trifluoroacetate. An axial/equatorial preference of 5:95 was achieved.

Experimental Section

General Methods. Reactions were conducted under argon in a 25-mL two-necked flask fitted with a rubber septum. Liquids were transferred via argon-flushed syringes. Benzene and toluene were distilled from sodium/benzophenone ketyl; tris(triphenylphosphine)rhodium(I) chloride and tris(tripenylphosphine)ruthenium(II) dichloride were obtained from Alfa, Danvers, MA; alkylsilanes were obtained from Petrarch Systems, Bristol PA, and used without purification. An authentic mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanol for GLC comparison was prepared by lithium aluminum hydride reduction of 4-*tert*-butylcyclohexanone in ether.[11] Triethylsilyl deuteride[12] and 2,2,6,6-tetradeuterio-4-*tert*-butylcyclohexanone[13] were prepared by literature methods.

GLC analyses were obtained on a Perkin-Elmer 3920 gas chromatograph fitted with a flame-ionization detector. Separations were provided by a 6 ft × $^1/_8$ in., 5% 2:1 FFAP/Bentone aluminum column.

Triethylsilane/Rhodium(I)-Catalyzed Reduction. To an orange homogeneous solution of 154 mg (1.00 mmol) of 4-*tert*-butylcyclohexanone and 45 mg (0.050 mmol) of tris(triphenylphosphine)rhodium(I) chloride in 5.0 mL of benzene was added 0.24 mL (1.5 mmol) of triethylsilane. The reaction mixture turned yellow and was heated at reflux for 1 h. The resulting deep red solution was concentrated by rotary evaporation. The residual oil was diluted with 5 mL of hexane, filtered, concentrated, and chromatographed on silica gel (3% ether–hexane) to afford 249 mg (92%) of *cis,trans*-[(4-*tert*-butylcyclohexyl)oxy]triethylsilane as a colorless liquid: IR (film) 2945, 1453, 1365, 1237, 1090, 1009, 843, 745 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.45–2.1 (br, ~q at 0.65, J = 7 Hz, and s at 0.85, 33 H), 3.45 (br s, ~1 H); mass spectrum, m/e (relative intensity) 270 (M$^+$, 1), 242 (22), 241 (100), 137 (23), 103 (93), 87 (11), 81 (16), 75 (66); exact mass calcd for $C_{16}H_{34}OSi$ m/e 270.2379, found 270.2381; GLC analysis, two major peaks (97% of total peak area) in an area ratio of 11:89, corresponding to the axial/equatorial isomers, respectively.

Diethylsilane/Rhodium(I)-Catalyzed Reduction. To an orange solution of 154 mg (1.00 mmol) of 4-*tert*-butylcyclohexanone and 9.0 mg (0.010 mmol) of tris(triphenylphosphine)-rhodium(I) chloride in 5.0 mL of benzene was added dropwise 0.15 mL (1.1 mmol) of diethylsilane. The reaction was mildly exothermic and turned yellow. After 15 min the solution was concentrated by rotary evaporation, and the residual oil was diluted with 3 mL of hexane. The resulting slurry was filtered, concentrated, and evaporatively distilled [60 °C (0.10 torr)] to afford 235 mg (97%) of *cis,trans*-[(4-*tert*-butylcyclohexyl)oxy]-diethylsilane as a colorless low melting solid: IR (film) 2960, 2102, 1463, 1371, 1240, 1090, 1057, 1012, 861, 830 cm^{-1}; ^{1}H NMR (CCl_4) δ 0.60–2.4 (br, with s at 0.87, 28 H), 3.45 (br s, 0.5 H), 3.97 (m, 0.5 H), 4.38 (m, 1 H); mass spectrum m/e (relative intensity) 242 (m$^+$, 15), 213 (58), 177 (17), 143 (49), 138 (73), 137 (54), 123 (58), 99 (59), 83 (65), 82 (77), 81 (100), 80 (61), 75 (48); exact mass calcd for $C_{14}H_{30}OSi$ m/e 242.2066, found 242.2054; GLC analysis, two major peaks (99% of total peak area) in a 47:53 area ratio corresponding to the axial/equatorial isomers, respectively.

Triethylsilane/Ruthenium(II)-Catalyzed Reduction. To a solution of 154 mg (1.00 mmol) of 4-*tert*-butylcyclohexanone, 48 mg (0.05 mmol) of tris(triphenylphosphine)ruthenium(II) dichloride, and 11 mg (0.05 mmol) of silver trifluoroacetate[14] in 5.0 mL of toluene was added 0.24 mL (1.5 mmol) of triethylsilane. The reaction mixture was heated at reflux and turned purple after several min. After 20 h at reflux, the solution was concentrated by rotary evaporation, diluted with 3 mL of hexane, filtered, concentrated, and evaporatively distilled [70 °C (0.10 torr)] to yield 260 mg (96%) of *cis,trans*-[(4-*tert*-butylcyclohexyl)oxy]-triethylsilane as a colorless liquid. GLC analysis: two major peaks (97% of the total peak area) in a 5:95 area ratio corresponding to the axial/equatorial isomers, respectively.

General Procedure for Hydrolysis of Silyl Ethers. A solution of the crude silyl ether and a few crystals of *p*-toluenesulfonic acid hydrate in 5 mL of 10% aqueous methanol was stirred at 25 °C for 1 h. An aliquot was removed for GLC analysis.

Registry No. 3a (R_3 = Et_3), 81256-40-8; **3a** (R_3 = Et_2, H), 81256-41-9; **3a** (R_3 = Ph_3), 81256-42-0; **3a** (R_3 = Me_2, Ph), 81256-43-1; **3a** (R_3 = OEt_3), 81256-44-2; **3a** (R_3 = Cl_3), 81256-45-3; **3a** (R_3 = Ph_2, H), 81256-46-4; **3b** (R_3 = Et_3), 81256-47-5; **3b** (R_3 = Et_2, H), 81256-48-6; **3b** (R_3 = Ph_3), 81256-49-7; **3b** (R_3 = Me_2, Ph), 81256-50-0; **3b** (R_3 = OEt_3), 81278-81-1; **3b** (R_3 = Cl_3), 81256-51-1; **3b** (R_3 = Ph_2, H), 81256-52-2; Et_3SiH, 617-86-7; Et_2SiH_2, 542-91-6; Ph_3SiH, 789-25-3; $PhMe_2SiH$, 766-77-8; $(EtO)_3SiH$, 998-30-1; Cl_3SiH, 10025-78-2; Ph_2SiH_2, 775-12-2; 4-*tert*-butylcyclohexanone, 98-53-3; tris(triphenylphosphine)rhodium(I) chloride, 14694-95-2; tris(triphenylphosphine)ruthenium(II) dichloride, 15529-49-4.

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[12] Doyle, M. P.; McOsker, C. C.; West, C. T. *J. Org. Chem.* **1975**, *41*, 1393.

[13] Geneste, P.; Lamaty, G. *Bull. Soc. Chim. Fr.* **1968**, 669.

[14] Janssen, D. E.; Wilson, C. V. "Organic Syntheses"; Rabjohn, N., Ed.; Wiley: New York, 1963, Collect. Vol. IV, p 547.

Conversion of 2,4,6-Trinitrobenzyl Chloride to 2,2′,4,4′,6,6′-Hexanitrostilbene by Nitrogen Bases

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In Shipp and Kaplan's report of the remarkably facile preparation of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) from 2,4,6-trinitrotoluene (TNT) and alkaline hypochlorite, it was disclosed that 2,4,6-trinitrobenzyl chloride (TNBzCl) is obtainable in 85% crude yield by quenching the reaction after only 1 min, and is converted to HNS by reaction with sodium hydroxide.[1] The sequence in eq 1 and 2 was

$$\underset{\text{TNT}}{\text{PiCH}_3} \xrightarrow{\text{OH}^-} \text{PiCH}_2^- \xrightarrow[\text{OCl}^-]{[\text{Cl}^+]} \underset{\text{TNBzCl}}{\text{PiCH}_2\text{Cl}} \qquad (1)$$

$$\underset{\text{TNBzCl}}{\text{PiCH}_2\text{Cl}} \xrightarrow{\text{OH}^-} \text{PiCHCl}^- \xrightarrow{\text{PiCH}_2\text{Cl}} \text{PiC(Cl)HCH}_2\text{Pi} \xrightarrow[-\text{HCl}]{\text{OH}^-} \underset{\text{HNS}}{\text{PiCH=CHPi}} \qquad (2)$$

Pi = picryl = 2,4,6-trinitrophenyl

suggested to account for these transformations. HNS was reportedly obtained in yields up to 50% from TNBZCl and up to 42% from TNT. The yields cited, however, included coprecipitated byproducts, largely 2,2′,4,4′,6,6′-hexanitrobibenzyl, which are removable by washing with acetone. On attempting to duplicate the crude HNS yield of 50% using TNBzCl and sodium hydroxide in the prescribed mole ratio of 1,[2] we obtained a 46% yield. This was reduced to 40% on washing with acetone.[3]

We report here that HNS can be obtained from TNBzCl in substantially improved yields by using certain nitrogen bases in place of sodium hydroxide. Bases in the pK_B range of 2.8–8.8 have been examined and are listed in Table I together with the yields of HNS obtained from

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[1] Shipp, K. G.; Kaplan, L. A. *J. Org. Chem.* **1966**, *31*, 857.

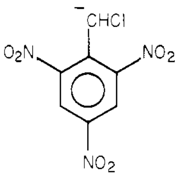
[2] No HNS is obtained when the NaOH/TNBzCl molar ratio equals 2.[1]

[3] The yield on starting with TNT and alkaline hypochlorite was similarly decreased from 42% to 37%.

[4] (a) Dean, J. A., Ed. "Lange's Handbook of Chemistry", 12th ed.; McGraw-Hill: New York, 1979; p 5–14. (b) Hall, J. L.; Fisher, J. F. *Proc. W. Va. Acad. Sci.* **1962**, *34*, 85; *Chem. Abstr.* **1963**, *59*, 3748*d*. (c) "CRC Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1979; p D-161.

them. The base/TNBzCl molar ratio was optimized at around 2.4 for triethylamine, isopropylamine, and ethanolamine (Table I), and this was used to compare the rest of the series. In general, bases with pK_B values from 3.0 to 5.0 gave higher yields of the acetone-washed product than did sodium hydroxide, producing in about 50% yield and above. Yields exceeding 60% were obtained with bases having pK_B values between 3.2 and 4.6, with some exceptions, notably methyl- and dimethylamines and ethylenediamine, which afforded yields of around 50%.[5] Cyclohexylamine, *n*-butyl- and isobutylamines, *N*,*N*-diethylethanolamine, and ethanolamine gave somewhat lower yields than isopropylamine and triethylamine which produced HNS in the highest yields, around 70%. Bases outside the pK_B range 3.0–5.0, specifically piperidine and morpholine and especially triethanolamine and pyridine, produced lower yields than sodium hydroxide.

Particularly in the case of amines affording yields over 60%, it is evident that the availability of hydroxide ion upon hydrolysis (1) is adequate, such that the desired reaction (eq 2), presumably requiring the intermediacy of the α-chlorotrinitrobenzyl anion (1),[1,6,7] is the major process occurring, and (2) is sufficiently limited that the formation of unwanted products, for example, an anionic σ complex such as 2, is minimized.[8,9] This situation, although dependent on the concentration of OH^-, is not readily achievable with sodium hydroxide due to its complete dissociation in water. With an amine (or ammonia) as the source of OH^-, all of the OH^- capable of being generated is not immediately available but is gradually available, as the well-known equilibrium in eq 3 is shifted by consumption of OH^-. Thus it is seen that 2 molar equiv of a suitable amine, potentially yielding 2 molar equiv of OH^-, can produce HNS in high yield, while 2 molar equiv of sodium hydroxide produces no HNS at all, as reported by Shipp and Kaplan.[1,10] Interfering side reactions are less important when OH^- is supplied in a continuous, "controlled" manner as from an amine than when OH^- is made available all at once as with sodium hydroxide.



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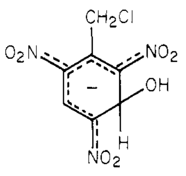

2

$$\text{amine} + H_2O \underset{}{\overset{K_b}{\rightleftharpoons}} \text{amine:}H^+ + OH^- \qquad (3)$$

This explanation for the difference in behavior of nitrogen bases and sodium hydroxide on reacting with TNBzCl is consistent with Bernasconi's and Fyfe et al.'s detection of several different processes dependent on base concentration in their studies of reactions of TNT in basic solution.[8,11] The key to obtaining high yields of HNS from TNBzCl, however, appears to be the controlled availability of OH^-, superimposed on the lowering of the OH^- concentration to a suitable level, in view of Shipp and Kaplan's finding that the yield of HNS is maximized at a sodium hydroxide/TNBzCl molar ratio of 1 and falls off to zero as the molar ratio is decreased to zero.[1,12]

Experimental Section

Caution! HNS and TNBzCl, like TNT, are explosive compounds and may detonate on grinding or impact.

Materials. TNBzCl was prepared by the method of Shipp and Kaplan,[1] adding a solution of 10 g (44 mmol) of TNT in 100 mL of THF and 50 mL of methanol to 100 mL of "5%" aqueous sodium hypochlorite (Clorox). The reaction was carried out at 0–15 °C for 1 min as prescribed;[1] however, for the purpose of this study, the product was isolated and purified by a modified procedure as follows. The reaction was quenched by the addition of 10 mL of concentrated hydrochloric acid to the reaction mixture. The mixture was stirred for a few seconds, after which the oil was allowed to separate for 0.5 h in the ice–salt bath. The clear, yellow-orange solvent phase was decanted, and the oil was washed with water several times in the reaction flask. The oil solidified, and the orange crystalline solids, slightly oily, were washed onto a filter with water and dried; yield 9.9 g (lit.[1] 10 g; 85%). The solids were taken up in 70 mL of hot benzene, and the solution was dried with 2 g of anhydrous magnesium sulfate. The solution was filtered, diluted with an approximately equal volume of hot hexane, and chilled 3 h, giving 6.0 g of yellow-orange needles, mp 77–81 °C (after losing solvent of crystallization). The crystals were taken up in 300 mL of boiling carbon tetrachloride, and the solution was filtered hot to remove 0.9 g of insoluble red-brown taffylike material. Concentration of the filtrate to approximately 125 mL and chilling overnight gave 4.1 g of fluffy yellow powder, mp 84–86 °C (lit.[1] mp 85 °C; cream-colored powdery solid from benzene–hexane). Further concentration and chilling gave an additional 0.5 g of product: mp 84–86 °C; NMR ($CDCl_3$) δ 5.13 (2 H, s, CH_2), 8.95 (2 H, s, picryl); IR (KBr) 3110 (s), 3070 (m), 3030 (w), 2885 (w), 1622 (s), 1605 (s), 1535 (vs), 1455 (s), 1410 (m), 1342 (vs), 1278 (s), 1275 (m), 1209 (m), 1172 (m), 1142 (w), 1091 (s), 944 (m), 929 (s), 924 (s), 893 (m), 836 (w), 819 (s), 799 (m), 753 (w), 730 (s), 716 (s), 639 (w), 554 (w), 536 (w), 373 (w) cm^{-1}.

The various nitrogen bases, diethylamine, ethylamine (70% in water), dimethylamine (25% in water), methylamine (40% in

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[5] The yields obtained from methyl- and dimethylamines and ethylenediamine appear, in particular, to be abnormally low, on the basis of a graph of yields as a function of pK_B's (Table I). In the case of dimethylamine, the lower yield is attributable at least in part to a side reaction producing a significant amount of byproduct whose identity remains inconclusive (see Experimental Section). Amines can react with trinitro aromatic compounds in a variety of ways including ring addition and addition to the nitro group. See: Strauss, M. J.; Taylor, S. P. B.; Reznick, A. *J. Org. Chem.* **1972**, *37*, 3076 and references therein. Except for the formation of highly colored solutions, however, no evidence is available to indicate any of these has occurred in the present work. Micellar effects of surfactants, producing accelerated formation of the 2,4,6-trinitrobenzyl anion in the reaction of TNT with amines, have been observed by: Okamoto, Y.; Wang, J. Y. *J. Org. Chem.* **1977**, *42*, 1261. Analogous effects are not seen to be a factor in the present study as constituted.

[6] No HNS was obtained at all from an attempted reaction of TNBzCl with triethylamine dissolved in toluene instead of water (see Experimental Section). (Subsequent addition of water to the highly colored reaction solution then caused HNS to form in 20% yield under these conditions.) This provided evidence against reaction of the amine per se with TNBzCl to remove the α-proton (cf. eq 2). If indeed the nitrogen base reacted in this manner, the yields obtained in this work should reflect the steric requirements of the bases. The data in Table I, however, show no evidence for this. On the contrary, of all the bases examined, triethylamine produced the highest yield of HNS.

[7] Formation of the 2,4,6-trinitrobenzyl anion from TNT in basic solution is well documented. Cf.: Fyfe, C. A., et al., ref 8 and references therein.

[8] Fyfe, C. A.; Malkiewich, C. D.; Damji, S. W. H.; Norris, A. R. *J. Am. Chem. Soc.* **1976**, *98*, 6983. See this reference and references therein for types of products that might arise from the interaction of bases with TNT and other nitro aromatic compounds.

[9] Piperidine (Table I) may prove to be a suitable base when the base/TNBzCl molar ratio is some value less than 2.4, and morpholine may prove to be suitable when the ratio is some value greater than 2.4.

[10] It is readily calculated from the dissociation constant of isopropylamine ($K_b = 4.27 \times 10^{-4}$ at 25 °C; cf. pK_B, Table I), for example, that an 0.82 M aqueous solution delivering 2 molar equiv of the amine with respect to TNBzCl, as employed in this study, initially provides only about 0.04 molar equiv of OH^-. (This is altered somewhat in practice by adding the solution to the TNBzCl dissolved in THF and methanol (see Experimental Section).

[11] Bernasconi, C. F. *J. Org. Chem.* **1971**, *36*, 1671.

[12] Salter, D. A.; Scilly, N. F.; Watson, K. E., U.S. Patent 4 085 152, 1978. These authors have reported that the yield of acetone-washed HNS is increased from 30–35% to 45–50% when the reaction of TNT with alkaline hypochlorite is carried out with certain nitrogen bases added up to 3 min *after* the start of the reaction (although TNBzCl is produced in 1 min; see above). In this process, both the hypochlorite and available sodium hydroxide are increased over that of Shipp and Kaplan.[1]

Table I. HNS from Nitrogen Bases and TNBzCl

base	pK_b[a]	base/TNBzCl molar ratio	HNS yield, %	
			crude	acetone washed
piperidine	2.88	2.4	41	36
diethylamine	3.07	2.4	56	52
dimethylamine	3.23	2.4	63[b]	50
triethylamine	3.28	2.0	71	
		2.4	75	70
		2.8	71	
cyclohexylamine	3.36	2.4	69	64
ethylamine	3.37	2.4	63	58
methylamine	3.38	2.4	53	49
n-butylamine	3.39	2.4	69	64
isopropylamine	3.47	1.6	71	
		2.0	75	69
		2.4	73	
		2.8	69	
isobutylamine	3.59	2.4	69	64
ethylenediamine	4.07, 7.15	2.4	55	51
N,N-diethylethanolamine	~4.3[c]	2.4	69	64
ethanolamine	4.50	1.2	61	
		2.0	65	
		2.4	69	64
		2.8	63	
ammonia	4.76	2.4	64	57
morpholine	5.30	2.4	43	39
triethanolamine	6.24	2.4	10	
pyridine	8.75[d]	2.4	4	

[a] In water at 25 °C.[4a] [b] Includes a byproduct not obtained on using any other amine (cf. footnote 5). [c] Temperature at which measurement was made was not specified.[4b] [d] Reference 4c.

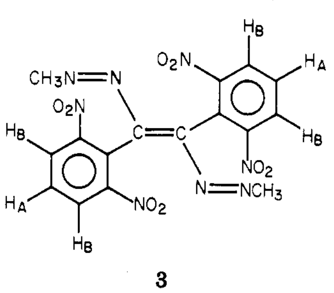
water), isopropylamine, cyclohexylamine, and *n*-butyl- and isobutylamines from Eastman, piperidine, morpholine, and ethanolamine from Fisher, *N,N*-diethylethanolamine and pyridine from Aldrich, and triethylamine, triethanolamine, ethylenediamine, and aqueous ammonia from Baker, were mostly the best grades commercially available and were used as received.

General Methods. Melting points were determined with a Mel-Temp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 457A grating infrared spectrophotometer. NMR spectra were obtained on a Varian T-60 NMR spectrometer with tetramethylsilane as an internal standard. The mass spectrum was obtained on a Du Pont 21-492 mass spectrometer by using a solids probe. The elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Reactions of TNBzCl with Nitrogen Bases (General Procedure). The reactions with ethanolamine exemplify the general procedure based on that of Shipp and Kaplan, which was used for all reactions summarized in Table I. TNBzCl (0.65 g, 2.5 mmol) was dissolved in THF (10 mL) and methanol (5 mL). Aqueous ethanolamine [6 mL of solutions delivering 0.18 (3.0), 0.30 (4.9), 0.36 (5.9), and 0.42 g (6.9 mmol) of amine and supplied from 20-mL stock solutions[13]] was added all at once with stirring several turns by means of a glass rod. The mixtures were allowed to stand for 15 min, after which the precipitated golden solid was collected on a filter and washed with methanol. The crude product was washed with hot acetone to give pale yellow HNS, mp 316–317 °C dec (lit.[1] mp 316 °C dec; pale yellow needles from nitrobenzene or DMF[14]). After evaporation of the solvent from the acetone extract, the residue was stirred with acetone without heating, and more HNS (~2–4%) was removed by filtration. Yields are summarized in Table I. The infrared spectrum was identical with that of an authentic sample of HNS prepared by the method of Shipp and Kaplan:[1,15] IR (KBr) 3100 (s), 3010 (w), 2890 (w), 1617 (s), 1600 (s), 1540 (vs), 1466 (w), 1405 (m), 1349 (vs), 1307 (w), 1268 (w), 1186 (w), 1176 (w), 1087 (m), 959 (m), 942 (w), 925 (s), 832 (w), 815 (w), 786 (w), 746 (s), 730 (s), 721 (s), 690 (w), 575 (w), 530 (w), 383 (w), 362 (w) cm^{-1}.

The product from other bases (Table I) varied in color from pale yellow to gray: mp ~315 °C dec; IR spectra identical with that of authentic HNS.

In the case of dimethylamine, the solid residue obtained from the acetone wash was extracted with several portions of boiling chloroform, affording a yellow solid (mp 264–267 °C) upon evaporation of the solvent. When a scaled-up preparation based on a six-fold increase in TNBzCl to 3.9 g (15.0 mmol) was carried out, the yield was 0.4 g. Crystallization from acetone afforded a yellow, scintillating, powdery solid, mp 268–269 °C. The following data were obtained and are consistent with a structure such as that represented by *trans*-1,2-bis(2,6-dinitrophenyl)bis(methylazo)ethylene (**3**): NMR (Me$_2$SO-d_6) δ 4.43 (6 H, s, CH$_3$), 8.73 (2 H, d, H$_A$), 9.17 (4 H, d, H$_B$); mass spectrum, *m/e* (relative intensity) 222 [(M/2)$^+$, 100], 176 [(M/2 − NO$_2$)$^+$, 10.8], 130 [(M/2 − 2NO$_2$)$^+$, 18.8], 43 [(CH$_3$N$_2$)$^+$, 6.0], 42 [(CH$_2$N$_2$)$^+$, 22.0]; IR (KBr) 3145 (s), 3105 (m), 3095 (m), 3050 (m), 1564 (s), 1530 (vs), 1489 (s), 1475 (s), 1434 (m), 1385 (s), 1340 (vs), 1308 (s), 1273 (s), 1191 (s), 1158 (s), 1083 (w), 1030 (s), 1011 (w), 945 (m), 935 (m), 916 (m), 862 (m), 843 (m), 833 (m), 824 (s), 746 (m), 739 (s), 736 (s), 672 (w), 560 (w), 501 (w), 354 (w) cm^{-1}.



3

Anal. Calcd for $C_{16}H_{12}N_8O_8$: C, 43.25; H, 2.72; N, 25.22. Found: C, 43.32; H, 2.84; N, 25.00.

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[13] Triethylamine was first dissolved in 3 mL of methanol and then diluted to 20 mL with water to form the stock solution.

[14] Very small samples of HNS are also crystallizable from acetone, benzene, and toluene. In the case of benzene, HNS cocrystallizes with a molecule of the solvent: NMR (Me$_2$SO-d_6) δ 7.15 (2 H, s, olefinic), 7.40 (6 H, s, benzene), 9.15 (4 H, s, picryl). The IR spectrum (KBr) was similar to that of HNS (see Experimental Section) with the following differences: band now absent at 1186 cm^{-1}; major new bands now present at 1483 (s), 912 (m), and 703 (s) cm^{-1}. The solvent of crystallization is lost when the sample is allowed to stand several days as indicated by the reapprearnace of the first band and gradual disappearance of the last three.

[15] For major IR assignments, see: Shipp, K. G. *J. Org. Chem.* **1964**, *29*, 2620.

Substantiating evidence, preferably chemical in nature, is needed before a firm identification can be made. To this end, an attempt to generate dinitrobenzoic acid in refluxing 70% nitric acid was unsuccessful. The pathway by which such a molecule as 3 might arise, moreover, is decidedly obscure.

Acknowledgment. Appreciation is expressed to Dr. T. Chen for the mass spectral determination and to M. Warman for obtaining the NMR spectra.

Registry No. 3, 81158-74-9; TNBzCl, 7176-28-5; HNS, 20062-22-0.

Nitrolysis of Dialkyl *tert*-Butylamines

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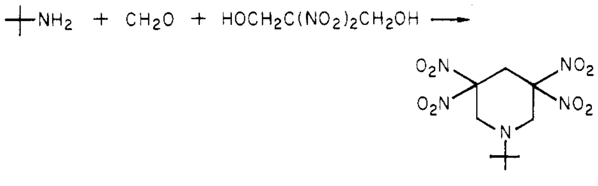
Received December 28, 1981

In the synthesis of secondary nitramines, especially cyclic ones, an N-blocking group is often required to control the course of Mannich condensations; the N substituent is subsequently removed by nitrolysis to give the nitramine. *N*-Acyl and *N*-alkyl groups have been used for this purpose with varying success.[1-5] Earlier work in our laboratory on *N*-*tert*-butyl-2,2,2-fluorodinitroethanamides[6] and -amines[7] suggested that the *tert*-butyl group might be particularly useful in this regard. We now report on the nitrolysis of *N*-*tert*-butylamines containing (mostly nitroalkyl) substituents of varying electron demand.

The amines 1-3 used as model compounds in the present work were obtained by the Mannich condensation of *tert*-butylamine with the appropriate nitroalkanes (eq 1-3), largely analogous to reported syntheses of similar tertiary and secondary amines.[8] The synthesis of 2 illustrates the utility of the N-blocking group since with ammonia 7-nitro-1,3,5-triazaadamantane is obtained.[9]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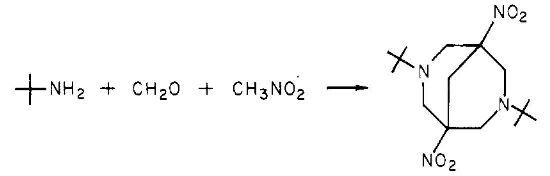
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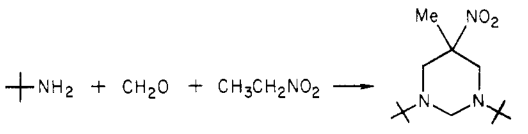
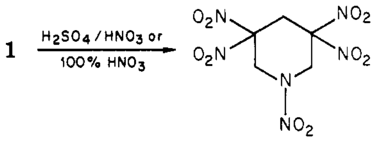

(3)

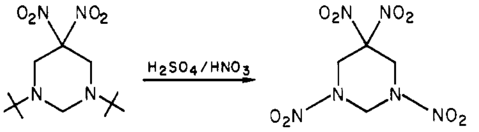
3

The facile conversion of *tert*-butylbis(2,2,2-fluorodinitroethyl)amine to bis(2,2,2-fluorodinitroethyl)amine in concentrated sulfuric acid[7] and the ability of mixed acid (H_2SO_4/HNO_3) to nitrate the latter[10] indicated that bis(2,2-dinitroalkyl)-substituted *tert*-butylamines should be nitrolyzed readily by mixed acid. This was shown to be the case for 1 which was converted to 4 in excellent yield with either mixed or 100% nitric acids (eq 4).


(4)

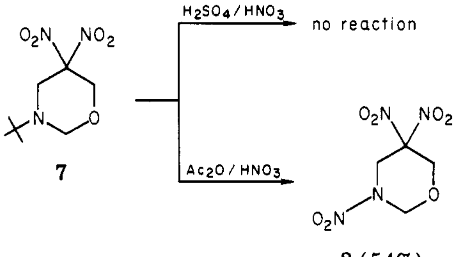
4 (81%, 96%)

For substrates with fewer β-nitro groups the situation is more complex. In some cases complete or partial nitrolysis occurred in mixed acid; some substrates were unreactive toward this reagent, but could be nitrolyzed with acetic anhydride/nitric acid or with 100% nitric acid alone. Thus, the diazine 5 was nitrolyzed quickly to 6 (eq 5) in mixed acid at room temperature. The analogous oxazine 7, however, was unreactive under the same conditions (except that decomposition occurred on extended exposure) but was nitrolyzed with the milder reagent Ac_2O/HNO_3 (eq 6). Similarly peculiar was the behavior of the nitrodiamines 2 and 3. Nitrolysis in mixed acid caused the displacement of only one *tert*-butyl group, whereas with 100% HNO_3, both *tert*-butyl groups were nitrolyzed (eq 7 and 8).


(5)

5

6 (85%)


(6)

7

8 (54%)

tert-Butyldimethylamine was studied as an example devoid of any nitro substituents. With mixed acid and with 90% or 100% HNO_3 no or only trace amounts of nitramines were produced. With nitric acid/acetic anhydride, dimethylnitramine was formed in about 15% yield. TLC analysis of the reaction mixture indicated that *tert*-butylmethylnitrosamine was also present; dimethylnitrosamine, however, was not formed. A higher yield of

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(1) E. E. Gilbert, J. R. Leccacorvi, and M. Warman in "Industrial and Laboratory Nitrations", L. F. Albright and C. Hanson, Eds., American Chemical Society, Washington, DC, 1976, p 327.

(2) G. F. Wright in "The Chemistry of the Nitro and Nitroso Groups", H. Feuer, Ed., Interscience, New York 1969, Part 1, Chapter 9.

(3) J. H. Robson and J. Reinhart, *J. Am. Chem. Soc.*, **77**, 107, 2453 (1955); see also ref 1 and 2.

(4) Y. Ogata, Y. Sawaki, and Y. Kuriyama, *Tetrahedron*, **24**, 3425 (1968).

(5) F. Chapman, P. G. Owston, and D. Woodstock, *J. Chem. Soc.*, **1949**, 1647; see also W. P. Norris, *J. Org. Chem.* **25**, 1244 (1960).

(6) H. G. Adolph, *J. Org. Chem.*, **37**, 747 (1972).

(7) W. H. Gilligan, *J. Org. Chem.*, **36**, 2138 (1971).

(8) H. Piotrowska, T. Urbanski, and K. Wejroch-Matacz, *Rocz. Chem.*, **45**, 1267, 2107 (1971).

(9) J. P. Jonak, S. F. Zakrevski, L. H. Mead, and L. D. Allshouse, *J. Med. Chem.*, **13**, 1170 (1972); U.S. Patent 3301854 (1967); *Chem. Abstr.*, **67**, 21936 (1967).

(10) R. G. Gafurov, S. I. Sviridov, F. Y. Natsibullin, and L. T. Eremenko, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1970**, 329.