The Synthesis of Some Fluorine-Containing Trinitrobenzenes[1]

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During an investigation of the methods of synthesis of fluorine-containing trinitrobenzenes, we made the following compounds: 1-fluoro- (I), 1,3-difluoro- (II), and 1,3,5-trifluoro-2,4,6-trinitrobenzene (III). Attempts to synthesize compounds of this type have been reported by Siele and Matsuguma.[4] We have found that while synthesis of the fluorodinitrobenzenes proceeds well in the conventional mixed-acid nitration medium, the introduction of the third nitro group is best effected using potassium nitrate and fuming sulfuric acid.[5] The infrared bands of the compounds prepared are given in Table I.

TABLE I

PRINCIPAL INFRARED BANDS[a]

$F_3C_6(NO_2)_3$	$F_2C_6H(NO_2)_3$	$FC_6H_2(NO_2)_3$	$F_3C_6H(NO_2)_2$	$F_3C_6H_2NO_2$[b]	$FC_6(NO_2)_3$-$(OC_2H_5)_2$	$(OH)_3C_6(NO_2)_3$
3.5 (2)[c]	3.3 (2)	3.3 (5)	3.2 (2)	3.3 (1)	3.4 (3)	6.1 (10)
6.2 (10)	6.2 (9)	5.3 (2)	6.1 (10)	6.2 (10)	3.5 (2)	6.4 (8)
6.4 (9)	6.5 (9)	6.2 (10)	6.5 (9)	6.5 (10)	6.2 (9)	6.6 (9)
6.5 (9)	6.8 (5)	6.5 (10)	6.8 (5)	6.8 (5)	6.5 (10)	7.4 (8)
6.9 (4)	7 (3)	6.8 (8)	7.4 (10)	6.9 (6)	6.8 (6)	
7.5 (10)	7.5 (10)	7.1 (8)	8.5 (6)	7.5 (10)	6.9 (7)	7.6 (9)
8.1 (8)	9.3 (9)	7.5 (10)	9.2 (8)	8.5 (5)	7.2 (8)	8.3 (9)
11 (4)	10.8 (5)	8.4 (7)	11.7 (6)	8.8 (8)	7.4 (10)	8.5 (9)
12.1 (1)	11.1 (3)	9.2 (9)	12 (4)	8.9 (7)	8.6 (9)	10.9 (4)
12.8 (4)	12.8 (6)	10.6 (6)	12.8 (5)	9.4 (9)	8.9 (10)	12 (2)
13.3 (2)	13.3 (5)	10.7 (8)	13.3 (3)	10 (7)	9.1 (9)	12.3 (4)
14.4 (7)	14.3 (6)	10.8 (9)		11.8 (7)	10 (10)	12.6 (6)
	14.7 (7)	12.9 (6)			11.5 (4)	
		13.2 (3)			11.8 (5)	13.2 (4)
		13.6 (9)			12 (5)	14.3 (5)
		13.9 (10)			12.2 (6)	
		14.1 (9)			12.7 (3)	
					13.5 (5)	
					13.8 (6)	
					14.2 (6)	

[a] Spectra run on a Perkin-Elmer 137 Infracord, slit program 25 μ, scanning speed of 12 min. [b] Liquid run as thin smear on sodium chloride plates, all others run as potassium bromide pellets. [c] Wave length given in microns; intensities in parentheses are normalized to 10.

We have found that the fluorines in each of the fluorotrinitrobenzenes are extremely sensitive to hydrolysis. For example, recrystallization of III from solvents containing small amounts of water gives rise to trinitrophloroglucinol. Because of the ease of hydrolysis, it is important that the dilution of the reaction mixture and the subsequent filtration and drying of the product be carried out as quickly as possible. This is accomplished by pouring the reaction mixture onto crushed ice, stirring, filtering at once, washing with water containing ice, and immediately drying the product under vacuum at room temperature.

The starting material for the synthesis of III, trifluoronitrobenzene (IV), was prepared from trichloronitrobenzene and potassium fluoride in dimethylsulfoxide using the procedure of Finger and Kruse.[6] We were unable to obtain pure IV by any means other than vapor phase chromatography. The crude IV forms an azeotrope with one or more of the many compounds in the react on mixture. The complexity of the reaction which yields IV may be demonstrated by considering the analysis of a fraction boiling between 65° and 95° at 20 mm. This fraction, when analyzed by means of vapor phase chromatography, showed twenty-two compounds varying from 52% to less than 0.01% of the mixture. Five of the components separated by gas chromatography and identified by mass spectrographic analysis are: trifluoronitrobenzene, 52%; trichlorofluorobenzene, 29%; dichlorodifluorobenzene, 8%; chlorodifluoronitrobenzene, 3%; and 2,4-dithiapentane, 3%. This separation indicates the compounds originate from the various combinations of reactions possible with potassium fluoride and trichloronitrobenzene and the thermal decomposition of the dimethylsulfoxide.

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EXPERIMENTAL

1,3,5-trifluoronitrobenzene was prepared by the method of Finger and Kruse,[6] and the azeotropic mixture boiling at 70–85°/20 mm. was used in preparation of trifluorodinitrobenzene.[7]

1,3,5-Trifluoro-2,4-dinitrobenzene. To a nitrating mixture of 25 ml. of white fuming (90%) nitric acid and 14 ml. of 30% fuming sulfuric acid was added 14 ml. of 1,3,5-trifluoro-2-nitrobenzene, followed by 10 ml. more of 30% fuming sulfuric acid. The mixture was heated carefully[8] to 75°; then slowly to 100° and held there for 2 hr. The nitration mixture was poured into ice and water, filtered, and washed. The 1,3,5-trifluoro-2,4-dinitrobenzene was separated from the impurities by washing with 150–200 ml. of 75% acetic acid. The acetic acid solution with the dissolved trifluorodinitrobenzene was diluted with approximately 1 l. of ice water, allowed to stand at 0° for about 0.5 hr., and filtered. Repeated recrystallizations from a cyclohexane–petroleum ether (b.p. 30–60°) mixture at 0° gave long white needles of 1,3,5-trifluoro-2,4-dinitrobenzene which melted at 57–58° (lit., m.p. 52–53°).

Anal. Calcd.: C, 32.45; N, 12.62; H, 0.45. Found: C, 33.27; N, 12.65; H, 0.55.

The predominant impurity, 1,3,5-trichloro-2-fluoro-4,6-dinitrobenzene, may be recrystallized from alcohol, giving platelets, m.p. 146–147°.

Anal. Calcd.: C, 24.72; N, 9.61; Cl, 36.94. Found: C, 25.56; N, 9.78; Cl, 35.10.

1,3,5-Trifluoro-2,4,6-trinitrobenzene. A flask with 9 g. of potassium nitrate was chilled in an ice water bath and 28 ml. of 30% fuming sulfuric acid was added slowly. The cold bath was removed, 5 g. of trifluorodinitrobenzene added, and the mixture then heated to 163° for 21 to 24 hr. The time required for the nitration was determined by sampling and infrared spectra.[9] The nitration mixture was poured slowly over 125 ml. of crushed ice. After thorough mixing, the product was filtered rapidly in a sintered glass crucible and washed with a small amount of cold water. Hydrolysis of trifluorotrinitrobenzene was kept at a minimum if ice was kept in the drowned nitration mixture up to the point of washing, where the last of the ice was melted. The solid was dried rapidly in vacuum, pumping to a pressure of about 1 micron; yield, 2.6 g. (43%).

Recrystallization from dry carbon tetrachloride gave long fine needles, m.p. 87°. X-ray analysis showed the crystal structure to be rhombohedral with $A = 16.8$ Å, $\alpha = 118° 18'$. Hexagonal indices (triple-cell), $a = 29.14$ Å, and $c = 6.576$ Å. The cell contained 21 formula units, which gave a density of 1.92.

Anal. Calcd: C, 26.80; N, 15.73; F, 21 34. Found: C, 26.67; N, 15.16; F, 19.94.

1-Fluoro-2,4,6-trinitrobenzene. A 125-ml. Erlenmeyer flask, fitted with an 18-in. air condenser, was charged with 21 g. of potassium nitrate, 56 ml. of 30% fuming sulfuric acid, and 10 g. of 1-fluoro-2,4-dinitrobenzene. The reaction mixture was heated, with stirring, at 120° (oil bath temperature) for 30–35 hr., then worked up in the same manner as the trifluoronitrobenzene; crude yield, 8.7 g. (70%). Recrystallization from carbon tetrachloride gave a m.p. of 122–123°.[10]

Anal. Calcd: C, 31.19; H, 0.86; N, 18.19. Found: C, 30.97; H, 0.96; N, 18.40.

1,3-Difluoro-2,4,6-trinitrobenzene. A nitration mixture of 9.58 g. of potassium nitrate, 28 ml. of 30% fuming sulfuric acid, and 5 g. of 1,3-difluoro-4,6-dinitrobenzene was placed in an apparatus similar to that used in the fluorodinitrobenzene nitration. After about 35 hr. at 140°, the product was worked up as before; yield, 2.5 g. (41%); recrystallization from dry carbon tetrachloride gave m.p. 147–148°.

Anal. Calcd: C, 28.81; N, 16.80. Found: C, 29.14; N, 16.72.

Trinitrophloroglucinol. Treatment of trifluorotrinitrobenzene with water resulted in the hydrolysis of the fluorine, giving trinitrophloroglucinol, m.p. 166.5–167°. The melting point was not depressed when mixed with an authentic sample, prepared by trinitration of phloroglucinol.

Anal. Calcd: C, 27.60; N, 16.09; H, 1.16. Found: C, 28.05; N, 16.34; H, 1.83.

1-Fluoro-3,5-diethoxy-2,4,6-trinitrobenzene. Trifluorotrinitrobenzene recrystallized from ethanol gave the corresponding fluorodiethoxytrinitrobenzene.

Anal. Calcd: C, 37.63; N, 13.16; H, 3.16; F, 5.95. Found: C, 37.57; N, 13.44; H, 3.32; F, 5.86.

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(7) Use of a fraction with a wider boiling range gave rise to an oil from which it was very difficult to isolate the trifluorodinitrobenzene.

(8) Rapid heating results in uncontrolled boiling of the reaction.

(9) If the dilution of the nitrating mixture was attempted before the nitration is complete, the product was usually a liquid or paste which could not be filtered. Since no other means of rapid separation were available, the product was likely to be lost at this point due to hydrolysis of the fluorines in the trifluorotrinitrobenzene. In order to avoid this problem, approximately 0.02 to 0.1 ml. of the nitration was taken a short time before the estimated time of completion and dropped into a centrifuge cone of crushed ice. The precipitated material was centrifuged out, decanted, and dried in vacuum to approximately 1 micron. (The time of contact of the trifluorotrinitrobenzene with cold water was kept to less than 5 min. during the filtration and centrifugation steps.) The sample was used to determine an infrared spectrum, the disappearance of trifluorodinitrobenzene 8.6- and 9.2-μ bands being taken as the criterion for complete nitration.

(10) Two allotropic forms of fluorotrinitrobenzene exist; m.p. 122–123° and 131–132°. The higher melting form was obtained from the first two preparations, but after repeated recrystallizations it changed to the lower melting form. Upon melting and resolidifying, the lower melting form reverts back to the higher melting allotropic form.

Some Constituents of *Calendula officinalis*

Robert Stevenson

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The composition of the constituents of the medicinal herb, marigold flowers (*Calendula officinalis*), has been the subject of frequent reports. The existence of carotenoid pigments was established by Zechmeister,[1] and the identification of individual components was undertaken by Goodwin.[2] The presence of a bitter principle was reported by Gedeon[3] and has been confirmed by the recent work of Suchý and Herout[4] who propose the name

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