185. *The Condensation of Deoxybenzoin with Aromatic Aldehydes and Ketones. Part I. Condensation with Salicylaldehyde.*

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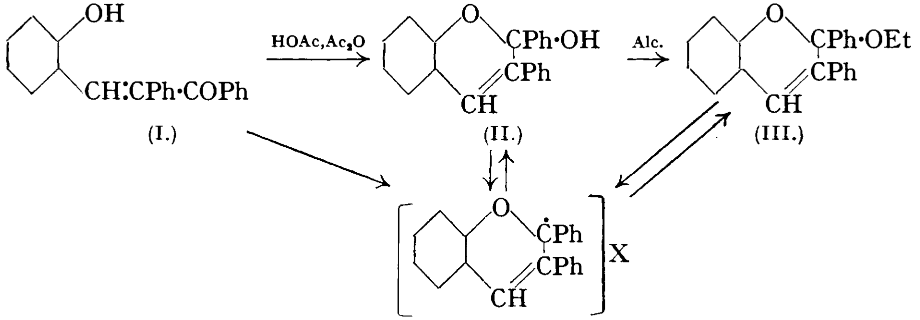
It is well known that deoxybenzoin condenses with aromatic aldehydes in the presence of both acidic and alkaline reagents (Japp and Klingemann, *Ber.*, 1888, **21**, 2934; Knoevenagel and Weissgerber, *Ber.*, 1893, **26**, 436; Klingemann, *Annalen*, 1893, **275**, 50; Stobbe and Wilson, *ibid.*, 1910, **374**, 237; Das and Ghosh, J., **1919**, **115**, 817; Singh and Mazumdar, *ibid.*, p. 821). With salicylaldehyde, however, condensation has hitherto only been effected in acids, with the formation of 3-phenylflavylium salts (Decker and Fellenberg, *Annalen*, 1909, **364**, 34; Gomberg and Cone, *ibid.*, 1909, **370**, 197; Das and Ghosh, *loc. cit.*; Singh and Mazumdar, *loc. cit.*; Löwenbein and Rosenbaum, *Annalen*, 1926, **448**, 223). It has now been achieved by alcoholic piperidine, after attempts with potassium hydroxide, sodium ethoxide, or diethylamine (cf. J., 1934, 1255; 1935, 1115; 1936, 256) had failed. The product was at first believed to be the dideoxybenzoin, but its reactions and molecular weight showed it to be *salicylidenedeoxybenzoin* (I). It does not agree in any way with Singh and Mazumdar's compound of the same name, m. p. 160° (*loc. cit.*). It does not behave as a typical chalkone. Although it is converted into 3-phenylflavylium chloride (separated as the ferrichloride) by hydrogen chloride in acetic acid in the normal manner, treatment with acetic anhydride or acetic acid produces 2 : 3-diphenylbenzo-2-pyranol (II), which is converted into the ethyl ether (III) by crystallisation from alcohol (compare Hill and Melhuish, J., 1935, 1161).

Contrary to Singh and Mazumdar's statement (*loc. cit.*), refluxing 3-phenylflavylium ferrichloride with alcoholic potassium hydroxide produces, not salicylidenedeoxybenzoin, but the pyranol ethyl ether (III).

The inter-relationship of the above compounds is shown by the following scheme :



EXPERIMENTAL.

Salicylidenedeoxybenzoin.—A solution of salicylaldehyde (5 c.c.) and deoxybenzoin (5 g.) in alcohol (50 c.c.) containing piperidine (5 c.c.) was kept for 3 days and poured into water (1 l.). When the precipitated oil solidified, the water was decanted, and the solid taken up in alcohol. The deep brown solution deposited pale brown crystals, which on recrystallisation from alcohol separated in almost colourless rhombs (2·5 g.), m.p. 129° [Found : C, 83·9; H, 5·6; *M* (Menzies–Wright), 312. $C_{21}H_{16}O_2$ requires C, 84·0; H, 5·3% ; *M*, 300].

Conversion into 3-*Phenylflavylium Ferrichloride.*—(a) Hydrogen chloride was rapidly passed through a solution of the above ketone (1 g.) in glacial acetic acid (10 c.c.) for 5 minutes with cooling, and the orange-yellow solution then treated with ferric chloride (0·5 g.) in glacial acetic acid (7 c.c.). The yellow crystals of the ferrichloride were separated after an hour, washed with dry ether, and recrystallised from acetic acid; m. p. 123—124° (Decker and Fellenberg, *loc. cit.*, give m. p. 123—124°).

(b) The ketone (2 g.) in acetic anhydride (30 c.c.) was cooled and stirred during the addition of ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.) so that the temperature did not rise above 30°. After an hour the product was collected and recrystallised from glacial acetic acid, forming yellow needles, m. p. and mixed m. p. 123°.

Action of Acetic Anhydride or Glacial Acetic Acid on Salicylidenedeoxybenzoin.—The ketone (1 g.) was stirred at room temperature for 1½ hours or refluxed with acetic anhydride (20 c.c.), and the solution poured into water. The white precipitate crystallised from aqueous alcohol in small, hard, colourless cubes, m. p. and mixed m. p. with authentic 2 : 3-diphenylbenzo-2-pyranol ethyl ether 78—79°.

The ketone (2 g.) was refluxed in glacial acetic acid (30 c.c.) for 10 minutes and poured into water. A portion of the white flocculent precipitate, crystallised from light petroleum (b. p. 60—80°), gave colourless hard crystals of the pyranol, m. p. 125°. Another portion, crystallised from alcohol, gave the ethyl ether, m. p. 80°.

Action of Alcoholic Potassium Hydroxide on 3-*Phenylflavylium Ferrichloride.*—The ferrichloride (3 g.) was refluxed with 10% alcoholic potassium hydroxide (130 c.c.) for 3 hours, the filtered solution poured into water (500 c.c.), and the precipitate crystallised from alcohol, giving colourless crystals, m. p. and mixed m. p. with 2 : 3-diphenylbenzo-2-pyranol ethyl ether, 79°.

3-*Phenylflavylium Chloride.*—Hydrogen chloride was passed through a solution of deoxybenzoin (5 g.) and salicylaldehyde (3 g.) in dry ether for 2 hours with cooling, and again for 1 hour after an interval of 24 hours. The long orange needles of the flavylium chloride were collected, washed with dry ether, and dried over calcium chloride in a vacuum desiccator; they darkened at 110—115° and had m. p. 158° (decomp.) (Found : C, 70·7; H, 4·7; Cl, 18·4. Calc. for $C_{21}H_{16}OCl_2$: C, 70·9; H, 4·6; Cl, 19·9%). Gomberg and Cone (*loc. cit.*) describe the salt as a dichloride crystallising in yellow needles (contrast Das and Ghosh; Singh and Mazumdar, *locc. cit.*).

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