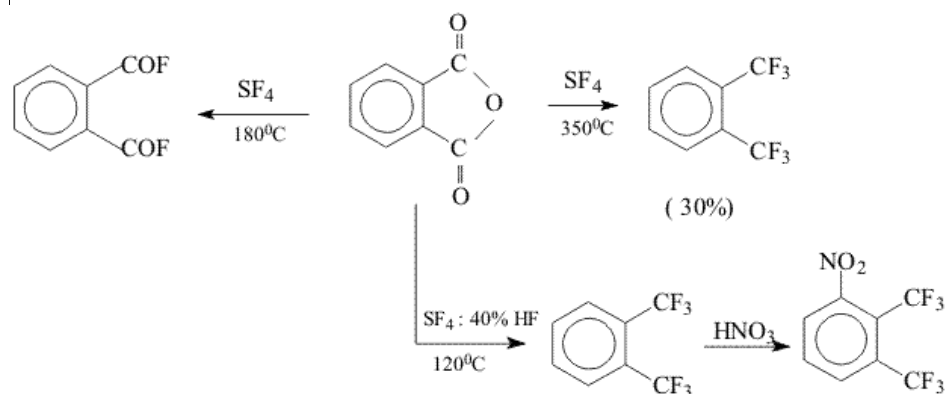


Fluorine-containing pyrazoles

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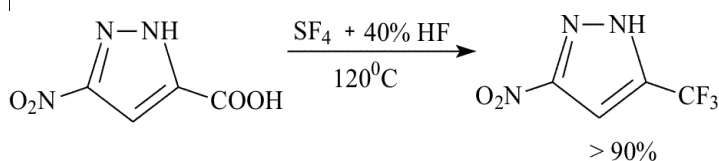
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It has been shown earlier that for production of 1,2-bis (trifluoromethyl) benzene from phthalic anhydride a temperature up to 350 °C is necessary [1,2].



During the process of development of a method to produce 2,3-bis(trifluoromethyl)nitrobenzene we succeeded in a considerable decrease in the reaction temperature by addition of a small quantity of hydrofluoric acid (40% solution of HF in H_2O) into the reaction mixture.

It turned out that the use of SF_4 with addition of hydrofluoric acid could be successfully used for substitution of carboxyl group in pyrazoles. Thus, by treatment of 3-carboxy-5-nitropyrazole with this mixture a corresponding pyrazole containing trifluoromethyl group was synthesized in a yield up to 90%.



Experimental

1,2-Bis(trifluoromethyl)benzene

Phthalic anhydride (45g, 0.3 mol) and hydrofluoric acid (7mL) were placed in a steel autoclave (250mL water capacity). The autoclave was cooled with dry carbonic acid at first and then with liquid nitrogen, then 85 mL of sulfur tetrafluoride (162g, 1.5 mol) preliminary condensed were poured from a trap. The autoclave was hermetically sealed, placed in a rocking furnace and heated at a temperature of 120°C for 10 hours. Next day the autoclave contents was poured on ice, methylene chloride was added, washed with water, dried with MgSO_4 and after distillation from CH_2Cl_2 the residue was distilled in vacuo. There was produced 35g (61%) of 1,2-bis(trifluoromethyl)benzene, $T_b = 420/15$ mm Hg (compare [2]).

3-trifluoromethyl-5-nitropyrazole

Similar to the above experiment from 3-carboxy-5-nitropyrazole (80g, 0.5 mol), hydrofluoric acid (10 mL) and 115 mL sulfur tetrafluoride (216g, 2.0mol) there was produced 83g of the product (90%), Melting Point = 65°C

Found, %: C, 26.32; H, 3.40; N, 22.42 $\text{C}_4\text{H}_6\text{N}_3\text{O}_4$,
 Calculated, %: C, 26.08; H, 3.26; N, 22.82. NMR: $^1\text{SF}_4$ 2 ppm. (CF_3)

References

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2. W.R. Hasek, W.C. Smilh., V.A. Engelhardt . I. Aw. Chem. Soc.,82,543 (1960)