Reactions of Alkylaminonitroalkenes

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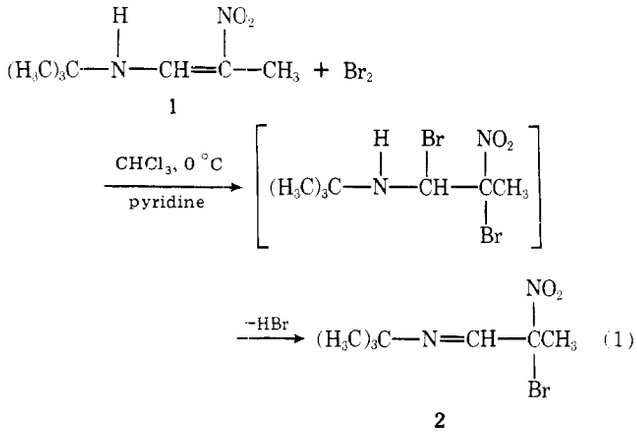
1-Alkylamino-2-nitro-1-alkenes react with bromine in the presence of amines to give α-bromo-α-nitroaldimines. In a novel and reversible amine interchange, secondary and primary amines react with secondary and tertiary aminonitroalkenes to give, respectively, tertiary and secondary aminonitroalkenes. These compounds are rapidly hydrolyzed by aqueous base to amines and nitroalkanes.

1-Alkylamino-2-nitro-1-alkenes have recently become available by the direct alkyl nitration of aldimines.[1] In this paper we are reporting on their reactions with bromine and amines.

Bromination. The reaction of bromine in chloroform with 1-(*tert*-butylamino)-2-nitro-1-propene (**1**) led to cleavage, as evidenced by the isolation of *tert*-butylammonium bromide. However, when the bromination of **1** was carried out in the presence of pyridine or diethylamine, *N*-(2-bromo-2-nitropropylidene)-*tert*-butylamine (**2**) was obtained in 77% yield. It is very likely that the intermediate in the formation of **2** is the dibromo compound which eliminates hydrogen bromide (eq 1).

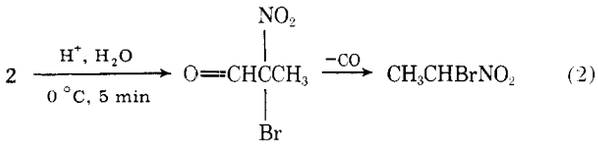


1

2

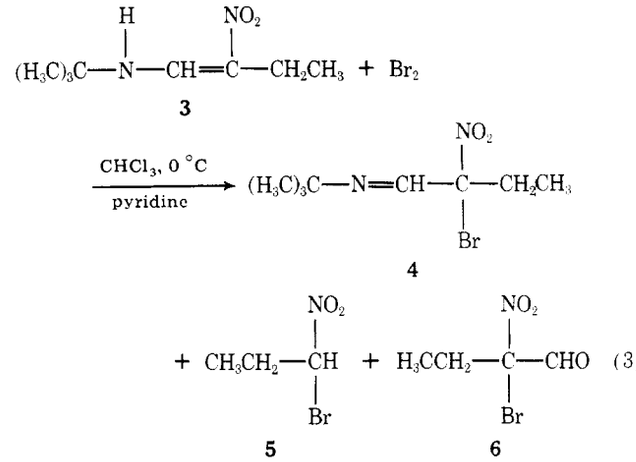
The structure of **2** was confirmed by its spectral data. The infrared spectrum showed absorptions at 1665 cm^{-1} (C=N) and at 1570 and 1339 cm^{-1} (NO_2). The position of the asymmetric NO_2 vibration frequency at 1570 cm^{-1} was particularly significant because it denoted the presence of an unconjugated NO_2 group.[2] The NMR spectrum of **2** was also consistent with the nitroimine structure, exhibiting singlet resonances for the *tert*-butyl, methyl, and azomethine protons at δ 1.22, 2.35, and 7.93, respectively.

Compound **2** was stable to brief neutral and alkaline washes but was rapidly hydrolyzed in dilute acid. Treatment of **2** with 1 equiv of 0.02 N hydrochloric acid at 0 °C for 5 min and distillation of the reaction mixture afforded 1-bromo-1-nitroethane (36%). 2-Bromo-2-nitropropanal was very likely an intermediate in the hydrolysis of **2.** Infrared analysis of the reaction mixture before distillation showed that the C=N band at 1665 cm^{-1} had disappeared and a new absorption at 1718 cm^{-1}, characteristic of the C=O group, was present (eq 2).



Compound **2** lost bromine when exposed to moisture and was reconverted to **1.**

Bromination of 1-(*tert*-butylamino)-2-nitro-1-butene (**3**) in the presence of pyridine gave a mixture which, based on NMR analysis, consisted of *N*-(2-bromo-2-nitrobutylidene)-*tert*-butylamine (**4**), 1-bromo-1-nitropropane (**5**), and a compound believed to be 2-bromo-2-nitrobutanal (**6**) (eq 3).



3

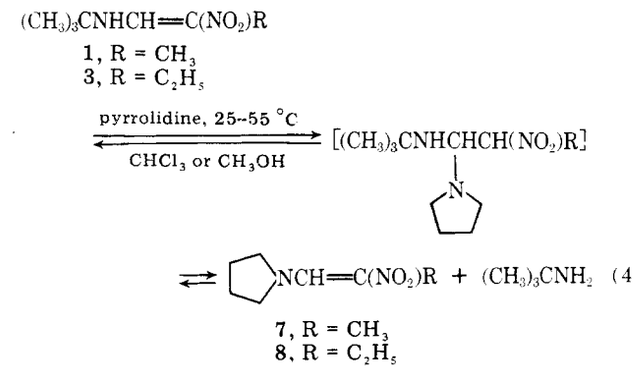
4

5 **6**

Distillation of the mixture in vacuo afforded fractions which contained all three components. The higher boiling fractions contained increasing amounts of **5** which might have been due to the thermal decomposition of **6.**

The presence of compounds **4** and **6** was established by their infrared absorptions at 1667 (CH=N) and 1748 cm^{-1} (C=O), respectively. In the NMR spectrum, **4** was identified by absorptions at δ 1.20 (*tert*-butyl) and 7.78 (CH=N), **5** by a triplet at δ 5.90 ($CHBrNO_2$), and **6** by a singlet at δ 9.40 (CHO).

Transamination. Upon treatment with pyrrolidine in either methanol or chloroform, the secondary aminonitroolefins **1** and **3** underwent amine interchange reactions to afford, respectively, 1-pyrrolidino-2-nitro-1-propene (**7**) and 1-pyrrolidino-2-nitro-1-butene (**8**) (eq 4). However, the reaction was



7, R = CH_3
8, R = C_2H_5

found to be of rather limited scope. For example, 1-cyclohexylamino-2-nitro-1-propene (**9**) failed to react with pyr-

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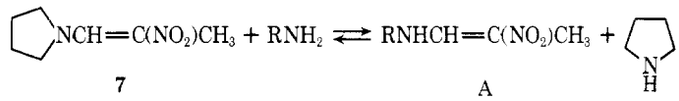
Table I. Reaction of 1-(Pyrrolidino)-2-nitro-1-propene (7) with Primary Amines



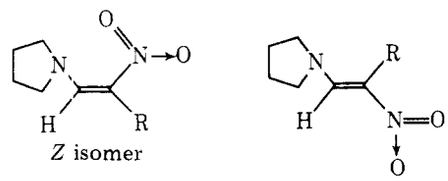
7 A

Amine, R	Registry no.	Amount, mol	Solvent	Temp, °C	Time, h	Yield of A, %	7 recovd, %
t-Bu	75-64-9	2.0	$CDCl_3$	40	22	74[a,b]	26[a,b]
		c	Neat	45	1.5	90	
i-Pr	75-31-0	2.2	$CHCl_3$	25	73	41[a]	41[a]
		c	Neat	45	1.0	42[d]	18[d]
n-Pr	107-10-8	1.1	$CHCl_3$	25	19	54[d]	11[d]
		1.1	MeOH	25	48	38[b]	14[b]

[a] Based on NMR analysis of the olefinic methyl singlets of compounds 7 and A. [b] Based on separation by preparative thin-layer chromatography. [c] The amine was used as the solvent. [d] Based on separation by column chromatography.

rolidine and was recovered in 76% yield. Furthermore, no reaction occurred when 1 was treated with piperidine, morpholine, diisopropylamine, or diethylamine. The failure of 1 to react with morpholine (pK_a 8.33), diethylamine (pK_a 11.04), and diisopropylamine (pK_a 11.13) may be attributed to the low nucleophilicity of the first and perhaps to steric hindrance in the latter two amines. The failure of 1 to react with piperidine was surprising since the pK_a values and steric requirements of both pyrrolidine (pK_a 11.27) and piperidine (pK_a 11.12) are similar.

Comparison of the NMR spectra of 7 and 8 with those of 3 revealed that the tertiary aminonitroolefins differed from the secondary aminonitroolefins in two important respects. Whereas the latter were shown to consist of a mixture of *Z* and *E* isomers, with the *Z* isomer predominating, the tertiary



Z isomer *E* isomer

R = CH_3 or C_2H_5

aminonitro compounds were found to consist solely of a single species. The positions of the olefinic proton resonances of 7 and 8 at δ 8.45 and 8.43, respectively, indicated that they were in the *E* rather than the *Z* configuration. The preference for the *E* configuration is believed to be a consequence of minimizing steric crowding. Molecular models show that the *E* isomers of 7 and 8 are less hindered than the *Z* isomers. In addition, the nonbonded p–p and p–π interactions between the amino and nitro groups are absent in the *E* isomer.

Additional evidence for the *E* configuration was obtained from the ultraviolet spectrum of 7, in which the long wavelength (K band) absorption [382 nm (log ϵ 4.17)] was displaced by 12 nm to longer wavelength, relative to the secondary aminonitroolefins 1 and 3. This bathochromic shift is not due to the loss of hydrogen-bonding ability in 7. Freeman and Emmons have shown that the disruption of intramolecular hydrogen bonding in aminonitroolefins leads to a hypsochromic shift of the K band absorption.[3] However, the observed bathochromic shift is consistent with the existence of the *E* isomer, for it is well-known that the less sterically hindered of two geometric isomers absorbs at the longer wavelength.[4,5]

The reversibility of the transamination reaction was established by reconversion of 7 to 1 upon treatment with *tert*-butylamine. The reaction was carried out in deuteriochloroform solution employing 2.0 molar equivalents of amine. Its progress was followed by the decrease of the olefinic methyl signal of 7 at δ 2.32 in the NMR spectrum and by the appearance of the olefinic methyl resonance of 1 at δ 2.08. The reaction progressed fairly rapidly, and after 20 min 50% of 1 was formed. The equilibrium was reached after 35 min when the amount of 1 had increased to 67%. After 22 h only a slight increase of 7 was indicated. Separation of the reaction products by preparative thin-layer chromatography afforded 70% of 1 and 30% of 7. Compound 1 consisted of a mixture of ca. 90% *Z* and 10% *E* isomers and was identical to the product obtained in the alkyl nitrate nitration of *N*-propylidene-*tert*-butylamine.[1] The NMR spectrum of recovered 7 indicated that it was 100% of the *E* configuration.

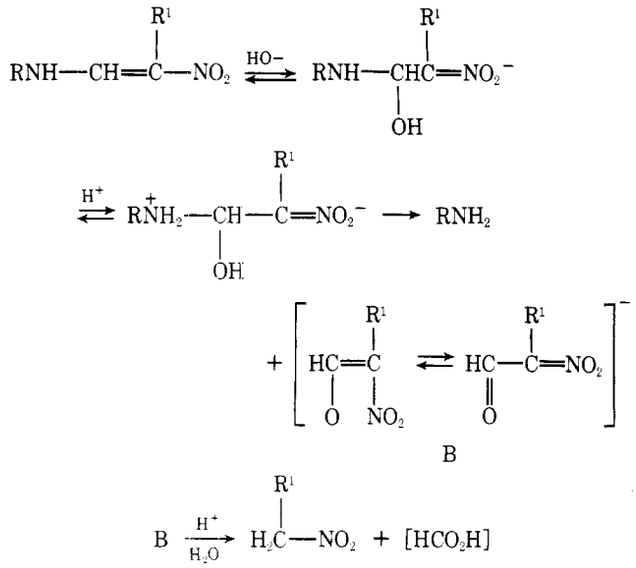
The reaction of 7 with primary amines appeared to be quite general. As shown in Table I, *tert*-butylamine, *n*-propylamine, and isopropylamine afforded the respective transamination products 1, 1-(*n*-propylamino)-2-nitro-1-propene (10), and 1-(isopropylamino)-2-nitro-1-propene (11). Compounds 1, 10, and 11 were identical with those obtained in the alkyl nitrate nitration of the respective aldimines.[1] The NMR spectra indicated that they were of the *Z* configuration. Thus, the reaction proceeded with inversion of configuration.

Aminonitroolefin 9, which did not react with pyrrolidine, underwent transamination with *tert*-butylamine readily. As determined by NMR, a mixture consisting of 1 (39%) and 9 (55%) was obtained. Separation of the mixture by column chromatography on neutral alumina could not be achieved, but NMR analysis of the mixture indicated that both 1 and 9 were of the retained *Z* configuration. The olefinic proton of 1 and 9 resonated at δ 7.09 and 7.03.[1]

The experimental evidence of the transamination reactions with aminonitroolefins suggests that the stereochemistry of the product is subject to thermodynamic control in the product-development step. In reactions involving the formation of secondary aminonitroolefins, the stereochemistry of the product was invariably of the *Z* configuration. This preference is believed to be due to intramolecular hydrogen bonding. In reactions involving the generation of tertiary aminonitroolefins, in which intramolecular hydrogen bonding is not possible, the less hindered *E* isomer appeared to be the exclusive product.

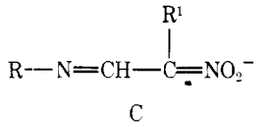
Hydrolysis. The secondary and tertiary aminonitroalkenes underwent rapid hydrolysis on treatment with aqueous potassium hydroxide to give the corresponding amines and nitroalkanes. The latter were obtained after acidification of the reaction mixture. For example, 1 and 7 were cleaved, respectively, to *tert*-butylamine, pyrrolidine, and nitroethane. The hydrolysis might occur by an addition–elimination-type reaction as shown in Scheme I. It is very likely that α-nitro al-

Scheme I



dehyes are intermediates in this reaction. Indirect evidence for this was reported by Hurd and Sherwood. Alkaline hydrolysis of 2-piperidino-1-nitroethene gave piperidine and the potassium salt of nitroethanal. The latter was directly oxidized to dipotassium nitroacetate.[6] It is suggested that on acidification the carbonyl group is eliminated as formic acid.

The possibility that the hydrolysis of a secondary aminonitroalkene, which contains an amino hydrogen, proceeded by the prior formation of a nitroimine salt C was unlikely,



based on the results of a control test. When the potassium salt of **1**, prepared by treating **1** with potassium amide in liquid ammonia, was dissolved in water, no *tert*-butylamine was observed in the strongly alkaline solution. Acidification with acetic acid led to a 67% recovery of **1**.

Experimental Section

***N*-(2-Bromo-2-nitropropylidene)-*tert*-butylamine (2).** To a solution of 1-(*tert*-butylamino)-2-nitro-1-propene (**1**,[1] 3.16 g, 0.02 mol) and pyridine (1.97 g, 0.025 mol) in 25 mL of chloroform at 0 °C was added dropwise during 15 min a solution of bromine (3.20 g, 0.020 mol) in 15 mL of chloroform. The reaction mixture was stirred at 0 °C for 30 min and then washed with three 25-mL portions of cold water and dried ($MgSO_4$). The chloroform was removed in vacuo, and the residue, a yellow oil, was distilled in vacuo to afford **2** (3.65 g, 77%): bp 64–65 °C (4.3 mm); n^{20}_D 1.4700; IR (neat) 1665 (C=N), 1570 and 1339 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.22 (s, 9, $(CH_3)_3C$), 2.35 (s, 3, CH_3), 7.93 (s, 1, CH=N).

Anal. Calcd for $C_7H_{13}BrN_2O_2$: C, 35.46; H, 5.53; Br, 33.70; N, 11.82. Found: C, 35.23; H, 5.44; Br, 33.94; N, 11.60.

Molecular weight ($(CH_3)_2CO$) Calcd: 237. Found: 244.1.

From the distillation residue there was recovered 0.02 g (1%) of **1**, mp 107–110 °C.

Hydrolysis of *N*-(2-Bromo-2-nitropropylidene)-*tert*-butylamine (2). To a solution of **2** (1.08 g, 4.6 mmol) in 25 mL of water at 0 °C was added 0.5 mL of 0.02 N hydrochloric acid. The reaction mixture was stirred at 0 °C for 5 min and then extracted with ether. The extracts were dried ($MgSO_4$) and the ether was removed in vacuo to afford 0.79 g of a mixture of 1-bromo-1-nitroethane and a compound believed to be 2-bromo-2-nitropropanal: IR ($CHCl_3$) 1718 (C=O), 1565 and 1346 cm^{-1} (NO_2).

Distillation of the mixture afforded 1-bromo-1-nitroethane (0.25 g, 36%) as a colorless lachrymatory liquid, bp 27–28 °C (5 mm); IR ($CHCl_3$) 1567 and 1348 cm^{-1} (NO_2) [lit.[7] bp 72–73 °C (48 mm); IR (neat) 1567 and 1354 cm^{-1} (NO_2)]; NMR ($CDCl_3$) δ 2.24 (d, 3, CH_3), 6.25 (q, 1, $CHBrNO_2$).

Bromination of 1-(*tert*-Butylamino)-2-nitro-1-butene (3). To a stirred solution of **3** (1.72 g, 0.01 mol) and pyridine (1.20 g, 0.015 mol) in 15 mL of chloroform at 0 °C was added dropwise during 15 min a solution of bromine (1.60 g, 0.01 mol) in 20 mL of chloroform. The reaction mixture was stirred for 1 h at 0 °C and then quickly washed with three 25-mL portions of ice water and dried ($MgSO_4$). Removing the chloroform in vacuo gave 2.24 g of a light yellow liquid which was shown by NMR to consist of a mixture of *N*-(2-bromo-2-nitrobutylidene)-*tert*-butylamine (**4**, 70%), 1-bromo-1-nitropropane (**5**, 10%), and a compound believed to be 2-bromo-2-nitrobutanal (**6**, 20%): IR (neat) 1748 (C=O), 1667 (C=N), 1567 and 1331 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.03 (t, 3, CH_3), 1.20 (s, 9, $(CH_3)_3C$), 2.60 (m, 2, CH_2), 5.90 (t, 1, $CHBrNO_2$), 7.78 (s, 1, CH=N), 9.40 (s, 1, CH=O).

Distillation of the mixture at reduced pressure afforded fractions which contained all three components. The higher boiling fractions contained increasing quantities of **5**.

1-Pyrrolidino-2-nitro-1-propene (7). To a stirred solution of 1-(*tert*-butylamino)-2-nitro-1-propene (**1**,[1] 1.58 g, 0.01 mol) in 50 mL of absolute methanol was added a solution of pyrrolidine (0.78 g, 0.011 mol) in 10 mL of absolute methanol. The reaction mixture was heated to 45 °C for 90 min and then cooled to room temperature and poured into 500 mL of absolute ether. The ethereal solution was concentrated in vacuo and the residue triturated with cold hexane to afford a mass of fine, bright yellow crystals. Recrystallation from hexane gave **7** (1.18 g, 76%) as yellow needles: mp 93–94 °C; UV max (95% C_2H_5OH) 382 nm (ϵ 14 800), 256 (1600); IR ($CHCl_3$) 1633 (C=C or C=N), 1375 and 1250 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 2.00 (m, 4, CH_2 ring), 2.32 (s, 3, CH_3), 3.59 (m, 4, CH_2 ring), 8.45 (s, 1, CH=C); mass spectrum (75 eV), *m/e* (relative intensity) 156 (100), 139 (44), 126 (16), 110 (44), 109 (91).

Anal. Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 54.05; H, 8.01; N, 17.79.

Molecular weight (C_6H_6) Calcd: 156. Found: 160.1.

1-Pyrrolidino-2-nitro-1-butene (8). To a solution of 1-(*tert*-butylamino)-2-nitro-1-butene (**3**,[1] 6.88 g, 0.04 mol) in 50 mL of chloroform was added a solution of pyrrolidine (3.12 g, 0.044 mol) in 10 mL of chloroform. The homogeneous orange solution was allowed to stand at room temperature for 115 h and then was poured into 500 mL of absolute ether and concentrated in vacuo. Triturating the residue with cold hexane gave 5.88 g of crude product as a lemon yellow solid. Recrystallization from hexane afforded 4.70 g of a mixture of **8** and **3**, mp 81.5–82.5 °C.

Chromatographing on a silica gel column (13 × 2.5 cm) and eluting with absolute ether gave an analytical sample of **8** (23%) as yellow needles, mp 82–82.5 °C; IR ($CHCl_3$) 1630 (C=N), 1390, 1271, and 1220 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.13 (t, 3, CH_3), 2.01 (m, 4, CH_2 ring), 2.75 (q, 2, CH_2CH_3), 3.62 (m, 4, CH_2 ring), 8.43 (s, 1, CH=C); mass spectrum (75 eV), *m/e* (relative intensity) 170 (33), 154 (16), 152 (10), 124 (14), 123 (26), 108 (52), 41 (100).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.34; H, 8.11; N, 16.51.

Molecular weight ($(CH_3)_2CO$) Calcd: 170.2. Found: 173.9.

Unreacted **3** was recovered in 23% yield.

Reaction of 1-Pyrrolidino-2-nitro-1-propene (7) with Primary Amines. A. Employing Excess *tert*-Butylamine. Compound **7** (0.50 g, 3.2 mmol) was dissolved in 20 mL of *tert*-butylamine, and the solution was refluxed for 90 min. The reaction mixture was cooled to room temperature, and excess *tert*-butylamine was removed in vacuo. The yellow solid was triturated with hexane, filtered, and washed with a small quantity of cold ether to afford 1-(*tert*-butylamino)-2-nitro-1-propene (**1**, 0.46 g, 90%) as a yellow amorphous powder, mp 108–113 °C. The IR and NMR spectra were identical with those of authentic **1**.[1]

B. Employing 2.0 Molar Equivalents of *tert*-Butylamine. To a solution of **7** (0.16 g, 0.01 mol) in 1.5 mL of deuteriochloroform was added *tert*-butylamine (0.15 g, 0.02 mol) dissolved in 1 mL of deuteriochloroform. The solution was stirred briefly and transferred to an NMR tube, and the spectrum was recorded from 5 min to 22 h. The progress of the reaction was monitored by observing the olefinic methyl signals of **7** and **1** at δ 2.32 and 2.08, respectively.

After 22 h, when the NMR spectrum indicated that the reaction was 74% complete, an aliquot of the reaction mixture was transferred to a preparative TLC plate (20 cm × 20 cm × 1 mm, silica gel PF 254) and eluted with absolute ether to afford two fractions. Each was washed from the silica with absolute methanol, and the methanol was removed in vacuo to afford unreacted **7** (17 mg, 30%) and **1** (39 mg, 70%). The IR and NMR spectra were identical with those of authentic samples.[1]

C. Employing 2.2 Molar Equivalents of Isopropylamine. To **7** (0.29 g, 1.9 mmol) dissolved in 10 mL of chloroform was added iso-

propylamine (0.24 g, 4.0 mmol) dissolved in 5 mL of chloroform. The reaction mixture was stirred briefly and allowed to stand for 73 h at room temperature. Then the solvent was removed in vacuo, and the residue was triturated with cold petroleum ether (30–60 °C) and filtered to give 0.23 g of a 50:50 mixture of 1-(isopropylamino)-2-nitro-1-propene (**11**, 41%) and unreacted **7** (41%), as determined by NMR analysis of the olefinic methyl singlets of **11** and **7** at δ 2.00 and 2.32, respectively.

D. Employing 1.1 Molar Equivalents of *n*-Propylamine. A solution of **7** (0.32 g, 2.0 mmol) and *n*-propylamine (0.13 g, 2.2 mmol) in 17 mL of absolute methanol was stirred at room temperature for 48 h. Then the reaction mixture was subjected to TLC plates on silica gel PF 254 and eluted with absolute ether to afford two fractions. Each fraction was washed from the silica gel with absolute methanol, and the methanol was evaporated in vacuo. In this manner a solid and a liquid product were obtained. Recrystallization of the solid material from hexane gave recovered **7** (47 mg, 14%), mp 88–90 °C.

The liquid was 1-(*n*-propylamino)-2-nitro-1-propene (**10**, 110 mg, 38%). The IR and NMR spectra were identical with those of authentic **10**.[1] The high-resolution mass spectrum of **10** exhibited a molecular ion at *m/e* 244.0906 (calcd *m/e* 244.0899).

Reaction of 1-Cyclohexylamino-2-nitro-1-propene (9) with Excess *tert*-Butylamine. Compound **9** (0.50 g, 2.7 mmol) was dissolved in 20 mL of *tert*-butylamine. The solution was refluxed for 1 h and cooled to room temperature, and excess *tert*-butylamine was removed in vacuo to afford 0.47 g of a mixture of unreacted **9** (55%) and 1-(*tert*-butylamino)-2-nitro-1-propene (**1**, 39%), as determined by NMR analysis of the olefinic methyl signals of **9** and **1** at δ 2.04 and 2.08, respectively.

Alkaline Hydrolysis of 1-(*tert*-Butylamino)-2-nitro-1-propene (1). Compound **1** (3.16 g, 0.02 mol) was dissolved in 25 mL of 2 N potassium hydroxide, and one-half of the hydrolysate was distilled into a receiver containing 5 mL of concentrated hydrochloric acid. Evaporating the distillate to dryness in vacuo and recrystallizing the residue from absolute ethanol gave *tert*-butylamine hydrochloride (1.89 g, 87%). The IR spectrum was identical with that of an authentic sample.

Benzamide: mp 138–139 °C (lit.[8] mp 134 °C).

The remainder of the hydrolysate was acidified to pH 1 with hydrochloric acid and extracted with ether. The ether extracts were washed first with a saturated potassium bicarbonate solution, then with water, and dried ($MgSO_4$). Evaporation of the ether in vacuo gave nitroethane (0.74 g, 45%): IR (neat) 1563 and 1370 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 1.57 (t, 3, CH_3), 4.45 (q, 2, CH_2NO_2).

Potassium *N*-Propylidene-*tert*-butylamine-2-nitronate. To a suspension of potassium amide (0.018 mol) in 150 mL of liquid ammonia at −40 °C was added **1** (3.16 g, 0.02 mol) in one portion. The reaction mixture was stirred for 30 min, and the ammonia was replaced with absolute ether (3 h). The suspension was filtered to give a solid which immediately began to darken on exposure to the atmosphere. The solid was dissolved in absolute ethanol and reprecipitated with absolute ether to afford the salt (3.17 g, 91%) as a cream-colored amorphous powder, mp 190–195 °C dec; IR (KBr) 1610 (C=N), 1524 and 1297 cm^{-1} (NO_2^-); NMR (Me_2SO-d_6) δ 1.07 (s, 9, $(CH_3)_3C$), 1.85 (s, 3 CH_3), 8.60 (s, 1, CH=N). Due to its instability the salt could not be purified sufficiently for elemental analysis. NMR analysis indicated that it was approximately 90% pure.

Acidification of Potassium *N*-Propylidene-*tert*-butylamine-2-nitronate. The salt (0.98 g, 5.0 mmol) was dissolved in 50 mL of distilled water at 0 °C, and the solution was acidified with 10% aqueous acetic acid to pH 5–6. The yellow suspension was extracted with three 15-mL portions of chloroform and dried ($MgSO_4$), and the chloroform was removed in vacuo to afford 1-(*tert*-butylamino)-2-nitro-1-propene (**1**, 0.53 g, 67%), mp 111–113 °C. The IR and NMR spectra were identical with those of authentic **1**.

Acknowledgment. The support of this work by a grant from the Eli Lilly and Company is greatly appreciated.

Registry No.—(*Z*)-**1**, 64331-63-1; (*E*)-**1**, 64331-62-0; **2**, 64957-53-5; (*Z*)-**3**, 64331-65-3; (*E*)-**3**, 64331-64-2; **4**, 64957-54-6; **5**, 5447-96-1; **6**, 64957-55-7; (*E*)-**7**, 64957-56-8; (*E*)-**8**, 64957-57-9; (*Z*)-**9**, 64331-56-2; 2-bromo-2-nitropropanal, 64957-58-0; 1-bromo-1-nitroethane, 563-97-3; pyrrolidine, 123-75-1; nitroethane, 79-24-3; potassium *N*-propylidene-*tert*-butylamine-2-nitronate, 65000-07-9; potassium amide, 17242-52-3.

References and Notes

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Notes

Fluoronitroanilines. Reaction Control via Hydrogen Bonding

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Recent work[1,2] has shown that although pentafluoronitrobenzene reacts with most nucleophiles to give predominantly displacement of a *p*-fluorine atom, it reacts with ammonia and methylamine to give mainly *o*-fluorine displacement. The higher percentage of ortho replacement for amine nucleophiles was attributed to hydrogen bonding between the attacking amine and the nitro group. However, evidence for the hydrogen-bonding hypothesis was not unequivocal since the ortho/para ratio for the reaction of ammonia and methylamine with pentafluoronitrobenzene (69:31 and 65:35, respectively) was not far from statistical and the preferential ortho (relative to para) directing effect of the fluorine atoms in nucleophilic substitution was a complicating factor.[3]

We have found that treatment of 2,4,6-trifluoronitrobenzene (**1**) with ammonia in tetrahydrofuran gives essentially all ortho-displacement product. Thin-layer chromatographic analysis[4] shows only trace amounts of two unidentified products in addition to the ortho-displacement product, 3,5-difluoro-2-nitroaniline (**2**), which was isolated in 88% yield (a small amount of unreacted **1** is also present). Similarly, treatment of 1,3-dinitro-2,4,6-trifluorobenzene (**3**) with ammonium hydroxide in tetrahydrofuran at −10 °C gives only one monoamine, 3,5-difluoro-2,6-dinitroaniline (**4**). A small amount of diamine, 2,6-dinitro-5-fluoro-1,3-phenylenediamine (**5**), is formed from further reaction of **4** with ammonia but no other products were detected by thin-layer chromatographic analysis.[5]

It is significant that substitution occurs exclusively at the more hindered ortho positions in compounds **1** and **3**. These results strongly support the hypothesis of Allen et al.[2] that the reaction of ammonia with fluoronitrobenzenes is controlled by the degree of hydrogen bonding in the reaction intermediates.[6] For compound **1**, stabilization of the reaction intermediate by hydrogen bonding can occur at the position ortho to nitro but not at the position para. For compound **3**, the in-