Novel Syntheses of 1,3,3-Trinitroazetidine

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Alternative methods for the synthesis of 1,3,3-trinitroazetidine (TNAZ) from epichlorohydrin, and benzhydrylamine have been developed. These approaches employ *N*-sulfonyl-3-(hydroxyimino)azetidines as penultimate intermediates and represent an improvement over previously published methods which require either diazo containing intermediates or involve low yielding procedures. Parallel methods employing *N*-benzhydryl- and *N*-benzyl-3-(hydroxyimino)azetidine were also investigated as alternate routes to TNAZ.

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Alternative syntheses for 1,3,3-trinitroazetidine (TNAZ) (**10**) have been the focus of some attention [1] due to its favorable detonation performance and melt-castable properties [2]. Until now, the only synthetic description to appear in the general literature suffers the disadvantage of a low yielding (8%) nitrolysis early on in a multi-step procedure starting from *t*-butylamine and epichlorohydrin [3], although this has since been improved to an overall yield of 9% (based on *t*-butylamine) [4] in semi-industrial scale trials. We now report attempts to develop processes circumventing the low yielding steps which employ inexpensive reagents and/or involve simple methodologies applicable for large scale work.

A report that *N*-tosyl-3-hydroxyiminoazetidine (**9**) underwent a smooth one-pot conversion to **10** [5] prompted us to focus on convenient approaches to **9**. *N*-Tosylazetidin-3-one (**8**), a precursor to **9**, has been previously reported [6], as have a number of other simple C-2-alkylated azetidin-3-ones [7-10]. The procedures quoted, provide the azetidin-3-ones by cyclization of the appropriate arylsulphonamoyl-1-diazo-2-alkanones. However, the involvement of diazo containing intermediates precludes such an approach since they are not well suited for scale-up.

Furthermore, of the limited number of azetidin-3-ones known, only the crystalline derivatives appear to have sufficient stability at ambient temperature to be convenient for further modification [11]. *N*-Benzhydrylazetidin-3-one (**5**) (mp 82°) was chosen as our initial target as it was easily accessible by oxidation of the corresponding azetidinol **4** [12][13] (which itself was available from condensation of epichlorohydrin (**1**) and benzhydrylamine (**2**) [14]). Moreover the hydrochloride of **5**, *i.e.* **6**, had been employed as hydrogenation substrate for the synthesis of azetidin-3-one hydrochloride (**7**) [11]. It followed, that this procedure could access **8** by an *in situ* reaction of tosyl chloride with the liberated free base of **7**.

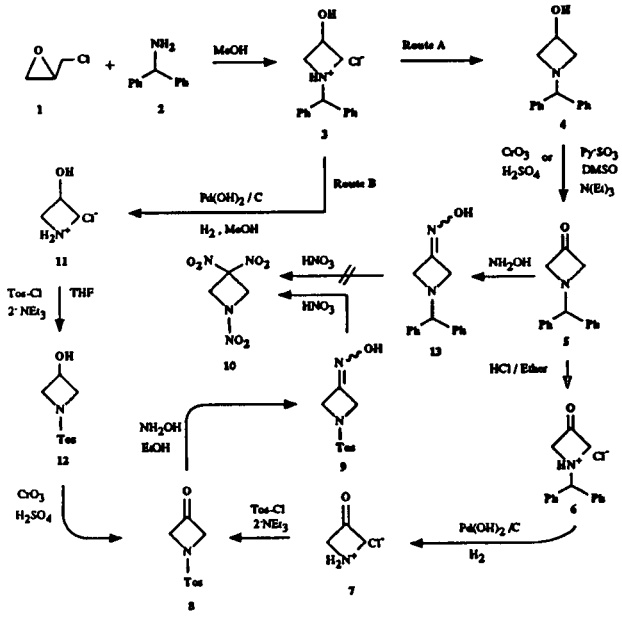
Accordingly we prepared **4** following the method of Anderson *et al.*, [14] in yields similar to those reported. Various oxidative techniques for the conversion of azetidinols to azetidinones have been employed, among them: pyridine-sulphur trioxide [13], trifluoroacetic anhydride, [11] and chromic anhydride [12]. Initially the latter of these appeared to be the method of choice based on considerations of cost *vs.* yield, and by adaptation of the method of Chatterjee *et al.*, [12] we isolated **5** in a yield of 58%. Following Baumann *et al.*, [11] the hydrogenolysis of hydrochloride (**6**) was achieved in methanol with a catalytic quantity of 20% palladium hydroxide on charcoal. In our hands however, we found the crystallization of **6** to be tedious. In addition, nmr studies of a vacuum dried sample indicated a contamination by significant quantities of crystal-bound methanol and another compound, presumably the dimethylketal 3,3-dimethoxyazetidine hydrochloride.

To minimize both the inconvenience and concomitant material losses, crude specimens of **7** were isolated from the methanolic solution and treated directly with tosyl chloride in ether in the presence of triethylamine. This process (Route A) (scheme 1) afforded **8** directly in a yield of 52% from **6**. Conversion of **8** to **9** was achieved in 93% yield by adaptating a published method [15] previously used for the oximation of 1-alkoxy-carbonylazetidin-3-ones.

The oxidative stage in this series of transformations towards **8** was also examined in an alternate route. In this pathway (Route B), the hydrogenolysis was carried out first on the hydrochloride (**3**). This approach had the added advantage that **3** was in fact the product initially isolated by the original condensation of the epichlorohydrin and benzhydrylamine. Thus, with minimal purification, **3** was catalytically reduced in a similar way as that used to reduce **6**. The hygroscopic product, azetidin-3-ol hydrochloride (**11**) was then liberated in the presence of tosyl chloride without isolation to afford the novel azetidin-3-ol (**12**) in an overall yield of 78% yield from **3**. However, the yields for the chromic acid oxidation of **12** to **8** were poor and offered no improvement over that of **4** to **5**.

In terms of our original goals, the yields and convenience of both these chromium mediated oxidations were not satisfactory, we therefore examined the pyridine-sul-

Scheme 1



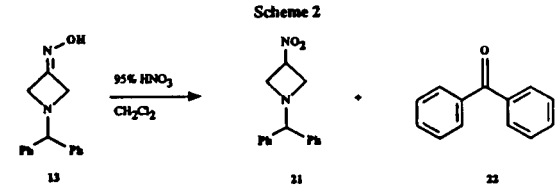
phur trioxide process advocated by Morimoto and coworkers [13]. Under the conditions described we could isolate **5** from **4** in 85% yield. With this improvement benzhydrylamine and epichlorohydrin can be converted to **9** in an overall yield of 21%. Disappointingly however, the pyridine-sulfur trioxide mediated oxidation of **12** gave **8** in only low yield thus diminishing the value of Route B.

With a reliable and high yielding route available for the preparation of **9** we examined its behavior under nitrolytic conditions. Treatment with 95% fuming nitric acid in refluxing methylene chloride afforded TNAZ (**1**) in 30-45% yield.

More recently it came to our attention that the benzhydryl group of *N*-benzhydryl-3-hydroxyiminoazetidine (**13**) had also been converted to TNAZ by treatment with fuming nitric acid in methylene chloride [16]. As this would greatly reduce the overall complexity of the present route to TNAZ we prepared **13** in essentially quantitative yield by treating **5** with hydroxylamine in ethanol. In our hands however, five equivalents of 95% fuming nitric acid in refluxing methylene chloride laboratory did not convert **13** to TNAZ but rather gave multicomponent mixtures from which *N*-benzhydryl-3-nitroazetidine (**21**) and benzophenone (**22**), could be isolated in 8% and 37% yields, respectively (Scheme 2). To determine if stronger nitrolytic conditions could complete the conversion, 98% fuming nitric acid was employed. However, TNAZ could not be isolated from the product mixture which was similar to the previous experiment albeit with a marginal shift in product distribution.

Even in light of the improvement offered by the use of **9**, the cost of benzhydrylamine still undermined the value of this procedure in terms of its commercial applicability.

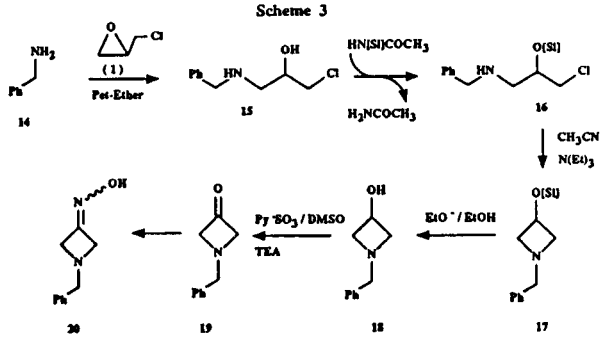
Scheme 2



We therefore examined a parallel procedure employing benzylamine, which is available at a fraction of the cost of benzhydrylamine. *N*-Benzylazetidin-3-ol (**18**) is available from a series of reactions starting from benzylamine (**14**) and epichlorohydrin (**1**). However, despite patent claims [17] that the initially formed alicylic aminoalcohol **15** could be prepared in a variety of organic solvents, we found **18** was only obtained if the original condensation was carried out in petroleum ether with **15** being protected as its *O*-silylether **16** prior to cyclization to the silyloxy azetidine **17** as described by Higgins *et al* [18][19]. Following the details in that description we found the purification of **17** by distillation to be somewhat capricious and strict adhesion to the experimental details decribed herein was necessary to afford **17** in 42% overall yield from **1**. The base catalyzed conversion of **17** to **18** was facile and could be achieved in a yield of 77% on a 0.09 mole scale.

With a viable method available to prepare **18**, we investigated its oxidation to *N*-benzylazetidin-3-one (**19**). Employing similar Swern oxidative conditions as used previously, **18** was treated with pyridine-sulfur trioxide in dimethyl sulfoxide. However, although complete consumption of starting material was indicated we were unable to isolate **19** by chromatographic methods. The apparent instability of **19** precluded its use as an alternative for **5**. However, since its oxime analogue **20** was expected to be more stable and might also be of some value as a TNAZ precursor we treated the crude product mixtures of **19** with hydroxylamine. This one pot procedure afforded the novel oxime adduct **20**, however it was available in only 17% yield (Scheme 3).

Scheme 3



Considering the failure of **13** to undergo conversion to TNAZ and the difficulty associated with obtaining gram quantities of **20** no attempt was made to examine the

nitrolytic behavior of the latter.

Thus TNAZ is available *via* **9** in a process which does not require the synthesis or participation of diazo containing materials and in an overall yield many times better than the previously reported [2] process.

EXPERIMENTAL

Melting points were recorded on a Bristoline hot-stage microscope and are uncorrected. The nmr spectra were recorded on either Varian VXR-300, GE-QE300 and/or Unity 500 MHz spectrometers. Chemical shifts are relative to internal tetramethylsilane for ^1H and ^{13}C spectra. All spectra were obtained from deuteriochloroform or deuteriochloroform/D_6-dimethyl sulfoxide solutions as noted, and are reported as chemical shift (δ) in ppm. Examination of the observed multiplicities for the H-2/4 and H-3 signals in the azetidin-3-ols and silyloxy derivatives were consistent with a non-first order system (AA'BB'X). Accordingly these signals have been recorded as multiplets. Microanalyses were carried out on a Carbo Erba 1106 elemental analyser. Mass measurements were made on a Finnigan Mat 95Q mass spectrometer.

N-Benzhydrylazetidin-3-ol Hydrochloride (**3**) and *N*-Benzhydrylazetidin-3-ol (**4**).

Compound **3** was prepared according to Lok *et al.*, [14] from benzhydrylamine and epichlorohydrin. The overall yield of **4** was 53%, mp 113-114°, lit [14] 113°.

N-Benzhydrylazetidin-3-one (**5**)

A solution of a pyridine-sulphur trioxide complex (5.00 g, 31.0 mmoles) in dimethyl sulfoxide (20 ml) was added dropwise to a stirred solution of **4** (1.19 g, 5.0 mmoles) and triethylamine (5.05 g, 50.0 mmoles). The mixture was then immersed in an oil bath pre-heated to 50° for 0.5 hours, poured into ice water (150 ml) and extracted into ethyl acetate (2 x 100 ml). The organic layer was washed with cold water (3 x 100 ml) and dried (magnesium sulphate). The solvent was removed *in vacuo* to a tan oil which solidified upon standing. The product was purified by collecting the appropriate fractions after elution (benzene/ethyl acetate 5:1) from a column of silica to yield a colorless solid (0.70 g, 60%), mp 78-80°, lit [13] 77-78°; ^1H nmr: δ 3.96, (s, 4H, $(CH_2)_2N$), 4.56, (s, 1H, $(Ph)_2CH$), 7.18, (m, 2H, ArH), 7.27, (m, 4H, ArH), 7.30, (m, 4H, ArH); ^{13}C nmr: δ 74.1, C-2; 77.7 $NC(Ph)_2$; (127.2, 127.4, 128.6, 142.3), Ar; 200.9, C(O).

N-Tosylazetidin-3-ol (**12**).

Palladium hydroxide (20% Pd on carbon) [20] (0.40 g) was added to a methanolic solution (60 ml) of **3** (3.30 g, 12.0 mmoles) and shaken under an atmosphere of hydrogen gas (55 psi) in a Parr hydrogenation apparatus for 72 hours. The mixture was filtered through a pad of Celite into a flask and the solvent removed *in vacuo*. The resulting semi-solid containing **11** was suspended in dry ether (3 x 60 ml) and the solvent decanted twice. Tosyl chloride (2.29 g, 12.0 mmoles) in ether (25 ml) was added followed by triethylamine (2.67 g, 26.4 mmoles) in ether (20 ml). The mixture was then stirred overnight and washed with dilute sodium bicarbonate (2 x 40 ml). The aqueous fraction was re-extracted with ether (3 x 50 ml) and the organic layers combined, dried over calcium chloride and concentrated to an oil which was passed down a short column of silica. Elution with chloroform and concentration of the appropriate fractions afforded a clear oil which crystallized slowly from ethyl acetate/hexane to a solid, (2.13 g, 78%) mp 103-104°; ^1H nmr: δ 2.44, (s, 3H, $PhCH_3$), 3.21, (d, J = 6.04 Hz, 1H, OH), 3.52 (m, 2H, $(CH_2)N$), 3.92, (m, 2H, $(CH'_2)N$), 4.40, (m, 1H, *CH*OH); ^{13}C nmr: δ 21.5, $ArCH_3$, 29.5, C-2; 60.0, C-3, (128.2, 129.8, 130.7, 144.3), Ar.

Anal. Calcd. for $C_{10}H_{13}NSO_3$: C, 52.85; H, 5.77; N, 6.17; Found: C, 52.76, H, 6.04; N, 5.95.

N-Tosylazetidin-3-one (**8**).

Method A.

A stream of dry hydrogen chloride gas was passed through a dry chilled ether solution (50 ml) of **5** (3.39 g, 14.3 mmoles) for 20 minutes. The precipitate of **6** (4.11 g, 95%) was collected by vacuum filtration and washed with dry ether (3 x 50 ml) air dried and dissolved in dry methanol (100 ml). Palladium hydroxide (20% Pd on carbon) (0.50 g) was added and the mixture shaken under a positive atmosphere of hydrogen gas (55 psi) for 72 hours. The suspension was passed through a pad of Celite into a flask and the solvent removed *in vacuo*. The residue was suspended in anhydrous ether (3 x 50 ml) and the solvent decanted twice. An ether solution (50 ml) of tosyl chloride (2.86 g, 15.0 mmoles) was added. This was followed by the dropwise addition of triethylamine (3.33 g, 33.0 mmoles) in ether (50 ml). The mixture was stirred at room temperature overnight, evaporated to dryness and partitioned between chloroform (150 ml) and dilute sodium bicarbonate (100 ml). The aqueous phase was re-extracted with chloroform (100 ml) and the combined organic fractions dried over calcium choride. Removal of the solvent afforded a pale semi-solid which was passed down a short column of silica by elution with chloroform. Concentration of the appropriate fractions gave **8** (1.75 g, 52%), mp 149°; ^1H nmr: δ 2.49, (s, 3H, $ArCH_3$); 4.62, (s, 4H, $(CH_2)_2N$), 7.40, (d, 2H, J = 8.5 Hz, ArH), 7.80, (d, 2H, J = 8.3 Hz, ArH); ^{13}C nmr: 21.6 $ArCH_3$, 72.4, C-2, (128.3, 130.1, 131.3, 145.1), Ar, 192.6, C(O).

Anal. Calcd. for $C_{10}H_{11}NO_3S$: C, 53.32; H, 4.92; N, 6.22; Found: C, 53.58, H, 4.95, N, 6.06.

Method B.

Sulfuric acid (0.36 g) was added dropwise to a chilled mixture of chromic anhydride (0.12 g, 1.2 mmoles), acetic acid (0.35 ml) 15% aqueous acetone (2 ml) and **12** (0.21 g, 1.0 mmole) at such a rate as to maintain the temperature between -5° and 0°. The mixture was then stirred at this temperature for 2 hours and then permitted to warm slowly to room temperature overnight. The chilled mixture was then quenched with concentrated aqueous ammonia until the *p*H $\cong$ 8. Coarse salt (100 g) was added and the slurry stirred with ether (4 x 100 ml). The decanted fractions were combined, dried over magnesium sulphate for several hours and the solvent removed in *vacuo* to a oil which was crystallized from hexane/benzene to a solid (0.10 g, 40%) identical with that isolated by method A.

N-Tosyl-3-(hydroxyimino)azetidine (**9**).

Hydroxylamine hydrochloride (1.00 g, 14.5 mmoles) and sodium hydroxide (0.58 g, 14.5 mmoles) were added to a ethanolic solution (10 ml) of **5** containing a few drops of water.

The solution was stirred at room temperature for 1 hour and refluxed for 1 hour. The mixture was concentrated to dryness then partitioned between chloroform (100 ml) and water (100 ml), the organic layer was separated and dried over magnesium sulphate and concentrated *in vacuo* to a solid which was recrystallized from ethyl acetate/hexane to colorless needles, (1.64 g, 96%); ^{1}H nmr: 2.46, (s, 3H, $ArCH_3$), 4.45, (s, 4H, $N(CH_2)_2$); 7.44, (d, J = 8.1 Hz, 2H, ArH), 7.75, (d, J = 8.3 Hz, 2H, ArH), 10.98, (s, 1H, NOH); ^{13}C nmr: 21.1, $ArCH_3$, 58.9, C-2/C-4, 59.2, C-2/C-4, (128.0, 129.7, 130.3, 142.1), Ar, 144.2, C=NOH.

Anal. Calcd. for $C_{10}H_{12}N_2O_3S$: C, 49.99; H, 5.03; N, 11.66; Found: C, 49.91; H, 4.90; N, 11.41.

N-Benzhydryl-3-(hydroxyimino)azetidine (**13**).

A mixture of hydroxylamine hydrochloride (0.70 g, 10 mmoles), sodium hydroxide (0.40 g, 10.0 mmoles) and **5** (0.19 g, 5.0 mmoles) in ethanol (50 ml) containing a few drops of water were stirred under reflux overnight. The mixture was then evaporated to dryness under reduced pressure and the residue partitioned between water (100 ml) and chlorofrom (2 x 100 ml). The organic fraction was dried (magnesium sulphate) and concentrated *in vacuo* to a crystalline material which recrystallized from ethyl acetate/hexane to afford colorless crystals (1.25 g, 99%), mp 165-166° lit [13] 169-170°; ^{1}H nmr: 3.82, (s, 4H, $(CH_2)_2N$), 4.61, (s, 1H, $(Ph)_2CH$, (7.18, 7.26, 7.45), (3 x m, 10H, ArH), 10.55, (s, 1H, OH); ^{13}C nmr: δ 59.9, C-2/4, 60.5, C-2/4, 75.92, $(Ph)_2C$, (127.0, 127.1, 128.5, 142.6), Ar, 148.6, C=NOH.

Anal. Calcd. for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.39; N, 11.10. Found: C, 76.12; H, 6.36, N, 11.06. $M^{+\cdot}$ = 252 amu.

1-Chloro-3-benzylpropan-2-ol (**15**) and *N*-Benzyl-3-(trimethylsilyloxy)azetidine (**17**).

Epichlorohydrin (**1**) (18.50 g, 0.20 mole) and benzylamine (**14**) (21.44 g, 0.20 mole) were stirred in petroleum ether (200 ml) at room temperature for 48 hours. The precipitate of **15** could be collected by vacuum filtration and recrystallized from toluene to a colorless crystalline material (36.70 g, 92%), mp 70-72° lit [17] 70-71°. For the conversion of **15** to **17** it was not necessary to isolate **15**. Thus under an atmosphere of nitrogen, *N*-trimethylsilylacetamide (26.20 g, 0.2 mole) was added to the suspension of **15** and the mixture refluxed for 3 hours. Upon cooling, a precipitate of acetamide was removed by filtration and the filtrate concentrated *in vacuo*. Acetonitrile (200 ml) and triethylamine (35.4 ml, 0.25 mole) were then added and the mixture refluxed for 3 days. The cooled mixture was filtered and the solvent removed at reduced pressure while avoiding temperatures above 40°. Petroleum ether (50 ml) was added and any further precipitate removed. The mixture was reconcentrated and then left under vacuum (1 mm Hg) for 0.5 hours and then flash distilled by immersion in a preheated oil bath (135°) at (85°/0.9 mm Hg) to afford **17** as a clear oil (20.10 g, 42%); ^{1}H nmr: δ -0.05, (s, 9H, $Si(CH_3)_3$), 2.74, (m, 2H, $(CH_2)N$), 3.52, (m, 4H, $[(CH'_2)N + PhCH_2]$), 4.27, (m, 1H, H-3), 7.10-7.25, (m, 10H, ArH); ^{13}C nmr: δ -0.5, $Si(CH_3)_3$, 61.8, C-3, 63.7, $PhCH_2$, 64.1, C-2/4, (126.7, 128.0, 128.2, 138.0), Ar.

N-Benzylazetidin-3-ol (**18**).

A methanolic solution (10 ml) of sodium methoxide (freshly prepared from sodium metal (5 mg)) was added to **17** (20.10 g, 85.5 mmoles) in methanol (150 ml) and stirred at room temperature for 1 hour. The solvent was removed at reduced pressure and the remaining oil dissolved in ether. Any precipitated material was removed by filtration and the filtrate reconcentrated and triturated with petroleum ether/diethyl ether. The product was then recrystallized from the same solvent mixture to a colorless solid (10.80 g, 77%) mp 64-65° lit [21] 66-67°; ^{1}H nmr: 2.89, (m, 2H, $(CH_2)N$), 3.51, (m, 2H, $(CH'_2)N$), 3.56, (s, 2H, $PhCH_2$), 4.30, (m, 1H, H-3), 5.70, (br s, 1H, OH), 7.28, (m, 5H, ArH); ^{13}C nmr: δ 61.5, C-3, 63.35, $PhCH_2$, 63.6, C-2/4, (127.2, 128.2, 128.5, 137.1), Ar.

N-Benzyl-3-(hydroxyimino)azetidine (**20**).

A solution of a pyridine-sulfur trioxide complex (10.00 g, 63.0 mmoles) in dimethyl sulphoxide (30 ml) was added dropwise to a stirred solution of **18** (1.63 g, 10.0 mmoles) and triethylamine (10.10 g, 100 mmoles). The stirred mixture was then immersed in an oil bath pre-heated to 40° for 0.5 hours, poured into ice water (150 ml) and extracted into ethyl acetate (2 x 100 ml). The organic layer was washed with cold water (3 x 100 ml) and dried (magnesium sulphate). The solvent was removed *in vacuo* to a tan oil (1.06 g) which was dissolved in ethanol (30 ml). Hydroxylamine hydrochloride (0.50 g, 72.0 mmoles) and sodium hydroxide (0.29 g, 72.0 mmoles) dissolved in water (2 ml) were added and the resulting solution stirred at room temperature overnight. The mixture was concentrated to dryness and the residue partitioned between chloroform (50 ml) and water (50 ml). The aqueous layer was reextracted with chloroform (50 ml) and the combined chloroform extracts dried (sodium sulphate) and concentrated at reduced pressure to a semi-solid material which was purified by elution (chloroform) from a column of silica to yield a material which was recrystallized from ethyl acetate/hexane to yield (0.20 g, 17%) **20** mp 110-111°; ^{1}H nmr: δ 3.79, (s, 2H, $PhCH_2$), 4.02, (m, 2H,$(CH_2)N$), 4.09, (m, 2H, $(CH'_2)N$), 7.29, (br s, 5H, ArH), 10.6, (br s, 1H, NOH); ^{13}C nmr: δ (61.1, 61.8, 62.8), C-2/4 + CH_2Ph, (127.4, 128.5, 128.6, 136.9) Ar, 150.3, C=NOH.

Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90. Found: C, 68.16; H, 6.86; N, 15.95.

Nitrolysis of *N*-Benzhydryl-3-(hydroxyimino)azetidine (**20**).

Fuming nitric acid (~95%) (0.99 ml, 27.8 mmoles) to a suspension of **20** (0.70 g, 2.78 mmoles) in dry methylene chloride (30 ml) and the mixture refluxed until the blue color no longer persisted (10 hours). The mixture was then poured onto ice (30 g) and neutralized by the addition of sodium bicarbonate. The mixture was extracted with chloroform (3 x 40 ml), dried over magnesium sulphate and concentrated under reduced pressure. Elution from a column of silica (hexane:ethyl acetate; 9:1) gave benzophenone (**22**) (0.19 g, 37%), and *N*-benzhydryl-3-nitroazetidine (**21**) (0.06 g, 8%); ^{1}H nmr: δ 3.60, (d, J = 6.34 Hz, 4H, H-2/4), 4.88, (s, 1H, $(Ph)_2CH$), 5.03, (m, 1H, H-3), 7.15-7.31, (m, 6H, ArH), 7.40, (m, 4H, Ar-H); ^{13}C nmr: 57.5, C-2; 72.1, Ph_2CHN, 77.4, C-3; (127.2, 127.5, 128.6, 140.9), Ar. A peak at m/z = 269.1286 amu was detected by high resolution chemical ionization mass spectrometry; Calcd. for $C_{16}H_{16}N_2O_2$ + H: requires 269.1290 amu.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.63; H, 6.03; N, 10.44.

1,3,3-Trinitroazetidine (**10**).

Fuming nitric acid (~95%) (0.74 ml, 17.5 mmoles) was added in one portion to a suspension of **9** (0.80 g, 3.33 mmoles) in

anhydrous methylene chloride (20 ml). The resulting dark blue solution was refluxed for 10 hours with the liberation of nitrous oxide and a progressive change in color from light blue through to yellow. The mixture was then poured onto ice and neutralized to *p*H = 7-8 and extracted with methylene chloride (3 x 50 ml), dried over magnesium sulphate and the solvent removed *in vacuo* to semi-solid which was passed down a short column of silica (chloroform) and concentrated to dryness. The residue was then recrystallized from carbon tetrachloride to afford white crystals in variable yield (30-45%) which melted at 100-101° lit [2] 103°. Methane positive chemical ionization mass spectrometry detected an ion at m/z = 193 which is accounted for by $[M+H]^+$. ^1H nmr: δ 5.20, (s, 4H, $N(CH_2)_2$). ^{13}C nmr: 63.3, C-2, 97.7, C-3.

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