

## Preparation and Photochemistry of Some Chlorine-substituted Derivatives of Deoxybenzoin and Bibenzyl

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A series of aryl *p*-chlorobenzyl ketones has been prepared and converted into the corresponding 1-aryl-2-*p*-chlorophenylethane derivatives (1). U.v. irradiation of two of the latter compounds (1a, b) in benzene results in replacement of the chlorine atom by a phenyl group, whereas other related compounds (1c, e, f) are stable. Irradiation of two isomeric chlorodeoxybenzoin (2a, b) gives the corresponding 1,2,3,4-tetra-arylbutane-1,4-diones (3).

OUR interest in the photochemistry of aromatic halogen compounds<sup>1-3</sup> arose from the discovery of the behaviour of the *p*-chlorobibenzyls (1a, b) which are converted on u.v. irradiation in benzene into the respective phenylated products (1c, d). In spite of previous intimations in the

literature that aromatic chloro-compounds are photochemically unreactive,<sup>4,5</sup> we have since shown that the

<sup>1</sup> G. E. Robinson and J. M. Vernon, *Chem. Comm.*, 1969, 977.  
<sup>2</sup> G. E. Robinson and J. M. Vernon, *J. Chem. Soc., (C)* 1970, 2586.

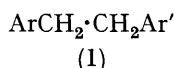
<sup>3</sup> G. E. Robinson and J. M. Vernon, *J. Chem. Soc. (C)*, 1971, 3363.

<sup>4</sup> W. D. Cohen, *Rec. Trav. chim.*, 1920, **39**, 243; H. Kobsa, *J. Org. Chem.*, 1962, **27**, 2293; E. J. Baum and J. N. Pitts, jun., *J. Phys. Chem.*, 1966, **70**, 2066; T. Matsuura and Y. Kitaura, *Bull. Chem. Soc. Japan*, 1968, **41**, 2483; T. Sato, S. Shimada, and K. Hata, *ibid.*, 1969, **42**, 766; other relevant literature is cited in ref. 3.

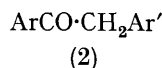
<sup>5</sup> R. K. Sharma and N. Kharasch, *Angew. Chem. Internat. Edn.*, 1968, **7**, 36.

replacement of chlorine by a phenyl substituent occurs quite generally for a variety of chlorobenzenes on irradiation in benzene. In some cases reductive dechlorination accompanies the phenylation reaction; some other compounds containing chlorine are more or less stable.

**Preparation of Materials.**—The deoxybenzoins (2a—f) were obtained by appropriate Friedel–Crafts acylation of chlorobenzene, benzene, biphenyl, and naphthalene; the last gave a mixture of (2e) and (2f) from which only the minor product, the  $\beta$ -isomer (2f), was separable in a pure state. Assignment of structure (2f) is based partly on the expectation of predominant formation of  $\alpha$ -naphthyl ketone, especially when the reaction is run in ethylene dichloride,<sup>6</sup> as well as on the singlet absorption ( $\tau$  1.45) in the n.m.r. spectrum of the minor product ascribed to the deshielded  $\alpha$ -hydrogen atom. A by-product from the preparation of (2a) had the composition  $C_{22}H_{17}ClO_2$ ; structure (2g) for this compound is consistent with its formation by further phenylacetylation of (2a), with its mass spectral fragmentation involving loss of benzyl and *p*-phenylacetylbenzyl groups from the molecular ion, and with the n.m.r. spectrum, which shows two singlet absorptions for benzylic methylene groups ( $\tau$  5.45 and 5.54) and the presence of four ring hydrogen atoms *ortho* to carbonyl groups.



- a; Ar = Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 b; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>; Ar' = Ph  
 c; Ar = *p*-Biphenyl; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 d; Ar = *p*-Biphenyl; Ar' = Ph  
 e; Ar =  $\alpha$ -Naphthyl; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 f; Ar =  $\beta$ -Naphthyl; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 g; Ar = Ar' = Ph



- a; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>; Ar' = Ph  
 b; Ar = Ph; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 c; Ar = *p*-Biphenyl; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 d; Ar = *p*-Biphenyl; Ar' = Ph  
 e; Ar =  $\alpha$ -Naphthyl; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 f; Ar =  $\beta$ -Naphthyl; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 g; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>; Ar' = *p*-PhCH<sub>2</sub>COC<sub>6</sub>H<sub>4</sub>

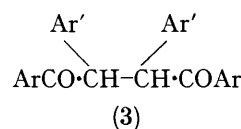
Wolff–Kishner reduction of the ketones (2b—f) gave the corresponding bibenzyl derivatives (1b—f), of which the  $\alpha$ -naphthyl compound (1e) was separated from a mixture of isomers, (1e) and (1f). The biphenyl derivatives (1c, d) were required for comparison with the irradiation products from (1a, b), and the naphthalene derivatives (1e, f) to test an explanation suggested for the stability of (1c). All new compounds were adequately characterised by elemental analysis, and by n.m.r. and mass spectral data. In both compounds (1c) and (2c) the biphenyl group must be substituted in the *para*-position by analogy with the formation of (2d)

and because the synthetic sample of (1c) was identical with the photochemical phenylation product from (1a).

**Irradiation of Bibenzyl Derivatives.**—When *p*-chlorobibenzyl (1b) in benzene was irradiated with a mercury-arc lamp until only a trace of (1b) remained, the products were *p*-phenylbibenzyl (1d) (62.5%) and bibenzyl (1g) (4.2%). This occurrence of phenylation and reduction processes is typical of the behaviour of other chlorobenzene derivatives.<sup>3</sup> *p,p'*-Dichlorobibenzyl (1a) behaved similarly, except that only one chlorine atom was replaced: the reaction mixture contained *p*-chloro-*p'*-phenylbibenzyl (1c) (54.5%) and *p*-phenylbibenzyl (1d) (2.5%) together with traces of (1a, b, and g). The minor product (1d) in the latter case must arise by the reduction–phenylation sequence, (1a)  $\rightarrow$  (1b)  $\rightarrow$  (1d), since the major product (1c) gave no (1d) on irradiation.

The stability of compound (1c) to irradiation may be compared to that of 4-chlorobiphenyl.<sup>1,7</sup> The chloro-compounds (1e, f) are similarly stable to irradiation in benzene, as is also  $\alpha$ -chloronaphthalene.<sup>3,8</sup> We ascribe the photochemical inertness of (1c, e, and f) to an intramolecular quenching effect, whereby the energy of the lowest excited state, determined by the more conjugated biphenyl or naphthalene chromophore, is insufficient to achieve homolysis of the carbon–chlorine bond (*cf.* 4-*p*-chlorobenzylbiphenyl<sup>2</sup>).

**Irradiation of Chlorodeoxybenzoins.**—Chlorodeoxybenzoins (2a, b) were both decomposed on irradiation in benzene, but no products of phenylation or reduction were detected like those obtained from other chlorobenzene derivatives.<sup>3</sup> Instead the corresponding dimers (3a, b) were isolated in very low yield; the molecular formula  $C_{28}H_{20}Cl_2O_2$  for both isomers was established by accurate mass measurements of the molecular ions, and the structure assignments are consistent with n.m.r. and mass spectral data (see Experimental section). Additionally benzaldehyde and



- a; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>; Ar' = Ph  
 b; Ar = Ph; Ar' = *p*-ClC<sub>6</sub>H<sub>4</sub>  
 c; Ar = Ar' = Ph

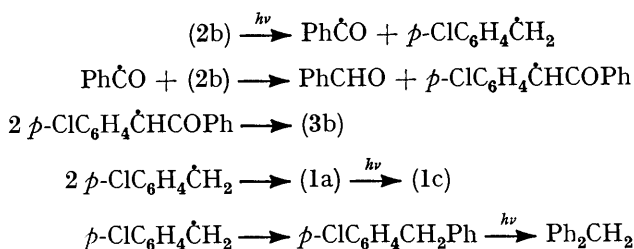
small amounts of biphenyl, diphenylmethane, and *p*-chlorodiphenylmethane were recognised in the reaction mixture from (2b) by g.l.c. and mass spectroscopic comparisons with authentic materials, and *p*-chloro-*p'*-phenylbibenzyl (1c) was isolated by column chromatography. The formation of these products can be accounted for by the following reaction scheme, which is analogous to that already proposed<sup>9</sup> for the photolysis of deoxybenzoin to benzaldehyde, bibenzyl (1g), and  $\alpha\alpha'$ -dibenzoylbibenzyl (3c).

<sup>8</sup> W. A. Henderson, jun., R. Lopresti, and A. Zweig, *J. Amer. Chem. Soc.*, 1969, **91**, 6049.

<sup>9</sup> J. Kenyon, A. R. A. A. Rassoul, and G. Soliman, *J. Chem. Soc.*, 1956, 1774.

<sup>6</sup> G. Baddeley, *J. Chem. Soc.*, 1949, S99.

<sup>7</sup> N. Kharasch, R. K. Sharma, and H. B. Lewis, *Chem. Comm.*, 1966, 418.



Biphenyl may arise by decarbonylation of benzoyl radicals, and reaction of phenyl radicals so produced with solvent. Similarly in the reaction mixture from (2a) were found trace amounts of diphenylmethane, bibenzyl (1g), 4-chlorobiphenyl, and dichlorobiphenyl. The formation of these products can be attributed to secondary reactions of benzyl and *p*-chlorobenzoyl radicals from photochemical cleavage of (2a). The primary photochemical process with dibenzyl ketone is a similar cleavage, followed by decarbonylation, and recombination of benzyl radicals to give bibenzyl (1g).<sup>10</sup>

#### EXPERIMENTAL

I.r. spectra of solids were recorded for Nujol mulls on a Pye Unicam SP200 spectrophotometer. <sup>1</sup>H N.m.r. spectra were measured at 60 MHz with tetramethylsilane as internal standard using a Perkin-Elmer R10 instrument. Low-resolution mass spectra were recorded on an A.E.I. M.S.12 operating at 70 eV, with a direct insertion probe and with facility for rapid scanning of g.l.c. peaks. High resolution mass spectral measurements were performed at the Physico-Chemical Measurements Unit, Aldermaston. G.l.c. analyses were on a Pye Series 104 chromatograph, using a 1.5 m × 4 mm column containing silicone gum rubber SE 30 as stationary phase supported on Celite at 200–250°. Alumina used for chromatography was Laporte type H. Light petroleum was the fraction b.p. 60–80°.

Phenylacetyl chloride was obtained as described<sup>11</sup> from the acid and phosphorus trichloride, and used without further purification. *p*-Chlorophenylacetic acid, m.p. 102–104° (lit.,<sup>12</sup> 105°), was prepared from *p*-chlorobenzyl chloride *via* conversion into the nitrile<sup>12</sup> and hydrolysis of the latter; the acid and thionyl chloride gave *p*-chlorophenylacetyl chloride (96%), b.p. 118–120°/7 mm, which was distilled before use.

*Preparation of Deoxybenzoin Derivatives (2a–d and g).*—The reaction between phenylacetyl chloride and chlorobenzene with aluminium chloride afforded benzyl *p*-chlorophenyl ketone (2a) (26%), m.p. 103–105° (from aqueous ethanol) (lit.,<sup>13</sup> 107.5°),  $\nu_{\text{max}}$  1686s cm<sup>-1</sup> (C=O stretch);  $\tau$  (CDCl<sub>3</sub>) 2.04 (2H, d,  $J_{2,3}$  8.7 Hz, ArH *ortho* to CO), 2.59 (2H, d, ArH *meta* to CO), 2.71 (5H, s, benzyl ArH), and 5.78 (2H, s, CH<sub>2</sub>);  $m/e$  230/232  $M^+$  7/2%, 139/141 (100/33,  $p\text{-ClC}_6\text{H}_4\text{CO}^+$ ), 111/113 (24/8,  $p\text{-ClC}_6\text{H}_4^+$ ), and 91 (13),  $m^*$  88.5 (139 → 111) and 84 (230 → 139). In a separate experiment using carbon disulphide as solvent,<sup>14</sup> the residue after distillation of the main product (2a) *in vacuo* was triturated with ether and recrystallised to yield *p*-chlorophenyl *p*-(phenylacetyl)benzyl ketone (2g) (0.4%), as prisms,

<sup>10</sup> G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlich, *Tetrahedron Letters*, 1963, 1863; P. S. Engel, *J. Amer. Chem. Soc.*, 1970, **92**, 6074; W. K. Robbins and R. H. Eastman, *ibid.*, pp. 6076, 6077.

<sup>11</sup> C. F. H. Allen and W. E. Barker, *Org. Synth.*, 1943, Coll. Vol. II, 156.

m.p. 172–175° (from ethanol–chloroform) (Found: C, 75.7; H, 5.0. C<sub>22</sub>H<sub>17</sub>ClO<sub>2</sub> requires C, 75.8; H, 4.9%),  $\nu_{\text{max}}$  1686s (C=O stretch), 1341, 1000, 830, 804, 747, 732, and 707 cm<sup>-1</sup> (Ar–H bend);  $\tau$  (CF<sub>3</sub>CO<sub>2</sub>H) 1.81 and 1.89 (4H two overlapping doublets, ArH *ortho* to CO), 2.24–2.94 (9H, m, ArH), 5.45 (2H, s, CH<sub>2</sub>), and 5.54 (2H, s, CH<sub>2</sub>),  $m/e$  348/350  $M^+$  1.9/0.6%, 257/259 (100/34,  $M - \text{PhCH}_2$ ), 139/141 (63/21,  $p\text{-ClC}_6\text{H}_4\text{CO}^+$ ), 111/113 (17/6,  $p\text{-ClC}_6\text{H}_4^+$ ), 91 (13), and 90 (10),  $m^*$  88.5 (139 → 111) and 75 (257 → 139).

A mixture of *p*-chlorophenylacetyl chloride, benzene, and aluminium chloride was heated under reflux for 6 h, then worked up to give *p*-chlorobenzyl phenyl ketone (2b) (66%), m.p. 134–135° (from ethanol) (lit.,<sup>15</sup> 133°),  $\nu_{\text{max}}$  1681 cm<sup>-1</sup> (C=O stretch);  $\tau$  (CDCl<sub>3</sub>) 1.87–2.19 (2H, m, ArH *ortho* to CO), 2.46–3.03 (7H, m, ArH), and 5.89 (2H, s, CH<sub>2</sub>);  $m/e$  230/232  $M^+$  4/1.3%, 125/127 (6/2,  $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$ ), 105 (100, PhCO<sup>+</sup>), and 77 (31),  $m^*$  56.5 (105 → 77).

A mixture of *p*-chlorophenylacetyl chloride, biphenyl, and aluminium chloride in carbon disulphide was heated under reflux for 4 h, and then worked up to give *p*-bi-phenyl *p*-chlorobenzyl ketone (2c) (25%) as needles, m.p. 192–194° (from ethanol–benzene) (Found: C, 78.3; H, 5.0. C<sub>20</sub>H<sub>15</sub>ClO requires C, 78.3; H, 4.9%),  $\nu_{\text{max}}$  1677s (C=O stretch), 1603, 1502, 1345, 1209 (benzene ring), 1100, 1031, 1010, 857, 830, 809, 778, 761, 735, and 702 cm<sup>-1</sup> (Ar–H bend);  $m/e$  306/308  $M^+$  3/1%, 181 (100,  $p\text{-PhC}_6\text{H}_4\text{CO}^+$ ), 153 (16), and 152 (26),  $m^*$  129 (181 → 153).

A mixture of phenylacetyl chloride, biphenyl, and aluminium chloride in carbon disulphide was heated under reflux for 1.5 h, and then worked up to give benzyl *p*-biphenyl ketone (2d) (19%), m.p. 148–150° (from ethanol–benzene) (lit.,<sup>16</sup> 150°),  $\nu_{\text{max}}$  1679s cm<sup>-1</sup> (C=O stretch);  $\tau$  (CDCl<sub>3</sub>) 1.91 (2H, d,  $J_{2,3}$  8.2 Hz, ArH *ortho* to CO), 2.22–2.84 (12H, m, ArH), and 5.75 (2H, s, CH<sub>2</sub>);  $m/e$  272  $M^+$  5%, 181 (100,  $p\text{-PhC}_6\text{H}_4\text{CO}^+$ ), 153 (18), 152 (28), and 91 (8),  $m^*$  129 (181 → 153).

*Preparation of p-Chlorobenzyl Naphthyl Ketones (2e and f).*—(i) Powdered anhydrous aluminium chloride (13.1 g) was added to naphthalene (11.2 g) and *p*-chlorophenylacetyl chloride (16.6 g) dissolved in carbon disulphide (40 ml). The mixture was heated 1 h under reflux, when it blackened and evolved hydrogen chloride. The resulting complex was decomposed with crushed ice and concentrated hydrochloric acid, and the product was extracted into benzene. The extract was washed with aqueous sodium carbonate, then with water, and dried (MgSO<sub>4</sub>). Evaporation gave a tarry solid which was chromatographed on alumina (300 ml). Elution with light petroleum–benzene (1:1 v/v) gave a buff-coloured solid which on recrystallisation afforded *p*-chlorobenzyl  $\beta$ -naphthyl ketone (2f) (4.5 g, 18%), m.p. 133–135° (from ethanol–benzene) (Found: C, 76.7; H, 4.8. C<sub>18</sub>H<sub>13</sub>ClO requires C, 77.0; H, 4.6%),  $\nu_{\text{max}}$  1676s (C=O stretch), 1099, 1025, 843, 835, 820, 776, 764, and 758 cm<sup>-1</sup> (Ar–H bend);  $\tau$  (CDCl<sub>3</sub>) 1.45br (1H, s,  $\alpha$ -H *ortho* to CO), 1.74–2.60 (6H, m, naphthyl ArH), 2.73 (4H, s, phenyl ArH), and 5.66 (2H, s, CH<sub>2</sub>);  $m/e$  155 C<sub>10</sub>H<sub>7</sub>CO<sup>+</sup>, 100%, 127 (71, C<sub>10</sub>H<sub>7</sub><sup>+</sup>), 126 (11), and 125 (6),  $m^*$  104

<sup>12</sup> R. von Walther and A. Wetzlich, *J. prakt. Chem.* [2], 1900, **61**, 169.

<sup>13</sup> S. S. Jenkins and E. M. Richardson, *J. Amer. Chem. Soc.*, 1933, **55**, 1618.

<sup>14</sup> N. P. Buu-Hoi and R. Royer, *Rec. Trav. chim.*, 1946, **65**, 251.

<sup>15</sup> P. Petrenko-Kritschenko, *Ber.*, 1892, **25**, 2239.

<sup>16</sup> V. Pápcke, *Ber.*, 1888, **21**, 1339.

(155  $\rightarrow$  127). After concentration of the mother liquor from recrystallisation, a further quantity of buff solid (2.8 g), m.p. 70—82°, was obtained. G.l.c. analysis of this material showed it to be a mixture of the  $\beta$ -naphthyl ketone (2f) with a major, more volatile component, presumably the  $\alpha$ -naphthyl isomer (2e). The n.m.r. spectrum of this mixture exhibited the two corresponding  $\text{CH}_2$  resonances at  $\tau$  5.66 ( $\beta$ -isomer) and 5.71 ( $\alpha$ -isomer) in intensity ratio *ca.* 1:4 in agreement with g.l.c. analysis. Several attempts at fractional crystallisation and sublimation *in vacuo* failed to separate the  $\alpha$ -naphthyl ketone (2e).

(ii) The above reaction was repeated at room temperature in ethylene dichloride as solvent, and worked up as before. The crude product (68%) obtained by evaporation of the benzene extract was a buff solid which did not require purification by chromatography. Its n.m.r. spectrum and g.l.c. analysis indicated a mixture of  $\alpha$ - and  $\beta$ -naphthyl ketones (2e and f) (*ca.* 2:1). Several recrystallisations from ethanol afforded the ketone (2f) (10%), m.p. 133—135°, identical with the sample obtained above.

**Preparation of Bibenzyl Derivatives (1a—f).**—*p,p'*-Dichlorobibenzyl (1a) was prepared by the reaction of *p*-chlorobenzylmagnesium chloride and *p*-chlorobenzyl chloride in refluxing ether; it had m.p. 98—100° (from light petroleum) (lit.,<sup>17</sup> 100°),  $\tau$  ( $\text{CDCl}_3$ ) 2.71 (4H, d,  $J_{2,3}$  8.7 Hz, ArH *ortho* to Cl), 2.95 (4H, d, ArH *meta* to Cl), and 7.17 (4H, s,  $2\text{CH}_2$ ); *m/e* 250/252/254  $M^+$  13/9/1.5%, 125/127 (100/33,  $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$ ).

Other bibenzyl derivatives were obtained by the Huang-Minlon modification<sup>18</sup> (using potassium hydroxide and hydrazine hydrate in diethylene glycol) of the Wolff-Kishner method of reduction of the corresponding ketones as follows: *p*-chlorobibenzyl (1b) (62%) from ketone (2b), m.p. 48—49° (from light petroleum) (lit.,<sup>19</sup> 49°),  $\tau$  ( $\text{CDCl}_3$ ) 2.62—3.10 (9H, m, ArH) and 7.12 (4H, s,  $2\text{CH}_2$ ); *m/e* 216/218  $M^+$  27/9%, 125/127 (62/20,  $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$ ), and 91 (100); *p-chloro-p'-phenylbibenzyl* (1c) (33%) from ketone (2c), isolated by chromatography of the crude product on alumina and elution with light petroleum-benzene (4:1 v/v), m.p. 119—120° (from ethanol) [Found:  $M^+$  292.1018 (mass spectrum).  $\text{C}_{20}\text{H}_{17}^{35}\text{Cl}$  requires  $M^+$  292.1019. Found: C, 82.5; H, 6.0. Required C, 82.1; H, 5.8%;  $\nu_{\text{max}}$  1497, 1413, 1098, 1021 (benzene ring), 844, 769, and 697  $\text{cm}^{-1}$  (Ar-H bend),  $\tau$  ( $\text{CDCl}_3$ ) 2.30—3.08 (13H, m, ArH) and 7.16 (4H, s,  $2\text{CH}_2$ ); *m/e* 292/294  $M^+$  19/6%, 167 (100,  $p\text{-PhC}_6\text{H}_4\text{CH}_2^+$ ), 165 (13), 152 (6), and 125/127 (3/1,  $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$ ); *p-phenylbibenzyl* (1d) (20%) from ketone (2d), m.p. 106—108° (from ethanol-benzene) (lit.,<sup>20</sup> 106°);  $\tau$  ( $\text{CDCl}_3$ ) 2.18—2.87 (14H, m, ArH) and 7.06 (4H, s,  $2\text{CH}_2$ ), *m/e* 258  $M^+$  21%, 167 (100,  $p\text{-PhC}_6\text{H}_4\text{CH}_2^+$ ), and 165 (11),  $m^*$  108 (258  $\rightarrow$  167); 1-*p-chlorophenyl-2- $\alpha$ -naphthylethane* (1e) (4%) from a mixture (*ca.* 4:1) of isomeric ketones (2e and f), isolated by fractional crystallisation of the reaction product, which was a mixture of (1e and f), the  $\alpha$ -naphthyl compound (1e) had m.p. 100—102° (from light petroleum) [Found:  $M^+$  266.0863 (mass spectrum).  $\text{C}_{18}\text{H}_{15}^{35}\text{Cl}$  requires  $M^+$  266.0862. Found: C, 80.3; H, 5.9. Required: C, 81.0; H, 5.7%;  $\nu_{\text{max}}$  1498 (benzene ring), 1095, 1020, 830, 802, and 782  $\text{cm}^{-1}$  (Ar-H bend);  $\tau$  ( $\text{CDCl}_3$ ) 2.09—3.07 (11H, m, ArH) and 7.05 (4H, s,  $2\text{CH}_2$ ); *m/e* 266/268  $M^+$  14/5%, 141 (100,  $\alpha\text{-C}_{10}\text{H}_7\text{CH}_2^+$ ),

<sup>17</sup> R. C. Fuson and H. G. Cooke, *J. Amer. Chem. Soc.*, 1940, **62**, 1180.

<sup>18</sup> Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487; (*cf.* L. J. Durham, D. J. McLeod, and J. Cason, *Org. Synth.*, 1963, Coll. Vol. IV, 510).

125/127 (8/3,  $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$ ), and 115 (21),  $m^*$  94 (141  $\rightarrow$  115) and 75 (266  $\rightarrow$  141); 1-*p-chlorophenyl-2- $\beta$ -naphthylethane* (1f) (38%) from ketone (2f), rods, m.p. 107.5—108.5° (from light petroleum) (Found: C, 81.0; H, 5.7.  $\text{C}_{18}\text{H}_{15}\text{Cl}$  requires C, 81.0; H, 5.7%),  $\nu_{\text{max}}$  1500 (benzene ring), 1100, 1030, 845, and 765  $\text{cm}^{-1}$  (Ar-H bend);  $\tau$  ( $\text{CDCl}_3$ ) 2.10—3.08 (11H, m, ArH) and 7.07 (4H, s,  $2\text{CH}_2$ ); *m/e* 266/268  $M^+$  14/5%, 142 (12), 141 (100,  $\beta\text{-C}_{10}\text{H}_7\text{CH}_2^+$ ), 125/127 (11/4,  $p\text{-ClC}_6\text{H}_4\text{CH}_2^+$ ), and 115 (18),  $m^*$  94 (141  $\rightarrow$  115) and 75 (266  $\rightarrow$  141). Understandably the spectra of the two naphthalene derivatives (1e and f) were almost indistinguishable, but g.l.c. analysis showed that each compound was obtained free of the other isomer; a mixed m.p. was depressed.

**Photolysis of Bibenzyl Derivatives (1).**—Solutions (0.8—1.0  $\times 10^{-2}\text{M}$ ) of the following bibenzyl derivatives in benzene (Fison's AnalaR grade) were irradiated through quartz with Hanovia 15-W low-pressure or 100-W medium-pressure mercury-arc lamps under a nitrogen atmosphere. After 24 h the reaction mixtures were concentrated by rotary evaporation and analysed by g.l.c. Products were identified by mixed injection with authentic compounds; quantitative measurements were made by calibrating the flame ionisation detector response to authentic compounds, and by using bibenzyl (1g) or *p*-terphenyl as internal standard.

*p,p'*-Dichlorobibenzyl (1a) gave *p*-chloro-*p'*-phenylbibenzyl (1c) (54.5%), *p*-phenylbibenzyl (1d) (2.5%), and traces of *p*-chlorobibenzyl (1b) and bibenzyl (1g). *p*-Chlorobibenzyl (1b) gave *p*-phenylbibenzyl (1d) (62.5%) and bibenzyl (1g) (4.2%) with unchanged (1b) (0.2%). *p*-Chloro-*p'*-phenylbibenzyl (1c) and the *p*-chlorophenethylnaphthalene derivatives (1e and f) were stable to irradiation (>90%), and no new products were detected in the reaction mixtures.

**Photolysis of *p*-Chlorobenzyl Phenyl Ketone (2b).**—The ketone (2b) (5.0 g) in benzene (950 ml) was irradiated (Hanovia 500-W medium-pressure lamp) through quartz under bubbling nitrogen for 24 h, after which g.l.c. analysis showed the presence of benzaldehyde (6%) and unchanged (2b) (39%). The reaction mixture was evaporated, and the tarry residue chromatographed on alumina (300 ml), from which elution with light petroleum gave a yellow oil (250 mg) which solidified. G.l.c. analysis of this material showed the presence of biphenyl, diphenylmethane, *p*-chlorophenyl(phenyl)methane, ketone (2b), and *p*-chloro-*p'*-phenylbibenzyl (1c); recrystallisation from ethanol gave (1c) (3%), m.p. and mixed m.p. 118—119°. Further elution with light petroleum-benzene (4:1 v/v) recovered starting material (2b) (7%), m.p. and mixed m.p. 134—135°. Further elution with light petroleum-benzene (2:3 v/v) gave a brown solid, which was triturated with ether and recrystallised to give 2,3-*bis-p-chlorophenyl-1,4-diphenylbutane-1,4-dione* (3b) (63 mg, 1.3%), as needles, m.p. 223—225° (from ethanol-benzene, 2:1 v/v) [Found:  $M^+$  458.0838 (mass spectrum).  $\text{C}_{28}\text{H}_{20}^{35}\text{Cl}_2\text{O}_2$  requires  $M^+$  458.0840],  $\nu_{\text{max}}$  1665s (C=O stretch), 1500, 1300, 1027 (benzene ring), 818, 721, and 695  $\text{cm}^{-1}$  (Ar-H bend);  $\tau$  [( $\text{CD}_3$ )<sub>2</sub>CO] 1.69—2.02 (4H, m, ArH *ortho* to CO), 2.32—2.80 (14H, m, ArH), and 4.34 (2H, s, CH); *m/e* 458/460/462  $M^+$  1.9/1.4/0.3%, 353/355/357 (1.1/0.7/0.1.  $M$  — PhCO), 336/338/340 (1.8/1.2/0.2,  $M$  — PhCO — OH), 248/250/252

<sup>19</sup> F. Bergmann, J. Weizmann, and D. Schapiro, *J. Org. Chem.*, 1944, **9**, 408.

<sup>20</sup> N. P. Buu-Hoi and R. Royer, *Rec. Trav. chim.*, 1951, **70**, 825.

(2·2/1·3/0·3,  $M - 2\text{PhCO}$ ), 178 (4), 165 (2), 105 (100,  $\text{PhCO}^+$ ), and 77 (27),  $m^*$  272 (458  $\longrightarrow$  353) and 56·5 (105  $\longrightarrow$  77).

*Photolysis of Benzyl p-Chlorophenyl Ketone (2a).*—The ketone (2a) in benzene was irradiated under the same conditions as those described above; the reaction mixture was then evaporated and chromatographed as above for the isomer (2b). Elution with light petroleum gave a pale yellow oil (30 mg), which g.l.c. analysis showed to contain biphenyl, diphenylmethane, bibenzyl (1g), 4-chlorobiphenyl, and a dichlorobiphenyl (probably the 4,4'-isomer, mass spectrum  $m/e$  222/224/226  $M^+$  100/65/11%). Elution with light petroleum-benzene (7:3 v/v) gave initially a pale yellow pasty solid, which afforded 1,4-bis-p-chlorophenyl-2,3-diphenylbutane-1,4-dione (3a) (20 mg, 0·4%) as rods, m.p. 153—155° (from light petroleum) [Found:  $M^+$  458·0844 (mass spectrum).  $\text{C}_{28}\text{H}_{20}^{35}\text{Cl}_2\text{O}_2$  requires  $M^+$

458·0840],  $\nu_{\text{max}}$  1666s (C=O stretch), 1593, 1293, 1256, 1206, 1098, 1018 (benzene ring), 860, 843, 811, 748, 738, 715, and 702  $\text{cm}^{-1}$  (Ar-H bend);  $\tau$  [( $\text{CD}_3$ )<sub>2</sub>CO] 1·90 (4H, d,  $J_{2,3}$  8·5 Hz, ArH *ortho* to CO), 2·54 (4H, d, ArH *ortho* to Cl), 2·86 (10H, s, ArH), and 4·43 (2H, s, CH);  $m/e$  458/460/462  $M^+$  1·6/1·2/0·2%, 319/321 (3·8/1·3,  $M - p\text{-ClC}_6\text{H}_4\text{CO}$ ), 302/304 (11/4), 139/141 (100/32,  $p\text{-ClC}_6\text{H}_4\text{CO}^+$ ), 111/113 (17/6,  $p\text{-ClC}_6\text{H}_4^+$ ), 91 (13), and 90 (10),  $m^*$  222 (458  $\longrightarrow$  319) and 199 (458  $\longrightarrow$  302). Further elution with light petroleum-benzene gave a mixture (145 mg) and finally recovered starting material (2a) (153 mg, 3%), m.p. and mixed m.p. 102—104°. Elution with solvents of increasing polarity afforded only intractable tars.

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