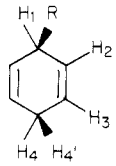
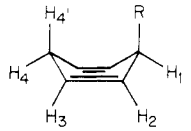
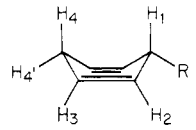
Table II. Coupling Constant Data for Various Structural Types of 1,4-Cyclohexadienes



4



5

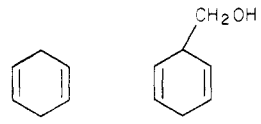


6

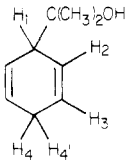
coupling constant	planar (4)[a]	rigid boat (5)[b]	rigid boat (6)[b]
$J_{1,4}$(cis)	8.3	2.6[c]	12.0
$J_{1,4'}$(trans)	7.5	4.7	4.7
J_{cis}/J_{trans}	1.11	<0.55	2.55
$J_{1,2}(J_{3,4})$	3.1	5.5	2.5
$J_{3,4'}$	3.0	2.5	5.5

[a] Data for compound 2 (from ref 12). [d] Data for 2,4a-dihydrotriptycene-2-carboxylic acid (from ref 13). [c] Although values for cis diequatorial coupling are not known for this geometry, a value of 2.6 Hz can be estimated by the method of Grossel (ref 6). However, his calculated values appear to be about 33% too high when compared to available experimental values.

spin decoupling in the presence of $Eu(fod)_3$, and the results are presented in Table I.



1 2



3

In a planar geometry, the $J_{1,4}/J_{1,4'}$ (cis/trans) ratio has been established as about 1.1 by previous experimental data (see Table II) as well as theoretical predictions.[6] As planar 1,4-dihydrobenzene begins to pucker (boat shaped) the homoallylic coupling constants react as follows (Table II): (1) the cis diaxial value becomes considerably larger, (2) the cis diequatorial value becomes much smaller, and (3) the trans axial/equatorial value decreases slightly. Hence, a substituted 1,4-dihydrobenzene with a single substituent in the pseudoaxial position of a boat geometry would show a J_{cis}/J_{trans} ratio of less than 1.1 since the cis relationship is pseudoequatorial/pseudoequatorial. A similar geometry with a pseudoequatorial substituent would show a J_{cis}/J_{trans} ratio of more than 1.1 since the cis relationship in this case is pseudoaxial/pseudoaxial. With **3**, the value is 0.96. Hence, we can conclude that **3** exists in a boat conformation with the substituent pseudoaxial as predicted by force field calculations. This conclusion is also supported by the vicinal coupling constants since $J_{3,4}$ and $J_{1,2}$ are slightly larger than that expected for a planar geometry, indicating a slight decrease in dihedral angle. We may conclude from the magnitude of the observed values that the extent of ring puckering is quite modest, suggesting a very shallow boat. It should also be noted that this representation is an average geometry and that significant oscillations about this conformation are expected.[5,7,8c]

Experimental Section

3-(2-Hydroxy-2-propyl)-1,4-cyclohexadiene. A solution of sodium amide in 60 mL of ammonia (-78 °C) was prepared from the metal (37 mmol) and a catalytic amount of ferric chloride. 1,4-Cyclohexadiene (2 g, 25 mmol) in 10 mL of dry THF (distilled from sodium/benzophenone) was then added and stirring was continued for 1 h. Dry acetone was then added followed by aqueous ammonium chloride. Ether extraction and microdistillation afforded a colorless oil in 39% yield: bp 36 °C (2 torr); 360-MHz NMR ($CDCl_3$) δ 5.85 (AB, 4 H, 2.8), (m, 1 H), 2.65 (m, 2 H), 1.8 (s, 1 H), 1.2 (s, 6 H). Anal. Calcd for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.50; H, 9.97.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences for support of this work (P.W.R.). We also thank the Lilly Research Laboratories for use of the Bruker 360-MHz NMR spectrometer.

Registry No. 1, 628-41-1; 3, 70338-15-7; acetone, 67-64-1.

Selectivity in Cycloadditions to Vinylheterocumulenes. [2 + 2] and [4 + 2] Cycloaddition of (Diethylamino)propyne to Vinyl Isocyanate and Vinyl Isothiocyanate[1]

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The mode of cycloaddition of unsaturated systems to heterocumulenes[3] varies depending on the chosen cumulative system as well as on the nature and extent of substitution at its terminal atoms. This stereochemical flexibility constitutes both a matter for mechanistic investigations and a versatile entry toward various small and medium ring size heterocycles. Particularly attractive in this respect are vinylheterocumulenes in that they have a carbon–carbon double bond adjacent to the cumulative system and can act as a 2-π-electron component by using one of the double bonds or as a 4-π-electron component by using one cumulative double bond and the vinyl group. Representative compounds of this class of heterocumulenes are vinylketenes[4] and vinylketenimines[5] whose site and peri selectivity in [2 + 2] and [4 + 2] cycloadditions have attracted considerable attention for the synthesis of four- and six-membered heterocycles. The ready availability and stability of vinyl isocyanate (**1a**) and vinyl isothiocyanate (**1b**), whose reactivities as cycloaddition partners are practically unexplored, led us to extend to these compounds our studies on cycloadditions to heterocumulenes.[6]

(1) Supported by a grant (No. 79.02122) from the National Research Council of Italy (CNR, Rome) on the basis of a joint research project between the Department of Organic Chemistry, University of Košice, Czechoslovakia, and the Laboratory of Organic Chemistry, University of Ferrara, Italy.

(2) On temporary leave from University of Košice.

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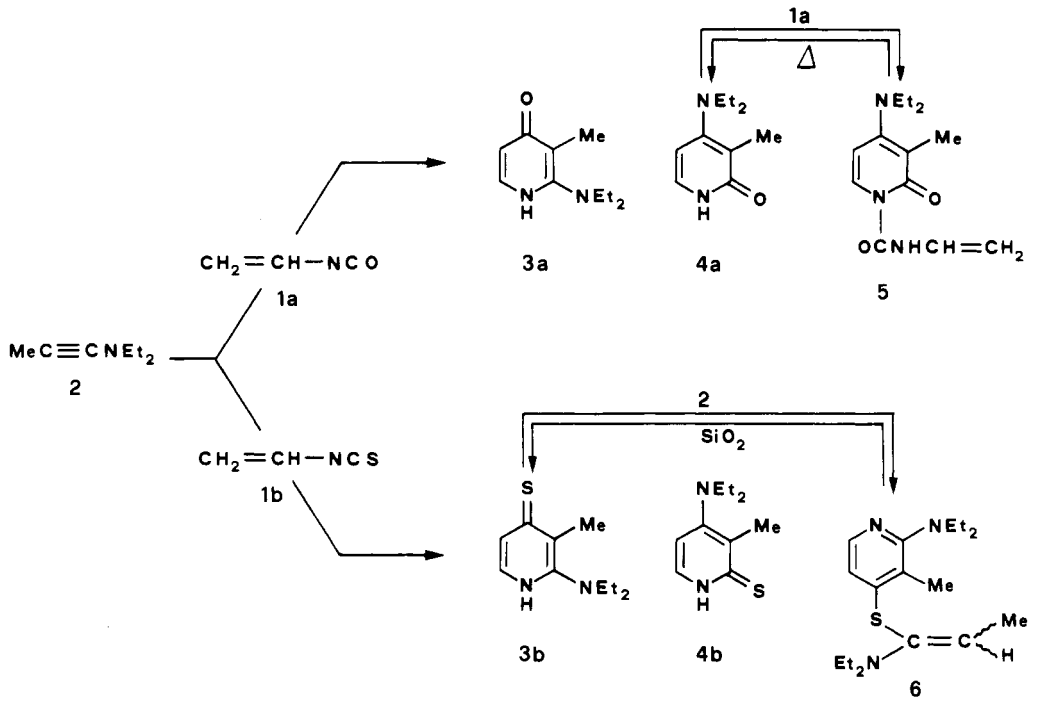
0022-3263/82/1947-3994$01.25/0

Scheme I



We report here the results of their reactions with 1-(diethylamino)propyne (**2**), a typical electron-rich dienophile.

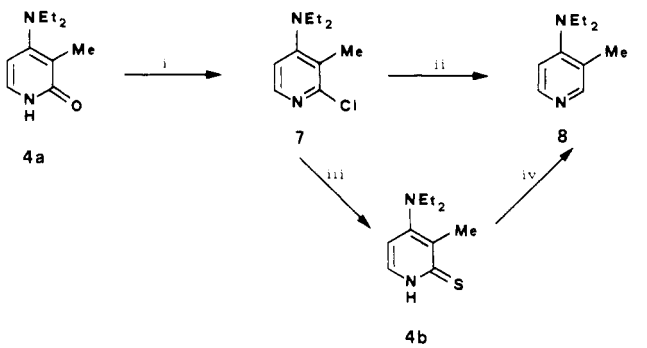
Addition of vinyl isocyanate (**1a**) to 1 molar equiv of ynamine **2** in ethyl ether caused a rapid exothermic reaction with formation of two 1:1 adducts, viz., the γ-pyridinone **3a** (3.7%) and the α-pyridinone **4a** (42%), together with the 2:1 adduct of *N*-carbamoyl-α-pyridone **5** (28.5%) (Scheme I). The formation of **5** from the addition of the α-pyridone **4a** initially formed to unreacted **1a** was indirectly proved by a control experiment showing in fact that the reaction between these compounds occurred rapidly at room temperature whereas fragmentation of **5** took place at higher temperature (ca. 130 °C).

The reaction between equimolar quantities of vinyl isothiocyanate (**1b**) and ynamine **2** in refluxing ethyl ether gave after chromatography over silica gel the two 1:1 adducts γ-pyridinethione **3b** (20%) and α-pyridinethione **4b** (ca. 3%) (Scheme I). In a subsequent experiment, the NMR spectrum of the reaction mixture resulting from 0.5 molar equiv of isothiocyanate **1a** and ynamine **2** indicated the presence of two 2:1 adducts in a 7.5:1 ratio, which were formulated as (*E*)- and (*Z*)-vinyl sulfides **6**, and no detectable amounts of pyridinethiones **3b** and **4b**.

The mixture of sulfides **6**, isolated as an uncrystallizable oil, gave on chromatography over silica gel the γ-pyridinethione **3b** (87%) and traces of the α-isomer **4b**. The formation of (*E*)- and (*Z*)-vinyl sulfides **6** from the addition of γ-pyridinethione **3b** initially formed to the unreacted ynamine **2** was indirectly proved by a control experiment with authentic samples of these compounds. This showed the substantial difference between the 2:1 addition processes which compete with the 1:1 cycloadditions of **2** to **1a** and **1b**. In the former case the α-pyridinone **4a**, the main 1:1 adduct, adds in the pyridinone form across the C=N bond of unreacted isocyanate **1a**, giving the urea derivative **5**, whereas in the latter the γ-pyridinethione **3b**, which is the major isomer in this case, adds in the thiolate form to the triple bond of the ynamine **2** with formation of sulfides **6**.

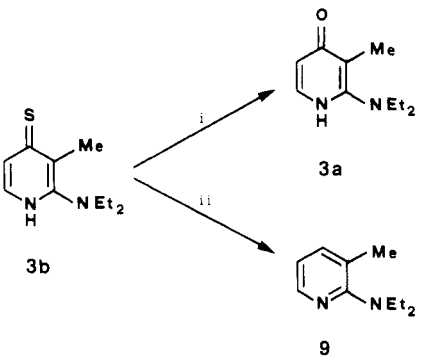
The structures of adducts **3** and **4** were assigned by following their conversion into 4- and 2-(diethylamino)-3-methylpyridines (**8** and **9**, Schemes II and III) and subsequent characterization of these compounds. The ^1H NMR spectrum[7] of **8** showed a broad singlet at δ 8.28 corresponding to the α-proton adjacent to the C_3 methyl group and two doublets at δ 8.27 and 6.77 with a coupling constant of $J_{\alpha,\beta}$ = 5.5 Hz corresponding to the two vicinal

Scheme II[a]



[a] Reagents: i, PCl_5–$POCl_3$; ii, $LiAlH_4$; iii, KSH; IV, Raney Ni.

Scheme III[a]



[a] Reagents; i, Mes·CNO; ii, Raney Ni.

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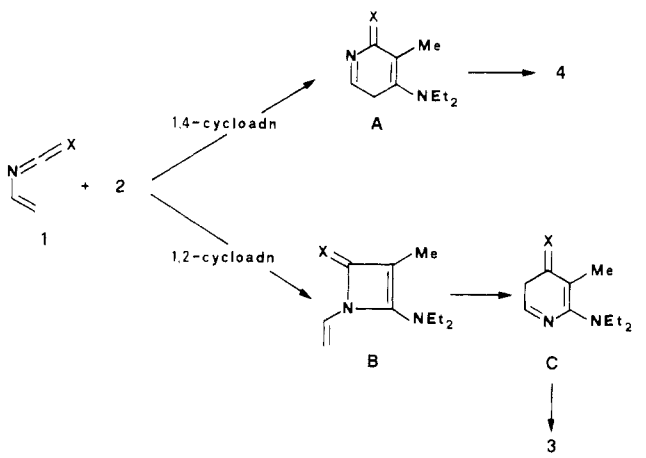
Scheme IV[a]



[a] a, X = O; b, X = S.

α' and β ring protons. Decoupling experiments proved that the slight broadening of the δ 8.28 and 8.27 signals was due to the long-range coupling of these protons with the C_3 methyl. The spectrum of compound **9** exhibited two doublets at δ 8.17 and 7.39, assigned to the α- and γ-protons, respectively, and a doublet for the β-proton at δ 7.78 ($J_{\alpha,\beta}$ = 7.83 Hz, $J_{\beta,\gamma}$ = 7.48 Hz). In this case the small couplings of the methyl group at C_3 with the α-proton ($J_{\alpha,Me}$ = 0.55 Hz) as well as with the γ-proton ($J_{\gamma,Me}$ = 0.67 Hz) were also measured. These features are only compatible with structures bearing the methyl group at C_3 for both pyridines and differing for the position of the diethylamino group, as actually shown in **8** and **9**. This safely excluded the possibility that we were dealing with different regioisomers than those reported in Schemes II and III.

The above results may be accommodated in a single (Scheme IV) where competing 1,4- and 1,2-cycloaddition reactions of the ynamine **2** to the vinylheterocumulene **1** takes place, the former pathway leading to the α-pyridinone and α-pyridinethione **4** and the latter to the γ-isomers **3**. Whereas the initial cycloadduct A which arises from the 1,4-cycloaddition is structurally stable and simply tautomerizes to **4**, the 1,2-cycloadduct B undergoes ring opening and electrocyclization to C which also is in equilibrium with its tautomer **3**. Since the 1,4-cycloadduct α-pyridinone **4a**, free and in the form of its *N*-carbamoyl derivative **5**, was the main product (yield 70%)[8] from the reaction of **2** with isocyanate **1a**, whereas the former 1,2-cycloadduct γ-pyridinethione **3b** was obtained in high yield (87%)[8] from the reaction of isothiocyanate **1b**, it may be deduced that the cycloadditions of ynamine **2** to vinylheterocumulenes **1a** and **1b** occur with reverse peri selectivity. Other α,β-unsaturated isocyanates are known to selectively undergo 1,4-cycloaddition by ynamines[9] and enamines[10] whereas there are no reports on the behavior of isothiocyanates.

In conclusion, the cycloadditions of vinyl isocyanate (**1a**) and vinyl isothiocyanate (**1b**) to 1-(diethylamino)propyne (**2**) illustrate differences in reaction mechanisms encountered in vinylheterocumulenes. Moreover, these reactions appear synthetically useful since simple transformations of their products, such as those described in Schemes II and III, make all α- and γ-pyridinones and pyridinethiones **4** and **3** equally available in large quantities.

Experimental Section

NMR spectra were recorded on a 80-MHz Bruker WP 80 spectrometer in the indicated solvent, and all chemical shifts are reported in parts per million (δ) downfield from Me_4Si as the internal standard. IR spectra were determined on a Perkin-Elmer Model 257 grating spectrometer. Mass spectra were recorded at 70 eV on a Varian Mat 112 high-resolution spectrometer. Analytical TLC was done on E. Merck silica gel 60 sheets whereas column chromatography used E. Merck silica gel 60 (70–230 mesh).

Materials. Commercial diethyl ether (Et_2O, Backer) was dried by being allowed to stand overnight over $CaCl_2$ followed by distillation over Na wire. 1-(Diethylamino)propyne (**2**, Fluka) was distilled prior to use. Vinyl isocyanate (**1a**) was prepared according to the literature procedure,[11] stored in sealed vials at −5 °C, and distilled prior to use: bp 40–42 °C (760 mmHg); ^{1}H NMR ($CDCl_3$) δ 4.8 (d, 1 H, $=CH_2$, J = 8.0 Hz), 5.0 (d, 1 H, $=CH_2$, J = 15 Hz), 6.12 (dd, 1 H, =CH, J = 8.0, 15.0 Hz).

Vinyl isothiocyanate (**1b**) was prepared by a modification of the method reported in a patent.[12] 2-Bromoethyl isothiocyanate[13] (28 g, 0.159 mol) was added dropwise to a 10 g (0.112 mol) of Et_3N containing 0.2 g of hydroquinone, and the solution was heated at 50 °C with stirring for an additional hour. Distillation through a short Vigreux column under slight vacuum gave 5 g (0.059 mol, 59%) of vinyl isothiocyanate (**1b**), bp 38–40 °C (70 mmHg). The residue from the distillation was treated with an abundant amount of water and extracted with chloroform. After evaporation of the solvent, distillation gave 10.6 g (0.06 mol) of unreacted 2-bromoethyl isothiocyanate, bp 103–104 °C (20 mmHg). Vinyl isothiocyanate (**1b**) showed the following: IR (film) 1613 (C=C), 2080, 2180 (NCS) cm^{-1}; ^{1}H NMR ($CDCl_3$) 5.08 (d, 1 H, $=CH_2$, J = 7.9 Hz), 5.3 (d, 1 H, $=CH_2$, J = 14.9 Hz), 6.2 (dd, 1 H, =CH, J = 7.9, 14.9 Hz).

Reaction of Vinyl Isocyanate (1a) with 1-(Diethylamino)propyne (2). A solution of isocyanate **1a** (3.2 g, 46 mmol) in 30 mL of Et_2O was added dropwise with stirring to a solution of ynamine **2** (5 g, 45 mmol) in 3 mL of Et_2O at such a rate as to maintain a gentle reflux of the solvent. After the mixture was allowed to stand overnight at room temperature, the solvent was evaporated under vacuum, and the residue was chromatographed (SiO_2; chloroform/acetone, 10:1, 5:1, 1:1) to give the following compounds in the following order.

***N*-(Ethenylcarbamoyl)-4-(diethylamino)-3-methyl-2-pyridinone (5)**: 3.2 g (12.9 mmol, 28.5%); oil; IR (CCl_4) 3450 (NH), 1735 (NHCO), 1640 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 12.9 (br s, 1 H, NH), 8.19 (d, 1 H, CH ring), 6.95 (m, 1 H, CH vinyl), 6.21 (d, 1 H, CH ring), 4.74 (m, 2 H, CH_2 vinyl), 3.49 (q, 4 H, CH_2), 2.08 (s, 3 H, CH_3), 1.16 (t, 6 H, CH_3). Anal. Calcd for $C_{13}H_{19}N_3O_2$: C, 62.65; H, 7.63; N, 16.87. Found: C, 62.73; H, 7.51; N, 16.68.

***N*,*N*-Diethylpropanamide**: 0.9 g (7 mmol, 15.5%); bp 90–91 °C (20 mmHg) [lit.[14] bp 91.5–92 °C (22 mmHg)]; IR (film) 1645 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.3 (m, 4 H, CH_2), 2.35 (q, 2 H, CH_2), 1.13 (m, 9 H, CH_3).

4-(Diethylamino)-3-methyl-2-pyridinone (4a): 3.4 g (18.9 mmol, 42%); mp 117–119 °C (from CCl_4–*n*-hexane, 1:1); IR (KBr) 3265 (NH), 1625 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 13.2 (br s, 1 H, NH), 7.22 (d, 1 H, =CH), 6.10 (d, 1 H, =CH), 3.13 (q, 4 H, CH_2), 2.07 (s, 3 H, CH_3), 1.08 (t, 6 H, CH_3); mass spectrum, *m/e* (relative intensity) 180 (M^+, 39), 166 (11), 165 (100), 151 (45), 137 (10), 80 (13), 53 (19). Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.66; H, 8.96; N, 15.56. Found: C, 66.87; H, 8.72; N, 15.61.

2-(Diethylamino)-3-methyl-4-pyridinone (3a): 0.3 g (1.7 mmol, 3.7%); mp 91–92 °C (from $CHCl_3$); IR (KBr) 3215 (NH), 1620 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.48 (d, 1 H, =CH), 7.28 (br

(8) More precise product distributions were determined from the ^{1}H NMR spectra of the crude reaction mixtures. From the reaction of isocyanate **1a** the ratio of **4a**/**3a** was 91:9, whereas from the reaction of **1b** the ratio of **4b**/**3b** was 10:90. Experimental details will be published in due course together with a study of the solvent effect on these cycloadditions.

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s, 1 H, NH), 6.29 (d, 1 H, =CH), 3.16 (q, 4 H, CH_2), 2.06 (s, 3 H, CH_3), 1.04 (t, 6 H, CH_3); mass spectrum, *m/e* (relative intensity) 180 (M^+, 22), 165 (30), 152 (11), 151 (100), 137 (31), 109 (11), 108 (13), 80 (11), 72 (36), 53 (16). Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.66; H, 8.96; N, 15.56. Found: C, 66.75; H, 8.76; N, 15.45.

Thermolysis of *N*-Carbamoyl-2-pyridinone 5. A sample of **5** (1.5 g, 6.4 mmol) was heated (oil bath at 130 °C) in vacuo (15 mmHg) for 2 h. While vinyl isocyanate (**1a**) distilled, the residue was crystallized (1.05 g, 5.83 mmol, 91%) and characterized as the α-pyridinone **4a**.

Preparation of *N*-Carbamoyl-2-pyridinone 5 from 4a and 1a. Equivalent quantities (ca. 0.5 mmol) of isocyanate **1a** and α-pyridinone **4a** were mixed in 0.8 mL of $CDCl_3$ in a NMR tube at room temperature. The spectrum of the solution which was recorded within few minutes was practically identical with that of adduct **5**.

Reaction of Vinyl Isothiocyanate (1b) with 1-(Diethylamino)propyne (2). Method A. A solution of isothiocyanate **1b** (3.06 g, 36 mmol) in 10 mL of Et_2O was added dropwise with stirring to a solution of ynamine **2** (4 g, 36 mmol) in 4 mL of Et_2O at such a rate that the solvent was maintained under gentle reflux. After the mixture was refluxed for an additional hour, the solvent was removed under reduced pressure to give 6.5 g of a deep red oil which was chromatographed (SiO_2; petroleum ether/acetone, 7:1, 5:1, 3:1, 1:1). The following fractions were obtained.

A mixture (2 g) of various products (TLC) from which by subsequent chromatography (SiO_2; petroleum ether/acetone, 7:1) was isolated 30 mg (0.14 mmol) of a pure compound [mp 106–107 °C (from $CHCl_3$)] whose spectroscopic data were consistent with those of the thioamide CH_2=CHNHC(S)CHMeC(O)NEt_2: IR (KBr) 3205 (NH), 1620 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 11.2 (br s, 1 H, NH), 7.55 (m, 1 H, =CH), 4.94 (dd, 2 H, $=CH_2$), 4.22 (q, 1 H, CH, J = 7.02 Hz), 3.38 (m, 4 H, CH_2), 1.56 (d, 3 H, CH_3, J = 7.02 Hz), 1.19 (m, 6 H, CH_3); mass spectrum, *m/e* 214 (M^+). Anal. Calcd for $C_{10}H_{18}N_2OS$: C, 55.99; H, 8.46; N, 13.06. Found: C, 56.14; H, 8.52; N, 13.12.

2-(Diethylamino)-3-methyl-4-pyridinethione (3b): 1.4 g (7.1 mmol, 20%); mp 95–96 °C (from Et_2O); IR ($CHCl_3$) 3420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.61 (d, 1 H, =CH), 6.95 (d, 1 H, =CH), 3.22 (q, 4 H, CH_2), 2.31 (s, 3 H, CH_3), 1.07 (t, 6 H, CH_3); mass spectrum, *m/e* (relative intensity) 196 (M^+, 33), 181 (35), 168 (11), 167 (100), 153 (29), 125 (10), 124 (21), 72 (46). Anal. Calcd for $C_{10}H_{16}N_2S$: C, 61.17; H, 8.22; N, 14.27. Found: C, 61.23; H, 8.15; N, 14.42.

4-(Diethylamino)-3-methyl-2-pyridinethione (4b): 0.25 g (1.3 mmol, 3.5%); mp 176–178 °C (from $CHCl_3$–CCl_4); IR ($CHCl_3$) 3393 cm^{-1}; ^1H NMR ($CDCl_3$) δ 13.6 (br s, 1 H, NH), 7.41 (d, 1 H, =CH), 6.48 (d, 1 H, =CH), 3.23 (q, 4 H, CH_2), 2.40 (s, 3 H, CH_3), 1.11 (t, 6 H, CH_3); mass spectrum, *m/e* relative intensity) 196 (M^+, 43), 181 (59), 168 (13), 167 (100), 151 (15), 125 (12), 72 (10). Anal. Calcd for $C_{10}H_{16}N_2S$: C, 61.17; H, 8.22; N, 14.27. Found: C, 61.12; H, 8.18; N, 14.35.

Method B. A solution of isothiocyanate **1b** (0.48 g, 5.6 mmol) in 9 mL of Et_2O was added dropwise in about 1 h to a solution of the ynamine **2** (1.39 g, 12.5 mmol) in 7 mL of the same solvent. After the mixture was stirred for an additional 1 h at room temperature, the solvent was removed under reduced pressure to give a deep red oil (1.7 g) which from the ^1H NMR spectrum appeared to be a mixture of (*E*)- and (*Z*)-vinyl sulfides **6** in a 7.5:1 ratio but whose stereochemistry was not assigned: ^1H NMR ($CDCl_3$) isomer A δ 8.02 (d, 1 H, =CH), 6.95 (d, 1 H, =CH), 5.62 (q, 1 H, =CH), 3.16 (q, 4 H, CH_2), 2.82 (q, 4 H, CH_2), 2.30 (s, 3 H, CH_3), 1.82 (d, 3 H, CH_3), 1.05 (t, 6 H, CH_3), 1.00 (t, 6 H, CH_3); isomer B δ 7.99 (d, 1 H, =CH); 6.76 (d, 1 H, =CH), 5.21 (q, 1 H, =CH), 3.16 (q, 4 H, CH_2), 3.06 (q, 4 H, CH_2), 2.29 (s, 3 H, CH_3), 1.82 (d, 3 H, CH_3), 1.05 (t, 6 H, CH_3), 1.00 (t, 6 H, CH_3).

The same reaction was carried out in an NMR tube. To a solution of about 30 mg (0.15 mmol) of ynamine **2** was added in one portion a 10% equiv. of isothiocyanate **1b** and the spectrum of the mixture was recorded. Subsequent amounts of **1b** were added after the disappearance of the vinyl signal in the reaction mixture (ca. 5–10 min). The overall addition of 0.5 equiv of **1b** produced the total disappearance of ynamine **2** (from the Me signal at 1.83 ppm) while the observed resonances were identical with those listed above for the mixture of *E* and *Z* sulfides **6**. Signals corresponding to pyridinethiones **3b** and **4b** were not observed.

A mixture of (*E*)- and (*Z*)-vinyl sulfides **6** in a 7.5:1 ratio was also obtained on treating in a NMR tube the 4-pyridinethione **3b** with 1 equiv of ynamine **2**.

Formation of 4-Pyridinethione 3b from Sulfides 6. A sample of vinyl sulfides **6** (0.6 g, 1.95 mmol) was chromatographed (SiO_2, petroleum ether/acetone, 3:1) to give 220 mg (1.7 mmol, 87%) of 4-pyridinethione **3b**.

4-(Diethylamino)-2-chloro-3-methylpyridine (7). A solution of 2-pyridinone **4a** (1 g, 5.6 mmol) in 3 mL of $POCl_3$ and 0.5 g of PCl_5 was refluxed for 2 h. The reaction mixture was poured into ice–water, brought to pH 13 with 15% aqueous NaOH, and extracted with Et_2O. Evaporation of the solvent gave 1 g (5.1 mmol, 91%) of 2-chloropyridine **7**: bp 114–115 °C (0.4 mmHg); ^1H NMR ($CDCl_3$) δ 7.98 (d, 1 H, =CH), 6.70 (d, 1 H, =CH), 3.08 (q, 4 H, CH_2), 2.25 (s, 3 H, CH_3), 1.02 (t, 6 H, CH_3); mass spectrum, *m/e* (relative intensity) 198 (M^+, 20), 185 (34), 184 (12), 183 (100), 155 (21).

4-(Diethylamino)-3-methyl-2-pyridinethione (4b) from 7. A solution of KOH (1.2 g, 21 mmol) in 10 mL of MeOH was saturated with H_2S; the solvent was removed under reduced pressure, and the residue was dissolved in 3 mL of ethylene glycol. To this solution was added the 2-chloropyridine **7** (1.5 g, 7.6 mmol), and the mixture was heated at 170–180 °C for 24 h. The mixture was brought to pH 7.8–8 by 10% aqueous HCl, the reaction was quenched with 20 mL of water, and the precipitate was filtered (1.1 g). This was crystallized from EtOH to give 0.9 g (4.6 mmol, 60%) of 2-pyridinethione **4b** (mp 175–177 °C), identical with the product obtained from the reaction of vinyl isothiocyanate (**1a**) with the ynamine **2**.

4-(Diethylamino)-3-methylpyridine (8). (A) From 2-Chloropyridine 7. To a suspension of $LiAlH_4$ (0.5 g, 13 mmol) in 6 mL of Et_2O was added dropwise a solution of **7** (0.4 g, 2 mmol) in 4 mL of Et_2O. After being refluxed for 3 h, the mixture was allowed to stand overnight at room temperature. The excess of $LiAlH_4$ was decomposed with 15% aqueous NaOH and the organic layer separated. This was washed with water and dried over KOH, and the solvent was evaporated under vacuum, leaving an oil which was distilled to give 0.2 g (1.2 mmol, 60%) of **8**: bp 76–77 °C (0.1 mmHg); ^1H NMR ($CDCl_3$)[7a] δ 8.28 (s, 1 H, =CH), 8.27 (d, 1 H, =CH), 6.77 (d, 1 H, =CH), 3.15 (q, 4 H, CH_2), 2.23 (s, 3 H, CH_3), 1.07 (t, 6 H, CH_3); mass spectrum, *m/e* (relative intensity) 164 (M^+, 34), 150 (13), 149 (100), 121 (25), 119 (10), 75 (17).

(B) From 2-Pyridinethione 4b. A mixture of **4b** (0.2 g, 1 mmol) and 1 g of Raney Ni (W_2) in 10 mL of EtOH was heated at reflux of the solvent for 2 h. After filtration of the Raney Ni, the solvent was removed under reduced pressure, leaving 40 mg (0.24 mmol, 24%) of the pyridine **8**, showing spectroscopic characteristics identical with those of the product obtained by method A.

2-(Diethylamino)-3-methyl-4-pyridinone (3a) from 4-Pyridinethione 3b. To a solution of **3b** (0.3 g, 1.5 mmol) in 10 mL of CH_3CN was added dropwise at room temperature a solution of 2,4,6-trimethylbenzonitrile oxide[15] (0.235 g, 1.46 mmol) in 5 mL of the same solvent. The mixture was stirred for 4 h and then refluxed for about 30 min. The solvent was removed under reduced pressure, and the residue was chromatographed (SiO_2; petroleum ether/acetone, 3:1) to give 110 mg (0.62 mmol, 43%) of mesityl isothiocyanate [mp 60–62 °C; IR (KBr) 2085 cm^{-1} (lit.[16] mp 61–62 °C)] and 200 mg (1.1 mmol, 75%) of 4-pyridinone **3a** [mp 91–92 °C (from $CHCl_3$)] which showed spectroscopic characteristics identical with those of the product obtained from the reaction of **1a** with **2**.

2-(Diethylamino)-3-methylpyridine (9). A mixture of 4-pyridinethione **3b** (0.25 g, 1.3 mmol) and 2 g of Raney Ni (W_2) in 10 mL of EtOH was heated at reflux of the solvent for 2 h. After filtration, the solvent was removed under reduced pressure, leaving 80 mg (0.49 mmol, 38%) of the pyridine **9**: oil; ^1H NMR ($CDCl_3$)[7b] δ 8.17 (d, 1 H, $=CH_\alpha$, $J_{H_\alpha-H_\beta}$ = 4.83 Hz), 7.39 (d, 1 H, $=CH_\gamma$, $J_{H_\gamma-H_\beta}$ = 7.48 Hz), 6.78 (dd, 1 H, $=CH_\beta$, $J_{H_\beta-H_\alpha}$ = 4.83 Hz, $J_{H_\beta-H_\gamma}$ = 7.48 Hz), 3.20 (q, 4 H, CH_2), 2.25 (s, 3 H, CH_3). The long-range couplings between the methyl at C_3 and protons of the ring were $J_{H_\alpha-Me}$ = 0.55 Hz and $J_{H_\gamma-Me}$ = 0.67 Hz.

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Registry No. **1a**, 3555-94-0; **1b**, 1520-22-5; **2**, 4231-35-0; **3a**, 82639-27-8; **3b**, 82639-29-0; **4a**, 82639-26-7; **4b**, 82639-30-3; **5**, 82639-25-6; (*E*)-**6**, 82639-31-4; (*Z*)-**6**, 82639-32-5; **7**, 82639-33-6; **8**, 39273-03-5; **9**, 35774-60-8; CH_2=CHNHC(S)$CHCH_3CONEt_2$, 82639-28-9; 2-bromoethyl isothiocyanate, 1483-41-6; *N*,*N*-diethylpropanamide, 1114-51-8.

Substituent Dependence of the Selectivity in the Cycloadditions of Vinylketenimines with Thiobenzophenone. 1,2- and 1,4-Addition Pathways

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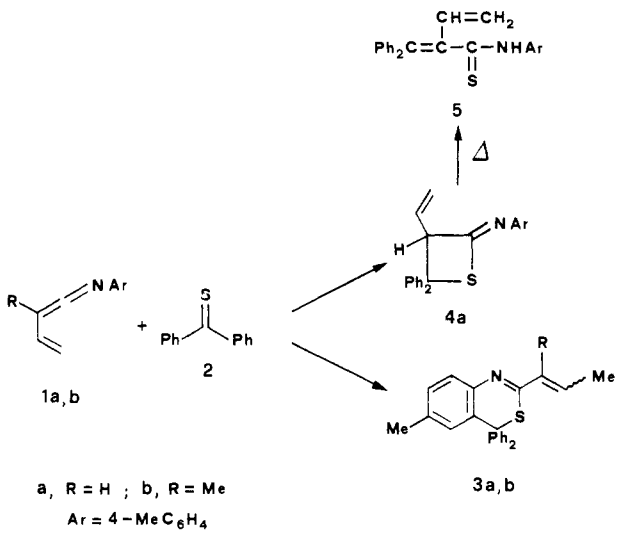
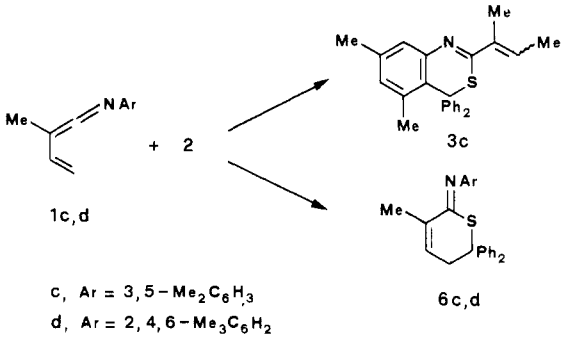
We recently reported[1] two modes of cycloaddition between thiobenzophenones and *C*-methyl and *C*-phenylketenimines, namely, 1,2-cycloaddition of the C=S bond of the thione across the cumulative C=C bond to give 2-iminothietanes and 1,4-cycloaddition across the C=N and one C=C bond of the *N*-aryl group of the cumulene to give 4*H*-3,1-benzothiazines. Another mode of cycloaddition which involves an unsaturated functionality flanking the carbon of the cumulene has been observed[2] with *C*-vinylketenimines and we report here a full account on the selectivity of their reactions with thiobenzophenone. We are investigating[3] the reactivity of other vinylheterocumulenes as a mechanistic probe of cumulene cycloadditions as well as a source of 1,3-diene equivalents for hetero-Diels–Alder reactions.

Four substituted *C*-vinylketenimines **1** were employed for the purposes of the present work, all compounds being stable and readily accessible by conventional preparative methods. Treatment of the C-monosubstituted derivative *N*-*p*-tolylvinylketenimine (**1a**), generated in situ from the corresponding amide by the triphenylphosphine dibromide–triethylamine method, with thiobenzophenone (**2**) at room temperature (Scheme I) gave a mixture (TLC) of the 4*H*-3,1-benzothiazine **3a** and 2-iminothietane **4a**. The presence of the latter adduct in the crude reaction mixture was inferred[1] from a singlet in the ^{1}H NMR spectrum at 5.5 ppm and a strong IR band at 1675 cm^{-1}. When the mixture was heated at 45 °C for 2 days, these signals disappeared and the α,β-unsaturated thioamide **5** (53%) together with the 4*H*-3,1-benzothiazine **3a** (21%) were isolated and identified through their spectroscopic characteristics. If it is accepted that the product distribution is under kinetic control as shown for other ketenimine–thioketone cycloadditions[1] and that the 2-iminothietane **4a** rearranges on heating exclusively to the thioamide **5**, the larger amount of the latter with respect to the benzothiazine **3a** (2.5:1 ratio) indicates the preference by the C=S bond of thioketone **2** for 1,2-cycloaddition across the C=C bond of the cumulative system of **1a** over the *N*-aryl 1,4-cycloaddition.

Scheme I



Scheme II



On the other hand, treatment the C-disubstituted derivative vinylmethylketenimine **1b** with **2** gave as a single product the 1,4-cycloadduct 4*H*-3,1-benzothiazine **3b** in ca. 80% yield (Scheme I). These results parallel our previous finding on the selectivity of *C*-methyl- and *C*-phenylketenimine–thioketone cycloadditions[1] where monosubstituted derivatives reacted according to the 1,2-cycloaddition mode whereas disubstituted compounds preferred the *N*-aryl 1,4-cycloaddition process. As already suggested, this variation of selectivity may be related to the inhibition by steric factors of the 1,2-cycloaddition which on the other hand should be favored by electronic effects.

The *N*-aryl 1,4-cycloaddition of thioketone **2** to ketenimines **1a** and **1b** indicates identical site selectivity as in the reaction of **1b** with (diethylamino)phenylacetylene,[4] a typical electron-rich dienophile, thus suggesting that the C=S bond of the thione **2** behaves as the electron-donor partner toward the heterodiene system C=N—C=C of **1a** and **1b**. However, this selectivity was substantially reduced by *m*-methyl groups in the *N*-aryl ring. Thus ketenimine **1c** with thioketone **2** (Scheme II) gave both *N*-aryl 1,4-cycloaddition to the corresponding 4*H*-3,1-benzothiazine

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(2) A preliminary account of this work has been presented at the 6th Colloque de Chimie Heterocyclique, Mulhouse, France, 1979, and has been reported in the form of a review paper: Dondoni, A. *Heterocycles* **1980**, *14*, 1547.

(3) Dondoni, A.; Kniezo, L.; Medici, A. *J. Org. Chem.*, previous paper in this issue.

(4) The indicated ynamine gives *N*-aryl 1,4-cycloaddition to **1b**, whereas the electron-poor dienophile dimethyl acetylenedicarboxylate gives *C*-vinyl 1,4-cycloaddition: Ghosez, L.; Sonveaux, E. *J. Am. Chem. Soc.* **1973**, *95*, 5417.

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