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Treatment of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (**1**) with picryl fluoride (PkF) in 1-methyl-2-pyrrolidinone (NMP) gave a mixture of a monopicryl and a dipicryl derivative of **1** in a ratio of 2:1, respectively, regardless of the initial concentrations of **1** and PkF. The products were identified as 5-nitro-2-picryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**2**) by X-ray crystallography and 5-nitro-2,4-dipicryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**4**) by ^{15}N labeling experiments.

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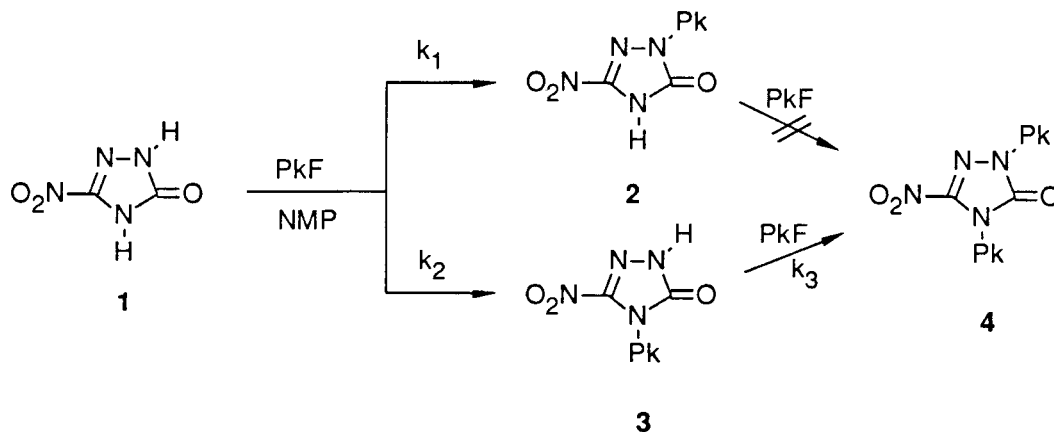
5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (**1**) is an explosive of current interest [1,2]. The N-H protons of this compound were determined in this Laboratory to be in the 2,4 positions in both the solid state and in solution by observing ^1H - ^{15}N coupling in the nmr spectra of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one- 4 - ^{15}N (**1a**) [3]. We were interested in preparing picryl derivatives of **1** both to determine the positions of substitution on **1** and to evaluate the explosive properties of the products.

Thus, treatment of **1** with picryl fluoride (PkF) in 1-methyl-2-pyrrolidinone (NMP) at 25° gave a mixture of a monopicryl and a dipicryl derivative of **1** in a ratio of 2:1, respectively, regardless of the initial concentrations of **1** and PkF. The initial ratios of **1** to PkF were varied between 1:3 and 3:1. The reactions were conveniently monitored by ^1H -nmr. The chemical shift of the picryl protons of the monopicryl derivative is $\delta = 9.36$ ppm and those of the dipicryl derivative are $\delta = 9.55$ ppm and 9.65 ppm in NMP. In reactions where PkF was in excess, the picryl peak of PkF [$\delta = 9.46$ ppm (d, $J = 6$ Hz)] was observed in the completed reaction mixtures in addition to those of the products; therefore, the monopicryl derivative is not intermediate in the formation of the dipicryl derivative. After

the product ratios were determined by ^1H -nmr, the products were precipitated with water and separated by fractional crystallization from acetone/ethanol. Similar results were obtained using *N,N*-dimethylformamide (DMF) as the reaction solvent; however, the aldehydic proton of DMF swamped the product region in the ^1H -nmr spectrum such that the reaction could not be conveniently monitored in this solvent.

The structure of the monopicryl derivative, as the NMP solvate, was determined by X-ray crystallography to be 5-nitro-2-picryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**2**) [4]. This structure was proposed by Sitzmann for a by-product of the reaction of picryl chloride with the potassium salt of 3,5-dinitro-1H-1,2,4-triazole [5]. An authentic sample of Sitzmann's compound was found to be identical (ir, ^1H -nmr and ^{13}C -nmr) with **2**.

The structure of the dipicryl derivative was determined by ^{15}N labeling as follows. Treatment of **1a** [3] with PkF in NMP produced a similar mixture of products that was resolved as described previously. The ^{13}C -nmr spectrum of the dipicryl derivative obtained from **1a** differed from that obtained from **1**. In addition to splitting the triazole carbons into doublets, the ^{15}N also split one of the picryl car-

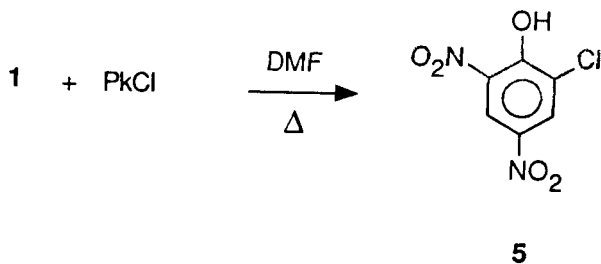


Where: Pk = 2,4,6-Trinitrophenyl, $k_1/k_2 = 2$, and $k_3 \gg k_1$

bons into a doublet; therefore, one of the picryl groups is attached to the ^{15}N at position 4. This evidence coupled with the strong carbonyl absorption observed in its ir spectrum suggests that the structure of the dipicryl derivative of **1a** is 5-nitro-2,4-dipicryl-2,4-dihydro-3H-1,2,4-triazol-3-one-4- ^{15}N (**4a**) and that of **1** is 5-nitro-2,4-dipicryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**4**). The ^{13}C -nmr spectrum of the 4- ^{15}N -labeled **2** (**2a**) showed splitting of the triazole carbons, but not of the picryl carbons.

Based upon the results presented thus far, it appears that **1** reacts with PkF to give initially a mixture of two monopicryl derivatives **2** and **3** in a ratio of 2:1, respectively. Compound **3** then reacts rapidly with another molecule of PkF to produce **4** and give the observed ratio of products.

Picryl chloride (PkCl) would not react with **1** in either NMP or DMF at 25°; however, in DMF at 90° a low yield of solid precipitated when the reaction mixture was diluted with water. Elemental analysis and the ^1H - and ^{13}C -nmr spectra of the product were consistent with a chlorodinitrophenol with nitro groups 1,3 to each other. We were surprised to find the product to be identical with an authentic sample of 2-chloro-4,6-dinitrophenol (**5**). In addition, **5** would not form when PkCl was heated in DMF at 90° in the absence of **1** or when **1** was heated with PkCl in NMP at 90°. Under no circumstances could **2** or **4** be obtained from reaction of **1** with PkCl.



EXPERIMENTAL

CAUTION! The compounds described herein are high explosives and should be handled with care.

Melting points were determined with a Mettler FP1 apparatus and are corrected. All ir spectra were determined with a Perkin-Elmer 283 spectrometer. All nmr spectra were determined with a JEOL FX90Q spectrometer. The ^1H - and ^{13}C -nmr shifts are referenced to internal tetramethylsilane = 0 and the ^{15}N shifts are referenced to external $1M$ $^{15}\text{NH}_4\text{NO}_3$ = 0. Microanalyses were performed by M. J. Naranjo, Los Alamos National Laboratory.

5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one was prepared as described previously [1]. Picryl fluoride was prepared according to a literature procedure [7]. Anhydrous 1-methyl-2-pyrrolidinone and *N,N*-dimethylformamide were purchased from the Aldrich Chemical Co., 2-chloro-4,6-dinitrophenol was purchased from K&K Laboratories, and picryl chloride purchased from Matheson, Coleman & Bell.

Reactions of 5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (**1**) with Picryl Fluoride (PkF). Preparation of 5-Nitro-2-picryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**2**) and 5-Nitro-2,4-dipicryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**4**).

A solution of **1** (0.65 g, 5 mmoles) and PkF (2.31 g, 10 mmoles) in anhydrous 1-methyl-2-pyrrolidinone (NMP) (5.0 ml) was allowed to stir at ambient temperature, protected from moisture, until the reaction was complete according to ^1H -nmr (~16 hours). The solution was diluted with ice-water to precipitate the products, which were collected by filtration, washed with water, and dried. The solid was dissolved in acetone and the boiling solution was treated with ethanol to precipitate **4**, which was recrystallized again from acetone/ethanol to yield 0.83 g (30%), mp 238°; ^1H -nmr (acetone- d_6): δ 9.42 (s, 2H), 9.56 (s, 2H); ^1H -nmr (NMP): δ 9.55 (s, 2H), 9.65 (s, 2H); ^{13}C -nmr (acetone- d_6): δ 124.1, 125.5, 126.4, 127.3, 147.1, 147.8, 148.6, 149.7, 150.3; ^{13}C -nmr (methyl sulfoxide- d_6): δ 122.0, 123.7, 125.8, 126.5, 145.7, 146.0, 146.5, 147.7, 148.5, 148.9; ir (potassium bromide): ν 3075, 2865, 1770, 1603, 1535, 1470, 1410, 1367, 1335, 1261, 1180, 1143, 1067, 1020, 990, 908, 855, 814, 795, 709, 646.

Anal. Calcd. for $\text{C}_{14}\text{H}_4\text{N}_{10}\text{O}_{15}$: C, 30.45; H, 0.73; N, 25.36. Found: C, 30.78; H, 0.76; N, 24.93.

The boiling filtrate was treated with water to precipitate **2**, which was collected by filtration and recrystallized from aqueous ethanol to yield 0.58 g (34%), identical with an authentic sample [5], mp 269°; ^1H -nmr (acetone- d_6): δ 9.28 (s, 2H), 11.02 (bs, 1H); ^1H -nmr (NMP): δ 9.36 (s); ^{13}C -nmr (acetone- d_6): δ 125.8, 126.7, 146.7, 148.6, 149.5, 150.9; ir (potassium bromide): ν 3345, 3100, 1767, 1722, 1641, 1621, 1569, 1554, 1472, 1423, 1383, 1350, 1321, 1240, 1216, 1198, 1170, 1151, 1099, 1031, 1010, 939, 929, 838, 828, 791, 776, 752, 742, 731, 722, 717, 637, 598, 531, 450, 421.

Anal. Calcd. for $\text{C}_8\text{H}_3\text{N}_5\text{O}_9$: C, 28.16; H, 0.89; N, 28.74. Found: C, 28.52; H, 0.69; N, 28.51.

In subsequent experiments **1** (5.0 mmoles) was treated with 5.0 and 15.0 mmoles of PkF, then PkF (5.0 mmoles) was treated with 10 and 15 mmoles of **1**, all in anhydrous NMP (5.0 ml), at ambient temperature for 16 hours. Integration of the picryl protons in the ^1H -nmr spectra of the completed reaction mixtures revealed that the ratio of products, **2** to **4**, was approximately 2:1 for all reactions.

Preparation of 5-Nitro-2-picryl-2,4-dihydro-3H-1,2,4-triazol-3-one-4- ^{15}N (**2a**) and 5-Nitro-2,4-dipicryl-2,4-dihydro-3H-1,2,4-triazol-3-one-4- ^{15}N (**4a**).

5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one-4- ^{15}N (**1a**) [3] (0.32 g, 2.5 mmoles) was treated with PkF (1.15 g, 5.0 mmoles) in NMP (2.5 ml) exactly as described above for **1**. Workup as described gave **2a**, 0.29 g (34%), mp 269°; ^1H -nmr (acetone- d_6): δ 9.26 (s, 2H), 11.0 (bs, 1H); ^{13}C -nmr (acetone- d_6): δ 125.7, 126.3, 146.6, 148.4, 149.5 (d, $J_{\text{CN}} = 29$ Hz), 150.9 (d, $J_{\text{CN}} = 29$ Hz); ^{15}N -nmr (acetone- d_6): 110.0 ppm ($^{15}\text{NH}_4\text{NO}_3 = 0$) and **4a**, yield 0.36 g (26%); mp 238°; ^1H -nmr (acetone- d_6): δ 9.42 (s), 9.56 (s); ^{13}C -nmr (acetone- d_6): δ 124.1 (d, $J_{\text{CN}} = 21$ Hz), 125.5, 126.4, 127.3, 147.1, 147.8, 148.6 (d, $J_{\text{CN}} = 22$ Hz), 149.7, 150.3; ^{13}C -nmr (methyl sulfoxide- d_6): δ 122.0 (d, $J_{\text{CN}} = 21$ Hz), 123.7, 125.8, 126.5, 145.7, 145.9 (d, $J_{\text{CN}} = 32$ Hz), 146.5, 147.7 (d, $J_{\text{CN}} = 22$ Hz), 148.5, 148.9; ^{15}N -nmr (acetone- d_6): 105.9 ppm ($^{15}\text{NH}_4\text{NO}_3 = 0$).

Reaction of **1** with Picryl Chloride (PkCl) in *N,N*-Dimethylformamide (DMF).

A solution of **1** (1.08 g, 8.3 mmoles) and PkCl (2.02 g, 8.2 mmoles) in DMF (15 ml) was heated at 90° for 16 hours. The resulting solution was poured into ice-water to precipitate a solid, which was recrystallized from acetone/ethanol to yield 0.60 g (33%) of 2-chloro-4,6-dinitrophenol (**5**), identical with a commercial sample, mp 110° (lit [6] mp 110-111°); ¹H-nmr (acetone-d₆): δ 8.66 (d, J = 2.5 Hz, 1H), 8.91 (d, J = 2.5 Hz, 1H), 9.8 (bs, 1H); ¹³C-nmr (acetone-d₆): δ 120.9, 126.1, 131.6, 135.5, 140.0, 156.0; ir (potassium bromide): ν 3080, 1605, 1590, 1538, 1520, 1457, 1417, 1335, 1260, 1142, 1060, 923, 910, 755, 729, 685, 630.

Anal. Calcd. for C₆H₃ClN₂O₅: C, 32.97; H, 1.38; N, 12.82. Found: C, 32.44; H, 1.20; N, 12.83.

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picryl-2,4-dihydro-3H-1,2,4-triazol-3-one (**2**); Dr. Michael E. Sitzmann, Naval Surface Warfare Center, for providing an authentic sample and ir spectrum of **2**; and Dr. Donald G. Ott, Los Alamos National Laboratory, for the sample of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one-4-¹⁵N (**1a**). This work was performed under the auspices of the US Department of Energy.

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