

533. *The Electrolysis of Some o-Benzoylbenzoic Acids in Pyridine at 93°.*

By P. J. BUNYAN and D. H. HEY.

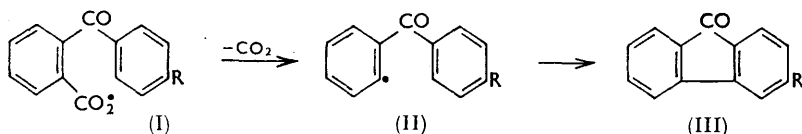
In the electrolysis of a series of five *o*-benzoylbenzoic acids at 93° in pyridine containing sodium methoxide and methanol the main neutral products were the benzophenone, the fluorenone, and the fluoren-9-ol. Under these conditions internuclear cyclisation is a general reaction.

In a previous communication<sup>1</sup> results were reported on the electrolysis of *o*-benzoylbenzoic acid and of four *para*-substituted *o*-benzoylbenzoic acids in methanol containing ~0.1 mol. of sodium methoxide at temperatures between 20° and 30°. It was considered that such reactions might give rise to *o*-benzoylphenyl radicals by decarboxylation and subsequently, by internuclear cyclisation, to fluorenones and/or fluoren-9-ols. The main products obtained in these reactions, however, were 3-arylphthalides and aryl methyl phthalates. In one case only was a fluorenone obtained, *o*-*p*'-bromobenzoylbenzoic acid giving 3-bromofluorenone; and with *o*-benzoylbenzoic acid a little fluoren-9-ol was isolated. The failure to obtain fluorenones or fluoren-9-ols as a general reaction is attributed to the comparatively low temperature of the reaction when the *o*-benzoylbenzoyloxy-radical initially formed is sufficiently stable to resist decarboxylation and to undergo rearrangement resulting in the formation of the mixed ester of phthalic acid. It was, therefore, decided to carry out the same electrolyses at a higher temperature. For this purpose methanol was replaced by a 21:4 v/v mixture of pyridine and methanol and the electrolyses were carried out at 93°.

Under these conditions the main neutral products consisted of the benzophenone, the fluorenone, and the fluoren-9-ol. Thus internuclear cyclisation is a general reaction. The current efficiency (40—50%) in these electrolyses was considerably higher than in the low-temperature electrolyses previously reported. The use of pyridine improves the

<sup>1</sup> Bunyan and Hey, *J.*, 1962, 324.

solvent properties of the medium and in general reduces the formation of polymers. It would thus appear that at the higher temperature the *o*-benzoylbenzoyloxy-radical (I)



initially formed at the anode loses carbon dioxide to give the *o*-benzoylphenyl radical (II), which (a) on intramolecular cyclisation gives the fluorenone (III) and by subsequent reduction the fluoren-9-ol, or (b) by hydrogen abstraction gives the benzophenone. The absence of the 3-arylphthalide is a probable consequence of the fact that the electrolyses are now conducted in an alkaline medium, since if *o*-carboxydiphenylmethanol is formed, the anion is likely to be discharged at the anode, giving rise directly to fluoren-9-ol by decarboxylation and intramolecular cyclisation.

The formation of fluorenones from *o*-benzoylphenyl radicals and cations, prepared from the diazonium salts of 2-aminobenzophenones, has already been reported.<sup>2</sup> Closely similar results have been obtained by Russell and Thomson<sup>3</sup> on oxidation of *o*-benzoylbenzoic acids with persulphate.

The yields of the neutral products obtained in the above reactions are summarised in Table I.

TABLE I.  
Electrolysis of benzoylbenzoic acids (0.1M) in pyridine at 93°. Yields of neutral products based on amount of acid not recovered.

Substituent at <i>p</i> -position	H	Cl	Br	Me	OMe
<i>p</i> -Substituted benzophenone (%)	6.4	14.6	—	12.5	13.0
3-Substituted fluorenone (%)	2.7	6.7	7.0	17.5	11.4
3-Substituted fluoren-9-ol (%)	6.3	5.5	1.6	2.2	2.5
Total cyclised products (%)	9.0	12.2	8.6	19.7	13.9

### EXPERIMENTAL

*Reagents and Apparatus.*—The *o*-benzoylbenzoic acids were prepared as previously described.<sup>1</sup> The apparatus used was identical with that previously described.<sup>1</sup> The cell, immersed in a thermostat-bath at 93°, was fitted with a reflux condenser.

*Electrolyses in Pyridine at 93°.*—*o*-Benzoylbenzoic acid. The acid (22.6 g., 0.1 mole) in pyridine (231 ml.) was introduced into the cell in a thermostat-bath at 93°, and methanol (44 ml.), in which sodium (0.23 g., 0.01 g.-atom) had been dissolved, was added with stirring. A constant potential of 120 v was maintained throughout the experiment. The current, initially 0.25 A, rapidly dropped to 0.16 A and then rose slowly to 0.17 A. The electrolysis was terminated after 30 hr. The internal temperature varied from 90° to 92° and the solution became dark red-brown. No solid was deposited. The electrolyte was transferred with methanol (75 ml.) to a distillation flask and methanol (115 ml.) (b. p. 65–67°/760 mm.) and pyridine (220 ml.) (b. p. 52–56°/50 mm.) were removed. The methanol fraction gave a slight precipitate on treatment with dimedone. The residue was extracted with boiling ether (5 × 200 ml.); during this operation a brown amorphous solid (A) (5.7 g.) separated. The combined ethereal extracts were washed successively with 2*N*-aqueous sodium hydroxide (10 × 20 ml.) and with water (3 × 50 ml.), and dried (MgSO<sub>4</sub>) (neutral extract B). To the solid residue A were added the combined alkaline washings, and subsequent filtration left a solid residue C (0.7 g.), which was washed successively with water, ethanol, and ether, and dried at 70° for 24 hr. Acidification of the ice-cold alkaline filtrate with hydrochloric acid precipitated a solid, which was collected, dried, boiled under reflux with chloroform (200 ml.)

<sup>2</sup> De Tar and Sagmanli, *J. Amer. Chem. Soc.*, 1950, **72**, 965; Hey and Mulley, *J.*, 1952, 2276; De Tar and Relyea, *J. Amer. Chem. Soc.*, 1954, **76**, 1680; De Tar and Whiteley, *ibid.*, 1957, **79**, 2498; De Tar, *Org. Reactions*, 1957, **9**, 409.

<sup>3</sup> Russell and Thomson, personal communication.

for 1 hr., and filtered. The residue after being dried at 70° for 24 hr. was a dark amorphous solid D (0.85 g.). The acid filtrate was also extracted with chloroform (5 × 20 ml.) and the dried (MgSO<sub>4</sub>) extracts were combined. Removal of the chloroform under reduced pressure left a brown oil, which was kept overnight with a saturated aqueous solution of sodium hydrogen carbonate (250 ml.). Phenols were extracted with chloroform (5 × 20 ml.) and the extracts were washed with water and dried (MgSO<sub>4</sub>). Acidification of the residual bicarbonate solution with hydrochloric acid liberated acids, which were also extracted with chloroform (5 × 20 ml.), washed, and dried (MgSO<sub>4</sub>). Removal of the chloroform under reduced pressure from the phenolic fraction gave a brown gum E (1.2 g.) while the acidic fraction left a brown gum (12.8 g.) from which boiling ethanol extracted *o*-benzoylbenzoic acid (3.9 g.), m. p. and mixed m. p. 121—126°, and left an insoluble residue weighing 8.9 g.

Removal of ether from the neutral extract B left a red oil, which on distillation gave, after the collection of pyridine and residual solvents, the following fractions: (i) a green mobile oil (2.23 g.), b. p. 82°/0.04 mm.; (ii) a yellow oil which partly solidified (2.04 g.), b. p. 108°/0.03 mm.; (iii) a yellowish brown oil (0.84 g.), b. p. 124°/0.05 mm.; and (iv) a thick red gum (0.43 g.), b. p. *ca.* 152°/0.04 mm. The residue weighed 0.885 g.

Fraction (i) was submitted to chromatography on active alumina. It was added in concentrated benzene solution and eluted successively with light petroleum (b. p. 40—60°) (1500 ml.), benzene (750 ml.), and finally ethanol (300 ml.). The light petroleum eluate gave benzophenone (0.885 g.) (infrared spectrum and 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 244—245°). The infrared spectrum of the product from the benzene eluate (1.22 g.) showed a peak at 1672 cm<sup>-1</sup> but no fluorenone could be identified. The product from the ethanol eluate (0.12 g.) was not identified.

Fraction (ii), on crystallisation from benzene–light petroleum (b. p. 80—100°) and then from water, gave fluoren-9-ol (0.73 g.), m. p. and mixed m. p. 158°; removal of the solvent from the mother-liquor left a residue (1.32 g.), which on chromatographic treatment as described above gave benzophenone (0.08 g.), fluorenone (0.35 g.) in yellow needles (from benzene–light petroleum), m. p. and mixed m. p. 83° (Found: C, 86.8; H, 4.4. Calc. for C<sub>13</sub>H<sub>8</sub>O: C, 86.6; H, 4.5%), and fluoren-9-ol (0.1 g.), m. p. and mixed m. p. 157—158° after crystallisation from water.

Fraction (iii) was also submitted to chromatography but the products could not be identified.

The following electrolyses were carried out on a 0.1M-scale, as described above for *o*-benzoylbenzoic acid, and the products were worked up in the same way. Details of the products isolated are summarised in Table 2.

*o*-*p'*-Chlorobenzoylbenzoic acid. The current, initially 0.14 A, rapidly dropped to 0.08 A and then rose slowly to 0.155 A during 48 hr.; then the electrolysis was terminated. The internal temperature remained at 90° and the solution developed a red colour. No solid was deposited but a small amount of a brown gum was deposited on the cathode. A slight precipitate was obtained when the recovered methanol was treated with dimedone. The following fractions were collected on distillation of the neutral fraction: (i) a pale green liquid (3.61 g.), b. p. 98—120°/0.02 mm.; (ii) a yellow oil, which solidified (3.00 g.), b. p. 120—142°/0.02 mm.; (iii) a viscous red oil (2.88 g.), b. p. 160°/0.02 mm.; (iv) a red gum (0.36 g.), b. p. *ca.* 180°/0.04 mm. The residue weighed 1.17 g. Fraction (i), on chromatography, gave 4-chlorobenzophenone (2.57 g.), m. p. and mixed m. p. after crystallisation from ethanol 74—75°, together with a yellow solid (0.34 g.) and a pale brown solid (0.35 g.). These two products (m. p. 134—140° and m. p. 150—156°) were combined with the corresponding products obtained from fraction (ii). Fraction (ii) crystallised from benzene–light petroleum, to give 3-chlorofluoren-9-ol in needles (0.32 g.), m. p. 167° (Found: C, 71.9; H, 4.4. C<sub>13</sub>H<sub>9</sub>ClO requires C, 72.0; H, 4.2%), which on oxidation with sodium dichromate in dilute acetic acid gave 3-chlorofluorenone, m. p. and mixed m. p. 159°.<sup>4</sup> The mother-liquor from the crystallisation of the 3-chlorofluoren-9-ol was submitted to chromatography on alumina, and elution with benzene (400 ml.) gave a yellow solid (0.83 g.), m. p. 134—140°, which was combined with the product, m. p. 134—140°, isolated as above from fraction (i). Recrystallisation from ethanol gave 3-chlorofluorenone (0.84 g.) in yellow needles, m. p. and mixed m. p. 159° (Found: C 72.6; H 3.3. Calc. for C<sub>13</sub>H<sub>7</sub>ClO: C, 72.7; H, 3.3%). A further quantity of 3-chlorofluoren-9-ol was obtained on elution with

<sup>4</sup> Heilbron, Hey, and Wilkinson, *J.*, 1938, 113.

ethanol (750 ml.) and this was added to the fraction of m. p. 150—156° isolated from fraction (i). Recrystallisation from benzene–light petroleum gave 3-chlorofluoren-9-ol, m. p. and mixed m. p. 167°. No products were isolated from fractions (iii) and (iv).

*o-p'-Bromobenzoylbenzoic acid.* The initial current was 0.18 A, which rapidly dropped to 0.13 A and then fell slowly to 0.03 A during 48 hr. The internal temperature was 88—90°. The solution became brown and some gum was deposited which was collected and dried at 70° (1.8 g.). No formaldehyde was found in the recovered methanol. Distillation of the neutral fraction gave: (i) a green oil which partially solidified (0.26 g.), b. p. ca. 97°/0.02 mm.; (ii) a yellow oil which solidified (1.50 g.), b. p. ca. 138°/0.02 mm.; (iii) a red gum (0.725 g.), b. p. 162°/0.01 mm. The residue weighed 0.54 g. Fraction (i), submitted to chromatography, gave from the light petroleum (b. p. 60—80°) eluate a white solid (0.06 g.), m. p. 40—50°, which was not identified, and a yellow solid (0.10 g.) identical with that from fraction (ii). Chromatographic treatment of fraction (ii) gave from the benzene (250 ml.) eluate a yellow solid (0.72 g.), which on admixture with the product from fraction (i) and crystallisation from ethanol gave 3-bromofluorenone (0.7 g.) in yellow needles, m. p. and mixed m. p. 163°.<sup>4</sup> Fraction (ii) also gave, on further elution with ethanol (500 ml.), a solid (0.19 g.), which on crystallisation from aqueous ethanol (charcoal) gave 3-bromofluoren-9-ol in needles, m. p. 172° (Found: C, 59.7; H, 3.9.  $C_{13}H_9BrO$  requires C, 59.8; H, 3.5%).

*o-p'-Toluoylbenzoic acid.* The initial current of 0.19 A rapidly dropped to 0.155 A and then rose slowly to 0.20 A during 26 hr. The internal temperature remained at 90°. The solution became deep red but no solid was deposited during the electrolysis. No formaldehyde was found in the recovered methanol. Distillation of the neutral fraction gave: (i) a yellow-green liquid (4.01 g.), b. p. 98°/0.01 mm.; (ii) a wine-coloured liquid (3.82 g.), b. p. ca. 138°/0.02 mm.; (iii) a yellow-red oil (0.32 g.), b. p. 164°/0.02 mm.; (iv) a red gum (0.39 g.), b. p. ca. 190°/0.02 mm. The residue weighed 0.89 g. Fraction (i), on chromatography and elution with light petroleum (b. p. 60—80°) (2500 ml.), gave a pale green oil (1.81 g.), which partially solidified and on recrystallisation from ether and then from aqueous ethanol gave 4-methylbenzophenone in needles, m. p. 55° (Found: C, 85.9; H, 6.0. Calc. for  $C_{14}H_{12}O$ : C, 85.7; H, 6.2%). Bruzau<sup>5</sup> recorded m. p. 55° for this ketone. The 2,4-dinitrophenylhydrazone had m. p. 203—204° after crystallisation from ethanol. Burton and Cheeseman<sup>6</sup> recorded m. p. 198—201°. Further elution with benzene (750 ml.) and then with ethanol (500 ml.) gave products (1.77 and 0.17 g.), which were combined with the analogous products obtained in the same way for fraction (ii). Chromatographic separation of fraction (ii) gave, on elution with light petroleum (b. p. 60—80°) (1500 ml.), a pale green oil (0.83 g.), which partly solidified. Recrystallisation from aqueous ethanol gave 3-methylfluorenone in yellow needles, m. p. 68° (Found: C 85.9; H, 5.0. Calc. for  $C_{14}H_{10}O$ : C, 86.6; H, 5.2%). Ritchie<sup>7</sup> has recorded m. p. 68° for this compound. Elution with benzene (750 ml.) gave an oily yellow solid (0.84 g.), which was combined with the corresponding product from fraction (i). This combined product could not be purified. A portion (1.86 g.) in concentrated sulphuric acid (24 ml.) at 0° was treated with potassium nitrate (2.4 g.) in concentrated sulphuric acid (24 ml.) at 0—4° as described by Chardonnens and Perriard.<sup>8</sup> The mixture was poured into ice–water and crystallisation of the product from aqueous acetone gave 3-methyl-2,7-dinitrofluorenone in pale yellow needles, m. p. 244—245° (Found: C, 59.0; H, 2.9. Calc. for  $C_{14}H_8N_2O_5$ : C, 59.2; H, 2.8%). Chardonnens and Perriard<sup>8</sup> record m. p. 242—243° for this compound. Further elution with ethanol (500 ml.) gave a buff-coloured solid (0.62 g.), which was combined with the corresponding product from fraction (i). Recrystallisation from aqueous ethanol and then from benzene–light petroleum (b. p. 80—100°) gave 3-methylfluoren-9-ol (0.39 g.) in needles, m. p. 146° (Found: C, 85.7; H, 6.0. Calc. for  $C_{14}H_{12}O$ : C, 85.7; H, 6.2%). Bermann *et al.*<sup>9</sup> recorded m. p. 146°.

*o-p'-Methoxybenzoylbenzoic acid.* The initial current of 0.1 A dropped rapidly to 0.07 A and then rose steadily to 0.12 A during 48 hr. The internal temperature remained at 88—90° and the solution became deep red. A small quantity of a white solid was deposited (0.15 g.). No formaldehyde was detected in the recovered methanol. Distillation of the neutral fraction

<sup>5</sup> Bruzau, *Ann. Chim. (France)*, 1934, **1**, 352.

<sup>6</sup> Burton and Cheeseman, *J.*, 1953, 832.

<sup>7</sup> Ritchie, *J. Proc. Roy. Soc., N.S. Wales*, 1946, **80**, 33.

<sup>8</sup> Chardonnens and Perriard, *Helv. Chim. Acta*, 1945, **28**, 593.

<sup>9</sup> Bergmann, Berthier, Fischer, Hirshberg, Lavie, Loewenthal, and Pullman, *Bull. Soc. chim. France*, 1952, 78.

gave: (i) a yellow oil which solidified at 0° (4.34 g.), b. p. 124—134°/0.01 mm., and (ii) a red gum (0.43 g.), b. p. ca. 160°/0.01 mm. The residue weighed 0.625 g. Fraction (i) on chromatography gave, on elution with light petroleum (b. p. 60—80°) (3 l.), a pale yellow oil (1.60 g.) which solidified. Recrystallisation from aqueous ethanol (charcoal) gave 4-methoxybenzophenone in needles m. p. 60—61° (Found: C, 79.85; H, 5.7. Calc. for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>: C, 79.2; H, 5.65%). Rennie<sup>10</sup> reported m. p. 60—61°. Elution with benzene (400 ml.) gave a yellow solid (1.39 g.), which on crystallisation from aqueous ethanol (charcoal) and then from light petroleum (b. p. 60—80°) gave 3-methoxyfluorenone in yellow needles, m. p. 99—100° (Found: C, 79.8; H, 4.9. Calc. for C<sub>14</sub>H<sub>10</sub>O<sub>2</sub>: C, 80.0; H, 4.8%). Arcus and Coombs<sup>11</sup> reported m. p. 99—100° for this compound. Elution with ethanol (750 ml.) gave a pale brown solid (0.64 g.), which on crystallisation from aqueous ethanol (charcoal) and then from light petroleum (b. p. 60—80°) gave 3-methoxyfluoren-9-ol (0.32 g.) in needles, m. p. 119° (Found: C, 78.9; H, 5.95. Calc. for C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>: C, 79.2; H, 5.65%). Arcus and Coombs<sup>11</sup> reported m. p. 120°.

TABLE 2.

Products of electrolysis from 0.1 mole of acid.

Acid	Neutral products			Acid and polymeric products				
	1 *	2 *	3 *	4	5	6	7	8
<i>o</i> -Benzoylbenzoic .....	0.965	0.40	0.93	0.70	0.85	1.20	3.90	8.90
<i>o-p'</i> -Chlorobenzoylbenzoic ...	2.57	1.17	0.98	3.4	0.44	0.81	4.38	3.70
<i>o-p'</i> -Bromobenzoylbenzoic ...	0.0	0.82	0.19	0.10	1.03	0.28	16.65	3.67
<i>o-p'</i> -Toluoylbenzoic .....	2.20	3.06	0.39	3.56	0.77	0.77	2.42	1.72
<i>o-p'</i> -Methoxybenzoylbenzoic	1.60	1.39	0.32	1.50	0.75	2.00	10.72	3.58

1 Benzophenone (g.).    3 Fluoren-9-ol (g.).    5 Solid D (g.).    7 Recovered acid (g.).  
 2 Fluorenone (g.).    4 Solid C (g.).    6 Phenols (g.).    8 Acidic polymer (g.).

\* These weights refer to slightly impure products as isolated from the column.

No products of cyclisation were obtained when similar experiments were carried out with *o*-phenoxybenzoic acid and with *NN*-diphenylanthranilic acid.

Thanks are accorded to the Department of Scientific and Industrial Research for the award of a Research Studentship to P. J. B.

KING'S COLLEGE (UNIVERSITY OF LONDON),  
STRAND, LONDON, W.C.2.

[Received, February 12th, 1962.]

<sup>10</sup> Rennie, *J.*, 1882, **41**, 228.

<sup>11</sup> Arcus and Coombs, *J.*, 1954, 3977.