Reaction of 1,3,5-Trifluorotrinitrobenzene with Nucleophiles

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1,3,5-Trifluorotrinitrobenzene (1) is shown to be a versatile intermediate for the preparation of symmetrical and unsymmetrical 1,3,5-substituted trinitrobenzene derivatives. Its reaction with a number of representative N, O, C, and halogen nucleophiles is described. An unusually large cation effect is reported for its reaction with the ambident anion of dinitromethane.

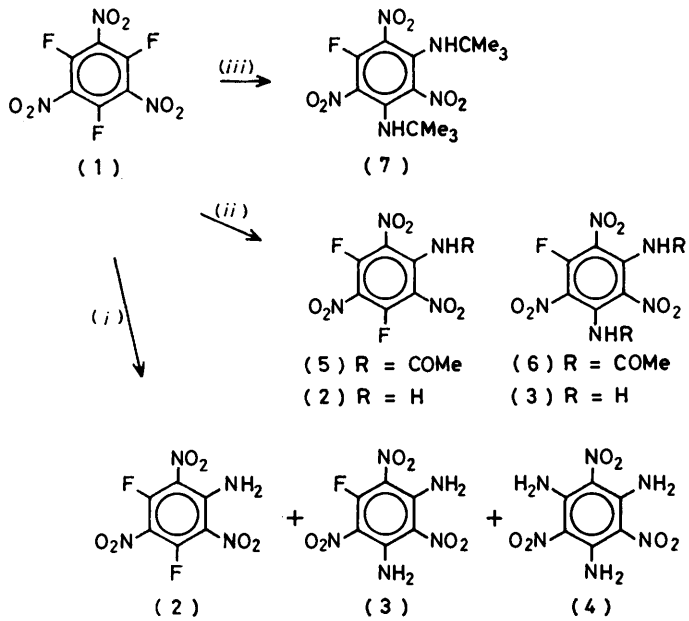
FULLY substituted derivatives of 1,3,5-trinitrobenzene are of interest for structure–property relationship studies [1] and are typically prepared by the reaction of 1,3,5-trichloro- [2] and 1,3,5-tribromo-trinitrobenzene [3] with suitable nucleophiles. However, the relatively low reactivity of these halogenonitrobenzenes often leads to complications, which include unwanted displacement or alteration of a nitro-group,[4] and incomplete substitution of halogen in the case of less reactive nucleophiles.[2a]

In view of the greater reactivity of fluorine in nucleophilic aromatic substitution,[5] the use of 1,3,5-trifluorotrinitrobenzene (1) should reduce if not eliminate these complications, and should permit the preparation of a much wider variety of compounds than has thus far been obtained from the other 1,3,5-trihalogenotrinitrobenzenes. Possibly because it was less readily available,[6] the behaviour of (1) with nucleophiles has not been studied. We report here on some representative reactions of this compound with N, O, C, and halogen nucleophiles.

RESULTS AND DISCUSSION

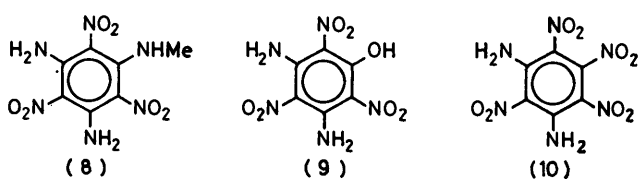
Reaction with Amines and Amides.—The superior reactivity of (1) is readily observed in its reaction with ammonia, which proceeds rapidly at −70 °C, and with 4 equiv. ammonia gives mainly (2) and (4) along with a small amount of (3). In contrast, the reaction of 1,3,5-trichlorotrinitrobenzene with an excess of ammonia requires several hours heating for complete substitution to occur.[2d] 1-Aminobutane also reacts very rapidly with (1) to give 1,3,5-tris(butylamino)trinitrobenzene.

Because of their rapidity these reactions are not suited for the synthesis of partially substituted compounds. Thus, attempts to conduct the reaction of (1) with ammonia under controlled conditions, which would afford pure (2) and (3) in good yield, were not successful. Therefore the reaction of (1) with acetamide and 2-amino-2-methylpropane was investigated in the hope that the lower reactivity or bulkiness of these reagents would permit better control of the extent of reaction. It was found that even the weakly nucleophilic acetamide reacts readily with (1) in refluxing benzene to produce (5) or (6) as the main product, depending on the amount of acetamide used, and on the reaction time. Compounds (5) and (6) are converted into the corresponding amines (2) and (3) in >90% yield by a brief treatment with concentrated sulphuric acid at ambient temperature. Compound (3) is obtained more conveniently and in better yield by reaction of (1) with 2 equiv. of 2-amino-2-methylpropane at −30 °C, followed by removal of the 2-methylpropyl groups with sulphuric or trifluoroacetic acid.[7]



SCHEME 1 (*i*) NH_3; (*ii*) $MeCONH_2$ at 80 °C; (*iii*) Me_3CNH_2, −30 °C

As expected, the fluorines in (2) and (3) are quite reactive, and both compounds undergo self-condensation at temperatures near their respective melting points. Compound (3) also reacted readily with methylamine to give (8), and was hydrolysed by aqueous acetic acid to the known diaminopicric acid (9).[8]



We also investigated briefly the use of 1,3-diaminotetranitrobenzene (10) as an alternative to (3) for the

preparation of 5-substituted-1,3-diaminotrinitrobenzenes. A drawback is that (10) is prepared from pentanitroaniline, a very sensitive explosive (see Experimental section). However, (10) does react readily with nucleophiles, *e.g.* with ammonia to give (4).

Reaction with Hydrazines.—1,3,5-Trichlorotrinitrobenzene has been reported to react with hydrazine in refluxing ethanol to form 1,3,5-trihydrazinotrinitrobenzene (13a).[2b] This report is in error,[9] and it appears that this compound has never been prepared. It was hoped that the greater reactivity of (1) would permit the preparation of (13a) under milder conditions and thus facilitate its isolation. We found that (1) reacts explosively with hydrazine in a variety of solvents. A solid product can only be isolated when the reaction is carried out at low temperatures, and at −70 °C in dichloromethane a reddish-black amorphous material is obtained which is characterized by a strong band in the i.r. at *ca.* 2 100 cm^{-1}. This product defied attempts to purify and further identify it, but the i.r. spectrum clearly shows that it is not (13a).*

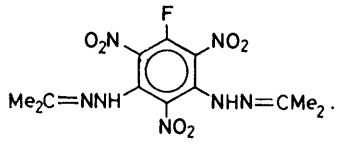
With hydrazine hydrochloride in methanol or aqueous acetonitrile (1) reacted rapidly at ambient temperature or below to produce similar darkly coloured solids exhibiting strong absorption in the i.r. near 2 100 cm^{-1}. In addition, these solids were quite sensitive to a mild hammer blow. These two features could be indicative of the presence of diazo- or azido-groups in these products. The formation of azido-groups could result from attack by hydrazine at the nitro-nitrogen, followed by elimination of two molecules of water. This process would be analogous to that observed in the reactions of 1,3,5-trichlorodinitrobenzene with hydrazine hydrate,[10] and of 1,3,5-trinitrobenzene with phenylhydrazine.[11] On the other hand, the presence of diazo-groups [12] is supported by the formation of a very similar material (i.r. spectrum) in the hydrolysis of (13b), where azido-group formation is improbable.[9]

A direct displacement of fluorine in (1) by hydrazine was observed in only one instance. When the crude product from the reaction of (1) with 4.5 equiv. hydrazine hydrochloride in methanol is treated with acetone and a strong acid, a small amount of 1-fluoro-3,5-bis-(2-propylenehydrazino)trinitrobenzene (11) is obtained.

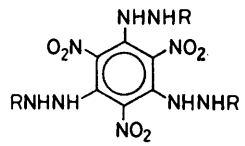
The reaction of (1) with acetylhydrazine is much less complicated and, depending on reactant ratio, yields (12) or (13b) as the main product. Compound (13b) is not identical with the compound prepared from 'trihydrazinotrinitrobenzene' and aqueous acetic acid and ascribed this structure.[2b,9] Reaction of (2) and (3) with acetylhydrazine gives the acetylhydrazino-amines (14) and (15).

Acid hydrolysis of (13b) does not yield 1,3,5-trihydrazinotrinitrobenzene.[9] The product has an infrared spectrum resembling strongly those of the reaction products of (1) with hydrazine hydrochloride (*vide supra*). It seems likely that (13a) was initially formed in both cases, and was further transformed under the reaction conditions.

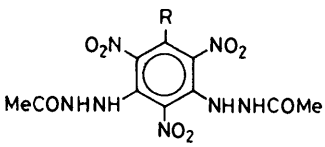
Reaction with Alkali Dinitromethides.—Eremenko and co-workers reported the synthesis of sodium picryl dinitromethide from picryl chloride and sodium dinitromethide.[13] We attempted the preparation of the difluoro-analogue (16) by the analogous reaction of 2 equiv. sodium dinitromethide with (1). However, in this reaction the fluorine was displaced with the oxygen of the anion to give on work-up potassium 3,5-difluoropicrate (18b). Only a trace of the desired C-attack product was observed. This type of leaving-group effect has been reported in the reaction of another



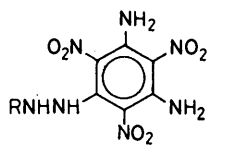
(11)



(13a) R = H
(13b) R = COMe



(12) R = F
(14) R = NH_2



(15) R = COMe

ambident nucleophile, nitrite ion, with 1-halogeno-2,4-dinitrobenzenes. In the case of ArF, O-attack was favoured by at least 10 : 1 over N-attack; whereas, in the case of ArCl, displacement occurred mainly by N-attack.[14]

In an attempt to obtain a more favourable balance of C- versus O-arylation of the dinitromethyl anion by (1), the effect of changing the cation to lithium was investigated.[15] The resulting effect was larger than expected: the yield of the C-arylation product (16) went from essentially zero to 43% [isolated (16b)]. The cation effect is generally not large in the alkylation of ambident anions and, moreover, a modest effect was anticipated in making only one jump in the alkali-metal series. A cation effect peculiar to the *gem*-dinitro-carbanion is suggested here which may have application to ambident anion control in other reactions with dinitromethides.† Characterization of (16b) included fluorination to give (17).

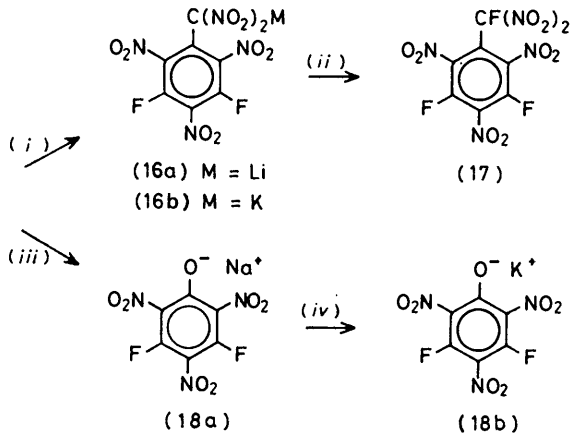
Reaction with Inorganic Salts.—Two examples were studied briefly, the reactions with sodium nitrite and with lithium bromide. In the first reaction, as in the reaction with alkali dinitromethide, (1) showed a pro-

* This material is a sensitive explosive and should be handled with care.

† The cation effect is usually attributed to an association between the more electronegative atom in the ambident anion and the cation which increases in strength with a decrease in cation size. A special effect may be operative here due to the possibility of formation of a six-membered ring involving the oxygens of the nitro-groups and the lithium cation.

nounced tendency towards mono-substitution: with 2 equiv. sodium nitrite in acetonitrile a 92% yield of difluoropicrate salt (18) was obtained. With lithium nitrite the result was the same, *i.e.* no cation effect was observed in this case.

Salts of difluoropicric acid (18a, b), as well as the free



SCHEME 2 (*i*) $LiCH(NO_2)_2$; (*ii*) F_2; (*iii*) 2 $NaNO_2$; (*iv*) KCl

acid, were readily converted into diaminopicric acid (9) by reaction with ammonia.

The reaction between (1) and lithium bromide in acetonitrile gave a mixture of 5-bromo-1,3-difluorotrinitrobenzene (48%) and 3,5-dibromo-1-fluorotrinitrobenzene (32%) which was not readily separable into its components.

EXPERIMENTAL *

Melting points are uncorrected. Elemental analyses were performed by Galbraith Labs, Inc., Knoxville, Tennessee. Mass spectra were obtained at the Cornell University Mass Spectrometry Facility, Ithaca, N.Y. ^1H N.m.r. spectra were run on a Varian HA-100 spectrometer; chemical shifts are downfield from $SiMe_4$ as *internal standard*. ^{19}F N.m.r. spectra are by Biomeasure Hopkinton, Massachusetts; chemical shifts are in p.p.m. upfield from $CFCl_3$ (internal standard). I.r. and u.v. spectra were obtained on commercial instruments under standard conditions. T.l.c. analyses were on plastic t.l.c. sheets (EM Reagents), 20 cm long, pre-coated with 0.25-mm silica gel F-254.

Reaction of (1) *with Ammonia.*—Gaseous ammonia (370 ml, 15.6 mmol) was added slowly (3.5 h) at −73 °C to a stirred solution of (1) (1.07 g, 4.0 mmol) in dry dichloromethane (100 ml). After 1 h cooling was stopped and the solvent was evaporated *in vacuo*. The residue (1.19 g) was triturated with ice–water, filtered off, dried *in vacuo*, and washed with boiling 1,2-dichloroethane (100 ml) to give insoluble (4) (0.22 g). Successive concentrations of the filtrate gave firstly a product which was mainly (3) (0.12 g, m.p. 215—220 °C), and then a product which was mainly (2) (0.5 g, m.p. 124—130 °C); (2), (3), and (4) were identified by comparison of their i.r. spectra with those of pure samples (see below).

* **CAUTION**: Many of the compounds reported here are **EXPLOSIVES** and should be handled with care. This is expecially true of materials which result from the reaction of (1) with hydrazine and its salts or derivatives.

1,3,5-*Tris(butylamino)trinitrobenzene.*—1-Aminobutane (0.82 g, 11.2 mmol), in water (2 ml) was reacted (20 h, room temperature) with (1) (0.5 g, 1.87 mmol) in dichloromethane (5 ml). The organic phase was filtered through a short column of silica gel, the filtrate evaporated, and the residue triturated with ether to give the title compound (0.5 g, 62%), m.p. 98—99 °C (lit.,[16] 86.5 °C). The product was pure by t.l.c. (toluene–ether–ethanol, 5 : 3 : 1); δ([$^2H_6$]Me_2SO) 3.31 (m, NCH_2 overlapped by NH), 3.27 (s, NH overlapped by NCH_2), 1.64 (m, CH_2-CH_2CH_2), 1.30 (m, CH_2CH_2Me), and 0.85 (t, CH_2Me); *m/e* (70 eV) 426 (M^+).

1-*Acetylamino*-3,5-*difluorotrinitrobenzene* (5) *and* 1,3-*Diacetylamino*-5-*fluorotrinitrobenzene* (6).—Acetamide (2.4 g, 40 mmol), dried at 60 °C for 16 h, was reacted with (1) (5.35 g, 20 mmol) by refluxing for 48 h in dry benzene (150 ml). Concentration (to 75 ml), addition of dry hexane (75 ml), and cooling gave a yellow solid which was stirred with ice–water (50 ml) for 10 min. The insoluble material (4.3 g) was dried and extracted with boiling, dry toluene (300 ml); the insoluble 1,3-*diacetylamino*-5-*fluorotrinitrobenzene* (6) (0.63 g), m.p. 322 °C (decomp.), was removed by filtration, and the toluene filtrate was concentrated and cooled to give 1-*acetylamino*-3,5-*difluorotrinitrobenzene* (5) (3.2 g), m.p. 188—189 °C (Found: C, 31.5; H, 1.25; N, 18.15; F, 12.6. $C_8H_4F_2N_4O_7$ requires C, 31.38; H, 1.32; N, 18.30; F, 12.41%); δ([$^2H_6$]acetone) 10.12 (s, 1 H, NH) and 2.19 (s, 3 H, Me).

In a similar experiment with a 3 : 1 molar ratio of acetamide to (1) and 73 h heating time, 2.7 g (20%) of insoluble (6), m.p. 321 °C (decomp.), was obtained after cooling and decanting the benzene, stirring the residue with cold water, and triturating the dried solid with boiling, dry toluene (150 ml). The identity of (6) was established by conversion to (3) (see below). A total of 4.6 g of (5) was also recovered from the benzene and toluene solutions by precipitation with hexane and trituration of the solid with ice–water.

An alternate procedure in which (1) (5 g) was heated in molten acetamide (10 g) at 80 °C for 1 h gave, after stirring the ground solid with cold water (100 ml), drying, extracting the residue with boiling, dry 1,2-dichloroethane (125 ml), and concentrating to 25 ml, compound (5) (3.0 g, 52.5%), m.p. 182—185 °C.

1-*Amino*-3,5-*difluorotrinitrobenzene* (2).—A solution of (5) (8.8 g) in concentrated sulphuric acid (115 ml) was kept for 10 min, then poured onto crushed ice. The precipitate was filtered off immediately, washed with cold water, and dried *in vacuo* to give 1-*amino*-3,5-*difluorotrinitrobenzene* (2) (7.45 g, 98%), m.p. 115—118 °C. The analytical sample was obtained from methylene chloride, m.p. 117—118.5 °C (Found: C, 27.55; H, 0.8; F, 14.6; N, 21.15. $C_6H_2F_2N_4O_6$ requires C, 27.28; H, 0.76; F, 14.39; N, 21.21%); δ([$^2H_6$]-benzene) 6.25 (s, NH); *m/e* 264 (M^+).

1,3-*Diamino*-5-*fluorotrinitrobenzene* (3).—(A) *From* (6). Compound (6) (2.7 g) was hydrolysed in concentrated sulphuric acid (60 ml) as above to give 1,3-*diamino*-5-*fluorotrinitrobenzene* (3) (1.85 g, 90%), m.p. 222—223 °C after crystallization from 1,2-dichloroethane (Found: C, 27.65; H, 1.45; F, 7.4; N, 26.65. $C_6H_4FN_5O_6$ requires C, 27.60; H, 1.54; F, 7.28; N, 26.82%); δ([$^2H_6$]acetone) 8.99 (s, NH); *m/e* (70 eV) 261 (M^+).

(B) *From* (7). 2-Amino-2-methylpropane (5.5 g, 75 mmol), in dry dichloromethane (1 500 ml) was added dropwise at 5 ml min^{-1} to a well stirred mixture of (1) (10.0 g, 37.4 mmol), potassium hydrogencarbonate (15.0 g, 150

mmol), and dry dichloromethane (400 ml) at −30 °C under nitrogen. Stirring for 15 h at room temperature, filtration, and evaporation of the solvent gave a product (14.2 g) which had three components by t.l.c. (benzene solvent). This mixture was stirred for 20 h in trifluoroacetic acid (50 ml) and dichloromethane (10 ml), and the yellow solid filtered off and extracted with boiling 1,2-dichloroethane (1 600 ml). Filtration gave insoluble (4) (1.15 g). Concentration of the filtrate to 150 ml gave (3) (6.93 g, 70%), m.p. 219—221 °C.

1,3-*Diamino*-5-*methylaminotrinitrobenzene* (8).—Methylamine was slowly bubbled into a mixture of (3) (2.0 g, 7.67 mmol) and acetonitrile (100 ml). After stirring for 15 h at room temperature, the solid was filtered off, triturated with water, and recrystallized from nitrobenzene (120 ml) to give 1,3-*diamino*-5-*methylaminotrinitrobenzene* (8) (1.43 g, 68%), m.p. 292—293 °C (decomp.) (Found: C, 31.0; H, 3.0; N, 30.7. $C_7H_8N_6O_6$ requires C, 30.89; H, 2.96; N, 30.88%); δ([$^2H_6$]Me_2SO) 10.64 (s, 1 H, N*H*Me), 9.89 (s, 4 H, NH_2), and 2.82 (d, 3 H, NH*Me*).

1,3-*Diamino*-5-*hydroxytrinitrobenzene* (9) *from* (3).—A slurry of (3) (2.0 g, 7.66 mmol) in acetic acid (25 ml) and water (1 ml) was stirred for 15 h, then acetic acid (200 ml) was added and the mixture was refluxed for 1 h. The hot solution was rapidly filtered and allowed to cool to give (9) (1.48 g, 74.6%), m.p. 276 °C (lit.,[8] 270 °C) (decomp.).

1,3-*Difluoro*-5-*hydroxytrinitrobenzene* via *Reaction of* (1) *with Sodium Nitrite*.—A stirred mixture of sodium nitrite (3.1 g, 45 mmol) and acetonitrile (50 ml) was treated dropwise with a solution of (1) (6.02 g, 22.5 mmol) in acetonitrile (30 ml). After 2 h the solvent was removed *in vacuo*, the orange paste was triturated with benzene (2 × 25 ml) to remove unreacted (1), 160 ml of 10% KCl solution was added and the mixture stirred for 1 h at 0 °C. Filtration and drying at 1 Torr over phosphorus pentaoxide gave (18b) (6.29 g, 92%), $\lambda_{max.}$ (H_2O) 345 (ε 10 300); precipitation of K^+ with BPh_4^- and of the picrate ion with $AsPh_4^+$ gave 12.7% K (Calc. 12.9%) and a weight of 97.8% of the theoretical for the picrate ion. In a similar experiment with lithium nitrite, (18b) was the only product detected; no N-arylation product was found.

Gaseous hydrogen chloride was bubbled through a suspension of (18b) (3.1 g, 10.2 mmol) in ether (250 ml) until the yellow colour turned to a light tan. After 0.5 h the mixture was filtered, and the solvent removed *in vacuo*, finally at 1 Torr, to give 1,3-*difluoro*-5-*hydroxytrinitrobenzene* (2.31 g, 85%). An analytical sample was obtained by sublimation at 115 °C/1 Torr followed by recrystallization from methylene chloride–hexane, m.p. 110.5—112 °C (Found: C, 26.75; H, 0.45; F, 14.3; N, 15.55. $C_6HF_2N_3O_7$ requires C, 27.19; H, 0.38; F, 14.33; N, 15.85%); δ_F (CD_2Cl_2) 113; *m/e* (70 ev) 265 (M^+).

1,3-*Diamino*-5-*hydroxytrinitrobenzene* (9) *from* 1,3-*Difluoro*-5-*hydroxytrinitrobenzene, and from* (18b).—(A). Ammonia gas was bubbled into a solution of 1,3-difluoro-5-hydroxytrinitrobenzene (8.17 g, 30.8 mmol) in benzene (250 ml); the yellow precipitate was stirred with concentrated hydrochloric acid (200 ml), filtered, washed with ether, and dried to give (9) (7.82 g, 98%), m.p. 275 °C (decomp.) (from nitrobenzene); δ([$^2H_6$]Me_2SO) 9.13 (s, NH) and 7.86 (s, OH).

(B). To (18b) (3.14 g) in water (100 ml) concentrated ammonium hydroxide (25 ml) was added. After 2 h the solution was acidified with concentrated hydrochloric acid. Work-up as above gave (9) (1.67 g, 62%).

1,3-*Diaminotetranitrobenzene* (10).—Dry ammonia gas (*ca.* 4 mmol) was allowed to diffuse from an addition funnel (volume 88 ml) during 90 h into a flask containing a stirred solution of aminopentanitrobenzene (0.63 g, 2 mmol)[17] in dry dichloromethane (60 ml). Filtration, washing the solid well with warm, dry dichloromethane, and concentration of the combined dichloromethane solutions to 20 ml yielded yellow 1,3-diaminotetranitrobenzene (10) (0.24 g, 43%), m.p. 190—191 °C (from dichloromethane) (Found: C, 25.05; H, 1.3; N, 29.0. $C_6H_4N_6O_8$ requires C, 25.01; H, 1.40; N, 29.17%); δ([$^2H_6$]-acetone) 8.97.

Reactions of (1) *with Hydrazine Hydrochloride*.—(A). Compound (1) (1 g, 3.75 mmol) was added to a stirred slurry of hydrazine hydrochloride (1.8 g, 26.2 mmol) in dry methanol (50 ml) at −40 °C. The yellow mixture was stirred at 0 °C for 1 h and at room temperature for 45 min, and was then filtered. Removal of the solvent *in vacuo* and trituration of the residue with tetrahydrofuran (50 ml) gave a brown solid with a strong i.r. band at 2 100 cm^{-1}; refluxing it with acetone produced no (11) as indicated by t.l.c. (dichloromethane), see below. A similar product (i.r.) was obtained when a solution of (1) (1.0 g) in dry acetonitrile (20 ml) was added dropwise at 0 °C to a stirred solution of hydrazine hydrochloride (1.80 g, 26.3 mmol) in water (20 ml), the mixture stirred for 1 h at 0 °C and 2 h at room temperature, and the organic phase freed from solvent.

(B). *Isolation of* (11). Compound (1) (1 g) was added to a stirred mixture of hydrazine hydrochloride (1.15 g, 16.8 mmol) in dry methanol (50 ml) at −45 °C. After 1 h at 0 °C concentrated hydrochloric acid (0.93 ml) was added. After filtration the solvent was removed at room temperature, the residue triturated with ether, and the ether solution filtered and evaporated. The brown solid was taken up in acetone, the filtered solution evaporated, and the solid triturated overnight with dichloromethane–tetrachloromethane (1 : 9). The residue was dissolved in dichloromethane and filtered through a column of silica gel to give (11) (0.1 g) as a red-orange solid, m.p. 175 °C (decomp.); δ([$^2H_6$]Me_2SO) 10.70 (s, 1 H, NH), 1.95 (s, 3 H, Me), and 1.90 (s, 3 H, Me); *m/e* 371 (M^+).

3,5-*Bis*-(2-*acetylhydrazino*)-1-*fluorotrinitrobenzene* (12).—Acetylhydrazine (0.55 g, 7.49 mmol) in acetonitrile (10 ml) was added dropwise at 0 °C to a stirred solution of (1) (1.0 g, 3.75 mmol) in acetonitrile (10 ml). Stirring for 2 h at room temperature and filtration gave 3,5-*bis*-(2-*acetylhydrazino*)-1-*fluorotrinitrobenzene* (12) (0.54 g, 38%), m.p. (after triturating the crude product with water for 10 min, filtering, drying, and recrystallizing twice from dry methanol) 212 °C (decomp.) (Found: C, 31.95; H, 2.65; F, 4.9; N, 25.95. $C_{10}H_{10}FN_7O_8$ requires C, 32.01; H, 2.69; F, 5.06; N, 26.13%); δ([$^2H_6$]Me_2SO) 10.08 (s, 1 H, NHN*H*COMe), 9.07 (s, 1 H, N*H*NHCOMe), and 1.72 (s, 3 H, NHNHCO*Me*); *m/e* (70 eV) 375 (M^+).

1,3,5-*Tris*-(2-*acetylhydrazino*)*trinitrobenzene* (13b).—Acetyl hydrazine (2.20 g, 30 mmol) in dry acetonitrile (50 ml) was added dropwise to a stirred solution of (1) (2.0 g, 7.49 mmol) in dry acetonitrile (20 ml), initially at 0 °C, later at room temperature. After 20 h stirring, acetylhydrazine (0.18 g, 2.44 mmol) in acetonitrile (5 ml) was added, followed by another 0.09 g 20 h later. After another 20 h stirring the product was filtered off, washed with acetone, and taken up in methanol (500 ml). The filtered solution was concentrated to 30 ml. On cooling to −20 °C 1,3,5-*tris*-(2-*acetylhydrazino*)*trinitrobenzene* (13b) (1.8 g, 56%) was obtained, m.p. 185 °C (decomp.). Trituration with acetone

for 18 h and then with dichloromethane provided an analytical sample, m.p. 190 °C (decomp.) (Found: C, 33.4; H, 3.5; N, 29.1. $C_{12}H_{15}N_9O_9$ requires C, 33.65; H, 3.29; N, 29.37); δ([$^2H_6$]Me_2SO) 9.78 (s, 1 H, N*H*COMe), 3.90 (br s, H_3O^+ from ionization of N*H*NHCOMe and H_2O in Me_2SO), and 1.68 (s, 3 H, Me).

Compound (13b) was also obtained from (12) by reacting with acetylhydrazine in acetonitrile at room temperature.

3,5-Bis-(2-acetylhydrazino)-1-aminotrinitrobenzene (14).—Acetylhydrazine (0.9 g, 12.1 mmol), in dry acetonitrile (21 ml) was added dropwise at 0 °C to a mixture of (2) (0.94 g, 3.56 mmol) and dry acetonitrile (20 ml). Additional acetylhydrazine (0.15 g, 2.2 mmol) was added after 24 h stirring at room temperature and after 30 h (0.12 g, 1.6 mmol). After stirring for another 48 h the yellow solid was triturated with acetone (30 ml, then 300 ml) at room temperature. The second acetone solution was filtered, concentrated to 20 ml, and cooled to −25 °C to give *3,5-bis-(2-acetylhydrazino)-1-aminotrinitrobenzene* (14) (0.3 g, 23%), m.p. 175 °C (decomp.). The analytical sample was prepared by an additional recrystallization from acetone as above (Found: C, 32.25; H, 3.25; N, 30.0. $C_{10}H_{12}N_8O_8$ requires 32.26; H, 3.25; N, 30.10); δ([$^2H_6$]Me_2SO) 10.76 (s, 0.3 H, N*H*NHCOMe), 10.09 (s, 2 H, NHN*H*COMe), 8.00 (s, 2 H, NH_2), 4.04 (br s, H_3O^+ from partial ionization of N*H*NHCOMe and H_2O in Me_2SO), and 1.71 (s, 6 H, Me).

5-(2-Acetylhydrazino)-1,3-diaminotrinitrobenzene (15).—A solution of acetylhydrazine (0.55 g, 7.66 mmol) in dry acetonitrile (25 ml) was added dropwise to a mixture of (3) (1.0 g, 3.83 mmol) in acetonitrile (15 ml) at room temperature to give, after stirring overnight, *5-(2-acetylhydrazino)-1,3-diaminotrinitrobenzene* (15) (1.19 g, 98.5%), m.p. 208 °C (decomp.) (Found: C, 29.9; H, 2.9; N, 30.4. $C_8H_9N_7O_7$ requires C, 30.48; H, 2.88; N, 31.11%); δ([$^2H_6$]Me_2SO) 10.27 (s, 1 H, NHN*H*COMe), 9.14 (s, 2 H, NH_2), 3.27 (s, H_3O^+ from ionization of NH_2, N*H*NHCOMe, and H_2O in Me_2SO), and 1.79 (s, 3 H, COMe); *m/e* (C.I., CH_4) 315 (M^+).

Hydrolysis of (13b).—A solution of (13b) (1.0 g) in concentrated hydrochloric acid (15 ml) was allowed to stand overnight, then diluted with ice–water (70 ml), filtered, and the solid dried to give an amorphous, dark brown material (0.15 g) with a strong i.r. band at 2 100 cm^{-1}, and no carbonyl absorption. Extraction of the filtrate with ether, evaporation of the ether, and drying of the residue gave a dark brown, amorphous solid (0.48 g) with a strong 2 100 cm^{-1} band in the i.r., and some carbonyl absorption (incomplete hydrolysis). Variation of acid concentration and reaction time gave either unreacted starting material or similar products as above, from which no pure compound could be isolated by crystallization or chromatography.

Reaction of (1) *with Lithium Dinitromethide; Preparation of* (16b).—A mixture of sodium dinitromethide (6.01 g, 47.0 mmol),[18] lithium chloride (2.0 g, 47.2 mmol), and dimethylformamide (26 ml) was stirred for 3 h under nitrogen. Lumps forming during the reaction were broken up mechanically. The mixture was cooled to 0 °C and a solution of (1) (6.27 g, 23.5 mmol) in dimethylformamide (8 ml) was added dropwise during 0.5 h. After stirring for an additional 0.5 h and pouring into a potassium chloride solution (10 g in 90 ml water), an orange precipitate formed on cooling to −10 °C, which was collected after 2 h, washed with water (4 × 5 ml) and ether (4 × 5 ml), and dried *in vacuo* to give (16b) (3.9 g, 43%); $\lambda_{max.}$ (H_2O) 363 nm. The structure was confirmed by reaction with fluorine (see below).

Reaction of sodium dinitromethide with (1) (ratio 2 : 1) in dimethylformamide at 0 °C, followed by drowning in 10% potassium chloride solution, gave a yellow precipitate, mostly (18b). This dissolved in water to leave only a trace of orange solid, presumably (16b).

(3,5-Difluoro-2,4,6-trinitrophenyl)fluorodinitromethane (17) *from* (16b).—A 300-ml 3-necked flask equipped with a magnetic stirring bar, thermometer, and gas inlet tube was charged with (16b) (3.0 g, 7.67 mmol) and a mixture of concentrated sulphuric acid (50 ml) and water (150 ml). The stirred mixture was cooled to −10 °C while a fluorine–nitrogen mixture (*ca.* 1 : 5) was bubbled in until the colour changed from orange to light yellow (1 h).[19] Filtration, washing with cold water, and drying *in vacuo* gave crude (17) (2.4 g). This was heated with tetrachloromethane (25 ml), and the solution filtered and cooled to −5 °C to give a yield of 1.25 g, m.p. 69—71 °C; with a second crop (0.5 g) from the mother-liquors, a total of 1.75 g (61%) of compound (17) was obtained as yellow plates. A *colourless material* resulted from several recrystallizations from tetrachloromethane with charcoal added, m.p. 71—72 °C (Found: C, 22.45; F, 15.6; N, 18.65. $C_7F_3N_5O_{10}$ requires C, 22.65; F, 15.36; N, 18.87); *m/e* (70 eV) 279 ($M^+ - 2NO_2$).

Reaction of (1) *with Lithium Bromide.*—A solution of (1) 4.0 g, 15 mmol) and lithium bromide (1.56 g, 18 mmol) in acetonitrile (20 ml) was stirred for 20 h at room temperature. Additional lithium bromide (0.41 g, 4.7 mmol) was added followed by stirring at 30 °C for 20 h. The solvent was removed *in vacuo*, the residue extracted with benzene (20 ml) and the benzene evaporated. This residue (4.5 g) was triturated with dichloromethane–hexane. Residual solid was phenolic material by i.r. analysis. The solution containing 4.25 g of product was analysed by ^{19}F n.m.r. (δ_F 114, s, and 119, s), which indicated a mixture of *1,3-dibromo-5-fluorotrinitrobenzene* (1.89 g, 32%) and *1-bromo-3,5-difluorotrinitrobenzene* (2.36 g, 48%). Purification was hindered by the sensitivity of the compounds to hydrolysis, which prevented liquid chromatography. A small amount of the monobromo-compound was obtained in >95% purity by sublimation followed by repeated crystallization from hexane, m.p. 112—116 °C; δ_F (CH_2Cl_2) 119; *m/e* (C.I., CH_4) 328, 330 ($M^+ + 1$, $^{79}/^{81}Br$). The dibromo-compound was present as an impurity with peaks at *m/e* 388, 390, 392 ($M^+ + 1$, Br isotopes).

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