

**Nitrocarbons. 4. Reaction of Polynitrobenzenes with Hydrogen Halides.  
Formation of Polynitrohalobenzenes<sup>1</sup>**

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Hexanitrobenzene and pentanitrobenzene in benzene solution react with hydrogen halides (HCl, HBr, HI, but not HF) at 25 °C to produce high yields of pentanitrohalobenzenes and 2,3,4,6-tetranitrohalobenzenes, respectively. Pentanitrofluorobenzene also reacts readily with HCl to yield 3-chloro-2,4,5,6-tetranitrofluorobenzene, but the other pentanitrohalobenzenes are much less reactive. 1,2,3,5- and 1,2,4,5-tetranitrobenzenes react rapidly with concentrated hydrochloric or hydrobromic acids at reflux to form picryl halides and 1-halo-2,4,5-trinitrobenzenes, respectively; pentanitrotoluene reacts very slowly under these conditions to form 3-halo-2,4,5,6-tetranitrotoluenes in lower yields. The scope and limitations of this regioselective reaction are defined, and comparison is made to related reactions. A mechanism is presented and discussed.

Reactions between nitroaromatics and hydrogen halides to yield halonitroaromatics or haloaromatics are known, although the number of examples is relatively few and applications appear to be of limited scope.<sup>2</sup> Yields are usually good (70–90%). Reaction types include (1) those involving displacement of a single nitro group leading to monohalogen substitution and (2) those in which all nitro groups are replaced by halogen. Monohalogen substitution has been observed only with polynitrobenzenes containing four or more nitro groups. An important reaction variable is the reaction temperature (reaction times are 0.25–4 h) and it is dependent on the number of nitro groups. Reaction at 25 °C has been reported only with pentanitroaniline which yields 3-halo-2,4,5,6-tetranitroanilines (Cl, Br, I).<sup>2a</sup> Tetranitroaromatics 1,2,3,5-tetranitrobenzene, 2,3,4,6-tetranitrophenol, and 2,3,4,6-tetranitroaniline required temperatures of 50 °C to reflux;<sup>2b</sup> the nitro flanked by two nitro groups is displaced leading to trinitromonohalo derivatives (Cl, Br, I). Reactions of the second type usually occur at 200–250 °C and lead to complete displacement of all nitro groups by halogen (Cl, Br) in di- and trinitrobenzenes and tetranitronaphthalenes, although decomposition occurs with nitro derivatives containing alkyl and hydroxyl groups.<sup>2c,d</sup> Nitrobenzene itself is more resistant to reaction (no reaction with HCl at 230 °C).<sup>2c</sup>

On the other hand, pentanitroaniline is much more reactive in the type 2 process; concentrated HCl at 80–90 °C for 3–4 h leads only to hexachlorobenzene.<sup>2a</sup> Partial displacement of nitro groups in polynitroaromatics other than monodisplacement has not previously been observed.

**Results and Discussion**

In the present work the reaction between selected polynitrobenzenes and hydrogen halides has been investigated. A facile reaction occurred between hexanitrobenzene (1), pentanitrobenzene (3), 1,2,3,5-tetranitrobenzene (5), or 1,2,4,5-tetranitrobenzene (7) and hydrogen halides (HCl, HBr, HI, but not HF) (Scheme I) to give monohalogen-substituted polynitrobenzenes in high yield. For example, pentanitrohalobenzenes **2a–c** are produced from hexanitrobenzene. The reaction is regioselective; halogen substitution occurs meta to the existing hydrogen in pentanitrobenzene leading exclusively to 2,3,4,6-tetranitrohalobenzenes **4a–c**. With 1 and 3 the reaction is conducted in a benzene solvent using either anhydrous hydrogen halide or concentrated aqueous hydrohalic acid at 25 °C. The tetranitrobenzenes and pentanitrotoluene react in concentrated HCl or HBr at reflux to yield picryl halides, 1-halo-2,4,5-trinitrobenzenes, or (very slowly in low yield) 3-halo-2,4,5,6-tetranitrotoluenes, respectively. Results are summarized in Table I.

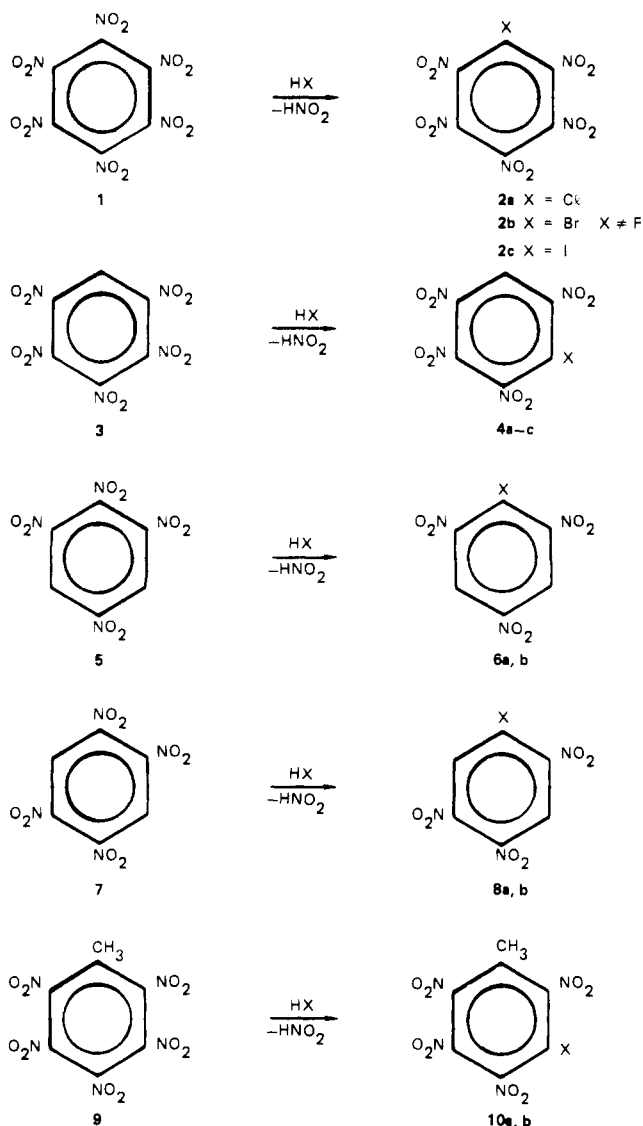
A mixture of the polynitrobenzene (hexa- or pentanitrobenzene) 1 or 3 and benzene is stirred vigorously with concentrated hydrohalic acid at 25 °C for periods of a few minutes to a few hours (procedure A). The monohalopolynitrobenzene product **2** or **4** is isolated from the dried benzene solution by simply removing the solvent. Yields of high purity crude product are often nearly quantitative

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## Scheme I



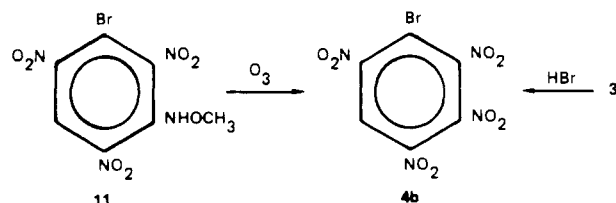
(Table I). Alternatively, anhydrous hydrogen halide (HCl, HBr) can replace the concentrated aqueous acid (procedure B). In a third procedure, the polynitrobenzene is heated at reflux with concentrated hydrohalic acid alone for 15 min (procedure C). 1,2,3,5- and 1,2,4,5-tetranitrobenzenes (5 and 7) were converted to picryl halides 6 and 1-halo-2,4,5-trinitrobenzenes 8, respectively, by this method. The reaction of 7 with HCl by procedure A is slow (12% in 30 min). The rates of reaction decrease in the order hexanitro > pentanitro > tetranitro. Pentanitrotoluene (9) is exceptional; it reacts very slowly in refluxing concentrated HCl or HBr to product low yields of 3-halo-2,4,5,6-tetranitrotoluenes 10a,b. A procedure reported previously for the conversion of pentanitroaniline into 3-halo-2,4,5,6-tetranitroanilines (concentrated hydrohalic acids alone at 25 °C)<sup>2a</sup> failed with the polynitro compounds of the present study. The addition of a cosolvent (benzene) was found to be necessary to obtain reaction of 1 and 3 at 25 °C owing to the poor solubility of the reactants in concentrated acid. However, with the tetranitrobenzenes 5 and 7 no cosolvent was required in refluxing acid.

The reaction is limited to the hydrogen halides HCl, HBr and HI. No reaction occurs with concentrated aqueous HF by procedures A or C and the reactants are recovered; under more vigorous conditions with hexanitrobenzene (90 °C, 2 h), trinitrophenylglucinol was the only isolated product. The hydrogen halide reactivity rates

decrease in the order HI > HBr > HCl >>> HF.

The new polynitro compounds pentanitro- and 2,3,4,6-tetranitrohalobenzenes are pale yellow crystalline solids and are stable for several months at 25 °C when stored in the dark in a dry atmosphere. The proton NMR spectra of pentanitrobenzene (3) and 2,3,4,6-tetranitrohalobenzenes 4a-c reveal an aryl proton chemical shift which is related to substituent electronegativity; signals for the corresponding 2,4,6-trinitrohalo compounds 6a-c appear at only slightly lower field (data for 6a,b in Table I); shifts for 3 and 1,2,3,5-tetranitrobenzene (5) are at  $\delta$  9.15 and 9.35, respectively;<sup>4</sup> the value for picryl iodide is  $\delta$  8.70. In 1,2,4,5-tetranitrobenzene, which lacks a nitro group para to hydrogen, the chemical shift is  $\delta$  8.59; thus the chemical shifts of  $\delta$  8.66 and 8.53, found in 8a and 8b, respectively, may be assigned to the protons at C-3 in the 2,4,5-trinitrohalobenzene products; the remaining signal would be that of the C-6 proton. Mass spectra reveal relatively strong molecular ions and  $[\text{M}-92]^+(\text{N}_2\text{O}_4)$ . The infrared spectra (KBr) show the absence of OH bands and the presence of strong NO<sub>2</sub> stretching bands near 1550 and 1310 cm<sup>-1</sup>.

The reaction of hydrogen halides with pentanitro- and tetranitrobenzenes and their derivatives is regioselective. Halogen substitution occurs at a position meta to an existing nonnitrosubstituent or hydrogen and ortho and para to nitro groups. 2,3,4,6-Tetranitrobromobenzene (4b), obtained by reaction of pentanitrobenzene with HBr, was identical with that prepared by oxidation of *N*-methoxy-3-bromo-2,4,6-trinitroaniline (11).<sup>3</sup> The latter compound was obtained by reaction of 1 equiv of methoxylamine with known 1,3-dibromo-2,4,6-trinitrobenzene.<sup>3</sup> The result is the first reported structure proof for a tetranitrohalobenzene product derived from a pentanitrobenzene.<sup>2a</sup>



The reaction of concentrated aqueous HI with pentanitrobenzene (3) by procedure A is exceptional. It yields a mixture of products owing to the reducing action of HI upon the primary product 2,3,4,6-tetranitroiodobenzene (4c). After a 40-min reaction at 25 °C, the isolated recrystallized product is a mixture of picryl iodide (6c) and 4c. Also seen in the <sup>1</sup>H NMR spectrum of the crude reaction product are signals corresponding to 1,2,3,5-tetranitrobenzene (5) and 1,3,5-trinitrobenzene (12). The reduction of picryl iodide with HI to 1,3,5-trinitrobenzene is a facile process.<sup>5</sup> The reaction of hexanitrobenzene with HI, on the other hand, is more rapid and selective; the only product detected after 6 min at 25 °C is pentanitroiodobenzene (2c, 72% yield). However, reaction for longer periods leads to a mixture of those same products which were obtained from pentanitrobenzene (3) (4c, 5, 6c, and 12) in addition to 2c and a trace of 3; see Experimental Section.

A striking feature of the polynitrobenzene-hydrogen halide reaction is the virtual absence of dihalogen-substituted products. Either monohalogen substitution or complete replacement of all nitro groups by halogen with

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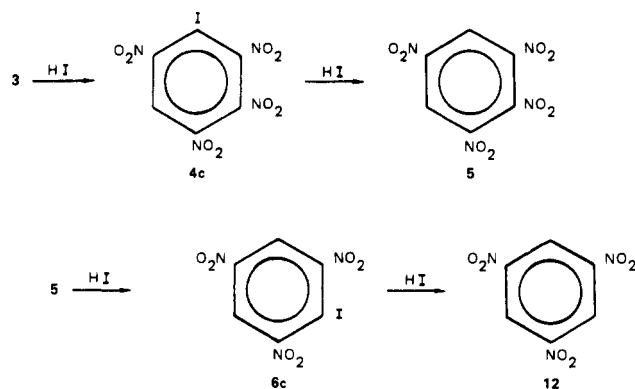
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Table I. Reaction of Polynitrobenzenes with Hydrogen Halides (HX) To Form Polynitrohalobenzenes

reactant	HX, X =	procedure <sup>a</sup>	product <sup>b</sup>	yield, <sup>c</sup> %	mp, <sup>d</sup> °C (recryst solv)	<sup>1</sup> H NMR shifts, <sup>e</sup> $\delta$ (singlets, CDCl <sub>3</sub> solvent)
1	Cl	A, B	2a	100	217–222 (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	
	Br	A, B	2b	100	225–230 (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	
	I	A	2c	72	229–232 (C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub> )	
3	Cl	A	4a	100	99–100 (CCl <sub>4</sub> )	8.90
	Br	A	4b	99	111–112 <sup>f</sup> (CHCl <sub>3</sub> )	8.78
	I	A	4c	(25) <sup>g</sup>	<sup>g</sup>	8.68
5	Cl	C	6a	67	80–81 <sup>h</sup> (CHCl <sub>3</sub> )	8.93
	Br	C	6b	74	120–122 <sup>i</sup> (C <sub>6</sub> H <sub>6</sub> )	8.81
7	Cl	C	8a	71, (89) <sup>j</sup>	112–116 <sup>j</sup> (C <sub>2</sub> H <sub>5</sub> OH)	8.66, 8.25 <sup>k</sup>
	Br	C	8b	64	119–121 <sup>l</sup> (C <sub>2</sub> H <sub>5</sub> OH)	8.53, 8.38 <sup>k</sup>
9	Cl	A	10a	(2) <sup>m</sup>	<i>m, n</i>	2.44 <sup>o</sup>
	Cl	C	10a	(11) <sup>m</sup>	<i>m, n</i>	2.44 <sup>o</sup>
	Br	C <sup>p</sup>	10b	(52) <sup>q</sup>	<i>q, r</i>	2.42 <sup>o</sup>
18	Cl	A	19	88	74–76 <sup>o</sup> (CCl <sub>4</sub> )	

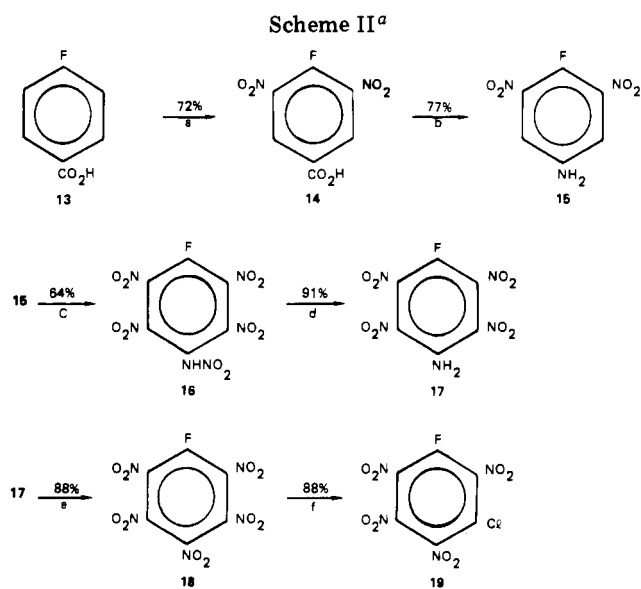
<sup>a</sup> Procedure A: concentrated aqueous hydrohalic acid, benzene, vigorous stirring, 25 °C, 0.1 to 4 h. Procedure B: anhydrous hydrogen halide in benzene solvent, 25 °C, 16 to 18 h. Procedure C: hydrohalic acid (HCl, HBr) at reflux 15 min. <sup>b</sup> Satisfactory elemental analyses ( $\pm 0.3\%$  for C, H, N, halogen) were obtained for all new compounds listed except those not isolated in a pure state (4c, 10a, 10b; see Experimental Section). <sup>c</sup> Yields (not optimized) of high purity products. The crude products are often very pure (various assay methods). <sup>d</sup> Melting points of pure recrystallized samples with solvent listed. <sup>e</sup> Chemical shifts ( $\delta$ ) referenced to tetramethylsilane as internal standard (30 °C). <sup>f</sup> Reported mp 113–114 °C. <sup>g</sup> Estimated yield. Product is a mixture (ca. 1:1) of picryl iodide and 4c; see Experimental Section; estimated yield of crude 4c is 25%. <sup>h</sup> Reported mp 83 °C. <sup>i</sup> Reported mp 122–123 °C. <sup>j</sup> Reported mp 116 °C; <sup>k</sup> the crude product contains some reactant 7. Yield in parentheses is based on unrecovered reactant. <sup>l</sup> Reported mp 120–121 °C. <sup>m</sup> Estimated yield with procedure C (after 15-min or 1-h reflux time) is 11%. After 15 min the product is mostly a mixture of 9 (75%) and 10a (15%) by <sup>1</sup>H NMR assay; estimated 2% reaction was observed with procedure A (2-h reaction time). <sup>n</sup> Crude product mixture, mp 214–220 °C. <sup>o</sup> Reactant 9,  $\delta$  2.57. <sup>p</sup> Reflux time 30 min. <sup>q</sup> Estimated yield. Product is mostly a mixture of 9 (17%) and 10b (60%) by <sup>1</sup>H NMR assay. <sup>r</sup> Crude product mixture, mp 169–173 °C.

more vigorous reaction conditions is the only observed result. The crude products obtained in the reactions



summarized in Table I revealed no NMR or mass spectra evidence of dihalogen substitution, with one exception. Pentanitrotoluene, which reacts most slowly of all reactive polynitroaromatics studied, produced a crude product by reaction with concentrated HBr (30-min reflux) containing a mixture of 3-bromo-2,4,5,6-tetranitrotoluene (10b) and a dibromonitrotoluene (possibly 3,5-dibromo-2,4,6-trinitrotoluene), as indicated by the mass spectra data and bromine analysis; the reaction with concentrated HCl was similar, but slower. The pentanitrohalobenzenes 4a–c do not react further with their own respective hydrogen halides. Also, treatment of 2,3,4,6-tetranitrobromobenzene (4b) with HCl, or 2,3,4,6-tetranitrochlorobenzene (4a) with HBr, at 25 °C gave only recovered reactants (<sup>1</sup>H NMR data). However, the more reactive HI was found to react to a limited extent with pentanitrochlorobenzene to produce a crude product containing some 3-iodo-2,4,5,6-tetranitrochlorobenzene (*M*<sup>+</sup> 418); about 7.5% conversion occurred at 25 °C after 15 min based on the iodine content of the crude product. Thus, in selected samples some dihalogen substituted products may be formed.

Pentanitrofluorobenzene (18), in contrast to the other pentanitrohalobenzenes 4a–c, was found to react rapidly and efficiently with HCl to produce a dihalogen compound, 3-chloro-2,4,5,6-tetranitrofluorobenzene (19, 88% yield).



<sup>a</sup> (a) HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, 95 °C; (b) NaNO<sub>2</sub>, 20% oleum, 25 °C; (c) HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, 25–30 °C; (d) CH<sub>3</sub>OC<sub>6</sub>H<sub>5</sub>, H<sub>2</sub>SO<sub>4</sub>; 25 °C; (e) 98% H<sub>2</sub>O<sub>2</sub>, 20% oleum, 25 °C; (f) concentrated HCl, C<sub>6</sub>H<sub>6</sub>, 25 °C.

We had earlier reported synthesis of 18 by peroxydisulfuric acid oxidation of 3,5-diacetamido-2,4,6-trinitrofluorobenzene.<sup>4</sup> An improved synthesis of 18 has been achieved (Scheme II). It involves nitration of 2,6-dinitro-4-fluoroaniline (15) to 2,3,5,6-tetranitro-4-fluoroaniline (17) (via 16), followed by peroxydisulfuric acid oxidation to 18.

Polynitroaromatics were found not to react with halide ions in neutral media. An acid catalyst is required. For example, hexanitrobenzene (1) in benzene, stirred vigorously at ambient temperature in separate experiments with aqueous solutions of either sodium chloride, tetrabutylammonium chloride, or tetrabutylammonium iodide, gave no polynitrohalobenzene products. Reaction of hexanitrobenzene in benzene with saturated aqueous sodium chloride and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) gave a product having the properties of a 1:1

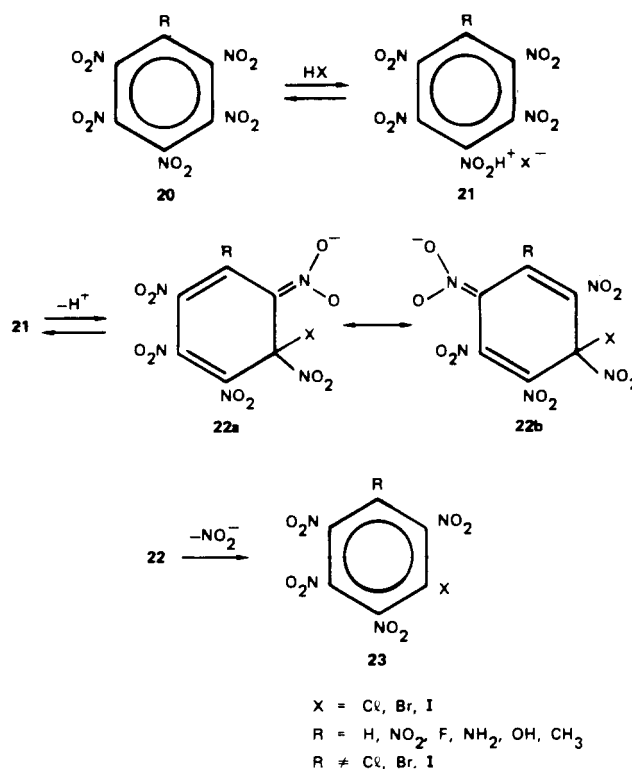
adduct of pentanitrophenol and 18-crown-6; however, the same product was also obtained when the aqueous sodium chloride was omitted.

The facile reaction of hydrogen halides with polynitroaromatics is unusual in that it has the characteristics of nucleophilic displacements which occur in basic media where Meisenheimer intermediates are involved. Polynitroaromatics readily undergo nitro displacements by hydroxide or alkoxide ions, ammonia, and amines. These displacements occur in a position meta to an existing nonnitro substituent or hydrogen. For example, pentanitroaniline reacts with ammonia to form 1,3,5-triamino-2,4,6-trinitrobenzene,<sup>6</sup> and hexanitrobenzene reacts with sodium hydroxide to yield trinitrochloroglucinol.<sup>7</sup>

The scope and limitations of the reaction between polynitroaromatics and hydrogen halides at 25–125 °C have been established and can be summarized. A reaction mechanism must accommodate the following facts. (1) The reaction occurs only in acid media. (2) The reaction is limited to the hydrogen halides HI, HBr, and HCl; no reaction occurs with HF. (3) The reaction rate is related to the nucleophilicity of the halide anion:  $I^- > Br^- > Cl^- \gg F^-$ , an order which also coincides approximately to the order of the corresponding hydrogen halide acidity. (4) Only one halogen is introduced by nitro displacement, independent of the halogen and the number of nitro groups present. (5) The nitroaromatic reactivity rate decreases with decreasing nitro substitution: hexanitro > pentanitro > tetranitro  $\gg$  trinitro. (6) The halogen substitution occurs with regioselectivity. The nitro group displaced is one meta to an existing group or hydrogen and oriented ortho to one or two nitro groups and para to one nitro group. (7) The reactivities of tetra- and pentanitrobenzenes are affected by substitution as indicated in the above discussions.

The reaction mechanism is considered to be a nucleophilic displacement of nitro by halide ion (Scheme III) and one in agreement with the principles and known facts of aromatic nucleophilic substitution. In strongly acidic medium an R-substituted polynitroaromatic (20) forms a protonated species (21) which is activated to attack by halide ion. Protonation is believed to occur predominantly on nitro with very little involvement of ipso C-protonation.<sup>8</sup> Ring attack by halide ion and proton loss leads to a Meisenheimer intermediate (22), stabilized significantly by planar resonance forms (e.g., 22a,b) involving exocyclic nitronate ions ortho and para to the entering halogen and ortho and para to the existing R group. Loss of nitrite ion from 22 leads to product 23. When R is a relatively small or planar group (H, F, NH<sub>2</sub>, OH, NO<sub>2</sub>), resonance stabilization of 22 is allowed. (Ring-substituted electron-withdrawing groups (F, NO<sub>2</sub>, NH<sub>3</sub><sup>+</sup>, OH<sub>2</sub><sup>+</sup>) would facilitate the displacement process.) On the other hand, when R is a relatively bulky and symmetrical group, even though electron withdrawing (i.e., Cl, Br, I), the well-known steric destabilization of nitronate resonance is encountered.<sup>9</sup> The planar nitro group, although large, can minimize its repulsion by assuming a tilted orientation to the benzene ring. The very sluggish reactivity of pentanitrotoluene may be attributed, for the most part, to steric inhibition of resonance in 22 by the relatively large, symmetrical methyl group.<sup>9</sup>

Scheme III



The fact that reaction of polynitroaromatics with halide at 25 °C occurs only in acidic medium suggests a protonated intermediate (21) or a closely related concerted process. The positively charged species (NO<sub>2</sub>H<sup>+</sup>) ortho to a ring nitro group would activate that nitro group to displacement by halide ion, in excess of the activation already provided by ring nitro groups and an electronegative R group. Numerous closely related examples of this type of process are known. These include the facile displacement in acidic medium of ortho and/or para nitro groups by halide ion from ortho and/or para nitro diazonium salts (activating group, N<sub>2</sub><sup>+</sup>) to yield mono- or dihalo diazonium salts.<sup>10</sup> Similarly, 2-nitro- and 4-nitropyridines undergo facile displacement of nitro by halide ion in acidic medium to form 2- or 4-halopyridines (pyridinium ion activation).<sup>11</sup>

The unique reaction of selected polynitroaromatics with hydrogen halides has synthetic utility, providing high yields of certain polynitrohalobenzenes from readily available reactants. Many of these products are difficult to synthesize by alternate routes.

### Experimental Section

Melting points were determined on a Kofler hot stage apparatus. NMR spectra were recorded on a Nicolet WB200 or Varian EM360 spectrometer and mass spectra on a Hewlett-Packard 5985 GC/MS system (70 eV).

**Warning!** All polynitro compounds described are explosives and should be handled with great care.

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**Reaction of Polynitrobenzenes with Hydrogen Halides (Procedure A).** A mixture of pentanitrobenzene (**3**)<sup>4</sup> (0.40 g, 1.32 mmol), benzene (10 mL), and concentrated HCl (20 mL) was stirred vigorously for 2 h at 25 °C. The benzene layer was dried (MgSO<sub>4</sub>) and concentrated to yield 0.39 g (100%) of 2,3,4,6-tetranitrochlorobenzene (**4a**); two recrystallizations from CCl<sub>4</sub> gave prisms, 0.10 g, mp 99–100 °C. The respective spectra of the crude and recrystallized samples were nearly identical (<sup>1</sup>H NMR, IR). Less vigorous stirring and/or shorter reaction times gave a mixture of recovered **3** and **4a**; for example, 47% reaction occurred after 20 min (<sup>1</sup>H NMR assay) under the above reaction conditions. Large losses usually occur on recrystallization of the polynitro products owing primarily to solubility behavior, not decomposition.

Procedure A was employed in the conversion of hexanitrobenzene (**1**) into pentanitrochlorobenzene (**2a**) (30 min, 25 °C; 100% yield of crude product, mp 206–210 °C; mp 212–214 °C after recrystallization from dichloroethane (50% recovery)). In the absence of benzene, no reaction was observed at 25 °C during 4.5 h nor at 100 °C during 15 min. Procedure A applied to 1,2,3,5-tetranitrobenzene (**5**) gave 12% conversion to picryl chloride (**6a**) (25 °C, 30 min; <sup>1</sup>H NMR assay). With 2,3,4,6-tetranitrobromobenzene in benzene, procedure A (25 °C, 40 min) gave recovered reactant (75%).

Pentanitrotoluene (**9**)<sup>4</sup> (60 mg) by procedure A (HCl, 25 °C, 2 h) gave 50 mg, mp 235–238 °C, containing principally unreacted **9**, and an estimated 2% 3-chloro-2,4,5,6-tetranitrotoluene (**10a**) based on material balance and chlorine analysis: found 0.22% Cl, calcd for C<sub>7</sub>H<sub>3</sub>ClN<sub>4</sub>O<sub>8</sub> 11.56%; M<sub>r</sub> 305.58. The mass spectrum revealed a strong molecular ion peak for unreacted **9** (317) and a very weak peak for **10a** (306): *m/e* (relative intensity) 317 M<sup>+</sup> (1.4), 306 (0.1), 224 (100), 213 (1.1).

Procedure A was employed with concentrated (48%) HBr in the conversion of pentanitrobenzene (**3**) into 2,3,4,6-tetranitrobromobenzene (**4b**) (4 h, 25 °C) and hexanitrobenzene (**1**) into pentanitrobromobenzene (**2b**) (2.5 h, 25 °C). When procedure A was applied to 2,3,4,6-tetranitrochlorobenzene (**4a**) (4 h, 25 °C), concentrated HBr gave no reaction.

Reaction of hexanitrobenzene (**1**) with concentrated HI (47%) by procedure A gave a 72% yield of crude pentanitroiodobenzene (**2c**, mp 158–230 °C; 6 min, 25 °C); its <sup>1</sup>H NMR spectrum revealed no proton signals; recrystallization from dichloroethane gave a pure product, 16% yield, mp 229–232 °C; decomposition occurred during recrystallization. In a parallel experiment with reaction time of 15 min the crude reaction product revealed (<sup>1</sup>H NMR, CDCl<sub>3</sub>) the presence of impurities, principally picryl iodide (**6c**) and trace amounts of 1,3,5-trinitrobenzene (**12**), 1,2,3,5-tetranitrobenzene (**5**), 2,3,4,6-tetranitroiodobenzene (**4c**), and pentanitrobenzene. Compare the results of the reaction of pentanitrobenzene with HI described in the following paragraph.

Reaction of concentrated HI (47%) with pentanitrobenzene (**3**) by procedure A gave a mixture of products, in addition to unreacted **3**; a dark brown or purple solution was produced during the reaction owing to iodine formation. Proton NMR signals (in CDCl<sub>3</sub>) were observed in crude, unrecrystallized reaction products at δ 9.45, 9.35, 9.15, 8.70, and 8.68, assigned (from values obtained on authentic samples) to 1,3,5-trinitrobenzene (**12**), 1,2,3,5-tetranitrobenzene (**5**), unreacted pentanitrobenzene (**3**), picryl iodide (**6c**), and 2,3,4,6-tetranitroiodobenzene (**4c**). Relative intensities (in parentheses) of these signals observed at various reaction times were as follows: 5 min, δ 9.45 (0), 9.35 (3), 9.15 (67), 8.70 (5, sh), 8.68 (49); 15 min, δ 9.45 (2), 9.35 (2), 9.15 (16), 8.70 (5, sh), 8.68 (29); 40 min, δ 9.45 (12), 9.35 (8), 9.15 (0), 8.70 and 8.68 (81 total); 60 min, δ 9.45 (70), 9.35 (0), 9.15 (0), 8.70 and 8.68 (83 total). The crude product obtained from 0.40 g of **3** after 40 min (0.30 g) contained no remaining reactant **3**. Weak <sup>1</sup>H NMR signals at δ 9.45 and 9.35 were assigned to 1,3,5-trinitrobenzene (**12**) and 1,2,3,5-tetranitrobenzene (**5**), respectively (about 1:1 ratio, estimated 20% by weight of the total product). The main product (80%) revealed a strong signal at δ 8.70 attributed to a mixture of picryl iodide (**6c**) and 2,3,4,6-tetranitroiodobenzene (**4c**); signals of **4c** and **6c** are not always completely resolved except at high resolution (200 MHz), and that of **4c** appears at δ 8.68. Two recrystallizations of the crude product from chloroform completely removed the noniodinated species **5** and **12** and left a product, mp 125–128 °C, containing only **4c** and **6c** (ca. 1:1 by <sup>1</sup>H NMR assay; signals at δ 8.70 and 8.68 only); attempts to resolve the

mixture by elution chromatography on silica gel were unsuccessful; the mass spectrum reveals strong molecular ions of both species (M<sup>+</sup> 384, 339). Anal. Calcd for C<sub>6</sub>H<sub>2</sub>IN<sub>3</sub>O<sub>6</sub>: C, 21.26; H, 0.59; I, 37.43, N, 12.40. Calcd for C<sub>6</sub>HIN<sub>4</sub>O<sub>6</sub>: C, 18.77; H, 0.20; I, 33.05; N, 14.59. Found: C, 20.07; H, 0.50; I, 35.69; N, 12.03.

Pentanitrochlorobenzene (**4a**, 50 mg) by procedure A (concentrated HI, 25 °C, 15 min) gave 33 mg, mp 145–180 °C, dec; mass spectrum, M<sup>+</sup> 418 assigned to 3-iodo-2,4,5,6-tetranitrochlorobenzene and stronger mass signals (M<sup>+</sup> 337, 339) of **4a**; estimated conversion to iodo product, 7.5% based on iodine analysis and material balance; found 3.62% I, calcd for C<sub>6</sub>ClIN<sub>4</sub>O<sub>6</sub> I, 30.33%; M<sub>r</sub> 418.45.

Hexanitrobenzene (**1**, 0.20 g, 0.57 mmol) and hydrofluoric acid (49% aqueous solution, 10 mL) in 5 mL of benzene were stirred at 25 °C for 2 h. Workup as in procedure A gave unreacted **1** (0.20 g), IR identical with an authentic sample. In a parallel experiment (16 h), **1** was again recovered (80%); no pentanitrofluorobenzene could be detected in the crude reaction product (mass spectrum). Heating **1** (0.20 g, 0.57 mmol) with concentrated hydrofluoric acid (30 mL) without added benzene on a steam bath (90 °C) for 2 h gave, after cooling, a precipitate of trinitrophenol; 0.06 g (40%); light yellow needles, mp 157–158 °C (unrecrystallized sample) (lit.<sup>7</sup> mp 161–164 °C); IR identical with that of an authentic sample.

Modifications of procedure A were investigated. Hexanitrobenzene (**1**, 0.20 g, 0.57 mmol) in 5 mL of benzene was stirred at 25 °C with saturated sodium chloride solution (10 mL) for 15 min. Workup as in procedure A gave only **1** (0.18 g, 90% recovery), which was identical with an authentic sample. In parallel experiments in which the sodium chloride solution was replaced with either tetrabutylammonium chloride or tetrabutylammonium iodide (25 °C, 1 h), amorphous products were obtained from which no pentanitrohalobenzene could be isolated.

In another modification of procedure A, a mixture of hexanitrobenzene (**1**, 0.20 g, 0.57 mmol) in 5 mL of benzene, 18-crown-6 (0.152 g), and saturated aqueous sodium chloride solution (10 mL) was stirred at 25 °C for 2 h. The usual workup gave 0.29 g of orange crystals; recrystallization from chloroform gave orange prisms, mp 160–162 °C. The same product was obtained in a parallel experiment in which the sodium chloride solution was omitted (25 °C, 15 h). From 0.20 g of **1** there was obtained 0.30 g (91%) of a 1:1 adduct of pentanitrophenol and 18-crown-6 (orange prisms, mp 160–176 °C; recrystallized from benzene, mp 167–168 °C) with partial resolidification to orange rectangular prisms of pentanitrophenol: mp 189–190 °C, lit.<sup>15</sup> mp 190 °C; mass spectrum, M<sup>+</sup> 319 (C<sub>6</sub>H<sub>5</sub>N<sub>5</sub>O<sub>11</sub>, M<sub>r</sub> 319.11); no molecular ions were observed in the mass spectrum corresponding to reactant hexanitrobenzene (M<sup>+</sup> 348) or product pentanitrochlorobenzene (M<sup>+</sup> 337, 339) (in the experiments where sodium chloride was included as reactant). Anal. Calcd for C<sub>18</sub>H<sub>25</sub>N<sub>5</sub>O<sub>17</sub>: C, 37.06; H, 4.32; N, 12.00. Found: C, 36.53; H, 4.45; N, 11.62.

**Reaction of Polynitrobenzenes with Hydrogen Halides (Procedure B).** Hydrogen bromide was bubbled into a solution of hexanitrobenzene (**1**, 0.20 g, 0.57 mmol) in dry benzene (5 mL) at 25 °C for 12 min (flask fitted with a calcium chloride tube). After standing at 25 °C for 16 h (excess HBr present), the solution was concentrated to dryness under reduced pressure to yield 0.22 g (100%) of crude pentanitrobromobenzene (**2b**): mp 225–230 °C; mp 210–230 °C (from CHCl<sub>3</sub>); mass spectrum, M<sup>+</sup> 381, 383; calcd for C<sub>6</sub>BrN<sub>5</sub>O<sub>10</sub>, 382.0. The procedure was also employed in the reaction of HCl (excess) with hexanitrobenzene to yield pentanitrochlorobenzene (**2a**); 100% yield.

**Reaction of Polynitrobenzenes with Hydrogen Halides (Procedure C).** A mixture of 1,2,3,5-tetranitrobenzene<sup>4</sup> (**5**, 0.20 g, 0.78 mmol) and concentrated HCl (10 mL) was heated under reflux for 15 min. After being cooled to 25 °C, the mixture was filtered and the collected product was washed with water; there was obtained 0.13 g (67%) of picryl chloride (**6a**), mp 80–81 °C, identical with an authentic sample (IR, <sup>1</sup>H NMR). In a parallel experiment, picryl bromide (**6b**), mp 120–122 °C (74% yield), was obtained similarly by using concentrated hydrobromic acid. Picryl iodide (**6c**) could not be obtained by this method, the product being reduced to 1,3,5-trinitrobenzene.<sup>5</sup> An authentic sample of

**6c**, mp 160–164 °C, was prepared by the procedure of Blatt and Gross.<sup>5</sup>

Procedure C was applied to the reaction of 1,2,4,5-tetranitrobenzene<sup>4</sup> (7, 50 mg) and 6 mL of concentrated HCl (15-min reflux). There was obtained a crude product (45 mg, mp 106–112 °C), shown by its mass spectrum to be a mixture of 2,4,5-trinitrochlorobenzene (**8a**) and reactant 7. Trituration of the crude mixture with chloroform at 25 °C extracted the product **8a**, leaving 15 mg of unreacted 7. Concentration of the extract to dryness gave 30 mg (71%) of crude **8a**, mp 105–114 °C (89% yield based on unrecovered 7). Recrystallization of the crude **8a** from ethanol gave long prisms: mp 112–116 °C (lit.<sup>13</sup> mp 116 °C); mass spectrum, *m/e* (relative intensity) 247 ( $M^+$ , 20.8), 249 ( $M^+$ , 6.8), 74 (100); calcd  $M_r$  for  $C_6H_2ClN_3O_6$  247.56. In a parallel experiment 1,2,4,5-tetranitrobenzene (**7**) reacted with boiling concentrated HBr to form 2,4,5-trinitrobenzobromobenzene (**8b**): long prisms, mp 117–118 °C (64% yield); mp 119–121 °C (from ethanol), lit.<sup>14</sup> mp 120–121 °C; mass spectrum, *m/e* (relative intensity) 293 ( $M^+$ , 15.6), 291 ( $M^+$ , 16.0), 74 (100); calcd  $M_r$  for  $C_6H_2BrN_3O_6$  292.02.

Pentanitrotoluene (**9**, 57 mg) was heated under reflux with concentrated HCl (5 mL) for 15 min to yield 43 mg of product: mp 214–220 °C; <sup>1</sup>H NMR ( $CDCl_3$ )  $\delta$  (peak heights in parentheses) 2.60 (5), 2.57 (35), 2.44 (7) assigned to an unidentified component, unreacted **9**, and 3-chloro-2,4,5,6-tetranitrotoluene (**10a**), respectively; mass spectrum, *m/e* (relative intensity) 317 (1.6), 308 (8.2), 306 (22.8), 289 (23.8), 259 (23.7), 297 (7.3), 295 (10.9), 213 (100); found Cl, 3.99%; calcd for  $C_7H_3ClN_4O_8$  Cl, 11.56,  $M_r$  306.58; calcd for  $C_7H_3Cl_2N_4O_8$  Cl, 23.95,  $M_r$  296.03. In a parallel run employing a reflux time of 1 h, 20 mg of product was obtained: <sup>1</sup>H NMR ( $CDCl_3$ )  $\delta$  (peak heights in parentheses) 2.60 (25), 2.57 (41), 2.44 (32). The yield of **10a**, estimated from the material balance, chlorine analysis, and NMR data is ca. 11–12% after either 15-min or 1-h reflux time.

Pentanitrotoluene (**9**, 53 mg) was heated under reflux with concentrated HBr (5 mL) for 0.5 h to yield 51 mg of product: mp 169–173 °C; <sup>1</sup>H NMR  $\delta$  (peak heights in parentheses) 2.57 (9), 2.42 (32), 2.31 (12) assigned to unreacted **9**, 3-bromo-2,4,5,6-tetranitrotoluene (**10b**), and a dibromotrinitrotoluene (possibly 3,5-dibromo-2,4,6-trinitrotoluene), respectively. Anal. Found C, 23.07; H, 0.79; Br, 28.16; N, 13.51. Calcd for  $C_7H_3BrN_4O_8$ : C, 23.95; H, 0.86; Br, 22.77; N, 15.96;  $M_r$  351.05. Calcd for  $C_7H_3Br_2N_4O_8$ : C, 21.84; H, 0.79; Br, 41.52; N, 10.92;  $M_r$  384.94. Mass spectrum, *m/e* (relative intensity) 385 (29.1), 383 (15.5), 370 (28.9), 368 (60.6); 352 (29.4), 350 (29.4), 75 (100). The yield of **10b**, estimated from the material balance and NMR data, is 52%.

**3,5-Dinitro-4-fluorobenzoic Acid (14)**. 4-Fluorobenzoic acid (**13**, Aldrich, 14.0 g, 0.10 mol) was added, with stirring, during 10 min to a mixture of oleum (30%  $SO_3$ , 63 mL) and 90% nitric acid (56 mL), keeping the temperature below 25 °C by ice-bath cooling. The resulting clear yellow solution was heated to 85 °C during 10 min (reflux condenser attached); the heating bath was then removed; after the initial exotherm had subsided, the reaction flask was then heated at 95 °C, while stirring, for 3 h. The mixture was then cooled and poured onto ice; filtration and washing with water gave 16.6 g (72%) of pure **14**: mp 235–237 °C (lit.<sup>16</sup> mp 220–222 °C); <sup>1</sup>H NMR ( $CD_3CN$ )  $\delta$  9.00 (d,  $J = 6$  Hz).

**3,5-Dinitro-4-fluoroaniline (15)**. To a solution of 3,5-dinitro-4-fluorobenzoic acid (**14**, 11.39 g, 49.5 mmol) in oleum (20%  $SO_3$ , 30 mL) was added ethylene dichloride (40 mL). While stirring and keeping the temperature below 25 °C (ice-bath cooling), sodium azide (3.70 g, 56.9 mmol) was added in small

portions during 3 min. The mixture was then heated under reflux for 1 h and cooled to 25 °C, and the ethylene dichloride layer was separated. The acid solution was poured over ice; filtration and washing with water gave 7.65 g (77%) of crude **15**, mp 146–148 °C. Recrystallization from ethylene dichloride gave 4.74 g of **15** as yellow-orange crystals: mp 149–150 °C; <sup>1</sup>H NMR ( $CD_3CN$ )  $\delta$  7.67 (d,  $J = 6$  Hz). Anal. Calcd for  $C_6H_4FN_3O_4$ : C, 36.01; H, 2.01; F, 9.49; N, 21.00. Found: C, 35.98; H, 1.91; F, 9.21; N, 20.72.

**4-Fluoro-2,3,5,6-tetranitroaniline (17)**. To 3,5-dinitro-4-fluoroaniline (**15**, 2.50 g, 12.4 mmol) dissolved in concentrated sulfuric acid (100 mL) was added 90% nitric acid (7 mL, 140 mmol) dropwise with stirring (20–25 °C). After being stirred at 25–30 °C for 4.5 h, the solution was extracted with methylene chloride (7  $\times$  100 mL); the extracts were stirred with  $MgSO_4$  and concentrated at 25 °C to leave 2.67 g (64%) of crude 4-fluoro-2,3,5,6-pentanitroaniline (**16**) as an orange-yellow solid, mp 95–102 °C dec, which was employed immediately in the next step.

A mixture of crude **16** (5.60 g, 16.7 mmol) and anisole (5.6 mL) in concentrated  $H_2SO_4$  (300 mL) was stirred at 25 °C for 1 h. The solution was extracted with  $CH_2Cl_2$  (5  $\times$  200 mL), and the extracts were stirred with  $MgSO_4$  and concentrated to yield 4.42 g (91%) of crude **17**; recrystallization from ethylene dichloride gave orange crystals, 2.77 g, mp 170–171 °C dec; IR (KBr) 3300, 3400  $cm^{-1}$  ( $NH_2$ ). Anal. Calcd for  $C_6H_2FN_5O_8$ : C, 24.76; H, 0.69; F, 6.53; N, 24.06. Found: C, 24.67; H, 0.75; F, 6.30; N, 23.96.

**Pentanitrofluorobenzene (18)**. A solution of 4-fluoro-2,3,5,6-tetranitroaniline (**17**, 0.50 g, 1.7 mmol) in oleum (20%  $SO_3$ , 25 mL) was chilled to 3 °C. Hydrogen peroxide (98%, 3.0 mL) was added dropwise during 10 min (temperature below 30 °C). After stirring at 25 °C for 16 h, the mixture was extracted with  $CH_2Cl_2$ , and the extracts were stirred with  $MgSO_4$  and concentrated to yield 0.48 g (88%) of crude **18**; recrystallization from  $CCl_4$  gave crystals: 0.25 g; mp 154–155 °C (lit.<sup>4</sup> mp 152–154 °C); <sup>19</sup>F NMR ( $CDCl_3$ )  $\delta$  -112.74 ppm from  $CFCl_3$ ; the infrared spectrum (KBr) was identical with that of an authentic sample of **18** prepared previously by an alternate route<sup>4</sup> (the  $NH_2$  bands of reactant **17** were absent).

**3-Chloro-2,4,5,6-tetranitrofluorobenzene (19)**. Pentanitrofluorobenzene (**18**, 0.20 g, 0.62 mmol) dissolved in benzene (5 mL) was stirred vigorously with 10 mL of concentrated HCl (25 °C, 2 h). The benzene layer was separated, dried with  $MgSO_4$ , and concentrated to yield 0.17 g (88%) of **19**; recrystallization from  $CCl_4$  gave pale yellow prisms: 0.08 g; mp 74–76 °C; <sup>19</sup>F NMR ( $CDCl_3$ )  $\delta$  -118.59 ppm from  $CFCl_3$ ; mass spectrum, *m/e* (relative intensity) 312 (5.1), 310 (15.7), 126 (34.0), 46 (100); calcd for  $C_6ClFN_4O_8$   $M_r$  310.54, see Table I. Anal. Calcd for  $C_6ClFN_4O_8$ : C, 23.21; Cl, 11.42; F, 6.12; N, 18.04. Found: C, 23.10; H, 0.26; Cl, 10.74; F, 5.59; N, 17.45.

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