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CHEMICAL REDUCTION OF 2, 4, 6-TRINITROTOLUENE (TNT) – INITIAL PRODUCTS

BY
Michael E. Sitzmann

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NAVAL ORDNANCE LABORATORY, WHITE OAK, SILVER SPRING, MARYLAND

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Michael E. Sitzmann

Naval Ordnance Laboratory
White Oak, Maryland

14 June 1973

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High purity model compounds were needed for comparison with the products formed during the biodegradation of TNT. Thus, an attempt to prepare twelve reduction products of TNT (amino, hydroxylamino, azo and azoxy compounds) was made. Eight of these compounds were successfully prepared. Most of the compounds were synthesized according to literature procedures or modifications of literature procedures; however, two of the compounds prepared, 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.

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CHEMICAL REDUCTION OF 2,4,6-TRINITROTOLUENE (TNT) - INITIAL PRODUCTS

This report describes the attempted synthesis of twelve reduction products of TNT for use as model compounds in a study of the biodegradation of TNT Eight compounds were successfully prepared, two of which have not previously been reported in the literature. This work was supported by Naval Ordnance Systems Command, ORD-033.

ROBERT WILLIAMSON II
Captain, USN
Commander

A. LIGHTBODY
By direction

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INTRODUCTION

In a study of the products from the biodegradation of 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.

RESULTS AND DISCUSSION

(See Table I for the structures of the compounds described in this section)

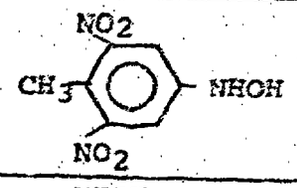
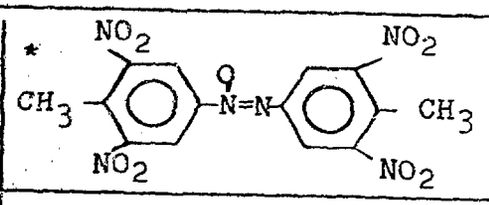
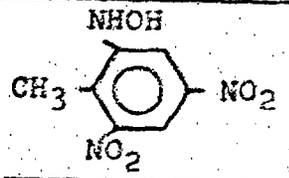
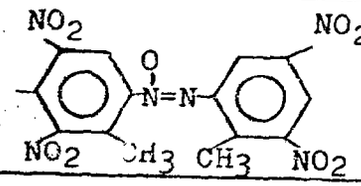
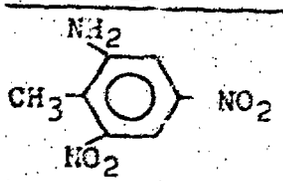
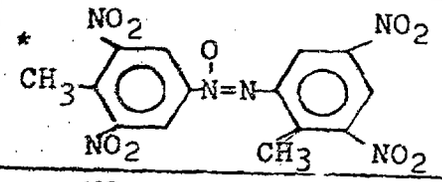
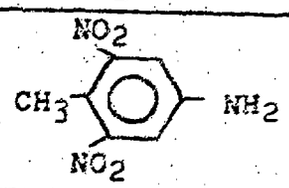
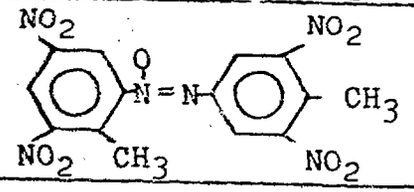
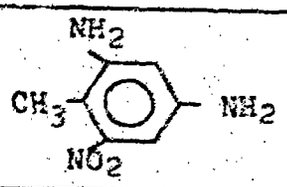
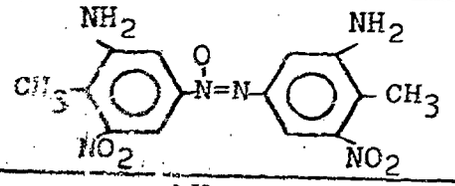
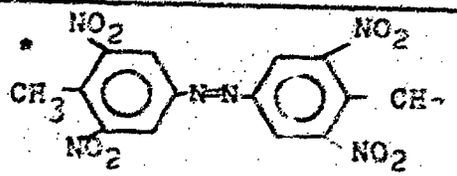
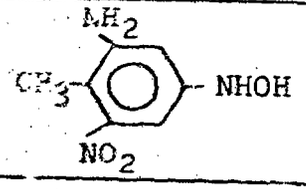
A. Hydroxylamino compounds

The compound, 2,6-dinitro-4-hydroxylaminotoluene (I) was prepared according to Elvoe (1) by reduction of TNT with ammonium sulfide in ethanol. The product contained a small amount of 4-amino-2,6-dinitrotoluene which was removed by column chromatography (silica gel, 70-230 mesh) to give I with a melting point of 144-146°. Elvoe reports 135-136°. Cohen and Dakin report 143-145° (2).

McGookin et. al. report the preparation of 4,6-dinitro-2-hydroxylaminotoluene (II) by reduction of TNT with sodium hydrogen sulfide in boiling water (3). Several attempts to prepare II by this method were unsuccessful. Mild oxidation of 2-amino-4,6-dinitrotoluene (III) with m-chloroperoxybenzoic acid gives II (presumably as an intermediate) but under the reaction conditions II is rapidly converted to the corresponding azoxy compound (VIII) and II cannot be isolated (see page 4). Brand and Eisenmenger (4) report the preparation of II in very small yield by the electrochemical reduction of TNT. No attempt was made to prepare II by this method.

TABLE I

REDUCTION PRODUCTS OF TNT

*		I	*		VII
		II	*		VIII
*		III	*		IX
*		IV			X
*		V			XI
*		VI			XII

*Compounds prepared in this study.

B. Amino compounds

McGookin et al describe the preparation of 2-amino-4,6-dinitrotoluene (III) by the Hofmann degradation of 4,6-dinitro-o-toluamide with sodium hypochlorite (3). Several attempts to follow the exact procedure were unsucessful in producing a pure compound. A modification of the procedure gave an increased yield and a higher melting product (mp 173-174° as compared to 155° reported by McGookin). The higher melting product gives an excellent elemental analysis for III. The product is reduced with alcoholic ammonium sulfide to yield 2,4-diamino-6-nitrotoluene. With m-chloroperoxybenzoic acid in methylene chloride, the product forms 4,4',6,6'-tetranitro-2,2'-azoxytoluene (VIII) the structure of which was confirmed by elemental analysis and nmr. Under the same conditions, authentic 4-amino-2,6-dinitrotoluene (IV) gives the corresponding 2,2',6,6'-tetranitro-4,4'-azoxytoluene (VII), a known compound. The nmr spectrum (acetone-d_6) of the product shows singlets at 7.77, 5.75 and 2.28 ppm in a ratio of 2:2:3. The addition of benzene resolves the peak at 7.77 ppm into two doublets at 7.74 and 7.64 ppm.

The 4-amino-2,6-dinitrotoluene (IV) (mp 171-172°) for this work was prepared by reduction of TNT with alcoholic ammonium sulfide. Brady and co-workers report 171° (5) for IV.

The procedure of Ruggli and Zaeslin (6) was used for the preparation of 2,4-diamino-6-nitrotoluene (V), mp 134-135°. Ruggli and Zaeslin report 135°.

C. Azo compounds

Amino compounds in the presence of hydroxylamino compounds can produce azo derivatives (7). The reaction occurs by addition of the amine to the nitroso compound formed from the disproportionation of the hydroxylamine:

$$2\ RNHOH \longrightarrow RNO + RNH_2 + H_2O$$

$$RNH_2 + RNO \longrightarrow RNHN(OH)R \longrightarrow RN{=}NR + H_2O$$

If both amino and hydroxylamino compounds are formed during the biodegradation of TNT, the formation of azo compounds such as 2,2',6,6'-tetranitro-4,4'-azotoluene (VI) from I and IV is possible. Compound VI was prepared according to the procedure of Brand and Eisenmenger (4). The product contained some 2,2',6,6'-tetranitro-4,4'-azoxytoluene (VII) which was removed by column chromatography to give a product with mp 266-268°. Brand and Eisenmenger report 248-250°. Elemental analysis confirmed the product was VI.

D. Azoxy compounds

Compound VII (2,2',6,6'-tetranitro-4,4'-azoxytoluene) was prepared by heating 2,6-dinitro-4-hydroxylamino toluene (I) with conc. hydrochloric acid according to the method of Brand and Eisenmenger (4). The melting point (2 5-216°) was the same as reported by the authors. Treatment of 4-amino-2,6-dinitrotoluene (IV) with m-chloroperoxybenzoic acid in methylene chloride also gives VII.

The preparation of 4,4',6,6'-tetranitro-2,2'-azoxytoluene (VIII) has not previously been reported in the literature. Compound VIII (mp 179-180°) was obtained by allowing a solution of 2-amino-4,6-dinitrotoluene (III) and m-chloroperoxybenzoic acid in methylene chloride to stand 16 hours at ambient temperature. The reaction presumably proceeds via formation of the intermediate 4,6-dinitro-2-hydroxylamino-toluene (II) (8).

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

Two routes to the azoxy compound are possible under these conditions:

$$\text{a)}\ RNHOH + RNO \longrightarrow RN(OH)\text{-}N(OH)R \longrightarrow R\text{-}\overset{O}{\overset{|}{N}}\text{=}N\text{-}R + H_2O$$

$$\text{b)}\ RNH_2 + RNO \longrightarrow RNHN(OH)R \longrightarrow RN\text{=}NR \xrightarrow{[O]} R\text{-}\overset{O}{\overset{|}{N}}\text{=}N\text{-}R$$

After 16 hours at ambient temperature essentially all the starting amino compound (III) was converted to the azoxy derivative VIII. Samples were removed from the reaction mixture after 1 hour and after 4 hours to determine if it would be feasible to isolate the intermediate hydroxylamine (II). Thin-layer chromatography of the samples showed mainly the azoxy compound (VIII) and the starting amine (III). There was a small amount of product that had an r_f slightly greater than the r_f of the azoxy product (VIII). This is probably the nitroso derivative. There was no evidence by thin-layer chromatographic analysis for the presence of appreciable amounts of the hydroxylamine (II). Apparently II is rapidly converted to the nitroso and azoxy compounds under the reaction conditions and cannot be isolated.

Cross-over azoxy products, 2,4'-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene (IX) and 2',4-dimethyl-3,3',5,5'-tetranitro-ONN-azoxybenzene (X) (9), are possible from the reaction of the 4- and 2-hydroxylamino compounds (I and II). Thin-layer chromatographic analysis indicated these cross-over products were formed (presumbly through I and II as intermediates) by the reaction of a mixture of III and IV with m-chloroperoxybenzoic acid. As expected, the previously identified azoxy compounds, VII and VIII, were also formed. However, one of the cross-over products was formed in much greater yield than the other. The cross-over azoxy product formed in larger yield was isolated by column chromatography. The compound (mp 169-170°) shows an nmr spectrum (DMSO-d_6) with aromatic ring protons at 9.07 ppm (singlet), 8.99 ppm (doublet) and 8.75 ppm (doublet). The ratio of protons is 2:1:1. For the 4-azoxy compound (VII) the ring

protons appear at 9.08 ppm (singlet) and 8.91 ppm (singlet) in a ratio of 1:1. The 2-azoxy compound (VIII) shows doublets at 9.28, 9.15, 8.96 and 8.77 ppm for the four ring protons (1:1:1:1 ratio). For azoxy compounds in which the substituents are identical (R-N=N-R' , where R = R'), Freeman has shown that the substituent attached to the oxidized nitrogen appears at lower field (10). Thus the protons appearing at 9.08 ppm in compound VII belong to the phenyl ring attached to the oxidized nitrogen. The mixed azoxy product melting at 169-170° 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.

E. Miscellaneous compounds.

Compounds such as 2,2'-diamino-6,6'-dinitro-4,4'-azoxytoluene (XI) could be expected to be formed during the biodegradation of TNT if the initial azoxy products were further reduced. Attempts to prepare XI by direct reduction of the 4-azoxy compound (VII) with ammonium sulfide gave a mixture of products which could not be separated.

The compound 2-amino-4-hydroxylamino-6-nitrotoluene (XII) was desired so it could be converted to the azoxy derivative (XI). An attempt to reduce III to XII failed. Reaction conditions similar to those used for the preparation of I from TNT were first tried. No reaction occurred and when more stringent conditions (additional ammonium sulfide) were employed, reduction proceeded to give the 2,4-diamino compound (V).

An attempt was made to prepare XI via the intermediate XII by oxidation of 2,4-diamino-6-nitrotoluene (V) with m-chloroperoxybenzoic acid in methylene chloride. A small amount (ca 5% of the weight of starting material) of red crystals (decomp. point 234°) was isolated. The red crystals crystallized as solvates which could not be broken up without decomposing the compound. All solvents tried gave similar results. However, the compound does not have the properties (r_f on thin-layer chromatography and the nmr spectrum) that XI would be expected to have.

EXPERIMENTAL

Preparation of:

1) 2,6-dinitro-4-hydroxylaminotoluene (I). See page 1 .

2) 4,6-dinitro-2-hydroxylaminotoluene (II). See page 1 .

3) 2-amino-4,6-dinitrotoluene (III).

Twenty-four grams (24 g) of 4,6-dinitro-o-toluamide was stirred with 160 ml of ice-cold 5.25% sodium hypochlorite (chlorox) for 30 minutes. 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 two hours. 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 minutes the mixture was cooled, filtered, and the bright yellow product crystallized from methanol to give 6.0g of 2-amino-4,6-dinitrotoluene, mp 173-174°. Anal. Calcd for $C_7H_7N_3O_4$: C, 42.64; H, 3.58; N, 21.31. Found: C, 42.59; H, 3.47; N, 21.16. The procedure described above is a modification of the method of McGookin et al (see page 3).

4) 4-amino-2,6-dinitrotoluene (IV). See page 3.

5) 2,4-diamino-6-nitrotoluene (V). See page 3 .

6) 2,2',6,6'-tetranitro-4,4'-azotoluene (VI).

The procedure according to Brand and Eisenmenger (4) 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 silca gel (70-230 mesh) using 50/50 benzene-hexane as the eluent. The azo product was crystallized from acetone to give red-orange crystals, mp 266-268°. Anal. Calcd for $C_{14}H_{10}N_6O_8$: C, 43.09; H, 2.58; N, 21.53. Found: C, 43.13; H. 2.57; N, 21.39. See also page 3 .

7) 2,2',6,6'-tetranitro-4,4'-azoxytoluene (VII). See page 4 .

8) 4,4'-6,6'-tetranitro-2,2'azoxytoluene (VIII).

To a solution of 1.5g (0.0076 mole) of 2-amino-4,6-dinitrotoluene in 75 ml of methylene chloride was added 3.0g (0.0147 mole) of m-chloroperoxybenzoic acid (assay 85%, Aldrich Chemical Co.). After the solution stood for 16 hours 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 1.3g of solid, mp 170-175°. The solid was dissolved in hot benzene and treated with charcoal, the solution was filtered and the filtrate cooled to give 0.65g of cream colored crystals, mp 179-180°. Concentration of the mother liquor gave a second crop (0.20g), mp 178-180°. The combined crops (0.85g, 55% of the theoretical) was recrystallized from benzene to give the analytical sample (0.65g, mp 179-180°). Anal. Calcd for $C_{14}H_{10}N_6O_9$: C, 41.39; N, 2,48; N, 20.69. Found: C, 41.64; H, 2.45; N, 20.82.

The nmr spectrum (DMSO-d_6) of VIII shows doublets at 9.28, 9.15, 8.96 and 8.77 ppm in addition to singlets at 2.59 and 2.48 ppm.

9) 2,4'-dimethyl-3,3'5,5'-tetranitro-ONN-azoxybenzene (IX).

To a solution of 0.50g (0.0025 mole) of 2-amino-4,6-dinitrotoluene and 0.75g (0.0038 mole)* of 4-amino-2,6-dinitrotoluene in 65 ml of

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* The excess of 4-amino-2,6-dinitrotoluene over the 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 cross-over azoxy products (IX and X) is very difficult.

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methylene chloride was added 2,5g (0.0123 mole) of m-chloroperoxybenzoic acid (assay 85%, Aldrich Chemical Co.). The reaction mixture was allowed to stand 16 hours at ambient temperature and filtered to remove precipitated 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 cross-over azoxy products (IX and X) were formed along with the 4-azoxy(VII) and 2-azoxy (VIII) compounds. However, one of the cross-over azoxy products was formed in much greater yield than the other. The methylene chloride was removed under reduced pressure leaving a residue from which 0.45g 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) in order to isolate the cross-over 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 cross-over azoxy product was crystallized from acetone-hexane to yield 100 mg of yellow crystals, mp 169-170°. Anal. Calcd for $C_{14}H_{10}N_6O_9$: C, 41.39; H, 2.48; N, 20.69. Found: C, 41.14; H, 2.31; N, 20.71.

The structure IX was assigned to the cross-over azoxy product melting at 169-170° on the basis of its nmr spectrum (DMSO-d_6) which shows a singlet at 9.07 ppm and doublets at 8.99 and 8.75 ppm (see page 4). The ratio of protons is 2:1:1. Two additional singlets at 2.56 and 2.52 ppm are also present.

10) 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.

11) 2,2'-diamino-6,6'-dinitro-4,4'-azoxytoluene (XI). See page 5 .

12) 2-amino-4-hydroxylamino-6-nitrotoluene (XII). See page 5 .

ACKNOWLEDGEMENT

The author is grateful to Miss Eleanore G. Kayser for the determination of the nmr spectra. He also wishes to thank Dr. John Hoffsommer for his helpful suggestions during the course of the project.

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6) P. Ruggli and H. Zaeslin, Helv. Chim Acta., 19, 438(1936).

7) P. A. S. Smith, The Chemistry of Open-chain Organic Nitrogen Compounds, W. A. Benjamin, Inc. N.Y., NY, Vol I, page 110; Vol II, page 4.

8) Ref. 7, Vol II, page 12, pages 321-322.

9) The I.U.P.A.C. Tentative Rules uses the infixes, -NNO- and -ONN-, for nomenclature of azoxy compounds. If it is necessary to number positions on both substituents, the convention is that when -ONN- is used, primed numbers refer to the positions on the group near the oxygen. Ref. 7 Vol II, page 271.

10) J. Freeman, J. Org. Chem., 28, 2508-11(1963).