Synthetic Methods and Reactions; XI[1]. A Convenient Direct Preparation of 1,3,5-Trinitrobenzene from *m*-Dinitrobenzene by Nitration with Nitronium Tetrafluoroborate in Fluorosulfuric Acid Solution

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Although the preparation of 1,3,5-trinitrobenzene from *m*-dinitrobenzene has been reported in low yield[2,3,4], 1,3,5-trinitrobenzene is usually prepared by indirect methods[5]. We have reported[6] recently mechanistic and kinetic studies of nitration of *m*-dinitrobenzene to 1,3,5-trinitrobenzene with nitronium tetrafluoroborate in fluorosulfuric acid at 95°. Under these conditions, however, the nitration is too slow to be of preparative use. Only a 40% yield (based on the isolated products) of 1,3,5-trinitrobenzene was observed even after several days. However, the recovery of nitro products was almost quantitative (98.8% based on the starting *m*-dinitrobenzene). We now would like to report the study of the preparative nitration of *m*-dinitrobenzene using nitronium tetrafluoroborate in fluorosulfuric acid solution to obtain 1,3,5-trinitrobenzene.

In our studies we have found that the rate of conversion of *m*-dinitrobenzene to 1,3,5-trinitrobenzene, as excepted, increases with increasing reaction temperature. However, the overall recovery of nitro products decreases with increased reaction temperature, due to oxidative side reactions. Thus it was necessary to carry out a detailed study to find optimal reaction conditions. The results of these studies at 150° are shown in the Table.

With a reaction time ~2h, one can obtain a 66% yield of 1,3,5-trinitrobenzene. However, since there is unreacted *m*-dinitrobenzene present (about 17%), a separation process (such as high pressure liquid chromatography) is needed in order to obtain pure 1,3,5-trinitrobenzene. A reaction time of 3h gave a ~62% yield of 1,3,5-trinitrobenzene with 95% purity. With 3.8h reaction time, 100% purity was achieved, but the yield dropped to about 50%.

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Table. Nitration of *m*-Dinitrobenzene to 1,3,5-Trinitrobenzene with Nitronium Tetrafluoroborate ($NO_2^{\oplus} BF_4^{\ominus}$) in Fluorosulfuric Acid (FSO_3H) Solution at 150°

Reaction Time (h)	Recovery of Nitro Compounds[a] (%)	1,3,5-Trinitrobenzene in Total Nitro Products[b] (%)	Yield of 1,3,5-Trinitrobenzene (%)
0	100	0	0
0.5	95.2	38.0	36.2
1.0	90.3	60.4	54.5
1.7	82.5	80.0	66.2
2.2	77.7	85.0	66.0
3.0	64.8	95.0	61.6
3.4	56.7	98.2	55.7
3.6	52.3	99.4	52.0
3.8	49.3	100	49.3
4.0	44.8	100	44.8
4.2	39.4	100	39.4

[a] Based on starting *m*-dinitrobenzene.

[b] Based on total nitro products isolated.

1,3,5-Trinitrobenzene:

Fluorosulfuric acid (200 ml) was placed in a 500 ml flask equipped with a magnetic stirring bar. To the stirred acid cooled in a dry ice/acetone bath nitronium tetrafluoroborate (100 g, 0.75 mol) and *m*-dinitrobenzene (42 g, 0.25 mol) were added, respectively. A reflux condenser was then attached and the reaction mixture was allowed to warm up to room temperature. Up to this point, no trinitrobenzene can be detected. The reaction vessel was then heated, while stirring the mixture, at 150°. After 3 h the reaction mixture was poured on to crushed ice (~ 500 g). The nitro products were extracted with dichloromethane, washed with 5% sodium hydrogen carbonate solution, and dried over magnesium sulfate. After removing solvent, 32.9 g (61.6%) of 1,3,5-trinitrobenzene (containing 5% of *m*-dinitrobenzene, based on G. L. C. analysis) was obtained.

In case of 3.8 h reaction time, under similar conditions, trinitrobenzene was analytically pure and was obtained in 49.3% yield. After recrystallization from alcohol (m.p. 122°), it gave physical characteristics and spectral properties (I.R. and N.M.R.) identical in aspects with an authentic analytical sample of highest purity.

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