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# Deprotonation of a Hindered Keteniminium Salt[1]

James A. Deyrup* and George S. Kuta

*Department of Chemistry, University of Florida, Gainesville, Florida 32611*

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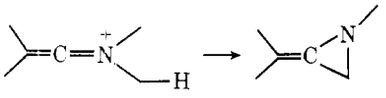
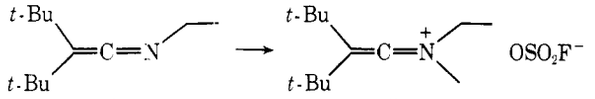
The synthesis of di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium fluorosulfonate (**2**) is described. This salt owes its unusual stability to the steric bulk of its substituents. Deprotonation of this salt with sodium bis(trimethylsilyl)-amide generated the corresponding azomethine ylide **9**. In 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

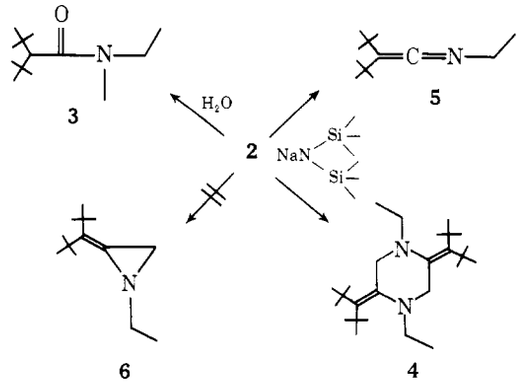
The sterically protected di-*tert*-butylketene-*N*-ethylimine **1** was synthesized from 2,2-di-*tert*-butylacetyl chloride[4] via a conventional procedure (see Experimental Section). The appropriate signals and multiplicities were found in its NMR spectrum. A strong and characteristic infrared maxium 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 $\delta$ 1.39 and a deshielded methyl singlet at $\delta$ 3.90, as well as the expected ethyl pattern at $\delta$ 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



3 5 2 6 4

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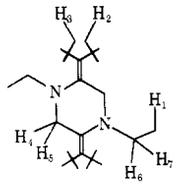
Table I. 100-MHz Proton Spectrum of Piperazine Dimer 4[a]



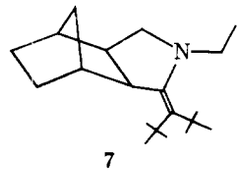
| Proton | δ | Multiplicity | J, Hz |
|---|---|---|---|
| $H_1$ | 1.07 | t | $J_{1,6(7)} = 7$ |
| $H_2$ | 1.30 | s | |
| $H_3$ | 1.33 | s | |
| $H_4$ | 2.60 | d | $J_{4,5} = 10$ |
| $H_5$ | 3.35 | d | $J_{5,4} = 10$ |
| $H_6$ | 3.02 | d of q | $J_{6,7} = 12$, $J_{6,1} = 7$ |
| $H_7$ | 2.72 | d of q | $J_{7,6} = 12$, $J_{7,1} = 7$ |

[a] $CDCl_3$ as solvent.

Although 1,4-cyclohexanedione is known to prefer a nonchair conformation,[12] the NMR pattern displayed by the endocyclic methylene group argues against such a flexible conformation. Molecular models suggest that 4 probably assumes a rigid chairlike conformation in which the two *N*-ethyl groups occupy axial positions. This conformation is consistent with the observed NMR spectrum.

Minor components appeared in the deprotonation product mixture which showed infrared absorption bands of rather weak intensity at ca. 2000 and 1640 $cm^{-1}$. These were interpreted as arising from dealkylation (to give **5**) and hydrolysis (to give **3**) during the prolonged reaction times. Attempts to encourage ring closure by performing the deprotonation in refluxing benzene again produced piperazine **4** in somewhat higher yield (59%). Deprotonation under the homogeneous conditions of hexamethylphosphoramide (HMPA) resulted in a drastic decrease in dimerization (21%), but only at the expense of hydrolysis to the amide **3** (52%). Further attempts to effect cyclization to **6** were abandoned, and attention was focused on the identity of the supposed "1,3-dipolar" precursor of **4**.

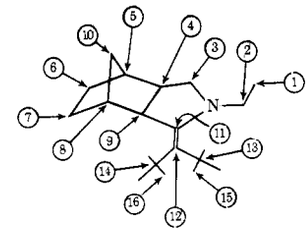
Stereospecific additions to 1,3-dipolarophiles have been of profound importance in establishing the intermediacy of azomethine ylides during the course of aziridine isomerizations.[13] These trapping experiments are now recognized as convincing evidence for the intervention of other 1,3-dipoles as well. Unfortunately, capture of in situ generated 1,3-dipoles by conventional trapping agents was subject to major experimental problems. Most desirable dipolarophiles would hardly withstand the severity of the strongly basic conditions required for dipole formation. Norbornene, however, was found to be inert to the silylamide base under the deprotonation conditions. Treatment of **2** with sodium bis(trimethylsilyl)-amide in the presence of a tenfold excess of norbornene formed the 1:1 adduct **7**. Attempted purification of **7** by



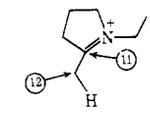
**7**

short-path distillation resulted in some sample decomposition with no substantial improvement in product quality. Spectroscopic analysis of adduct **7** before distillation revealed a parent ion at *m/e* 289.2761 (calcd for $C_{20}H_{35}N$, 289.2769). Complete analysis of the mass spectrum suggested the presence of at least one other component. The identity and relative percentage of this by-product(s), however, was not determined. NMR spectral analysis showed the expected nonequivalent *tert*-butyl signals at δ 1.35 and 1.50, a methyl triplet at δ 1.00, as well as unresolved methylene and norbornyl multiplets in the range δ 1.0–3.0. $^{13}C$ NMR (Table II) proved to be helpful in establishing the presence of the olefinic linkage carrying the *tert*-butyl groups. These olefinic carbons appeared as singlets at δ 141.6 and 124.8 downfield from internal $Me_4Si$ and are in agreement with typical shifts for $sp^2$-hybridized carbons. The assignments made in Table II were based on the multiplicities extracted from single frequency off-resonance decoupling data together with typical chemical-shift values for model norbornyl and pyrrolidine derivatives.[14] The infrared spectrum contained a weak band at ca. $1625^{-1}$ characteristic of the enamine functionality.[5]

Table II. $^{13}C$ Chemical-Shift Data for 7 and 8



**7**

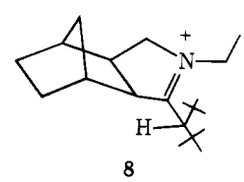


**8**

| δ[a] (7) | δ[a] (8) | Multiplicity | Assignment |
|---|---|---|---|
| 16.0 | 13.0 | q | 1 |
| 26.2 | 27.2 | t | 6 |
| 31.1 | 31.8 | q | 16 |
| 31.6 | 29.5 | t | 7 |
| 32.6 | 32.7 | q | 15 |
| 33.6 | 36.7 | s | 14 |
| 36.0 | 36.8 | s | 13 |
| 36.7 | 40.3 | d | 5 |
| 41.1 | 40.7 | d | 8 |
| 41.8 | 34.2 | t | 10 |
| 44.3 | 48.0 | t | 2 |
| 51.1 | 42.8 | d | 4 |
| 54.6 | 60.2 | d | 9 |
| 57.4 | 64.5 | t | 3 |
| 124.8 | 59.9 | s (7) d (8) | 12 |
| 141.6 | 195.2 | s | 11 |

[a] Chemical shifts are reported downfield from internal $Me_4Si$ with deuteriochloroform as a solvent. Some of these assignments where there are similar shifts and multiplicities may be interchanged.

Interestingly, adduct **7** was derivatized during an attempted purification via column chromatography to a compound which gave an immediate precipitate with silver nitrate. An identical product was formed from hydrochloric acid treatment of **7**. This product is assigned the hydrochloride structure **8** formed



**8**

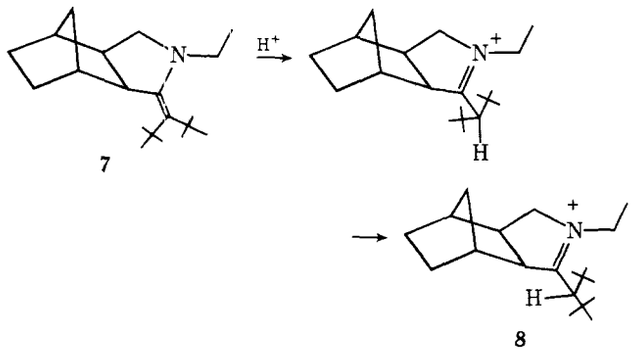
from the protonation of the enamine moiety of **7**.

The NMR spectrum of this derivative was much more informative than that of **7**. The postively charged nitrogen greatly deshields the adjacent exo- and endocyclic pairs of methylene protons while separating the $H_{3a}$ and $H_{7a}$ endo protons by approximately 0.75 ppm. The exo configuration of adduct **7** is based on the ample literature precedent for the preferred exo addition of 1,3-dipoles to norbornene.[13a,13f,14] The $^{13}C$ spectrum provided valuable structural data. The loss of one olefinic C, the shift of the other to 195, and the multi-

**Table III. A Partial Tabulation of Mass Spectral Fragmentations Obtained from 7 and 8**

| | Rel Intensity, % | |
|---|---|---|
| *m/e* | 7 | 8 |
| 289 | 1.8 | 2.0 |
| 274 | 2.6 | 3.3 |
| 233 | 13.5 | 13.4 |
| 232 | 19.6 | 23.0 |
| 219 | 17.5 | 16.7 |
| 218 | 100.0 | 100.0 |

Scheme II



7 8

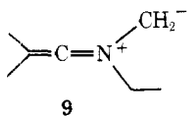
plicity change of $C_{12}$ from a singlet to a doublet are in agreement with C protonation of the enamine. The presence of an infrared band at 1620 $cm^{-1}$ [15] also supports the presence of the iminium functionality ($C{=}N^+$). High-resolution mass spectrometry failed to show a parent ion at *m/e* 326 for the hydrochloride salt **8**. Instead, a pseudo parent ion at *m/e* 289.2763 (calcd for $P^+ - HCl$, 289.2769) was observed. The conspicuous loss of HX from salts has been noted to occur in other systems.[3,16] A tabulation of the major fragmentations of **8** is given in Table III. These are compared with *m/e* values obtained from the mass spectral analysis of freshly prepared **7**. The great similarity of these two spectra supports the proposed structural relationship.

The iminium bond of the hydrochloride salt **8** was inert toward attack by a variety of reagents, including methyllithium (addition and/or deprotonation), sodium borohydride (reduction), sodium iodide (dealkylation), and aqueous sodium hydroxide (deprotonation and/or hydrolysis). The unusual proclivity of adduct **7** to scavange HCl and the marked resistance of **8** toward deprotonation warrant further comment.

Analysis of molecular models show that extreme crowding between the *tert*-butyl groups and the norbornyl skeleton in **7** is unavoidable (if approximately normal enamine geometry is maintained). Substantial steric relief, though, is experienced on protonation when rotation of the carbon bearing the *tert*-butyl group assumes a thermodynamically more stable conformation (cf. Scheme II). Conversely, deprotonation of **8** would require rotation of the *tert*-butyl groups into a sterically demanding conformation in which the proton would be in a periplanar arrangement with the p orbital of the iminium bond.

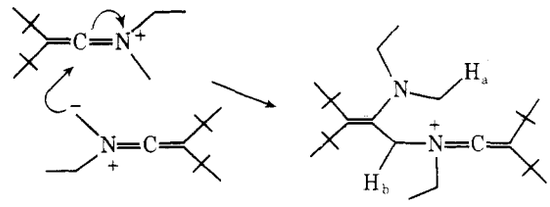
## Discussion

The experimental observations of dimerization and stereospecific addition to norborene can be explained in terms of intermediate ylide **9**. An alternative stepwise path to dimer



9

Scheme III



10

**7** must be considered (Scheme III). Thus, stepwise addition of dipole **9** to iminium salt **2** could yield **10**. Although deprotonation of **10** could occur at $H_a$ to give **4** after cyclization, $H_a$ is no longer acidic and it would appear that $H_b$ would be lost with greater ease.[17] We thus prefer the alternative concerted 3 + 3 cycloaddition which has ample literature precedent.

The failure of 1,3 dipole **9** to cyclize to methylene aziridine **6** is surprising.[18] Steric arguments would, if anything, tend to favor **6** over dimer **4**. It should be noted, however, that the electrocyclic ring closure proceeds with concomitant destruction of $\pi$ bonding. It is known the substituents which can stabilize charge facilitate the concerted and reversible thermal ring opening of aziridines. Aziridines which lack such stabilizing substituents tend to sustain carbon–carbon or carbon–nitrogen scission and polymerize when subjected to thermal ring-opening conditions. It is possible, therefore, that the lack of ring closure of **9** results from the lack of groups which would facilitate loss of $\pi$ overlap.

It should also be noted that the intermediate **9** has a $\pi$ bond orthoganal to the azomethine ylide $\pi$ system. The localized $\pi$ bond is directed toward the opposite partner in the cycloaddition reaction and potentially set up for weak bonding and resultant transition state energy lowering. This rationale is similar to that proposed for 2 + 2 cycloadditions involving ketenes.[21]

## Experimental Section

Melting and boiling points are recorded in degrees centigrade and are uncorrected. Melting points were determined with a Thomas-Hoover Unimelt capillary melting-point apparatus using 1.6–1.8 × 90 mm Kimax capillary tubes. Boiling points were determined by conventional distillation techniques or by microcapillary methods. Infrared spectra were recorded on a Perkin-Elmer Model 137 sodium chloride prism spectrometer and calibrated at 1601 $cm^{-1}$ with a polystyrene film. Nuclear magnetic resonance spectra were recorded on a Varian Model A60-A analytical spectrometer for 60-MHz proton spectra and a Varian Model XL-100 spectrometer for 100-MHz proton and proton-decoupled spectra. Carbon-13 nuclear magnetic resonance spectra were obtained from a Varian Model XL-100 spectrometer operating at a probe frequency of 25.16 MHz. All chemical shifts ($\delta$) in designated solvents are reported in parts per million (ppm) downfield from tetramethylsilane as an internal standard. Routine low-resolution mass spectra, exact mass, and molecular weight data were measured on an AEI-MS-30 double-beam spectrometer at an ionizing potential of 70 eV. Microanalyses were carried out by Atlantic Microlab, Inc., Atlanta, Georgia, and in all cases are in agreement with assigned structures. Where noted, reactions and manipulations of moisture-sensitive compounds were carried out in a Labconco drybox purged with a continuous stream of nitrogen. Solvent evaporations were performed at reduced pressure on a Büchi Rotoavapor-R rotary evaporator equipped with a water aspirator.

***N*-Ethyl-2,2-Di-*tert*-butylacetamide.** Anhydrous ethylamine (15.0 g, 0.333 mol) was placed in a 2 × 30 cm Fischer and Porter Carius tube previously cooled to 0–5 °C with an ice–water bath. 2,2-Di-*tert*-butylacetyl chloride (8.92 g, 46.8 mmol) was added directly to the chilled ethylamine without stirring. The Carius tube was sealed, removed from the ice–water bath, shaken to effect mixing of reagents, and then positioned over a magnetic stirrer where the mixture was stirred for 84 h. The greenish product mixture was evaporated to dryness. The residue was again taken up in chloroform, washed with dilute hydrochloric acid, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent left a pale-yellow solid. Recrystallization from hexane afforded *N*-ethyl-2,2-di-*tert*-butylacetamide

(7.7 g, 82%) as colorless prisms: mp 133–134 °C; IR (KBr) 3230 (N–H, stretch), 1640 (C=O), 1545 $cm^{-1}$ (N–H, bend); NMR ($CDCl_3$) δ 1.10 (s, 18 H), 1.13 (t, $J$ = 7 Hz, 3 H), 1.65 (s, 1 H), 3.23 (q, $J$ = 7 Hz, 2 H), 5.25 (br, 1 H).

Anal. Calcd for $C_{12}H_{25}NO$: C, 72.36; H, 12.56; N, 7.06. Found: C, 72.33; H, 12.63; N, 7.02.

**Di-*tert*-butylketene-*N*-ethylimine (1).** A solution of *N*-ethyl-2,2-di-*tert*-butylacetamide (2.00 g, 10.1 mmol) in 25 mL of benzene was prepared in a 100-mL round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar. Phosphorus pentachloride (2.29 g, 11.0 mmol) was added and the resulting suspension refluxed for approximately 30 min. Benzene and phosphoryl chloride were removed by evaporation at reduced pressure, and the remaining traces of phosphoryl chloride was chased with 20 mL of benzene. The crude imidoyl chloride was treated directly with triethylamine (5.57 g, 7.99 mL, 55.0 mmol) in 50 mL of benzene, and the resulting mixture was refluxed for 2 h. The precipitated triethylamine hydrochloride was removed by suction filtration and the filtrate concentrated at reduced pressure to a brown liquid. Vacuum distillation (Kugelrohr, 40–60 °C/0.25 mmHg) gave di-*tert*-butylketene-*N*-ethylimine (1.60 g) contaminated to the degree of approximately 25% by what appeared to be 2,2-di-*tert*-butylacetonitrile: IR (liquid film) 1998 $cm^{-1}$ (C=C=N); NMR ($CDCl_3$) δ 1.21 (s, 18 H), 1.23 (t, $J$ = 7 Hz, 3 H), 3.39 (q, $J$ = 7 Hz, 2 H); MS $m/e$ calcd for $C_{12}H_{23}N$, 181.1830; found, 181.1827.

**Di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium Fluorosulfonate (2).** Freshly prepared di-*tert*-butylketene-*N*-ethylimine (1.60 g) was rinsed from the Kugelrohr bulb into a 100-mL round-bottomed flask with 50 mL of anhydrous ether. The flask was then set up for magnetic stirring and protected from atmospheric moisture with a calcium sulfate drying tube. Methyl fluorosulfonate (1.51 g, 1.02 mL, 13.3 mmol) was syringed into the ketenimine solution, and the resulting mixture was stirred at room temperature for approximately 30 min. Precipitation of the keteniminium fluorosulfonate salt as a white flocculent suspension took place within seconds after the introduction of the methyl fluorosulfonate. The colorless solid was collected on a small Büchner funnel by suction filtration and washed several times with anhydrous ether. Recrystallization from chloroform–diethyl ether afforded di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium fluorosulfonate (1.50 g) as a white powder: mp 224–228 °C (dec); IR (KBr) 2000 $cm^{-1}$ (C=C=N); NMR ($CDCl_3$) δ 1.39 (s, 18 H), 1.48 (t, $J$ = 7 Hz, 3 H), 3.90 (s, 3 H), 4.11 (q, $J$ = 7 Hz, 2 H).

***N*-Methyl-*N*-ethyl-2,2-di-*tert*-butylacetamide (3).** Di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium fluorosulfonate (0.250 g, 0.847 mmol) and 15 mL of distilled water were placed in a 25-mL Erlenmeyer flask. The solution was made basic by adding 5 mL of 10% aqueous sodium hydroxide, and the resulting mixture was stirred at room temperature for approximately 10 h. Extraction into three 25-mL portions of diethyl ether followed by drying over anhydrous magnesium sulfate and evaporation at reduced pressure produced *N*-methyl-*N*-ethyl-2,2-di-*tert*-butylacetamide (0.157 g, 87%) as a pale-yellow liquid. Vacuum distillation (Kugelrohr, 100–110 °C/0.3 mmHg) gave an analytically pure sample as a colorless solid: mp 33.5–35.5 °C; IR ($CCl_4$) 1640 $cm^{-1}$ (C=O); NMR ($CDCl_3$) δ 1.07 (s, 18 H), 1.20 (t, $J$ = 7 Hz, 3 H), 2.45 (s, 0.75 H), 2.49 (s, 0.25 H), 2.83 (s, 0.75 H), 3.0 (s, 2.25 H), 3.39 (q, $J$ = 7 Hz, 2 H); MS $m/e$ calcd for $C_{13}H_{27}NO$, 213.2092; found, 213.2092.

**Treatment of Di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium Fluorosulfonate (2) with Sodium Bis(trimethylsilyl)amide. *N,N'*-Diethyl-2,5-bis(2,2,4,4-tetramethyl-3-pentylidene)piperazine (4).** In a drybox, di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium fluorosulfonate (0.638 g, 2.16 mmol), sodium bis(trimethylsilyl)amide (0.595 g, 3.25 mmol), and 25 mL of dry benzene were placed in a 100-mL round-bottomed flask equipped with a magnetic stirring bar and a calcium sulfate drying tube. The resulting heterogeneous slurry was stirred at room temperature under nitrogen atmosphere for a period of 28 h. During this time, the mixture became somewhat more homogeneous and assumed a bright yellow appearance. The fluorosulfonate salts and excess silylamide base were removed by suction filtration through a bed of Celite, and the clear yellow filtrate evaporated at reduced pressure to a yellow oil (0.406 g). Crystallization from ethyl acetate produced colorless flakes of *N,N'*-diethyl-2,5-bis(2,2,4,4-tetramethyl-3-pentylidene)piperazine in two crops (0.2182 g, 52%): mp 154–156 °C; IR ($CHCl_3$) 1600 $cm^{-1}$ (C=CN); NMR 60 MHz ($CDCl_3$) δ 1.07 (t, $J$ = 7 Hz, 6 H), 1.30 (s, 9 H), 1.43 (s, 9 H), 2.33–3.58 (m, 8 H); NMR 100 MHz ($CDCl_3$) δ 1.07 (t, $J$ = 7 Hz, 6 H), 1.31 (s, 9 H), 1.43 (s, 9 H), 2.60 (d, $J_{AB}$ = 10 Hz, 2 H, endocyclic $CH_2$), 2.74 (d of q, $J_{A'B'}$ = 11.5 Hz, $J_{H,CH3}$ = 7 Hz, 2 H, exocyclic $CH_2$), 3.01 (d of q, $J_{A'B'}$ = 11.5 Hz, $J_{H,CH_3}$ = 7 Hz, 2 H, exocyclic $CH_2$), 3.35 (d, $J_{AB}$ = 10 Hz, 2 H, endocyclic $CH_2$); NMR $^{13}C$ ($CDCl_3$) δ 13.0 (q, $CH_3CH_3$), 33.8 (q, *t*-Bu), 42.5 (t, exocyclic $CH_2$), 45.2 (t, endocyclic $CH_2$), 45.2 (t, endocyclic $CH_2$), 141.3 (s, exocyclic, C=C), 147.1 (s, endocyclic, C=C); MS $m/e$ calcd for $C_{26}H_{50}N_2$, 390.3973; found, 390.3977.

**Treatment of Di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium Fluorosulfonate (2) with Sodium Bis(trimethylsilyl)amide in Refluxing Benzene.** In a drybox, di-*tert*-butylketene-*N*-ethyliminium fluorosulfonate (0.500 g, 1.69 mmol), sodium bis(trimethylsilyl)amide (0.466 g, 2.54 mmol), and 20 mL of dry benzene were combined in a 100-mL round-bottomed flask containing a small magnetic stirring bar. The flask was removed from the drybox, positioned over a magnetic stirrer, and equipped with a reflux condenser and a nitrogen atmosphere. The reaction mixture was refluxed for 6.5 h before being filtered through a small Büchner funnel containing a bed of Celite. The yellow filtrate was evaporated to an oil (0.404 g), diluted with approximately 8 mL of ethyl acetate, and placed in a refrigerator freezer. After several hours, crystalline flakes of piperazine dimer (0.197 g, 59.7%, mp 154–156 °C) appeared and were collected by suction filtration. The mother liquor was examined spectroscopically and was found by comparison with an authentic sample to contain mostly *N*-methyl-*N*-ethyl-2,2-di-*tert*-butylacetamide.

***exo*-*N*-Ethyl-1-(2,2,4,4-tetramethyl-3-pentylidene)perhydro-4,7-methanoisoindole (7) and *exo*-*N*-Ethyl-1-(2,2,4,4-tetramethyl-3-pentyl)-3a,4,5,6,7,7a-hexahydro-4,7-methano-3*H*-isoindolinium Chloride (8).** Di-*tert*-butylketene-*N*-methyl-*N*-ethyliminium fluorosulfonate (0.400 g, 1.36 mmol), norbornene (1.28 g, 13.6 mmol), and 15 mL of dry benzene were combined in a 50-mL round-bottomed flask equipped with a magnetic stirring bar and a calcium sulfate drying tube. The flask was transferred to a drybox and positioned over a magnetic stirrer where sodium bis(trimethylsilyl)amide (0.75 g, 4.09 mmol) was added. The resulting suspension was then stirred at room temperature under nitrogen atmosphere for 23 h. The golden reaction mixture was passed through a filter funnel containing a bed of Celite, and the yellow filtrate was evaporated at reduced pressure to remove solvent and excess norbornene. After removing the residual traces of solvent by evaporation at high vacuum, *exo*-*N*-ethyl-1-(2,2,4,4-tetramethyl-3-pentylidene)-perhydro-4,7-methanoisoindole (0.386 g, 98.5%) was obtained as an acid-sensitive pale-yellow oil: IR ($CHCl_3$) 1625 $cm^{-1}$ (C=CN); NMR ($CDCl_3$) δ 1.00 (t, $J$ = 7 Hz, Me), 1.35 (s, *t*-Bu), 1.50 (s, *t*-Bu), 1.0–3.0 (m, methylene and norbornyl); MS $m/e$ calcd for $C_{21}H_{35}N$, 289.2769; found, 289.2761.

The crude isoindole (7) was diluted with approximately 5 mL of benzene and applied to a neutral alumina column (1.25 × 10 cm) packed in petroleum ether (65–100 °C). Five 40-mL fractions were collected with chloroform and discarded. A sixth and final 40-mL fraction was obtained with anhydrous methanol, evaporated to a golden oil, and then diluted with ethyl acetate which produced colorless platelets of *exo*-*N*-ethyl-1-(2,2,4,4-tetramethyl-3-pentyl)-3a,4,5,6,7,7a-hexahydro-4,7-methano-3*H*-isoindolinium chloride (0.289 g, 65.3%): mp 176–179 °C (dec); IR ($CHCl_3$) 1620 $cm^{-1}$ (C=N); NMR ($CDCl_3$) δ 1.25 (s, 9 H), 1.28 (s, 9 H), 1.50–1.80 (br m, 6 H, $H_5$, $H_6$, $H_8$), 1.53 (t, $J$ = 7 Hz, 3 H), 2.50 (br s, 1 H, $H_7$), 3.00 (s, 1 H, exocyclic CH), 3.43 (br d, $J_{3a,7a}$ = 8 Hz, 1 H, $H_{7a}$), 4.08–5.18 (m, 4 H, endocyclic and exocyclic $CH_2$); MS $m/e$ calcd for $C_{20}H_{35}N$, 289.2769; found, 289.2763.

Anal. Calcd for $C_{20}H_{35}N{\cdot}HCl{\cdot}H_2O$: C, 69.82; H, 11.14; N, 4.07. Found: C, 69.84; H, 11.15; N, 4.07.

**Registry No.**—1, 64200-90-4; 2, 64200-92-6; 3, 64200-93-7; 4, 64200-94-8; 7, 64200-95-9; 8, 64200-96-0; ethylamine, 75-04-7; 2,2-di-*tert*-butylacetyl chloride, 29571-65-1; *N*-ethyl-2,2-di-*tert*-butylacetamide, 64200-97-1; *N*-ethyl-2,2-di-*tert*-butylacetimidyl chloride, 64200-98-2; 2,2-di-*tert*-butylacetonitrile, 62796-07-0; methyl fluorosulfonate, 421-20-5; norbornene, 498-66-8.

## References and Notes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Chemical Co., Inc. This reagent has been established to be a severe poison. All manipulations were carried out in a well-ventilated hood and protective rubber gloves were worn when making transfers.
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# Vinylogous Systems. 4. Mass Spectra of Vinylogous Ureas and Ureides[1]

James S. Docken, Everin C. Houkom, Roger A. Jorgenson, Daryl L. Ostercamp,* Gloria A. Tweed, and Richard G. Werth

*Department of Chemistry, Concordia College, Moorhead, Minnesota 56560*

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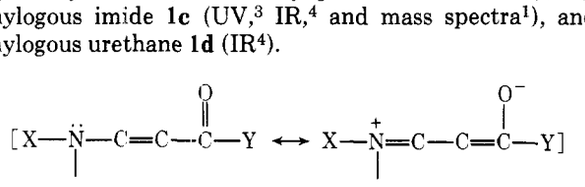
The mass spectra of 16 acyclic and isocyclic vinylogous ureas **1a** and 18 acyclic, isocyclic, and heterocyclic vinylogous ureides **1b** are reported and discussed. Preferred fragmentation pathways for both **1a** and **1b** are dominated by cleavage at the ends of the conjugated system, with the enaminone core (N—C=C—C=O) being retained within either a charged daughter ion or an ejected neutral fragment. Such decomposition usually furnishes the base peak in the mass spectrum, and is very often a primary step as well.

In continuation of our studies of elongated functional groups in which nitrogen is the electron donor and carbonyl the acceptor, we wish to report the syntheses and mass spectra of some vinylogous ureas **1a,** β-amino α,β-unsaturated amides, and vinylogous ureides **1b,** β-amido α,β-unsaturated amides. Our main goal was to provide a further evidence of the importance of resonance stabilization within the enaminone core of **1**. The competing cross conjugation which exists in **1a–d** is apparently minimal, as shown by spectral results for **1a** (UV[2]), vinylogous imide **1c** (UV,[3] IR,[4] and mass spectra[1]), and vinylogous urethane **1d** (IR[4]).



**1a**, X = R; Y = $NR_2$
**b**, X = RC(O); Y = $NR_2$
**c**, X = RC(O); Y = R
**d**, X = R; Y = OR
**e**, X = R; Y = R

Electron impact-induced fragmentations of vinylogous amides **1e**[5–7] and imides **1c**[1,8] have been reported, and distinct analogies between the behavior of **1a** and **1e,** and of **1b** and **1c** also, were to be expected. Thus, the formation of a relatively stable β-amino α,β-unsaturated acylium ion from **1a** would be reasonable, although we were unsure whether oxazolium and/or isoxazolium daughter ions would be as important for **1b** as they are in the fragmentation of **1c**. Compounds prepared for the present investigation are collected in Tables I and II.

## Experimental Section

Melting and boiling points are uncorrected. Common reagents were freshly distilled (amines from BaO) under a dry atmosphere. Commercial samples of anhydrous alcohol, acrylic anhydride (Aldrich Chemical Co.), and reagent grade acetic anhydride were used. Propiolamide (Terro-Marine Bioresearch) was sublimed under vacuum. Reaction progress and product purity were monitored by thin-layer chromatography. Preparative chromatography was carried out on columns dry packed with Florisil. Solvents were evaporated under reduced pressure on a rotary evaporator with a bath of suitable temperature. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Mass spectra were obtained on either an A.E.I. MS-30 or MS-902 mass spectrometer using a direct-insertion probe under the following conditions: electron voltage 70 eV, ion source temperature 200–250 °C, probe temperature 75–230 °C.[9] Accurate mass measurements were also obtained for compounds **2e, 2h, 2k, 8a–c, 12a, 12n,** and **19a,** as well as for selected peaks of compounds **2d** and **19d.** Infrared spectra were recorded on a Beckman IR-8. Deuteration of compound **12f** was carried out in $CDCl_3$ by shaking with $D_2O$ for 6 h, NMR measurements showing no evidence for exchange except at NH, where it was complete.

**Preparation of Compounds.** A number of the compounds were synthesized according to the literature, including **2a,**[10] **2b,**[11] **2c,**[12] **2h,**[13] **8d,**[14] **12a,**[15] **12h,**[15] **19a,**[16] and **19b.**[16] Such procedures were also used to prepare many of the new compounds reported in Tables I and II. The following experimental directions are illustrative.

**β-Amino-*N,N*-pentamethylenecrotonamide (2d).** A solution of piperidine (7.72 g, 0.0907 mol) in dry ether (30 mL) was added dropwise under a dry atomosphere to a stirred solution of diketene (7.63 g, 0.0907 mol) in dry ether (30 mL). The reaction solution was refluxed for 45 min, cooled to ice temperature, and then saturated with $NH_3$ for 4 h. Removal of the ether left a thick oil which did not solidify in the refrigerator overnight. Using Becker's[17] method, a catalytic amount of $NH_4NO_3$ was added to the thick liquid, and the mixture was saturated with $NH_3$ for 5 h at 80 °C. Cooling gave a crystalline mass, which upon recrystallization from ethyl acetate and chromatography (ether) of the mother liquor yielded 12.59 g (83%) of **2d,** mp 78–79 °C. Recrystallization from cyclohexane–ether and subsequent sublimation at 68 °C (0.1 mm) gave pure **2d,** mp 79–80 °C.

**2-Aminocyclopentene-1-*N*-ethylcarboxamide (2e).** A solution of 2-oxocyclopentane-1-*N*-ethylcarboxamide[18] [4.10 g, 0.0264 mol, bp 102–107 °C (0.5 mm), mp 83–84 °C, lit.[19] mp 84 °C] in absolute ethanol (50 mL) was saturated with $NH_3$ for 2 h on each of five suc-

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