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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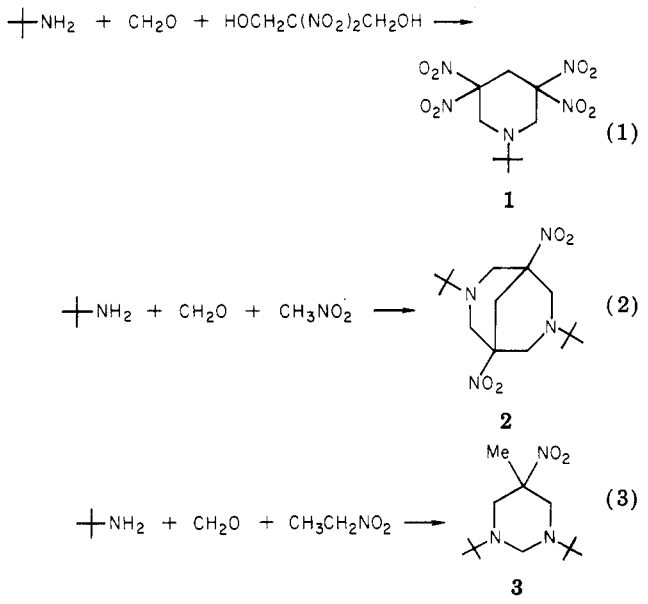
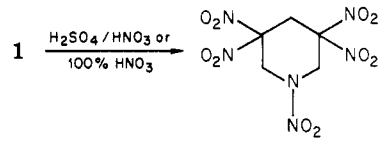
In the synthesis of secondary nitramines, especially cyclic ones, an N-blocking group is often required to control the course of Mannich condensations; the N substituent is subsequently removed by nitrolysis to give the nitramine. *N*-Acyl and *N*-alkyl groups have been used for this purpose with varying 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),



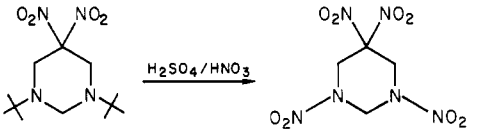
largely analogous to reported syntheses of similar tertiary and secondary amines.[8] The synthesis of **2** illustrates the utility of the N-blocking group since with ammonia 7-nitro-1,3,5-triazaadamantane is obtained.[9]

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).



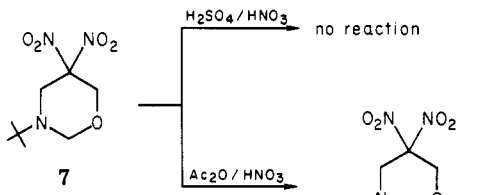
4 (81%, 96%)

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



5 **6** (85%)

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



7 **8** (54%)

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).

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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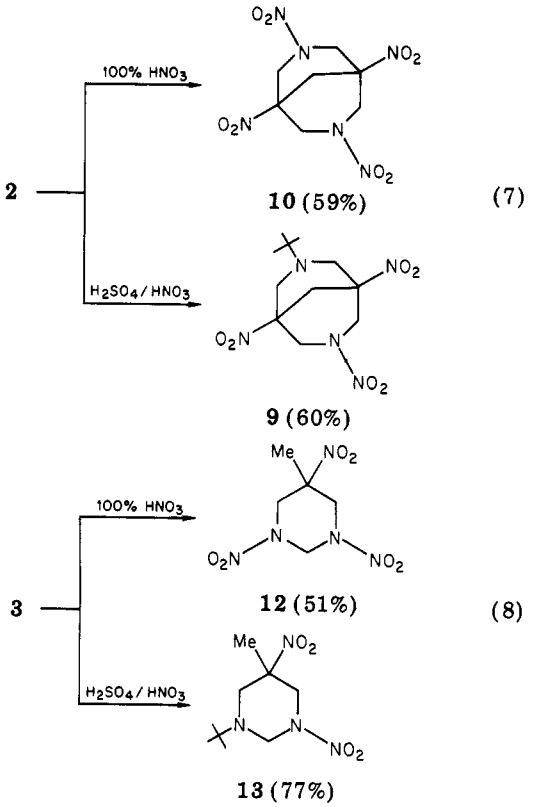


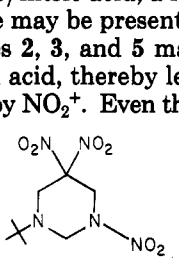
(7)

(8)

dimethylnitramine, 55%, was obtained by using the amine hydrochloride for nitrolysis. As in the nitration of secondary amines,[2] chloride ion appears to have a catalytic effect in the nitrolysis of the tertiary amine also.

The results obtained have thus confirmed the expectation that dialkyl *tert*-butylamines can be nitrolyzed readily to the corresponding dialkylnitramines. The nitrolyses occur in preparatively useful yields ranging from 55% to 85% for a variety of nitro-substituted and unsubstituted amines. Improvement of the yields may be possible since attempts at their optimization were generally not made.

A possible explanation of the differing behavior of substrates **2**, **3**, **5**, and **7** toward the three nitrolysis agents used here may be based on differences in the basicities of the nitrogens. Effects of basicity on the nitration of secondary amines[2] and the nitrolysis of hexamine and other methylenediamines,[11] of the *N*-alkyl group in 2,4-dinitroanilines,[2] and of 1-alkyl-3,6-dinitroperhydro-1,3,6-triazepines[5] have been previously noted. The lack of reactivity of **7**, **9**, and **13** in mixed acid may thus be due to their complete protonation at the *tert*-butyl nitrogens in this medium which would prevent attack by NO_2^+ or a similar nitrating species. In the less acidic media, 100% HNO_3 and acetic anhydride/nitric acid, a larger amount of unprotonated substrate may be present, and nitrolysis proceeds. The diamines **2**, **3**, and **5** may be largely *mono*protonated in mixed acid, thereby leaving the second N vulnerable to attack by NO_2^+. Even the fact that **14**, which



14

must be an intermediate in the mixed-acid nitrolysis of **5** to **6**, undergoes further nitrolysis in that medium while **9** and **13** do not can be rationalized on the basis of differences in the basicities of the remaining *tert*-butyl nitrogens.

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Table I. Properties and Analyses of Nitrolysis Products[d]

compd	mp, °C	^{1}H NMR, δ
6	153–154	6.13 (s, NCH_2N),[a] 5.23 (s, CCH_2N)
8	88–89	4.68 (s, 2 H),[b] 5.18 (s, 2 H), 5.45 (s, 2 H)
10	273–274 dec	3.30 (s, CCH_2C),[c] 4.24 (d, NCHC), 5.39 (d, NCHC)
9	93–94	1.03 (s, 9 H),[c] 2.67 (d, 2 H), 2.81 (m, 2 H), 3.64 (d, 2 H), 3.81 (d, 2 H), 5.40 (d, 2 H)
12	167–168	1.80 (s, 3 H),[c] 4.12 (d, 2 H), 5.18 (d, 1 H), 5.41 (d, 2 H), 7.05 (d, 1 H)
13	100.5–102	1.12 (s, 9 H),[b] 1.56 (s, 3 H), 2.67 (d, 1 H), 3.63 (d, 1 H), 3.72 (d, 1 H), 4.11 (d, 1 H), 5.02–5.21 (m, 2 H)

[a] $CDCl_3$/1 drop of Me_2SO-d_6. [b] CD_2Cl_2. [c] Acetone-d_6. [d] Satisfactory analytical values (±0.3% for C, H, and N) were reported for all compounds in this table.

Experimental Section

Caution: Several of the compounds reported herein, especially **4**, **6**, **8**, and **10**, are sensitive explosives and should be handled with appropriate care. Elemental analyses were obtained commercially. ^{1}H NMR spectra are from various sources; chemical shifts are given in parts per million from Me_4Si.

1-*tert*-Butyl-3,3,5,5-tetranitropiperidine (1). Glacial AcOH was added to 1 mL of *tert*-butylamine in 15 mL of H_2O to a pH of 6, followed by addition of 1.6 g 2,2-dinitro-1,3-propanediol. During 6 days of stirring the mixture at room temperature the pH was adjusted periodically to 6 as necessary with AcOH or NaOAc. The crude product was filtered off; extraction of the filtrate with CH_2Cl_2 and washing of the extract with H_2O gave an additional crop: total yield 0.25 g (15%); mp 136–137 °C (from MeOH/H_2O); ^{1}H NMR (CD_2Cl_2) δ 1.16 (s, CH_3), 3.71 (s, CCH_2C), 4.03 (s, CCH_2C).

Anal. Calcd for $C_9H_{15}N_5O_8$: C, 33.65; H, 4.71; N, 21.80. Found: C, 33.61; H, 4.73; N, 21.88.

3,7-Di-*tert*-butyl-1,5-dinitro-3,7-diazabicyclo[3.3.1]nonane (2). To an ice-cooled solution of 36.5 g of *tert*-butylamine in 150 mL of MeOH was added 30 g of AcOH with stirring, followed by 20.4 g of nitromethane and 30.0 g of paraformaldehyde. The mixture was heated to a mild reflux for 4 days, kept at ca. −10 °C overnight, and filtered. The dark brown solid was triturated with 100 mL of a pH 6 buffer solution to give 7.2 g of crude product which was purified by a combination of chromatography on silica gel (CH_2Cl_2) and recrystallization from MeOH. Additional product can be obtained by adding the initial filtrate to 1500 mL of H_2O, stirring several h, filtering off the solid, and chromatographing it on silica gel (CH_2Cl_2). The initial solid fractions were combined and purified as above. The pH 6 buffer wash was made basic and extracted with CH_2Cl_2, and the extract was washed with H_2O, and dried. Chromatography and recrystallization as above gave a further crop of product: total yield 3.7 g (7%); mp 135–136 °C; ^{1}H NMR ($CDCl_3$) δ 1.11 (s, CH_3), 2.64 (s, CCH_2C), 3.01 (AB q, NCH_2C).

Anal. Calcd for $C_{15}H_{28}N_4O_4$: C, 54.86; H, 8.59; N, 17.06. Found: C, 55.07; H, 8.59; N, 17.09.

1,3-Di-*tert*-butyl-5-methyl-5-nitrohexahydro-1,3-diazine (3). To 1.5 g of nitroethane in 10 mL of MeOH were added 4 mL of 36% formaldehyde solution and 2 mL of *tert*-butylamine, and the mixture was stirred overnight and cooled to ca. −10 °C. The solid was filtered, washed with H_2O, and recrystallized from MeOH/H_2O. The initial crop was a mixture, the second crop afforded 0.2 g of **3**, mp 106–109 °C. Additional material can be obtained by fractional crystallization of the initial crop: ^{1}H NMR (CD_2Cl_2) δ 1.08 (s, 18 H), 1.46 (s, 3 H), 2.31 (d, 2 H), 2.88 (d, 2 H), 3.59 (d, 2 H), 3.85 (d, 1 H).

Anal. Calcd for $C_{13}H_{27}N_3O_2$: C, 60.67; H, 10.58; N, 16.33. Found: C, 60.59; H, 10.63; N, 16.22.

Nitrolysis. The nitrolyses were carried out by three general methods. Properties and analytical data for new products are listed in Table I.

Method A. The dialkyl *tert*-butylamine was added to concentrated H_2SO_4 with cooling in ice. To this mixture was added at 0 °C a mixture of 90% HNO_3 and concentrated H_2SO_4. After being stirred, the solution was poured onto ice and the product isolated as described below.

Method B. The dialkyl *tert*-butylamine was added to 100% HNO_3 at 0 °C under N_2. After being stirred, the solution was poured onto ice and the product isolated as described below.

Method C. To acetic anhydride under N_2 was added 100% HNO_3, keeping the temperature below 20 °C. To this solution at 5–10 °C was added the dialkyl *tert*-butylamine in AcOH. After being stirred, the solution was poured onto ice and the product isolated as described below.

1,3,3,5,5-Pentanitropiperidine (4). Method A, with 0.2 g of 1 in 3 mL of H_2SO_4 and a mixture of 0.8 mL of HNO_3 and 1.3 mL of H_2SO_4 and after overnight stirring at room temperature, filtering off of the solid, washing with water, and recrystallization (CH_2Cl_2/hexane), gave 0.15 g (81%) of **4**. Method B, with 0.1 g of **1** and 2 mL of HNO_3 and after 3 days at room temperature, filtering off of the solid, extraction of the filtrate (CH_2Cl_2), and purification of the product as in method A, gave 0.09 g (96%) of **4**. The products were identical by melting point and IR with an authentic sample.

1,3,5,5-Tetranitrohexahydro-1,3-diazine (6). Method A, with 7.5 g of **5** in 100 mL of H_2SO_4 and a mixture of 17 mL of HNO_3 and 27 mL of H_2SO_4 and after 1 h at 0 °C and 2 h at room temperature, extraction (CH_2Cl_2), drying ($MgSO_4$), concentration, addition of hexane, and cooling, gave 6.05 g (87%) of **6**.

3,5,5-Trinitrotetrahydro-1,3-oxazine (8). Method C, with 2 mL of Ac_2O, 0.8 mL of HNO_3 and 1.0 g of **7** in 2 mL of AcOH and after warming of the mixture to room temperature over 4 h and overnight stirring at room temperature, extraction (CH_2Cl_2), washing with H_2O, and purification by recrystallization (CH_2Cl_2/hexane), gave 0.56 g (54%) of **8**.

1,3,5,7-Tetranitro-3,7-diazabicyclo[3.3.1]nonane (10). Method B, with 0.2 g of **2** and 2.0 mL of HNO_3 and after 0.5 h at 0 °C and 3 days at room temperature, filtering off of the solid, extraction of the filtrate (CH_2Cl_2), washing of the extract with dilute K_2CO_3 solution and H_2O, and recrystallization (CH_2Cl_2/hexane) of the combined product, gave 0.11 g (59%) of **10**.

7-*tert*-Butyl-1,3,5-trinitro-3,7-diazabicyclo[3.3.1]nonane (9). Method A, with 0.1 g of **2** in 2.5 mL of H_2SO_4 and a mixture of 0.6 mL of HNO_3 and 1 mL of H_2SO_4 and after 1 h at 0 °C and 1 h at room temperature, extraction (CH_2Cl_2), washing with dilute K_2CO_3 solution and H_2O, and recrystallization (MeOH/H_2O), gave 0.06 g (62%) of **9**.

1-*tert*-Butyl-3,5-dinitro-5-methyl-1,3-hexahydrodiazine (13). Method A, with 0.1 g of **3** in 2.5 mL of H_2SO_4 and a mixture of 0.6 mL of HNO_3 and 1.0 mL of H_2SO_4 and after 15 min at 0 °C, extraction (CH_2Cl_2), washing with H_2O, and recrystallization of the crude product (MeOH/H_2O), gave 0.07 g (77%) of **13**.

5-Methyl-1,3,5-trinitrohexahydro-1,3-diazine (12). Method B, with 5 mL of HNO_3 and 0.1 g of **3** and after 15 min at 0 °C and 6 h at 35–45 °C, filtering off the solid, and recrystallization (CH_2Cl_2/hexane), gave 0.043 g (51%) of **12**.

Nitrolysis of *tert*-Butyldimethylamine. To 10 mL of Ac_2O at 0–5 °C was added 2.9 mL of oxide-free 90% HNO_3, followed by a solution of 1.0 g of *tert*-butyldimethylamine in 3.0 mL of AcOH. The mixture was stirred 2 days at room temperature and poured onto ice. After the mixture was stirred 2 h, the product was extracted (CH_2Cl_2). The aqueous phase was made basic (Na_2CO_3) and extracted again (CH_2Cl_2). The combined extracts were washed (dilute $NaHCO_3$), dried ($MgSO_4$), and concentrated by distillation. Addition of hexane and chilling gave 0.143 g (16%) of dimethylnitramine. Further concentration gave no additional product.

Nitrolysis of *tert*-Butyldimethylamine Hydrochloride. The same procedure as above was used with 11.5 mL of Ac_2O, 2.5 mL of oxide-free HNO_3, and a solution of 2.0 g of the amine hydrochloride in 2 mL of AcOH. A workup as above gave 0.51 g of dimethylnitramine as a first crop. Further concentration gave another 0.21 g (total yield 55%).

Acknowledgment. This work was supported by the Energetic Materials Division, U.S. ARRADCOM, Dover, NJ, and the Office of Naval Research, Mechanics Division, Code 432.

Registry No. **1**, 81340-11-6; **2**, 81340-12-7; **3**, 65478-96-8; **4**, 71706-07-5; **5**, 34924-01-1; **6**, 81360-42-1; **7**, 33923-30-7; **8**, 81340-13-8; **9**, 81340-14-9; **10**, 81340-15-0; **12**, 81340-16-1; **13**, 81340-17-2; *tert*-butylamine, 75-64-9; 2,2-dinitro-1,3-propanediol, 2736-80-3; nitromethane, 75-52-5; nitro ethane, 79-24-3; *tert*-butyldimethylamine, 918-02-5; dimethylnitramine, 4164-28-7; *tert*-butyldimethylamine hydrochloride, 6338-78-9.

Competing β Fragmentation in Regeneration of Alcohols from Arenesulfonates with Arene Anion Radicals

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The recovery of alcohols from alkyl arenesulfonates through reductive cleavage with arene anion radicals has found considerable use,[1] since the process usually proceeds in excellent yield with few side reactions such as elimination, racemization, or epimerization.[2] Recently, Cavazza et al. reported that benzylic and allylic tosylates undergo considerable C–O cleavage on treatment with sodium–naphthalene or sodium–anthracene.[3] Yields of alcohol were sometimes as low as 30%, and sizeable amounts of products characteristic of further reaction of allylic or benzylic radicals or anions were also found.[3] We report that certain other types of arenesulfonate esters are prone to a different side reaction which yields products characteristic of carbon radicals produced by cleavage of the C–C bond β to the O–S bond of the sulfonate ester.

For example, neopentyl tosylate (**1**) on treatment with sodium–naphthalene in tetrahydrofuran (THF) yields both neopentyl alcohol and a mixture of what appears to be 1- and 2-*tert*-butyldihydronaphthalene. Traces of isobutane could also be observed in most reaction mixtures. Under similar conditions the *p*-toluenesulfonate ester of 2-methyl-2-phenylpropanol (neophyl tosylate, **2**) affords a sizeable amount of cumene as well as neophyl alcohol and traces of what appear to be alkylated dihydronaphthalenes. Typical results are shown in Table I.

In our original studies neopentyl tosylate was observed to give an anomalously low yield of alcohol (ca. 85%) even under quite favorable conditions (large excess of sodium naphthalene, 0 °C).[2] Further work showed that the yield of alcohol was even poorer under the conditions used in this study (slight excess of anion radical, 25 °C) and that changing the solvent from THF to 1,2-dimethoxyethane (DME) resulted in a further drop in yield. In addition, small amounts of two long-retention-time materials were observed on gas chromatographic (GC) analysis. The

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