Heteroatom Chemistry
Volume 4, Number 1, 1993

Synthesis and Stability of 2,4,6-Trinitrobenzylamine

Michael E. Sitzmann* and Horst G. Adolph

Energetic Materials Division, Naval Surface Warfare Center, Silver Spring, MD 20903-5000

Received 30 January 1992

ABSTRACT

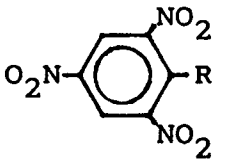
2,4,6-Trinitrobenzylamine was synthesized via 2,4,6-trinitrophenylacetic acid and 2,4,6-trinitrobenzyl isocyanate. The title compound decomposes at room temperature but forms a stable hydrochloride and acetyl derivative.

INTRODUCTION

Amino-substituted 2,4,6-trinitrobenzenes are exceptionally stable, both chemically and thermally, due to electronic and hydrogen bonding interactions of the amino and nitro substituents [1]. A mixture of 1,3,5-trinitrobenzene and ammonia, on the other hand, reacts readily to form Meisenheimer adducts and their follow-on products [2]. When the amino group is attached to the trinitrobenzene via an alkane chain, the basicity of the amino group and thus its propensity to form Meisenheimer adducts is expected to decrease with decreasing chain length. Therefore, one might postulate that the title compound (**4**) should be stable, while the longer chain ω-trinitrophenyl alkylamines might not be. A search of the literature revealed that no trinitrophenyl alkylamines have been reported.

RESULTS AND DISCUSSION

We now describe the synthesis and isolation of **4**, using the sequence shown below which involves 2,4,6-trinitrophenylacetic acid (**1**) and 2,4,6-trinitrobenzyl isocyanate (**3**) as intermediates. This synthesis approach was attractive, because **4** is initially isolated as the hydrochloride which is expected to be stable, independent of the stability of the free base **4** itself.

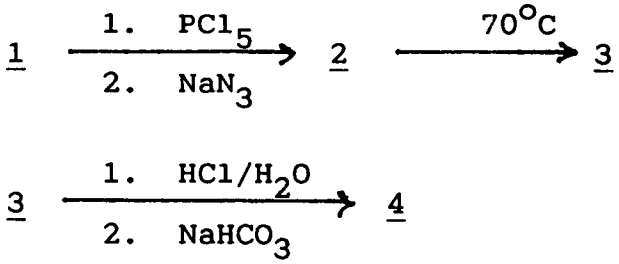


1: R = CH_2COOH

2: R = $CH_2C(O)N_3$

3: R = CH_2NCO

4: R = CH_2NH_2



Bonecki [3] reported that chromic acid oxidation of 2-(2,4,6-trinitrophenyl)ethanol in sulfuric acid gives mixtures of **1** and trinitrobenzoic acid, whereas the oxidation of 2-(2,4,6-trinitrophenyl)ethyl acetate in the same medium was claimed to give **1** in good yield and purity. In our experience, oxidation of both the acetate and the alcohol by the chromic-sulfuric acid procedure gives a mixture of **1** and trinitrobenzoic acid. This mix-

*To whom correspondence should be addressed

1042-7163/93/$5.00 + .25

ture is difficult to separate. It was found that the sodium salt of **1** decarboxylates more readily than that of trinitrobenzoic acid. Therefore, selective decarboxylation did not give pure **1**. Oxidation of 2-(2,4,6-trinitrophenyl)ethanol with CrO_3 in acetic acid, however, gave a 70% yield of fairly pure **1** which could be purified further by recrystallization.

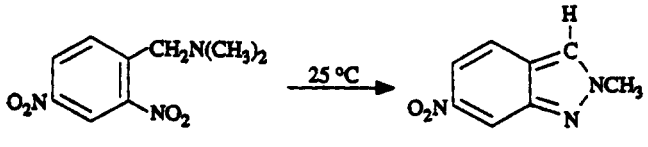
Conversion of **1** to the isocyanate **3** proved to be straightforward. Anticipated complications in the conversion of the acid chloride to the azide, involving possible abstraction of a labile benzyl hydrogen by azide ion, did not materialize. As expected, hydrolysis of **3** in aqueous hydrochloric acid formed the hydrochloride of **4** as a stable, crystalline salt which showed no sign of change after 18 months storage at room temperature.

Treatment of **4** hydrochloride with aqueous sodium hydrogen carbonate solution in the presence of ether followed by rapid solvent removal gave **4** as a brown solid which decomposed gradually at room temperature and more slowly at −15°C. (After 1 week at −15°C, about 80–90% of the original **4** remained.) A solution of **4** in d_3-MeCN showed no signs of change in the ^{1}H NMR spectrum after 5 hours at room temperature; after 4 days, however, complete decomposition of **4** had occurred.

In addition to salt formation, **4** is sufficiently nucleophilic for acylation (see the Experimental section) and, probably, carbonyl addition and alkylation reactions. As shown for the reaction with acetic anhydride, **4** can be generated in situ for this purpose from the hydrochloride.

Although trinitrobenzyl compounds form strongly colored anions on reaction with bases [4], the use of trinitrobenzyl as a tagging moiety has apparently not been pursued. Our results show that **4** is stable and reactive enough for synthesis of a variety of nitrogen compounds containing an N-trinitrobenzyl group. Additionally, **3** can serve to attach a trinitrobenzyl group to hydroxy and other compounds capable of addition to an isocyanate.

A referee suggested that the thermal instability of **4** may be related to the high yield, slow conversion of N,N-dimethyl-2,4-dinitrobenzylamine at room temperature to **5** [5].



100%

This conversion appears to be accompanied by upfield shifts of the ^{1}H signals, especially for H_5 and H_6, in the dinitrobenzylamine.

Similar upfield signals (at δ 8.82 and 8.70 in CD_3CN) were observed by us during the slow decomposition of **4** under nitrogen at room temperature. These absorptions appeared as doublets with a coupling constant of about 1.5 cps and may be due to meta-coupled nonequivalent aromatic protons. However, these signals disappeared on further storage of the CD_3CN solution. The formation of isolable, well-defined products in the decomposition of **4** was not observed in our work.

EXPERIMENTAL

Caution

Most trinitrobenzyl compounds reported here are moderately strong explosives and should be handled with appropriate care. Trinitrophenylacetyl azide is easily detonated and should be isolated in analytical quantities only. Melting points are uncorrected. ^{1}H NMR spectra were determined on a Varian EM 390 spectrometer using TMS internal standard. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

*2,4,6-Trinitrophenylacetic Acid (**1**).* A solution of 7.5 g (0.0292 mol) of 2-(2,4,6-trinitrophenyl)ethanol in 85 mL of acetic acid was stirred at 20°C during the addition of 18 g (0.18 mol) of chromium trioxide in two portions. The reaction is exothermic initially and cooling is necessary to hold the temperature at 20°C. The mixture was stirred overnight (immersed in a water bath) before it was poured into ice water (350 mL). An insoluble solid (1.0 g; 2-(2,4,6-trinitrophenylethyl) trinitrophenylacetate on the basis of its ^{1}H NMR spectrum) was removed by filtration, and the filtrate was extracted with ether (100 mL, then 2 × 75 mL). The combined ether extracts were washed with 15% hydrochloric acid (2 × 30 mL) and then dried ($MgSO_4$) before the volatiles were removed to give 6.0 g (74%) of nearly pure trinitrophenylacetic acid (^{1}H NMR analysis). Crystallization from dichloroethane (180 mL) gave 4.6 g, mp 173–175°C; Ref. 163–165°C [3]; ^{1}H NMR (acetone d_6): δ 4.47 (s, 2H), 9.33 (s, 2H).

2,4,6-Trinitrophenylacetyl Chloride. Phosphorus pentachloride (2.5 g, 0.012 mol) was added to a mixture of 2.7 g (0.01 mol) of 2,4,6-trinitrophenylacetic acid and 25 mL of dichloroethane stirred in a water bath at 40–45°C in portions. The violet-colored solution was slowly heated to 60°C and held for 5 minutes to give an amber-colored solution from which the volatiles were removed. The solid product, after being stirred with hexanes and drying, weighed 2.85 g (99%), mp 87–90°C; ^{1}H NMR ($CDCl_3$): δ 4.90 (s, 2H), 9.30 (s, 2H).

*2,4,6-Trinitrophenylacetyl Azide (**2**) and 2,4,6-Trinitrobenzyl isocyanate (**3**).* Sodium azide (0.9 g, 0.014 mol) and water (15 mL) were added to a so-

lution of 2.8 g (0.0097 mol) of 2,4,6-trinitrophenylacetyl chloride in dichloromethane (30 mL) stirred at 22°C. The mixture was stirred vigorously for 1 hour before the dichloromethane solution was separated and dried ($MgSO_4$). A sample from this solution exhibited IR (film): 2160 (N_3), 1725 (C=O), 1555, 1350 (NO_2)cm^{-1}, and ^1H NMR ($CDCl_3$): 4.40 (s, 2H), 9.22 (s, 2H), consistent with 2,4,6-trinitrophenylacetyl azide. The dichloromethane solution was concentrated to 15 mL before dry dichloroethane (40 mL) was added and solvent was distilled off to a volume of 25 mL. After 3.5 hours at 70°C, the solution was treated with charcoal and filtered and volatiles were removed under reduced pressure until crystals began to form. Hexanes were added to give 2.4 g, (90%) of **3**, mp 114–117°C. Crystallization from dichloroethane raised the mp to 116–118°C. ^1H NMR ($CDCl_3$): δ 5.10 (s, 2H), 9.17 (s, 2H); IR (KBr): 2305 (N=C=O), 1545, 1355 (NO_2)cm^{-1}. Anal. calcd. for $C_8H_4N_4O_7$: C, 35.83; H, 1.50; N, 20.89. Found: C, 35.72; H, 1.48; N, 20.65.

*2,4,6-Trinitrobenzylamine (**4**) Hydrochloride.* Conc. hydrochloric acid (3.5 mL) diluted with 7 mL of water was stirred at 65°C, while 0.63 g (0.00235 mol) of 2,4,6-trinitrobenzyl isocyanate was added over 2 minutes. The mixture was held at 75°C for 45 minutes before it was cooled, and a small amount of insoluble solid was removed by filtration. The filtrate was evaporated under reduced pressure to give 0.66 g (100%) of crystals, **4** hydrochloride, mp 198°C. Crystallization from methanol-dichloromethane raised the mp to 202°C; ^1H NMR (D_2O with 3-(trimethylsilyl)-1-propane-sulfonic acid, sodium salt hydrate as internal standard): δ 4.70 (s, 2H), 9.53 (s, 2H). Anal. calcd. for $C_7H_7N_4O_6Cl$: C, 30.18; H, 2.53; N, 20.11; Cl, 12.72. Found: C, 29.35; H, 2.89; N, 19.36; Cl, 11.89. Calcd. for $C_7H_7H_4O_6Cl \times 0.5\ H_2O$: C, 29.23; H, 2.80; N, 19.48; Cl, 12.32.

*2,4,6-Trinitrobenzylamine (**4**).* A solution containing 50 mg of **4** hydrochloride in 2 mL of water was stirred with ether (5 mL), while sodium bicarbonate was slowly added until the aqueous phase was basic to pH paper. The ether phase was separated and dried (Na_2SO_4) and the ether was quickly removed under reduced pressure to give a brown solid; ^1H NMR (CD_3CN): δ 4.20 (s, 2H), 9.00 (s, 2H).

N-(2,4,6-trinitrobenzyl)acetamide. A mixture of 0.15 g (0.54 mmol) of **4** hydrochloride and 2.5 mL of acetic anhydride was stirred, while pyridine was slowly added dropwise until all material was dissolved. After 3 minutes, the solution was poured into water to give an insoluble solid (0.09 g) which was removed by filtration. Extraction of the filtrate with dichloromethane gave additional solid (0.03 g) with the same melting point (130–131°C), which was not raised by the crystallization from dichloromethane-hexanes; ^1H NMR ($CDCl_3$): δ 1.96 (s, 3H, CH_3), 5.00 (d, 2H, CH_2), 6.4 (broad, NH), 9.08 (s, 2H, picryl H). Anal. calcd. for $C_9H_8N_4O_7$: C, 38.04; H, 2.84; N, 19.71. Found: C, 38.00; H, 2.89; N, 19.60.

ACKNOWLEDGMENTS

This work was supported by the Wright Laboratory, Munitions Division, Eglin AFB, FL. We thank Dr. P. R. Bolduc for advice and encouragement.

REFERENCES

[1] S. Zeman, *Thermochimica Acta*, 1979, 269; H. H. Cady, A. C. Larson, *Acta Cryst.*, 1965, 485; J. R. Holden, *Acta Cryst.*, 1967, 545; J. R. Holden, C. Dickinson, *J. Phys. Chem.*, 1972, 3597.

[2] T. N. Hall: Polynitroaromatic Addition Compounds, in H. Feuer (ed): *The Chemistry of the Nitro and Nitroso Groups Part 2*, Interscience Publishers, New York, p. 352 (1970).

[3] Z. Bonecki, T. Urbanski, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1961, 461.

[4] C. A. Fyfe, C. D. Malkiewich, S. W. H. Damji, A. R. Norris, *J. Am. Chem. Soc.*, 1976, 6983; G. P. Sollot, *J. Org. Chem.*, 1982, 2471.

[5] J. H. Boyer, P. F. Pagoria, T. P. Pillai, M. D. Pace, D. Stec, *J. Chem. Res., 5*, 1986, 416.