893. *Allylbenzene Compounds. Part III.* Pyrolysis of Methyl 2-Allyloxy-3 : 4-dimethoxybenzoate.*

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Pyrolysis of methyl 2-allyloxy-3 : 4-dimethoxybenzoate yields methyl 5-allyl-2-hydroxy-3 : 4-dimethoxybenzoate, the structure of which is demonstrated by conversion by standard methods into 4 : 5 : 6-trimethoxy*iso*phthalic acid.

IN view of the formation of 1-allyl-3 : 4-dihydroxy-5-methoxybenzene by the pyrolysis of 1-allyloxy-2-hydroxy-3-methoxybenzene (Trikojus and White, *J.*, 1949, 436) in contrast to the normal *o*-migration of the allyl group from 1-allyloxy-2 : 3-dimethoxybenzene and 1-allyloxy-2-ethoxy-3-methoxybenzene, it seemed of interest to examine the pyrolysis of methyl 2-allyloxy-3 : 4-dimethoxybenzoate in which *o*-migration of the allyl group is prevented by the carbomethoxy-group.

The product of the pyrolysis has been identified as that of a *p*-migration of the allyl group, by conversion into 5-allyl-2 : 3 : 4-trimethoxybenzoic acid with methyl sulphate and alkali in acetone, followed by rearrangement with alcoholic potassium hydroxide to 2 : 3 : 4-trimethoxy-5-propenylbenzoic acid. The latter, on oxidation with permanganate, formed 4 : 5 : 6-trimethoxy*iso*phthalic acid in good yield, demonstrating the correctness of the structures mentioned above.

EXPERIMENTAL

M. p.s are corrected. Analyses are by Drs. Weiler and Strauss, Oxford.

Methyl 2-Hydroxy-3 : 4-dimethoxybenzoate.—Best yields (cf. Beilstein, 4th edn., **10**, 465) were obtained by treatment of 2-hydroxy-3 : 4-dimethoxybenzoic acid (Baker and Savage, *J.*, 1938, 1602) (28 g.) in ether (280 ml.) with excess of ice-cold ethereal diazomethane, until there was no further evolution of nitrogen. On evaporation, methyl 2-hydroxy-3 : 4-dimethoxybenzoate remained and formed colourless needles, m. p. 76—77°, from alcohol (25·1 g., 83%). Esterification with methanol and sulphuric acid gives somewhat smaller yields (*ca.* 70%).

Methyl 2-Allyloxy-3 : 4-dimethoxybenzoate.—Methyl 2-hydroxy-3 : 4-dimethoxybenzoate (25·2 g.), allyl bromide (20 ml.), potassium carbonate (powdered, anhydrous; 34·6 g.), and acetone (100 ml.) were refluxed for 8 hours, cooled, diluted with water, and extracted with ether. The extract was washed with 10% sodium hydroxide solution and with water, dried (Na_2SO_4), and distilled. *Methyl 2-allyloxy-3 : 4-dimethoxybenzoate* was obtained as a pale yellow oil, b. p. 111—113°/0·05 mm. (27·4 g., 91%) (Found : C, 61·9; H, 6·5. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%).

Pyrolysis of Methyl 2-Allyloxy-3 : 4-dimethoxybenzoate.—Methyl 2-allyloxy-3 : 4-dimethoxybenzoate (26 g.) was heated in a bath to 180° (in about 40 minutes). The temperature in the liquid then rose to 12° above that of the bath (bath at 203°). After 2 hours' heating the temperatures of liquid and bath remained equal at 230°, and after cooling the product was dissolved in ether and extracted with sodium hydroxide solution. Acidification of this extract yielded *methyl 5-allyl-2-hydroxy-3 : 4-dimethoxybenzoate* (isolated with ether), b. p. 129—133°/0·07 mm. (15·2 g.), as a colourless oil (Found : C, 61·9; H, 6·5. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%).

From the smaller, high-boiling fraction (b. p. 136—143°/0·07 mm.) *5-allyl-2-hydroxy-3 : 4-dimethoxybenzoic acid* separated (5·1 g.), and formed clusters of colourless needles, m. p. 91°, from aqueous acetic acid (Found : C, 60·5; H, 5·85. $C_{12}H_{14}O_5$ requires C, 60·5; H, 5·9%). The same acid was obtained by saponification of the methyl ester with aqueous sodium hydroxide.

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* Part II, *J.*, 1950, 2810.

It was not esterified with methanol–sulphuric acid, but readily formed methyl 5-allyl-2-hydroxy-3 : 4-dimethoxybenzoate on treatment with diazomethane in ether.

2-Acetoxy-5-allyl-3 : 4-dimethoxybenzoic Acid.—5-Allyl-2-hydroxy-3 : 4-dimethoxybenzoic acid (2 g.), acetic anhydride (2·8 ml.), and sulphuric acid (1 drop) were heated at 60° for 15 minutes. On addition of water, the *acetate* solidified and formed long colourless prisms, m. p. 98·5—99·5°, from light petroleum (Found: C, 60·0; H, 5·9. $C_{14}H_{16}O_5$ requires C, 60·0; H, 5·8%).

Methyl 2-Acetoxy-5-allyl-3 : 4-dimethoxybenzoate.—Methyl 5-allyl-2-hydroxy-3 : 4-dimethoxybenzoate (100 mg.), acetic anhydride (50 mg.), and pyridine (0·5 ml.) were refluxed for 2 hours and kept for 18 hours at room temperature. On addition of water, the *acetate* solidified and formed colourless hexagonal prisms, m. p. 50·5°, from light petroleum (60—80°) (Found: C, 61·1; H, 6·2. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2%). The same compound (m. p. and mixed m. p.) was obtained by treatment of 2-acetoxy-5-allyl-3 : 4-dimethoxybenzoic acid with diazomethane in ether.

5-Allyl-2 : 3 : 4-trimethoxybenzoic Acid.—Methyl 5-allyl-2-hydroxy-3 : 4-dimethoxybenzoate (6·5 g.) in acetone (150 ml.) was treated with methyl sulphate (2 × 5·5 ml.) and 10% sodium hydroxide solution (3 × 50 ml.) at the b. p. while being stirred. Heating and stirring were continued for 3 hours, the acetone was distilled off, and after acidification the crude product was extracted with ether, and the ethereal solution shaken with charcoal, filtered, and evaporated, yielding *5-allyl-2 : 3 : 4-trimethoxybenzoic acid,* which formed plates, m. p. 83° (5 g., 77%), from light petroleum (b. p. 60—80°) (Found: C, 61·9; H, 6·4. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%). The same acid was obtained in slightly better yield (90%) from a similar methylation of 5-allyl-2-hydroxy-3 : 4-dimethoxybenzoic acid.

2 : 3 : 4-Trimethoxy-5-propenylbenzoic Acid.—5-Allyl-2 : 3 : 4-trimethoxybenzoic acid (4·3 g.) was heated for 48 hours at 100° with alcohol (60 ml.) and potassium hydroxide (15·6 g.). After steam-distillation and acidification, the product separated as an oil and was extracted with ether. When a solution in light petroleum was kept at 0°, colourless plates of *2 : 3 : 4-trimethoxy-5-propenylbenzoic acid* separated, and after 2 further crystallisations from light petroleum had m. p. 65—67° (1·2 g., 30%) (Found: C, 62·1; H, 6·5. $C_{13}H_{16}O_5$ requires C, 61·9; H, 6·4%).

Oxidation of 2 : 3 : 4-Trimethoxy-5-propenylbenzoic Acid.—This acid (500 mg.) in acetone (40 ml.) was treated with potassium permanganate (1·5 g.) in small portions, with shaking. The reaction was completed by heating to the b. p., and the solvent removed in steam. On addition of dilute sulphuric acid and dissolution of the manganese dioxide with sulphur dioxide, 4 : 5 : 6-trimethoxy*iso*phthalic acid separated in plates (300 mg.), m. p. 191°, and on crystallisation from water formed colourless, pointed prisms, m. p. 192°, alone or mixed with an authentic sample prepared by Feist and Awe's method (*Ber.*, 1926, **59**, 175) (Found: C, 51·6; H, 4·8. Calc. for $C_{11}H_{12}O_7$: C, 51·6; H, 4·7%).

Thanks are offered to Miss K. Thieberg for preparing the authentic sample of 4 : 5 : 6-trimethoxy*iso*phthalic acid.

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