(49) The band nearest the baseline was found to contain triadduct (**10**). An NMR spectrum of the crude product mixture showed **5b** and **10** to be the only products formed.
(50) Repeated attempts to obtain a correct elemental analysis on **5a** always gave results that were too low in C, H, and N. Given the extreme reactivity of octamethylsemibullvalene toward oxygen,[10] a reasonable hypothesis is that **5a**, itself a peralkylated semibullvalene, underwent some oxidation prior to being analyzed.

Alkyl Nitrate Nitration of Active Methylene Compounds. Nitration of Aldimines[1]

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The alkyl nitrate nitration of aldimines **1** derived from aldehydes and aliphatic or alicyclic amines affords the corresponding 1-alkylamino-2-nitro-1-alkenes **2**. The spectral data of **2** show the presence of both the *Z* and *E* isomers, the former predominating in both the solid state and in nonpolar solvents.

In continuation[2] of our studies of the alkyl nitration, we are now reporting on its application to the synthesis of 1-alkylamino-2-nitro-1-alkenes **2** (eq 1).

$$\underset{\mathbf{1}}{RN{=}CHCH_2R'} \xrightarrow[2.\ NH_4Cl]{1.\ KNH_2\text{–liquid } NH_3\text{–}RONO_2} \underset{\mathbf{2}}{RNCH{=}CR'} \quad (1)$$
(H on the CH, NO_2 on the CR′)

Methods that have been used to prepare **2** include the condensation of sodium nitromalonaldehyde with hydrochlorides of primary and secondary amines;[3] the condensation of α-nitro ketones with primary aromatic amines;[4] the reaction of morpholine and piperidine with alkoxyalkylidenemalonic esters and nitromethane;[5] the reaction between sodium methazonate and salts of primary[6a] and secondary amines;[6b] the reaction of vicinal dinitroalkenes[7a] or chloronitroalkenes[7b] with amines; and the condensation of nitroalkanes with N,N-disubstituted amide acetals[8] or with amide–dimethyl sulfate complexes.[9]

A consideration of the available methods has shown that they are limited in scope. Moreover, they suffer from the lack of readily available starting materials and frequently from low yields.

The nitration reaction in eq 1 was studied in several base–solvent systems with *N*-propylidene-*tert*-butylamine [**3**, R = $C(CH_3)_3$; R′ = CH_3] and *N*-butylidene-*tert*-butylamine [**4**, R = $C(CH_3)_3$; R′ = C_2H_5] as model compounds. As shown in Table I, the highest yields of 1-(*tert*-butylamino)-2-nitro-1-propene (**5**) and of 1-(*tert*-butylamino)-2-nitro-1-butene (**6**) (53 and 51%, respectively) were obtained in the potassium amide–liquid ammonia system when the molar ratio of **1** to base to nitrating agent was 1:2:1.5 and when 30 min was allowed for both anion formation and nitration. It is of interest that in a control test only 18% of **3** was recovered when it was subjected to potassium amide in liquid ammonia. A considerable amount of polymeric material was formed which was not identified. Only tar-like material was obtained when **3** was nitrated in lithium amide–liquid ammonia.

Nitration of **4** in *n*-butyllithium–hexane did not give **6** but, instead, afforded (*N*-*tert*-butyl)-4-aminooctane (**7**) which arose from a nucleophilic attack of butyllithium on the azomethine carbon[10] (eq 2). Nitrations of **4** with *n*-propyl nitrate were successful in lithium diisopropylamide employing hexane or THF as solvents, but the yield of **6** did not exceed 30%.

In order to determine the scope of the reaction, aldimines of varied structures were nitrated. Variations in the alkylamino moiety had some effect on the yield of the aminonitroalkenes **2** as indicated in Table II. The low yield of 1-(isopropylamino)-2-nitro-1-propene (**8**) is probably due to its instability. It decomposed on recrystallization from hot hexane with the evolution of oxides of nitrogen and also on standing at ambient temperatures.

$$\underset{\mathbf{4}}{(H_3C)_3CN{=}CH(CH_2)_2CH_3} \xrightarrow[2.\ H^+]{1.\ BuLi\text{–}C_6H_{14}\text{–}n\text{-}PrONO_2} \underset{\mathbf{7}}{H_3C(CH_2)_2CH(CH_2)_3CH_3} \quad (2)$$
(HNC(CH₃)₃ on the CH)

As shown in Table II, aldimines derived from primary aliphatic aldehydes underwent nitration in the potassium amide–liquid ammonia system to afford the expected aminonitroalkenes.

An interesting side reaction was observed in the nitration of *N*-ethylidene-*tert*-butylamine [**9**, R = $C(CH_3)_3$; R′ = H] with *N*-propyl nitrate. In addition to 1-(*tert*-butylamino)-2-nitroethene (**10**) there was also formed compound **5** in 10% yield (eq 3). Only **10** was obtained when **9** was nitrated with

$$\underset{\mathbf{9}}{(CH_3)_3CN{=}CHCH_3} \xrightarrow{1.\ KNH_2\text{–liquid } NH_3} \quad (3)$$
$$\xrightarrow[2.\ EtONO_2]{3.\ NH_4Cl} \underset{\mathbf{10}}{(CH_3)_3CNHCH{=}CHNO_2}$$
$$\xrightarrow[2.\ n\text{-}PrONO_2]{3.\ NH_4Cl} \underset{\mathbf{5}}{(CH_3)_3CNHCH{=}C(NO_2)CH_3} + \mathbf{10}$$

ethyl nitrate. Traces of **5** were also found in nitrations of **4** and *N*-heptylidene-*tert*-butylamine with *n*-propyl nitrate.

The formation of **5** in these reactions is very likely due to aldehyde interchange between the aldimines and propanal. In a control test it was established that **3** was formed in addition to considerable amounts of aldol condensation products when **4** was treated with propanal in potassium amide–liquid ammonia (eq 4).

$$\mathbf{4} + H_3CCH_2CHO \xrightarrow[2.\ NH_4Cl]{1.\ KNH_2\text{–liquid } NH_3} \underset{\mathbf{3}}{(H_3C)_3CN{=}CHCH_2CH_3} + \mathbf{4} \quad (4)$$

The formation of propanal in the nitrations with *n*-propyl

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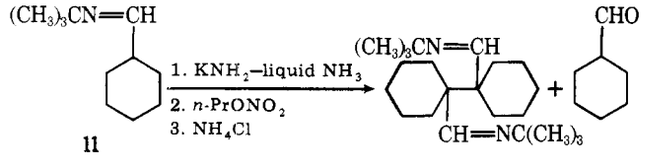
nitrate is not unexpected for it has been well established that primary alkyl nitrates undergo elimination reactions in alkaline media to give aldehydes.[11]

Alkyl nitrate nitrations of aldimines derived from α-branched aldehydes did not lead to *tert*-α-nitroaldimines. Instead, products were obtained which resulted both from dimerization of the aldimine and aldehyde interchange. For example, nitration of cyclohexylmethylidene-*tert*-butylamine (11) with *n*-propyl nitrate afforded 1,1′-bis(cyclohexylmethylidene-*tert*-butylamine) (**12**, 18%), cyclohexanecarboxaldehyde, and compound **5** (eq 5). The structure of **12** was

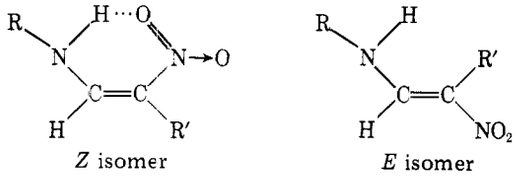


11 12 + **5** (5)

assigned on the basis of its NMR spectrum which showed singlets at 1.20 and 7.34 ppm for the *tert*-butyl and methine protons, respectively. The cyclohexyl rings were indicated by two types of ring protons, namely, a 16-proton multiplet at 1.80 ppm and a four-proton multiplet at 2.00 ppm. The latter is ascribed to the axial hydrogens in the 2 and 6 positions which are shielded by the imino groups.

Recently, we reported that alkyl nitrations of 2- and 4-isopropylpyridines led with dimerization to the 2,3-bis(pyridyl)-2,3-dimethylbutanes. It was shown that the nitroisopropylpyridines were intermediates in these transformations.[12] It is possible, although it has not been verified, that a tertiary nitro compound such as *N*-(1-nitrocyclohexylmethylidene)-*tert*-butylamine was the precursor in the formation of dimer **12**.

Spectra of Compounds 2. A study of the NMR spectra of compounds **2** clearly confirmed their structures as aminonitro olefins. In solution, both *E* and *Z* isomers were present. The *Z* isomer predominated in nonpolar solvents due to its increased stability through intramolecular hydrogen bonding. The *Z* and *E* isomers were distinguishable by the different chemical shifts of the olefinic protons. For example, in $CDCl_3$ they appeared in compound **5** as doublets at 7.09 and 8.41 ppm which integrated to a value of 0.9 and 0.1 protons, respectively. The *E* isomer absorbed at lower field because of the de-



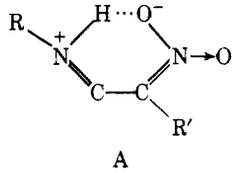
Z isomer *E* isomer

R = alkyl; R′ = H, alkyl

shielding effect of the *cis*-nitro group.[13] The resonances appeared as doublets due to vicinal HCNH coupling between the amino and olefinic protons. The existence of the coupling was demonstrated by deuterium exchange and spin-decoupling experiments. Irradiation of the NH absorption at 9.6 ppm caused the collapse of the olefinic proton resonances to singlets. Moreover the large coupling constant of 14 Hz is indicative of the trans conformation for the amino and olefinic protons.[14]

Addition of $(CD_3)_2SO$ to a $CDCl_3$ solution of **5** caused a change of the *Z*/*E* isomer ratio from 9:1 to 1:1. A similar solvent-promoted isomerization has also been observed with α-nitroarylidenephenylhydrazines.[15]

In the solid-state infrared spectra (KBr, CsI) of compounds **2**, the presence of the NH group was clearly apparent as a single, moderately intense absorption at 3200 cm^{-1}. In chloroform solution, this band was replaced by two weak absorptions at 3570–3330 cm^{-1} (concentration dependent) and at 3279–3225 cm^{-1} (concentration independent). These were assigned, respectively, to the free and associated (hydrogen bonded) forms of **2**. All of compounds **2** exhibited a sharp absorption at 1660–1630 cm^{-1}. This band, which is very likely due to the C=C vibration, possibly also reflects contribution from the C=N stretching vibrations of the dipolar structure A. Similar absorptions have been observed in the spectra of aminonitroacroleins[16] and aminonitroalkenes.[6a,17]



A

The conjugative effect of the alkylamino group was also seen in the shift to lower frequencies of the nitro group to 1371–1353 cm^{-1}. In nitroalkenes the asymmetric stretching vibration of the nitro group occurs at 1550–1500 cm^{-1}.[18]

The mass spectra of **2** exhibited molecular ions which corresponded to the appropriate molecular formulas. In compounds **2** which contained the *tert*-butylamino moiety, frag-

Table I. Effect of Various Base–Solvent Systems on the Yield of $(H_3C)_3CNHCH{=}C(NO_2)R$ (5, R = CH_3; 6, R = CH_2CH_3)

Base–solvent	5, yield, %	6, yield, %
KNH_2–liquid NH_3[a]	53	51
$NaNH_2$–liquid NH_3[a]	44	
$LiNH_2$–liquid NH_3[a]	0[b]	
n-BuLi–hexane[c]		0[d]
$(i\text{-Pr})_2$NLi–hexane[c,e]		30
$(i\text{-Pr})_2$NLi–THF[c,f]		28

[a] The molar ratio of 1 to base to *n*-propyl nitrate was kept at 1.0:2.0:1.5 in approximately 200 mL of solvent. Acidifications were carried out in situ with ammonium chloride. [b] Extensive tar formation was observed. [c] The molar ratio of 1 to base to *n*-propyl nitrate was 1:1:1.5. The reaction mixture was acidified with hydrogen chloride. [d] A 40% yield of (*N*-*tert*-butyl)-4-octanamine (**7**) was isolated. [e] When the molar ratio of base was increased to two, the yield of **6** was only 14%. [f] The reaction mixture was acidified in situ with glacial acetic acid.

Table II. Preparation of $RNHCH{=}C(NO_2)R'$[a,b]

R	R′	Yield, %	Mp, °C
$t\text{-}C_4H_9$	H	21[c,d]	81–82
$n\text{-}C_3H_7$	CH_3	54	*e*
$i\text{-}C_3H_7$	CH_3	40	62.5–63 dec
$i\text{-}C_4H_9$	CH_3	70	*e*
$t\text{-}C_4H_9$	CH_3	51	113–113.5
C_6H_{11}	CH_3	50	101–101.5
$t\text{-}C_4H_9$	C_2H_5	51[f]	91.5–92
$n\text{-}C_6H_{13}$	C_2H_5	67	*e*
$t\text{-}C_4H_9$	$n\text{-}C_5H_{11}$	46[f]	77.5–78

[a] Satisfactory analytical data were reported for all new aldimines and new alkylaminonitroalkenes. [b] Nitrations were performed in 150–200 mL of liquid ammonia at −33 °C, employing 0.10 mol of imine, 0.20 mol of potassium amide, and 0.15 mol of *n*-propyl nitrate. Anion formation and nitration times were 30 min. Acidification was performed in situ with 0.22 mol of ammonium chloride. [c] About 10% of 1-(*tert*-butylamino)-2-nitropropene (**5**) was also obtained as determined by NMR. [d] The yield was 13.8% when using ethyl nitrate. [e] Undistillable liquid. [f] Traces of **5** were present in the crude reaction mixture as determined by NMR.

mentation was dominated by the loss of methyl and isobutylene. Compounds **2** which did not contain the *tert*-butylamino group generally exhibited one or more ions which indicated the loss of the fragments OH, NO_2, or HNO_2. The frequent occurrence of the P − OH and P − HNO_2 ions suggests a molecular geometry in which the nitro group and a hydrogen atom are in close proximity, enabling the concerted loss of these fragments. This is consistent with the existence of **2** in the *Z* configuration.

Experimental Section

Apparatus. Nitrations were performed in a 300- or 500-mL four-necked flask equipped with a mechanical stirrer, dry ice condenser, thermometer, and pressure-equalizing addition funnel. The ammonia was passed through a potassium hydroxide tower prior to liquefaction.

***N*-Propylideneisobutylamine.** The following modification of the method of Campbell et al.[19] is representative of the procedure employed for the preparation of aldimines.

To 58.0 g (1.00 mol) of freshly distilled propanal at −20 °C was added dropwise, with stirring and cooling, 73.0 g (1.00 mol) of freshly distilled isobutylamine, while maintaining the temperature below −5 °C. Solid potassium hydroxide (~10 g) was added, and the reaction mixture was allowed to warm to room temperature while the aqueous layer separated (~1 h). The organic phase was stored over potassium hydroxide at 5 °C overnight and then distilled from fresh potassium hydroxide through a 40-cm Todd column packed with 0.25-in. glass helices to give *N*-propylisobutylamine (45.8 g, 40%): bp 115–116 °C; $n^{21}D$ 1.4092; IR ($CHCl_3$) 1669 cm^{-1} (C=N); NMR ($CDCl_3$) 0.89 [d, 6, $(CH_3)_2CH$], 1.08 (t, 3, CH_2CH_3), 1.4–2.5 [m, 3, CH_2CH_3 and $(CH_3)_2CH$], 3.19 (d, CH_2N), and 7.62 ppm (t, 1, CH=N).

***N*-Heptylidene-*tert*-butylamine (83%):** bp 51–52 °C (3 mm); $n^{21}D$ 1.4269; IR (neat) 1667 cm^{-1} (C=N); NMR ($CDCl_3$) 1.16 (m, 20, CH_2 and CH_3), 2.17 (m, 2, CH_2), and 7.60 ppm (t, 1, CH=N).

***N*-Butylidene-*n*-hexylamine (63%):** bp 107–110 °C (48 mm); $n^{20}D$ 1.4290; IR (neat) 1681 cm^{-1}; NMR ($CDCl_3$) 0.90 (t, 6, CH_3), 1.45 (m, 10, CH_2), 2.20 (m, 2, CH_2CH=N), 3.34 (t, 2, CH_2N), and 7.60 ppm (t, 1, CH=N).

***N*-Cyclohexylmethylidene-*tert*-butylamine (71%):** bp 54–54.4 °C (3 mm); $n^{20}D$ 1.4515; IR (neat) 1669 cm^{-1} (C=N); NMR ($CDCl_3$) 1.14 [s, 9, $(CH_3)_3C$], 1.2–2.2 (m, 11, CH_2 and CH, ring), and 7.42 ppm (d, 1, CH=N).

1-(*tert*-Butylamino)-2-nitro-1-propene (5). The following experiment is typical of the procedure employed in the nitration of aldimines.

To 150 mL of liquid ammonia at −33 °C was added a catalytic amount of ferric nitrate and freshly cut potassium metal (7.82 g, 0.20 g-atom). After the potassium amide had formed (15–30 min), freshly distilled *N*-propylidene-*tert*-butylamine[20] (11.3 g, 0.10 mol) was added in one portion. The reaction mixture was stirred at −33 °C for 0.5 h and then cooled to −60 °C, and *n*-propyl nitrate (15.8 g, 0.15 mol) was added during 5–8 min, while maintaining the temperature below −40 °C (*Caution:* cooling must be maintained during the addition of the nitrating agent, as long as the vigorous exotherm persists). The nitration mixture was stirred for an additional 25 min at −33 °C and then acidified at −40 °C with ammonium chloride (11.8 g, 0.22 mol).

The ammonia was replaced with absolute ether, the inorganic salts were filtered off, and the ether was removed in vacuo to give an orange oil. The oil was triturated with hexane, cooled to induce crystallization, and filtered. The orange amorphous solid (9.53 g, 60%) was dissolved in hexane, treated with decolorizing carbon, and recrystallized to afford 1-(*tert*-butylamino)-2-nitro-1-propene (**5**) (8.38 g, 53%): yellow needles; mp 113–113.5 °C; UV λ_{max} (95% C_2H_5OH) 370 nm (log ϵ 4.86) and 260 (3.11); IR ($CHCl_3$) 3236 (NH), 1645 (C=C or C=N), 1355, 1318, and 1239 cm^{-1} (NO_2); NMR ($CDCl_3$) 1.38 [s, 9, $(CH_3)_3C$], 2.06 (s, 3, CH_3), 7.09 (d, 0.9, C=CH, *Z* isomer, *J* = 14 Hz), 8.41 (d, 0.1, C=CH, *E* isomer, *J* = 14 Hz), and 9.6 ppm (br, 1 NH); mass spectrum (75 eV) *m/e* (rel intensity) 158 (42), 143 (38), 102 (22), 84 (17), 57 (100); mol wt (C_6H_6) calcd 158.2, found 162.0.

1-(*n*-Propylamino)-2-nitro-1-propene. From potassium (7.82 g, 0.20 g-atom), *N*-propylidene-*n*-propylamine[21] (9.90 g, 0.10 mol), *n*-propyl nitrate (15.8, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 200 mL of liquid ammonia, there was obtained 23.5 g of a dark brown liquid which did not crystallize.

A 5.00-g portion was chromatographed on a 13 × 2.5 cm silica gel column and eluted with ether to afford 1-(*n*-propylamino)-2-nitro-1-propene (1.70 g, 54%): nondistillable yellow liquid; $n^{22}D$ 1.5793; UV λ_{max} (95% C_2H_5OH) 370 nm (log ϵ 3.97) and 257 (2.90); IR ($CHCl_3$) 3279 (NH), 1660 (C=C or C=N), 1366, 1325, and 1239 cm^{-1} (NO_2); NMR ($CDCl_3$) 0.99 (t, 3, CH_3), 1.67 (m, 2, CH_2), 2.07 (s, 3, CH_3), 3.40 (m, 2, CH_2), 7.10 (d, 0.9, C=CH, *Z* isomer, *J* = 14 Hz), 8.36 (d, 0.1, C=CH, *E* isomer, *J* = 14 Hz), and 9.5 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 144 (31), 127 (1.1), 115 (19), 98 (1.1), 97 (9.0), 68 (23), 58 (72), 43 (100), 41 (98); mol wt [$(CH_3)_2CO$] calcd 144.17, found 143.16.

1-(Isopropylamino)-2-nitro-1-propene (8). From potassium (7.82 g, 0.20 g-atom), *N*-propylideneisopropylamine[22] (9.90 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 100 mL of liquid ammonia, there was obtained an amorphous red-orange solid (9.53 g, 66%). Recrystallization from hexane afforded **8** (5.73 g, 40%): yellow needles; mp 62.5–63 °C dec; UV λ_{max} (95% C_2H_5OH) 368 nm (log ϵ 4.21) and 262 (3.00); IR ($CHCl_3$) 3247 (NH), 1647 (C=C or C=N), 1360, 1299, and 1235 cm^{-1} (NO_2); NMR ($CDCl_3$) 1.28 [d, 6, $(CH_3)_2CH$], 2.00 (s, 3, CH_3), 3.67 [m, 1, $(CH_3)_2CH$], 7.08 (d, 0.9, C=CH, *Z* isomer, *J* = 14 Hz), 8.33 (d, 0.1, C=CH, *E* isomer, *J* = 14 Hz), and 9.4 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 144 (77), 129 (43), 111 (17), 97 (20), 85 (28), 82 (41), 58 (82), 56 (41), 55 (41), 43 (100).

1-(Isobutylamino)-2-nitro-1-propene. From potassium (7.82 g, 0.20 g-atom), *N*-propylideneisobutylamine (11.3 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 150 mL of liquid ammonia, there was obtained 24.1 g of a dark orange oil which did not crystallize. The oil was chromatographed on a 30 × 2.5 cm silica gel column and eluted with ether. The ether was removed in vacuo and the product was rechromatographed to afford 1-(isobutylamino)-2-nitro-1-propene (10.5 g, 70%): yellow-brown liquid; $n^{21}D$ 1.5832; UV λ_{max} (95% C_2H_5OH) 369 nm (log ϵ 3.98) and 243 (3.15); IR ($CHCl_3$) 3270 (NH), 1658 (C=C or C=N), 1371, 1323, and 1239 cm^{-1} (NO_2); NMR ($CDCl_3$) 0.95 [d, 6, $(CH_3)_2CH$], 1.0 [m, 1, $(CH_3)_2CH$], 2.05 (s, 3, CH_3), 3.27 (t, 2, CH_2N), 7.08 (d, 0.9, C=CH, *Z* isomer, *J* = 14 Hz), 8.28 (d, 0.1, C=CH, *E* isomer, *J* = 14 Hz), and 9.5 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 158 (39), 142 (2), 125 (4), 115 (65), 111 (10), 69 (36), 58 (100).

1-Cyclohexylamino-2-nitro-1-propene. From potassium (13.1 g, 0.34 g-atom), *N*-propylidenecyclohexylamine[23] (23.3 g, 0.17 mol), *n*-propyl nitrate (35.1 g, 0.33 mol), and ammonium chloride (19.8 g, 0.36 mol), in 150 mL of liquid ammonia, there was obtained an amorphous yellow-orange solid (18.3 g, 60%). Recrystallization from hexane gave 1-cyclohexylamino-2-nitro-1-propene: 15.7 g (50%); lustrous yellow plates; mp 101–101.5 °C; UV λ_{max} (95% C_2H_5OH) 370 nm (log ϵ 4.09) and 258 (2.86); IR ($CHCl_3$) 3225 (NH), 1652 (C=C or C=N), 1364, and 1299 cm^{-1} (NO_2); NMR ($CDCl_3$) 1.0–2.0 (m, 10, CH_2, ring), 2.04 (s, 3, CH_3), 3.0–3.6 (br, 1, CH, ring), 7.03 (d, 0.9, C=CH, *Z* isomer, *J* = 14 Hz), 8.32 (d, 0.1, C=CH, *E* isomer, *J* = 14 Hz), and 9.5 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 184 (76), 167 (10), 149 (20), 141 (26), 138 (19), 121 (metastable), 109 (18), 103 (22), 83 (58), 67 (28), 55 (100), 41 (66), 36.5 (metastable).

2-(*tert*-Butylamino)nitroethene (10). From potassium (7.82 g, 0.20 g-atom), *N*-ethylidene-*tert*-butylamine[24] (9.90 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 150 mL of liquid ammonia, there was obtained a red-brown oil (8.41 g, 58%) which did not crystallize. A 3.31-g portion was chromatographed twice on a 30 × 2.5 cm silica gel column and eluted with ether to afford 1.82 g of a yellow semisolid mixture of **10** (21%) and **5** (10%), as determined by NMR: IR ($CHCl_3$) 3333 (NH) and 1645 cm^{-1} (C=C or C=N); NMR ($CDCl_3$) 1.40 [s, 9, $(CH_3)_3C$], 2.07 (s, 1.0, $C=CCH_3$), 6.52 (d, 0.5, $CH=CHNO_2$), 7.14 [d, 0.33, $CH=C(NO_2)-CH_3$, *J* = 14 Hz], 7.20 (quartet, 0.50, $CH=CHNO_2$, *J* = 14, 6 Hz), and 9.6 ppm (br, 1, NH).

When ethyl nitrate was the nitrating agent, there was obtained after a similar workup **10** (2 g, 13.8%): mp 81–82 °C (hexane); UV λ_{max} (95% C_2H_5OH) 353 nm (log ϵ 4.29) and 230 (3.26); IR ($CHCl_3$) 3257 (NH), 1637 (C=C or C=N), 1353, 1319, and 1232 cm^{-1} (NO_2); NMR ($CDCl_3$) 1.40 [s, 9, $(CH_3)_3C$], 6.50 (d, 1, $CH=CHNO_2$ *J* = 6 Hz), 7.04 (q, 1, $CH=CHNO_2$, *J* = 14, 6 Hz), and 9.5 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 144 (28), 129 (36), 115.5 (metastable), 89 (11), 72 (13), 59 (38), 41 (100); mol wt [$(CH_3)_2CO$] calcd 144.17, found 144.01.

1-(*tert*-Butylamino)-2-nitro-1-butene (6). From potassium (7.82 g, 0.20 g-atom), *N*-butylidene-*tert*-butylamine[20] (12.7 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 150 mL of liquid ammonia, there was obtained an orange amorphous solid (11.7 g, 68%). Recrystallization from hexane afforded **6** (8.69 g, 51%): pale yellow needles; mp 91.5–92 °C; UV λ_{max} (95% C_2H_5OH) 370 nm (log ϵ 4.13) and 259 (2.58); IR ($CHCl_3$) 3247 (NH), 1646 (C=C or C=N), 1362, 1325, and 1235 cm^{-1} (NO_2); NMR

($CDCl_3$) 1.12 (t, 3, CH_3), 1.37 [s, 9, $(CH_3)_3C$], 2.47 (m, 2, CH_2), 7.05 (d, 0.9, C=CH, *Z* isomer, J = 14 Hz), 8.37 (d, 0.1, C=CH, *E* isomer, J = 14 Hz), and 9.7 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 172 (39), 157 (26), 143.1 (metastable), 116 (8), 101 (29), 72 (18), 57 (100), 41 (36).

1-(*tert*-Butylamino)-2-nitro-1-heptene. From potassium (7.82 g, 0.20 g-atom), *N*-heptylidene-*tert*-butylamine (16.9 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 100 mL of liquid ammonia, there was obtained an orange waxy solid (11.1 g, 52%). Recrystallization from hexane gave 1-(*tert*-butylamino)-2-nitro-1-heptene (9.78 g, 46%): waxy yellow plates; mp 77.5–78 °C; UV λ_{max} (95% C_2H_5OH) 370 nm (log ϵ 4.20) and 260 (3.04); IR ($CHCl_3$) 3247 (NH), 1650 (C=C or C=N), 1368, 1325, 1238, and 1227 cm^{-1} (NO_2); NMR ($CDCl_3$) 0.90 (t, 3, CH_3), 1.33 (m, 6, CH_2), 1.38 [s, 9, $(CH_3)_3C$], 2.38 (m, 2, CH_2), 6.97 (d, 1, C=CH, *Z* isomer, J = 14 Hz), and 9.6 ppm (br, 1, NH).

1-(*n*-Hexylamino)-2-nitro-1-butene. From potassium (7.82 g, 0.20 g-atom), *N*-butylidene-*n*-hexylamine (15.5 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 150 mL of liquid ammonia, there was obtained a dark red oil (17.7 g, 76%).

A 2.67-g portion of this oil was chromatographed on a 15 × 2.5 cm silica gel column and eluted with ether. The ether was removed in vacuo and the procedure was repeated to afford 1-(*n*-hexylamino)-2-nitro-1-butene (2.01 g, 67%): light orange, nondistillable liquid; $n^{20}D$ 1.5485; UV λ_{max} (95% C_2H_5OH) 370 nm (log ϵ 3.85) and 244 (3.00); IR ($CHCl_3$) 3247 (NH), 1647 (C=C or C=N), 1362, and 1235 cm^{-1} (NO_2); NMR ($CDCl_3$) 0.85–2.0 (m, 14, CH_2 and CH_3), 2.45 (m, 2, CH_2), 3.42 (m, 2, CH_2), 7.00 (d, 0.9, C=CH, *Z* isomer, J = 14 Hz), 8.31 (d, 0.1, C=CH, *E* isomer, J = 14 Hz), and 9.6 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 200 (36), 185 (45), 154 (19), 129 (20), 112 (35), 72 (56), 55 (42), 43 (100), 41 (70); mol wt [$(CH_3)_2CO$] calcd 200.28, found 200.99.

Nitration of *N*-Cyclohexylmethylidene-*tert*-butylamine. From potassium (7.82 g, 0.20 g-atom), *N*-cyclohexylmethylidene-*tert*-butylamine (**11**, 16.7 g, 0.10 mol), *n*-propyl nitrate (15.8 g, 0.15 mol), and ammonium chloride (11.8 g, 0.22 mol), in 200 mL of liquid ammonia, there was obtained, upon trituration with hexane and filtering, 4.22 g of a yellow-white solid: mp 119–123 °C. A 2.38-g sample was sublimed at 65–70 °C (0.4 mm) to afford a yellow and a white fraction. These were mechanically separated and each fraction was sublimed. The procedure was repeated four times.

Fraction 1 was **1-(*tert*-butylamino)-2-nitro-1-propene (5,** 0.36 g, 4%), mp 105–108 °C. The IR, NMR, and mass spectra were identical with those of authentic **5**.

Fraction 2 was **1,1′-bis(cyclohexylmethylidene-*tert*-butylamine) (12,** 1.70 g, 18%): colorless needles; mp 128.5–129 °C; IR ($CHCl_3$) 1658 cm^{-1} (C=N); NMR ($CDCl_3$) 1.20 [s, 9, $(CH_3)_3C$], 1.8 (m, 8, CH_2, ring), 2.00 (m, 2, H, axial, ring), and 7.34 ppm (s, 1, N=CH); mass spectrum (75 eV) *m/e* 332 (calcd *m/e* 332); mol wt [$(CH_3)_2CO$] calcd 332, found 320. Anal. Calcd for $C_{22}H_{40}N_2$: C, 79.45; H, 12.12; N, 8.42. Found: C, 78.99; H, 11.92; N, 8.60.

Distillation of the hexane filtrate in vacuo gave a mixture of cyclohexanecarboxaldehyde (0.28 g, 2%) and recovered **11** (3.73 g, 23%) as determined by GLC. Hydrolysis of the mixture in the presence of 2,4-dinitrophenylhydrazine reagent gave cyclohexanecarboxaldehyde dinitrophenylhydrazone, mp 168–169 °C. A mixture melting point determination with authentic cyclohexanecarboxaldehyde dinitrophenylhydrazone gave no depression.

Reaction of *n*-Butylidene-*tert*-butylamine (4) with *n*-Butyllithium. To a stirred solution of *n*-butyllithium (0.11 mol) in 150 mL of hexane at −20 °C, under nitrogen, was added *n*-butylidene-*tert*-butylamine[20] (12.7 g, 0.10 mol). After allowing 0.5 h for anion formation, the reaction mixture was cooled to −70 °C and *n*-propyl nitrate (15.8 g, 0.15 mol) added dropwise to the rapidly stirred solution, while maintaining the temperature below −40 °C (*Caution:* vigorous exotherm). After 0.5 h the nitration mixture was saturated with dry hydrogen chloride at −40 °C to afford a gelatinous suspension. Extracting with chloroform, filtering, and removing the chloroform in vacuo gave a brown resinous material (19.8 g).

A 5.00-g portion was chromatographed on a silica gel column and eluted with ether to afford (*N*-*tert*-butyl)-4-octylamine (**7,** 1.83 g, 40%): colorless crystals; mp 99–101 °C; IR ($CHCl_3$) 1600 cm^{-1} (C=N); NMR ($CDCl_3$) 0.97 (m, 3, CH_3), 1.53 [s + m, 19, $(CH_3)_3C$ and CH_2], 3.0 (br, 1, CH), and 8.9 ppm (br, 1, NH); mass spectrum (75 eV) *m/e* (rel intensity) 185 (8), 170 (33), 142 (94), 128 (100), 86 (81), 72 (85), 52.1 (metastable), 40.5 (metastable).

Reaction of *N*-Butylidene-*tert*-butylamine (4) with Propanal in Potassium Amide–Liquid Ammonia. To a stirred suspension of potassium amide (0.20 mol) in 200 mL of liquid ammonia at −40 °C was added *N*-butylidene-*tert*-butylamine[20] (**4,** 12.7 g, 0.10 mol). After stirring 0.5 h, the reaction mixture was cooled to −55 °C and propanal (5.81 g, 0.10 mol) added during 5 min (*Caution:* exotherm) while maintaining the temperature below −40 °C. After allowing an additional 25 min for reaction, the mixture was acidified with ammonium chloride (11.8 g, 0.22 mol) at −40 °C and the ammonia replaced with absolute ether. The reaction mixture was filtered and the ethereal filtrate carefully concentrated in vacuo to a volume of ~100 mL. The remainder of the ether was removed by distillation through a 40-cm Todd column packed with 0.25-in. glass helices. The residue remaining from the distillation was redistilled in vacuo from solid potassium hydroxide to afford two fractions.

Fraction 1 [1.50 g; bp 35–40 °C (20 mm); $n^{20}D$ 1.4120] consisted of a mixture of **4** (8%) and *N*-propylidene-*tert*-butylamine (5%), as determined by GLC.

Fraction 2 [1.92 g: bp 80–90 °C (10 mm); $n^{20}D$ 1.4659] consisted of at least six high boiling compounds (by GLC). The presence of olefinic protons in the NMR spectrum indicated that these compounds were products of aldol condensation. They were not identified.

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Registry No.—**4,** 6852-59-1; (*E*)-**5,** 64331-62-0; (*Z*)-**5,** 64331-63-1; (*E*)-**6,** 64331-64-2; (*Z*)-**6,** 64331-65-3; **7,** 64331-66-4; (*E*)-**8,** 64331-67-5; (*Z*)-**8,** 64331-68-6; **10,** 64331-69-7; **11,** 53188-66-2; **12,** 64331-70-0; *N*-propylideneisobutylamine, 6898-80-2; propanal, 123-38-6; isobutylamine, 78-81-9; *N*-heptylidene-*tert*-butylamine, 6852-61-5; heptanal, 111-71-7; *N*-butylidenehexylamine, 64331-71-1; butanal, 123-72-8; hexylamine, 111-26-2; *N*-propylidene-*tert*-butylamine, 7020-81-7; propyl nitrate, 627-13-4; *N*-propylidenepropylamine, 7707-70-2; (*Z*)-1-(propylamino)-2-nitro-1-propene, 64331-52-8; (*E*)-1-(propylamino)-2-nitro-1-propene, 64331-53-9; *N*-propylideneisopropylamine, 28916-23-6; (*Z*)-1-(isobutylamino)-2-nitro-1-propene, 64331-54-0; (*E*)-1-(isobutylamino)-2-nitro-1-propene, 64331-55-1; *N*-propylidenecyclohexylamine, 1195-49-9; (*Z*)-1-cyclohexylamino-2-nitro-1-propene, 64331-56-2; (*E*)-1-cyclohexylamino-2-nitro-1-propene, 64331-57-3; *N*-ethylidene-*tert*-butylamine, 7020-80-6; ethyl nitrate, 625-58-1; (*E*)-1-(*tert*-butylamino)-2-nitro-1-heptene, 64331-58-4; (*Z*)-1-(*tert*-butylamino)-2-nitro-1-heptene, 64331-59-5; (*E*)-1-(hexylamino)-2-nitro-1-butene, 64331-60-8; (*Z*)-1-(hexylamino)-2-nitro-1-butene, 64331-61-9; cyclohexanecarboxaldehyde dinitrophenylhydrazone, 3335-68-0; *tert*-butylamine, 75-64-9; cyclohexanecarboxaldehyde, 62043-61-0.

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Deprotonation of a Hindered Keteniminium Salt[1]

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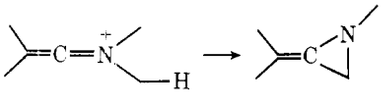
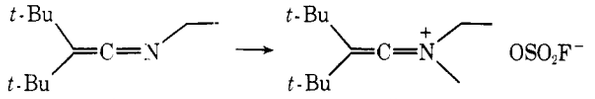
The synthesis of di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium fluorosulfonate (**2**) is described. This salt owes its unusual stability to the steric bulk of its substituents. Deprotonation of this salt with sodium bis(trimethylsilyl)-amide generated the corresponding azomethine ylide **9**. In the absence of added dipolarophiles, **9** dimerizes to the piperazine **4**. In the presence of norbornene, however, **9** adds in 1,3-dipolar fashion to give **7**. The novel chemical properties of **4**, **7**, and **8** are discussed.

We had previously observed that deprotonation of certain iminium salts could lead to aziridines via ring closure of an intermediate 1,3-dipolar azomethine ylide.[2] Our interest in the synthesis and chemistry of methylene aziridines led us to consider an extension of this reaction to keteniminium salts.



Several procedures were tried in our attempts to prepare keteniminium salts. Although these attempts yielded interesting chemistry, the salts proved much too reactive for general use in our deprotonation studies.[3] One notable exception, di-*tert*-butylketene-*N*-ethyl-*N*-methyliminium fluorosulfonate (**2**), could be prepared in high yield by alkylation of the corresponding ketenimine (**1**) with methyl fluorosulfonate.



1 2

Results

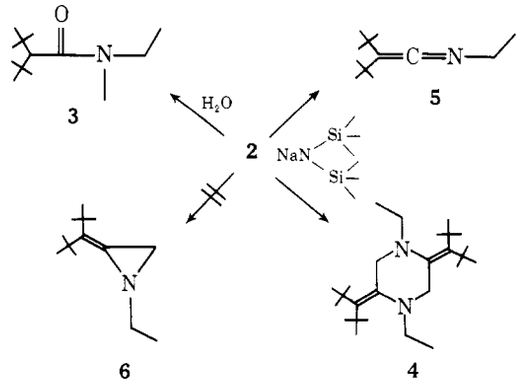
The sterically protected di-*tert*-butylketene-*N*-ethylimine **1** was synthesized from 2,2-di-*tert*-butylacetyl chloride[4] via a conventional procedure (see Experimental Section). The appropriate signals and multiplicities were found in its NMR spectrum. A strong and characteristic infrared maxium at 1998 cm^{-1} assignable to the heterocumulene functionality, C=C=N—, was also observed.[5,6] Attempts to isolate an analytical sample of **1** completely free from di-*tert*-butylacetonitrile[7] either by conventional distillation techniques or by column chromatography resulted in only slight purification. Nevertheless, the alkylation was performed by syringing a twofold excess of methyl fluorosulfonate[8] into a stirred ethereal solution containing ketenimine **1**. Keteniminium fluorosulfonate salt **2** precipitated as a white flocculent solid. This material was determined by spectroscopic analysis to be completely free of nitrile and/or alkylated nitrile by-products.

Keteniminium salt **2** proved to be remarkably stable (mp 224–228 °C with decomposition) considering the known chemistry of other heterocumulenes.[9,10] It is very soluble in polar solvents such as chloroform, ethanol, or water and could be recrystallized from methylene chloride–ether. It was inert toward neutral hydrolysis conditions and it could be recovered unchanged after stirring in water at room temperature for 2 h or more. The infrared spectrum of **2** showed a band of medium intensity at 2000 cm^{-1} which is at somewhat lower frequency than expected for a ketenimine with a positively charged heteroatom. Schiff bases, for example, show appreciable infrared shifts to higher frequency upon protonation or alkylation.[6] Present in the NMR spectrum was a low-field *tert*-butyl signal at δ 1.39 and a deshielded methyl singlet at δ 3.90, as well as the expected ethyl pattern at δ 1.48 (triplet) and 4.11 (quartet). As further structural proof, **2** was hydrolyzed in aqueous base to tertiary amide **3** (Scheme I).

The deprotonation of **2** was performed in benzene using sodium bis(trimethylsilyl)amide as a sterically hindered, nonnucleophilic strong base.[2] Thus, a slurry of **2** in benzene with excess base for 24 h produced the piperazine dimer **4** in 52% yield rather than the intended aziridine **6**. The dimeric structure of **4** was confirmed by its high-resolution mass spectrum which showed a parent ion at *m/e* 390.3977 (calcd for $C_{26}H_{50}N_2$, 390.3973). The NMR spectrum of **4** proved unexpectedly complex. The endocyclic methylene group (H_4, H_5) appeared as a sharp AB quartet (coupling constants and shifts shown in Table I).

The exocylic methylene protons (H_6, H_7) appeared as a quartet of quartets pattern which collapsed to a simple AB system upon spin decoupling of the methyl protons (H_1). The geminal nonequivalence of these protons (H_6, H_7) can be attributed to restricted rotation of the *N*-ethyl groups of **4**.[11] Inspection of molecular models shows extensive steric interaction between the *N*-ethyl substituent and its neighboring *tert*-butyl group.

Scheme I



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