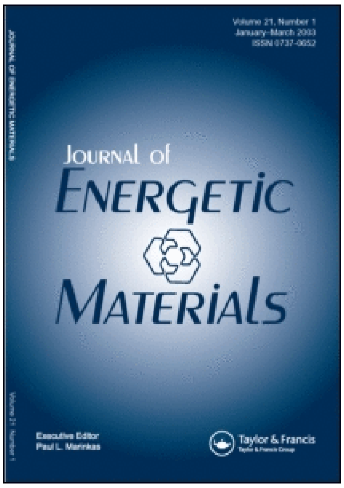

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Synthesis of ^{15}N-labeled isomers of 5-Nitro-2,4-Dihydro-3H-1,2,4-Triazol-3-One (NTO)

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To cite this Article Oxley, Jimmie C. , Smith, James L. , Yeager, Kirk E. , Coburn, Michael D. and Ott, Donald G.(1995) 'Synthesis of ^{15}N-labeled isomers of 5-Nitro-2,4-Dihydro-3H-1,2,4-Triazol-3-One (NTO)', Journal of Energetic Materials, 13: 1, 93 — 105

To link to this Article: DOI: 10.1080/07370659508019345

URL: http://dx.doi.org/10.1080/07370659508019345

SYNTHESIS OF ^{15}N-LABELED ISOMERS OF 5-NITRO-2,4-DIHYDRO-3H-1,2,4-TRIAZOL-3-ONE (NTO)

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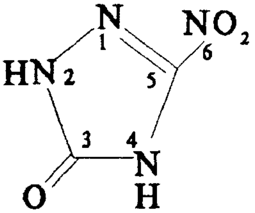
ABSTRACT

The synthetic routes to ^{15}N labeled 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) isomers are reported. Isomers labeled on N(6), N(4) and both N(1) and N(2) have been made. These compounds were identified by ^{1}H, ^{13}C, and ^{15}N NMR and by mass spectral analysis. In many cases unequivocal NMR and mass spectral assignments were made.



Journal of Energetic Materials Vol. 13, 93-105 (1995)
Published in 1995 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Although 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one (NTO) has been known for a number of years,[1] only recently has it received attention as a potentially insensitive explosive.[2] As part of an ongoing program to study the thermal decomposition mechanisms of a number of energetic materials, NTO and labeled isomers were examined. Herein we describe the synthetic routes to 5-nitro-2,4-dideutro-3H-1,2,4-triazol-3-one (d2NTO) and 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one labeled with ^{15}N on the nitro group [NTO (N6)], on the isolated ring nitrogen [NTO (N4)], and on the vicinal nitrogens [NTO (N1,2)]

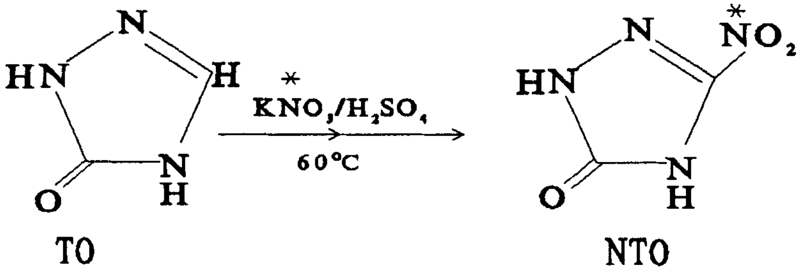
EXPERIMENTAL METHOD

All spectra were obtained on a JEOL GSX high resolution Fourier transform NMR spectrometer equipped with a 5 mm broadband probe. Resonance frequencies for ^{1}H, ^{13}C, and ^{15}N were 399.65 MHz, 100.40 MHz, and 40.40 MHz, respectively. Natural abundance ^{13}C spectra were obtained with proton decoupling. The ^{15}N spectra for the ^{15}N-labeled compounds were obtained with single pulse gated decoupling without nuclear Overhauser enhancement. Samples were weighed and dissolved (1% to 5%) into deuterated dimethyl sulfoxide(DMSO) unless otherwise noted. The ^{1}H NMR spectra were referenced to tetramethylsilane (0 ppm) added to the sample. The ^{13}C NMR spectra were referenced to the DMSO solvent septet

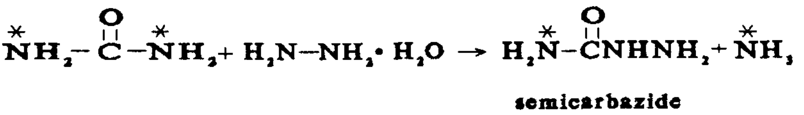
(39.5 ppm). The ^{15}N NMR chemical shifts were referenced to aqueous solutions (0.1M) of ammonium chloride (0 ppm) present in sealed co-axial capillaries. [By this method, the ^{15}N resonance of nitromethane was 358 ppm.] Most electron impact (70 eV) mass spectra were obtained on a Finnagan model 8222 double focusing magnetic sector mass spectrometer. The spectrum of 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one-1,2-^{15}N was acquired on a Finnagan TSQ 700 quadrupole mass spectrometer.

Deuterated NTO: The d2-NTO was prepared by dissolving previously recrystallized NTO (1.7 g) in 25 mL of D_2O (MSD isotope, 99.8%). A few drops of D_2SO_4 were necessary to promote the exchange reaction. The mixture was heated at 55-60°C for 1 hour under nitrogen atmosphere and then cooled in an ice bath. The product was washed with a large quantity of ice water, vacuum filtered, and dried under vacuum overnight to yield 1.5 g (88%) of a white solid. Mass spectral analysis indicated over 90% conversion to the fully deuterated species with about 10% mono deuterated impurity. No evidence of the presence of protonated species was observed. Deuterated TO (2,4-dihydro-3H-1,2,4-triazol-3-one) was prepared in a similar fashion; however, mass spectral analysis indicates deuteration was not complete. From the relative abundances of the mass fragments 87 and 86, it was estimated mono- and di-deuterated TO were formed in approximately equal amounts.

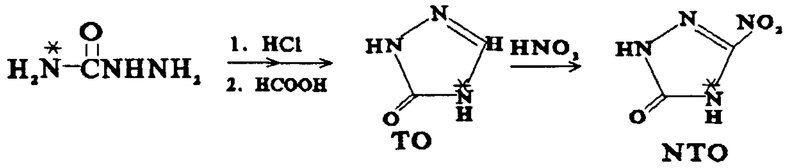
5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one-6-^{15}N [NTO(N6)]: ^{15}N-NO$_2$-labeled NTO was prepared by nitrating TO with a $K^{15}NO_3/H_2SO_4$ mixture, rather than nitric acid. Concentrated H_2SO_4 (1.5 mL) was added to 1.0 g (9.9 mmol) $K^{15}NO_3$, and the mixture was stirred 30 minutes. Solid TO (0.81 g, 9.6 mmol) was added to the slurry, a condenser was put in place, and the mixture was heated at 60°C for 2 hours. Some orange fumes were observed in the condenser during that time. The mixture was allowed to cool to ambient temperature slowly before a few pieces of ice were added. The white NTO precipitate was removed by filtration, washed with 5 X 7 mL cold water, and dried. Yield was 0.9 g (70% based on the labeled compound). (The filtrate was analyzed by ^{13}C NMR and found to contain no NTO.) The NMR chemical shifts of the NTO are given in Table I. The mass spectral fragmentation pattern is shown in Table II.



2,4-Dihydro-3H-1,2,4-triazol-3-one-4-^{15}N [TO(N4)]: The ^{15}N-labeled semicarbazide was prepared from urea-1,3-^{15}N and hydrazine hydrate. Urea-1,3-^{15}N (2.0g, 0.033 mol) and hydrazine hydrate (2 mL, 0.04 mol) were heated in a pressure reactor with stirring at 100° to 118°C for 4 to 5 hours. After heating was discontinued, the reaction mixture was allowed to stir overnight before the reactor was vented, and the contents were filtered. The solid was washed repeatedly with water until only an insoluble gray residue remained. The combined filtrate was evaporated to a white paste on a rotary evaporator. Analysis (^{13}C NMR) of the white paste indicated semicarbazide and urea. The semicarbazide/urea paste was slurried in water (10 mL) and cooled in an ice bath while concentrated HCl (2 mL) was added. The solution was stirred 5 minutes before the water was removed on a rotary evaporator, leaving a mixture of semicarbazide-4-^{15}N hydrochloride and urea. This mixture was refluxed with 98% formic acid (2.5 mL) for 1.5 hours. The resulting white paste was dissolved in the minimum of hot water (about 5 mL), and the solution was cooled undisturbed for several days. The solid that crystallized was collected by filtration, washed with a little ice water, and dried. A second crop of crystals was obtained by allowing the filtrate to evaporate slightly. The combined yield of TO (N4) was 1.6 g (58%). The NMR chemical shifts are given in Table I.

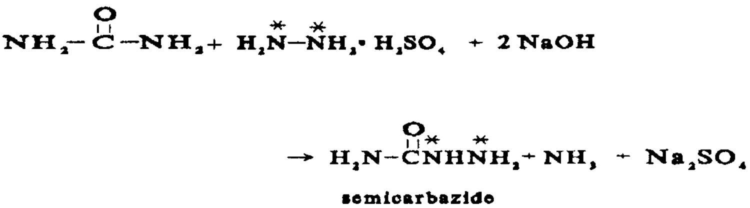


$$\overset{*}{N}H_2-\overset{O}{\overset{||}{C}}-\overset{*}{N}H_2 + H_2N-NH_2\cdot H_2O \rightarrow H_2\overset{*}{N}-\overset{O}{\overset{||}{C}}NHNH_2 + \overset{*}{N}H_3$$

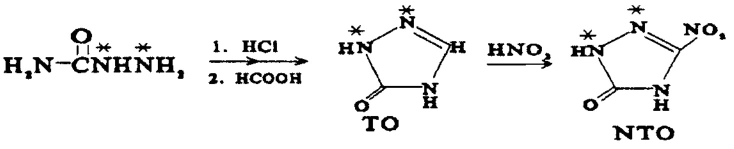


5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one-4-^{15}N [NTO (N4)]: Solid TO (N4) (1.0 g, 0.012 mol) was added over 10 minutes to concentrated nitric acid (6 mL) at 40°C-55°C. After complete addition, the solution was heated at 75°C for 1.5 hours, during which time copious brown fumes evolved and a white precipitate formed. After the mixture had cooled to ambient temperature, the crystals were collected by filtration, washed with cold water (3 x 1.5 mL) and dried to yield 1.35 g (86%) of NTO (N4). The NMR chemical shifts of the product are given in Table I, and the major mass spectral fragments are listed in Table II.

5-Nitro-2,4-dihydro-3H-1,2,4-triazol-3-one-1,2-^{15}N [NTO(N1,2)]: In a pressure reactor, urea (1.0 g, 0.017 mol) was dissolved in water (2.0 mL) and hydrazine-$^{15}N_2$ sulfate (2.0 g 0.015 mol) was added with stirring. The resulting slurry was treated with sodium hydroxide (1.2 g, 0.03 mol), and the mixture was heated in a sealed 25 mL reactor between 100° and 118°C for 6-7 hours. Heating was discontinued, and the mixture was allowed to stir at ambient temperature overnight. Workup of this reaction mixture and conversion of the semicarbazide to TO(N1,2) followed the same procedure described for TO(N4). However, the TO(N1,2) was contaminated with sodium sulfate in addition to urea in this instance and could not be obtained in pure form (NMR, Table I). Thus, 0.16 g of the dried mixture was dissolved in fuming nitric acid (90%) (10 mL), and the solution was heated at 75°C for 5 minutes. The resulting solution was evaporated to dryness on a rotary evaporator, and the residue was taken up in ice water (10 mL). The undissolved solid was collected by filtration, washed with ice water, and dried to yield 0.18 g (75%) of NTO (N1,2). The NMR chemical shifts and mass spectral data are given in Tables I and II, respectively.



$$NH_2-\overset{O}{\overset{\|}{C}}-NH_2 + H_2\overset{*}{N}-\overset{*}{N}H_2\cdot H_2SO_4 + 2\,NaOH \rightarrow H_2N-\overset{O}{\overset{\|}{C}}\overset{*}{N}H\overset{*}{N}H_2 + NH_3 + Na_2SO_4$$



DISCUSSION

Synthesis Condensation of urea and hydrazine hydrate in a minimum of water under mild pressure and heat resulted in the formation of semicarbazide. The stoichiometry of the reaction was adjusted in each synthesis so that the ^{15}N-labeled reactant was the limiting reagent. However,a large excess of urea was avoided to prevent excessive formation of carbazide. The water insoluble gray residue removed in the filtration step at the completion of the condensation was assumed to be carbazide. A white paste was isolated at this point by removing water from the filtrate with a rotary evaporator; ammonia and excess hydrazine, if any, were removed in this step. The ^{13}C-NMR of the white paste typically showed the presence of both semicarbazide and excess urea; their chemical shifts were in the 160-170 ppm range depending on the acidity of the D_2O solution. Separation of the semicarbazide and urea was unnecessary at this point and was more readily effected after formation of TO.

Cyclization of the semicarbazide with formic acid required the presence of a strong acid. Accordingly, hydrochloric acid was used to convert the semicarbazide to the hydrochloride prior to treatment with formic acid. When the TO, thus formed, contained excess urea, the TO was recrystallized from water to separate it from the more soluble urea. However, when hydrazine sulfate and sodium hydroxide were used to generate hydrazine in the initial step, the sodium sulfate by-product was found to precipitate out with the TO.

Nitration of the TO was accomplished by use of nitric acid or by generation of nitric acid from potassium nitrate and sulfuric acid. Observation of this step suggested that substitution of the nitro group into the TO ring was not effected unless large amounts of nitrogen dioxide were evolved in the reaction. This observation indicates substitution of the nitro group into TO is a nitrosation/oxidation rather than actual nitration reaction.

NMR Spectra The compound NTO(N4) was first synthesized in order to assign the positions of the two NTO protons.[3] Observation of the ^1H spectra of NTO ^{15}N-labeled on N(1) and N(2) revealed ^{15}N coupling (8 and 108 Hz) only to the upfield proton resonance (13.7 ppm), indicating this resonance belonged to the proton on N(1). In all cases the downfield resonance of the N(4) proton (14.4 ppm) was small and broad, which is expected of the acidic proton. A resonance was not observed at 14.4 ppm in the ^1H spectrum of the N(6)-labeled NTO. There was, however, a small broad resonance on the left side of the proton resonance at 13.7 ppm, suggesting that it might have shifted far enough upfield to be masked by the resonance of the N(1) proton.

NMR resonances (^{13}C) were observed at 154 ppm for the carbonyl C(3) in NTO and 156 ppm for the corresponding carbon in TO; C(5) exhibited a resonance at 148 ppm for C-NO_2 in NTO and at 136 ppm for C-H in TO. The ^{13}C spectra were decoupled from proton, but coupling to ^{15}N was observed. The carbonyl carbon C(3) exhibited 17 Hz coupling in the NTO isomer labeled at N(4) and 16 Hz coupling in the isomer labeled at N(1) and N(2). Labeling of the nitro group nitrogen N(6) effected splitting of C(5) (29 Hz). In contrast, labeling of the ring nitrogens on either side of the C(5) carbon [N(1) or N(4)] did not appear to produce splitting. However, this observation, may be an artifact, resulting from the relative weakness of this carbon resonance compared to that of the carbonyl carbon C(3). In fact, in TO(N4) where the C(5) resonance was stronger, ^{15}N coupling was observed to C(5) as well as to C(3) (11 and 19 Hz, respectively).

Observation of the ^{15}N NMR spectrum of all three isotopically labeled NTO isomers allowed unequivocal assignment of the N(6) and N(4) ^{15}N resonances. The resonance of the N(6) nitro group was in the expected region (328 ppm). The protonated nitrogen N(4) exhibited a nitrogen resonance at 120 ppm, similar to that observed for the N(4) ^{15}N-labeled TO (Table I). The spectra of NTO ^{15}N-labeled on both N(2) and N(1) exhibited two resonances, coupled to each other by 13 Hz. A reasonable assignment

TABLE I
NMR Spectra of NTO and TO

	Carbon 13						Proton					Nitrogen 15*			
	ppm		J_{CN}	ppm		J_{CN}	ppm		ppm		J_{HN}	ppm	J_{NN}	ppm	J_{NN}
	CO			CNO2			N(4)H		N(1)H						
NTO	154	s		148	br		14.4	br	13.7	s					
NTO (N6)	154	s		148	d	29			13.7	s		328	s		
NTO (N4)	154	d	17	148	br		14.4	br	13.7	s		120	s		
NTO(1,2)	154	d	16	148	br		14.4	br	13.8	dd	8,108	249	d13	156	d13

	Carbon 13						Proton						Nitrogen 15*	
	ppm		J_{CN}	ppm		J_{CN}	ppm		ppm		ppm	J_{HN}	ppm	
	CO			CH			NH		NH		CH			
TO	156	s		136	s		11.5	s	11.4	s	7.8	s		
TO (N4)	156	d	19	136	d	11	11.5	br	11.3	br	7.8	d,7	122	s
TO(N1,2)	162	br		137	br						7.5	dd 5,13 **		

* s = singlet; d = doublet; dd = doublet of doublets; br = broad. J is given in Hz.
** TO(N1,2) spectra were obtained on a crude sample in D_2O.

appears to be that the resonance of N(2) bonded to proton should be similar to that of N(4) and, accordingly, is assumed to be the resonance at 156 ppm. The N(1) nitrogen, double bonded to the carbon holding the nitro group, would be the resonance farther downfield (249 ppm).

Mass Spectra Previous studies[4,5] have attempted to assign the mass spectral fragmentation pattern of NTO; but our study using ^{15}N-labeled compounds now provides unequivocal assignment of the important fragments. At variance with the previous reports is the assignment of the NTO m/e 85 as TO. NTO (N6) exhibited no peak at m/e 85 but rather a fragment of m/e 86, while NTO (N1,2) exhibited a large peak at m/e 85 and no peak at 87. This evidence indicates that the NTO fragment 85 is not the triazolone ring. The 85 fragment contains N(6), N(4), and neither N(1) nor N(2); thus, it was assigned as H(O)CN(4)=CN(6), appearing to indicate that under electron impact the triazolone ring comes apart by elimination of hydrazine. Loss of NO_2 would be expected and was observed in most spectra (m/e 46 or 47). Loss of NO was also evidenced in the observation of a NTO fragment of m/e 100 or 101. TO, itself, (parent m/e 85) was not observed, but the parent minus one or two protons (or NTO - HONO or NTO - H_2NO_2) was observed in the spectra of all isomers (Table II).

TABLE II
Principal Fragments in the Mass Spectra of NTO

	NTO	NTO(N6)	NTO(N4)	NTO(N1,2)
NTO	130 L	131 L	131 L	132 L
NTO - N(6)O	100 T	100 T	101 T	
H(O)CN(4)=CN(6)	85 M	86 S	86 M	85 L
TO - H	84 M	84 M	85 M	86 M
TO - 2H	83 L	83 L	84 L	85 L
$N(6)O_2$	46 T	47 T	46 T	

ACKNOWLEDGMENTS

Part of this work was performed under the auspices of the US Department of Energy and part was funded by Eglin Air Force Base and the Office of Naval Research.

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