The Preparation and Hydrolysis of Some Esters of 2 : 4 : 6-*Triphenylbenzoic Acid. Part I. Preparation of the Esters.*

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1 : 3 : 5-Triphenylbenzene was converted into the monobromo-derivative, which was isolated in two forms, one metastable. Oxidative degradation confirmed the structure previously suggested for the monobromide. 2 : 4 : 6-Triphenylbenzoic acid was prepared from the monobromide, and esterified either by the silver salt method or by interaction with diazo-alkanes.

1 : 3 : 5-TRIPHENYLBENZENE was most conveniently prepared by condensation of acetophenone with the agency of hydrogen chloride at 60° (Engler and Berthold, *Ber.*, 1874, **7**, 1125). Condensation by means of a mixture of potassium pyrosulphate and concentrated sulphuric acid resulted mainly in the production of tar and a very low yield of 1 : 3 : 5-triphenylbenzene, contrary to the experience of Kohler and Blanchard (*J. Amer. Chem. Soc.*, 1935, **57**, 367).

Two identical methods for the preparation of a monobromo-derivative of 1 : 3 : 5-triphenylbenzene are reported in the literature, by direct bromination in carbon disulphide at room temperature. In one case the melting point of the product was reported as 108° (Engler and Berthold, *loc. cit.*), and in the second as 129° (Kohler and Blanchard, *loc. cit.*). The first sample prepared by the present authors had a melting point of 105—107°, which changed after a few days to 129·5°. All subsequent preparations carried out at the University College of North Wales yielded a product melting initially at 129·5°. The preparation was repeated at University College, London, and on the first occasion yielded a product which melted at 108°, resolidified, and melted again at 129°. On storage the substance changed its initial melting point to 129°, and again all subsequent preparations melted at this temperature. Recrystallisation of the higher-melting form under various conditions also failed to yield the metastable form.

X-Ray powder photographs of the two forms of bromotriphenylbenzene were taken. The samples were mounted in a Lindemann glass capillary, and rotated slowly while being cooled by a stream of liquid air. For ease of comparison both photographs were taken on the same plate by the movable-sector technique. The patterns obtained from the two forms were not identical, indicating a difference of crystalline form or molecular structure.

Two other examples of fugitive melting points in derivatives of *s*-triphenylbenzene are known; 2-cinnamoyl-1 : 3 : 5-triphenylbenzene (Kohler and Blanchard, *loc. cit.*) and *n*-propyl triphenylbenzoate (see below). The persistent glass-like nature of the analytically pure *iso*butyl triphenylbenzoate may also be connected with this behaviour.

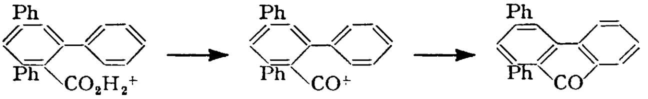
It is interesting to speculate whether the compounds in question are monotropic substances, such as benzophenone, or whether the dimorphism results from some restricted rotation of the substituent phenyl groups.

Previously it has been assumed that when triphenylbenzene is brominated, the bromine atom enters the central nucleus. Such arguments as have been adduced for this view are based on steric considerations, *e.g.*, that when the bromine atom is replaced by an acetyl group the product behaves like a methyl ketone with substituents in both *ortho*-positions. For a study of the effect of *ortho*-substituents on the hydrolysis of esters of the required triphenylbenzoic acid a more direct proof of the position of the bromine atom in the molecule was felt to be desirable. The position taken up by the bromine atom is limited to the central nucleus, or to one of the six available *ortho*-positions in the three substituent phenyl groups, by the observation that attempts to prepare triphenylbenzoyl chloride from the derived triphenylbenzoic acid resulted only in the formation of 1 : 3-diphenylfluorenone (Kohler and Blanchard, *loc. cit.*). Oxidation might, therefore, be expected to yield either a mixture of bromotrimesic and benzoic acid, or of trimesic, benzoic, and *o*-bromobenzoic acid, the last two in the proportion of 2 : 1 (cf. the oxidation of nitrotriphenylbenzene; Vorlander Fischer, and Willie, *Ber.*, 1929, **62**, 2836). Numerous oxidations were carried out, but in every case the main product of the reaction was benzoic acid. The only other product, obtained in very small amount, was an acid with an equivalent weight corresponding roughly to that of a bromodiphenylbenzoic acid. Both *o*-bromobenzoic acid and bromotrimesic acid (a crude sample was prepared by oxidation of bromomesitylene) are known to be stable under the reaction conditions employed, and it was observed that *o*-bromobenzoic acid can be separated from relatively large quantities of admixed benzoic acid by chromatography of aqueous solutions of their sodium salts on a column of alumina, first washed with dilute nitric acid, then washed neutral with water. Careful analysis, using this method, of the benzoic acid product from the oxidations failed to reveal any admixed *o*-bromobenzoic acid.

The failure to detect *o*-bromobenzoic acid suggests that the bromine atom is located in the central nucleus, also that in such a system the central nucleus is very much more susceptible to oxidising agents than the substituent phenyl groups.

1 : 3 : 5-Triphenylbenzoic acid was prepared from bromotriphenylbenzene by the Grignard reaction with xylene as solvent and diethylaniline as catalyst (Kohler and Blanchard, *loc. cit.*), and with less initial difficulty by using dibutyl ether as solvent (Marvel *et al., J. Amer. Chem. Soc.*, 1928, **50**, 2810).

Methyl (Kohler and Blanchard, *loc. cit.*), ethyl, *n*-propyl (dimorphic), *iso*propyl, *iso*butyl, and *tert.*-butyl triphenylbenzoate were prepared, either by the silver salt method, or by interaction of the acid with the appropriate diazo-alkane in ethereal solution. Other methods of esterification were unsatisfactory. In particular, reaction of the acid with the appropriate alcohol in concentrated sulphuric acid solution, a method normally successful with "sterically hindered" acids (Meyer, *Monatsh.*, 1904, **25**, 1201), resulted only in the formation of 1 : 3-diphenylfluorenone, presumably owing to the formation, and immediate cyclisation in this medium, of an acylium ion from the acid. Formation of this intensely yellow fluorenone derivative would, therefore, provide evidence for the incursion of Day and Ingold's mechanism *A*'1 (*Trans. Faraday Soc.*, 1941, **37**, 686), subsequently $A_{Ac}1$, in acid-catalysed hydrolysis of these esters.



Kohler and Blanchard (*loc. cit.*) have reported adversely on the application of the silver salt method of esterification to triphenylbenzoic acid. However, the method succeeds if the silver salt is prepared by double decomposition of the sodium salt with silver nitrate. Direct interaction of the acid with silver nitrate gives a precipitate which actually contains much co-precipitated silver nitrate, and reaction of this with an alkyl halide naturally results in a poor yield of ester.

EXPERIMENTAL

Oxidation of 1-*Bromo*-2 : 4 : 6-*triphenylbenzene.*—1-Bromo-2 : 4 : 6-triphenylbenzene (10 g.) in glacial acetic acid (50 ml.) was heated to *ca.* 95° on a boiling-water bath, and a solution of chromium trioxide (50 g.) in glacial acetic acid (80 ml.) and water (20 ml.) gradually added. The mixture was then poured into a solution of sodium carbonate (400 g.) in water (500 ml.), and the precipitated chromium hydroxide filtered off and washed with hot sodium carbonate solution. On cooling, the combined alkaline filtrates deposited fine crystals. These were filtered off and dissolved in hot water, and the solution was acidified. The resultant precipitate (0·06 g.) was dissolved in aqueous sodium hydroxide, re-precipitated with acid, and finally crystallised from glacial acetic acid, then having m. p. 305—309° (Found: equiv., 372. Calc. for $C_{19}H_{13}O_2Br$: equiv., 353).

The alkaline filtrate was then acidified with nitric acid and exhaustively extracted with ether. Evaporation of the ethereal extract yielded pure benzoic acid (6 g.). Chromatography of the sodium salt showed that no *o*-bromobenzoic acid was present.

2 : 4 : 6-*Triphenylbenzoic Acid.*—A conventional Grignard apparatus was modified by the addition of a tap sealed on to the base of the flask, and the provision of an exterior asbestos mantle carrying an electric heater. The apparatus was first flooded with nitrogen, and then

ethyl bromide (7 ml.) in diethyl ether (100 ml.) was added to magnesium turnings (5 g.) in the flask. When the reaction became vigorous, the apparatus was drained through the attached tap, solid bromotriphenylbenzene (26 g.) and di-*n*-butyl ether (30 ml.) containing a trace of iodine were immediately added, the flow of nitrogen being maintained, and the flask was then heated until reaction commenced. More di-*n*-butyl ether (250 ml.) was run in during 30 min.; then, slowly, so that reaction was maintained, bromotriphenylbenzene (20 g.) in xylene (100 ml.) was added. After this the mixture was boiled for 3 hr., then cooled, and a slow current of dry carbon dioxide passed in, through a wide delivery tube, for 3 hr. A white solid separated. Sulphuric acid (25 ml.) in water (75 ml.) was added and the organic solvents were removed in steam. The semi-solid residue was separated by filtration and extracted with boiling benzene (100 ml.), and the filtered benzene solution shaken when cold with an excess of aqueous sodium hydroxide. A brown layer of sodium triphenylbenzoate formed between the two layers. This was separated and boiled with dilute sulphuric acid. The resultant white triphenylbenzoic acid (30 g.) was crystallised from glacial acetic acid; it had m. p. 251° (Found : C, 85·3; H, 5·1. Calc. for $C_{25}H_{18}O_2$: C, 85·7; H, 5·1%).

Ethyl 2 : 4 : 6-*Triphenylbenzoate*.—An ethereal solution of diazoethane was prepared from ethylamine (20 g.) (Adamson and Kenner, *J.*, 1935, 286; 1937, 1554), and cooled to 0°. Solid triphenylbenzoic acid was added gradually with stirring, until the yellow colour of the solution was discharged. Excess of acid was removed by extraction with aqueous sodium hydroxide, and the solution then dried and concentrated. The resultant *ethyl* 2 : 4 : 6-*triphenylbenzoate* (25 g.), recrystallised from ethanol, had m. p. 95° (Found : C, 85·9; H, 6·1. $C_{27}H_{22}O_2$ requires C, 85·7; H, 5·8%).

n-*Propyl* 2 : 4 : 6-*Triphenylbenzoate*.—*n*-Propylamine (25 g.) was converted into diazopropane by the method of Adamson and Kenner (*loc. cit.*). Concentration of the mixture yielded a colourless oil, crystallisable from ethanol. Two crops of crystals were obtained, having m. p. 72·5° and 92° respectively. These were combined, a 70% solution in benzene chromatographed through alumina, and the column developed with a 2% solution of ethanol in benzene. Under ultraviolet light two narrow zones were visible at the top of the column, which on elution with ethanol yielded only traces of material. The colourless non-fluorescent lower section of the column was also eluted with ethanol. Evaporation yielded three successive crops of crystals. The first crop melted at 72·5°, resolidified, melted again at 91·5°, and on cooling and reheating melted initially at 91·5° (Found : C, 85·6; H, 6·3. $C_{22}H_{24}O_2$ requires C, 85·7; H, 6·1%). The second and third crops melted at 91° (Found : C, 86·2; H, 6·5%). The main bulk of the *ester* was recrystallised from ethanol (m. p. 92°; yield 15 g.).

A sample prepared by the silver salt method melted initially at 92°.

iso*Butyl* 2 : 4 : 6-*Triphenylbenzoate*.—Diazo*iso*butane was prepared from *iso*butylamine (25 g.) and treated with triphenylbenzoic acid as above. Evaporation yielded an oily *ester* (4 g.) which was poured in benzene (30 c.c.) on alumina (27 × 2·5 cm.) and eluted with benzene. The appearance of the ester in the eluate was detected by measuring the refractive index of successive 5-c.c. samples. The solution containing the purified ester on evaporation yielded a colourless gum with no definite m. p.; it did not crystallise (Found : C, 85·1; H, 6·6. $C_{29}H_{26}O_2$ requires C, 85·7; H, 6·4%).

Silver 2 : 4 : 6-*Triphenylbenzoate*.—Triphenylbenzoic acid (19 g.) was dissolved in hot ethanol (350 c.c.) and exactly neutralised with aqueous 1·04N-sodium hydroxide. On addition of silver nitrate (9·3 g.) in water (30 c.c.) a creamy-white precipitate of the silver salt was obtained. This was filtered off, washed with 1 : 1 ethanol–water, and dried *in vacuo* (yield 21·3 g.).

Methyl 2 : 4 : 6-*Triphenylbenzoate*.—Silver triphenylbenzoate (15 g.), methyl iodide (24 c.c.), and di-*n*-butyl ether (80 c.c.) were refluxed together for 2 hr., then cooled, and filtered from silver iodide, and the solvent was removed under reduced pressure. The residual yellow oil, crystallised from methanol–acetic acid, had m. p. 89·5°.

The ester was also prepared by use of ethereal diazomethane (Kohler and Blanchard, *loc. cit.*); it then had m. p. 91° (Found : C, 85·2; H, 5·2. Calc. for $C_{26}H_{20}O_2$: C, 85·7; H, 5·5%).

iso*Propyl* 2 : 4 : 6-*Triphenylbenzoate*.—Silver triphenylbenzoate (3·87 g.), *iso*propyl iodide (4 c.c.), and benzene (10 c.c.) were heated at 95° for 12 hr. The mixture was then filtered, extracted with aqueous sodium hydroxide, dried, and evaporated. The residual reddish oil was dissolved in ether and extracted with aqueous sodium thiosulphate to remove iodine. The dried solution on evaporation yielded the *ester* which, crystallised from glacial acetic acid, had m. p. 82° (0·4 g.) (Found : C, 85·0; H, 6·0. $C_{28}H_{24}O_2$ requires C, 85·7; H, 6·1%).

tert.-*Butyl* 2 : 4 : 6-*Triphenylbenzoate*.—Silver triphenylbenzoate (54 g.), *tert.*-butyl bromide (48·5 g.), and benzene (150 c.c.) were shaken together in a glass-stoppered bottle for 24 hr.

Filtration, extraction with aqueous sodium hydroxide, and evaporation yielded the *ester* which, crystallised from ethanol, had m. p. 101·5° (34 g.) (Found : C, 85·9; H, 6·5. $C_{29}H_{26}O_2$ requires C, 85·7; H, 6·4%).

Attempted Esterification in Sulphuric Acid.—Triphenylbenzoic acid (1 g.) was shaken with 100% sulphuric acid (20 c.c.) for 10 min. and the dark solution then poured into cold methanol (200 c.c.). The mixture was concentrated, diluted with water, and extracted with ether, and the combined extracts were evaporated to dryness. The residual yellow solid was poured in benzene (15 c.c.) on a column of alumina, the column developed with benzene containing 5% of ether, and the prominent yellow zone cut out and eluted with ethanol. Evaporation yielded 1 : 3-diphenylfluorenone, m. p. and mixed m. p. 182—183°. Nothing was obtained by elution of the remaining part of the column.

Separation of o- *and* p-*Bromobenzoic and Benzoic Acid.*—A 3% aqueous solution of equal parts of the sodium salts of benzoic, *o*-bromobenzoic, and *p*-bromobenzoic acid was poured on a 60-cm. column of alumina, which had been washed with N-nitric acid and then washed neutral with water. The column was developed with water (50 c.c.) and cut arbitrarily into 3-cm. sections which were eluted with water. The order of adsorption from the top of the column was *o*-bromobenzoate, benzoate, and *p*-bromobenzoate.

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