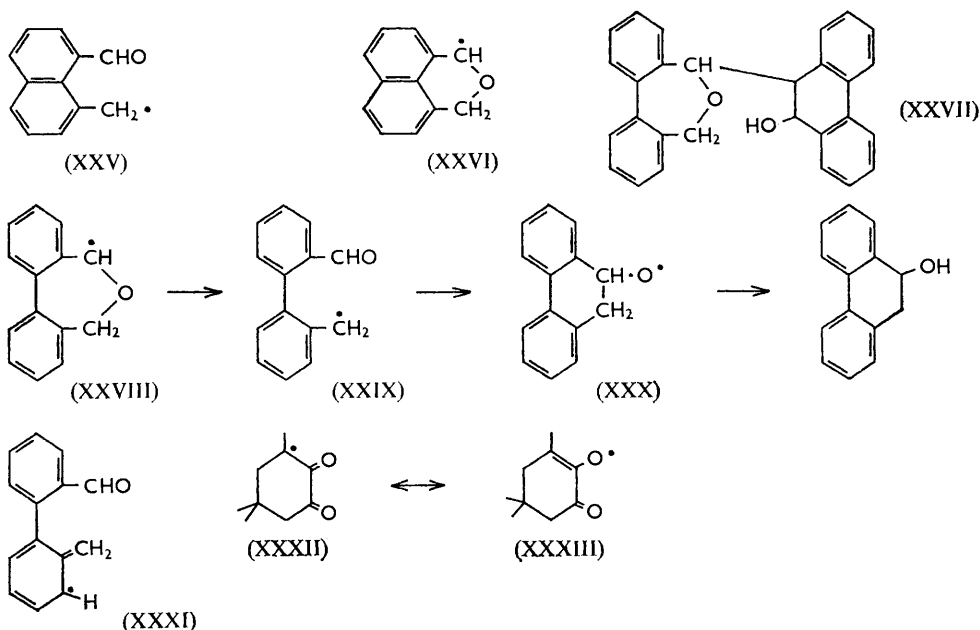
⁶ Gray and Williams, *Chem. Rev.*, 1959, **59**, 239; Jaffé, Prosen, and Szwarc, *J. Chem. Phys.*, 1957, **27**, 416.

⁷ Huang, Lee, and Malhotra, unpublished results.

⁸ Rust, Seubold, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 3258; see also ref. 1a.

⁹ Eastham, Huffaker, Raaen, and Collins, *J. Amer. Chem. Soc.*, 1956, **78**, 4323; Selman and Eastham, *Quart. Rev.*, 1960, **14**, 230.

as the major product, accompanied by traces of phenanthrene, 9-phenanthrol, phenanthraquinone, bisdiphenan, and the substituted diphenan (XXVII) whose structure was inferred from its elemental analysis and infrared absorption.



To account for the ring contraction to the dihydrophenanthrol the radical (XXVIII) first formed is envisaged to disproportionate to the benzyl radical (XXIX), which then adds intramolecularly to the aldehyde group to give the dihydrophenanthroxy-radical (XXX) as indicated. This then abstracts a hydrogen atom from the surrounding ether to form the dihydrophenanthrol.

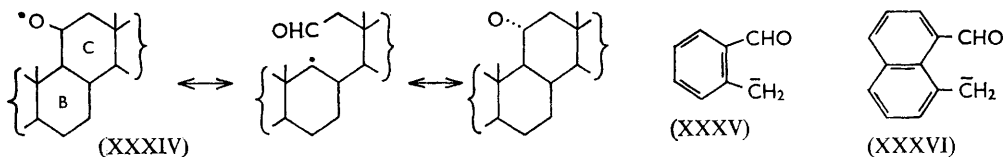
This striking difference in behaviour between the diphenan and the phthalan radicals can be explained on steric grounds. In the diphenan radical, the presence of the seven-membered system renders the benzene rings non-planar, and thus the benzyl radical (XXIX) generated on disproportionation is capable of being stabilised by resonance hybrids such as (XXXI), which, unlike the 2-formylbenzyl radical, is not subject to the same extent of steric inhibition of resonance. The subsequent cyclisation reaction, which calls for the addition of a benzyl radical to the carbon atom in a carbonyl function to yield an oxy-radical, might occasion surprise but could well be feasible considering the driving forces at hand to facilitate the reaction, namely (a) the gain in resonance energy through attainment of a large measure of coplanarity of the benzene rings, (b) a favourable polar effect, which would be expected to operate in the addition of the nucleophilic benzyl radical to the positive end of a polarised system, and (c) steric assistance accruing from the favourable disposition of the reacting centres.

In support of the postulated reaction a few analogies are available. The radical (XXXII) derived from isophorone oxide has been found to react as the enol-oxy-radical (XXXIII),¹⁰ and can therefore be regarded as a vinylogue of the benzyl radical (XXIX). Similarly, the ring opening and closure, involving in the latter process the addition of an alkyl radical to the carbon atom in an aldehyde group, postulated as intermediate steps in the epimerisation of the oxy-radical (XXXIV) derived from the steroid alcohol, 3 β ,20 β -diacetoxy-11 β -hydroxy-5 α -pregnane¹¹ may also be considered, in certain respects, an

¹⁰ Reusch and Johnson, *J. Amer. Chem. Soc.*, 1962, **84**, 1759.

¹¹ Hensler, Kalvoda, Anner, and Wettstein, *Helv. Chim. Acta*, 1963, **46**, 352.

analogy. Again, the addition of benzyl radicals (from substituted toluenes and t-butoxy-radicals) to maleic anhydride¹² can also be looked upon as an analogous process in that, in either case, the benzyl radical adds, as a nucleophilic radical, to the positive end of a polarised double bond. Further study of this type of addition reaction seems worthwhile.



It is of interest to note that the steric control of resonance, which occurs in the radicals derived from phthalan and naphthalan, has also been observed in the anionic rearrangement of these ethers. In the reaction with potassium amide in liquid ammonia, it has been found that, whilst diphenan rearranges extensively to 9,10-dihydro-9-phenanthrol (90% yield), and dibenzyl ether gives 1,2-diphenylethanol (55% yield), phthalan and naphthalan are entirely unaffected.¹³ Since the reaction probably proceeds by a mechanism similar to that operative in the Wittig rearrangement,¹⁴ namely, the intermediate formation of an ion-pair followed by addition of the anion to the "incipient" carbonyl group, the failure of phthalan and naphthalan to undergo the reaction is expected. The anions (XXXV) and (XXXVI) which would be derived from these substances would, as in the radicals described above, be subject to steric suppression of resonance, and their formation is therefore not favoured.

EXPERIMENTAL

Melting points were taken on a Kofler micro hot-stage apparatus. Infrared spectra were determined with a Hilger H800 spectrophotometer. Microanalyses are by Dr. W. Zimmerman (Melbourne) and Mrs. H. K. Tong (Singapore). Light petroleum had b. p. 60–80°, and alumina was neutral and activated (Merck).

General Procedure.—The ether (1 mole) and di-t-butyl peroxide (approx. 0.2 mole) were sealed under nitrogen in a Carius tube and heated at 120–125° for 22 hr. The volatile products were removed by distillation under a partial vacuum, and the other products worked up by standard methods. Since in almost all cases there was unchanged peroxide, and quantitative isolation of this in presence of large quantities of other materials presented difficulty, only relative yields of products (including polymers) are recorded.

cis-Stilbene Oxide.—The reaction mixture from *cis*-stilbene oxide¹⁵ (11.0 g., 56 mmoles) and di-t-butyl peroxide (1.5 g., 10.3 mmoles) was transferred quantitatively into a distillation flask with the aid of carbon tetrachloride (10 ml.), and the volatile products distilled at 30–50° (bath)/2 mm. into two receivers connected in series and cooled at –80° (acetone–solid carbon dioxide). Quantitative analysis of the distillate by infrared spectroscopy¹⁶ indicated the presence of di-t-butyl peroxide (6.0 mmoles, 58% recovery), t-butyl alcohol (6.9 mmoles), and acetone (1.4 mmoles), giving 4.7 : 1 for the ratio alcohol : acetone. The residue from the distillation was heated with methanol (3 × 20 ml.), and the colourless solid which remained undissolved collected by filtration, m. p. 254–257° (0.49 g.). This was *meso*- $\alpha\alpha'$ -dibenzoylbibenzyl (m. p. and mixed m. p., and comparison of infrared absorption with a sample obtained from deoxybenzoin as described below). The filtrate, on cooling, deposited a mixture of solids, m. p. 30–60° (8.4 g.). This was collected, and the mother-liquor was concentrated and chilled, to give *cis*-stilbene oxide, m. p. and mixed m. p. 36–38° (0.5 g.). A portion (2.0 g.) of the above solid mixture was adsorbed on alumina (150 g.) and eluted with light petroleum–benzene, giving (i) unreacted *cis*-stilbene oxide (1.5 g.), (ii) a colourless compound, m. p. 158–160 (0.11 g.) shown to be racemic $\alpha\alpha'$ -dibenzoylbibenzyl by m. p. and mixed m. p. and by comparison of

¹² Shechter and Barker, *J. Org. Chem.*, 1956, **21**, 1473.

¹³ Weinheimer, Kantor, and Hauser, *J. Org. Chem.*, 1953, **18**, 801.

¹⁴ Schöllkopf and Walter, *Angew. Chem.*, 1961, **73**, 545.

¹⁵ Cope, Trumbull, and Trumbull, *J. Amer. Chem. Soc.*, 1958, **80**, 2844.

¹⁶ Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

infrared spectrum with a sample obtained from deoxybenzoin, and (iii) *meso*- $\alpha\alpha'$ -dibenzoylbibenzyl (~10 mg.). Based on 42% decomposition of the di-*t*-butyl peroxide, the yields of the *meso*- and racemic dimers are 32 and 27%, respectively.

Pure *cis*-stilbene oxide, after being heated alone under identical conditions, was recovered unchanged (m. p. and infrared absorption).

trans-Stilbene Oxide.—The reaction product from *trans*-stilbene oxide¹⁵ (10.3 g., 53 mmoles) and di-*t*-butyl peroxide (1.0 g., 6.9 mmoles) was dissolved in hot methanol (100 ml.) and filtered to remove yellow resinous material (0.24 g.). The filtrate on cooling deposited *trans*-stilbene oxide (6.8 g.) which was filtered off. The filtrate was concentrated to an oily residue (2 g.) which was chromatographed on alumina (120 g.), giving (i) a further quantity of *trans*-stilbene oxide (1.1 g.) and (ii) *meso*- $\alpha\alpha'$ -dibenzoylbibenzyl, m. p. 255–257° (0.1 g.), identified as described earlier. The ratio of *t*-butyl alcohol to acetone, determined as above, was 0.77 : 1.

trans-Stilbene oxide, after being heated alone under the same conditions, was totally recovered (m. p. and infrared).

Deoxybenzoin.—Deoxybenzoin (10.5 g., 53.6 mmoles) and di-*t*-butyl peroxide (1.5 g., 10.3 mmoles) were heated, and the volatile products isolated as described above. Quantitative analysis by infrared spectroscopy indicated the presence of acetone (2.4 mmoles), *t*-butyl alcohol (4.2 mmoles), and di-*t*-butyl peroxide (4.0 mmoles). The residue after distillation was treated with hot methanol (3 \times 30 ml.), and the insoluble material (0.48 g.) filtered off and recrystallised from benzene, giving *meso*- $\alpha\alpha'$ -dibenzoylbibenzyl as needles, m. p. 255–257° (lit.,¹⁷ 254–255°). The filtrate was concentrated, and gave a solid residue (9.8 g.), a portion (2.0 g.) of which was chromatographed on alumina (150 g.). Elution with light petroleum–benzene followed by benzene afforded (i) unreacted deoxybenzoin (1.8 g.) and (ii) racemic $\alpha\alpha'$ -dibenzoylbibenzyl (45 mg.), prisms, m. p. 160–162° (from ethanol) (lit.,¹⁷ 161°). No tarry material was formed.

Phthalan.—The reaction mixture from phthalan¹³ (16.3 g., 136 mmoles) and di-*t*-butyl peroxide (1.8 g., 12.3 mmoles) was distilled to remove unreacted phthalan (b. p. ~52°/0.2 mm., 13.5 g.), and the solid residue (1.5 g.) dissolved in light petroleum–benzene and adsorbed on alumina (120 g.). Elution with the same solvent mixture gave (i) phthalan (0.3 g.) (infrared spectrum), (ii) *iso*-*bis*phthalan (0.15 g.), m. p. 102–104°, plates from aqueous methanol, ν_{\max} (CCl₄) 1078, 1048, 726 cm.⁻¹ [Found: C, 80.3; H, 6.1%; *M* (Rast), 242. C₁₆H₁₄O₂ requires C, 80.6; H, 5.9%; *M*, 238], (iii) *bis*phthalan, m. p. 127–129° (decomp.) (0.34 g.), needles from aqueous methanol, ν_{\max} (CCl₄) 1067, 1048, 728, 717 cm.⁻¹ [Found: C, 80.6; H, 6.2%; *M* (Rast), 232], and (iv) phthalide, m. p. and mixed m. p. 72–73° (0.3 g.). In contact with air, solutions of both the above dimers in petroleum deposited phthalide after *ca.* 12 hr.

o-Tolualdehyde.—*o*-Tolualdehyde (35 g., 292 mmoles) and di-*t*-butyl peroxide (2.6 g., 17.8 mmoles) were heated in the usual manner for 32 hr. The mixture was dissolved in peroxide-free ether (200 ml.) and extracted with saturated aqueous sodium hydrogen carbonate. Acidification of this extract gave *o*-toluic acid (0.26 g.), m. p. and mixed m. p. 103–105°. Concentration of the ether solution deposited *iso*- $\alpha\alpha'$ -*di*-(2-methylbenzoyloxy)-2,2'-*dimethyl*bibenzyl (1.3 g.), which was filtered off and washed with light petroleum (3 \times 15 ml.), m. p. 164–171°, and further purified by chromatography on alumina in benzene, giving a product (90% recovery), m. p. 173–174°, which crystallised in needles from benzene–ethanol, ν_{\max} (CCl₄) 1728, 1251, 1071, 729 cm.⁻¹ [Found: C, 80.5; H, 6.6%; *M* (Rast), 421. C₂₁H₃₀O₄ requires C, 80.3; H, 6.3%; *M*, 479]. The filtrate was concentrated, and distilled under nitrogen, giving unreacted *o*-tolualdehyde (26 g.; b. p. 64–66°/0.2 mm.) and a partially solid residue. The latter was separated by trituration with light petroleum into (a) a solid component (0.8 g.) whose m. p. (125–143°) and infrared spectrum indicated that it was a mixture of the isomeric $\alpha\alpha'$ -*di*-(2-methylbenzoyloxy)-2,2'-*dimethyl*bibenzyls, and (b) an oil (4 g.) which on chromatography on alumina (300 g.), yielded (i) *o*-tolualdehyde (0.4 g.), (ii) *t*-butyl *o*-toluate, b. p. 80–100°(bath)/0.2 mm. (0.2 g.), ν_{\max} (CCl₄) 1711, 1387, 1380sh, 1365, 727 cm.⁻¹ (Found: C, 75.2; H, 8.5. C₁₂H₁₆O₂ requires C, 75.0; H, 8.4%), (iii) $\alpha\alpha'$ -*di*-(2-methylbenzoyloxy)-2,2'-*dimethyl*bibenzyl (0.45 g.), m. p. 155–157°, plates from ethanol, ν_{\max} (CCl₄) 1728, 1256, 1071, 975, 729 cm.⁻¹ [Found: C, 80.5; H, 6.5%; *M* (Rast), 435], (iv) a mixture of the above isomeric bibenzyls, m. p. 139–170° (1.0 g.), (v) the *iso*-bibenzyl, m. p. 173–174° (0.2 g.), (vi) the keto-ester (XXII) (0.6 g.), m. p. 85–86° (from aqueous methanol), ν_{\max} (CCl₄) 1721bs, 1246, 1079, 964, 945, 913, 729 cm.⁻¹

¹⁷ Knoevenagel, *Ber.*, 1888, **21**, 1358.

[Found: C, 80.5; H, 6.4%; *M* (Rast), 467]. $C_{40}H_{36}O_5$ requires C, 80.5; H, 6.1%; *M*, 596], and (vii) intractable oils (0.8 g.) with strong absorption at 1720 cm^{-1} .

The products are thus the substituted bibenzyl (3.8 g., 32 mmoles), toluic acid (0.26 g.), *t*-butyl *o*-toluate (0.2 g.), the keto-ester (XXII) (0.6 g.), and intractable oils (0.8 g.).

Hydrolysis of Iso- α '-di-(2-methylbenzoyloxy)-2,2'-dimethylbibenzyl.—The bibenzyl (0.4 g.) methanol (35 ml.) and aqueous potassium hydroxide (20%; 35 ml.) were heated under reflux for 26 hr. After removal of methanol and dilution with water, ether extraction gave *iso*-2,2'-dimethylhydrobenzoin (0.2 g.), m. p. 105—106°, needles from light petroleum, ν_{max} (Nujol) 3350, 787, 763, 750, 729 cm^{-1} (Found: C, 79.7; H, 7.7. $C_{16}H_{18}O_2$ requires C, 79.3; H, 7.5%). Acidification of the aqueous layer gave *o*-toluic acid, m. p. and mixed m. p. 103—105° (0.19 g.).

Hydrolysis of α '-Di-(2-methylbenzoyloxy)-2,2'-dimethylbibenzyl.—Under similar conditions (36 hr.) the bibenzyl (0.38 g.) gave 2,2'-dimethylhydrobenzoin (0.17 g.), m. p. 117—119°, needles from light petroleum, ν_{max} (Nujol) 3445, 3275, 791, 759, 726 cm^{-1} (Found: C, 79.5; H, 7.7%), and *o*-toluic acid (0.1 g.), m. p. and mixed m. p. 104—105°.

Periodic Acid Oxidation.—*iso*-2,2'-Dimethylhydrobenzoin (96 mg.), methanol (3 ml.), and aqueous potassium periodate (0.1 g. in 15 ml.) were allowed to stand at room temperature (27°) for 24 hr. Dilution with water and ether extraction gave *o*-tolualdehyde (89 mg.) identified by its infrared spectrum. Similar cleavage of 2,2'-dimethylhydrobenzoic (75 mg.) also gave *o*-tolualdehyde (66 mg.).

Hydrolysis of the Keto-ester (XXII).—The keto-ester (0.45 g.), methanol (40 ml.), and aqueous potassium hydroxide (20%; 40 ml.) were heated under reflux in an atmosphere of nitrogen for 30 hr. After removal of methanol, acidification and isolation with ether afforded a solid product, m. p. 90—135°. Extraction of the mixture with boiling light petroleum left a residue (95 mg.) which crystallised from benzene–light petroleum as needles, m. p. 158—160°, identified as 2,2'-dimethylbenzic acid by mixed m. p. and comparison of infrared spectrum with a sample prepared as described by Shacklett and Smith.¹⁸ The methyl ester, prepared by reaction with diazomethane, crystallised from aqueous methanol as plates, m. p. 81—82° (Found: C, 75.7; H, 6.7. $C_{17}H_{18}O_3$ requires C, 75.7; H, 6.7%). Concentration of the petroleum extracts gave *o*-toluic acid, m. p. and mixed m. p. 103—105° (280 mg.).

Naphthalan.—Naphthalan¹³ (8.0 g.; 47 mmoles) and di-*t*-butyl peroxide (2.0 g., 13.7 mmoles) were heated in the usual manner for 22 hr. After removal of volatile material under reduced pressure, a portion (3.1 g.) of the solid residue (8.0 g.) was chromatographed on alumina (150 g.). Elution with light petroleum–benzene gave (i) unreacted naphthalan (1.8 g.), and (ii) a mixture of solids (0.8 g.) from which was obtained by fractional crystallisation *iso*-bis-naphthalan (0.4 g.), m. p. 168—171°, plates from ethanol, ν_{max} ($CHCl_3$) 1085, 1070, 1055 cm^{-1} [Found: C, 85.0; H, 5.4%; *M* (Rast), 303. $C_{24}H_{18}O_2$ requires C, 85.2; H, 5.4%; *M*, 338], and *bis*naphthalan (80 mg.), m. p. 192—195°, rods from benzene–ethanol, ν_{max} ($CHCl_3$) 1086, 1068 cm^{-1} [Found: C, 84.9; H, 5.4%; *M* (Rast), 298]. Further elution with ether gave a brown gum (0.6 g.) which showed strong absorption at 1720 cm^{-1} . The lactone band of naphthalide is reported¹⁹ to be at 1727 cm^{-1} . Chloroform solutions of the two bisnaphthalans, on standing in contact with air for 12 hr., showed the same absorption at 1720 cm^{-1} .

Diphenan.—Diphenan¹³ (16 g., 82 mmoles) and di-*t*-butyl peroxide (2.5 g., 17 mmoles) were heated under nitrogen in a Carius tube at 120—125° for 27 hr. After removal of volatile material under reduced pressure, a portion (5.4 g.) of the dark brown viscous residue (17 g.) was chromatographed on alumina (180 g.). Elution with light petroleum and then benzene gave (i) phenanthrene (15 mg.), m. p. and mixed m. p. 99—100° (ii) unreacted diphenan (3.9 g.), and (iii) *bis*diphenan (45 mg.), m. p. 266—267°, needles from cyclohexane–ethanol, ν_{max} ($CHCl_3$) 1074, 1046 cm^{-1} (Found: C, 86.5; H, 5.6. $C_{28}H_{22}O_2$ requires C, 86.1; H, 5.7%). Elution with ether and with 5% methanol in ether gave a brown gum which on re-chromatography (alumina, 80 g.) gave (iv) the crossed dimer (XXVII) of diphenan and 9-dihydrophenanthrol (25 mg.), m. p. 240—242°, needles from light petroleum, ν_{max} ($CHCl_3$) 3235, 1116, 1054, 1038 cm^{-1} (Found: C, 86.4; H, 5.6. $C_{28}H_{22}O_2$ requires C, 86.1; H, 5.7%), (v) dihydrophenanthrol (320 mg.), m. p. 103—104° (from aqueous methanol), identified by dehydration to phenanthrene (mixed m. p. and infrared spectrum) and by elemental analysis (Found: C, 85.5; H, 6.4. Calc. for $C_{14}H_{12}O$: C, 85.7; H, 6.2%), and (vi) phenanthraquinone (10 mg.), identified by m. p. and mixed m. p. 205—207° and by comparison of infrared absorption with authentic material.

¹⁸ Shacklett and Smith, *J. Amer. Chem. Soc.*, 1953, **75**, 2654.

¹⁹ Corran and Whalley, *J.*, 1958, 4719.

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Another portion (4.8 g.) of the reaction mixture was extracted with 5% aqueous sodium hydroxide (2×50 ml.). On acidification, and extraction with ether, a brown gum (158 mg.) resulted, which on sublimation at $120\text{--}140^\circ(\text{bath})/0.1$ mm. afforded 9-phenanthrol (5 mg.), m. p. and mixed m. p. $153\text{--}155^\circ$.

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