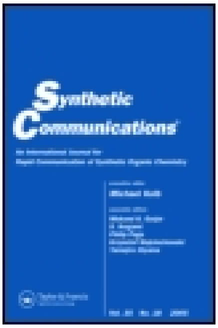

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# A New Synthesis of Alkyl-N,N-dinitramines by Direct Nitration of Isocyanates

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# A NEW SYNTHESIS OF ALKYL-N,N-DINITRAMINES BY DIRECT NITRATION OF ISOCYANATES

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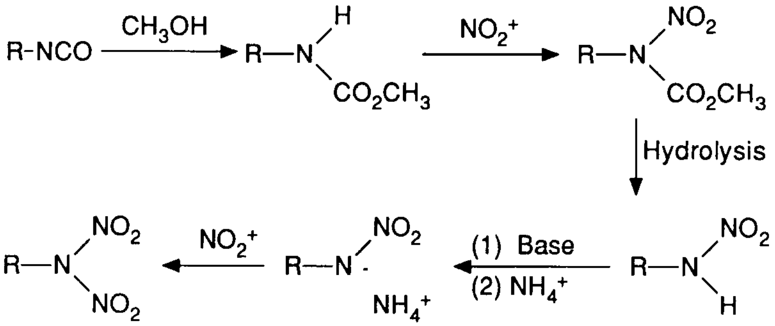
## ABSTRACT

A facile conversion of aliphatic isocyanates to N,N-dinitramines has been developed. An aliphatic isocyanate is treated with a mixture of nitronium fluoroborate and nitric acid in acetonitrile giving fair yields and simplifing the existing synthesis.

The N,N-dinitramine function is a highly labile functional group accessible only by difficult preparative procedures. Recently, renewed interest has developed in preparing N,N-dinitramines as possible energetic groups for propellant applications. The established method,[1] takes four steps and involves the preparation of an alkyl nitramine via the N-nitromethylcarbamate followed by nitration with nitronium ion, according to Equation 1.



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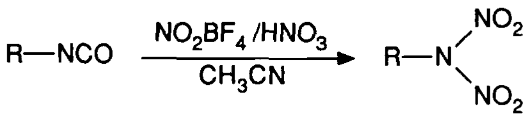
We report here a new, simple, one-step synthesis of N,N-dinitramines from aliphatic isocyanates, using stoichiometric quantities of nitronium tetrafluoroborate and nitric acid in acetonitrile as the nitrating system, according to Equation 2.

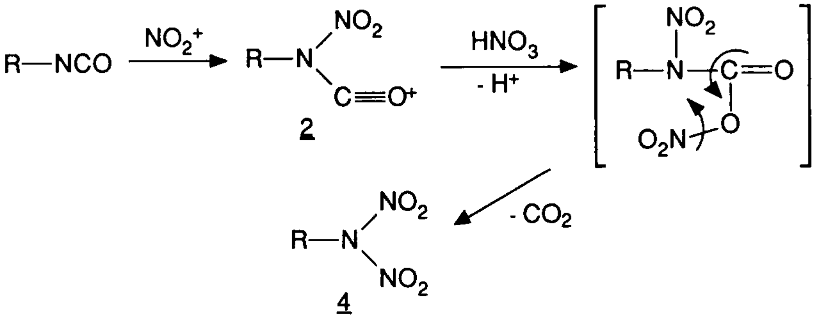


$$R{-}NCO \xrightarrow[CH_3CN]{NO_2BF_4/HNO_3} R{-}N(NO_2)_2 \qquad (2)$$

This route differs from the previous work in that it is only one step instead of four, and requires the presence of both nitric acid and high quality nitronium tetrafluoroborate in the reaction medium. If either reagent is absent, no N,N-dinitramine is formed.

We propose the simple mechanism shown in Scheme I, in accordance with the observation of Ledebev et al (Scheme I) who reacted isocyanates with nitronium ions in the absence of nitric acid to give monoalkyl-mononitramino compound via intermediate 2.[2] Adding an aliphatic isocyanate to a preformed, ice-cooled mixture of acetonitrile, nitric acid, and nitronium tetrafluoroborate results in the initial formation of the corresponding acylium ion 2 to which $HNO_3$ is added, then losing a proton and $CO_2$, to give the corresponding aliphatic N,N-dinitramine 4. Consistent with this mechanism is our observation that no N,N-dinitramines are formed when the reaction is run in the absence of free nitric acid which presumably acts as a nucleophile toward acylium ion 2. An alternative to the proposed mechanism below is the direct addition of $N_2O_5$ (formed by the reaction of $NO_2BF_4$ with $HNO_3$) across the alkyl isocyanate giving the same reactive intermediate shown below also giving 4.

This reaction is most successful with primary alkyl isocyanates. When 1-adamantyl isocyanate was subjected to the conditions of this procedure, only a trace (<1%) of the desired N,N-dinitramine was formed, with the remainder of the substrate transformed into a complex mixture. This result indicates a high sensitivity either to steric hindrance or to the stability of the ternary carbonium ion or radical formed if the dinitramine group leaves and then rearranges. We would expect that the dinitramide groups is an excellent leaving group and obviously quite



Scheme 1: Proposed Mechanism for N,N-Dinitramine Synthesis

Table I

| Substrate | Product | Yield |
|---|---|---|
| *n*-Butyl isocyanate | 1-(N,N-Dinitramino) butane | 35% |
| Methyl isocyanate | N,N-Dinitramino-methane | 30% |
| 1-Adamantyl isocyanate | 1-(N,N-Dinitramino) adamantane | <1% |
| Hexamethylene diisocyanate | 1,6-bis(N,N-Dinitramino)hexane | 10% |
| Ethane-1,2-diisocyanate | 1,2-bis(N,N-Dinitramino)ethane | -0- |
| 2-(Trimethylsilyl-ethyl)-1-isocyanate | 1-(N,N-Dinitramino)-2-trimethylsilyl-ethane | 25 |

labile when attached to a ternary position such as the 1-position of adamantane. Hexamethylene diisocyanate is converted in 10% yield, the square of the yield obtained for monofunctional substrates, indicating that the two distant functional groups are not interacting in this case.

The substrates investigated are shown in Table I, along with the yields. The overall yields from this route are no better than those of previous syntheses, but the transformation is accomplished in one rather than four steps.

## EXPERIMENTAL

*CAUTION*: All the products described in this paper are potentially explosive and should be handled in 0.5-g quantities and stored at 0°C. All NMR spectra were obtained on a Varian EM-360 spectrometer. IR spectra were obtained on a Perkin-Elmer 1420 Infrared spectrophotometer. Elemental analysis could not be obtained because of the marked instability of the products. All thin-layer chromatography was run by elution of $CHCl_3$ over silica gel.

**General Procedure for Conversion of Isocyanates to N,N-Dinitramines.** To an ice-cooled mixture of 1.45 g (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% $HNO_3$ (under argon) was added 10 mmol of aliphatic isocyanate, avoiding fume-off by controlling the rate of addition as appropriate. The reaction mixture was then stirred for 15 min at 0°C, diluted to 25 mL with $CHCl_3$, filtered rapidly through a 1 x 3-in. plug of $SiO_2$, and eluted with 100 mL of $CHCl_3$. Chromatography of the crude product, elution $CHCl_3$ over $SiO_2$, and collection of the fastest moving UV-active material ($R_f = 0.5$) yielded the desired dinitramines in fair quantity. N,N-Dinitro-1-butylamine and N,N-dinitromethylamine show spectral properties identical to those of known samples synthesized by established methods.[1]

**1-Adamantyl-N,N-dinitramine:** IR (Neat) 2900, 1610 (s), 1270 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.2-2.5 (m) TLC: $R_f = 0.7$ ($CHCl_3/SiO_2$) bleaches $I_2$.

**1,6-bis(N,N-dinitramino)hexane:** IR (Neat 2940, 2860, 1640 (s), 1600 (s), 1340 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 4.1 (t, 4H, J = 6 Hz, $CH_2$-N) $\delta$ 1.2-1.9 (m, 6H, $CH_2$) TLC: $R_f = 0.5$ ($CHCl_3/SiO_2$) bleaches $I_2$.

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