Picrylamino-substituted Heterocycles. III. 1,2,4-Triazoles (1,2)

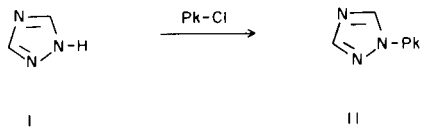
Michael D. Coburn and Thomas E. Jackson (3)

University of California, Los Alamos Scientific Laboratory

This paper describes the synthesis of various picryl- and picrylamino-substituted 1,2,4-triazoles and 3,3′-bi-1,2,4-triazolyls. These compounds were prepared by condensing the appropriate 1,2,4-triazole or amino-1,2,4-triazole with a picryl halide. The proton n.m.r. spectra, crystal densities, thermal stabilities, and drop-weight impact sensitivities of the resulting compounds were determined.

The picryl- and picrylamino-substituted 1,2,4-triazoles and 3,3′-bi-1,2,4-triazolyls have been prepared and evaluated as potential high explosives as part of our continuing effort in the field of picrylamino-substituted heterocycles. The n.m.r. spectra of these compounds were determined as dimethylsulfoxide solutions; the chemical shifts are expressed in δ units.

Condensation of 1,2,4-triazole (I) with picryl chloride gave 1-picryl-1,2,4-triazole (II). The n.m.r. spectrum of II consists of two equivalent singlets corresponding to the C-3 proton (8.42 δ) and the C-5 proton (9.20 δ) of the



I II

Pk = Picryl

triazole ring, followed by a singlet corresponding to the two picryl protons (9.33 δ). The chemical shifts of the C-3 and C-5 protons of 1-acetyl-1,2,4-triazole (4) in dimethylsulfoxide are 8.28 δ and 9.29 δ, respectively. Thus it appears that the picryl group and the acetyl group have nearly the same deshielding effect (5) on the C-5 proton of the triazole ring.

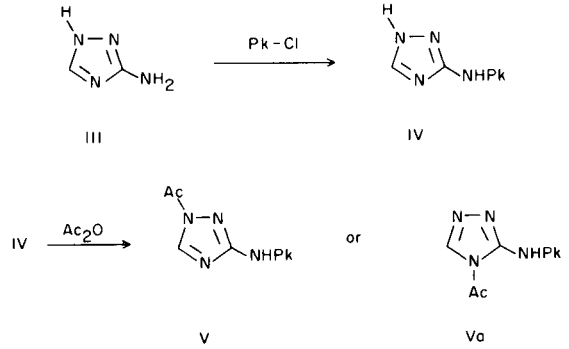
The reaction of 3-amino-1,2,4-triazole (III) with picryl chloride afforded 3-picrylamino-1,2,4-triazole (IV) rather than an *N*-picryl-3-amino-1,2,4-triazole. Treatment of IV with acetic anhydride provided an acetyl derivative which contains a carbonyl band at 1753 cm^{-1} in its infrared spectrum. Considering the carbonyl absorption frequencies of the acetyl derivatives of 3-amino-1,2,4-triazole given in Table I, it appears evident that the acetyl group is on one of the triazole ring nitrogens rather than the 3-amino group. Furthermore, the n.m.r. chemical shift of the triazole C-5 proton of the acetyl derivative is 9.18 δ, which clearly indicates that this proton is deshielded. Therefore, the acetyl derivative of IV is either 1-acetyl-3-picrylamino-1,2,4-triazole (V) or 4-acetyl-3-picrylamino-1,2,4-triazole (Va). This conclusion is supported by the fact that the

TABLE I

Carbonyl Absorption Frequencies (a)

1,2,4-Triazole	*N*-Acetyl (cm^{-1})	3-Acetylamino (cm^{-1})
1-Acetyl-	1765	
2-Acetyl-3-amino	1732	
3-Acetylamino		1689
1(4)-Acetyl-3-acetylamino-	1745	1689
1(4)-Acetyl-3-picrylamino-	1753	

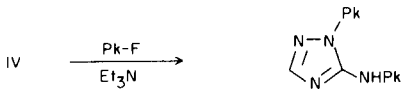
(a) The values presented in this table (except the last one) were taken from K. T. Potts, *Chem. Revs.*, 61, 87 (1961).



chemical shift of the C-5 proton of 1(4)-acetyl-3-acetylamino-1,2,4-triazole (6) is 9.12 δ, while those of 2-acetyl-3-amino-1,2,4-triazole (6) and 3-acetylamino-1,2,4-triazole

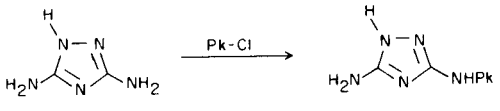
(6) are 7.60 δ and 7.84 δ, respectively. The chemical shift of the picryl protons of IV is 8.98 δ and that of V is 9.04 δ.

When IV was heated with picryl fluoride in the presence of triethylamine, an *N*-picryl-3-picrylamino-1,2,4-triazole was obtained. The chemical shift of the triazole C-5 proton of the product is 8.50 δ; thus, the C-5 proton is not deshielded and the compound appears to be 2-picryl-3-picrylamino-1,2,4-triazole (VI). The chemical shift of the aryl protons of the 3-picrylamino group is 8.95 δ and that of the 2-picryl protons is 9.23 δ.

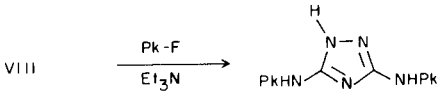


VI

3,5-Diamino-1,2,4-triazole (VII) condensed with one molecule of picryl chloride to give 3-amino-5-picrylamino-1,2,4-triazole (VIII), which, when heated with picryl fluoride in the presence of triethylamine, was converted to 3,5-bis(picrylamino)-1,2,4-triazole (IX). The chemical



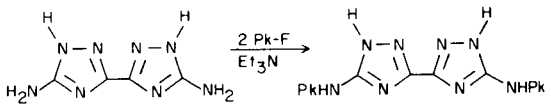
VII VIII



IX

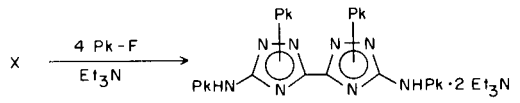
shift of the picryl protons is 8.91 δ for VIII and 8.99 δ for IX. When IX was heated with picryl fluoride in the presence of triethylamine, only unreacted IX and a considerable amount of black tar was recovered.

Treatment of 5,5′-diamino-3,3′-bi-1,2,4-triazolyl (7) (X) with two molar equivalents of picryl fluoride in the presence of triethylamine produced 5,5′-bis(picrylamino)-3,3′-bi-1,2,4-triazolyl (XI). The chemical shift of the aryl protons of the two equivalent picrylamino groups is 9.01 δ.

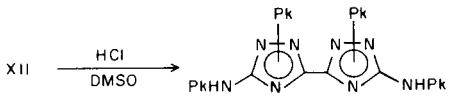


X XI

When X was treated with four molar equivalents of picryl fluoride in the presence of an excess of triethylamine, *N*,*N*′-dipicryl-5,5′-bis(picrylamino)-3,3′-bi-1,2,4-triazolyl (XIII) was isolated as a stable complex with two molecules of triethylamine (XII). Free XIII was liberated by treating a dimethylsulfoxide solution of XII with an excess of hydrochloric acid.



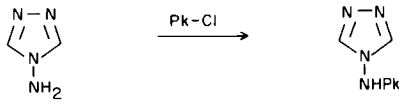
XII



XIII

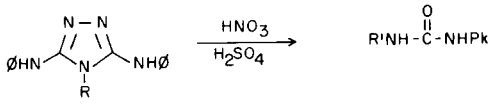
The chemical shift of the aryl protons of the two picrylamino groups of XIII was observed at 8.79 δ and an equivalent peak, corresponding to the protons of the two *N*-picryl groups, was observed at 9.25 δ.

4-Picrylamino-1,2,4-triazole (XV) was obtained from the reaction of 4-amino-1,2,4-triazole (XIV) with picryl chloride. The n.m.r. spectrum of XV contained two equivalent peaks corresponding to the two picryl protons (9.30 δ) and the C-3 and C-5 triazole protons (8.77 δ).



XIV XV

During the course of this work we tried to prepare IX by nitrating 3,5-dianilino-1,2,4-triazole (8) (XVI). This experiment resulted in the oxidative cleavage of the triazole ring to give picrylurea (XVII). Similarly, *s*-dipicrylurea (XIX) was obtained by nitrating 3,5-dianilino-4-phenyl-1,2,4-triazole (9) (XVIII).



XVI (R = H) XVII (R' = H)

XVIII (R = Ø) XIX (R' = Pk)

Some of the physical and explosive properties of the picryl- and picrylamino-substituted 1,2,4-triazoles are given in Table II, and their n.m.r. chemical shifts are summarized

TABLE II

Physical and Explosive Properties of the Picryl- and Picrylamino-substituted 1,2,4-Triazoles

Compound	m.p. (dec.)	Thermal Stability (a)	Crystal Density (g./ml.)	Impact Sensitivity (b)
1-Picryl-1,2,4-triazole	228°	220°	1.70	> 320 cm.
3-Picrylamino-1,2,4-triazole	310°	300°	1.94	> 320 cm.
2-Picryl-3-picrylamino-1,2,4-triazole	260°	150°	1.80	> 320 cm.
3-Amino-5-picrylamino-1,2,4-triazole	275°	270°	1.85	230 cm.
3,5-bis(Picrylamino)-1,2,4-triazole	272°	270°	1.81	240 cm.
4-Picrylamino-1,2,4-triazole	225°	220°	1.78	314 cm.
5,5′-bis(Picrylamino)-3,3′-bi-1,2,4-triazolyl	---	340°	1.80	> 320 cm.
N,N′-Dipicryl-5,5′-bis(picrylamino)-3,3′-bi-1,2,4-triazolyl	---	150°	1.83	---

(a) Temperature of the beginning of the first exotherm in differential thermal analysis at 10°/min. (b) Determined with the LASL Type 12 machine (2.5 kg. weight, sample on sandpaper). The 50% points of several common explosives are: PETN, 11 cm.; RDX, 23 cm.; TNT, 160 cm.

TABLE III

N.M.R. Data for the Picryl- and Picrylamino-substituted 1,2,4-Triazoles (a)

Compound	δ C-H (p.p.m.) Picrylamino	*N*-Picryl	Triazole
1-Picryl-1,2,4-triazole		9.33	8.42, 9.20
3-Picrylamino-1,2,4-triazole	8.98		8.36
1(4)-Acetyl-3-picrylamino-1,2,4-triazole	9.04		9.18
2-Picryl-3-picrylamino-1,2,4-triazole	8.95	9.23	8.50
3-Amino-5-picrylamino-1,2,4-triazole	8.91		
3,5-bis(Picrylamino)-1,2,4-triazole	8.99		
4-Picrylamino-1,2,4-triazole	9.30		8.77
5,5′-bis(Picrylamino)-3,3′-bi-1,2,4-triazolyl	9.01		
N,N′-Dipicryl-5,5′-bis(picrylamino)-3,3′-bi-1,2,4-triazolyl	8.79	9.25	

(a) Determined with a Varian A-60A spectrometer as dimethylsulfoxide solutions using tetramethylsilane as an internal standard. All of the spectra which contain more than one peak were integrated, and the ratios of the peaks were consistent with the structural assignments.

TABLE IV

Chemical Shifts of the C-3(5) Protons of the 1,2,4-Triazoles Employed as Model Compounds (a)

Compound	δC-H (p.p.m.)
1,2,4-Triazole	8.52
1-Acetyl-1,2,4-triazole	8.28, 9.29
3-Amino-1,2,4-triazole	7.71
3-Acetylamino-1,2,4-triazole	7.84
2-Acetyl-3-amino-1,2,4-triazole	7.57
1(4)-Acetyl-3-acetylamino-1,2,4-triazole	9.12
4-Amino-1,2,4-triazole	8.57
4-Acetylamino-1,2,4-triazole	8.66

(a) Determined with a Varian A-60A spectrometer as dimethylsulfoxide solutions using tetramethylsilane as an internal standard.

in Table III. Table IV contains the n.m.r. data for the 1,2,4-triazoles employed as model compounds.

EXPERIMENTAL (10)

1-Picryl-1,2,4-triazole (II).

A solution of 1,2,4-triazole (1.72 g., 0.025 mole) and picryl chloride (2.48 g., 0.01 mole) in 50 ml. of γ-butyrolactone was stirred at 25° for 16 hours. The mixture was diluted with 1 l. of water and the precipitated solid was collected by filtration and dried. The crude product was recrystallized from acetone-hexane to give 2.50 g. (88%) of 1-picryl-1,2,4-triazole, m.p. 228° dec.

Anal. Calcd. for $C_8H_4N_6O_6$: C, 34.30; H, 1.44; N, 30.00. Found: C, 34.10; H, 1.25; N, 30.06.

3-Picrylamino-1,2,4-triazole (IV).

A solution of 3-amino-1,2,4-triazole (2.10 g., 0.025 mole) and picryl chloride (2.48 g., 0.01 mole) in 50 ml. of dimethylformamide was heated at 100° for 5 hours, then poured into 400 ml. of ice and water. The crude product was collected by filtration and recrystallized from γ-butyrolactone. The product was washed repeatedly with methanol and dried to yield 2.51 g. (85%), m.p. 310° dec.

Anal. Calcd. for $C_8H_5N_7O_6$: C, 32.55; H, 1.71; N, 33.22. Found: C, 32.67; H, 1.93; N, 33.05.

1(4)-Acetyl-3-picrylamino-1,2,4-triazole (V).

3-Picrylamino-1,2,4-triazole (1.36 g., 0.0046 mole) was refluxed with 25 ml. of acetic anhydride for 1.5 hours. The resulting solution was stirred in 150 ml. of water until the excess acetic anhydride was hydrolyzed, and the solid was collected by filtration. The product was recrystallized from acetone to give 0.95 g. (60%), m.p. 215°.

Anal. Calcd. for $C_{10}H_7N_7O_7$: C, 35.62; H, 2.09; H, 29.08. Found: C, 35.56; H, 2.13; N, 28.99.

2-Picryl-3-picrylamino-1,2,4-triazole (VI).

Picryl fluoride (11) (2.31 g., 0.01 mole) was added to a solution of 3-picrylamino-1,2,4-triazole (2.95 g., 0.01 mole) and triethylamine (1.4 ml., 0.01 mole) in 50 ml. of dimethylsulfoxide. The resulting solution was heated at 70° for 5 hours, then poured into 400 ml. of ice and water. The mixture was acidified with concentrated hydrochloric acid and the solid was collected by filtration, washed with water, and dried. The material was recrystallized twice from acetone-ethanol to provide 3.78 g. (75%) of 2-picryl-3-picrylamino-1,2,4-triazole, m.p. 260° dec.

Anal. Calcd. for $C_{14}H_6N_{10}O_{12}$: C, 33.21; H, 1.19; N, 27.67. Found: C, 33.49; H, 1.41; N, 27.79.

3-Amino-5-picrylamino-1,2,4-triazole (VIII).

A solution of 3,5-diamino-1,2,4-triazole (2.48 g., 0.025 mole) and picryl chloride (2.48 g., 0.01 mole) in 50 ml. of dimethyl sulfoxide was heated at 70° for 5 hours, then poured into 400 ml. of ice and water. The crude product was collected by filtration and recrystallized from γ-butyrolactone-ethanol (treatment with Norite was necessary) to yield 1.86 g. (60%), m.p. 275° dec.

Anal. Calcd. for $C_8H_6N_8O_6$: C, 30.98; H, 1.95; N, 36.13. Found: C, 30.71; H, 1.93; N, 36.08.

3,5-bis(Picrylamino)-1,2,4-triazole (IX).

Picryl fluoride (11) (1.15 g., 0.005 mole) was added to a solution of 3-amino-5-picrylamino-1,2,4-triazole (1.55 g., 0.005 mole) and triethylamine (0.7 ml., 0.005 mole) in 50 ml. of dimethyl sulfoxide. The resulting solution was heated at 70° for 5 hours, diluted with 100 ml. of ethanol, and the crude product was precipitated by adding water. The dark solid was collected by filtration, washed first with water then with ethanol, and dried. After the product had been recrystallized twice from acetone-ethanol, it was necessary to dry it in an oven at 140° for 48 hours in order to remove the last traces of solvents. The yield of pure 3,5-bis(picrylamino)-1,2,4-triazole, m.p. 272° dec., was 0.89 g. (34%).

Anal. Calcd. for $C_{14}H_7N_{11}O_{12}$: C, 32.26; H, 1.35; N, 29.56. Found: C, 32.48; H, 1.61; N, 29.45.

5,5′-bis(Picrylamino)-3,3′-bi-1,2,4-triazolyl (XI).

5,5′-Diamino-3,3′-bi-1,2,4-triazolyl (7) (0.42 g., 0.0025 mole) was added to a stirred solution of picryl fluoride (11) (1.30 g., 0.0056 mole) and triethylamine (1.0 ml., 0.007 mole) in 50 ml. of dimethylsulfoxide. The mixture was heated at 70° for 5 hours, then poured into 400 ml. of ice and water. The mixture was acidified with concentrated hydrochloric acid and the solid was collected by filtration, washed with water, and dried. Two recrystallizations of the product from acetone gave 0.15 g. (10%) of 5,5′-bis(picrylamino)-3,3′-bi-1,2,4-triazoylyl which begins to decompose without melting at 340°.

Anal. Calcd. for $C_{16}H_8N_{14}O_{12}$: C, 32.66; H, 1.37; N, 33.33. Found: C, 32.66; H, 1.54; N, 33.57.

N,N′-Dipicryl-5,5′-bis(picrylamino)-3,3′-bi-1,2,4-triazolyl (XIII).

A mixture of 5,5′-diamino-3,3′-bi-1,2,4-triazolyl (7) (0.42 g., 0.0025 mole), picryl fluoride (11) (2.54 g., 0.011 mole), and triethylamine (3.1 ml., 0.022 mole) in 50 ml. of dimethylsulfoxide was heated at 75° for 5 hours, then poured into 250 ml. of ice and water. The precipitated solid was collected by filtration, washed with water, and recrystallized twice from acetone-ethanol to give 0.97 g. (32%) of the red triethylamine complex (XII), m.p. 260° dec.

Anal. Calcd. for $C_{40}H_{40}N_{22}O_{24}$: C, 39.61; H, 3.32; N, 25.41. Found: C, 39.36; H, 3.23; N, 25.19.

The triethylamine complex (0.97 g., 0.0008 mole) was dissolved in 50 ml. of dimethylsulfoxide to form a dark red solution.

Concentrated hydrochloric acid was added to the stirred solution until its color changed from dark red to light yellow. The solution was diluted with water to precipitate the product, which was collected by filtration, washed with water, and recrystallized from acetone-methanol to yield 0.64 g. (79%) of *N,N'*-dipicryl-5,5'-bis-(picrylamino)-3,3'-bi-1,2,4-triazolyl. The compound does not melt, but differential thermal analysis indicates that slow decomposition begins at 150°. The material gradually darkens on heating and turns completely black at about 220°.

Anal. Calcd. for $C_{28}H_{10}N_{20}O_{24}$: C, 33.28; H, 1.00; N, 27.72; O, 38.00. Found: C, 32.85; H, 1.43; N, 27.44; O, 37.91.

4-Picrylamino-1,2,4-triazole (XV).

A solution of 4-amino-1,2,4-triazole (2.12 g., 0.025 mole) and picryl chloride (2.48 g., 0.01 mole) in 50 ml. of dimethylsulfoxide was heated at 70° for 5 hours, then poured into 400 ml. of ice and water. The dark solid was collected by filtration, washed with water, and recrystallized from acetone-ethanol (treatment with Norite was necessary) to give 1.27 g. (43%) of 4-picrylamino-1,2,4-triazole, m.p. 225° dec.

Anal. Calcd. for $C_8H_5N_7O_6$: C, 32.55; H, 1.71; N, 33.22. Found: C, 32.41; H, 1.67; N, 32.99.

Model Compounds.

Commercial 1,2,4-triazole, 3-amino-1,2,4-triazole, and 4-amino-1,2,4-triazole were acetylated according to literature procedures (4, 6, 12) to give the various acetyl derivatives listed in Table IV.

Nitration of 3,5-Dianilino-1,2,4-triazole (XVI).

Concentrated nitric acid (5 ml.) was added dropwise to a solution of 3,5-dianilino-1,2,4-triazole (8) (0.10 g., 0.0004 mole) in concentrated sulfuric acid (5 ml.) at 0-10°. The resulting dark red solution was heated at 60° for 1.5 hours, then cooled to 0°. The product which crystallized from the nitrating mixture was collected by filtration, washed repeatedly with water, and dried to yield 0.09 g. (42%) of picrylurea, m.p. 200-202° dec. [lit. (13) m.p. 201-203°].

Anal. Calcd. for $C_7H_5N_5O_7$: C, 31.01; H, 1.86. Found: C, 30.84; H, 1.73.

Nitration of 3,5-Dianilino-4-phenyl-1,2,4-triazole (XVIII).

Absolute nitric acid (10 ml.) was added dropwise to a solution of 3,5-dianilino-4-phenyl-1,2,4-triazole (9) (1.0 g., 0.003 mole) in concentrated sulfuric acid (10 ml.) at 0-10°. The resulting dark red solution was heated at 70° for 1.5 hours, then cooled to 0°. The solid which crystallized from the nitrating mixture was removed by filtration, washed with water, dried, and recrystallized from acetone-benzene to give 0.46 g. (31%) of *s*-dipicrylurea, m.p. 209-210° dec. [lit. (14) m.p. 209°]. The infrared spectrum of the product is identical with that of authentic *s*-dipicrylurea (14).

Acknowledgment.

The authors are grateful to Drs. P. N. Neuman and L. C. Smith for helpful criticism of the manuscript.

REFERENCES

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) Part I, *J. Heterocyclic Chem.*, 3, 365 (1966). Part II, *ibid.*, 5, 83 (1968).

(3) Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

(4) M. R. Atkinson and J. B. Polya, *J. Chem. Soc.*, 141 (1954).

(5) K. T. Potts, and T. H. Crawford, *J. Org. Chem.*, 27, 2631 (1962).

(6) B. G. van den Bos, *Rec. Trav. Chim.*, 79, 836 (1960).

(7) R. N. Shreve and R. K. Charlesworth, U. S. Patent, 2,744,116.

(8) F. Kurzer and K. Douraghi-Zadeh, *J. Chem. Soc.*, 932 (1965).

(9) F. Kurzer and K. Douraghi-Zadeh, *ibid.*, 3912 (1965).

(10) Microanalyses by M. J. Naranjo. Crystal densities by Marion L. Clancy. Drop weight impact sensitivities by C. E. Hannaford. All melting points are corrected.

(11) G. C. Shaw and D. L. Seaton, *J. Org. Chem.*, 26, 5227 (1961).

(12) H. G. O. Becker, K. Heimburger and H. J. Timpe, *Wiss. Z. Tech. Hochsch. Chem. Leuna-Merseburg.*, 8, 118 (1966).

(13) M. Giua, *Gazz. Chim. Ital.*, 55, 665 (1925).

(14) R. T. C. Loh and W.M. Dehn, *J. Am. Chem. Soc.*, 48, 2958 (1926).

Received February 1, 1968 Los Alamos, N. M. 87544