331. *Triarylpyrylium Borofluorides.*

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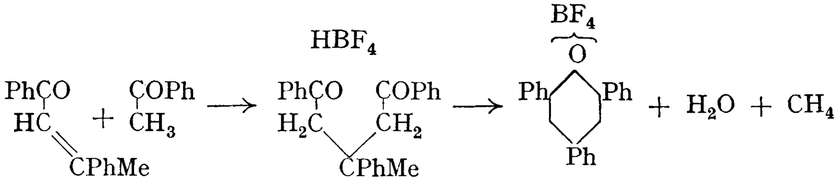
It is doubtful whether the new synthesis of β-diketones described by Meerwein and Vossen (*J. pr. Chem.*, 1934, **141**, 149), whereby methyl ketones and acid anhydrides are treated with boron trifluoride, is a general one, but a good case is represented by the preparation of benzoylacetone.

In attempting an extension of the process, but still using acetophenone, we obtained 2 : 4 : 6-*triphenylpyrylium borofluoride*, convertible into the known triphenylpyrylium ferrichloride of Dilthey (*J. pr. Chem.*, 1916, **94**, 53; **95**, 116). A better yield of the same salt was obtained when an equivalent mixture of acetophenone and phenyl styryl ketone was treated with boron trifluoride. The latter type of synthesis was applied to the preparation of 2 : 4 : 6-*tri*-p-*methoxyphenylpyrylium borofluoride*; the yields were superior to those obtained by the use of ferric chloride as in Dilthey's process (*loc. cit.*).

The mechanism of the reaction (from acetophenone) is obscure. The most natural suggestion is that shown below :



This would harmonise with the absence of strong oxidising agents in the system and with the elimination of methane in Riehm's synthesis (*Annalen*, 1887, **238**, 16) of triphenylpyridine from acetophenone and ammonium chloride (cf. Engler and Heine, J., 1873, **28**, 1036) and the similar decomposition of the Guareschi compounds (Guareschi, *Chem. Zentr.*, 1897, i, 927). Methane does not, however, appear to be a product of the reaction, so the fate of the methyl group has not been determined.

The first stage of the process with acetophenone and phenyl styryl ketone is doubtless the formation of benzylidenediacetophenone.

EXPERIMENTAL.

2 : 4 : 6-*Triphenylpyrylium Borofluoride*.—(A) Acetophenone (10 g.) was saturated with boron trifluoride prepared from potassium borofluoride (19 g.), boric anhydride (3·5 g.), and concentrated sulphuric acid (60 c.c.) according to Krause and Nitsche's method (*Ber.*, 1921, **54**, 2784). Heat was evolved and the colour changed from pale yellow to deep greenish-yellow. The reaction was completed by heating at 120° for 15 minutes. After cooling, the mass was shaken with benzene and water, and the solid collected; it crystallised from alcohol in fine yellow needles, m. p. 225—226° (yield, 2·4 g. or 22%).

(B) A mixture of phenyl styryl ketone (8 g.) and acetophenone (4·8 g.) was heated until homogeneous and was then saturated with boron trifluoride prepared from potassium borofluoride (38 g.), boric anhydride (6·5 g.), and sulphuric acid (125 c.c.); the mixture became deep cherry-red and the temperature rose to 90°. On cooling, the melt became very viscous; it was shaken with benzene and water and the yellow precipitate was collected, washed, and dried (yield, 4·6 g. or 61%).

2 : 4 : 6-*Triphenylpyrylium borofluoride* is insoluble in benzene and its pale greenish-yellow solution in concentrated sulphuric acid exhibits an intense greenish-blue fluorescence. The alcoholic and acetone solutions also are fluorescent (Found: C, 67·5; H, 4·6. $C_{23}H_{17}OF_4B,0{\cdot}66H_2O$ requires C, 67·7; H, 4·5%). The results are difficult to interpret except as suggested. The presence of boron and fluorine was confirmed qualitatively, and when the salt was heated with sulphuric acid boron trifluoride was evolved. When the borofluoride was shaken with an excess of aqueous sodium acetate containing a little alcohol, the yellow colour gradually disappeared owing to the formation of the pseudo-base, which was then taken up in ether. The separated ethereal solution was mixed with a saturated solution of ferric chloride in concentrated hydrochloric acid; the 2 : 4 : 6-triphenylpyrylium ferrichloride precipitated crystallised from acetone–benzene in yellow needles, m. p. 227° alone or mixed with the product of Dilthey's process (*loc. cit.*).

2 : 4 : 6-*Tri*-p-*methoxyphenylpyrylium Borofluoride*.—(A) *p*-Methoxyacetophenone (10 g.) was treated like acetophenone in the previous example; the mixture gradually became dark bluish-red. Impure 2 : 4 : 6-trianisylpyrylium borofluoride was isolated as a maroon precipitate (yield, not greater than 10%). A much better method is the following.

(B) *p*-Methoxyphenyl *p*-methoxystyryl ketone (5·4 g.) and *p*-methoxyacetophenone (3 g.) were mixed at 70° and boron trifluoride (from potassium borofluoride, 19 g.) was passed in until saturation occurred; the colour changed from pale yellow to deep bluish-red. A small sample being non-fluorescent in alcohol or acetone solution, the mixture was heated at 120° for 15 minutes. It was then cooled and worked up as previously described; the brick-red semi-crystalline product was freed from initial materials by washing with benzene (yield, 3·8 g. or 32·7%).

2 : 4 : 6-*Tri*-p-*methoxyphenylpyrylium borofluoride* crystallised from glacial acetic acid in small, thin, orange prisms, m. p. 345—347° (Found: C, 63·9; H, 4·9. $C_{26}H_{23}O_4F_4B$ requires C, 64·2; H, 4·7%), soluble in alcohol or acetone to yellow, greenish-yellow fluorescent solutions. Directly treated with aqueous picric acid, it afforded the picrate in orange needles, m. p. 270° (lit., 278°).

The pseudo-base was rendered to ether in the presence of aqueous sodium carbonate, and the tri-*p*-methoxyphenylpyrylium ferrichloride prepared from the ethereal solution. The derivative crystallised from acetic acid in glistening brown plates and flat prismatic needles, m. p. 270° alone or when mixed with an authentic specimen.

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