480. *The Partial Hydrolysis of Benzenesulphonic Esters of Polyhydric Phenols*

By EMMANUEL M. KAMPOURIS

The benzenesulphonic esters of pyrocatechol, resorcinol, quinol, and phloroglucinol were prepared by an improved method. These esters were hydrolysed to hydroxy-esters, which can be methylated. The resulting methoxy-esters were then hydrolysed to methoxy-phenols.

THE dibenzenesulphonic esters of resorcinol and quinol, and the tribenzenesulphonic ester of phloroglucinol were first prepared by Georgescu.[1] The same esters and the pyrocatechol dibenzenesulphonate have now been prepared by benzenesulphonylation of the phenols with benzenesulphonylchloride and calcium hydroxide in aqueous solution. This method generally gives better yields and purer products than those obtained by benzenesulphonylation in pyridine. By this method phloroglucinol, in the form of its dihydrate, can be quantitatively esterified to the triester; in pyridine on the other hand, a mixture, consisting of the tri-, di-, and mono-esters is obtained in low yield. However, if specially dehydrated phloroglucinol is used, the yield is increased and a product consisting mainly of triester can be obtained. From this product the triester can be isolated by taking advantage of its insolubility in dilute solutions of alkalis, whilst the di- and the mono-ester, which are precipitated together by acidification of the alkaline solution, can be separated by extraction with benzene, in which the monoester is almost insoluble. All these esters are stable in hot solutions of inorganic acids, and do not react with hot concentrated nitric acid, which acts as a solvent; on the other hand, they are hydrolysed by alkalis.

The partial hydrolysis of the esters was carried out by the method used for the partial hydrolysis of pyrogallol tribenzenesulphonate,[2] modified to proceed stepwise until hydrolysis was complete. The hydroxy-esters obtained in this way can be useful in synthesis,

[1] M. Georgescu, *Ber.*, 1891, **24**, 416.

[2] E. Kampouris, Thesis, Techn. Univ. of Athens, 1955; E. Sakellarios, E. Kampouris, and J. Sakellarios, *Ber.*, 1961, **94**, 2544.

and the partially methylated polyhydric phenols were prepared by their use as intermediates.

The methylation of the dibasic phenol monoesters with dimethyl sulphate gave the corresponding methoxy-esters, which were also prepared from guaiacol, resorcinol monomethyl ether,[3] and quinol monomethyl ether [3] by benzenesulphonylation with benzenesulphonyl chloride in pyridine. These methoxy-esters were hydrolysed to the monomethyl ethers of pyrocatechol, resorcinol, and quinol. The phloroglucinol dibenzenesulphonate was methylated to the methoxy-diester, prepared also by benzenesulphonylation in pyridine of phloroglucinol monomethyl ester.[4] This methoxy-diester can be hydrolysed in two stages, yielding first the *O*-methylphloroglucinol monobenzenesulphonate, and then phloroglucinol monomethyl ether. The *O*-methylphloroglucinol monobenzenesulphonate was methylated to the di-*O*-methyl monoester, which was also prepared by methylation of the monoester, and by benzenesulphonylation of the phloroglucinol dimethyl ether.[4] Finally, this di-*O*-methyl monoester was hydrolysed to the phloroglucinol dimethyl ether.

Experimental

Pyrocatechol Dibenzenesulphonate.—Powdered calcium hydroxide was added in portions at 30—35°, to a stirred mixture of pyrocatechol (11 g.) in water (500 ml.) and benzenesulphonyl chloride (38 g.), until the liquid was permanently alkaline to litmus. Stirring was continued for an hour; the reaction product, which separated as a sticky mass, gradually solidifying and dispersing. After 24 hr., the solid was separated, crushed in a mortar, and dispersed in water; it was then acidified with hydrochloric acid, filtered off, washed with water, and dried to give *pyrocatechol dibenzenesulphonate* (38 g., 96%), which was crystallised from acetone and then from trichlorethylene to give prisms, m. p. 155—156° (Found: S, 16·2. $C_{18}H_{14}O_6S_2$ requires S, 16·4%). The following were prepared in a similar way: (*a*) resorcinol dibenzenesulphonate forming prisms, m. p. 69° (from methanol) (lit.,[1] m. p. 69—70°) (Found: S, 16·5. Calc. for $C_{18}H_{14}O_6S_2$: S, 16·4%); (*b*) quinol dibenzenesulphonate forming prisms, m. p. 118—119° (from glacial acetic acid) (lit.,[1] m. p. 120—121°) (Found: S, 16·3. Calc. for $C_{18}H_{14}O_6S_2$: S, 16·4%). The dibenzenesulphonate crystallised from benzene in long rods, containing solvent, and readily disintegrated in air (Found: C_6H_6, 16·5. Calc. for $C_{18}H_{14}O_6S_2,C_6H_6$: C_6H_6, 16·7%); and (*c*) phloroglucinol tribenzenesulphonate was obtained in 95% yield by a similar reaction from phloroglucinol dihydrate (16·2 g.) dispersed in water (150 ml.) and benzenesulphonyl chloride (56 g.). Crystallisation from methanol gave leaves, m. p. 122° (lit.,[1] m. p. 115—117°) (Found: S, 17·4. Calc. for $C_{24}H_{18}O_9S_3$: S, 17·6%).

Pyrocatechol Monobenzenesulphonate (*Partial Hydrolysis of the Diester*).—A 20% aqueous methanolic solution of potassium hydroxide (58 ml.) was added dropwise at 30—35° to a stirred dispersion of pulverised pyrocatechol dibenzenesulphonate (39 g.) in methanol (150 ml.). The reaction was continued at 30—35° until the diester disappeared, when the temperature was raised to 40—45° for 15 min. The resulting solution was diluted with water to 1,500 ml., decolourised with a few drops of sodium hyposulphite solution, acidified with hydrochloric acid, and stirred for 2 hr. to assist deposition. After being kept at about 0° for 2 days, the precipitate was broken up, filtered off, washed with cool water, and dried to give pyrocatechol monobenzenesulphonate (22 g.; 88%). This compound is sparingly soluble in petroleum, readily in trichlorethylene, benzene, and xylene, and very soluble in methanol. It crystallises from trichlorethylene–xylene (1 : 1 v/v) in prisms, m. p. 65—66° (Found: S, 12·65. $C_{12}H_{10}O_4S$ requires S, 12·8%). Acetylation gave pyrocatechol benzenesulphonate acetate, m. p. 86° (from methanol). Methylation with dimethyl sulphate gave *pyrocatechol methyl ether benzenesulphonate*, which crystallised in needles (from methanol), m. p. 52—53 (Found: S, 12·0. $C_{13}H_{12}O_4S$ requires S, 12·1%). The following were similarly prepared:

(*a*) *Resorcinol monobenzenesulphonate.* The sulphonate is soluble in methanol and readily soluble in warm benzene and toluene. It crystallises from toluene in prisms, m. p. 90—91° (Found: S, 12·95%. $C_{12}H_{10}O_4S$ requires S, 12·8%). Acetylation yielded resorcinol benzene sulphonate acetate, as prisms (from methanol), m. p. 57—58. Methylation gave resorcinol

[3] F. Ullman, *Annalen*, 1903, **327**, 116.

[4] (*a*) H. Weidel and J. Pollak, *Monatsh.*, 1900, **21**, 22; (*b*) D. D. Pratt and R. Robinson, *J.*, 1924, **125**, 193.

methyl ether benzenesulphonate, m. p. 43—44° (from methanol) (Found: S, 12·4. $C_{13}H_{12}O_4S$ requires S, 12·1%).

(*b*) *Quinol monobenzenesulphonate.* The quinol monobenzene sulphonate prepared by hydrolysis of the diester was obtained as the monohydrate, which was slightly soluble in warm water, forming needles, m. p. 43—44° (Found: H_2O, 6·95. $C_{12}H_{10}O_4S,H_2O$ requires H_2O, 6·7%). The anhydrous monoester is readily soluble in methanol, benzene and trichlorethylene, and crystallises from anhydrous xylene in prisms, m. p. 76° (Found: S, 12·7. $C_{12}H_{10}O_4S$ requires S, 12·8%). The acetate forms plates (from methanol), m. p. 48—49°. The methoxy-ester forms needles (from methanol), m. p. 49—50° (Found: S, 11·9. $C_{13}H_{12}O_4S$ requires S, 12·1%).

(*c*) *Phloroglucinol dibenzenesulphonate.* Hydrolysis of the phloroglucinol triester (27·3 g.) dispersed in methanol (100 ml.) by 20% aqueous methanolic potassium hydroxide (29 ml.) gives phloroglucinol dibenzenesulphonate in 90% yield, as prisms (from benzene), m. p. 120—121° (Found: S, 16·0. $C_{18}H_{14}O_7S_2$ requires S, 15·8%). Acetylation gave the phloroglucinol dibenzene-sulphonate acetate as prisms (from methanol), m. p. 81°. Methylation yielded phloroglucinol monomethyl ether dibenzenesulphonate, m. p. 92° (from benzene) (Found: S, 15·0. $C_{19}H_{16}O_7S_2$ requires S, 15·25%).

Phloroglucinol Monobenzenesulphonate (*Partial Hydrolysis of the Diester*).—A 20% solution of potassium hydroxide (56 ml.) was added at 50—55° over a period of 10 min. to a stirred solution of phloroglucinol dibenzenesulphonate (20·3 g.) in methanol (80 ml.). The reaction mixture was then kept at 60—65°, under reflux for 15 min. and the resulting greenish brown solution was diluted to 1 l. with water, decolourised with a few drops of sodium hyposulphite solution, acidified with hydrochloric acid, stirred for 1 hr. to assist deposition, and then kept overnight at about 0°. The precipitated needles were filtered off, washed with cold water, and dried over calcium chloride to give phloroglucinol monobenzenesulphonate monohydrate (11·3 g.; 80%). Crystallisation from water gave needles that lost water of crystallisation at about 102° and melted at 163—164° (Found: H_2O, 6·55. $C_{12}H_{10}O_5S,H_2O$ requires H_2O, 6·3%). The monohydrate (2·5 g.) was dissolved in boiling benzene (250 ml.), 100 ml. of the solvent were distilled off, and the solution was filtered. The anhydrous monoester separated as small needles, m. p. 163—164° (Found: S, 11·8. $C_{12}H_{10}O_5S$ requires S, 12·0%). Acetylation gave the phloroglucinol benzenesulphonate diacetate, as prisms (from benzene), m. p. 95—96°. Methylation with dimethyl sulphate yielded phloroglucinol dimethyl ether benzene-sulphonate as long flattened plates (from methanol), m. p. 75° (Found: S, 11·1%. $C_{14}H_{14}O_5S$ requires S, 10·9%).

Pyrocatechol.—To a stirred dispersion of pulverised pyrocatechol dibenzenesulphonate (11·7 g.), or to a solution of the monoester (7·5 g.), in methanol (50 ml.), both kept at 50—55°, was added during 10 min. a 20% solution of potassium hydroxide (50 ml. for the diester; 34 ml. for the monoester). The mixture was then kept at 60—65° for 30 min., diluted to 500 ml. with water, decolourised with a few drops of sodium hyposulphite solution, acidified, and kept at 0—5° for 24 hr. The unhydrolysed monoester was filtered off, the filtrate was extracted with ether and the ether evaporated leaving pyrocatechol (2·7 g.; 80%). Resorcinol and quinol were similarly prepared. Phloroglucinol in 75% yield was prepared from phloroglucinol monoester monohydrate (14·2 g.) in methanol (20 ml.) by the addition of a 40% solution of potassium hydroxide (42 ml.).

Pyrocatechol Monomethyl Ether (*Guaiacol*).—A 20% solution of potassium hydroxide (34 ml.) was added, at 50—55°, during 5 min., to a stirred solution of pyrocatechol methyl ether benzene-sulphonate (10·6 g.; prepared in 96% yield by methylation of the monoester with dimethyl sulphate) in methanol (50 ml.). The reaction was then continued at 60—65° for 30 min., the resulting methanolic solution was diluted to 500 ml. with water, decolourised, acidified, and extracted with benzene; the benzene extract was evaporated leaving guaiacol (4·5 g.; 90%). Acetylation gave the acetate, b. p. 239° (lit.,[5] 235—240°). Resorcinol monomethyl ether, b. p. 243—244° (lit.,[6] 238—244°; 243·8°) and quinol monomethyl ether, m. p. 55—56° (from petroleum–trichloroethylene), lit.,[7] 56°, were similarly prepared. Acetylation gave resorcinol mono-methyl ether acetate, b. p. 254—255° (lit.,[8] 254—256°), and quinol monomethyl ether acetate,

[5] F. Tiemann and P. Koppe, *Ber.*, 1881, **14**, 2020.
[6] P. Pfeiffer and J. Oberlin, *Ber.*, 1924, **57***B*, 208; M. Lecat, *Ann. Soc. sci. Bruxelles*, 1929, **49***B*, 112.
[7] R. Robinson and J. C. Smith, *J.*, 1926, 393.
[8] O. Wallach and M. Wüsten, *Ber.*, 1883, **16**, 152.

m. p. 33—34° (from petroleum), lit.,[9] 31—32°. The quinol monomethyl ether was precipitated from aqueous solution as the hexahydrate, as leaves, m. p. 23° (Found: H_2O, 46·95. $C_7H_8O_2,6H_2O$ requires H_2O, 46·5%).

Phloroglucinol Monomethyl Ether Monobenzenesulphonate (*Partial Hydrolysis of the Methoxydiester*).—A 20% solution of potassium hydroxide (24 ml.) was added dropwise at 40—45° to a stirred dispersion of pulverised phloroglucinol methyl ether dibenzenesulphonate (12·6 g.; prepared in 95% yield by methylation of the diester) in methanol (50 ml.). The reaction was continued at 40—45° until the diester had disappeared and the temperature was then raised to 50—55° for 10 min. The resulting reddish solution was diluted to 500 ml. with water, decolourised, acidified, stirred for 1 hr. and kept at about 0° overnight. The product was filtered off, washed with water, and dried to give phloroglucinol monomethyl ether monobenzenesulphonate (6·8 g., 90%) as prisms (from benzene), m. p. 111—112° (Found: S, 11·7. $C_{13}H_{12}O_5S$ requires S, 11·4%). Methylation with dimethyl sulphate gave the phloroglucinol dimethyl ether benzenesulphonate in 95% yield.

Phloroglucinol Monomethyl Ether.—Phloroglucinol monomethyl ether monobenzenesulphonate (11·2 g.) dissolved in methanol (50 ml.) was hydrolysed with 20% potassium hydoxide (56 ml.). The procedure was similar to that described for the hydrolysis of the pyrocatechol monoester to pyrocatechol. The yield (3·8 g.; 68%) of phloroglucinol monomethyl ether, m. p. (from benzene) 77—79° (lit.,[4a,10] 75—78°; 78—81°). Acetylation yielded the phloroglucinol methyl ether diacetate as needles (from methanol) m. p. 77° (lit.,[10] 74°). Similarly, the phloroglucinol dimethyl ether was prepared in 75% yield from a solution of phloroglucinol dimethyl ether benzenesulphonate (14·7 g.) in methanol (50 ml.) and a 20% solution of potassium hydroxide (56 ml.). Crystallisation from petroleum gave fine, stellate, crystals, m. p. 36—37° (lit.,[4a] 36—38°). Methylation with dimethyl sulphate yielded phloroglucinol trimethyl ether, m. p. 52—53° (from petroleum) lit.,[11] 52·5°; 54—55°.

DRECA LABORATORIES, 4 AMORGOU ST., PIRAEUS 18, GREECE. [*Received, July 29th*, 1964.]

[9] A. Klemenc, *Monatsh.*, 1914, **35**, 90.
[10] J. Herzig and F. Aigner, *Monatsh.*, 1900, **21**, 436.
[11] W. Will, *Ber.*, 1888, **21**, 603; J. Herzig and Br. Erthal, *Monatsh.*, 1911, **32**, 498.