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For the first time, we have demonstrated the possibility of obtaining substituted pyrylium tetrafluoroborates (Ia-c) as a result of the acylation of phenylacetylene by an oxonium complex generated in situ by reacting the corresponding acyl fluorides with boron trifluoride etherate. At the same time, the direct use of acyl fluoborates as acylating agents resulting in the polymerization of phenylacetylene.

$$RCOF + (C_2H_5)_2O \rightarrow BF_3 \rightarrow I(C_2H_6)_2OC - RI^+BF_4$$

$$2 C_6H_6C = CH + I(C_2H_6)_2OC - RI^+BF_4$$

$$C_6H_6$$

$$RF_4$$

Ia $R=CH_3$; Ib $R=C(CH_3)_3$; Ic $R=C_6H_5$

This method makes it possible to vary the radical R as a function of the acyl fluoride used and to obtain the difficultly accessible 2-alkylated pyrylium tetrafluoroborates.

A 20-ml portion of CHCl₃ at room temperature is given an addition of 1.4 g (0.01 mole) of boron trifluoride etherate and 0.08 mole of the corresponding acyl fluoride. The mixture is stirred for 1 h, then cooled to -30° C, and given a dropwise addition of a solution of 1.8 g (0.02 mole) of phenylacetylene in 20 ml of CHCl₃. The reaction mixture obtained is stirred at room temperature for 24 h, and the precipitate formed is separated and recrystallized. The yields of compounds Ia-c are 15, 30, and 35%, and their mp's are 238-240, 252-254, and 218-220°C, respectively (from acetic acid).

Literature data: mp's of Ia-c, 242-245 [1], 253-256 [2], 214-216 [2] respectively. The structures of compounds Ia-Ic were confirmed by data from PMR spectroscopy.

LITERATURE CITED

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