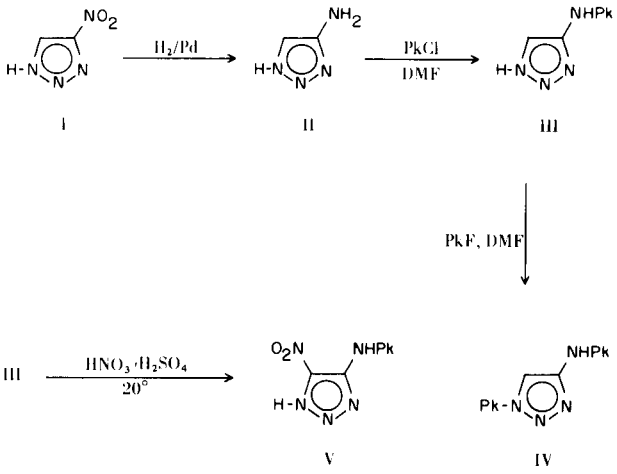
Picryl Derivatives of 4-Amino-1*H*-1,2,3-triazole (I)

Peter N. Neuman

University of California, Los Alamos Scientific Laboratory

During the course of our research, we required a readily accessible supply of 4-amino-1*H*-1,2,3-triazole (II) for its subsequent conversion to picryl-substituted explosives. In searching the available literature we found that II had been prepared by the basic hydrolysis of 8-azaguanine (2), by the thermally induced Curtius rearrangement of 1*H*-1,2,3-triazole-4-carboxylic acid azide (3), and by the sodium-liquid ammonia reduction of 5-amino-1-benzyl-1*H*-1,2,3-triazole (4); however, in these procedures, II was isolated either as an impure substance or as a derivative.

We have prepared the free amine in 92% yield by selectively hydrogenating the nitro function of 4-nitro-1*H*-1,2,3-triazole (I) (5) over 5% palladium-on-charcoal. Compound I was to a certain degree resistant to hydrogenation, and we found that a large amount of the palladium catalyst and a relatively lengthy reduction time were necessary in order to assure its complete conversion to II. In most instances the amine could be utilized directly without additional purification in ensuing synthetic applications. The condensation of II with picryl chloride, for example, furnished 4-picrylamino-1*H*-1,2,3-triazole (III) which then condensed with picryl fluoride to give 1-picryl-4-picrylamino-1*H*-1,2,3-triazole (IV). The nitration of III with mixed acids afforded 5-nitro-4-picrylamino-1*H*-1,2,3-triazole (V), a labile substance. Compound V is unstable above 75° and decomposes with the evolution of gas in many organic solvents.



Pk = 2,4,6-trinitrophenyl

Nmr spectra were also obtained for these compounds, and their chemical shifts are given in the Experimental section. An analysis of the spectra of model compounds supports IV as the structure of the second condensation product. A comparison of the chemical shifts of the triazolyl C-H proton of III and IV reveals that attachment of a picryl group onto III shifts this signal 0.86 ppm downfield in DMSO. This large downfield shift would have

TABLE I

Physical Properties of Triazolyl Explosives

Compound	Melting Point (°C)	Thermal Stability (°C)	Crystal Density (g./cc.)	Impact Sensitivity (cm.)
4-Picrylamino-1*H*-1,2,3-triazole (III)	228 (dec.)	220 (a)	1.78 (b)	103 (c)
5-Nitro-4-picrylamino-1*H*-1,2,3-triazole (V)	236 (dec.)	75	1.82	(d)
1-Picryl-4-picrylamino-1*H*-1,2,3-triazole (IV)	161-162 (dec.)	120	1.75	35

(a) Temperature of the first exotherm in differential thermal analysis at 10° per minute. (b) Obtained by M. Clancy by the sink-float procedure. (c) Performed by C. E. Hannaford with the LASL Type 12 machine (2.5 kg. weight, sample on sandpaper). The 50% points of some common explosives are: PETN, 11 cm; RDX, 23 cm; TNT, 160 cm. (d) Sensitive to a hammer blow.

been observed only if the picryl group were on the 1-position. Jacquier (6) recently observed a similar shift when he found that the picryl group of 1-picryl-1*H*-1,2,3-triazole displaced the signal arising from the adjacent proton 0.89 ppm downfield relative to 1*H*-1,2,3-triazole in DMSO.

Some physical and explosive properties of III, IV, and V are given in the Table below.

EXPERIMENTAL (7)

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

Some 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.

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

A mixture of 3.00 g. of 4-nitro-1*H*-1,2,3-triazole, 3.00 g. of 5% palladium-on-charcoal, and 150 ml. of absolute ethanol was shaken in a Paar hydrogenator under a constant pressure of 60 psi of hydrogen for 6 hours at room temperature. The catalyst was carefully removed by vacuum filtration, and the solvent was evaporated under reduced pressure, leaving an oily residue which crystallized on standing overnight. Traces of solvent were removed under vacuum to give 2.03 g. (92%) of the triazole.

This product was dissolved in absolute ether, and the solution was filtered by gravity. The filtrate was concentrated and chilled to give 1.38 g. (62%) of white crystals, m.p. 74-75°. The nmr spectrum of II showed two broad singlets centered at τ 3.67 (1H) and 5.03 (2H) and a sharp singlet at τ 2.97 (1H).

Anal. Calcd. for $C_2H_4N_4$: C, 28.57; H, 4.80; N, 66.64. Found: C, 28.66; H, 4.65; N, 66.44.

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

A solution of 1.44 g. of 4-amino-1*H*-1,2,3-triazole, 4.23 g. of picryl chloride, and 30 ml. of dry dimethylformamide was stirred at room temperature for 24 hours. The solution was then poured into 1.5 liters of water. The precipitated product was collected, washed with water, and recrystallized from acetone-water to give 4.03 g. (76%) of orange crystals, m.p. 228° dec. The nmr spectrum of III exhibited sharp singlets at τ 1.03 (2H) and 2.23 (1H) and broad singlets centered at τ -4.57 (1H) and -0.45 (1H).

Anal. Calcd. for $C_8H_5N_7O_6$: C, 32.55; H, 1.71; N, 33.22. Found: C, 32.60; H, 1.76; N, 33.01.

1-Picryl-4-picrylamino-1*H*-1,2,3-triazole (IV).

A solution of 4.03 g. of 4-picrylamino-1*H*-1,2,3-triazole, 3.16 g. of picryl fluoride, and 50 ml. of dry dimethylformamide was stirred at room temperature for 24 hours. This solution was poured into 1.5 liters of water, and to this aqueous solution was added concentrated hydrochloric acid until the product began to precipitate. This product was isolated as before and recrystallized from acetone-water to give 1.06 g. (15%) of pale yellow crystals, m.p. 161-162° dec. The nmr spectrum of IV displayed sharp singlets at τ 0.65 (2H), 0.97 (2H), and 1.37 (1H), and a broad singlet centered at τ -0.60 (1H).

Anal. Calcd. for $C_{14}H_6N_{10}O_{12}$: C, 33.21; H, 1.19; N, 27.67. Found: C, 33.66; H, 1.25; N, 27.78.

5-Nitro-4-picrylamino-1*H*-1,2,3-triazole (V).

To a stirred solution of 1.00 g. of 4-picrylamino-1*H*-1,2,3-triazole and 20 ml. of 96% sulfuric acid was added 10 ml. of 100% nitric acid portionwise, the solution being maintained at 20-25° with cooling. During the latter stages of addition, evolution of gas commences. After being stirred at 20° for 1 hour, the solution was poured over crushed ice, and the precipitate was collected, washed with water, and dried to give 0.86 g. of a yellow solid. Recrystallization of this substance from acetone-benzene gave 0.34 g. (30%) of large yellow crystals, m.p. 236° dec. The nmr spectrum of V in acetone-d_6 exhibited a sharp singlet at τ 0.74 (2H) and broad singlets centered at τ -1.66 (1H) and -1.00 (1H).

Anal. Calcd. for $C_8H_4N_8O_8$: C, 28.55; H, 1.19; N, 32.94. Found: C, 28.44; H, 1.39; N, 33.03.

REFERENCES

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

(2a) *Japan.* **10**, 468 (1959); *Chem. Abstr.*, **54**, 18555c (1960). (b) S. Yamada, T. Mizoguchi, and A. Ayata, *Yakugaku Zasshi*, **77**, 441 (1957); *Chem. Abstr.*, **51**, 12107g (1957).

(3) S. Yamada, T. Mizoguchi, and A. Ayata, *Yakugaku Zasshi*, **77**, 452 (1957); *Chem. Abstr.*, **51**, 14697 (1957).

(4) J. R. E. Hoover and A. R. Day, *J. Am. Chem. Soc.*, **78**, 5832 (1956).

(5) D. Pocar, S. Maiorana, and P. Dalla Croce, *Gazz. Chim. Ital.*, **98**, 949 (1968).

(6) J. Elguero, E. Gonzalez, and R. Jacquier, *Bull. Soc. Chim. France*, 2998 (1967).

(7) Combustion analyses were performed by M. J. Naranjo. The nmr spectra were taken on a Varian A-60A spectrometer as, unless otherwise stated, DMSO solutions using TMS as an internal standard.

Received July 6, 1970 Los Alamos, New Mexico 87544