544. *Allylbenzene Compounds. Part II.* 2 : 4 : 6-Trimethoxyallylbenzene.*

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2 : 4 : 6-Trimethoxyallylbenzene has been obtained by the pyrolysis of 3 : 5-dimethoxyphenyl allyl ether, followed by methylation of the resultant phenol. The allyl group in 2 : 4 : 6-trimethoxyallylbenzene is unusually stable to alkali, but at 130° it rearranges to 2 : 4 : 6-trimethoxypropenylbenzene which forms 2 : 4 : 6-trimethoxybenzoic acid on oxidation.

Three trimethoxyallylbenzenes have been reported to occur in Nature : elemicin, the identification of which as 3 : 4 : 5-trimethoxyallylbenzene by Semmler (*Ber.*, 1908, **41**, 1768, 1918) was confirmed by Mauthner's synthesis (*Annalen*, 1917, **414**, 250; cf. Hahn and Wassmuth, *Ber.*, 1934, **67**, 696), calamol, isolated by Qudrat-i-Khuda, Mukherjee, and Ghosh (*J. Indian Chem. Soc.*, 1939, **16**, 583) from the rhizome of *Acorus calamus* (variety " ghore bacha ") and believed by them to be " 2 : 3 : 5-, 2 : 3 : 6-, or 3 : 4 : 6- "trimethoxyallylbenzene, and 2 : 4 : 5-trimethoxyallylbenzene (Rao and Subramanian, *Current Sci.*, 1935, **3**, 552; *Chem. Abstr.*, 1935, **29**, 6585; 1934, **28**, 3523).

A fourth isomer, 2 : 4 : 6-trimethoxyallylbenzene, has now been synthesised. Allylation of 3 : 5-dimethoxyphenol and pyrolysis of the allyl ether gave a phenol, which is undoubtedly 3 : 5-dimethoxy-2-allylphenol, since no anomalous rearrangements of allyl ethers are known when both *ortho*-positions are unsubstituted (cf. Tarbell, *Organic Reactions*, 1944, **2**, 1). Methylation of the phenol with diazomethane or with methyl sulphate gave 2 : 4 : 6-trimethoxyallylbenzene.

Unlike the other known allylbenzenes, the refractive index of 2 : 4 : 6-trimethoxyallylbenzene was only slightly increased on prolonged heating of the compound with saturated alcoholic potassium hydroxide. However, on being heated with potassium hydroxide at 130° it isomerized readily to 2 : 4 : 6-trimethoxypropenylbenzene which was isolated as a crystalline solid and oxidised to 2 : 4 : 6-trimethoxybenzoic acid, identified by comparison with an authentic specimen, obtained from 2 : 4 : 6-trihydroxybenzoic acid. The latter was obtained by Will's method (*Ber.*, 1885, **18**, 1323) and methylated in two stages, diazomethane giving the intermediate methyl 2-hydroxy-4 : 6-dimethoxybenzoate from which either 2 : 4 : 6-trimethoxybenzoic acid or its methyl ester could be obtained by treatment with methyl sulphate and alkali. This method is preferable to those described in the literature (Beilstein, 4th Edn., **10**, 469).

Experimental.

3 : 5-*Dimethoxyphenyl Allyl Ether*.—Phloroglucinol dimethyl ether (Pratt and Robinson, *J.*, 1924, **125**, 188) (4·8 g.), allyl bromide (4·3 g.), potassium carbonate (freshly dried and sieved) (5·0 g.), and acetone (dried over potassium carbonate) (25 ml.) were refluxed for 7 hours and cooled, and water (100 ml.) added. The 3 : 5-*dimethoxyphenyl allyl ether* which separated was extracted with ether, washed with 5% sodium hydroxide solution, dried (K_2CO_3), and distilled. It formed a colourless oil, b. p. 156—162°/18 mm., b. p. 105—106°/0·4 mm. (Found : C, 68·2; H, 7·45. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%). From the alkaline washings phloroglucinol dimethyl ether (1·5 g.) was recovered.

3 : 5-*Dimethoxy-2-allylphenol*.—3 : 5-Dimethoxyphenyl allyl ether (12·7 g.) was heated in an oil-bath at 200—210° for 1 hour. Rearrangement began at about 180°; the temperature of the liquid rose more rapidly than that of the bath until it exceeded the bath-temperature, and after 25—30 minutes fell 1—2° below it again. On cooling, the product was dissolved in 5% sodium hydroxide solution, washed with ether to remove any unchanged allyl ether, acidified, and extracted with ether. After being dried (Na_2SO_4), evaporated, and distilled, the 3 : 5-*dimethoxy-2-allylphenol* (10·2 g.), b. p. 168—170°/18 mm., b. p. 120—121°/0·5 mm., solidified, and formed long colourless prisms, m. p. 42—43°, from light petroleum (b. p. 60—80°) (Found : C, 68·2; H, 7·5. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%).

2 : 4 : 6-*Trimethoxyallylbenzene*.—(a) *By diazomethane*. 3 : 5-Dimethoxy-2-allylphenol (5 g.) in methanol (20 ml.) was treated with an ethereal solution of diazomethane prepared from nitroso-

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* *J.*, 1949, 436, is considered to be Part I.

methylurea (20·6 g.). After 60 hours at room temperature the solvents were evaporated; 2 : 4 : 6-*trimethoxyallylbenzene* distilled as a colourless oil, b. p. 163—167°/22 mm., n_D^{18} 1·5377.

(b) *With methyl sulphate.* 3 : 5-Dimethoxy-2-allylphenol (15 g.) in methanol (30 ml.) was stirred and treated with methyl sulphate (15 g.) and excess of 20% sodium hydroxide solution for 30 minutes. After 15 minutes' boiling, and cooling, the 2 : 4 : 6-trimethoxyallylbenzene was extracted with ether, washed with water, dried (Na_2SO_4), and distilled. It (12·2 g.) had b. p. 156—158°/20 mm., b. p. 82—84°/0·07 mm., n_D^{14} 1·5388, n_D^{18} 1·5370, $n_D^{30\cdot5}$ 1·5322 (Found : C, 68·9; H, 7·7. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). Light absorption : Maximum, 2700—2730 A.; ε = 875.

Heating 2 : 4 : 6-trimethoxyallylbenzene (1 g.) with potassium hydroxide (1 g.), water (1·5 ml.), and alcohol (5 ml.) at the boiling point for 10 hours and recovery of the oil by addition of water and extraction with ether gave a product (0·7 g.), b. p. 157°/19 mm., n_D^{14} 1·5389, n_D^{18} 1·5370, $n_D^{30\cdot1}$ 1·5329.

Heating it (1 g.) with potassium hydroxide (2·6 g.) and alcohol (10 ml.) for 48 hours on a steam-bath gave an oil (0·7 g.), b. p. 167—168°/25 mm., n_D^{18} 1·5425. Increasing the time of heating to 75 hours did not give any further increase in the refractive index of the product.

2 : 4 : 6-*Trimethoxypropenylbenzene.*—2 : 4 : 6-Trimethoxyallylbenzene (3·9 g.) was dissolved in amyl alcohol (B.D.H. AnalaR; 30 ml.) and heated with potassium hydroxide (pellets; 10 g.) in an oil-bath at 125—140° for 22 hours. The amyl alcohol was removed by steam-distillation, and the residue cooled, whereupon 2 : 4 : 6-trimethoxypropenylbenzene crystallised (3·5 g.) and was filtered off. It formed long colourless prisms, m. p. 74—74·5°, from methanol (Found : C, 69·0; H, 7·7. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%). Light absorption : Maximum, 2675 A.; ε = 18,870.

2 : 4 : 6-*Trimethoxybenzoic Acid.*—(a) *By oxidation.* 2 : 4 : 6-Trimethoxypropenylbenzene (1·6 g.) was dissolved in acetone (75 ml.) and shaken with potassium permanganate (powdered; 3·3 g.) added in small portions during 30 minutes. The reaction was completed at the boiling point, and the acetone removed by steam-distillation. On cooling, sulphur dioxide was passed into the residue until the manganese dioxide dissolved and the acid was then extracted with ether, the ethereal solution extracted with sodium carbonate solution, and the acid precipitated by addition of dilute sulphuric acid. 2 : 4 : 6-Trimethoxybenzoic acid (0·1 g.) was filtered off and formed plates and prisms, m. p. 143° (decomp.), from aqueous methyl alcohol, alone or mixed with an authentic specimen prepared by method (b) below (Found : C, 56·45; H, 5·8. Calc. for $C_{10}H_{12}O_5$: C, 56·6; H, 5·7%).

(b) *From* 2 : 4 : 6-*Trihydroxybenzoic Acid.* 2 : 4 : 6-Trihydroxybenzoic acid (m. p. 206°, decomp.) (2·8 g.) was prepared in 55% yield by boiling phloroglucinol (3·8 g.), potassium hydrogen carbonate (15 g.), and water (30 ml.) for 10 minutes, cooling the mixture and pouring it into dilute hydrochloric acid. The product was dissolved in methanol (30 ml.) and ether (100 ml.) and treated with diazomethane from nitrosomethylurea (15 g.) at 5°, the temperature being allowed to rise to 20° during 1 hour. The excess of diazomethane was destroyed with acetic acid, the solvents were evaporated, and the methyl 2-hydroxy-4 : 6-dimethoxybenzoate (2·2 g.) was isolated as colourless needles, m. p. 105—106°, from methanol.

Treatment of methyl 2-hydroxy-4 : 6-dimethoxybenzoate (10 g.) in acetone (100 ml.), at the boiling point, with methyl sulphate (3 × 10 ml.) and 10%-potassium hydroxide solution (4 × 100 ml.), distillation of the solvents, and cooling and acidification of the residue gave 2 : 4 : 6-trimethoxybenzoic acid (7·9 g.), as colourless needles and plates (from 20% aqueous methanol), m. p. 142° (decomp.) after drying over phosphoric oxide.

If the methylation mixture was refluxed for two hours before removal of the solvents, the product was decarboxylated to phloroglucinol trimethyl ether, which crystallised on cooling, whilst cooling the reaction mixture two minutes after addition of the potassium hydroxide resulted in the separation of methyl 2 : 4 : 6-trimethoxybenzoate, which formed colourless prisms, m. p. 68—69°, from aqueous methanol and was hydrolysed to 2 : 4 : 6-trimethoxybenzoic acid when boiled for 1 hour with 5% aqueous alcoholic potassium hydroxide.

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