Anal. Calcd for $C_6H_{14}ClO_3P$: Cl, 17.7. Found: Cl, 17.6.

The infrared spectrum of the product had peaks at 2940 cm^{-1} (aliphatic C—H), 1260 cm^{-1} (P → O), 1100 cm^{-1} (C—O—C), 1020 cm^{-1}, 962 cm^{-1} (P—O—C).

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Chemical Reduction of 2,4,6-Trinitrotoluene—Initial Products

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High-purity model compounds were needed for comparison with the products formed during the biodegradation of 2,4,6-trinitrotoluene (TNT). Thus, an attempt to prepare 12 reduction products of TNT (amino, hydroxylamino, azo, and azoxy compounds) was made. Eight of these compounds were successfully prepared, two of which (4,4′,6,6′-tetranitro-2,2′-azoxytoluene and 2,4′-dimethyl-3,3′,5,5′-tetranitro-ONN-azoxybenzene) have not previously been reported in the literature. Improvements were made in the purity and method of preparation of several of the compounds previously reported in the literature.

In a study of the products from the biodegradation of 2,4,6-trinitrotoluene (TNT), it was necessary to have a series of the initial reduction products of TNT for use as model compounds. These compounds were desired in high purity so that their presence among the biodegradation products of TNT could be determined quantitatively using such methods as thin-layer chromatography, gas chromatography, and ultraviolet spectroscopy. It was thought that the initial biodegradation products of TNT might include hydroxylamino, amino, azo, and azoxy compounds. Thus, the preparation of representative compounds from each of these classes was undertaken.

Hydroxylamino compounds: 2,6-dinitro-4-hydroxylaminotoluene (I) and 4,6-dinitro-2-hydroxylaminotoluene (II). Compound I, prepared according to Elvove (3), contained a small amount of 4-amino-2,6-dinitrotoluene (IV) which was removed by column chromatography.

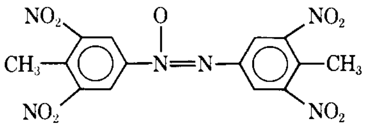
Attempts to prepare II by the method of McGookin et al. (5) or by the oxidation of 2-amino-4,6-dinitrotoluene (III) with *m*-chloroperoxybenzoic acid were unsuccessful. In the latter case, II was rapidly converted to the azoxy derivative under the reaction conditions and could not be isolated.

Amino compounds: 2-amino-4,6-dinitrotoluene (III), 4-amino-2,6-dinitrotoluene (IV) (1), and 2,4-diamino-6-nitrotoluene (V)(6). Attempts to prepare III by the method of McGookin et al. (5) did not yield a pure compound, but a modification of the procedure gave a yield of high-purity product. Reduction of III with alcoholic ammonium sulfide yielded 2,4-diamino-6-nitrotoluene (V), and oxidation of III with *m*-chloroperoxybenzoic acid in methylene chloride yielded 4,4′,6,6′-tetranitro-2,2′-azoxytoluene (VIII).

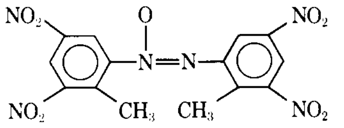
Azo compounds: 2,2′,6,6′-tetranitro-4,4′-azotoluene (VI). Compound VI was prepared by a modification of the procedure of Brand and Eisenmenger (2). (See Experimental section.)

Azoxy compounds: 2,2′,6,6′-tetranitro-4,4′-azoxytoluene (VII), 4,4′,6,6′-tetranitro-2,2′-azoxytoluene (VIII), 2,4′-dimethyl-3,3′,5,5′-tetranitro-ONN-azoxybenzene

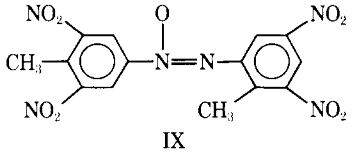
(IX), and 2',4-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene (X).



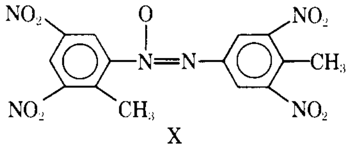
VII



VIII

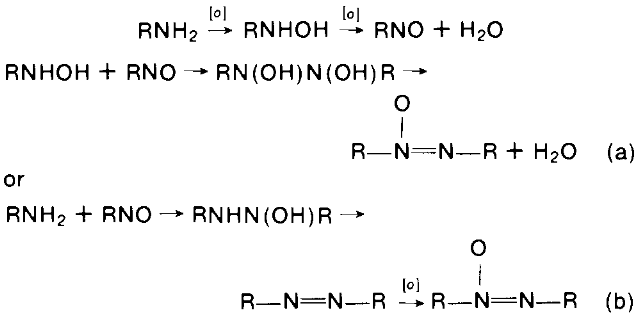


IX



X

Mild oxidation of aromatic amines can produce azoxy compounds as illustrated below (*7*).



$$RNH_2 \xrightarrow{[o]} RNHOH \xrightarrow{[o]} RNO + H_2O$$

$$RNHOH + RNO \rightarrow RN(OH)N(OH)R \rightarrow R\text{—}\overset{\overset{\displaystyle O}{|}}{N}\text{=}N\text{—}R + H_2O \qquad (a)$$

or

$$RNH_2 + RNO \rightarrow RNHN(OH)R \rightarrow R\text{—}N\text{=}N\text{—}R \xrightarrow{[o]} R\text{—}\overset{\overset{\displaystyle O}{|}}{N}\text{=}N\text{—}R \qquad (b)$$

Treatment of 4-amino-2,6-dinitrotoluene (IV) and 2-amino-4,6-dinitrotoluene (III) with *m*-chloroperoxybenzoic acid in methylene chloride yielded VII and VIII, respectively. [Compound VII was also prepared by heating 2,6-dinitro-4-hydroxylaminotoluene (I) with concentrated hydrochloric acid according to the method of Brand and Eisenmenger (2).]

Thin-layer chromatographic analysis indicated that both crossover products, IX and X, were formed by oxidation of a mixture of III and IV. The crossover product formed in largest yield was isolated by column chromatography (see Experimental section). The product was assigned the structure IX by comparing its nmr spectrum with those of VII and VIII (see Table I for nmr data). For azoxy compounds in which the substituents are identical ($R\text{—}\overset{\overset{\displaystyle O}{|}}{N}\text{=}N\text{—}R'$, where $R\text{=}R'$), Freeman has shown that the substituent attached to the oxidized nitrogen appears at the lower field (*4*). Thus, the protons appearing at 9.08 ppm in compound VII belong to the phenyl ring attached to the oxidized nitrogen. The crossover product shows a singlet at 9.07 ppm and therefore was assigned the structure IX rather than X which would be expected to have a singlet near 8.91 ppm.

Miscellaneous compounds: 2,2'-diamino-6,6'-dinitro-4,4'-azoxytoluene (XI) and 2-amino-4-hydroxylamino-6-nitrotoluene (XII). Attempts to prepare XI by reduction of VII with ammonium sulfide gave a mixture of products which could not be separated. The preparation of XI by mild oxidation of 2,4-diamino-6-nitrotoluene (V) with *m*-chloroperoxybenzoic acid was also unsuccessful.

Reaction conditions similar to those used for the preparation of I from TNT did not reduce 2-amino-4,6-dinitrotoluene (III) to XII. When more stringent reaction conditions were employed, the product was V.

Experimental

Melting points for TNT reduction products are given in Table II. The melting points were taken on a Thomas-Hoover apparatus and are corrected. Silica gel HF-254 was used for tlc, and the spots were visualized with uv light. Nmr spectra were determined on a Varian HA-100 spectrometer. Elemental analyses (C, H, N) were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., for compounds III, VI, VIII, and IX and were in agreement with theoretical values.

2-Amino-4,6-dinitrotoluene (III). Twenty-four grams of 4,6-dinitro-*o*-toluamide was stirred with 160 ml of ice-cold 5.25% sodium hypochlorite (Clorox) for 30 min. The unreacted amide was removed by filtration, and ice-cold 25% sulfuric acid was quickly added to the cold filtrate. The precipitated solid was removed by filtration, washed quickly with cold water, and then boiled with water for 2 hr. At this time the hot mixture was filtered, and the insoluble white solid obtained was heated with boiling dilute sodium bicarbonate. The white solid rapidly turned bright yellow. After 15 min the mixture was cooled and filtered, and the bright yellow product crystallized from methanol to give 6.0 grams of 2-amino-4,6-dinitrotoluene, mp 173–174°. The procedure described above is a modification of the method of McGookin et al. (*5*).

2,2',6,6'-Tetranitro-4,4'-azotoluene (VI). The procedure according to Brand and Eisenmenger (2) yielded a mixture of VI and the azoxy compound VII. Several crystallizations from benzene concentrated the azo compound VI in the mother liquors. The combined mother liquors were subjected to column chromatography on silica gel (70–230 mesh) by use of 50/50 benzene–hexane as the eluent. The azo product was crystallized from acetone to give red-orange crystals, mp 266–268°.

4,4',6,6'-Tetranitro-2,2'-azoxytoluene (VIII). To a solution of 1.5 grams (0.0076 mole) of 2-amino-4,6-dinitrotoluene in 75 ml of methylene chloride was added 3.0 grams (0.0147 mole) of *m*-chloroperoxybenzoic acid (assay 85%, Aldrich Chemical Co.). After the solution stood for 16 hr at ambient temperature, the white solid that precipitated (*m*-chlorobenzoic acid) was removed by filtration. The methylene chloride filtrate was extracted with 5% aqueous sodium bicarbonate to remove the remaining *m*-chlorobenzoic acid. The methylene chloride was allowed to evaporate in a current of air in the hood, leaving 1.3 grams of solid, mp 170–175°. The solid was crystallized twice from benzene to give 0.85 grams (55%) of cream-colored crystals, mp 179–180°.

2,4'-Dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene (IX). To a solution of 0.50 gram (0.0025 mole) of 2-amino-4,6-dinitrotoluene and 0.75 gram (0.0038 mole) of 4-amino-2,6-dinitrotoluene in 65 ml of methylene chloride was added 2.5 grams (0.0123 mole) of *m*-chloroperoxybenzoic acid (assay 85%, Aldrich Chemical Co.). (The excess of 4-amino-2,6-dinitrotoluene over 2-amino-4,6-dinitrotoluene was used to diminish the amount of 4,4',6,6'-tetranitro-2,2'-azoxytoluene (VIII) formed. The separation of VIII from the crossover azoxy products (IX and X) is difficult).

The reaction mixture was allowed to stand 16 hr at ambient temperature and filtered to remove precipitated

Table I. Nmr Data for Aminodinitrotoluenes and Azoxy Compounds[a]

Compound	Solvent	Aliphatic-H	Aromatic-H	NH_2
2-Amino-4,6-dinitrotoluene (III)	Acetone-d_6	2.28 s	7.77 s[b]	5.75 s
4-Amino-2,6-dinitrotoluene (IV)	Acetone-d_6	2.26 s	7.33 s	5.60 s
2,2′,6,6′-Tetranitro-4,4′-azoxytoluene (VII)	DMSO-d_6	2.55 s, 2.52 s	9.08 s, 8.91 s	
4,4′,6,6′-Tetranitro-2,2′-azoxytoluene (VIII)	DMSO-d_6	2.59 s, 2.48 s	9.28 d, 9.15 d 8.96 d, 8.77 d	
2,4′-Dimethyl-3,3′,5,5′-tetranitro-ONN-azoxybenzene (IX)	DMSO-d_6	2.56 s, 2.52 s	9.07 s 8.99 d, 8.75 d	

[a] s = singlet, d = doublet. Chemical shifts are in δ units. [b] Addition of benzene resolves the peak at 7.77 into two doublets at 7.74 and 7.64.

Table II. Physical Properties of TNT Reduction Products

Compound	Mp, °C	Lit, mp, °C	Lit ref
2,6-Dinitro-4-hydroxylaminotoluene (I)	144–46	135–36	3
2-Amino-4,6-dinitrotoluene (III)	173–74	155	5
4-Amino-2,6-dinitrotoluene (IV)	171–72	171	1
2,4-Diamino-6-nitrotoluene (V)	134–35	135	6
2,2′,6,6′-Tetranitro-4,4′-azotoluene (VI)	266–68	248–50	2
2,2′,6,6′-Tetranitro-4,4′-azoxytoluene (VII)	215–16	216	2
4,4′,6,6′-Tetranitro-2,2′-azoxytoluene (VIII)	179–80	[a]	[a]
2,4′-Dimethyl-3,3′,5,5′-tetranitro-ONN-azoxybenzene (IX)	169–70	[a]	[a]

[a] Compound is new to the literature.

m-chlorobenzoic acid. Extraction of the methylene chloride filtrate with 5% aqueous sodium bicarbonate removed the remaining *m*-chlorobenzoic acid. Thin-layer chromatographic analysis of the methylene chloride solution indicated that both crossover azoxy products (IX and X) were formed along with the 4-azoxy (VII) and 2-azoxy (VIII) compounds. However, one of the crossover azoxy products was formed in much greater yield than the other. The methylene chloride was removed under reduced pressure, leaving a residue from which 0.45 gram of the 4-azoxy compound (VII) was obtained by fractional crystallization from benzene. The benzene mother liquor was subjected to column chromatography on silica gel (70–230 mesh) to isolate the crossover azoxy product formed in the larger yield.

Benzene–hexane mixtures were used as the eluent, and several passes through the column were necessary to effect sufficient separation. The crossover azoxy product was crystallized from acetone–hexane to yield 100 mg of yellow crystals, mp 169–170°. The structure IX was assigned to the crossover azoxy product with mp 169–170° on the basis of its nmr spectrum (see discussion, section on azoxy compounds).

2′,4-Dimethyl-3,3′,5,5′-tetranitro-ONN-azoxybenzene (X). Thin-layer chromatographic analysis indicated X was formed in small amounts during the preparation of IX as described above. No attempt was made to isolate this compound.

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