LXXX.—*The Bromination of* m-*Methoxycinnamic Acid.*

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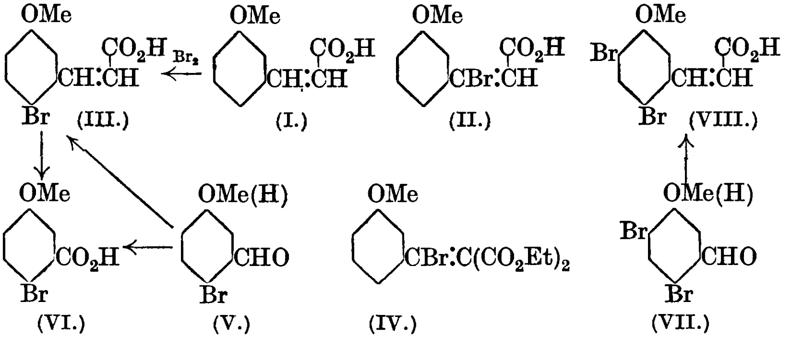
BAUER and VOGEL (*J. pr. Chem.*, 1913, **88**, 341) found that *m*-methoxycinnamic acid (I), when treated with one molecular proportion of bromine in glacial acetic acid, gave a substance, m. p. 186°, to which they attributed the constitution (II), since on oxidation it gave *m*-methoxybenzoic acid. They did not specify the temperature of bromination, but we have found that the bromination is effected slowly in acetic acid at the ordinary temperature, and that the acid produced, m. p. 189°, is 6-*bromo*-3-*methoxycinnamic acid* (III), its constitution being established as shown. The 6-position of the bromine atom in the bromination product (V) of *m*-methoxy (or *m*-hydroxy)-benzaldehyde has been proved by Pschorr (*Annalen*, 1912, **391**, 23). The cinnamic acid (III) prepared from this 6-bromo-3-methoxybenzaldehyde melted at 189° and was identical with the one mentioned above.

Bauer and Vogel gave no evidence for the formula (IV) which they attributed to the bromination product of ethyl *m*-methoxybenzylidenemalonate (*loc. cit.*). After hydrolysis, elimination of carbon dioxide, and oxidation, the acid obtained from this product is 6-bromo-3-methoxybenzoic acid (VI). It is possible that the bromination product of *m*-methoxybenzylidenemalonic acid also has the bromine in the 6-position, and not in the side chain as Bauer and Vogel state.

By the action of two molecules of bromine upon *m*-methoxycinnamic acid in glacial acetic acid solution, Bauer and Vogel (*loc. cit.*, p. 341) obtained a substance which they regarded as β : 6-dibromo-3-methoxycinnamic acid (formula as II), because it could be converted into 6-bromo-3-methoxybenzoic acid. Actually,



however, the bromination product is a complex mixture, from which, after oxidation, 4(or 2) : 6-dibromo-3-methoxybenzoic acid (m. p. 203°) can be isolated, identical with the acid produced by oxidation of the 4(or 2) : 6-dibromo-3-methoxybenzaldehyde (VII) obtained from 6-bromo-3-hydroxybenzaldehyde (Hodgson and Beard, J., 1925, **127**, 877). The second bromine atom entering the nucleus may be in position 2 or 4 (compare Hodgson and Beard, J., 1926, 148, who state that the direct chlorination of *m*-hydroxybenzaldehyde gives chiefly the 2- and not the 6- or the 4-chloro-derivative).

4(or 2) : 6-Dibromo-3-methoxybenzaldehyde was converted into 4(or 2) : 6-*dibromo*-3-*methoxycinnamic acid* (VIII), m. p. 234°, and this into the corresponding benzoic acid, m. p. 203°, on oxidation.

Bromination of *m*-methoxycinnamic acid with one molecular proportion of bromine therefore gives the 6-bromo-derivative in large amount, and with two molecular proportions of bromine, two bromine atoms, to some extent, enter the nucleus. These reactions are abnormal, for bromination of cinnamic acids usually affects the double bond in the side chain, producing dibromides (Manchot, *Annalen*, 1912, **387**, 257).

EXPERIMENTAL.

m-Methoxycinnamic acid (m. p. 117°) is best prepared from the corresponding aldehyde by the action of malonic acid in pyridine, and not by the Perkin reaction, which even after prolonged treatment gives a very poor yield.

Bromination of m-*Methoxycinnamic Acid.*—The acid (10 g.) was brominated (1 mol. of bromine) in glacial acetic acid (200 c.c.) according to the directions of Bauer and Vogel (*loc. cit.*). After 2 days, much practically pure crystalline matter was collected and in the following 8 days a further quantity of less pure material separated. By crystallisation from benzene, colourless needles (4 g.), m. p. 189°, of 6-*bromo*-3-*methoxycinnamic acid* (III) were obtained (Found : C, 46·8; H, 3·5. $C_{10}H_9O_3Br$ requires C, 46·7; H, 3·6%). It is oxidised by permanganate (without the production of potassium bromide) to give 6-bromo-3-methoxybenzoic acid (m. p. 162°) (VI). 6-Bromo-3-methoxycinnamic acid was also synthesised from 6-bromo-3-methoxybenzaldehyde (m. p. 76°, prepared after Pschorr and also Hodgson and Beard, J., 1925, **127**, 877) by means of malonic acid in pyridine.

After the brominating liquor had stood for 10 days, it was diluted with water, and gave a solid, m. p. 108—140°, from which nothing pure could be crystallised; but it undoubtedly contained a cinnamic acid dibromide derivative, because, when it was warmed with sodium acetate, bromide was produced together with an oily, styrene-like substance.

Bromination of m-*Methoxybenzylidenemalonate.*—This substance, b. p. 205—208°/17 mm., prepared after Bauer and Vogel, was heated on the water-bath with bromine (1 mol.) in 100% acetic acid for 3 hours; bromination was then complete. The product obtained on pouring the mixture into water was hydrolysed with sodium hydroxide, and the acid (m. p. 173—183°, decomp.) obtained on acidification was dried and heated at 180° until the evolution of carbon dioxide ceased. The product, after crystallisation from benzene, melted at 189° before and after admixture with 6-bromo-3-methoxycinnamic acid. They were also found identical in other respects.

The Action of Two Molecules of Bromine on m-*Methoxycinnamic Acid.*—*m*-Methoxycinnamic acid (10 g.) was heated on the water-bath with bromine (2 mols.) after Bauer and Vogel, who record no temperature; bromination was complete in 8 hours. The product obtained on pouring the mixture into water separated from dilute acetic acid (without the application of heat) in colourless crystals, m. p. 130—163°. This substance at once reduced permanganate in cold acetone, and when it was treated with cold alkali or sodium acetate an oil of styrene-like character and a bromide were formed. The bromine was evidently partly in the side chain. The acid (m. p. 130—163°), after being ozonised in dilute acetic acid solution at the ordinary temperature, melted at 157—165° and contained Br, 52·8% (Calc. for 3Br, 57·5; for 2Br, 47·3%). The product, on oxidation with permanganate, gave a small quantity of 4(or 2) : 6-dibromo-3-methoxybenzoic acid, m. p. 203°, which was identified by the method of mixed melting point.

Monobromination of 6-bromo-3-methoxycinnamic acid produced the mixed acids, m. p. 157—165°. Bromination therefore takes place partly at the double bond in the side chain and partly in the nucleus.

4(or 2) : 6-*Dibromo*-3-*methoxycinnamic acid* (VIII) was synthesised for purposes of comparison. 4(or 2) : 6-Dibromo-3-hydroxybenzaldehyde (m. p. 139°) was prepared after Hodgson and Beard (*loc. cit.*), but instead of isolating the monobromo-derivatives of 3-hydroxybenzaldehyde it was found advantageous to heat the aldehyde with one mol. of bromine in chloroform and, when that had reacted, to add the second mol. of bromine. Subsequent methylation and steam distillation gave 4(or 2) : 6-dibromo-3-methoxybenzaldehyde, m. p. 110° as found by Hodgson and Beard. This was converted into the corresponding cinnamic acid exactly as in the preparation of 6-bromo-3-methoxycinnamic acid. 4(or 2) : 6-*Dibromo*-3-*methoxycinnamic acid* separates from acetic acid in colourless prisms, m. p. 234° (Found: equiv., 334·7. $C_{10}H_8O_3Br_2$ requires equiv., 336). It decolorises permanganate in cold acetone solution and is oxidised, without the formation of bromide, to give 4(or 2) : 6-dibromo-3-methoxybenzoic acid, m. p. 203°.

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[*Received, November* 21*st*, 1927.]