Internuclear Cyclisation. Part X. The Preparation of 3 : 4-Benzocoumarin.*

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Phenyl *o*-aminobenzoate has been converted into 3 : 4-benzocoumarin by a variety of methods, and the by-products formed in these reactions have been identified.

As part of work on the extension of the Pschorr phenanthrene synthesis to heterocyclic systems, the synthesis of 3 : 4-benzocoumarin (I) from phenyl *o*-aminobenzoate (II), first reported by Rule and Bretscher (*J.*, 1927, 925), has been reinvestigated, and the reaction extended to include some recently introduced methods of ring closure (Hey and Osbond, *J.*, **1949**, 3164; Heacock and Hey, *J.*, 1952, 1508). Rule and Bretscher (*loc. cit.*) described the synthesis of 3 : 4-benzocoumarin in 14% yield by the diazotisation of phenyl *o*-aminobenzoate in alcoholic solution with amyl nitrite followed by decomposition of the diazonium salt with copper powder. Phenol and salicylic acid were obtained as by-products.

The present communication describes the application of five different procedures for the decomposition of the diazonium salt. Phenyl *o*-aminobenzoate (II) was prepared by (*a*) the reduction of phenyl *o*-nitrobenzoate (III), obtained from *o*-nitrobenzoyl chloride and phenol, and (*b*) the preferential hydrolysis with cold concentrated sulphuric acid for a long period of the benzenesulphonamido-group in phenyl *o*-benzenesulphonamidobenzoate (IV), prepared from benzenesulphonylanthraniloyl chloride and phenol (cf. Schroeter and Eisleb, *Annalen*, 1909, **367**, 101).

The yields of 3 : 4-benzocoumarin and the nature of the by-products formed in these reactions are shown in the Table. The major by-product was phenyl benzoate produced by deamination. Deamination in place of ring closure has been previously observed in

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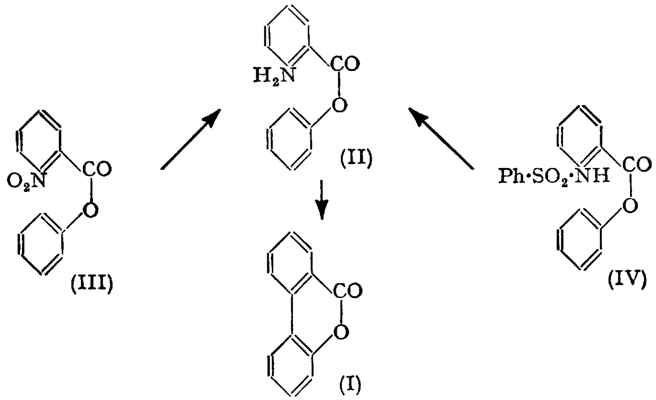
* Part IX, preceding paper.

similar reactions (Hey and Mulley, *J.*, 1952, 2276). Other by-products obtained included diphenyl diphenate, and salicylic and benzoic acids produced by the fortuitous hydrolysis of the ester linkage. The maximum yield of 3 : 4-benzocoumarin was obtained by decomposition of an aqueous solution of the diazonium sulphate with copper powder. No 3 : 4-benzocoumarin was obtained on thermal decomposition of the diazonium fluoroborate in boiling light petroleum, which gave the normal replacement reaction with the formation of phenyl *o*-fluorobenzoate (cf. Balz and Schiemann, *Ber.*, 1927, **60**, 1186).



Ring-closure experiments with phenyl o-*aminobenzoate.*

	Experimental conditions	Yield (%) of 3 : 4-benzocoumarin	By-products
(*a*)	Action of heat on aq. diazonium sulphate	6	Salicylic acid (22%)
(*b*)	Action of Cu on aq. diazonium sulphate	19·2	—
(*c*)	Addition of aq. Na_2CO_3 and Cu to aq. diazonium sulphate	9	Phenyl benzoate (14%) Benzoic acid (20·5%)
(*d*)	Action of Cu on solid diazonium fluoroborate in acetone	6·3	Phenyl benzoate (34·8%) Diphenyl diphenate (22·5%)
(*e*)	Diazonium fluoroborate in boiling light petroleum (b. p. 80—100°)	—	Phenyl *o*-fluorobenzoate (31%)
* (*f*)	Action of Cu on diazonium chloride in alcohol	14	Phenol Salicylic acid

* Rule and Bretscher (*loc. cit.*).

Authentic specimens of the hitherto unknown esters, diphenyl diphenate and phenyl *o*-fluorobenzoate, have been prepared from the acid chlorides and phenol in pyridine.

EXPERIMENTAL

Phenyl o-*Nitrobenzoate.*—An ethereal solution of *o*-nitrobenzoyl chloride (from 16·7 g. of acid) was added slowly to a solution of phenol (9·4 g.) in pyridine (60 c.c.). The ether was evaporated and the clear pyridine solution was boiled for a few minutes, cooled, and poured into water. A red solid separated, which on recrystallisation from aqueous alcohol (charcoal) afforded *phenyl* o-*nitrobenzoate* (12 g.) in pale yellow prisms, m. p. 52—53° (Found : C, 64·4; H, 3·8. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7%). Cahn (*J.*, 1932, 1400), who recorded no analyses, reported m. p. 42—43°, b. p. 164—165°/21 mm.

Phenyl o-*Benzenesulphonamidobenzoate.*—Benzenesulphonylanthraniloyl chloride (7 g.) and phenol (2·35 g.) were boiled under reflux in dry benzene (100 c.c.) for 21 hr. Removal of the solvent by distillation left a white solid, from which *phenyl* o-*benzenesulphonamidobenzoate* (7·5 g.) was obtained in colourless needles, m. p. 103—105°, on recrystallisation from methanol (Found : C, 64·3; H, 4·2. $C_{19}H_{15}O_4NS$ requires C, 64·6; H, 4·3%).

Phenyl o-*Aminobenzoate.*—(*a*) A solution of the nitro-ester (9·5 g.) in alcohol (200 c.c.) and a suspension of Raney nickel (10 g.) in the same solvent were shaken with hydrogen at atmospheric pressure until the required quantity of hydrogen had been absorbed. The suspension was filtered and the filtrate concentrated under reduced pressure. The base was obtained as a brown oil, which was dissolved in benzene and adsorbed on an alumina column (10 × 2 cm.). Elution of the column with the same solvent, followed by concentration of the eluant, afforded pure phenyl *o*-aminobenzoate (4 g.) in colourless needles, m. p. 72—73°. Schmidt (*J. pr. Chem.*, 1887, **36**, 372), who prepared this compound by the action of isatoic acid on phenol, recorded m. p. 70°. Cahn (*loc. cit.*) gave m. p. 71°.

(*b*) A suspension of iron filings (80 g.) in 5% acetic acid (100 c.c.) was heated on a steam-bath, with stirring, until no more hydrogen was evolved. The nitro-ester (20 g.) was added slowly and the mixture stirred on a steam-bath for 1 hr. The solution was neutralised with aqueous sodium carbonate, and charcoal added to assist filtration. After filtration, both residue and filtrate were repeatedly extracted with hot benzene. The combined benzene extracts were concentrated to give the crude base as a brown oil, which was purified chromatographically as described under (*a*). Pure phenyl *o*-aminobenzoate (10 g.) was obtained in colourless needles, m. p. 72°.

(*c*) A solution of phenyl *o*-benzenesulphonamidobenzoate (7 g.) in concentrated sulphuric acid (30 c.c.) was set aside at room temperature for 5 days, after which it was poured into a mixture of ice and aqueous ammonia. A solid separated, which on recrystallisation from benzene–light petroleum (b. p. 80—100°) gave phenyl *o*-aminobenzoate (2·7 g.) in colourless needles, m. p. 72°.

Preparation of 3 : 4-*Benzocoumarin*.—(*a*) Phenyl *o*-aminobenzoate (2·6 g.) in concentrated sulphuric acid (10 c.c.) and water (100 c.c.) was diazotised at 0° with a solution of sodium nitrite (1 g.) in water (10 c.c.). After being stirred for 1 hr. at 0° the filtered pale yellow-green solution was heated on a steam-bath for 1 hour. The product was extracted with chloroform, and the chloroform solution was washed with dilute aqueous sodium hydroxide. Evaporation of the dried (Na_2SO_4) extract afforded a dark red oil (0·5 g.), which was dissolved in benzene–light petroleum (b.p. 60—80°) (3 : 1) and adsorbed on an alumina column (20 × 2 cm.). When the column was washed with benzene–light petroleum (b. p. 60—80°) (700 c.c.) and benzene (1000 c.c.) a pale yellow waxy solid was obtained, which on recrystallisation from light petroleum (b. p. 80—100°) gave 3 : 4-benzocoumarin (0·15 g.) in colourless needles, m. p. 92·5°. Rule and Bretscher (*loc. cit.*) recorded m. p. 93—94° for this compound. Further washing of the column with benzene, benzene–ether, and methanol gave a series of tars. Acidification of the sodium hydroxide washings and extraction with chloroform gave a black solid (1·78 g.), which was adsorbed from benzene on alumina (20 × 2 cm.). Elution of the column with the same solvent (1000 c.c.) gave salicylic acid (0·56 g.) in needles, m. p. and mixed m. p. 158°, from benzene–light petroleum (b. p. 80—100°).

(*b*) Phenyl *o*-aminobenzoate (2·9 g.) was diazotised as described above in concentrated sulphuric acid (10 c.c.) and water (200 c.c.) with sodium nitrite (1 g.) in water (10 c.c.). To the filtered solution copper powder * (3 g.) was slowly added, and nitrogen was evolved in the cold. The solution was stirred at room temperature overnight, the diazonium salt completely decomposing. The resulting suspension was filtered, and both filtrate and residue were repeatedly extracted with hot chloroform. Concentration of the dried (Na_2SO_4) extract yielded a brown tar (2·25 g.), which was adsorbed from benzene–light petroleum (b. p. 60—80°) on alumina (20 × 2 cm.). When the column was washed with benzene–light petroleum (b. p. 60—80°) (2 : 1) (1300 c.c.) and benzene (1700 c.c.) a light-coloured solid was obtained, which on recrystallisation from benzene–light petroleum (b. p. 80—100°) gave 3 : 4-benzocoumarin (0·51 g.) in colourless needles, m. p. 91—92°. Further washing of the column with benzene–chloroform (1 : 1) (500 c.c.) afforded only a trace of a brown solid. The brown solid obtained from concentration of the final washings (methanol, 500 c.c.; acetic acid, 500 c.c.) was dissolved, as far as possible, in benzene, and adsorbed on a silica gel column (20 × 2 cm.), but elution with benzene (700 c.c.) afforded only a trace of a brown unidentifiable solid.

(*c*) Phenyl *o*-aminobenzoate (2·3 g.) was diazotised, as described above, in concentrated sulphuric acid (10 c.c.) and water (100 c.c.) with sodium nitrite (0·7 g.) in water (10 c.c.). The filtered solution was decomposed by the addition of excess of aqueous sodium carbonate and copper powder (3 g.). Nitrogen was evolved in the cold, and the suspension was stirred at room temperature for 24 hr. The mixture was filtered and both filtrate and residue were extracted with chloroform. Concentration of the dried (Na_2SO_4) chloroform extract afforded a dark brown tar (1·4 g.), which was adsorbed from benzene–light petroleum (b. p. 60—80°) (4 : 1) on alumina (20 × 2 cm.). When the column was washed with benzene–light petroleum (b. p. 60—80°) (4 : 1) (300 c.c.) a yellow solid was obtained, which on recrystallisation from light petroleum (b. p. 40—60°) gave phenyl benzoate (0·3 g.) in colourless prisms, m. p. 67—68°,

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* In all the reactions described in this paper the copper powder was prepared by precipitation from aqueous copper sulphate with zinc dust.

undepressed on admixture with an authentic specimen. Further washing of the column with the same solvent (1300 c.c.) gave an off-white solid, which on recrystallisation from light petroleum (b. p. 60—80°) gave 3 : 4-benzocoumarin (0·18 g.) in colourless needles, m. p. 89—90°. Final elution of the column with benzene, benzene–chloroform, and chloroform gave a series of brown tars. Acidification of the original alkaline solution and extraction with chloroform gave a dark red crystalline solid, contaminated with some tar. The product was dissolved in a mixture of benzene and light petroleum (b. p. 60—80°) (2 : 1) and adsorbed on a silica gel column (20 × 2 cm.). Washing with benzene (1500 c.c.) gave colourless crystals, m. p. 105—107°, which on recrystallisation from water gave benzoic acid (0·27 g.) in needles, m. p. and mixed m. p. 120—121°.

(*d*) A suspension of phenyl *o*-aminobenzoate (5 g.) in concentrated hydrochloric acid (20 c.c.) and water (40 c.c.) was diazotised at 0° with sodium nitrite (2 g.) in water (10 c.c.). The solution was diluted with water (40 c.c.) to keep the diazonium chloride in solution. After being stirred for 1 hr. at 0—5° the solution was filtered and sodium fluoroborate (10 g.) in water (20 c.c.) was added, with stirring, at 0°. The diazonium fluoroborate (6·9 g.) was collected and dried *in vacuo*. The fluoroborate (4·9 g.) was suspended in " AnalaR " acetone (50 c.c.) to which copper powder (3·5 g.) was added. Nitrogen was freely evolved in the cold, and the reaction was complete in 1 hr. The product was filtered into an excess of cold water. The residue was repeatedly extracted with hot acetone and boiling water, and the combined aqueous-acetone solution extracted with chloroform. On concentration, the dried (Na_2SO_4) chloroform solution gave a light brown gum (3·28 g.), which was adsorbed from benzene–light petroleum (b. p. 60—80°) (2 : 1) on alumina (20 × 2 cm.). Elution of the column with this solvent (150 c.c.) gave a pale yellow waxy solid, m. p. 50—60°, which on recrystallisation from light petroleum (b. p. 40—60°) gave phenyl benzoate (0·85 g.) in prisms, m. p. and mixed m. p. 66°. Further washing of the column with the same solvent (200 c.c.) gave a yellow solid, m. p. 62—75°, which on repeated crystallisation from light petroleum (b. p. 80—100°) gave colourless prisms, m. p. 80—81° (0·68 g.). A mixed m. p. with an authentic specimen of diphenyl diphenate (m. p. 83°) showed no depression. Continued washing of the column with this solvent (700 c.c.), with benzene–light petroleum (b. p. 60—80°) (4 : 1) (400 c.c.), and with benzene (400 c.c.), gave a light brown solid, which on recrystallisation from light petroleum (b. p. 40—60°) afforded 3 : 4-benzocoumarin (0·2 g.) in colourless needles, m. p. 91—92°. Washing of the column with benzene–chloroform (1 : 1) (700 c.c.) and chloroform (200 c.c.) gave a brown solid, which on recrystallisation from benzene–light petroleum (b. p. 80—100°) gave buff-coloured needles, m. p. 182° (Found : C, 77·6; H, 5·4%; *M*, 227). Final elution of the column with methanol (1000 c.c.) and glacial acetic acid (500 c.c.) afforded a brown glass, which was dissolved, as far as possible, in benzene and adsorbed on a silica gel column (20 × 2 cm.). Washing of the column with benzene (400 c.c.) gave only a minute quantity of a buff-coloured solid.

(*e*) The diazonium fluoroborate (2·0 g.), prepared as described above, was suspended in sodium-dried light petroleum (b. p. 80—100°), and the suspension was boiled under reflux for 44 hr. A large amount of dark insoluble material was produced, from which the pale yellow solution was decanted. The residue was extracted with benzene and the benzene extract and light petroleum solution were combined and concentrated (charcoal) to give phenyl *o*-fluorobenzoate (0·43 g.) in pale yellow prisms, m. p. and mixed m. p. 66—68°.

Diphenyl Diphenate.—Diphenoyl dichloride, prepared from diphenic acid (10 g.) by the method of Bell and Robinson (*J.*, 1927, **1698**), was added to a solution of phenol (10 g.) in pyridine (50 c.c.). After being kept at room temperature for 2 days, the solution was poured into water. Crystallisation of the solid which separated from aqueous methanol (charcoal) and then from benzene–light petroleum (b. p. 80—100°) gave *diphenyl diphenate* (12·2 g.) in prisms, m. p. 83° (Found : C, 79·6; H, 4·9. $C_{26}H_{18}O_4$ requires C, 79·2; H, 4·6%).

Phenyl o-*Fluorobenzoate*.—*o*-Fluorobenzoic acid (2·0 g.), prepared by Slothouwer's method (*Rec. Trav. chim.*, 1914, **33**, 324), was boiled under reflux with thionyl chloride (20 c.c.) for 24 hr. After removal of the excess of thionyl chloride *in vacuo*, a solution of phenol (1·5 g.) in pyridine (10 c.c.) was added. After being heated on a water-bath for 30 min., the solution was poured into water and the resulting brown oil extracted with benzene and adsorbed on an alumina column (10 × 2 cm.). Washing of the column with benzene (1000 c.c.) afforded a yellow solid which, on recrystallisation from light petroleum (b. p. 40—60°), gave *phenyl* o-*fluorobenzoate* (1·3 g.) in pale yellow prisms, m. p. 70—71° (Found : C, 72·5; H, 4·4. $C_{13}H_9O_2F$ requires C, 72·2; H, 4·2%).

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