52, 103563-25-3; (Z)-EtCH=CHEt, 7642-09-3; (E)-MeCH=CHMe, 624-64-6; $Me_2C=CH_2$, 115-11-7; $Me_2C=CHMe$, 513-35-9; $Me_2C=CMe_2$, 563-79-1; (Z)-MeCH=CHMe, 590-18-1; EtCOCl, 79-03-8; $Me_2CHCOCl$, 79-30-1; MeCOCl, 75-36-5; $Ph_3P^+CHMeCO_2MeBr^-$, 2689-62-5; (Z)-EtCH=CH$(CH_2)_4$CHO, 2277-19-2; $Me_2C=CH(CH_2)_2CH(Me)CH_2CHO$, 106-23-0; $Me_2C=CH(CH_2)_2CH(Me)CH_2CO_2H$, 502-47-6; (Z)-EtCH=CH$(CH_2)_4CO_2H$, 41653-99-0; $H_2C=CH(CH_2)_4CO_2H$, 1119-60-4; $H_2C=CEt_2$, 760-21-4; $H_2C=CH_2$, 74-85-1; (Z)-MeCH=C(Cl)CH_2CO_2Me, 103563-26-4; (E)-MeCH=C(Cl)CH_2CO_2Me, 103563-27-5; $H_2C=C(Me)(CH_2C(Me_2))_3CH_3$, 15796-04-0; $Ph_3P^+CH_2CO_2Me$ Br^-, 1779-58-4; $H_2C=CH(CH_2)_4COCl$, 21430-12-6; (Z)-EtCH=CH$(CH_2)_4COCl$, 103563-28-6; $Me_2C=CH(CH_2)_2CH(Me)CH_2COCl$, 36392-06-0; $EtACl_2$, 563-43-9.

Synthesis and Ring Expansion of Vinylazetidines. A Synthesis of Hydroazocines[1]

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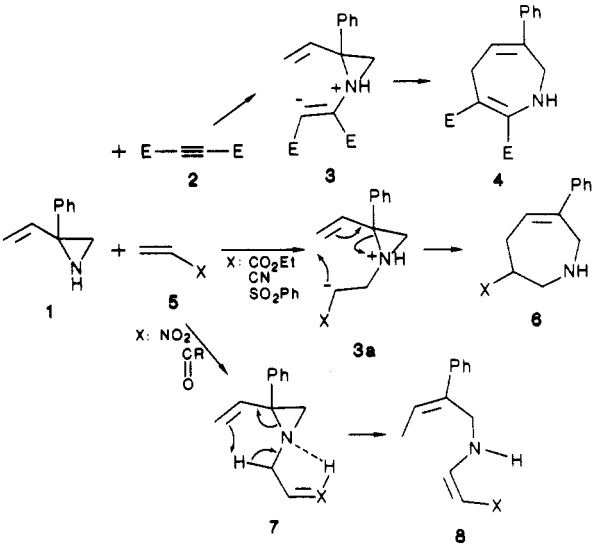
Received January 31, 1986

A synthesis of 2-vinylazetidines **11a–c** by means of $ClSO_2NCO$ addition to 1,3-dienes followed by AlH_3 reduction is described. One example (**11a**) underwent Michael additions with several olefinic and acetylenic substrates. The 1,2-divinylazetidines obtained with the latter reagents underwent Cope rearrangements when heated and gave rise to tautomeric mixtures of 3,4,7,8- and 1,4,7,8-tetrahydroazocines (**21** and **22**).

The chemistry of azocines and of their hydro derivatives is largely unexplored[2] because of the unavailability of good methods for their preparation. Recently we reported a ring expansion reaction of 2-vinylaziridines **1** to hydroazepines **4** or **6** during their reaction with olefinic or acetylenic substrates.[3] Thus vinylaziridine **1** reacts with dimethyl acetylenedicarboxylate (**2**) at 20 °C to produce dihydroazepine **4** in excellent yield. Since even olefins **5** (X: COOEt, CN, or SO_2Ph) react with **1** by way of ring expansion to the tetrahydroazepines **6**, both reactions were postulated to proceed via a Michael addition to produce the zwitterionic intermediates **3**; the latter then undergo ring closure with cleavage of the three-membered ring. However, not all olefinic Michael acceptors led to formation of seven-membered rings. When the intermediate carbanionic species **3a** is stabilized by a nitro or a carbonyl function, the reaction takes a different course and leads, via an ene reaction on **7**, to enamine species **8**. In order to test the scope of the above ring expansion reactions and whether they can be applied to the synthesis of hydroazocines, we decided to investigate the reaction of 2-vinylazetidines with unsaturated substrates. We report here the synthesis of vinylazetidines **11** and reaction of **11a** with olefinic and acetylenic Michael acceptors.

Results and Discussion

While 2-vinylaziridines **1** can be prepared from readily available azirines,[4] a general method for synthesis of 2-vinylazetidines is not available.[5] As an entry into vinylazetidines, we utilized the chlorosulfonyl isocyanate (CSI) addition to olefins.[6] Reaction of $ClSO_2NCO$ with isoprene



followed by sodium sulfite workup[7] furnished vinylazetidinone **10a**.[8] Reduction of **10a** to 2-vinylazetidine **11a** presented unexpected difficulties. Although lithium aluminium hydride reduction of azetidinones to azetidines is a well-known reaction,[9] its application to **10** led surprisingly to concomitant reduction of the vinyl side chain. The NMR spectrum of the product (**12**) revealed the absence of olefinic protons, and instead the typical pattern of a CH_3CH_2 group was visible. An additional highly coupled signal for the CH_2-4 group, centered at 3.4 ppm, indicated conversion to the azetidine system. An analogy for an intramolecular C=C reduction by LAH can be found during the reduction of a carbonyl adjacent to an allenic function.[10] On the other hand, DIBAL, $HAlCl_2$, or H_2AlCl, which were reported[11] to be reagents of choice for reduction of azetidinones, were ineffective for reduction of **10**. Finally, we succeeded in generating **11a** in 73% yield by AlH_3 reduction of **10a**. In a similar manner 2,3-di-

(1) Small Rings. 29. For paper 28, see: Hassner, A., Wiegand, N. *J. Org. Chem.*, in press.
(2) See, for instance: (a) Paquette, L. A.; Kakihana, T.; Hansen, J. F.; Philips, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 152. (b) Paquette, L. A.; Kakihana, T.; Kelly, J. F. *J. Org. Chem.* **1971**, *36*, 435. (c) Nakatsubo, F.; Cocuzza, A. J.; Keeley, D. E.; Kishi, Y. *J. Am. Chem. Soc.* **1977**, *99*, 4835. (d) Moore, J. A.; Anet, F. A. L. *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; 1984; Vol. 7, Chapter 5.19, p 653. Pergamon Press, Oxford.
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(4) (a) Chaabouni, R.; Laurent, A. *Synthesis* **1975**, 464. (b) Hassner, A.; Costa, R.; McPhail, A. T.; Butler, W. *Tetrahedron Lett.* **1981**, *22*, 3691.
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(7) Durst, T.; Sullivan, M. J. *J. Org. Chem.* **1970**, *35*, 2043.
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(9) See: Paquette, L. A.; Kakihana, T.; Kelly, J. F. *J. Org. Chem.* **1971**, *36*, 435.
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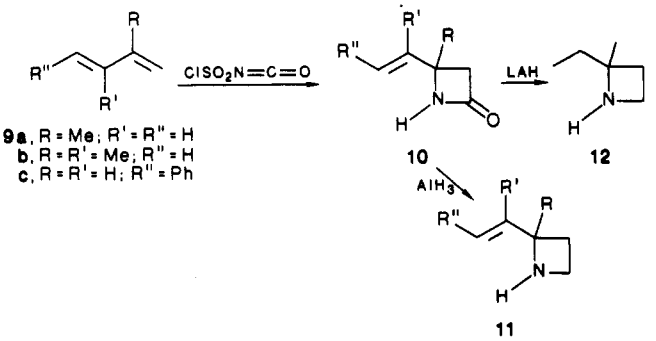
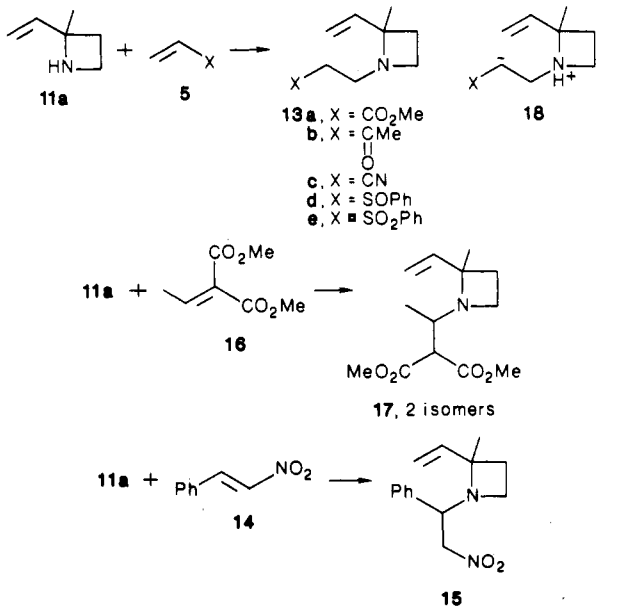
methylbutadiene (**9b**) and 1-phenylbutadiene (**9c**) were converted via the azetidinone to the 2-vinylazetidines **11b** and **11c** albeit in poor yield.

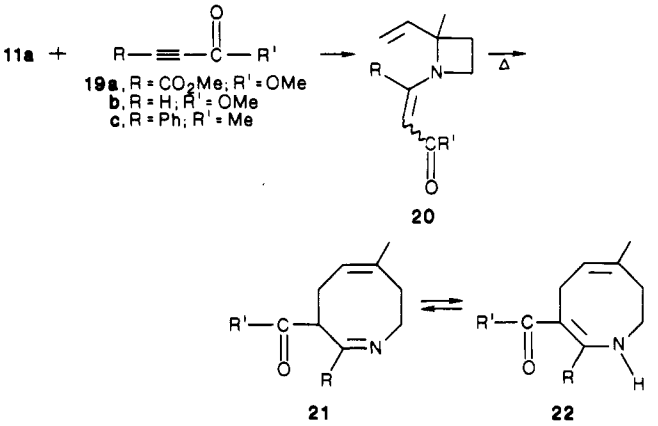


Reaction of azetidine **11a** with several unsaturated substrates (**5a–e**) proceeded smoothly at room temperature but produced only the Michael adducts **13** in nearly quantitative yields. These reaction products still showed in the H NMR spectrum a quaternary methyl group at 1.3 ppm and the typical splitting pattern for the intact vinyl group (at 6.0, 5.2, and 5.0 ppm). In the azetidine CH_2CH_2 moiety of the adducts, each proton appeared as a distinct doublet of doublets of doublets system, the CH_2X group gave an almost regular triplet, whereas the NCH_2 in the side chain was a complicated multiplet because of second-order effects. In the sulfoxide **13d** each peak was a twin due to the presence of two diastereomers. ^{13}C NMR spectra (correlated by off-resonance decoupling) also indicated the presence of the $C{=}CH_2$ group at 112 and 143 ppm and were completely consistent with structures **13**. No ring expansion products, as had been found in the reaction of vinylaziridines **1** with **5**, were observed. Nitrostyrene **14** or the diester **16** likewise led only to Michael adducts **15** or **17**, respectively, both as a mixture of the two possible diastereomers. No ring opening of the azetidine was observed, in contrast to the ring cleavage of vinylaziridine **1** to enamine **8**, which occurs on reaction with nitrostyrene **14**[3] and dimethyl ethylidenemalonate (**16**).[12]



The intermediate in the Michael addition of **11** to **5** is expected to be **18**, the four-membered-ring analogue of **3a**. Apparently, proton transfer occurs in **18** in preference to ring closure. Since aziridines are much weaker bases than azetidines,[13] the difference in behavior between vinylazetidine **11** which leads to **13** and vinylaziridine **1** which leads to **6** or **8** must be attributed to the greater propensity of the three-membered ring for ring opening.

Addition of vinylazetidine **11a** to acetylenic substrates **19** likewise stopped at the Michael addition stage (**20**). This again points to the greater ease with which vinylaziridines undergo ring opening compared to vinylazetidines. The divinylazetidine structures of **20a–c** were indicated by their ^1H and ^{13}C NMR spectra. Typical $CH{=}CH_2$ absorptions in both H and C NMR and the C-3 and C-4 absorptions near 31 and 46 ppm, respectively, were evident, as were the new enamine carbon absorptions near 152 and 85 ppm, their location highly dependent upon the nature of the R and R′ substituents.



The 1,2-divinylazetidine structure of **20** permitted a thermal aza-Cope rearrangement to tetrahydroazocines to take place. In the case of **20a** and **20c**, heating at 100 °C produced a tautomeric mixture of the imine form **21** and the enamine form **22** in a ratio of 18:82 and 7:93, respectively, as determined by ^1H NMR. The major component in the mixture of the tautomers, e.g., **22a**, had a relatively simple proton spectrum due to the apparent plane of symmetry in the molecule, caused by rapid nitrogen inversion: a doublet for CH_2-4 near 3.3 ppm, a triplet with fine splitting for the adjacent olefinic proton, an olefinic methyl singlet, a triplet for CH_2-7 at 2.4, and a quartet-shaped signal for the methylene adjacent to NH. The imine form **21**, because of its asymmetry, showed more complicated signals which we were able to assign with the help of homodecoupling experiments. Significant is the doublet of doublets for the C-3 proton at 4.52 ppm in **21a** and at 4.31 ppm in the imino ketone form **21c**. In the ^{13}C NMR spectra, C-3 appeared at 47.46 ppm for ester **21a** and at 66.03 ppm for ketone **21c**, both as doublets in off-resonance decoupled spectra. Ring expansion of **20b** required 140 °C and led solely to the enamine **22b**, which polymerized on standing in air.

Michael addition of **11** to **19a** and **19b** occurred stereospecifically since ^1H and ^{13}C NMR spectra indicate **20a** and **20b** to be a single isomer (in the case of **20b**, the olefinic coupling constants are consistent with the trans β-aminoacrylate structure). Enamino ketone **20c** on the other hand, exists as a 1:1 mixture of conformers with an appreciable barrier to rotation, as indicated by its ^1H and ^{13}C NMR spectra. The ^1H NMR signals of **20c** are considerably broadened and in both spectra two sets of signals were seen. Heating up to 57 °C causes the peaks in the proton spectrum to move with further broadening except for the acetyl methyl singlet at 1.62 ppm which appeared

(12) Hassner, A.; Andisik, D., unpublished results.

(13) The pK_a of azetidines is about 11, while that of aziridines is 8–9.

throughout as a sharp line. From NMR line widths we have estimated the activation energy of this dynamic process to be $G^* = 16.1 + 0.2$ kcal/mol at 42 °C. It appears that this dynamic phenomenon is caused by slow rotation about the N—C=C σ-bond of the enamino ketone.[14]

Experimental Section

Melting points were obtained on a Fischer-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 177 and 457 grating infrared spectrometers. Mass spectra were obtained with a Finnigan 4021 EI CI mass spectrometer. The NMR spectra were recorded at 300.1 (^{1}H) and 75.5 (^{13}C) MHz on a Bruker AM 300 spectrometer. Unless otherwise specified, spectral data refer to $CDCl_3$ solutions, with tetramethylsilane as internal reference. Elemental analyses were performed by the microanalytical laboratory at the Hebrew University, Jerusalem. Reagent-grade solvents were distilled prior to use. Merck silica gel 60 (230–400 mesh), Merck pre-coated preparative liquid chromatography plates, 2 mm, silica gel 60 F-254, and Merck silica gel 60 PF_{254} containing gypsum for radial chromatography were used as chromatographic materials. Azetidinones **10a** and **10b** were prepared following the reported procedure.[8]

4-(*trans*-2-Phenylethenyl)azetidin-2-one (10c). To a solution of *trans*-1-phenyl-1,3-butadiene (**9c**) (390 mg, 3.00 mmol) in 10 mL of dry ether under argon atmosphere was added via syringe a slight excess of CSI (440 mg, 3.11 mmol) at −50 °C. The mixture was allowed to warm up to 0 °C and stirred for 4 h at this temperature. Then the mixture was poured into 20 mL of cold 10% aqueous Na_2SO_3 solution and after 1-h stirring was extracted with ether. The ether extracts were washed with water, dried with Na_2SO_4, and filtered, and the solvent was evaporated. The remaining yellow oil (274 mg) was separated by preparative liquid chromatography with ether as eluent, yielding 61 mg (11.7%) of β-lactam **10c** as a colorless oil, which crystallized upon standing: mp 116–119 °C (ether); IR (KBr) 3155 s (NH), 1758, (C=O), 1722, 1695, 1644, 1395, 1358, 1279, 1188, 1140, 984, 970, 743, 688 cm^{-1}; ^{1}H-NMR δ (ppm) 2.81 (ddd, J = 15, 2.5, 1 Hz, CH-3 cis), 3.29 (ddd, J = 15, 5.5, 1 Hz, CH-3 trans) 4.30 (dddd, J = 7.5, 5.5, 2.5, 1 Hz, CH-4), 6.23 (dd, J = 16, 7.5 Hz, CH-4a), 6.37 (br s, NH), 6.63 (d, J = 16 Hz, CH-4b), 7.2–7.7 (m, C_6H_5); ^{13}C NMR δ (ppm) 167.6 (C=O), 45.5 (C-3), 49.3 (C-4), 128.6 (C-4a), 132.3 (C-4b), 128–135.8 (Ph); MS, EI (20 eV), m/e (relative intensity) 173 (38, M$^+$), 144 (30), 130 (100, M$^+$ − H_2CCOH and/or M$^+$ − HNCO), 115 (15), 104 (17), 91 (12). Anal. Calcd for $C_{11}H_{11}NO$ (173.21): C, 76.27, H, 6.40; N, 8.09. Found: C, 76.38 H, 6.48; N, 7.97.

AlH_3 Reduction of Azetidinones 10. 2-Methyl-2-vinylazetidine (11a). To a suspension of $LiAlH_4$ (5.06 g, 133 mmol) in 200 mL of dry ether under argon was added dropwise, with stirring and ice-bath cooling, 100% sulfuric acid (6.50 g, 66.4 mmol). After stirring for an additional hour, azetidinone **10a** (5.55 g, 50 mmol) was added dropwise, and the mixture was stirred for 6 days. The mixture was cooled, 2.0 g of water was added, and after 1 h of stirring the mixture was filtered and the aluminium hydroxide was washed several times with ether. The combined ether solutions were distilled over a short Vigreux column to give 1.59 g of azetidine **11a** as a mixture with ether (determined by NMR) whereas 1.98 g of pure **11a** was collected as a colorless liquid: bp 107–110 °C; yield 73.5%; IR (neat) 3280 (b, NH), 1635, 960, 770, 715 cm^{-1}; ^{1}H NMR δ (ppm) 1.4 (s, Me) 2.06 (br s, NH), 2.1–2.3 (m, CH_2-3), 3.36–3.5 (m, CH_2-4), 4.14 (dd, J = 18, 1.5 Hz, H-2b), 4.02 (dd, J = 10.5, 1.5 Hz, H-2b), 6.09 (dd, J = 18, 10.5 Hz, H-2a); ^{13}C NMR δ (ppm) 145.2 (C-2a), 110.5 (C-2b), 63.2 (C-2), 40.3 (C-4), 32.8 (C-3), 27.9 (Me). Anal. Calcd for $C_6H_{11}N$ (97.16): C, 74.17; H, 11.41. Found: C, 74.3; H, 11.1.

2-Methyl-2-(2-propenyl)azetidine (11b). Reduction of azetidinone **10b** (3.76 g, 30.0 mmol) with AlH_3 yielded 0.905 g (27.1%) of azetidine **11b** as a colorless liquid: bp 140–150 °C (Kugelrohr); IR (neat) 3280 (NH), 1645, 1100, 892 cm^{-1}; ^{1}H NMR δ (ppm) 1.44 (s, Me), 1.71 (dd, J = 1.5, 0.8 Hz, Me), 1.9 (br s, NH), 2.07 (ddd, J = 10.5, 8.8, 7.8, H-3), 2.38 (ddd, J = 10.5, 8.3, 7.8, H-3), 3.26 (ddd, J = 8.8, 7.7, 4.6 Hz, H-4), 3.54 (ddd, J = 8.3, 7.8, 7.7, H-4), 4.78 (dq, J = 1.5, 0.8, H-2b), 4.87 (dq, J = 1.5, 1.5, H-2b); ^{13}C NMR δ (ppm) 151.6 (C-4a), 107.6 (C-4b), 65.9 (C-4), 39.8 (C-2), 32.4 (C-3), 27.6 (Me), 17.5 (Me).

2-(*trans*-2-Phenylethenyl)azetidine (11c). Azetidinone **10c** (180 mg, 1.04 mmol) was reduced with AlH_3 prepared from $LiAlH_4$ (168 mg, 4.22 mmol) and 100% sulfuric acid (210 mg, 2.14 mmol). After 5 days of stirring, 10 mL of ether was added and then 2 mL of 40% aqueous NaOH and 2 g of ice. After 1 h, the phases were separated and the aqueous phase was extracted twice with ether. The combined etheral solutions were washed with water, dried with Na_2SO_4, and filtered. Evaporation gave a colorless oil which was purified by Kugelrohr distillation yielding 100 mg of **11c** as colorless oil (60%): ^{1}H NMR δ (ppm) 2.24 and 2.4 (m, CH_2-3), 2.51 (br s, NH), 3.36 and 3.59 (m, CH_2-4), 4.47 (m, H-2), 6.42 (m, 2 H), 7.1–7.4 (m, Ph); ^{13}C NMR δ (ppm) 132.9 (C-2b), 129.3 (C-2a), 126-136 (Ph), 60.4 (C-2), 43.6 (C-4), 28.5 (C-3).

Reduction of Azetidinone 10a with $LiAlH_4$. Azetidinone **10a** (555 mg, 5.00 mmol), diluted with 2 mL of dry ether, was added dropwise to a suspension of $LiAlH_4$ (950 mg, 25.0 mmol) in 55 mL of dry ether, and the resulting mixture was refluxed for 1.5 days under an argon atmosphere. Then 1.0 mL of water, 1.0 mL of 15% NaOH, and again 2.6 mL of water were added while stirring. The $Al(OH)_3$ precipitate was filtered off and washed with ether. The combined organic layers were dried and evaporated, and the residue was distilled in a Kugelrohr apparatus to yield 310 mg (62.5%) of **2-ethyl-2-methylazetidine (12)** as a colorless liquid: bp 110–125 °C; IR (film) 3260 (NH), 1450, 1363, 1250, 1110, 956, 720 cm^{-1}; ^{1}H NMR δ (ppm) 0.87 (t, J = 7.5 Hz, Me), 1.27 (s, CH_3), 1.60 (q, J = 7.5 Hz, CH_2-2a), 1.98 (ddd, J = 11, 9, 6 Hz, CH-3), 2.11 (ddd, J = 11, 9, 6.8 Hz, CH-3), 2.4 (br s, NH), 3.36 (ddd, J = 9, 8.3, 6, CH-4), 3.46 (ddd, J = 9, 8.3, 6.8, CH-4). Anal. Calcd for $C_6H_{13}N$ (99.17): C, 72.66; H, 13.21 Found: C, 71.9; H, 12.7.

Reactions of Azetidine 11a with H_2C=CHX (5). Azetidine **11a** was either treated with **5** neat or in an inert, low-boiling solvent such as CH_2Cl_2. The progress of the addition was monitored by NMR using a $CDCl_3$ solution of the reactants.

***N*-(2-Carbomethoxyethyl)-2-methyl-2-vinylazetidine (13a).** To azetidine **11a** (194 mg, 2.00 mmol) was added methyl acrylate (**5a**) (190 mg, 2.09 mmol), and the mixture was kept for 5 h at room temperature. Subsequent Kugelrohr distillation gave after a short forerun 305 mg (83.3%) of adduct **13a** as a colorless liquid: $bp_{0.25}$ 50–70 °C; IR (Film) 1740 (C=O), 1000, 920 cm^{-1}; MS, EI (30 eV), m/e (relative intensity) 184 (100, M$^+$ + 1), 168 (80), 156 (14), 110 (73); ^{1}H NMR δ (ppm) 1.28 (s, Me), 1.86 (ddd, J = 10.5, 8, 5 Hz, H-3), 2.10 (ddd, J = 10.5, 8, 5 Hz, H-3), 6.01 (dd, J = 17.5, 10.5, H-2a), 2.34 (t, J = 7.5 Hz, CH_2), 2.6 (m, CH_2), 3.1 (ddd, J = 8, 7, 6.5 Hz, H-4), 3.23 (ddd, J = 8, 6.5, 5 Hz, H-4), 3.67 (s, OMe), 5.15 (dd, J = 17.5, 1.5 Hz, H-2b), 5.06 (dd, J = 10.5, 1.5 Hz, H-2b); ^{13}C NMR δ (ppm) 172.8 (C=O), 143.4 (C-2a), 112.5 (C-2b), 66 (C-2), 51.4 (OMe), 49.1 (C-4), 46.6 (C-1a), 33.2 (C-1b), 31 (C-3), 19 (Me).

***N*-(3-Oxobutyl)-2-methyl-2-vinylazetidine (13b).** To a solution of azetidine **11a** (204 mg, 2.10 mmol) in 2 ml of CH_2Cl_2 was added vinyl methyl ketone (150 mg, 2.14 mmol). After 5 h at room temperature, the solvent was evaporated and the residue was purified by Kugelrohr distillation to give 313 mg (89.3%) of adduct **13b** as a colorless liquid: $bp_{0.25}$ 60–70 °C; IR (film) 1725, 1715 (C=O), 1640, 1000, 925 cm^{-1}; MS, EI (30 eV), m/e (relative intensity) 168 (55, M$^+$ + 1), 152 (60), 140 (14), 124 (7), 110 (100), 100 (56); ^{1}H NMR δ (ppm) 1.29 (s, Me), 1.85 (ddd, J = 10, 8.2, 4.7 Hz, H-3, 2.09 (ddd, J = 10, 8.2, 7, H-3), 2.14 (s, Me), 2.44 (t, J = 7.2 Hz, CH_2), 2.58 (m, CH_2), 3.09 (ddd, J = 8.2, 7, 6.7 Hz, H-4), 3.21 (ddd, J = 8.2, 6.7, 4.7 Hz, H-4), 5.06 (dd, J = 11, 1.5 Hz, H-2b), 5.13 (dd, J = 17.5, 1.5 Hz, H-2b), 6.02 (dd, J = 17.5, 11 Hz, H-2a); ^{13}C NMR δ (ppm) 207.6 (C=O), 143.4 (C-2a), 112.5 (C-2b), 65.8 (C-2), 49 (C-4), 45.7 (C-1a), 42.1 (C-1b), 30.9 (C-3), 30 (Me), 20 (Me).

***N*-(2-Cyanoethyl)-2-methyl-2-vinylazetidine (13c).** In the same manner from azetidine **11a** (97 mg, 1.00 mmol) and acrylonitrile (54 mg, 1.02 mmol) was obtained 113 mg (75.3%) of **13c** as a colorless liquid: $bp_{0.6}$ 70–80 °C; IR (film) 2250 (C≡N), 1000, 925 cm^{-1}; ^{1}H NMR δ (ppm) 1.3 (s, Me), 1.91 (ddd, J = 10.5, 8, 8.5 Hz, H-3), 2.11 (ddd, J = 10.5, 8.5, 7 Hz, H-3), 2.33 (t, J = 7 Hz, CH_2), 2.66 (m, CH_2), 3.18 (dt, J = 8, 6.5 Hz, H-4), 3.31 (ddd,

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J = 8, 6.5, 4.5 Hz, H-4), 5.09 (dd, J = 10.5, 1.5 Hz, H-2b), 5.21 (dd, J = 17.5, 1.5 Hz, H-2b), 6.01 (dd, J = 17.5, 10.5 Hz, H-2a); ^{13}C NMR δ (ppm) 142.9 (C-2a), 118.9 (C≡N), 113.1 (C-2b), 66.3 (C-2), 49.3 (C-4), 46.9 (C-1a), 31.2 (C-3), 20.1 (Me), 17.2 (C-1b); MS, EI (30 eV), m/e (relative intensity) 151 (100, M^+ + 1), 135 (26), 110 (80). Anal. Calcd for $C_9H_{14}N_2$ (150.22): C, 71.95; H, 9.39; N, 18.65. Found: C, 71.88; H, 9.58; N, 18.77.

***N*-[2-(Phenylsulfinyl)ethyl]-2-methyl-2-vinylazetidine (13d)** was obtained by treating azetidine **11a** (388 mg, 4.00 mmol) with phenyl vinyl sulfoxide (609 mg, 4.00 mmol) for 20 h at room temperature. Chromatography of the resulting oil (silica gel, EtOAc) gave 822 mg of **13d** as a viscous liquid (82.4%): IR (film) 1365, 1355, 990, 970, cm^{-1}; ^{1}H NMR δ (ppm) 1.29 and 1.30 (s, Me), 1.89 (m, H-3), 2.12 (m, H-3), 2.77 (m, CH_2), 3.14 and 3.26 (m, CH_2-4), 5.06 and 5.08 (dd, J = 11, 1.5 Hz, H-2b), 5.14 and 5.22 (dd, J = 17.5, 1.5 Hz, H-2b), 6.01 and 6.04 (dd, J = 17.5, 11 Hz, H-2a), 7.5 (m), 7.63 (m); ^{13}C NMR δ (ppm) 143.4 and 142.8 (C-2a), 112.9 and 113 (C-2b), 66 and 66.1 (C-2), 56.2 and 56.5 (C-1b), 48.9 and 49.2 (C-4), 44.1 and 44.2 (C-1a), 30.9 and 31 (C-3), 19.6 and 20.3 (Me); MS, EI (24 eV), m/e (relative intensity) 250 (42, M^+ + 1), 232 (4), 182 (16), 124 (100), 108 (58), 95 (24).

***N*-[2-(Phenylsulfonyl)ethyl]-2-methyl-2-vinylazetidine (13e)** was obtained from **11a** (100 mg, 1.03 mmol) and phenyl vinyl sulfone (168 mg, 1.00 mmol) in 2 mL of CH_2Cl_2 kept at room temperature for 15 h. After evaporation of the solvent, the remaining oil was purified by chromatography on silica gel with ether as eluent, yielding 244 mg (92.0%) of **13e** as a colorless, viscous liquid: IR (film) 920, 740, 690 cm^{-1}; ^{1}H NMR δ (ppm) 1.21 (s, Me), 1.81 (ddd, J = 10.5, 8, 5 Hz, H-3), 2.11 (ddd, J = 10.5, 8.5, 7 Hz, H-3), 2.71 (m, CH_2), 3.12 (t, J = 7.5 Hz, CH_2), 3.0 (ddd, J = 8, 7, 6.5 Hz, H-4), 3.08 (ddd, J = 8.5, 6.5, 5 Hz, H-4), 5.03 (dd, J = 11, 1.5 Hz, H-2b), 5.09 (dd, J = 17.5, 1.5 Hz, H-2b), 5.91 (dd, J = 17.5, 11 Hz, H-2a), 7.75 (m, Ph); ^{13}C NMR δ (ppm) 142.7 (C-2a), 112.9 (C-2b), 127–139 (Ph), 65.9 (C-2), 54.4 (C-1b), 48.6 (C-4), 44.2 (C-1a), 30.7 (C-3), 19.8 (Me); MS, EI (29 eV), m/e (relative intensity) 266 (92, M^+ + 1), 250 (77), 198 (67), 124 (45), 123 (65), 110 (100), 108 (67), 96 (50). Anal. Calcd for $C_{14}H_{19}NSO_2$ (265.3): C, 63.38; H, 7.22, N, 5.28. Found: C, 62.91; H, 7.14, N, 5.19.

Reaction of 11a with β-Nitrostyrene (14) and Dimethyl Ethylidenemalonate (16). To a solution of β-nitrostyrene (**14**) (75 mg, 0.50 mmol) in 0.4 mL of $CDCl_3$ was added **11a** (49 mg, 0.50 mol). The NMR spectrum of the reaction mixture after 5 h showed complete reaction with formation of a 50:50 mixture of two diastereomeric forms of **15**: 7.2–7.4 (m, Ph), 6–6.1 (m, H-2a) 4.9–5.22 (m, CH_2-2b), 4.4–4.6 (m, H-1a), 4.2–4.33 M, CH_2-1b), 2.9–3.18 (m, CH_2-4), 2–2.1 and 1.74–1.95 (m, CH_2-3), 1.33 (ss, 2 Me); ^{13}C NMR δ (ppm) 19.8, 22.3 (Me), 30.3, 31.0 (CH_2-3), 47.3, 47.5 (CH_2-4), 63.61, 63.67, 63.74, 63.79 (CH-Ph), 66.2, 66.8 (C-2), 79.4, 79.5 (CH_2NO_2), 113.5 (CH_2=C), 141.8, 144.1 (CH=C), 127–137 (Ph); MS, CI, m/e (relative intensity) 247.66 (25, MH^+), 217.56 (M^+ - NO), 186.56, (100, M^+ - CH_2NO_2), 179.52 (5).

A mixture of azetidine **11a** (100 mg, 1.03 mmol) and ethylidene malonate **16** (158 mg, 1.00 mmol) was kept for 24 h at room temperature. The NMR spectrum showed complete formation of the Michael adduct **17** as a 40:60 mixture of two diastereomers: ^{1}H NMR 6.16 (m, H-2a), 5.1 (m, CH_2-2b), 3.7–3.75 (ssss, OMe), 3.42 (dd, H-1b), 3.2 (m, 3 H, H-4 + H-1a), 1.9 (m, CH_2-3), 1.34 (s, Me), 1.07 (dd, 1a-Me); MS, EI, m/e (relative intensity) 256.70 (100, MH^+), 240.60 (7), 188.46 (11), 124.40 (90).

***N*-((*E*)-2-Carbomethoxyvinyl)-2-methyl-2-vinylazetidine (20b).** To a solution of **11a** (485 mg, 5.00 mmol) in ether (8 mL) was added dropwise the equivalent amount (420 mg) of methyl propiolate **19b**. After 15 h at room temperature, the reaction mixture was filtered through a small amount of silica gel and the solvent was evaporated, yielding 893 mg of **20b** (98.6%) as an almost colorless liquid: IR (film) 1690 (C=O), 1600, 1100, 925, 790 cm^{-1}; ^{1}H NMR δ (ppm) 1.49 (s, Me), 2.26 (m, CH_2-3), 3.62 (s, OMe), 3.78 (t, J = 7.5 Hz, CH_2-4), 4.46 (d, J = 13 Hz, H-1b), 5.13 (dd, J = 11, 1 Hz, H-2b), 5.19 (dd, J = 17, 1 Hz, H-2b), 5.99 (dd, J = 17, 11 Hz, H-2a), 7.34 (d, J = 13 Hz, CH=C); ^{13}C NMR δ (ppm) 169.2 (C=O), 147.4 (C-1a), 141.1 (C-2a), 113.5 (C-2b), 84.6 (C-1b), 69.8 (C-2), 50.2 (OMe), 45.9 (C-4), 31.5 (C-3), 24.4 (Me); MS, EI (30 eV), m/e (relative intensity) 182.52 (100, MH^+), 150.40 (11, M^+ - MeOH), 122.38 (1), 114.34 (38). Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.35; H, 8.29. Found: C, 65.9; H, 8.4.

***N*-(1,2-Dicarbomethoxyvinyl)-2-methyl-2-vinylazetidine (20a).** To a solution of **19a** (425 mg, 3.00 mmol) in ether (5 mL) was added dropwise azetidine **11a** (300 mg, 3.09 mmol). Removal of the volatile components gave 720 mg of a yellow oil that crystallized upon dilution with 0.5 mL of ether and maintaining the temperature at −10 °C, finally yielding 510 mg of **20a** (70.8%) as slightly yellow crystals: mp 52–52.5 °C (ether); ^{1}H NMR δ (ppm) 1.58 (s, Me), 2.19 (ddd, J = 11, 9, 5 Hz, H-3), 2.32 (dd, J = 16, 9 Hz, H-3), 3.61 (s, OMe), 3.84 (br, OMe and CH_2-4), 4.46 (br s, H-1b), 5.18 (br d, J = 11 Hz, H-2b), 5.22 (br d, J = 17.5 Hz, H-2b), 6.04 (dd, J = 17.5, 11 Hz, H-2a); ^{13}C NMR δ (ppm) 167.6 (C=O), 164.8 (C=O), 152 (br, C-1a), 140.3 (br, C-2a), 114.7 (br, C-2b), 83.8 (br, C-1b), 71.3 (C-2), 52.5 (OMe), 50.6 (OMe), 46.1 (C-4), 31.7 (C-3), 22.2 (b, Me); MS, CI, m/e (relative intensity) 240.62 (100, MH^+), 208.52 (13, M^+ - MeOH), 180.50 (1.6, M^+ - MeOCOH), 172.46 (78 M^+ - C_5H_8). Anal. Calcd for $C_{12}H_{17}NO_4$ (239.27): C, 60.24; H, 7.16; N, 5.85. Found: C, 60.02; H, 7.14; N, 5.68.

Phenylbutynone Adduct 20c. To a solution of phenylbutynone **19c** (144 mg, 1.00 mmol) in 0.8 mL of $CDCl_3$ was added at −15 °C azetidine **11a** (110 mg, 1.13 mmol). The mixture was allowed to warm to room temperature within several hours and was kept at 30 °C for an additional 8 h. Then it was passed through a short column of silica gel to remove polar impurities and the product was further purified by radial chromatography with 1:1 EtOAc–hexane as eluent; 203 mg of ***N*-(3-oxo-1-phenyl-1-butenyl)-2-methyl-2-vinylazetidine (20c)** (84%) was obtained as a colorless oil: IR (film) 1646, 1604, 1005, 990, 960, 920, 882, 820, 770, 725, 700 cm^{-1}; ^{1}H NMR δ (ppm) 1.14 and 1.72 (s, Me), 1.62 (s, Ac), 2.16 (m, H-3), 3.49 and 3.8 (m, H-4), 4.75 and 5.31 (dd, J = 17.5, 1 Hz, H-2b), 4.83 and 5.26 (dd, J = 10.5, 1 Hz, H-2b), 4.99 and 5.21 (s, H-1b), 5.85 and 6.13 (dd, J = 17.5, 10.5 Hz, H-2a), 7.33 (m, Ph); ^{13}C NMR δ (ppm) 194 and 194.7 (C=O), 159.4 and 161.4 (C-1a), 140.1 and 141.9 (C-2a), 127–135 (Ph), 112.9 and 114.5 (C-2b), 98.4 and 100.1 (C-1b), 70.26 and 71.3 (C-2), 46.4 and 46.55 (C-4), 30.5 and 31.3 (C-3), 29.49 (Ac), 21.9 and 25.2 (Me); MS, EI (30 eV), m/e (relative intensity) 242 (21, M^+ + 1), 198 (70), 174 (36), 84 (100).

Aza-Cope Rearrangement of 1,2-Divinylazetidines 20. Formation of 6-Methyl-2,3-dicarbomethoxy-3,4,7,8-tetrahydroazocine (21a) and 6-Methyl-2,3-dicarbomethoxy-1,4,7,8-tetrahydroazocine (22a). Dimethyl acetylenedicarboxylate adduct **20a** (100 mg, 0.42 mmol) in 0.3 mL of $CDCl_3$ was heated for 14 h in a 100 °C bath in a closed NMR tube behind a safety shield. The resulting solution, containing an 18:82 mixture of the tautomers **21a** and **22a**, was filtered through silica gel and the solvent was removed. The oily residue crystallized from ether by standing at 0 °C, giving 80 mg (80%) of colorless prisms of the enamine form **22a**, mp 109–110 °C, which converted within minutes back to the mixture of tautomers by dissolution in $CDCl_3$: IR (KBr) 3330 (NH), 1725, 1655, 1580, 1105, 1068, 760 cm^{-1}. **22a**: ^{1}H NMR δ (ppm) 1.72 (br s, Me), 2.46 (t, J = 5.5 Hz, CH_2-7), 3.25 (d, J = 8.5 Hz, CH_2-4), 3.66 (s, OMe), 3.7 (m, CH_2-8), 3.79 (s, OMe), 4.93 (br t, J = 7 Hz, NH), 5.51 (tq, J = 8.5, 1.5 Hz, H-5); ^{13}C NMR δ (ppm) 169.5 (C=O), 168.6 (C=O), 148.5 (C-2), 135.7 (C-6), 121.7 (C-5), 99 (C-3), 51.50 (OMe), 52.7 (OMe), 43.3 (C-8), 38.7 (C-4), 25.9 (Me), 24.1 (C-7). **21a**: 1.65 (br s, Me), 2.5 (m, H-7), 2.69 (ddd, J = 17, 5.5, 2.5 Hz, H-7), 2.39 (dt, J = 14, 9 Hz, H-4), 3.05 (ddd, J = 14, 12, 9 Hz, H-4), 3.7 (s, OMe), 3.86 (s, OMe) 3.97 (ddd, J = 10.5, 6.25 Hz, H-8), 4.33 (ddd, J = 13, 10.5, 5.5 Hz, H-8), 4.52 (dd, J = 12, 8 Hz, H-3), 5.41 (tq, J = 8.5, 1.5 Hz, H-5); ^{13}C NMR δ (ppm) 170.6 (C=O), 165.4 (C=O), 159 (C-2), 136.9 (C-6), 119.8 (C-5), 53.2 (OMe), 52.5 (OMe), 50.6 (C-8e, 47.5 (C-3), 33.4 (C-4), 27.9 (C-7), 26 (Me). Anal. Calcd for $C_{12}H_{17}NO_4$ (239.27): C, 60.25; H, 7.16; N, 5.85. Found: C, 60.30; H, 7.20; N, 5.75.

Methyl 6-Methyl-1,4,7,8-tetrahydroazocine-3-carboxylate (22b). 20b (108 mg, 0.60 mmol) was heated in C_6D_5Br solution (0.4 mL) in an NMR tube at 140 °C for 1 h. The solvent was removed in vacuo via Kugelrohr distillation and the residue was diluted with a few drops of ether and crystallized at −10 °C to give 59 mg (54.6%) of **22b** as colorless prisms: mp 76–84 °C; IR (KBr) 3320 (NH), 1645, 1600, 1100, 860, 770 cm^{-1}; ^{1}H NMR δ (ppm) 1.71 (br s, Me), 2.44 (tq, J = 6, 1 Hz, CH_2-7), 3.25 (d, J = 8.5 Hz, CH_2-4), 3.64 (s, OMe), 3.71 (br q, J = 6 Hz, CH_2-8), 4.82 (br, NH), 5.6 (tq, J = 8.5, 1 Hz, H-5), 7.47 (d, J = 8 Hz, H-2); ^{13}C NMR δ (ppm) 169.7 (C=O), 147.7 (C-2), 133.7 (C-6), 124.2

(C-5), 96.6 (C-3), 50.5 (OMe), 40.4 (C-8), 40 (C-4), 26.2 (Me), 22.4 (C-7).

3-Acetyl-6-methyl-2-phenyl-1,4,7,8-tetrahydroazocine (22c). **20c** (120 mg, 0.50 mmol) was thermolyzed for 20 h as described for **20a**. After evaporation the residue was recrystallized from 1:6 CH_2Cl_2/hexane, yielding 99 mg (82.5%) of enamine form **22c** as yellow needles: mp 166–167 °C; ^1H NMR δ (ppm) 1.46 (s, Ac), 1.72 (br s, Me), 2.49 (br t, J = 6.5 Hz, CH_2-7), 3.47 (d, J = 8.5 Hz, CH_2-4), 3.81 (br q, J = 6.5 Hz, CH_2-8), 4.5 (br, NH), 5.53 (tq, J = 8.5, 1.5 Hz, H-5), 7.39 (m, H-2); ^{13}C NMR δ (ppm) 198.1 (C=O), 161.8 (C-2), 141.3 (C-6), 128-134 (Ph), 122.8 (C-5), 109.7 (C-3), 44.6 (C-8), 36.9 (C-4), 29.9 (Ac), 25.9 (Me), 25.8 (C-7). Imine tautomer **21c**: ^{13}C NMR δ (ppm) 204.1 (C=O), 166.1 (C=N), 127–137 (Ph), 119.6 (C-5), C-6 not resolved, 66 (C-3), 50.2 (C-8), 33.8 (C-4), 29.6 (Ac), 27.5 (Me), 26.2 (C-7). Anal. Calcd for $C_{16}H_{19}NO$ (241.34): C, 79.63; H, 7.94; N, 5.80. Found: C, 79.74; H, 8.02; N, 5.84. MS, EI (24 eV), m/e (relative intensity) 241 (20, M^+), 226 (4), 198 (100), 170 (41), 156 (20), 83 (52).

Acknowledgment. We thank Dr. H. E. Gottlieb for helping interpretation of NMR-spectra, Dr. K. Murthy for valuable assistance and the Minerva Foundation for fellowship support (to N.W.). A grant from the Israel Academy of Sciences and Humanities in support of this research is greatfully acknowledged.

Registry No. **5a**, 96-33-3; **5b**, 78-94-4; **5c**, 107-13-1; **5d**, 20451-53-0; **5e**, 5535-48-8; **9c**, 16939-57-4; **10a**, 20012-94-6; **10b**, 103564-07-4; **10c**, 103564-07-4; **11a**, 103564-08-5; **11b**, 103564-09-6; **11c**, 103564-10-9; **12**, 103564-11-0; **13a**, 103564-12-1; **13b**, 103564-13-2; **13c**, 103564-14-3; **13d**, 103564-15-4; **13e**, 103564-16-5; **14**, 102-96-5; **15** (isomer 1), 103564-17-6; **15** (isomer 2), 103564-18-7; **16**, 17041-60-0; **17** (isomer 1), 103564-19-8; **17** (isomer 2), 103564-20-1; **19a**, 762-42-5; **19b**, 922-67-8; **19c**, 1817-57-8; **20a**, 103564-21-2; **20b**, 103564-22-3; **20c**, 103564-23-4; **21a**, 103564-24-5; **21c**, 103564-25-6; **22a**, 103564-26-7; **22b**, 103564-27-8; **22c**, 103564-28-9; $ClSO_2NCO$, 1189-71-5.

Reactions of Alkylidenecarbenes Derived from N,N-Disubstituted-2-oxopropanamides: The Formation of 3-Pyrrol-2-ones and 2-Butynamides

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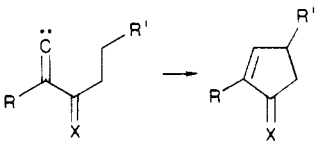
Received December 30, 1985

Activation of C–H bonds toward insertion by an alkylidenecarbene was examined in the reaction of N,N-disubstituted-2-oxopropanamides with diethyl (diazomethyl)phosphonate under basic reaction conditions. The intermediate alkylidenecarbene expected to be formed yielded two types of products, viz., 3-pyrrol-2-ones and 2-butynamides. A solvent effect that alters the relative ratio of the two products was observed. A mechanistic interpretation is offered for this effect and for the ratio of pyrrolones obtained from 2-oxopropanamides that are unsymmetrically substituted at nitrogen.

Development of methodologies for the formation of five-membered rings has recently been of considerable interest, primarily because of efforts to synthesize polyquinoids.[1] One of the approaches that has received increasing attention involves generation of a carbene and its subsequent intramolecular 1,5 C–H insertion.[2-4] For example, such an insertion reaction of alkylidenecarbenes (R_2C=C:), 1,[5] yields cyclopentenes and cyclopentenones (eq 1).[2]



X = H_2, O (1)

Several different synthetic approaches to alkylidenecarbenes have been developed, and they appear to produce intermediates sharing some common trends in their reactivities.[2] Preeminent among these is the preference for insertion into a tertiary C–H bond over a secondary C–H bond, which in turn is greatly favored over a primary C–H bond.[2d,i,k] On a first-order basis, the observed selectivity can be ascribed to the differences in bond dissociation energies of the various C–H bonds.[6] The present paper describes investigations intended to probe further the role of bond dissociation energies in defining the success of C–H insertion by alkylidenecarbenes **1**. Of particular interest was the possibility that heteroatoms would activate C–H bonds α to them toward the insertion reaction.

The effect of a heteroatom on the strength of a C–H bond α to it is substantial, as reflected in the reported bond

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