5.1 (dd, 1.2 H, J = 6, 1 Hz, Z isomer), 4.88 (dd, 0.8 H, J = 7, 1 Hz, E isomer); mass spectrum, m/e 282 ($M^{+\cdot}$), 105, 77. Anal. Calcd for $C_{17}H_{14}O_4$: C, 72.31; H, 5.00. Found: C, 72.36; H, 5.27.

1,3-Bis[(2,2-dimethylpropanoyl)oxy]-2-(phenylselenyl)-propane (5d). t-BuCOCl (914 μL) was added to diol **5b** (817 mg) and a 4-(dimethylamino)pyridine (1 mg) in pyridine (15 mL) at 0 °C. After stirring at room temperature for 3 h, rotary evaporation and chromatography on silica (hexane–Et_2O gradient) gave **5d** (1.4 g, 92%) as a colorless oil: IR (film) 1730, 1580, 1480, 1460, 1395, 1365, 1280, 1150, 1030, 950, 770, 740, 690 cm^{-1}; NMR ($CDCl_3$) δ 7.7–7.5 (m, 2 H), 7.4–7.2 (m, 3 H) 4.32 (d, 4 H, J = 6.5 Hz), 3.57 (quintet, 1 H, J = 6.5 Hz), 1.23 (s, 18 H); mass spectrum, m/e 400 ($M^{+\cdot}$ ^{80}Se), 298, 243, 141, 85, 57. Anal. Calcd for $C_{19}H_{28}O_4Se$: C, 57.14; H, 7.07. Found: C, 57.03; H, 6.88.

1,3-Bis[(2,2-dimethylpropanoyl)oxy]propene (10c). O_3 was bubbled through **5d** (0.800 g) in CH_2Cl_2 (15 mL) at −78 °C until blue. The solution was purged with N_2, Et_3N, (0.8 mL) was added, and the solution was allowed to warm up to room temperature over 1 h. Workup as for **10b** gave **10c** (442 mg, 91%) as a colorless oil: IR (film) 1730, 1670, 1480, 1460, 1400, 1365, 1280, 1130, 1035, 940 cm^{-1}: NMR ($CDCl_3$) δ 7.44 (d, 0.6 H, J = 12.5 Hz, E isomer), 7.23 (d, 0.4 H, J = 6 Hz, Z isomer), 5.6 (dt, 0.6 H, J = 12.5, 7 Hz, E isomer), 5.13 (dt, 0.4 H, J = 7, 6 Hz, Z isomer), 4.78 (d, 0.8 H, J = 7 Hz, Z isomer), 4.60 (d, 1.2 H, J = 7 Hz, E isomer); mass spectrum m/e 242 ($M^{+\cdot}$), 157, 85. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.44; H, 9.12.

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Registry No. **1b**, 99018-30-1; **1c**, 99018-31-2; **3a**, 86728-47-4; **3b**, 99033-17-7; **4a**, 99018-32-3; **4b**, 99018-33-4; **4c**, 99018-34-5; **5a**, 99018-35-6; **5b**, 99018-36-7; **5c**, 99018-37-8; **5d**, 99018-38-9; **6**, 65349-59-9; **7**, 99018-39-0; **8**, 99018-40-3; **9**, 99018-41-4; (*E*)-**10a**, 31447-25-3; (*Z*)-**10a**, 31447-24-2; (*E*)-**10b**, 99018-42-5; (*Z*)-**10b**, 99018-43-6; (*E*)-**10c**, 99018-44-7; (*Z*)-**10c**, 99018-45-8; **11**, 869-29-4; PhCOCl, 98-88-4; t-BuCOCl, 3282-30-2; 2-methyl-3-buten-2-ol, 115-18-4; 3-methyl-2-(phenylselenyl)-1,3-butanediol, 99018-46-9; allyl alcohol, 107-18-6; ethyl 2,3-epoxybutyrate, 19780-35-9.

N-Protected α-Amino Ketones from Enamines and (Ethoxycarbonyl)nitrene[1]

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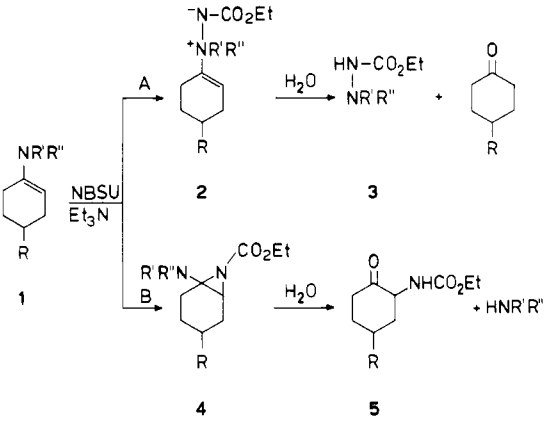
Recently, we reported a new synthesis of *N*-(ethoxycarbonyl)-α-amino ketones, via the thermolysis of ethyl azidoformate in enol trimethylsilyl ethers.[2]

Previously we studied[3] the reaction of (ethoxycarbonyl)nitrene (EtOCON), generated from *N*-[(4-nitrophenyl)sulfonoxy]urethane (NBSU) and enamines.[4]

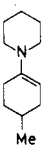
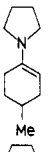
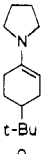
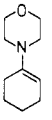
Scheme I



a, R′···R″ = -$(CH_2)_5$- (piperidine)
b, R′···R″ = -$(CH_2)_4$- (pyrrolidine)
c, R′···R″ = -$(CH_2CH_2)_2O$- (morpholine)
d, R′···R″ = -$(CHMeCH_2)_2$- (*cis*-2,5-dimethylpyrrolidine)
e, R′ = Me; R″ = Ph (*N*-methylaniline)

x, R = H
y, R = Me
z, R = t-Bu

Table I.[a] **Reaction of Enamines, NBSU, and Et_3N in Dichloromethane**

entry[b]	1	2	3	5
ay		42 (53)	30 (47)	
by		14 (31)	41 (36)	19 (33)
bz		9 (10)	25 (28)	24 (62)
cx		23 (80)	14 (16)	5 (4)

[a] Absolute yields in percent; GC percentages are given in parentheses. [b] See Scheme I.

For this reaction we showed that the reaction outcome could be partially shifted from aminimides (N–N ylides), as the main products, to α-amino ketone derivatives,[5] depending on the reaction conditions used in the generation of the nitrene.

In this paper we describe the results of our efforts directed toward a more selective preparation of α-amino ketones and toward the isolation of the α-amino ketone precursors. At this time the two routes can be illustrated

(1) Part of this paper has been presented at the "XV Congresso Nazionale della Società Chimica Italiana", Grado, Italy, September 16–21 1984, Abstract p 437.

(2) Lociuro, S.; Pellacani, L.; Tardella, P. A. *Tetrahedron Lett.* **1983**, *24*, 593.

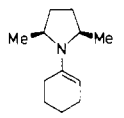
(3) Pellacani, L.; Pulcini, P.; Tardella, P. A. *J. Org. Chem.* **1982**, *47*, 5023.

(4) For a very recent review on (ethoxycarbonyl)nitrene, see: Lwowski, W. In "Azides and Nitrenes"; Scriven, E. F. V., Ed.; Academic Press, Inc.: Orlando, FL, 1984. For recent reviews on enamines, see: (a) Hickmott, P. W. *Tetrahedron* **1982**, *38*, 1975, 3363. (b) Pitacco, G.; Valentin, E. In "The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives"; Patai, S., Ed.; John Wiley & Sons: New York, 1982; Supplement F, part 1, Chapter 15, p 623. (c) Granik, V. G. *Russ. Chem. Rev.* **1984**, *53*, 383.

(5) α-Amino ketones, besides the general methods of preparation (Mayer, D. In "Houben-Weyl, Methoden der Organischen Chemie", 4th ed.; Müller, E., Ed.; G. Thieme Verlag: Stuttgart, 1977; Vol. VII/2c, p 2253) have been obtained from azides and masked ketones such as enamines (Alder, K., Stein, G. *Liebigs Ann. Chem.* **1933**, 501, 1) or enol acetates (Keana, J. F. W.; Keana, S. B.; Beetham, D. *J. Org. Chem.* **1967**, *32*, 3057) as well as by chromous chloride promoted addition of *N*-chlorourethanes to enamines, enol ethers, or enol acetates (Driguez, H.; Paton, J. M.; Lessard, J. *Can. J. Chem.* **1977**, *55*, 700. Driguez, H.; Vermes, J. P.; Lessard, J. *Can. J. Chem.* **1978**, *56*, 119). An example of α-amino aldehydes from treatment of enamines with chloramine-T has been reported: Dyong, I. D.; Lam-Chi, Q. *Angew. Chem.* **1979**, *91*, 997.

0022-3263/85/1950-5365$01.50/0

Table II.[a] Reaction of Enamines, NBSU, and Et_3N in Dichloromethane

entry[b]	1	3	4	5
dx		1 (6)	(79)	27 (15)
ex		7 (19)	(68)	37 (13)

[a] See Table I. [b] See Scheme I.

in Scheme I. By hydrolysis aminimides **2** gave substituted hydrazines **3** and ketones (path A), while α-amino ketones **5** should be the hydrolysis products of undetected aziridines **4** (path B). Actually these aziridines belong to the class of aminals,[6] compounds quite sensitive to hydrolysis. For these early considered substrates, we noted also that pyrrolidine enamines gave higher amounts of α-amino ketones than piperidine enamines, under the same reaction conditions. This difference might be due to the different overlap between the nitrogen lone pair and the π electrons of enamines, as reflected in the chemical shift of the vinylic proton in the ^1H NMR spectra,[7] as well as in the chemical shift of the C-2 in the ^{13}C NMR spectra.[8]

First we confirmed that other pyrrolidine enamines derived from substituted cyclohexanones such as 4-methyl- and 4-*tert*-butylcyclohexanone **1by** and **1bz** gave α-amino ketone derivatives **5** as well as aminimides **2** and substituted hydrazines **3**, as a result of the addition on both possible sites, the nitrogen lone pair (path A) and the double bond (path B). Inversely an other piperidine enamine such as **1ay** failed to give **5y**. The products formed, yields, and GC percentages are reported in Table I. Substrates **1by** and **1bz** are also interesting with respect to the stereochemical results: 4-alkyl-2-amino ketones **5y** and **5z** are both cis. This could be simply due to thermodynamic reasons, the more stable isomer being always formed. Attempts to equilibrate[9] **5y** gave only the starting material, as confirmed by chromatographic and spectral data. Ketones recovered from the hydrolysis of aminimides **1ay** and **1by** were identical with starting ketones and no 1,2-carbonyl shift was observed.

We considered also morpholine enamine **1cz**. The amount of p–π conjugation in this product is comparable to that of the piperidine enamines but the results of chlorocarbene addition, namely the high stability of the cyclopropane adduct, suggested this experiment.[10] However this substrate gave a high quantity of aminimide **2cx** (80% by GC) and only a low amount (4% by GC) of α-amino ketone **5z**. The other minor product obtained was, as usual, the substituted hydrazine **3c** (16% by GC).

However, even in these cases we were not able to detect the precursors of α-amino ketones. In order to trap the expected aziridines and to force the nitrene addition on the double bond we decided to test the enamines derived from less basic or more crowded amines (Table II), on the basis of the known behavior of enamines in the alkylation reaction.[11]

For the latter approach we chose enamine **1dx** formed from *cis*-2,5-dimethylpyrrolidine and cyclohexanone. This substrate when submitted to the usual reaction conditions gave as the main product (79% by GC) an adduct **4dz**, as deduced from GC-MS analysis. This compound, highly sensitive to hydrolysis, could not be isolated either by column chromatography or by HPLC, and gave, in a few hours at room temperature, *N*-(ethoxycarbonyl)-α-aminocyclohexanone (**5x**) (27% absolute yield) and *cis*-2,5-dimethylpyrrolidine. The yields of **5x** are variable in repeated runs, due to loss of material (probably the polymerization of the aziridine is an important side reaction). The substituted hydrazine **3d** was isolated as a minor product (1%).

Enamine **1ex** derived from *N*-methylaniline, a weak base, and cyclohexanone gave a main product (68% by GC), which was isolated by HPLC and was identified by spectral data as aziridine **4ex**. This was the first case in which we isolated this kind of adduct.[12] Nevertheless, **4ex** easily decomposed to **5x** and *N*-methylaniline on standing at room temperature. Other products in the reaction mixture was substituted α-amino ketone **5x** and hydrazine **3e** (13% and 19% by GC, respectively) and they were the only products isolated by silica gel column chromatography (37% and 7%, respectively).

In conclusion, the use of enamines with a sterically hindered or weakly basic amine components favors the addition of EtOCON to the double bond and the isolation of α-amino ketone derivatives as the nearly exclusive product, although in moderate yields. Moreover, in one case, the isolation of an aziridine intermediate was possible. Further work is in progress with the aim of expanding the synthetic utility of the reaction.

Experimental Section

GC analyses were performed on a Carlo Erba 4100 gas chromatograph with a column of 3% SP 2250 (2 m × 2 mm) on 100/120 Supelcoport. GC/MS was done on a Kratos MS 80, at an ionization potential of 70 eV coupled to a Carlo Erba 4160 gas chromatograph with a column of 3% SP 2250 (2 m × 2 mm) on 100/120 Supelcoport. High-resolution mass spectra (HRMS) were obtained on a Kratos MS 80 spectrometer (15 000 resolution). ^1H NMR spectra were recorded on a Varian EM-360 spectrometer and on a Bruker WP-80 SY spectrometer with Me_4Si as an internal standard. ^{13}C NMR spectra were obtained on a Bruker WP-80 SY spectrometer and on a Varian CFT-20 spectrometer with $CDCl_3$ as an internal standard. Infrared spectra (IR) were obtained on a Perkin-Elmer 257 infracord instrument. The separation by high-performance liquid chromatography (HPLC) was done on a Violet Clar 002 instrument, equipped with a Violet Clar 001 microprocessor and a variable wavelength detector Violet Clar 004 (set at 254 nm). Solvents were HPLC-grade. Dichloromethane was distilled over $CaCl_2$. Triethylamine was dried by allowing it to stand over KOH and then was distilled from $LiAlH_4$. NBSU[13] and enamines **1ay**,[14] **1by**,[15] **1bz**,[16] **1cx**,[17] **1ex**[18,19] were

(6) Duhamel, L. In "The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives"; Patai, S.; Ed.; John Wiley & Sons: New York, 1982; Supplement F, Part 2, Chapter 20, p 849.
(7) Gurowitz, W. D.; Joseph, M. A. *J. Org. Chem.* **1967**, *32*, 3289.
(8) Tourwé, D.; Van Binst, G.; De Graaf, S. A. G.; Pandit, U. K. *Org. Magn. Reson.* **1975**, *7*, 433.
(9) Fabrissin, S.; Fatutta, S.; Malusà, N.; Risaliti, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 686.
(10) (a) Ohne, M. *Tetrahedron Lett.* **1963**, 1753. (b) Wolinsky, J.; Chan, D.; Novak, R. *Chem. Ind. (London)* **1965**, 720. (c) Pandit, U. K.; De Graaf, S. A. G.; Braams, G. T.; Raaphorts, J. S. T. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 799. (d) De Graaf, S. A. G.; Pandit, U. K. *Tetrahedron* **1973**, *29*, 2141, 4263. (e) De Graaf, S. A.; Pandit, U. K. *Tetrahedron* **1974**, *30*, 1115.
(11) Curphey, T. J.; Hung, J. C.; Chu, C. C. C. *J. Org. Chem.* **1975**, *40*, 607.
(12) It is known that a related but structurally different aziridine could be distilled below 150 °C without appreciable decomposition and when heated at 180 °C for 1 h a complete rearrangement occurred: Sato, Y.; Kojima, H.; Shirai, H. *J. Org. Chem.* **1976**, *41*, 3325.
(13) Lwowski, W.; Maricich, T. J. *J. Am. Chem. Soc.* **1965**, *87*, 3630.
(14) Knowles, A. M.; Lawson, A.; Boyd, G. V.; Newberry, R. A. *J. Chem. Soc. C* **1971**, 598.
(15) Kovar, K. A.; Schielein, F.; Dekker, T. G.; Albert, K.; Breitmaier, E. *Tetrahedron* **1979**, *35*, 2113.

prepared by standard procedures. Boiling points are referred to an external bath.

***cis*-1-Cyclohexenyl-2,5-dimethylpyrrolidine (1dx)** was prepared by dissolving cyclohexanone in an excess of *cis*-2,5-dimethylpyrrolidine and anhydrous ether and stirring the solution over molecular sieves (Union Carbide, 3-Å $^1/_8$ in. pellets (Fluka)) at room temperature for 42 h: bp 118 °C (4 mmHg); IR (CCl_4) 1625 cm^{-1}; ^1H NMR (neat) δ 4.2 (m, 1 H, CH=C), 3.6–3.1 (m, 2 H, C*H*CH_3), 2.2–1.2 (m, 12 H), 1.0 (d, 6 H, CHC*H*$_3$); mass spectrum, *m/z* (relative intensity) 179 (M^+, 35), 178 (20), 165 (14), 164 (100), 137 (27), 136 (16), 122 (10), 98 (20), 54 (18), 51 (14); HRMS, M^+, 179.1670, calcd for $C_{12}H_{21}N$, 179.1673.

Reaction of NBSU with Enamines. Procedure A. To a stirred solution of 5 mmol of enamine, 50 mmol of triethylamine, and 10 mL of dichloromethane in an atmosphere of N_2 was added 5 mmol of NBSU in 1 h at room temperature. After 2 h more of stirring, petroleum ether (bp 30–50 °C) was added, and the precipitate thus formed was filtered off (80–90%). The filtrate was concentrated in vacuo and the residue was chromatographed on silica gel with a mixture of benzene and ethyl acetate (95:5 generally). A good separation was always obtained, and a reverse order of elution was found with respect to the GC retention times.

Procedure B. See procedure A, but 5 mmol of triethylamine was used.

With 1-(4-methylcyclohexenyl)piperidine (1ay) (procedure A) as starting material two products were collected: **2ay** (42%) and **3a**[3] (30%).

2ay: IR (CCl_4) 1705 cm^{-1}; ^1H NMR (CCl_4) δ 5.3 (m, 1 H, CH=C), 4.0 (q, 2 H, CH_2O), 3.0 (m, 4 H, CH_2N), 2.6–1.4 (m, 13 H), 1.3 (t, 3 H, CH_2CH_3), 1.0 (d, 3 H, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 155.2 (COO), 136.9 (*C*=CH), 122.5 (C=*C*H), 60.8 (CH_2O), 52.9 (CH_2N), 33.1, 31.0, 27.8, 27.5, 26.6 (*C*H_2CH_2N), 23.6, 21.2 (*C*HCH_3), 14.6 (CH_2CH_3); mass spectrum, *m/z* (relative intensity) 266 (M^+, 26), 193 (44), 154 (11), 142 (21), 110 (23), 84 (100); HRMS, M^+, 266.1975, calcd for $C_{15}H_{26}N_2O_2$, 266.1988.

With 1-(4-methylcyclohexenyl)pyrrolidine (1by) (procedure A) as starting material three products were collected: **2by** (14%), **3b**[3] (41%), and **5y** (19%).

2by: IR (CCl_4) 1705 cm^{-1}; ^1H NMR (CCl_4) δ 5.3 (m, 1 H, CH=C), 4.0 (q, 2H, CH_2O), 3.0 (m, 4 H, CH_2N), 2.3–1.5 (m, 11 H), 1.2 (t, 3 H, CH_2CH_3), 1.0 (d, 3 H, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 154.7 (COO), 138.1 (*C*=CH), 122.9 (C=*C*H), 61.0 (CH_2O), 50.7 (CH_2N) 33.1, 30.9, 27.7 (two overlapped peaks), 23.3 (*C*H_2CH_2N), 21.3 (CH*C*H$_3$), 14.7 (CH_2CH_3); mass spectrum, *m/z* (relative intensity) 252 (M^+, 100), 183 (18), 179 (41), 154 (14), 141 (16), 110 (11), 70 (23), 69 (14), 55 (11), 54 (11), 44 (14), 43 (11), 42 (11), 41 (18); HRMS, M^+, 252.1833, calcd for $C_{14}H_{24}N_2O_2$, 252.1837.

5y: bp 130 °C (5 mmHg); IR (CCl_4) 3420, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5 (br, 1 H, NH), 4.3 (dd, 1 H, CHN, *J* = 6 Hz, *J* = 12 Hz), 4.1 (q, 2 H, CH_2O), 2.7–1.8 (m, 7 H), 1.2 (t, 3 H, CH_2CH_3), 1.0 (d, 3 H, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 207.4 (CO), 155.9 (COO), 60.9 (CH_2O), 58.3 (CHN), 43.6, 40.0, 35.8, 30.8 (*C*HCH$_3$), 20.7 (CH*C*H$_3$), 14.5 (CH_2CH_3); mass spectrum, *m/z* (relative intensity) 199 (M^+, 42), 181 (22), 179 (26), 164 (11), 155 (47), 142 (100), 128 (83), 115 (11), 114 (14), 98 (25), 90 (39), 84 (14), 82 (12), 81 (14), 70 (25), 62 (11), 56 (22), 43 (11), 41 (19); HRMS, M^+, 199.1205, calcd for $C_{10}H_{17}NO_3$, 199.1209. An acidic equilibration of this ketone was attempted. An ethanolic solution of **5y** (0.05 mmol in 1 mL) was heated overnight at 100 °C with 20% hydrochloric acid (0.067 mL). The solution was concentrated in vacuo, diluted with water, and extracted with chloroform. The residue was found to be identical with the starting ketone by GC, IR, ^1H NMR, and mass spectrum.

With 1-(4-*tert*-butylcyclohexenyl)pyrrolidine (1bz) (procedure A) as starting material three products were collected: **2bz** (9%), **3b** (25%), and **5z** (24%).

2bz: IR (CCl_4) 1705 cm^{-1}; ^1H NMR (CCl_4) δ 5.3 (m, 1 H, CH=C), 4.0 (q, 2 H, CH_2O), 3.0 (m, 4 H, CH_2N), 2.3–1.5 (m, 11 H), 1.2 (t, 3 H, CH_2CH_3), 0.8 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 154.7 (COO), 138.4 (*C*=CH), 123.4 (C=*C*H), 61.0 (CH_2O), 50.7 (CH_2N), 43.4 (*C*$C(CH_3)_3$), 32.2 (*C*$(CH_3)_3$), 29.0, 27.3 (C(*C*$H_3)_3$), 26.1, 24.2, 23.4 (*C*H_2CH_2N), 14.7 (CH_2CH_3); mass spectrum, *m/z* (relative intensity) 294 (M^+, 53), 221 (65), 211 (13), 210 (95), 168 (23), 141 (46), 112 (12), 96 (27), 82 (15), 70 (89), 69 (17), 57 (100); HRMS, M^+, 294.2301, calcd for $C_{17}H_{30}N_2O_2$, 294.2306.

5z: bp 138 °C (5 mmHg); IR (CCl_4) 3420, 1710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.4 (br, 1 H, NH), 4.1 (dd, 1 H, CHN, *J* = 6 Hz, *J* = 12 Hz), 4.0 (q, 2 H, CH_2O, 2.7–1.4 (m, 7 H), 1.1 (t, 3 H, CH_2CH_3), 0.8 (s, 9 H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 207.5 (CO), 155.9 (COO), 60.8 (CH_2O), 58.7 (CHN), 45.7 (*C*$C(CH_3)_3$), 39.9, 36.9, 32.4 (*C*-$(CH_3)_3$), 28.7, 27.6 (C(*C*$H_3)_3$), 14.5 (CH_2CH_3); mass spectrum, *m/z* (relative intensity) 241 (M^+, 7), 184 (100), 156 (14), 128 (28), 90 (28), 67 (13), 62 (13), 57 (26), 56 (17), 55 (13); HRMS, M^+, 241.1672, calcd for $C_{13}H_{23}NO_3$, 241.1677.

With 4-cyclohexenylmorpholine (1cx) (procedure B) as starting material three products were collected: **2cx** (23%), **3c** (14%), and **5x**[20] (5%).

2cx: IR (CCl_4) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.4 (m, 1 H, CH=C), 4.0 (q, 2 H, CH_2O), 3.6 (t, 4 H, ring CH_2O), 2.9 (t, 4 H, CH_2N), 2.3–1.4 (m, 8 H), 1.2 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 155.1 (COO), 136.7 (*C*=CH), 124.1 (C=*C*H), 67.4 (ring CH_2O), 61.1 (CH_2O), 52.2 (CH_2N), 28.0, 24.6, 22.0, 21.7, 14.5 (CH_3); mass spectrum, *m/z* (relative intensity) 254 (M^+, 100), 181 (47), 170 (18), 169 (32), 141 (13), 140 (55), 96 (45), 86 (34), 69 (20), 56 (22), 55 (21); HRMS, M^+, 254.1622, calcd for $C_{13}H_{22}N_2O_3$, 254.1630.

3c:[21] mp 110.0–111.5 °C (ethyl acetate–ethanol); IR (CCl_4) 3315, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.8 (br, 1 H, NH), 4.1 (q, 2 H, CH_2O), 3.8 (t, 4 H, ring CH_2O), 2.8 (t, 4 H, CH_2N), 1.2 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 155.3 (COO), 66.5 (ring CH_2O), 61.2 (CH_2O), 56.3 (CH_2N), 14.5 (CH_3); mass spectrum, *m/z* (relative intensity) 174 (M^+, 26), 101 (100), 86 (54), 85 (42), 62 (21), 57 (59), 56 (34), 55 (35); HRMS, M^+, 174.1007, calcd for $C_7H_{14}N_2O_3$, 174.1004.

With *cis*-1-cyclohexenyl-2,5-dimethylpyrrolidine (1dx) (procedure B) as starting material two products were collected: **3d** (1%) and **5x** (27%).

3d:[22] bp 110 °C (1 mmHg); IR ($CHCl_3$) 3420, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.1 (br, 1 H, NH), 4.1 (q, 2 H, CH_2O), 2.7 (m, 2 H, CH), 2.2–1.3 (m, 4 H, ring CH_2), 1.2 (t, 3 H, CH_2CH_3), 1.1 (d, 6 H, CHC*H*$_3$); mass spectrum, *m/z* (relative intensity) 186 (M^+, 18), 171 (71), 143 (16), 125 (25), 113 (51), 99 (11), 98 (100), 97 (14), 85 (25), 83 (38), 82 (23), 70 (11), 69 (15), 59 (10), 57 (12), 56 (31), 55 (37); HRMS, M^+, 186.1367, calcd for $C_9H_{18}N_2O_2$, 186.1368.

The main products **4dx** could not be isolated, owing to its high instability: mass spectrum, *m/z* (relative intensity) 266 (M^+, 98), 251 (100), 224 (9), 221 (9), 210 (13), 209 (22), 195 (13), 193 (20), 122 (11).

With *N*-cyclohexenyl-*N*-methylaniline (1ex) (procedure B) as starting material two products were collected: **3e** (7%) and **5x** (37%). A sample of the aziridine **4ex** was isolated by HPLC with a mixture of hexane and ethyl acetate (9:1): IR (CCl_4) 1740, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4–6.5 (m, 5 H), 4.0 (q, 2 H, CH_2O), 2.9 (s, 3 H, CH_3N), 2.7 (m, 1 H), 2.1–1.5 (m, 8 H), 1.2 (t, 3 H, CH_2CH_3); mass spectrum, *m/z* (relative intensity) 274 (M^+, 97), 259 (18), 201 (21), 199 (18), 186 (26), 185 (100), 184 (34), 157 (34), 107 (22), 98 (17), 91 (13), 77 (30); HRMS, M^+, 274.1702 calcd for $C_{16}H_{22}N_2O_2$, 274.1681.

3e:[23] IR (CCl_4) 3420, 1710 cm^{-1}; ^1H NMR (CCl_4) δ 7.2–6.4 (m, 5 H, C_6H_5), 5.5 (br, 1 H, NH), 4.0 (q, 2 H, CH_2O), 3.0 (s, 3 H, CH_3N), 1.2 (t, 3 H, CH_3CH_2); ^{13}C NMR ($CDCl_3$) δ 155.6 (COO), 149.7, 129.1, 119.8, 112.8 (C_6H_5), 61.6 (CH_2O), 41.0 (CH_3N), 14.5 (CH_3); mass spectrum, *m/z* (relative intensity) 194 (M^+, 80), 121 (100), 106 (12), 105 (26), 92 (10), 77 (12); HRMS, M^+, 194.1050,

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calcd for $C_{10}H_{14}N_2O_2$, 194.1055.

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Registry No. **1ay**, 31882-35-6; **1by**, 39716-23-9; **1bz**, 4147-00-6; **1cx**, 670-80-4; **1dx**, 98945-50-7; **1ex**, 10468-26-5; **2ay**, 98945-51-8; **2by**, 98945-52-9; **2bz**, 98945-54-1; **2cx**, 98945-55-2; **3a**, 4663-84-7; **3b**, 83487-79-0; **3c**, 98945-58-5; **3d**, 98945-56-3; **3e**, 40887-55-6; **4ex**, 98945-57-4; **5x**, 13640-77-2; **5y**, 98945-53-0; **5z**, 86296-10-8; NBSU, 2955-74-0; cyclohexanone, 108-94-1; *cis*-2,5-dimethylpyrrolidine, 39713-71-8; (ethoxycarbonyl)nitrene, 2655-26-7.

Synthesis and Reactivity of *N*-Mesitylcyclopropylideneazomethine

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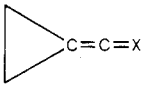
Allenylidenecyclopropanes **1** are quite stable compounds whose chemistry has been widely investigated.[1] For instance they have been reported to react with very electrophilic partners, such as chlorosulfonyl isocyanate and 4-phenyl-4*H*-1,2,4-triazolin-3,5-dione to give bis(alkylidene)cyclopentane derivatives, through addition across the cumulative double bond and the ring opening of the cyclopropane moiety. On the other hand, the heteroanalogues of **1**, such as the ketenes **2** and ketene imines **3** have not been reported to date.

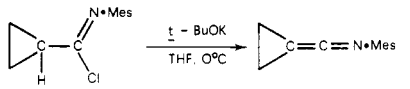


X = CR_2 (**1**); X = O (**2**); X = NR (**3**)

Compounds **2** have been characterized as 2 + 2 cyclodimers[2] only, while their behavior toward other cycloaddition partners has not been reported.

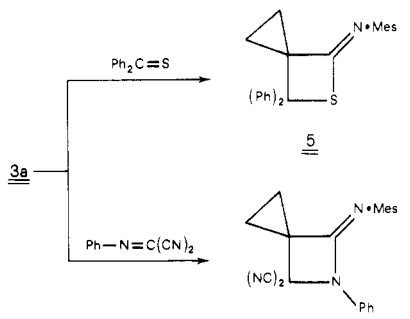
We have undertaken the synthesis of the ketene imines **3**, which are expected to be more resistant to dimerization, owing to their lower electrophilicity,[3] and endowed with a substantially greater reactivity with respect to the allenylidenecyclopropanes.

Treatment of *N*-mesitylcyclopropylformimidoyl chloride (**4**) with potassium *tert*-butoxide in THF at 0 °C gives the *N*-mesitylcyclopropylideneazomethine (**3a**), as indicated by a strong IR band at 2080 cm^{-1} (see Experimental Section). Quite remarkably, the cyclopropylidene moiety



4 **3a**

Mes = 2, 4, 6 - Me_3 - C_6H_2 -



5

6

moves the cumulene absorption to consistently higher frequencies ($\Delta\nu$ = 80–30 cm^{-1}) with respect to that usually observed for the C=C=N (2000–2050 cm^{-1}) group.[4] While **3a** appeared sufficiently stable, when in solution, attempts to isolate it as a pure material failed, due to a rapid decomposition. Reactions of **3a**, generated in situ, were carried out with appropriate reactants. In particular thiobenzophenone and *N*-(dicyanomethylene)aniline added in a 2 + 2 fashion to the C–C double bond of **3a** to give the corresponding spiro derivatives **5** and **6**, respectively. The structure of compound **5** was established by an X-ray crystal structure analysis (Figure 1). Spectroscopic data for **5** and **6** (see Experimental Section) are consistent with the assigned structure. It is worthy of note the relatively upfield ^{13}C NMR resonance (47.03 ppm) of C_3 of the spiro

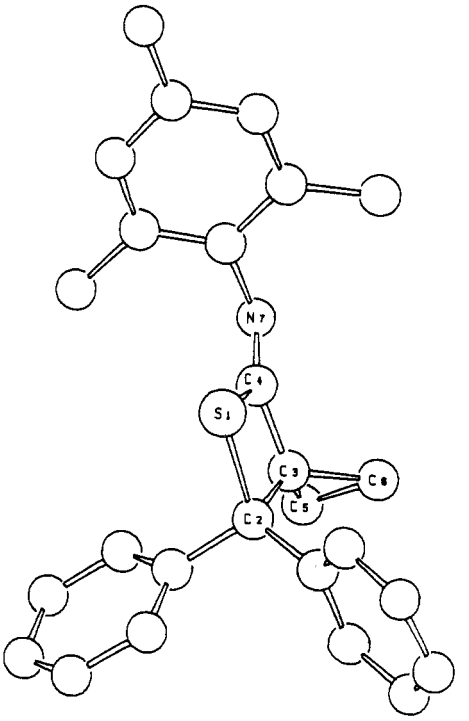


Figure 1. Structure of the spiro[2.3]hexane **5** in the solid state from a single-crystal X-ray analysis.

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