

TABLE I
NMR Spectra of 1,2,3-Triazoles (a)

Compound	Ar-H ()	Het-H ()
1 <i>H</i> -1,2,3-Triazole		2.09 (s)
4-Nitro-1 <i>H</i> -1,2,3-triazole (IX)		0.95 (s)
1-Picryl-1 <i>H</i> -1,2,3-triazole (I)	0.65 (s)	1.20 (d) 1.93 (d) $J_{4,5} = 1.2$ Hz
2-Picryl-2 <i>H</i> -1,2,3-triazole (II)	0.62 (s)	1.56 (s)
2-Picryl-4-nitro-2 <i>H</i> -1,2,3-triazole (III)	0.50 (s)	0.68 (s)
1-Picryl-4-nitro-1 <i>H</i> -1,2,3-triazole (X)	0.74 (s)	-0.05 (s)
1-(3,5-Dinitrophenyl)-4-nitro-1 <i>H</i> -1,2,3-triazole (XII)	0.79 (d) 1.07 (t) $J_{2,4} = 2.0$ Hz	-0.37 (s)
4-(4-Nitrophenyl)-1 <i>H</i> -1,2,3-triazole (VII)	1.78 (q)	1.40 (s)
4-(2,4-Dinitrophenyl)-1 <i>H</i> -1,2,3-triazole (VIII)	1.25 (d) 1.48 (q) 1.83 (d) $J_{3,5} = 2.5$ Hz $J_{5,6} = 8.5$ Hz	1.57 (s)
1-(3-Nitrophenyl)-4-nitro-1 <i>H</i> -1,2,3-triazole (XIII)	1.63 (m)	-0.25 (s)
1-(3,4-Dinitrophenyl)-4-nitro-1 <i>H</i> -1,2,3-triazole (XV)	1.24 (m)	-0.35 (s)
1-(4-Nitrophenyl)-4-nitro-1 <i>H</i> -1,2,3-triazole (XIV)	1.58 (m)	-0.22 (s)

(a) The spectra were run on a Varian A-60A spectrometer as DMSO solutions with TMS as an internal standard.

TABLE II
Physical Properties of 1,2,3-Triazoles

Compound	Melting Point (°C)	Thermal Stability (°C) (a)	Crystal Density (g/cc) (b)	Impact Sensitivity (cm) (c)
1-Picryl-1 <i>H</i> -1,2,3-triazole (I)	224 dec	150	1.70	11
2-Picryl-2 <i>H</i> -1,2,3-triazole (II)	211-212	335	1.69	200
1-Picryl-4-nitro-1 <i>H</i> -1,2,3-triazole (X)	233 explodes	165 (d)	1.85	9
2-Picryl-4-nitro-2 <i>H</i> -1,2,3-triazole (III)	165-166	235	1.75	67
1-(3,5-Dinitrophenyl)-4-nitro-1 <i>H</i> -1,2,3-triazole (XII)	194	210	1.74	56
1-(3,4-Dinitrophenyl)-4-nitro-1 <i>H</i> -1,2,3-triazole (XV)	160	210	1.73	51
4-Nitro-1 <i>H</i> -1,2,3-triazole (IX)	158-159	158	1.72	25

(a) Temperature of the beginning of the first exotherm in differential thermal analysis at 10° per minute. (b) Obtained by M. Clancy by the sink-float method. (c) Determined with the LASL Type 12 machine (2.5 kg. weight, sample on sandpaper) by C. E. Hannaford and F. M. Muse. The 50% points of several common explosives are: PETN, 11 cm; RDX, 23 cm; TNT, 160 cm. (d) At 5° per minute.

The nitration of 4-phenyl-1*H*-1,2,3-triazole (VI) gave 4-(2,4-dinitrophenyl)-1*H*-1,2,3-triazole (VIII). Although a variety of nitration conditions failed to generate the target compound, 4-picryl-1*H*-1,2,3-triazole, these experiments do establish, for the first time, that in the presence of mixed

acids the *C*-triazolyl moiety activates the phenyl ring towards electrophilic substitution in the *ortho-para* positions.

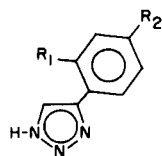
The stages of successive substitution of VI were well defined and could be readily monitored by controlling the temperature of the nitrating medium. Nitration of VI with

TABLE III
Condensations of 1,2,3-Triazole

Solvent	Pk-X	Yield of Product (s) (%)	1-Picryltriazole (%)	2-Picryltriazole (%)
Dioxane	Cl	90	100	0
DMF	Cl	85	100	0
DMSO	Cl	89	100	0
Dioxane	F	94	100	0
DMF	F	96	100	0
DMSO (a)	F	94	56	44
DMSO (b)	F	96	22	78
Dioxane	NO ₂	94	100	0
DMF	NO ₂	67	100	0
DMSO	NO ₂	58	100	0

(a) Picryl fluoride added to a solution of 1,2,3-triazole and DMSO after a few hours. (b) 1,2,3-Triazole added to a solution of picryl fluoride and DMSO.

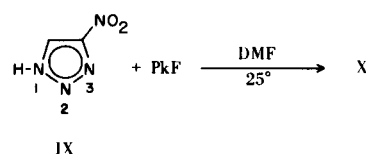
mixed acids at 0°, for example, led to the formation of 4-(4-nitrophenyl)-1*H*-1,2,3-triazole (VII), a compound that Harvey (4) has recently prepared by solvolizing the adduct obtained from tosyl azide and *p*-nitrophenacylmethylene-triphenylphosphorane. At 80° either VI or VII could be transformed into 4-(2,4-dinitrophenyl)-1*H*-1,2,3-triazole (VIII). That this nitrated triazole was indeed VIII was demonstrated unambiguously by the intermediacy of VII



VI, R₁ = R₂ = H
VII, R₁ = H, R₂ = NO₂
VIII, R₁ = R₂ = NO₂

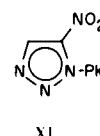
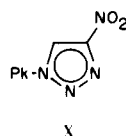
in the VI→VII→VIII conversion and by its nmr spectral properties (see Table I). On treatment with a mixture of sodium nitrate and fuming sulfuric acid at 120°, VIII was partially degraded to water-soluble products.

While attempts to nitrate 1-picryl-1*H*-1,2,3-triazole (I) and 1-(4-nitrophenyl)-4-nitro-1*H*-1,2,3-triazole to 1-picryl-4-nitro-1*H*-1,2,3-triazole (X) failed, the condensation of 4-nitro-1*H*-1,2,3-triazole (IX) and picryl fluoride in DMF at room temperature gave this compound. Kahn and Lynch (10) have used a similar approach in preparing several *N*-

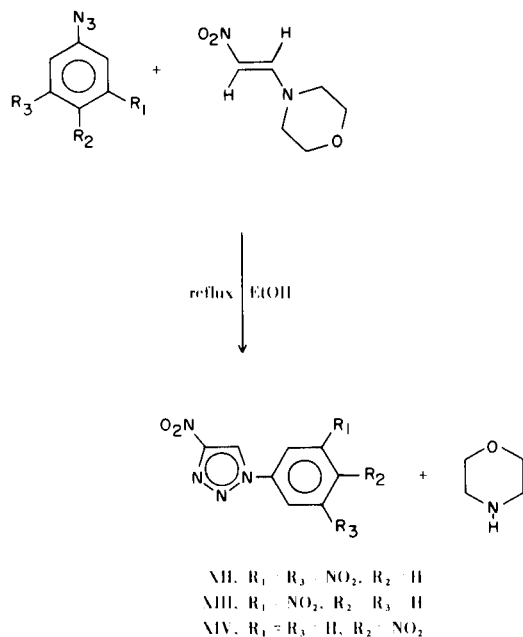


(2,4-dinitrophenyl)nitroazoles which cannot be obtained by direct nitration of corresponding *N*-phenylazoles.

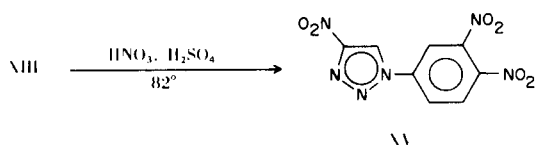
The steric requirements of the attacking nucleophile (IX) coupled with the spectral properties of the condensation product were used in establishing X as the correct structure. Since the steric effect of the 4-nitro group (IX) does not extend to the 1-position, nucleophilic displacements effected by this site are more likely to occur than displacements effected by the 3-position. Examination of the nmr spectra of model compounds (see Table I) supports this argument. A comparison of the triazolyl C-H proton signals of triazole and of I reveals that the picryl group deshields the 4- and the 5-positions 0.16 and 0.89 ppm respectively. Although the shielding effects of any functional group are not strictly additive, we can predict, nevertheless, that terminal *N*-picrylation of IX should shift the triazolyl proton from τ 0.95 to approximately τ 0.06 and 0.79 for X and XI respectively. The condensation product registered a one-proton singlet at τ -0.05, which shows close correspondence to the calculated chemical shift of X.



The recent work of Pocar (5) provided us with a novel method for the preparation of some unusually substituted nitrophenyltriazoles. These investigators found that the 1,3-dipolar addition of aryl azides to 1-morpholino-2-nitroethene furnished 1-aryl-4-nitro-1*H*-1,2,3-triazoles in good yields. In a similar fashion this enamine and 3,5-dinitrophenyl azide led to the formation of 1-(3,5-dinitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XII). An attempt to nitrate XII with mixed acids was unsuccessful.



With 3-nitrophenyl azide as the dipolar species, we obtained the corresponding 1-(3-nitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XIII). On treatment with mixed acids XIII was converted to 1-(3,4-dinitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XV). The structure of the nitration product was



assigned on the basis of the following experimental evidence.

In similarly substituted nitrophenylpyrazoles, Finar and Hurlock (6) have found that nitration of 1-(3-nitrophenyl)- and 1-(3-nitrophenyl)-4-nitropyrazole with mixed acids at 100° gives 1-(3,4-dinitrophenyl)-4-nitropyrazole.

On examining spectra (see Table I) of compounds with the skeletal structure of 1-phenyl-4-nitro-1*H*-1,2,3-triazole, we find the triazolyl proton of X (τ -0.05) at a higher field

than the corresponding proton of nitrated XIII (τ -0.35) and of XII, XIII, and XIV (τ -0.22 to -0.37), although the picryl group is the more electronegative substituent. Lynch (7) has observed a similar diamagnetic shielding mechanism operating in other phenyl heterocycles and attributes the increased shielding to the introduction of *ortho*-nitro groups that lead to large deviations from coplanarity, "with consequent reduction of inter-ring paramagnetic effects" (7b). We must conclude, therefore, that substitution of the phenyl ring most likely occurred at a position other than *ortho* to the triazolyl group.

To confirm our structural assignment, we attempted to prepare XV by Pocar's method using 3,4-dinitrophenyl azide as the dipolar species; however, the azide was unfortunately labile under the conditions normally employed to effect addition.

EXPERIMENTAL (8)

Caution! These compounds are sensitive explosives. It is imperative that the utmost care be exercised in their preparation and final utilization. See Table II for further details.

Many of the compounds are thermally unstable below their melting points; therefore, capillaries were inserted in the block approximately 10° below the melting point of the compound of interest. The melting points are corrected, and heating rates of 1° per minute were used.

1-Picryl-1*H*-1,2,3-triazole (I).

A solution of 4.20 g. of 1*H*-1,2,3-triazole, 13.40 g. of picryl fluoride, and 100 ml. of dry DMF, protected from atmospheric moisture, was stirred at room temperature for 3 days. This solution was then poured with stirring into 2 l. of water. The precipitated product was collected by filtration, washed with water, and dried. The product was then dissolved in a minimal amount of acetone (about 400 ml.), and to this stirred solution was added 1.5 l. of water, dropwise at first, until crystallization was induced, at which time the flow was increased to a slow, steady stream. The precipitated product was again collected by filtration, washed with water, and dried to give 14.6 g. (90%) of white crystals, m.p. 224° dec. [lit. (2) m.p. 230°].

Anal. Calcd. for $\text{C}_8\text{H}_4\text{N}_6\text{O}_6$: C, 34.30; H, 1.44; N, 30.00. Found: C, 34.20; H, 1.47; N, 30.16.

2-Picryl-2*H*-1,2,3-triazole (II).

To a solution of 3.35 g. of picryl fluoride, 2.20 ml. of triethylamine, and 40 ml. of dry DMSO was added 1.00 g. of 1*H*-1,2,3-triazole in one portion. The resulting solution was allowed to stir for 1 hour at room temperature protected from atmospheric moisture. This solution was then poured into 800 ml. of water, and the product was collected by filtration, washed with water, and dried. The product mixture was recrystallized from ethanol-acetone, collected by filtration, washed with small portions of cold ethanol, and dried to give 1.50 g. (37%) of small white needles, m.p. 211-212°.

Anal. Calcd. for $\text{C}_8\text{H}_4\text{N}_6\text{O}_6$: C, 34.30; H, 1.44; N, 30.00. Found: C, 34.12; H, 1.40; N, 30.31.

Condensation of 1*H*-1,2,3-Triazole with Various Picrylating Agents.

The following procedure was used in studying the condensation

of 1*H*-1,2,3-triazole with picryl fluoride, picryl chloride, and 1,2,3,5-tetranitrobenzene in dioxane, DMF, and DMSO.

A solution of 3.6 mmoles of picrylating agent, 7.2 mmoles of 1*H*-1,2,3-triazole, and 15 ml. of solvent was stirred at room temperature under a dry atmosphere for from 3 to 48 hours depending on the agent being used. The solution was then poured into 200 ml. of water. The product mixture was collected by filtration, washed thoroughly with water, and dried under vacuum. DMSO solutions of the unrecrystallized material were then analyzed by nmr spectroscopy. These analyses are compiled in Table III.

2-Picryl-4-nitro-2*H*-1,2,3-triazole (III).

Method A.

A solution of 1.00 g. of 2-picryl-2*H*-1,2,3-triazole, 10 ml. of 96% sulfuric acid, and 20 ml. of 100% nitric acid was stirred at 85° for 1 hour. This solution was then poured over crushed ice, and the product was collected by filtration, washed with water, and dried. The product was recrystallized twice from ethanol-acetone to give 0.96 g. (83%) of white crystals, m.p. 165-166°.

Anal. Calcd. for C₈H₃N₇O₈: C, 29.55; H, 0.93; N, 30.16. Found: C, 29.33; H, 0.96; N, 30.09.

Method B.

To a solution of 6.81 g. of 2-(2,4-dinitrophenyl)-4-nitro-2*H*-1,2,3-triazole and 75 ml. of 30% fuming sulfuric acid was added 20 g. of sodium nitrate portionwise with stirring. The resulting solution was heated at 145° for 16 hours. Once the solution had cooled to room temperature, it was poured over an excess of crushed ice. The crude product was then collected by filtration, washed with water, and dried. Recrystallization of this substance from absolute ethanol gave 2.82 g. (36%) of white crystals, m.p. 167-168°.

The infrared spectra of III prepared by Methods A and B were identical.

4-(4-Nitrophenyl)-1*H*-1,2,3-triazole (VII).

To a stirred solution of 20 ml. of 96% sulfuric acid and 20 ml. of 100% nitric acid at 0° was added 2.00 g. of 4-phenyl-1*H*-1,2,3-triazole portionwise at such a rate that the temperature never exceeded 5°. On completion of the addition the resulting solution was allowed to stir for 1 hour at 0° before it was poured over crushed ice. The crude product was collected by filtration, washed with water, dried, and recrystallized from absolute ethanol to give 1.30 g. (50%) of white needles, m.p. 197-198° [lit. (4) m.p. 198-199°].

Anal. Calcd. for C₈H₆N₄O₂: C, 50.53; H, 3.18; N, 29.46. Found: C, 50.53; H, 3.32; N, 29.65.

4-(2,4-Dinitrophenyl)-1*H*-1,2,3-triazole (VIII).

Method A.

A solution of 1.00 g. of 4-phenyl-1*H*-1,2,3-triazole, 10 ml. of 100% nitric acid, and 10 ml. of 96% sulfuric acid was refluxed for 20 hours at 90°. This solution was then poured over crushed ice and collected by filtration, and the precipitate was recrystallized from ethanol-water to give 0.57 g. (35%) of pinkish rods, m.p. 181-182°.

Anal. Calcd. for C₈H₅N₅O₄: C, 40.86; H, 2.14; N, 29.78. Found: C, 40.55; H, 2.15; N, 29.61.

Method B.

To a cooled, stirred solution of 15 ml. of 100% nitric acid and 15 ml. of 96% sulfuric acid was added 1.00 g. of 4-(4-nitrophenyl)-1*H*-1,2,3-triazole portionwise. The resulting solution was then heated at 86° for 3 hours, allowed to cool to room temperature,

and poured over crushed ice. The crude product was isolated as before and recrystallized from ethanol-water to give 0.49 g. (40%) of pinkish needles, m.p. 176-177°.

The infrared spectra of VIII prepared by Methods A and B were identical.

1-Picryl-4-nitro-1*H*-1,2,3-triazole (X).

A solution of 8.12 g. of picryl fluoride, 4.00 g. of 4-nitro-1*H*-1,2,3-triazole, and 100 ml. of dry DMF was stirred at room temperature under a dry atmosphere for 24 hours. The solution was poured with stirring into 1 l. of water. The crude product was collected by filtration, washed thoroughly with several portions of water, and dried. This product was dissolved in a minimal amount of hot methyl ethyl ketone. The solution was chilled, and the material that crystallized was collected by filtration and washed with cold ether to give 3.28 g. of product, m.p. 233° (explodes).

The volume of the mother liquor was reduced until crystallization was induced, and a second crop of 1.97 g. was isolated, m.p. 233° (explodes). The total yield was 5.25 g. (46%).

Anal. Calcd. for C₈H₃N₇O₈: C, 29.55; H, 0.93; N, 30.16. Found: C, 29.32; H, 0.64; N, 30.04.

1-Morpholino-2-nitroethene.

This preparation gives better yields than Hurd and Sherwood's method (9).

To a stirred solution of 54.0 g. of ethyl ethoxymethylenemalonate and 30.5 g. of nitromethane was added 43.5 g. of morpholine in one portion. The morpholine initiates the reaction, which becomes exothermic at first. In a few minutes the product usually begins to crystallize from solution.

After 2 hours the product was collected by filtration and washed with cold ether to give 16.3 g. of a granular yellow product. A second crop was obtained by slowly adding cold ether to the filtrate with stirring. This product was isolated as previously described to give an additional 3.7 g. of small yellow-orange needles.

The crops were combined and recrystallized from absolute ethanol to give 19.5 g. of large yellow crystals, m.p. 140-141° [lit. (9) m.p. 140-141°].

4-Nitro-1*H*-1,2,3-triazole (IX).

The following procedure is an improvement over Pocar's method (5).

A solution of 28.0 g. of 1-morpholino-2-nitroethene, 35.0 g. of tosyl azide, and 400 ml. of absolute ethanol was refluxed for 48 hours. When this solution was chilled, 20-25 g. of tosyl morpholide crystallized and was collected by filtration. Evaporation of the solvent under reduced pressure left a tarry, oily residue. To this residue was added 100 ml. of chloroform, and the resulting combination was swirled until the crystalline nitrotriazole was liberated from the oily residue. Washing the filtered triazole thoroughly with chloroform usually furnished 12.4 g. (60%) of white crystals, m.p. 158-159° [lit. (5) m.p. 161-162°].

1-(3,5-Dinitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XII).

A solution of 6.60 g. of 3,5-dinitrophenyl azide, 5.00 g. of 1-morpholino-2-nitroethene, and 150 ml. of absolute ethanol was refluxed in the absence of light for 7 days. The solution was chilled and collected by filtration. The crude product was dissolved in boiling ethanol-acetone and treated with charcoal. The volume of the solvent was reduced, and the resulting solution was chilled to give 2.70 g. (30%) of white crystals, m.p. 194°.

Anal. Calcd. for C₈H₄N₆O₆: C, 34.30; H, 1.44; N, 30.00. Found: C, 34.10; H, 1.18; N, 30.20.

1-(3-Nitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XIII).

A solution of 8.20 g. of 3-nitrophenyl azide, 7.90 g. of 1-morpholino-2-nitroethene, and 100 ml. of absolute ethanol was refluxed for 4 days in the dark. When the solution cooled, the product crystallized and was collected by filtration. Recrystallization of this triazole from ethanol-acetone gave 6.56 g. (56%) of tan crystals, m.p. 168-169°.

Anal. Calcd. for $C_8H_5N_5O_4$: C, 40.86; H, 2.14; N, 29.78. Found: C, 40.89; H, 2.23; N, 29.85.

1-(3,4-Dinitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XV).

To a solution of 2.50 g. of 1-(3-nitrophenyl)-4-nitro-1*H*-1,2,3-triazole and 10 ml. of 96% sulfuric acid was added 15 ml. of 100% nitric acid with stirring and cooling. The resulting solution was heated at 82° for 1.5 hours and poured over crushed ice. The crude product was isolated as before and recrystallized from ethanol-acetone to give 2.07 g. (70%) of pale tan needles, m.p. 160°.

Anal. Calcd. for $C_8H_4N_6O_6$: C, 34.30; H, 1.44; N, 30.00. Found: C, 34.15; H, 1.31; N, 30.04.

1-(4-Nitrophenyl)-4-nitro-1*H*-1,2,3-triazole (XIV).

This compound was prepared by Pocar's method (5).

Acknowledgment.

The author wishes to thank Professor G. J. Fonken for his advice and for reading the manuscript.

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