

Nitro Derivatives of 1-Picrylbenzotriazole (1).

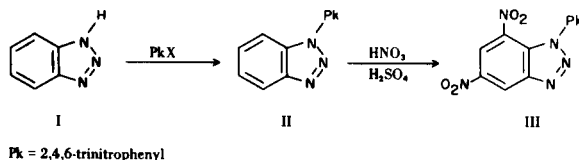
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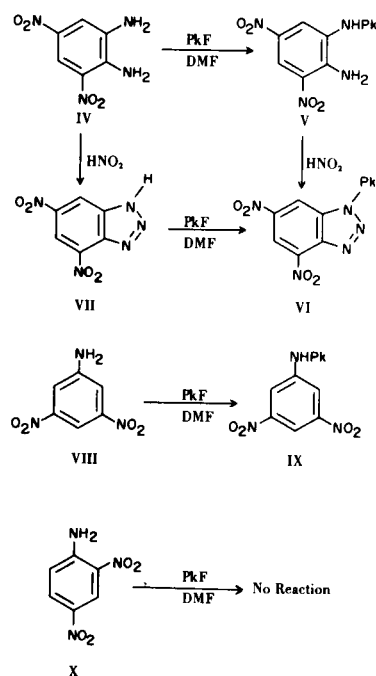
The synthesis of the isomeric 4,6-, 5,6-, and 5,7-dinitro-1-picrylbenzotriazoles has been accomplished. The nmr spectra of these compounds and the mononitro derivatives of 1-picrylbenzotriazole were determined and the substituent effects of the nitro and picryl groups on the chemical shifts of the various benzotriazole protons are discussed.

The reaction of benzotriazole (I) with picryl chloride in ethanol has been reported to yield 1-picrylbenzotriazole (II) as the major product along with a small amount of 2-picrylbenzotriazole (2). The reaction was repeated in this laboratory to yield II, but the byproduct that resulted was identified as the picrate of I by comparing it with an authentic sample obtained from the reaction of I with picric acid. Compound II was also the exclusive product of the reaction of I with picryl fluoride. Nitration of II produced a dinitro derivative that was assigned the structure of 5,7-dinitro-1-picrylbenzotriazole (III) after the other possible products had been synthesized unequivocally as described in the following paragraphs.



3,5-Dinitro-*o*-phenylenediamine (IV) (3) was allowed to react with picryl fluoride in DMF to yield 2,4-dinitro-6-picrylaminoaniline (V), which was treated with nitrous acid to form 4,6-dinitro-1-picrylbenzotriazole (VI). Treatment of IV with nitrous acid provided 4,6-dinitrobenzotriazole (VII) (4), which condensed with picryl fluoride in DMF to produce VI by an alternate route. That the 1-amino group of IV is significantly more nucleophilic than the 2-amino group was demonstrated when 3,5-dinitroaniline (VIII) reacted with picryl fluoride in DMF to give 1,3-dinitro-5-picrylaminoaniline (IX), while 2,4-dinitroaniline (X) failed to react with picryl fluoride under identical conditions.

4,5-Dinitro-*o*-phenylenediamine (XI) (5) was converted to 5,6-dinitrobenzotriazole (XII) with nitrous acid. The product reacted with picryl fluoride in DMF to give 5,6-dinitro-1-picrylbenzotriazole (XIII). An alternate



route to XIII involves the condensation of 4-nitro-*o*-phenylenediamine (XIV) with picryl chloride in ethanol to form 4-nitro-2-picrylaminoaniline (XV), followed by the treatment of XV with nitrous acid to yield 6-nitro-1-picrylbenzotriazole (XVI), which was nitrated with fuming nitric acid to XIII. The assignment of structure XV was based upon the report that XIV reacts with 1-chloro-2,4-dinitrobenzene to give 2-(2,4-dinitroanilino)-4-nitroaniline (2). Nitration of XVI with a mixture of nitric and sulfuric acids gave a labile trinitro derivative of II. One of the nitro groups of the product was easily replaced by a methoxy group when the crude product was dissolved in methanol. Although there is no direct evidence for the structures of these products, it appears reasonable to

TABLE I
Nmr Spectra of the Benzotriazoles (a)

Benzotriazole	Picryl Protons	δ_{C-H} (ppm)			Coupling Constants (cps)
		C-4	Benzotriazole C-5	Protons C-6	
5-Nitro-		8.87(d)		8.32(q)	2(4,6); 10(6,7)
4,6-Dinitro-			9.47(d)		2(5,7)
5,6-Dinitro		9.01(s)			9.01(s)
5-Nitro-1-picryl-	9.59(s)	9.32(d)		8.69(q)	2(4,6); 9(6,7)
6-Nitro-1-picryl	9.55(s)	8.62(d)	8.42(q)		9(4,5); 2(5,7)
4,6-Dinitro-1-picryl-	9.57(s)		9.60(d)		2(5,7)
5,6-Dinitro-1-picryl-	9.63(s)	9.48(s)			9.22(s)
5,7-Dinitro-1-picryl-	9.50(s)	9.28(d)		9.83(d)	2(4,6)
5,7-Dinitro-6-methoxy-1-picryl- (b)	9.48(s)	9.59(s)			

(a) Determined with a Varian A-60A spectrometer as DMSO- d_6 solutions using tetramethylsilane as an internal standard. (b) The 6-methoxy protons appear as a singlet at 4.12 δ .

TABLE II
Condensation of the Triazoles and Amines with Picryl Halides

Reactants (moles)	Reaction Solvent (ml.)	Reaction Temp. ($^{\circ}$ C)	Reaction Time (hr.)	Recrystallization Solvent	Product(s) (% yield)	M.p. ($^{\circ}$ C)
I(0.01), PkF(0.01)	DMF(20)	25	3	Acetone-ethanol	II(96)	212 (a)
IV(0.01), PkF(0.01)	DMF(20)	25	24	None (b)	V(91)	281 dec.
VII(0.01), PkF(0.01)	DMF(20)	25	24	Acetone-ethanol	VI(95)	309 dec.
VIII(0.01), PkF(0.01)	DMF(20)	25	24	Acetone-ethanol	IX(62)	275
XII(0.01), PkF(0.01)	DMF(20)	25	48	Acetone-ethanol	XIII(60)	226 dec.
XIV(0.02), PkCl(0.02), NaOAc(0.02)	Ethanol(300)	Reflux	5	Acetone-ethanol	XV(63)	256 dec.
XIX(0.01), PkCl(0.01), NaOAc(0.01)	Ethanol(100)	Reflux	5	None	XVI (c) XX	

(a) Lit. (2) m.p. 212 $^{\circ}$. (b) The product was purified by digestion in boiling ethanol. (c) Nmr analysis indicated the crude to be XV (44%) and XX (56%). Attempts to resolve the mixture failed.

assume that XIII is an intermediate in the formation of the trinitro compound and, in view of the observed directive influence of the 1-picryl group on the nitration of II, that the 7-position of XIII would be more susceptible to nitration than the 4-position. Thus, 1-picryl-5,6,7-trinitrobenzotriazole (XVII) seems to be the most plausible structure for the trinitro derivative and 5,7-dinitro-6-methoxy-1-picrylbenzotriazole (XVIII) is probably the product of its reaction with methanol. 5-Nitrobenzotriazole (XIX), obtained from the reaction of XIV with nitrous acid (6), reacted with picryl chloride in ethanol to provide a mixture of XVI and its isomer, 5-nitro-1-

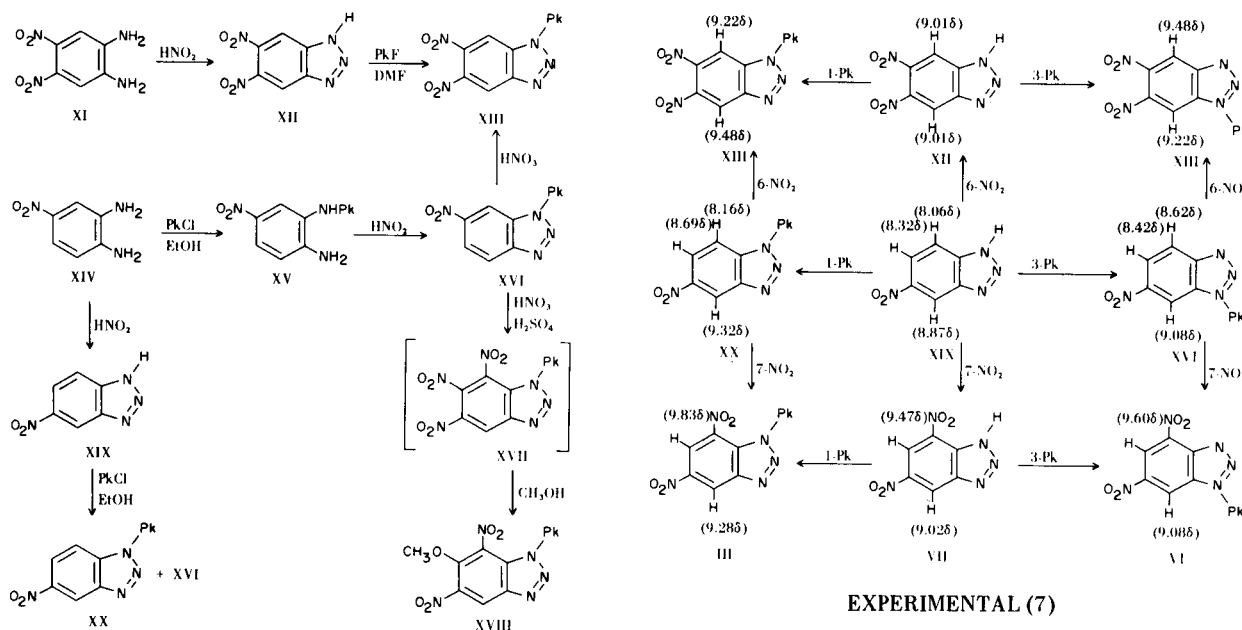
picrylbenzotriazole (XX). The mixture was not resolved, but the nmr spectrum of XX was obtained by subtracting the spectrum for XVI from that of the mixture.

The nmr spectra of the benzotriazole derivatives prepared in this study are described in Table I. The substituent effects of the nitro and picryl groups on the chemical shifts of the various benzotriazole protons are illustrated below using 5-nitrobenzotriazole (XIX) as the focal compound.

Note that the nitro group deshields the adjacent proton by approximately 1.0 ppm in each case, while it has little, if any, effect on the other protons. Introduction

TABLE III
Elemental Analyses

Compound	Molecular Formula	Calculated, %			Found, %		
		C	H	N	C	H	N
III	C ₁₂ H ₄ N ₈ O ₁₀	34.30	0.95	26.67	34.62	0.88	26.67
V	C ₁₂ H ₇ N ₇ O ₁₀	35.22	1.72	23.96	35.55	2.13	23.87
VI	C ₁₂ H ₄ N ₈ O ₁₀	34.30	0.96	26.67	34.16	0.83	26.92
IX	C ₁₂ H ₆ N ₆ O ₁₀	36.56	1.53	21.32	36.78	1.48	21.26
XII·H ₂ O	C ₆ H ₅ N ₅ O ₅	31.73	2.22	30.83	31.87	2.31	30.75
XIII	C ₁₂ H ₄ N ₈ O ₁₀	34.30	0.96	26.67	34.41	1.22	26.45
XV	C ₁₂ H ₈ N ₆ O ₈	39.57	2.21	23.07	39.53	1.92	22.93
XVI	C ₁₂ H ₅ N ₇ O ₈	38.41	1.34	26.13	38.69	0.86	26.23
XVIII	C ₁₃ H ₆ N ₈ O ₁₁	34.68	1.34	24.89	34.82	1.33	25.12
I-PkOH	C ₁₂ H ₇ N ₆ O ₇	41.51	2.03	24.20	41.43	2.18	24.12



of the picryl group in the 1-position of XIX deshields the C-4 proton by 0.45 ppm, but it has only a small effect on the C-7 proton (0.10 ppm). Conversely, introduction of the picryl group in the 3-position of XIX deshields the C-4 proton by 0.21 ppm, and the C-7 proton by 0.56 ppm. A similar trend is observed for the introduction of a picryl group to the 1- and 3-positions of VII and XII. A reasonable explanation for these observations is that the picrylation for the 1(3)-position localizes the 2,3(1,2) π bond and that the resultant anisotropic effect of the localized π bond significantly deshields the proton closest to it. The less significant deshielding of the other benzotriazole protons may be caused by the strong electron-withdrawing effect of the picryl group.

Caution! Most of the compounds prepared in this study are explosives with impact sensitivities comparable to that of RDX.

Condensation of the Benzotriazoles and Amines with Picryl Halides.

The appropriate quantities of the reactants and solvent indicated in Table II were mixed and allowed to react under the conditions given in the table. The resulting mixtures were diluted with approximately ten times their volumes of water to precipitate the products, which were collected by filtration, washed with water, dried and recrystallized from the indicated solvents. The yields and melting points or explosion temperatures of the purified products are given in Table II and the elemental analyses of the new compounds prepared in this study are given in Table III. When a mixture of products was formed the composition for the crude product was determined by nmr spectroscopy and is reported in footnotes to Table II.

5,7-Dinitro-1-picrylbenzotriazole (III).

1-Picrylbenzotriazole (II) (3.3 g., 0.01 mole) was added to a mixture of fuming nitric acid (90% nitric acid) (25 ml.) and concentrated sulfuric acid (25 ml.) at 5-10°. The resulting solution was heated under reflux for 2 hours, cooled to 25°, and poured over crushed ice (~ 500 g.). The precipitated solid was collected by filtration, washed with water, and recrystallized from acetone-ethanol to give 3.06 g. (73%) of III, m.p. 263°.

4,6-Dinitro-1-picrylbenzotriazole (VI).

2,4-Dinitro-6-picrylaminoaniline (V) (2.0 g., 0.0049 mole) was dissolved in concentrated sulfuric acid (100 ml.). The solution was cooled to 5° with an ice bath and was treated dropwise with a 10% aqueous solution of sodium nitrite (20 ml.) while the temperature was kept below 15°. The resulting solution was stirred at 25° for one hour, then it was poured over crushed ice (~ 500 g.). The solid was collected by filtration, washed with water, and recrystallized from acetone-ethanol to yield 1.3 g. (63%) of VI, m.p. 309° dec., which was identical in all respects with the product obtained from the reaction of 4,6-dinitrobenzotriazole (VII) with picryl fluoride (see Table IV).

5,6-Dinitrobenzotriazole (XII).

A slurry of 4,5-dinitro-*o*-phenylenediamine (XI) (5) (7.0 g., 0.035 mole) in 300 ml. of concentrated hydrochloric acid was treated dropwise with 90 ml. of a 10% aqueous solution of sodium nitrite at 5-10°. After the resulting mixture had stirred at 25° for one hour it was chilled to 0° and the product was removed by filtration, washed with water, and air-dried to provide 6.6 g. (83%) of analytically pure crystals of the monohydrate of XII, m.p. 144°. Anhydrous XII was obtained when the monohydrate was dried in an oven at 80° overnight.

6-Nitro-1-picrylbenzotriazole (XVI).

4-Nitro-2-picrylaminoaniline (XV) (2.0 g., 0.0055 mole) was dissolved in concentrated sulfuric acid (40 ml.). The solution was cautiously diluted with 20 ml. of water with ice cooling, then 14 ml. of a 10% aqueous solution of sodium nitrite was added dropwise at 5-10°. The resulting mixture was allowed to stir at 25° for one hour, then the product was removed by filtration, washed with water, and recrystallized from acetone-ethanol to yield 1.76 g. (85%) of XVI, m.p. 270° dec.

Nitration of 6-Nitro-1-picrylbenzotriazole (XVI).

(a) A solution of XVI (5.0 g., 0.013 mole) in 50 ml. of fuming nitric acid (90% nitric acid) was heated under reflux for 24

hours, cooled to 25°, and poured over crushed ice (~ 500 g.). The precipitated solid was collected by filtration, washed with water, and recrystallized from acetone-ethanol to give 2.45 g. (45%) of 5,6-dinitro-1-picrylbenzotriazole (XIII), m.p. 226° dec., identical in all respects with the product of the reaction of 5,6-dinitrobenzotriazole (XII) with picryl fluoride (see Table IV).

(b) To a mixture of fuming nitric acid (90% nitric acid) (10 ml.) and concentrated sulfuric acid (10 ml.) was added XVI (1.0 g., 0.0026 mole) at 25°. The solution was refluxed for one hour, cooled at 25°, and poured over crushed ice (~ 200 g.). The solid was removed by filtration, washed with ice water, and dried to yield impure 1-picryl-5,6,7-trinitrobenzotriazole (XVII), which was immediately dissolved in the minimum amount of boiling methanol. The solution was concentrated until crystallization began to occur and was chilled in the freezer. The crystals were collected, washed with a little methanol, and dried to provide 0.57 g. (49%) of 5,7-dinitro-6-methoxy-1-picrylbenzotriazole (XVIII), m.p. 228° dec.

Picrate of Benzotriazole.

Benzotriazole (I) (0.6 g., 0.005 mole) and picric acid (1.15 g., 0.005 mole) were dissolved in ethanol (30 ml.) with heating. The clear solution was diluted with water (30 ml.) and chilled in the freezer. The crystals of the picrate of I were collected and dried to give 1.60 g. (91%), m.p. 175°. The product was identical in all respects with the by-product of the reaction of I with picryl chloride (2).

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REFERENCES

- (1) This work was performed under the auspices of the U.S. Atomic Energy Commission.
- (2) M. Kamel, M. I. Ali and M. M. Kamel, *Tetrahedron*, **23**, 2863 (1967).
- (3) L. Horner, U. Schwenk and E. Junghanns, *Ann. Chem.*, **579**, 212 (1953).
- (4) R. Nietzki and H. Hagenbach, *Ber.*, **30**, 543 (1897).
- (5) G. W. H. Cheeseman, *J. Chem. Soc.*, 1170 (1962).
- (6) T. Zincke, *Ann. Chem.*, **311**, 290 (1960).
- (7) Elemental analyses by M. J. Naranjo. All melting points are corrected.