2,4,6-Trimethylpyrylium Tetrafluoroborate from Acetyl Fluoride and Boron Trifluoride

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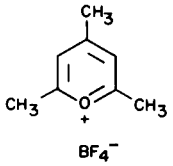
Acetyl fluoroborate in contact with acetyl fluoride turns with time into a brown oil which displays a green-yellow fluorescence under UV irridiation. From this oil 2,4,6-trimethylpyrylium tetrafluoroborate (I) was isolated. (The compound was also isolated from old samples of acetyl fluoride sealed into glass ampoules; this is probably due to partial decomposition of acetyl fluoride with subsequent attack on the glass and formation of boron trifluoride. This observation is a "one component synthesis" of a pyrylium salt from a two-carbon compound; the syntheses recorded up to the present (1) require either one component containing at least five carbon atoms or several components as starting materials.

Propionyl fluoride and butyryl fluoride saturated with boron trifluoride also turn brown and fluorescent. However, attempts to isolate pyrylium compounds from the brown materials have so far been unsuccessful.



I

EXPERIMENTAL

When a stream of boron trifluoride (2) was passed at 0° through pure acetyl fluoride (3), acetyl fluoroborate precipitated just as from solutions in chloroform (4). The yellow reaction mixture, which displayed a green-yellow fluorescence under UV light, was sealed into glass ampoules and kept at room temperature. The crystals disappeared within a few days and the color of the liquid became dark brown. After a week the ampoules were opened and held over boiling water to expel the unreacted acetyl fluoride. The brown oily residue dissolved completely in hot ethanol. Upon cooling white crystals precipitated, the precipitation being completed by addition of ether. (The same crystals were obtained by extracting the oil with hot water and cooling, but the yield was poorer). Up to 4 g. of 2,4,6-trimethylpyrylium tetrafluoroborate was obtained from 100 g. of acetyl fluoride. The salt was recrystallized from ethanol, m.p. 205-208° (previously reported m.p. (5) 206-208°).

Anal. Calcd. for $C_8H_{11}BF_4O$: C, 45.78; H, 5.25; F, 36.20; B, 5.15. Found: C, 45.90; H, 5.41; F, 35.3; B, 5.2.

The UV spectrum (in ethanol) and the NMR spectrum (in deuterium oxide) were identical with those of 2,4,6-trimethylpyrylium perchlorate (6,7). The IR-spectrum (in potassium bromide) had the following bands in common with potassium fluoroborate, 3400 (m), 2900 (m), 2830 (m), 1300 (m), 1255 (m), 1150 (sh), 1080 (vs), 1050 (sh), 805 (m), 765 (m), 520 (s) and 515 (s) cm^{-1}. In addition the spectrum of the compound had the following lines of the perchlorate (8), 1650 (s), 1550 (s), 1460 (m), 1380 (m) and 1350 (m) cm^{-1} and several weak bands. The highest m/e value of the mass spectrogram was 123 (corresponding to $C_8H_{11}O^+$). The identity of the crystals was further proven by their conversion into *sym*-collidine picrate (m.p. 155-156°) and *m*-xylenol (identified as the tribromide derivative (m.p. 166°) by the methods applied to the perchlorate (9,10).

2,4,6-trimethylpyrylium tetrafluoroborate was also synthesized in a 40% yield by passing boron trifluoride through a mixture of 5 ml. of *t*-butyl alcohol and 25 ml. of acetic anhydride.

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