MHz) δ 2.30 (s, 3 H), 5.20 (d, 1 H, J = 12.0 Hz), 5.50 (d, 1 H, J = 16.0 Hz), 6.80–8.60 (m, 17 H). This material was immediately used in the next step.

To a solution containing 1.0 g of the above oil in 10 mL of dry tetrahydrofuran was added 150 mg of sodium hydride. The mixture was allowed to stir at 25 °C for 20 min, and then 100 mL of pentane was added. The resulting precipitate was filtered and dried under vacuum to give 680 mg of a solid. This material was heated in 20 mL of dry benzene at 80 °C for 4 h. The precipitate that formed was filtered, and the resulting oil was subjected to thick-layer chromatography using a 1:1 ether–pentane mixture as the solvent. The major component isolated from the thick-layer plate contained 195 mg of 3-(*o*-vinylphenyl)-4-phenylpyrazole (**40**) as a clear oil: IR (neat) 3.28, 6.90, 8.55, 10.31, 12.19, 13.16, 14.70 μm; NMR ($CDCl_3$, 100 MHz) δ 5.05 (d, 1 H, J = 12.0 Hz), 5.60 (d, 1 H, J = 16.0 Hz), 6.65 (dd, 1 H, J = 16.0, 12.0 Hz), 6.90–7.80 (m, 11 H).

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.68; H, 5.81; N, 11.29.

Thermolysis of the Sodium Salt of 1-Phenyl-3-(*o*-vinylphenyl)-2-propen-1-one Tosylhydrazone (41). To a solution containing 5 mL of 3.0 N aqueous sodium hydroxide solution and 3 mL of 95% ethanol was added 1.2 g of acetophenone. The mixture was cooled to 0 °C, and 1.32 g of *o*-vinylbenzaldehyde[68] in 2 mL of ethanol was added dropwise. After being stirred for 48 h at 25 °C, the mixture was poured into 20 mL of water and extracted with ether. The ether layer was dried over magnesium sulfate, and the solvent was removed under reduced pressure. The resulting oil solidified on standing to give 2.15 g (88%) of 1-phenyl-3-(*o*-vinylphenyl)-2-propen-1-one: mp 27–28 °C; IR (KBr) 6.02, 6.25, 6.80, 6.94, 7.25, 7.58, 8.26, 9.90, 10.31, 10.99, 13.51, 14.71 μm; NMR ($CDCl_3$, 100 MHz) δ 5.35 (d, 1 H, J = 12.0 Hz), 5.56 (d, 1 H, J = 16.0 Hz), 6.85–8.15 (m, 12 H); UV (methanol) 252 nm (ε 15900), 310 (15000).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.12; H. 6.06.

To a solution containing 1.17 g of the above ketone in 5 mL of ethanol was added 1.03 g of tosylhydrazine. The mixture was heated at reflux for 8 h and was then concentrated under reduced pressure. The resulting oil was crystallized from ethanol to give 1.15 g (56%) of the tosylhydrazone derivative **41**: mp 91–92 °C; IR (KBr) 2.92, 6.29, 7.25, 8.62, 12.50, 13.16, 14.38 μm; NMR ($CDCl_3$, 100 MHz) δ 2.36 (s, 3 H), 5.20 (d, 1 H, J = 10.0 Hz), 5.45 (d, 1 H, J = 16.0 Hz), 6.50–7.60 (m, 17 H), 7.80 (d, 2 H, J = 8.0 Hz), 8.10 (br s, 1 H).

To a solution containing 804 mg of the above compound in 10 mL of tetrahydrofuran was added 144 mg of sodium hydride under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min, and then 70 mL of pentane was added. The resulting precipitate was filtered and dried under vacuum to give 690 mg of a white solid. This material was heated in 30 mL of dry benzene for 4 h. The remaining solid was filtered, and the solvent was removed under reduced pressure. The resulting oil was crystallized from hexane to give 235 mg (81%) of 3-(*o*-vinylphenyl)-5-phenylpyrazole (**42**) as a white crystalline solid: mp 88–89 °C; IR (KBr) 3.11, 6.17, 6.25, 6.33, 6.92, 7.25, 10.42, 11.24, 12.66, 13.42, 14.71 μm; NMR ($CDCl_3$, 100 MHz) δ 5.08 (d, 1 H, J = 12.0 Hz), 5.50 (d, 1 H, J = 16.0 Hz), 6.50 (s, 1 H), 6.70–7.70 (m, 11 H); UV (methanol) 353 nm (ε 33000), 238 (32100); mass spectrum, *m/e* 246 (M^+), 215, 169, 143, 130, 118, 77.

Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.79; H, 5.77; N, 11.35.

Acknowledgment. We gratefully acknowledge the National Cancer Institute for generous support of this research.

Registry No. 1, 71312-47-5; 1·Na, 74346-37-5; 2, 2387-34-0; 3, 74346-38-6; 5, 71312-53-3; 7, 62708-42-3; 8, 73774-60-4; 8·Na, 73774-54-6; 10, 73774-58-0; 11, 74346-39-7; 12, 73774-57-9; 13, 15677-15-3; 14, 95-13-6; 15, 73774-56-8; 16, 73774-59-1; 17, 74346-40-0; 17·Na, 74346-41-1; 18, 74346-42-2; 19, 74346-43-3; 20, 74365-62-1; 21, 74365-63-2; 22, 74346-44-4; 23, 63949-51-9; 24, 30021-35-3; 27, 74346-45-5; 28, 74346-46-6; 28·Na, 74346-47-7; 30, 74346-48-8; 31, 74346-49-9; 32, 74346-50-2; 33, 25033-22-1; 34, 74346-51-3; 39, 74346-52-4; 39·Na, 74346-53-5; 40, 74346-54-6; 41, 74346-55-7; 41·Na, 74346-56-8; 42, 74346-57-9; 5-hexenal, 764-59-0; tosylhydrazine, 1576-35-8; cyclopentene, 142-29-0; diazomethane, 334-88-3; 1-amino-*trans*-2,3-diphenylaziridine, 28161-60-6; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8; *o*-(*trans*-2-butenyl)benzaldehyde, 74346-58-0; diazoethane, 1117-96-0; *exo*-1,1a,6,6a-tetrahydrocycloprop[*a*]indene-1-carboxaldehyde, 74346-59-1; *o*-(*cis*-2-butenyl)benzaldehyde, 74346-60-4; *o*-(3-butenyl)benzaldehyde, 70576-29-3; 1,2-dihydronaphthalene, 447-53-0; *o*-vinylbenzaldehyde, 28272-96-0; phenylacetaldehyde, 122-78-1; 2-phenyl-3-(*o*-vinylphenyl)propen-1-al, 74346-61-5; acetophenone, 98-86-2; 1-phenyl-3-(*o*-vinylphenyl)-2-propen-1-one, 74346-62-6.

Selectivity in Ketenimine–Thioketone Cycloadditions. 1. 1,4- and 1,2-Addition Pathways and the Synthesis of 4*H*-3,1-Benzothiazines, 2-Iminothietanes, and Thioacrylamides[1]

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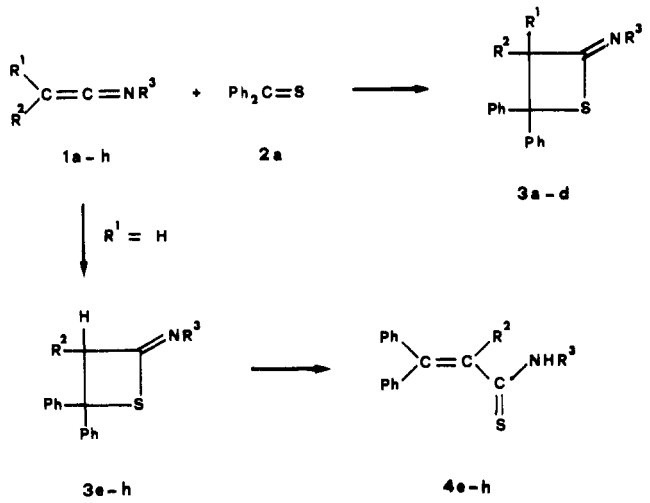
Received January 21, 1980

The cycloadditions of thiobenzophenones to ketenimines take place at different sites of the cumulene depending on the extent of substitution and the nature of the substituents. C,C-Disubstituted ketenimines whose nitrogen bears an alkyl or an ortho,ortho'-disubstituted aryl undergo 1,2-cycloaddition by the C=S bond of the thione across the cumulene C=C bond to give four-membered 1:1 adducts, viz., 2-iminothietanes. An identical cycloaddition takes place from C-monosubstituted ketenimines irrespective of the nature of the N substituent. 2-Iminothietanes formed in these cases are unstable and rearrange to thioacrylamides. On the other hand, C,C-disubstituted ketenimines whose nitrogen is flanked by a phenyl or a meta- or para-substituted phenyl undergo 1,4-cycloaddition by the C=S bond of the thione across the formal heterodiene system formed by the C=N bond of the cumulene and one of the C=C bonds of the *N*-aryl group to yield as final products six-membered ring adducts, viz., 4*H*-3,1-benzothiazines. Evidence for the formation of an intermediate is provided by NMR and IR spectroscopy and, indirectly, by the isolation of a diadduct from 2 mol of thione and 1 mol of ketenimine. *N*-Phenylmethylketenimine, however, reacts with thiobenzophenone according to both the 1,2- and 1,4-cycloaddition modes to give the corresponding 2-iminothietane and 4*H*-3,1-benzothiazine in almost equal amounts. The product distribution, as monitored by following the reaction at intervals by NMR spectroscopy, is under kinetic control.

There is ample documentation on the participation of ketenimines[3] as 2-π-electron components in cycloaddition reactions with 2-π- and 4-π-electron (1,3-dipole) systems to give four- and five-membered 1:1 adducts, respectively.

0022-3263/80/1945-3766$01.00/0

Scheme I[a]



[a] a, $R^1 = R^2 = Ph$, $R^3 = CH_3$; b, $R^1 = R^2 = Ph$, $R^3 = 2,4,6\text{-}(CH_3)_3Ph$; c, $R^1 = R^2 = CH_3$, $R^3 = 2,6\text{-}(CH_3)_2Ph$; d, $R^1 = R^2 = CH_3$, $R^3 = 2,4,6\text{-}(CH_3)_3Ph$; e, $R^1 = H$, $R^2 = Ph$, $R^3 = c\text{-}C_6H_{11}$; f, $R^1 = H$, $R^2 = Ph$, $R^3 = 2,4,6\text{-}(CH_3)_3Ph$; g, $R^1 = H$, $R^2 = Ph$, $R^3 = CH_3$; h, $R^1 = H$, $R^2 = Ph$, $R^3 = Ph$.

Significant examples of [2 + 2] cycloadditions are the reactions with nitrosobenzenes,[3a] ketones,[4a] isocyanates,[4b] and azobenzenes,[4c] whereas examples of [4 + 2] cycloadditions with 1,3-dipolar systems are the reactions with nitrones[5] and trimethylsilyl azide.[3a] Addition across the C=C bond of the cumulative system is the rule in these reactions, whereas the cycloadditions across the C=N bond are limited to a few cases, such as the reactions with *N*-(diethylamino)methylacetylene[6a] and hydrazoic acid.[6b] These cycloadditions may be interpreted on the basis of the frontier molecular orbital theory[7] as the result of the dominant LUMO (cumulene)–HOMO (cumulenophile) interaction in the early stages of the reaction followed by an electron transfer from the HOMO (cumulene) to the LUMO (cumulenophile) which determines the ring closure across the C=C bond of the cumulene in a concerted or nearly concerted process. The presence of electron-withdrawing groups in the cumulene, for their ability to stabilize 1,4-dipolar intermediates, may favor the stepwise mechanism which in some cases results in reactions across the C=N bond of the cumulene.

We wish to report here the results from our studies on the reactions between ketenimines and thioketones and show that, in addition to the usual patterns described above, these heterocumulenes undergo a less common cycloaddition mode which involves the cumulene C=N bond and the conjugated C=C bond of the *N*-aryl ring. This paper deals with the general scope and outcome of the reactions from the synthetic point of view, whereas the interpretation of their site selectivity and mechanism will be examined in the following paper. A partial report of this research has already been presented.[8]

Table I. Relevant Spectral Data[a] of 2-Iminothietanes 3e-h

	^1H NMR, ppm	IR, cm^{-1} [b]
3e	0.8-2.4 (b, 10 H), 2.78-3.25 (br, 1 H), 5.70-5.85 (br, 1 H), 6.6-7.7 (15 H)	1700-1680
3f[c]	2.12 (s, 6 H), 2.2 (s, 3 H), 6.13 (1 H)	1712-1680
3g	3.16 (d, 3 H, J = 2 Hz), 6.04 (q, 1 H)	1700-1670
3h	6.15 (s, 1 H)	1685-1665

[a] In CCl_4. [b] C=N functional group. [c] Mass spectrum, m/e 433 (M^+), 256, 235, 177

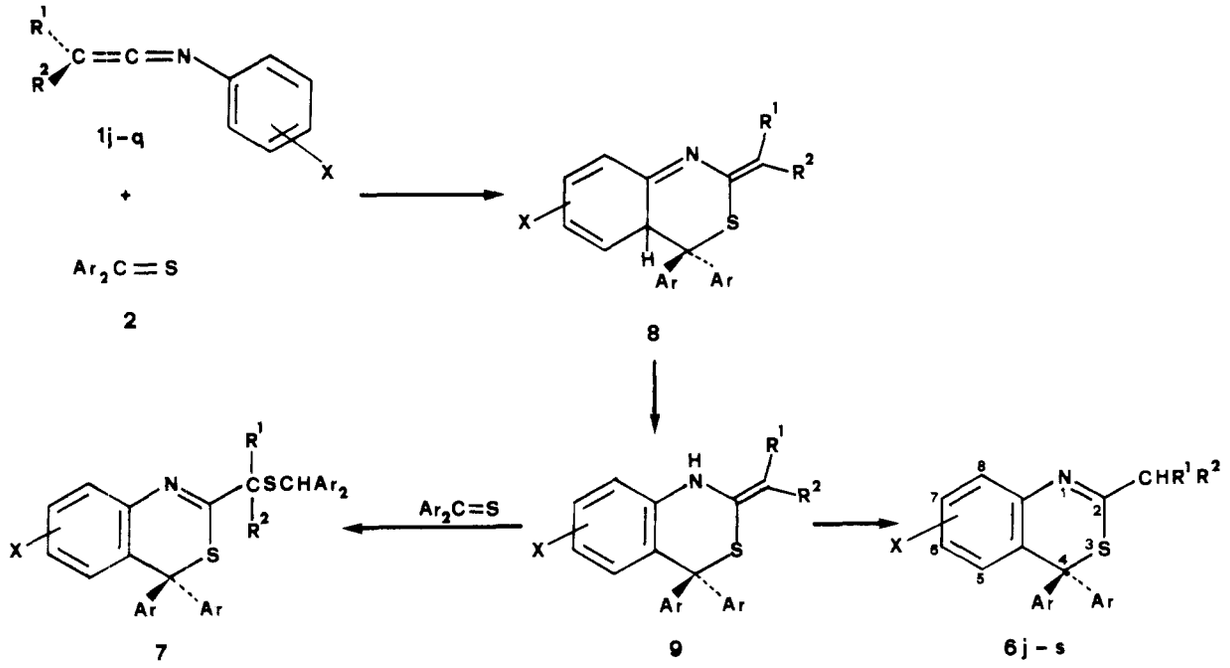
Results and Discussion

1,2-Cycloaddition. A. Formation of 2-Iminothietanes 3. The reactions of *C,C*-diphenyl- and *C,C*-dimethylketenimines **1a–d** with 1.1 molar equiv of thiobenzophenone (**2a**) in deoxygenated methylene dichloride gave 1:1 cycloadducts which were shown to be the 2-iminothietane derivatives **3a–d** (Scheme I). On a preparative scale the yields were modest (30–50%), but in small scale reactions followed by NMR spectroscopy they were almost quantitative. The structure of 2-iminothietanes **3a–d** stemmed from their IR, NMR, and mass spectra as well as an X-ray analysis. Relevant spectral features were a strong IR band at ca. 1680 cm^{-1} and two ^{13}C NMR peaks for the nonequivalent aliphatic quaternary carbons and a low-field signal (170–190 ppm) for the imino carbon; the mass spectra showed major fragments with m/e values corresponding to tetraphenylethylene (for **3a** and **3b**) or to diphenylisobutylene (for **3c** and **3d**). The structure of **3c** was determined by an X-ray diffraction study.[9] This showed that the puckering of the four-membered ring avoids the eclipsing of the groups at C_3 and C_4 and relieves the bond and angle strains which would be present in a strictly planar arrangement. Thus, 2-iminothietanes **3a–d** were indefinitely stable at room temperature and decomposed at their melting points into various fragments, including the starting reactants.

B. Formation of Thioacrylamides 4. Under the same conditions, *C*-phenylketenimines **1e–h** underwent an identical stereoselective 1,2-cycloaddition by thiobenzophenone (**2a**) to form 3-monosubstituted 2-iminothietanes **3e–h** which rearranged into thioacrylamides **4e–h** (Scheme I). In fact, although cycloadducts **3e–h** were stable compounds as long as they remained in the sealed reaction vials at room temperature, they were unstable at higher temperatures and during the workup operations of the reaction mixtures, thus preventing their isolation in a pure form. The spectroscopic characteristics of 2-iminothietanes **3e–h** (Table I) were, therefore, obtained from the observation of the reaction solutions. The main features were a strong IR band at ca. 1680 cm^{-1} (C=N) and a singlet in the ^1H NMR spectrum at ca. 6 ppm which was assigned to the hydrogen of C_3 of the thietane ring. A convincing proof that this low-field singlet corresponded to an aliphatic rather than an olephinic hydrogen was provided by the

(1) Presented in part at the 2nd International Symposium on Acetylenes, Allenes, and Cumulenes, Nottingham, England, Sept 5, 1977.
(2) (a) University of Ferrara. (b) Laboratory of the Consiglio Nazionale delle Ricerche.
(3) Reviews on ketenimine cycloadditions: (a) G. R. Krow, *Angew. Chem., Int. Ed. Engl.*, **10**, 435 (1971); (b) N. P. Gambaryan, *Russ. Chem. Rev. (Engl. Transl.)*, **45**, 630 (1976); (c) L. Ghosez and M. J. O'Donnell in "Pericyclic Reactions", Vol. II, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, Chapter 2.
(4) (a) L. A. Singer and P. D. Bartlett, *Tetrahedron Lett.*, 1887 (1964); A. Weidler-Kubanek and M. Litt, *J. Org. Chem.*, **33**, 1844 (1968); (b) Naser-ud-Din, J. Riegl, and L. Skattebøl, *J. Chem. Soc., Chem. Commun.*, 271 (1973); (c) M. W. Barker and M. E. Coker, *J. Heterocycl. Chem.*, **4**, 155 (1967).
(5) M. W. Barker and J. H. Gardner, *J. Heterocycl. Chem.*, **5**, 881 (1968).
(6) (a) L. Ghosez and C. de Perez, *Angew. Chem., Int. Ed. Engl.*, **10**, 184 (1971); (b) G. L'abbé, J.-P. Dekerk, A. Verbruggen, and S. Toppet, *J. Org. Chem.*, **43**, 3042 (1978).
(7) Reference 3c, p 93.
(8) A. Dondoni, A. Battaglia, P. Giorgianni, G. Gilli, and M. Sacerdoti, *J. Chem. Soc., Chem. Commun.*, 43 (1977).
(9) For a full account of the structure of **3c**, see V. Bertolasi and G. Gilli, *Acta Crystallogr., Sect. B*, **B34**, 3403 (1978).
(10) Identical behavior is likely to be followed by *N*-alkylketenimines in general.

Scheme II[a]



[a] 6j, $R^1 = R^2 = p$-ClPh, X = 6-CH_3, Ar = Ph; 6k, $R^1 = R^2$ = Ph, X = 6-CH_3, Ar = Ph; 6l, $R^1 = R^2$ = Ph, X = 6-CH_3, Ar = p-CH_3Ph; 6m, $R^1 = R^2$ = Ph, X = 6-Cl, Ar = Ph; 6n, $R^1 = R^2 = CH_3$, X = H, Ar = Ph; 6o, $R^1 = R^2 = CH_3$, X = 6-CH_3, Ar = Ph; 6p, $R^1 = R^2 = CH_3$, X = 6-OCH_3, Ar = Ph; 6q, $R^1 = R^2 = CH_3$, X = 5-OCH_3, Ar = Ph; 6q′, $R^1 = R^2 = CH_3$, X = 7-OCH_3, Ar = Ph; 6r, $R^1 = R^2 = CH_3$, X = 6-CH_3, X = 6-CH_3, Ar = p-ClPh; 6s, $R^1 = R^2 = CH_3$, X = 6-CH_3, Ar = p-CH_3Ph; 7p, $R^1 = R^2 = CH_3$, X = 6-OCH_3, Ar = Ph; 7q′, $R^1 = R^2 = CH_3$, X = 7-OCH_3, Ar = Ph.

value[11] of the J_{CH} (134.5 Hz) measured from ^{13}C satellites of the 6.13-ppm peak in the ^1H NMR spectrum of **3f**. Accordingly, the mass spectrum of **3f** showed fragments at m/e 256 [$(Ph_2C{=}CHPh)^+$], 235 [$(PhCH{=}C{=}NMes)^+$], and 177 [$(MesN{=}C{=}S)^+$]. The conversion of cycloadducts **3e–h** into thioacrylamides **4e–h** was carried out by heating the reaction solutions at 80–90 °C for 5 h. The rearrangement **3** → **4** can be formulated to occur through the migration of hydrogen from C_3 to nitrogen and rupture of the S–C_4 bond of the thietane ring, but whether these processes are concerted or take place in successive steps is a point which at present cannot be decided. Results for a typical experiment where reactants and products were monitored at intervals by NMR are shown in Figure 1 (see the paragraph at the end of the paper regarding supplementary material).

In addition to spectroscopic evidence (see Experimental Section) and conversion in some cases into amides, conclusive evidence for the structure of thioacrylamides **4** came from a single-crystal X-ray analysis[12] of compound **4f**. It is worth noting that in the solid state the molecule is blocked in the *E,E′* conformation about the C–C and C–N bonds of the thioamidic group and that the N–H tautomer is preferred over the S–H isomer.

Hence, ketenimines **1a–h** undergo a thermally induced 1,2-cycloaddition by thiobenzophenone (**2a**) across the cumulene C=C bond to give as a primary product[13] the 2-iminothietane derivatives **3**, some of which were not isolated because of their tendency to isomerize to thioacrylamides **4**. This site selectivity is in line with that most commonly observed in ketenimine cycloadditions.[4] Moreover, the regiochemistry of the cycloaddition is as expected, as bonding occurs between the electrophilic central carbon of the cumulene[3a,c] and the sulfur of the C=S group whose nucleophilic character is well documented both in reactions leading to open-chain compounds[14] (thione *S*-oxides) and in cycloaddition reactions.[15] An identical 1,2-cycloaddition by thiobenzophenones has been reported to take place across the C=C bond of ketenes.[16]

1,4-Cycloaddition. Formation of 4*H*-3,1-Benzothiazines 6. The reactions of *C,C*-diaryl- and *C,C*-dimethylketenimines **1j–q** with a slight excess of the aromatic thiones **2** gave the 1:1 six-membered-ring cycloadducts, 4*H*-3,1-benzothiazines **6**, in good yields (ca. 80%) and, in some cases, very modest amounts (5–6%) of adducts **7** from 2 mol of thione and 1 mol of ketenimine (Scheme II). When the reactions were carried out with a twofold molar excess of the thione with respect to the ketenimine, the yields of **7** rose to ca. 20%. The structure of 4*H*-3,1-benzothiazines **6** stemmed from spectroscopic evidence and the X-ray analysis[17] of compound **6k**. The main spectroscopic features of compounds **6** are an IR band at ca. 1590 cm^{-1} (C=N bond of the thiazine ring[18]) and a ^1H NMR singlet at ca. 5.05–5.10 ppm for the Ar_2CH proton (compounds **6j–m**) or a septet and a doublet at ca. 2.6 and 1.05 ppm, respectively (J = 6.5 Hz), for the Me_2CH group (compounds **6n–s**); the mass spectra showed a

(11) L. M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Oxford, 1969, Chapters 4 and 5.

(12) For a full account of the crystal structure of **4f**, see V. Bertolasi and G. Gilli, *Cryst. Struct. Commun.*, **7**, 517 (1978).

(13) As shown in Figure 2 and in similar experiments carried out at low temperature (-30 °C), the NMR spectra of the reaction solutions did not reveal the presence of any transient species preceeding the formation of cycloadduct **3**.

(14) A. Battaglia, A. Dondoni, P. Giorgianni, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc. B*, 1547 (1971).

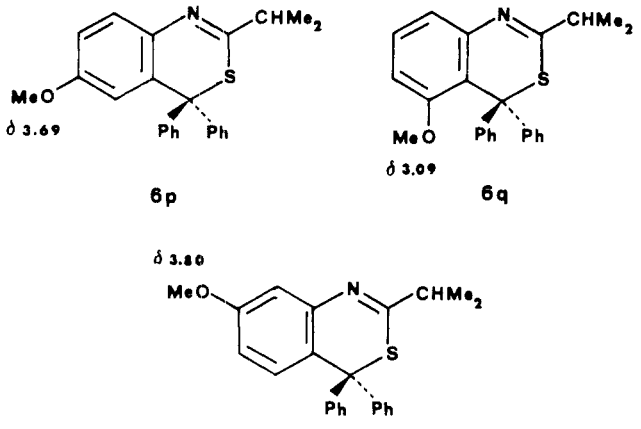
(15) A. Battaglia, A. Dondoni, G. Maccagnani, and G. Mazzanti, *J. Chem. Soc. B*, 2096 (1971).

(16) H. Kohn, P. Charumilind, and Y. Gopichand, *J. Org. Chem.*, **43**, 4961 (1978).

(17) M. Sacerdoti, V. Bertolasi, G. Gilli, A. Dondoni, and A. Battaglia, *Acta Crystallogr., Sect. B*, **B33**, 2816 (1977).

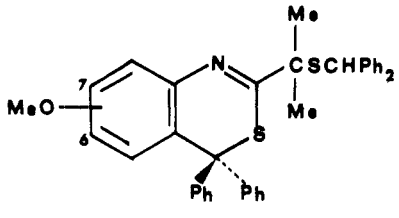
(18) R. G. Visser, J. P. B. Baaij, A. C. Brouwer, and H. J. T. Bos, *Tetrahedron Lett.*, 4343 (1977).

breakdown pattern containing a peak for $(M - CHR_2)^+$ (R = Ar or Me). The reaction of *N*-(*m*-methoxyphenyl)dimethylketenimine (**1q**) with thiobenzophenone (**2a**) gave the two isomeric benzothiazines **6q** and **6q′** arising from



the cyclization of the thione on the two nonequivalent ortho positions of the *N*-aryl ring of **1q**. The NMR spectrum of the minor product **6q** (8%) exhibited the methoxyl resonance at 3.09 ppm ($CDCl_3$) and a very complex pattern in the aromatic region, whereas the spectrum of the major isomer **6q′** (74%) showed the methoxyl resonance at lower field (3.80 ppm) and the typical ABX pattern observed for the isomer **6p** derived from ketenimine **1p**.

The structure of the 2:1 adducts **7p** and **7q′** was assigned on the basis of their spectroscopic characteristics. The NMR spectra of **7p** showed, in addition to patterns identical with those for benzothiazine **6p**, two singlets at 1.08 (6 H) and 4.95 ppm (1 H) and peaks at 53.13 and 54.87 ppm for quaternary and tertiary carbons, respectively. The molecular ion could not be observed in the mass spectrum; prominent peaks were present at *m/e* 404 $[(M - Ph_2CH)^+]$, 372 $[(M - Ph_2CHS)^+]$, and 330 $[(M - Ph_2CHSMe_2)^+]$. The elemental analysis was satisfactory. Similar evidence was obtained for **7q′**.



7p,q′

Reasonable pathways which account for the formation of adducts **6** and **7** are outlined in Scheme II. The addition of the C=S bond of the thione across the C=N bond of the cumulene and the C=C bond of the *N*-aryl ring leads to cycloadduct **8** which rearranges by hydrogen migration to the more stable 4*H*-3,1-benzothiazine **6**. The first step in Scheme II can be viewed as a 1,4-cycloaddition of the thione to the ketenimine which acts as a formal heterodiene. Although the mechanism of formation of **8** and the way of its evolution to the isolable product **6** are points for further studies, other schemes which exclude the adduct **8** along the reaction pathway leading to **6** are hardly conceivable. Moreover, a transient species showing spectroscopic features consistent with **9** has been detected, as it is exemplified for the reaction of *N*-(*p*-tolyl)dimethylketenimine (**1o**) with thiobenzophenone (**2a**) (Figure 2, see

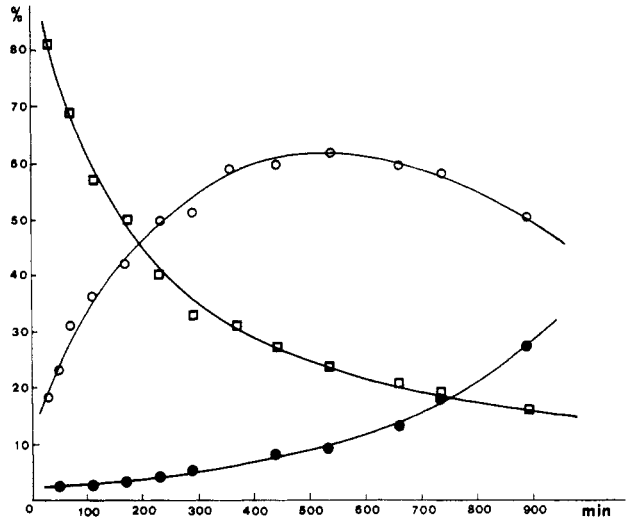


Figure 3. Reaction of *N*-(*p*-tolyl)dimethylketenimine (**1o**, 0.232 M) with thioketone (**2a**, 0.255 M) in $(CD_3)_2CO$ at ca. 25 °C: percentages of ketenimine **1o** (squares), benzothiazine **6o** (full circles), and a transient species (open circles) vs. time (from CH_3 signal intensities of ^1H NMR spectra).

paragraph at the end of the paper regarding supplementary material). The NMR spectra of the reaction mixture recorded at low extent of conversion of the ketenimine showed the presence of two peaks of increasing intensity, one lying downfield (1.82 ppm) and the other upfield (1.44 ppm) with respect to the $=CMe_2$ singlet (1.64 ppm) of the ketenimine. The signals at 1.82 and 1.44 ppm can be assigned to two nonequivalent methyls of an isopropylidene group as required for both intermediates **8** and **9**. On the other hand, the resonances of the $CHMe_2$ group (doublet at 1.01 ppm and septet at 2.60 ppm) of the benzothiazine **6o** became apparent only after ca. 50% conversion of ketenimine **1o** and afterward increased steadily, whereas the intensity of the two singlets at 1.82 and 1.44 ppm decreased and had totally disappeared at infinite time. The trends of the intensities of the three sets of signals at 1.64, 1.82, and 1.01 ppm (Figure 3) are those typical for consecutive reactions and indicate that the observed transient species is an intermediate of the benzothiazine **6o**. The structure **9** rather than **8** for the intermediate is suggested by a transient medium-intensity IR absorption at 3435 cm^{-1} (CCl_4) which can be attributed to the NH group. Moreover, adduct **8** is expected to be quite unstable, owing to its tendency to restore the aromatic system. Finally, the formation of the 2:1 adduct **7** observed in some cases can derive from the addition[19] of a molecule of thioketone to the isopropylidene C=C bond of **9** in competition with the hydrogen migration leading to the benzothiazine **6**.

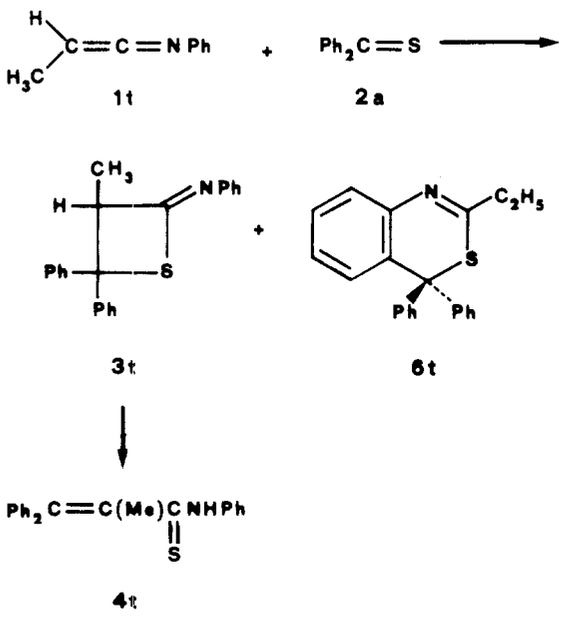
The 4*H*-3,1-benzothiazines **6** were the only isolable products from reactions of thiobenzophenones **2** with *N*-arylketenimines **1j–q** in solvents of different characteristics as well as at low temperature (−15 °C) and in the presence of Et_3N.[20]

The faculty of ketenimines for employing one double bond of the cumulative system and one of the *N*-aryl group

(19) Adducts **7** were isolated only from the reactions of *C,C*-dimethylketenimines **1n–q**. Owing to the relatively low-lying LUMO (see the accompanying paper), it is likely that the thione can behave as an electron acceptor toward the enamine **9** to give a cyclic or open-chain adduct having the sulfur atom of the thione bonded to the terminal carbon of the enamine system and whose subsequent rearrangement leads to the observed product **7**.

(20) The reasons for these experiments came from the observations[18] that the acid-catalyzed rearrangement of 2-iminothietanes to benzothiazines is inhibited by the presence of Et_3N.

Scheme III



in *thermal* cycloaddition reactions is substantiated by two other significant examples, viz., the reactions with ynamines[21] and vinyl ethers.[22] On the other hand, it has been recently reported[18] that *N*-arylketenimines such as **1n** and **1o** undergo a *photochemically* induced 1,2-cycloaddition by cyclic thiones (thiantrone, xantenethione, and thioxantenethione) to form 2-iminothietane derivatives.

Concurrent 1,2- and 1,4-Cycloadditions. Unlike ketenimines **1a–q** examined in the preceding sections, *N*-phenylmethylketenimine[23] (**1t**) exhibited a dual behavior as a cycloaddition partner with thiobenzophenone (**2a**) since it reacted according to both the 1,4- and the 1,2-addition modes to produce 4*H*-3,1-benzothiazine **6t** and 2-iminothietane **3t** in a 1:1.1 ratio; the cycloadduct **3t** was satisfactorily stable at room temperature but rearranged on being heated to the thioacrylamide[24] **4t** (Scheme III). Cycloadducts **3t** and **6t** proved by NMR spectroscopy to form through two parallel pathways. The ^{1}H NMR spectra of the reaction solution (Figure 4, see paragraph at the end of the paper regarding supplementary material) exhibited two systems of peaks: system A, δ 4.88 (q), 1.10 (d, J = 7.3 Hz); system B, δ 2.43 (q), 1.01 (t, J = 7.7 Hz). System A is assigned to the $CHCH_3$ resonances of 2-iminothietane **3t** and system B to the C_2H_5 resonances of benzothiazine **6t**. The intensities of the signals of systems A and B increased steadily until the ketenimine **1t** (doublet at 1.62 ppm for the CH_3) had totally disappeared, but their ratio remained constant. The spectrum of the reaction mixture showed no substantial changes after 2 days at room temperature, but when the compound was heated at ca. 100 °C for a few hours, system A disappeared and was replaced by the broad singlet at 2.33 ppm of the thioacrylamide **4t**. These observations indicated that benzothiazine **6t** (1,4-cycloadduct) and 2-iminothietane **3t** (1,2-cycloadduct) were both products deriving from two parallel pathways, whereas the thioacrylamide **4t** was produced by the iminothietane **3t** in a subsequent process. In preparative-scale experiments, the products **3t**, **4t**, and **6t** were isolated and fully characterized. In refluxing benzene, 2-iminothietane **3t** isomerized within 2 h to the thioamide **4t**, whereas benzothiazine **6t** was recovered unaltered after 1 day under the same conditions.

Table II. Preparations and Characteristics of Ketenimines 1a-t ($R^1R^2C{=}C{=}NR^3$)

	R^1	R^2	R^3	bp (mm) or mp, °C	method[a]
1a	Ph	Ph	CH_3	98-105 (0.001)	B
1b	Ph	Ph	2,4,6-$(CH_3)_3$Ph	56-59[b]	C
1c	CH_3	CH_3	2,6-$(CH_3)_2$Ph	64-65 (0.01)	A
1d	CH_3	CH_3	2,4,6-$(CH_3)_3$Ph	48-49 (0.001)	D
1e	H	Ph	*c*-C_6H_{11}	98-105 (0.05)	D
1f	H	Ph	2,4,6-$(CH_3)_3$Ph	*c*	D
1g	H	Ph	CH_3	24 (0.001)	D
1h	H	Ph	Ph	*c*	D
1j	*p*-ClPh	*p*-ClPh	*p*-CH_3Ph	79-80[b]	C
1k	Ph	Ph	*p*-CH_3Ph	82-84[b]	C
1m	Ph	Ph	*p*-ClPh	67-69[b]	C
1n	CH_3	CH_3	Ph	30-35 (0.002)	A
1o	CH_3	CH_3	*p*-CH_3Ph	57-59 (0.002)	A
1p	CH_3	CH_3	*p*-CH_3OPh	65-67 (0.004)	A
1q	CH_3	CH_3	*m*-CH_3OPh	60-61 (0.005)	A
1t	H	CH_3	Ph	*c*	D

[a] A, from the imidoyl chloride and Et_3N;[27a] B, from the amide and P_2O_5;[27b] C, from the amide and the mixture $Ph_3P/Br_2/Et_3N$;[27c] D, see the Experimental Section. [b] Recrystallized from pentane. [c] Polymerized on distillation.

Conclusions

The results reported in the preceding sections show that ketenimines **1** may equally undergo 1,2- and 1,4-cycloadditions by thiobenzophenones **2**, this selectivity depending on the extent and type of substitution at the terminal carbon of the cumulene and on the nature of the group on nitrogen as well. The 1,2-cycloaddition of the C=S bond of the thione takes place across the C=C bond of the cumulene to form a four-membered adduct 2-iminothietane **3**, while the 1,4-cycloaddition involves the C=N bond of the cumulene and the C=C of the aryl group bonded to nitrogen and leads to a six-membered-ring adduct, 4*H*-3,1-benzothiazine **6**. In the former case, the ketenimine can be viewed as acting as a 2-π-electron system and in the latter as a *formal* 4-π-electron heterodiene.

The 1,2- and 1,4-cycloadducts do not convert into each other under the reaction conditions. Even 2-iminothietane **3t**, where both possibilities of conversion to benzothiazine **6t** and thioamide **4t** are in principle available, rearranged to thioamide **4t** only. These observations differ from those reported for the photochemical cycloadditions[18] between ketenimines and thiones where the iminothietanes resulted and rearranged to benzothiazines.

The results of the present work as well as those of other recent reports[18,21,22] enlarge considerably the role of ketenimines in synthetic organic chemistry.

Experimental Section

General Methods. Chemical shifts for both the ^{13}C and ^{1}H NMR spectra are given as δ values in parts per million from Me_4Si.

(21) E. Sonveaux and L. Ghosez, *J. Am. Chem. Soc.*, **95**, 5417 (1973).
(22) D. P. Del'tsova and N. P. Gambaryan, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, 858 (1976).
(23) Ketenimine **1t** is a slightly yellow oil which rapidly polymerizes but is satisfactorily stable in a CCl_4 solution.
(24) The ^{1}H NMR spectrum ($CDCl_3$) of **4t** at room temperature exhibits two signals at 2.28 and 2.33 ppm of relative intensities 1:3, which coalesce in a single broad band at ca. 60 °C. This indicates the presence of two nonequivalent methyls which may belong to two conformers and/or two tautomers.

The formations of products and intermediates were followed at intervals in sealed NMR tubes, previously freeze–thaw degassed under high vacuum. Low-resolution mass spectra were recorded at an ionizing voltage of 70 eV. Preparative plate chromatography was done with a 2-mm-thick layer of silica gel on glass plates. Melting points are uncorrected. All solvents were purified by the usual methods before use.[25]

Starting Materials. The preparations of thiobenzophenones **2** have been reported previously.[26] Ketenimines **1** (Table II) were prepared according to standard procedures.[27] NMR and IR data for compounds **1** are collected in Table III (see paragraph at the end of the paper regarding supplementary material). A slight modification of the reported procedure[27c] was employed for the isolation and purification of C-monosubstituted derivatives **1e–h** and **1t**. To a stirred solution of PPh_3 (47 mmol) in 250 mL of CCl_4 was added at room temperature an equivalent amount of Br_2 (2.5 mL) in 50 mL of the same solvent. Triethylamine (47 mmol) and the amide (2 mmol) were added under an argon atmosphere, and the mixture was refluxed for 4–5 h. After cooling, the reaction mixture was filtered, and the solvent was concentrated to 100 mL in vacuo at room temperature. Addition of 150 mL of pentane and cooling at −25 °C produced a further amount of precipitate. After filtration and complete removal of the solvent, the same procedure was repeated three times, each time with a smaller amount of pentane (70, 30, and 15 mL). Rapid evaporation of the solvent at −15 °C under high vacuum (1×10^{-3} torr) gave an oily residue which polymerized within a few hours. After solution of the oil in a suitable solvent, the amount of ketenimine (65–85%) was determined by ^1H NMR (PPh_3 and small amounts of polymeric materials being the impurities). Ketenimine solutions were satisfactorily stable at room temperature for at least 2 days.

Synthesis of 2-Imino-3,3,4,4-tetrasubstituted Thietanes 3a–d. A description of the generalized procedure follows. Equimolar solutions of thione **2a** and ketenimines **1a–d** were introduced separately by a syringe in the two arms of an h-shaped Carius tube previously purged with argon. The solutions were quickly freeze–thaw degassed under high vacuum and mixed after the tube was sealed. The reaction mixture was thermostated at the selected temperature for the time required for the intense blue color of the thione to fade. Evaporation of the solvent in vacuo gave a red-brown oil from which were obtained by chromatography (silica, CH_2Cl_2) the unreacted thioketone, some ketone, and the iminothietane **3**. The adducts **3**, whose yields refer to amounts from chromatographic separation, were recrystallized from the proper solvents.

2-(Methylimino)-3,3,4,4-tetraphenylthietane (3a). Thiobenzophenone **2a** (2.27 mmol) and ketenimine **1a** (2.27 mmol) in CCl_4 (10 mL) at 45 °C for 8 days gave **3a**: 0.46 g (50% yield); mp 165–167 °C (from methanol); IR (CCl_4) 1670 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 3.31 (s, Me), 6.98–7.38 (m, 20 H, arom); ^{13}C NMR ($CDCl_3$) δ 66.64 (1 C, quat), 83.2 (1 C, quat), 164.5 (C=N); mass spectrum, m/e absence of M^+ (405), 332, 207, 198, 192. Anal. Calcd. for $C_{28}H_{23}NS$: C, 82.92; H, 5.72; N, 3.45. Found: C, 82.85; H, 5.78; N, 3.52.

2-(Mesitylimino)-3,3,4,4-tetraphenylthietane (3b). Thione **2a** (2.02 mmol) was reacted with ketenimine **1b** (2.02 mmol) in CCl_4 (10 mL) at 45 °C for 15 days (50% of thione remained unreacted). There was obtained 0.31 g (30% yield) of **3b**: mp 156–159 °C (from ethanol); IR (CCl_4) 1655 cm^{-1} (C=N); ^1H NMR (CCl_4) δ 2.05 (s, 2 Me), 2.20 (s, Me), 6.6–7.4 (m, 22 H, arom); ^{13}C NMR ($CDCl_3$) δ 66.9 (1 C, quat), 83.4 (1 C, quat), 166.4 (C=N); mass spectrum, m/e 509 (M^+), 332, 311, 198. Anal. Calcd. for $C_{36}H_{31}NS$: C, 84.83; H, 6.13; N, 2.75. Found: C, 84.80; H, 6.07; N, 2.73.

2-[(2,6-Dimethylphenyl)imino]-3,3-dimethyl-4,4-diphenylthietane (3c). Thiobenzophenone **2a** (3 mmol) and ketenimine **1c** (3 mmol) in $CHCl_3$ (15 mL) at 60 °C for 3 days (25% of the thione remained unreacted) gave 0.34 g (30% yield) of **3c**: mp 125–127 °C (from methanol); IR (CCl_4) 1680 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.43 (s, 2 Me), 2.1 (s, 2 Me), 6.7 (m, 3 H, arom), 6.82–7.3 (m, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 65.3 (1 C, quat), 66.3 (1 C, quat), 169.4 (C=N); mass spectrum, m/e 371 (M^+), 209, 173. Anal. Calcd. for $C_{25}H_{25}NS$: C, 80.82; H, 6.78; N, 3.77. Found: C, 80.75; H, 6.76; N, 3.80.

2-(Mesitylimino)-3,3-dimethyl-4,4-diphenylthietane (3d). Thione **2a** (2.67 mmol) and ketenimine **1d** (2.67 mmol) in CCl_4 (10 mL) at 45 °C for 8 days gave 0.58 g (55% yield) of **3d**: mp 118–120 °C (from ethanol); IR (KBr) 1680 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ 1.48 (s, 2 Me), 2.18 (s, 2 Me), 2.25 (s, 1 Me), 6.86 (s, 2 H, arom), 7.16–7.45 (m, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 65.5 (1 C, quat), 66.6 (1 C, quat), 169.5 (C=N); mass spectrum, m/e 385 (M^+), 208,177. Anal. Calcd. for $C_{26}H_{27}NS$: C, 80.99; H, 7.06; N, 3.63. Found: C, 81.01; H, 7.09; N, 3.56.

Synthesis of α,β-Unsaturated Thioamides 4e–h. General Procedure. The reactions were carried out in the apparatus described above and were followed at intervals by ^1H NMR. In all cases the transient iminothietane was detected spectroscopically (Table I). After the disappearance of the ketenimine, the reaction vessel was thermostated at a higher temperature, and conversion of the thietane to thioacrylamide was also followed by ^1H NMR. After evaporation of the solvent in vacuo, the reaction mixture was chromatographed (silica, CH_2Cl_2) to give unreacted thione, some ketone, and the thioamide (yield refers to this amount) which was recrystallized from the proper solvent.

***N*-Cyclohexyl-2,3,3-triphenylthioacrylamide (4e).** Thiobenzophenone **2a** (11.62 mmol) was reacted with ketenimine **1e** (11.62 mmol) in CCl_4 (14 mL) at 45 °C for 17 h and then at 80 °C for 15 h; yield of **4e** 80%: mp 201–204 °C (from methanol); IR (CCl_4) 3390 cm^{-1} (NH); ^1H NMR (CCl_4) δ 0.55–1.88 (br, 10 H), 3.75–4.28 (br, 1 H), 6.58–7.33 (m, 16 H); mass spectrum, m/e 397 (M^+), 314, 299. Under reflux with 15% HCl, the thioamide **4e** was converted to the corresponding amide: mp 191–192 °C (from ethanol); IR (CCl_4) 3345 (NH), 1670 (CO) cm^{-1}; mass spectrum, m/e 381 (M^+), 288, 283, 255. Anal. Calcd. for $C_{27}H_{27}NS$: C, 81.57; H, 6.85; N, 3.52. Found: C, 81.64; H, 6.79; N, 3.51.

***N*-Mesityl-2,3,3-triphenylthioacrylamide (4f).** Thione **2a** (3.93 mmol) was reacted with ketenimine **1f** (3.93 mmol) in CCl_4 (14 mL) at 40 °C for 14 h and then at 95 °C for 36 h; yield of **4f** 90%: mp 220–224 °C (from benzene–petroleum ether); IR (CS_2) 3350 cm^{-1} (NH); ^1H NMR (CD_2Cl_2) δ 1.78 (s, 2 Me), 2.21 (s, Me), 6.88 (s, 2 H), 7.12–7.78 (m, 15 H), 8.69 (br, NH); mass spectrum, m/e 433 (M^+), 418, 400. Anal. Calcd. for $C_{30}H_{27}NS$: C, 83.10; H, 6.28; N, 3.23. Found: C, 83.17; H, 6.25; N, 3.26.

***N*-Methyl-2,3,3-triphenylthioacrylamide (4g).** Thione **2a** (1.26 mmol) was reacted with ketenimine **1g** (1.26 mmol) in CCl_4 (12 mL) at room temperature for 4 h and then at 50 °C for 17 h; yield of **4g** 60%: mp 218–220 °C (from benzene–petroleum ether); IR (CCl_4) 3410 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 2.92 (d, Me, J_{H-CH_3} = 5.37 Hz), 7.04–7.12 (m, 16 H); mass spectrum, m/e 329 (M^+), 314, 296, 253, 166. Anal. Calcd. for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.25. Found: C, 80.14; H, 5.76; N, 4.20.

***N*-Phenyl-2,3,3-triphenylthioacrylamide (4h).** Thione **2a** (2.27 mmol) was reacted with ketenimine **1h** (2.27 mmol) in CCl_4 (20 mL) at 25 °C for 29 h; yield of **4h** 70%: mp 212–217 °C (from benzene–petroleum ether); IR (CS_2) 3380 cm^{-1} (NH); ^1H NMR ($CDCl_3$) δ 6.88–7.45 (m, 15 H), 8.51 (br, NH); mass spectrum, m/e 391 (M^+), 314, 299, 166. Anal. Calcd. for $C_{27}H_{21}NS$: C, 82.83; H, 5.41; N, 3.58. Found: C, 82.81; H, 5.47; N, 3.59.

IR Detection of Transient 3-Monosubstituted 2-Iminothietanes 3e–h. Thiobenzophenone **2a** (0.707 mmol) was reacted with an equivalent amount of ketenimines **1e–h** in 10 mL of CCl_4 under an argon atmosphere. The reaction course was followed at intervals by IR in a 0.5-mm NaCl cell previously purged with argon. Bands in the NH region (ca. 3350 cm^{-1}) were absent in the early stage of the reaction, whereas a strong peak at ca. 1700 cm^{-1} (C=N) (Table I) was present and increased with time. After disappearance of the ketenimine peak at ca. 2000 cm^{-1}, the simultaneous decrease of the C=N peak and the appearance of the NH band of the thioamide were observed.

^{13}C–H Coupling Constant Detection in the 2-Iminothietane 3f. Thiobenzophenone **2a** (0.232 mmol) was reacted with ketenimine **1f** (0.20 mmol) in a mixture of 0.5 mL of CCl_4 and 0.05 mL of $(CD_3)_2CO$. Once the C–H signal at 4.73 ppm of **1f** had

(25) A. Weissberger, "Techniques of Organic Chemistry", Vol. VII, Interscience, New York, 1955.
(26) L. Lunazzi, G. Maccagnani, G. Mazzanti, and G. Placucci, *J. Chem. Soc. B*, 162 (1971).
(27) (a) C. L. Stevens and J. C. French, *J. Am. Chem. Soc.*, **76**, 4398 (1954); (b) C. L. Stevens and G. H. Singhal, *J. Org. Chem.*, **29**, 34 (1964); (c) H. J. Bestmann, J. Lienert, and L. Mott, *Justus Liebigs Ann. Chem.*, **718**, 24 (1968).

totally disappeared, the $J(^{13}C-H)$ was measured from the satellite bands of the 6.13-ppm signal. In three different recordings the values were 134.5 ± 0.5 Hz. In Table I are also given the mass spectral data of a solution of **3f** recorded before its conversion to **4f**.

Synthesis of 4*H*-3,1-Benzothiazines 6. General Procedure. The general operative conditions for the mixing of the reactants were as described above. Details on each reaction and the characteristics of adducts **6** are given below. All benzothiazines **6** presented a strong IR band at ca. 1590 cm^{-1} (in CCl_4, exocyclic C=N). In this section are also described the spectroscopic detection of an intermediate and the isolation of 2:1 adducts **7**.

2-[Bis(4-chlorophenyl)methyl]-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine (6j). Thiobenzophenone **2a** (2.1 mmol) was reacted with ketenimine **1j** (2.1 mmol) in CCl_4 (10 mL) at 30 °C for 5 days. Chromatographic workup (silica, 1:3 CH_2Cl_2–petroleum ether) yielded 85% of **6j**: mp 195–198 °C dec (from benzene–pentane); ^1H NMR ($CDCl_3$) δ 2.20 (s, 1 Me), 5.1 (s, $CHPh_2$), 6.25–7.4 (m, 21 H, arom); mass spectrum, *m/e* 549 (M^+), 314, 165. Anal. Calcd. for $C_{34}H_{25}NCl_2S$: C, 74.17; H, 4.58; N, 2.54. Found: C, 74.11; H, 4.53; N, 2.59.

2-(Diphenylmethyl)-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine (6k). Thione **2a** (2.1 mmol) was reacted with ketenimine **1k** (2.1 mmol) in CCl_4 (10 mL) at 30 °C for 5 days; yield of **6k** 85%: mp 234–239 °C dec (from DMF); ^1H NMR ($CDCl_3$) δ 2.1 (s, Me), 5.05 (s, $CHPh_2$), 6.8–7.1 (m, 23 H, arom); mass spectrum, *m/e* 481 (M^+), 314, 167. Anal. Calcd. for $C_{34}H_{27}NS$: C, 84.78; H, 5.65; N, 2.91. Found: C, 84.70; H, 5.69; N, 2.86.

2-(Diphenylmethyl)-4,4-ditolyl-6-methyl-4*H*-3,1-benzothiazine (6l). Ditolyl thioketone (**2b**) was reacted with ketenimine **1k** (0.11 mmol) in CCl_4 (10 mL) at 35 °C for 6 days; yield of **6l** 85%: mp 149–154 °C dec (from CH_2Cl_2–pentane); ^1H NMR (CCl_4–C_6D_6; 0.5–0.2 mL) δ 2.1 (s, Me), 2.23 (s, 2 Me), 5.15 (s, $CHPh_2$), 5.35–7.4 (m, 23 H, arom); mass spectrum, *m/e* 509 (M^+), 340, 167. Anal. Calcd. for $C_{36}H_{31}NS$: C, 84.83; H, 6.13; N, 2.75. Found: C, 84.75; H, 6.09; N, 2.79.

2-(Diphenylmethyl)-4,4-diphenyl-6-chloro-4*H*-3,1-benzothiazine (6m). Thione **2a** (0.1 mmol) was reacted with ketenimine **1m** (0.1 mmol) in $CDCl_3$ (0.6 mL) at 25 °C for 15 h and then at 80 °C for 2 h; yield of **6m** 85%: mp 238–245 °C dec (from $CHCl_3$–pentane); ^1H NMR ($CDCl_3$) δ 5.21 (s, $CHPh_2$), 6.55–7.20 (m, 23 H, arom); mass spectrum, *m/e* 502 (M^+), 335, 167. Anal. Calcd. for $C_{33}H_{24}NClS$: C, 78.94; H, 4.82; N, 2.79. Found: C, 78.83; H, 4.79; N, 2.83.

2-Isopropyl-4,4-diphenyl-4*H*-3,1-benzothiazine (6n). Thione **2a** (9 mmol) was reacted with ketenimine **1n** (9 mmol) in THF (15 mL) at 30 °C for 5 days; yield of **6n** 80%: mp 143–146 °C (from benzene–pentane); ^1H NMR ($CDCl_3$) δ 1.05 (d, 2 Me), 2.73 (m, 1 H, J_{H-CH_3} = 6.75 Hz), 6.43–7.55 (m, 14 H, arom); mass spectrum, *m/e* 343 (M^+), 300. In another experiment thione **2a** (3 mmol) was reacted with **1n** (3 mmol) in benzene (10 mL) to which was added (1%) Et_3N at −15 °C for 15 days. The yield of **6n** was 85%. Anal. Calcd. for $C_{23}H_{21}NS$: C, 80.42; H, 6.16; N, 4.08. Found: C, 80.44; H, 6.18; N, 4.13.

2-Isopropyl-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine (6o). Thione **2a** (3.03 mmol) was reacted with ketenimine **1o** (3.03 mmol) in CCl_4 (8 mL) at 30 °C for 40 h. After evaporation of the solvent, column chromatography (silica, 2:1 CH_2Cl_2–pentane) yielded **6o** 80%: mp 124–127 °C (from ethanol); ^1H NMR ($CDCl_3$) δ 1.04 (d, 2 Me), 2.21 (s, Me), 2.65 (m, 1 H, J_{H-CH_3} = 6.75 Hz), 6.35 (m, 1 H, arom), 7.1–7.48 (m, 12 H, arom); mass spectrum, *m/e* 357 (M^+), 342, 314. Similar results were obtained from reactions in CH_2Cl_2, $CH_3C{\equiv}N$, and $Me_2C{=}O$. Anal. Calcd. for $C_{24}H_{23}NS$: C, 80.63; H, 6.49; N, 3.92. Found: C, 80.70; H, 6.45; N, 3.99.

2-Isopropyl-4,4-diphenyl-6-methoxy-4*H*-3,1-benzothiazine (6p). Thione **2a** (2.83 mmol) was reacted with ketenimine **1p** (2.60 mmol) in THF (15 mL) at 30 °C for 7 days. Column chromatography (silica, benzene) yielded 80% of **6p**: mp 140–142 °C (from CH_2Cl_2–pentane); ^1H NMR ($CDCl_3$) δ 1.04 (d, 2 Me), 2.71 (m, 1 H, J_{H-CH_3} = 6.83 Hz), 3.69 (s, Me), 6.1 (d, 1 H, X of ABX, J_{AX} = 2.85 Hz), 6.86 (dd, 1 H, A of ABX, J_{AB} = 8.4 Hz), 7.31 (d, 1 H, B of ABX), 7–7.41 (mm, 11 H, arom); ^{13}C NMR ($CDCl_3$) δ 19.76 (2 Me), 39.9 (CH), 55.19 (OMe), 59.49 (C of C–S), 112.4, 113.2, 127.4, 127.7, 128.0, 129.7 (1 C, arom), 130.69 (1 C, arom), 138.2 (1 C, arom), 142.9 (2 C, arom of Ph_2C), 158.4 (1 C, arom), 167.8 (s, C=N); mass spectrum, *m/e* 373 (M^+), 342, 333. Anal. Calcd. for $C_{24}H_{23}NOS$: C, 77.17; H, 6.21; N, 3.75. Found: C, 77.11; H, 6.28; N, 3.71.

Benzothiazines 6q and 6q′ from Ketenimine 1q. Thione **2a** (4.1 mmol) was reacted with ketenimine **1q** (1.95 mmol) in CCl_4 (15 mL) at 25 °C for 18 h and then at 30 °C for 15 h. After workup of the reaction mixture through column chromatography (silica, 2:1 benzene–pentane) the two benzothiazines **6q** and **6q′** were obtained in a 0.12:1 ratio (overall yield 85%). For **6q**: mp 112–114 °C dec (from $MeC{\equiv}N$); ^1H NMR ($CDCl_3$) δ 1.06 (d, 2 Me), 2.68 (m, 1 H, J_{H-CH_3} = 6.71 Hz), 3.09 (s, Me), 6.73–7.40 (m, 13 H, arom); mass spectrum, *m/e* 373 (M^+), 358, 342, 330. Anal. Calcd. for $C_{24}H_{23}NOS$: C, 77.17; H, 6.21; N, 3.75. Found: C, 77.13; H, 6.23; N, 3.77. For **6q′**: mp 97–101 °C (from pentane at −50 °C); ^1H NMR ($CDCl_3$) δ 1.06 (d, 2 Me), 2.68 (m, 1 H, J_{H-CH_3} = 6.71 Hz), 3.8 (s, 1 Me), 7.08 (d, 1 H, X of ABX, J_{AX} = 2.84 Hz), 6.76 (dd, 1 H, A of ABX, J_{AB} = 8.5 Hz), 6.54 (d, 1 H, B of ABX); mass spectrum, *m/e* 373 (M^+), 358, 342, 330. Anal. Calcd. for $C_{24}H_{23}NOS$: C, 77.17; H, 6.21; N, 3.75. Found: C, 77.22; H, 6.19; N, 3.69.

2-Isopropyl-4,4-bis(4-chlorophenyl)-6-methyl-4*H*-3,1-benzothiazine (6r). Thione **2c** (1 mmol) was reacted with ketenimine **1o** (1 mmol) in CCl_4 (12 mL) at 25 °C for 24 h and then at 35 °C for 2 days; yield of **6r** 80%: mp 125–132 °C dec (from benzene–pentane); ^1H NMR ($CDCl_3$) δ 1.04 (d, 2 Me), 2.23 (s, Me), 2.64 (m, 1 H, J_{H-CH_3} = 6.75 Hz), 6.25 (m, 1 H, arom), 6.9–7.3 (m, 10 H, arom); mass spectrum, *m/e* 426 (M^+), 383.

2-Isopropyl-4,4-ditolyl-6-methyl-4*H*-3,1-benzothiazine (6s). Thione **2b** (3.14 mmol) was reacted with ketenimine **1o** (3.14 mmol) in CCl_4 (8 mL) at 20 °C for 4 days and then at 40 °C for 3 days. After evaporation of the solvent, high-pressure column chromatography (silica, 1:9 ethyl acetate–petroleum ether) allowed a satisfactory separation of the benzothiazine from ditolyl ketone; yield of **6s** 65%: mp 128–130 °C (from benzene–pentane); ^1H NMR ($CDCl_3$) δ 1.04 (d, 2 Me), 2.21 (s, Me), 2.23 (s, 2 Me, arom), 2.62 (m, 1 H, J_{H-CH_3} = 6.4 Hz), 6.39 (d, X of ABX), 6.68–7.39 (m, 10 H, arom); mass spectrum, *m/e* 385 (M^+), 342. Anal. Calcd. for $C_{26}H_{27}NS$: C, 80.99; H, 7.06; N, 3.63. Found: C, 81.05; H, 7.11; N, 3.58.

Isolation of Adduct 7p from Thiobenzophenone (2a) and Ketenimine 1p. Thiobenzophenone **2a** (7 mmol) was reacted with ketenimine **1p** (3.3 mmol) in benzene (10 mL) at 35 °C for 2 days. Workup of the reaction mixture through column chromatography (silica, benzene) afforded in the order of elution the adduct **7p** and the benzothiazine **6p** in a 0.47:1 molar ratio (overall yield 85%). The adduct **7p** was recrystallized from benzene–pentane: mp 122–132 °C dec; IR (C_2Cl_4) 1618 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08 (s, 2 Me), 3.66 (s, OMe), 4.95 (s, $CHPh_2$), 6.15 (d, 1 H, X of ABX, J_{AX} = 3.0 Hz), 6.97 (dd, 1 H, A of ABX, J_{AB} = 8.7 Hz), 7.5 (d, 1 H, B of ABX), 6.16–7.18 (m, 22 H, arom); ^{13}C NMR ($CDCl_3$) δ 28.04 (2 Me), 53.13 (1 C), 55.28 (OCH_3), 55.5 ($CHPh_2$), 60.36 (C–S), 112.31, 113.2, 126.77, 127.35, 127.68, 128.2, 128.31, 128.55, 129.7, 131.56, 138.03, 142.1, 142.33, 158.94 (C, arom), 166.52 (C=N); mass spectrum, *m/e* absence of M^+ (571), 404, 372, 330. Anal. Calcd. for $C_{37}H_{33}NOS_2$: C, 77.72; H, 5.82; N, 2.45; S, 11.22. Found: C, 77.93; H, 5.91; N, 2.35; S, 10.93.

Isolation of adduct 7q′ from Thiobenzophenone (2a) and Ketenimine 1q. Thiobenzophenone **2a** (4.1 mmol) was reacted with ketenimine **1q** (1.94 mmol) in CCl_4 (14 mL) at 25 °C for 18 h and then at 30 °C for 15 h. Workup of the reaction mixture through column chromatography (silica, 2:1 benzene–pentane) afforded in the following order the adduct **7q′** and benzothiazines **6q** and **6q′** in a molar ratio of 0.16:0.12:1 (overall yield 96%). The adduct **7q′** was recrystallized from benzene–pentane: mp 146–147 °C dec; IR (C_2Cl_4) 1590 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 2 Me), 3.87 (s, OMe), 5.0 (s, $CHPh_2$), 7.0 (d, 1 H, X of ABX, J_{AX} = 2.68 Hz), 6.78 (dd, 1 H, A of ABX, J_{AB} = 8.8 Hz), 6.52 (d, 1 H, B of ABX), 6.44–7.25 (m, 23 H, arom); mass spectrum, *m/e* absence of M^+ (571), 404, 372, 330. Anal. Calcd. for $C_{37}H_{33}NOS_2$: C, 77.72; H, 5.82; N, 2.45; S, 11.22. Found: C, 77.68; H, 5.85; N, 2.4; S, 10.95.

Spectroscopic Detection of Intermediates 9 from *C,C*-Dimethyl-Substituted Ketenimines 1n–q and Thiobenzophenone (2a). The reactions were followed at intervals by ^1H NMR or by IR. A description of two typical experiments is given below.

^{1}H NMR Detection. A solution of ketenimine **1n** (0.158 mmol) and thiobenzophenone (**2a**, 0.22 mmol) in CCl_4 (0.6 mL) in a freeze–thaw-degassed, sealed NMR tube was examined at intervals, following the disappearance of the peak at 1.68 ppm (s, 2 Me of **1n**) and the formation of two peaks at 1.84 and 1.58 ppm, respectively, which equally increased up to 45–55% of conversion of the reagents. After reaching a maximum, the two peaks slowly disappeared and were replaced by the benzothiazine signals.

IR Detection. Thiobenzophenone (**2a**, 2.46 mmol) was reacted with ketenimine **1o** (2.0 mmol) in CCl_4 (6 mL) under an argon atmosphere at room temperature. The reaction course was followed at intervals in a NaCl cell (0.5 mm) previously purged with argon. Bands in the 3370–3430-cm^{-1} region (NH) were observed immediately, which increased with time. After reaching a maximum, the bands slowly disappeared.

Reaction of *N*-Phenylmethylketenimine (1t) with Thiobenzophenone (2a). Thiobenzophenone **2a** (1.47 mmol) was reacted with ketenimine **1t** (1.30 mmol) in CCl_4 (10 mL) at 25 °C for 30 h. After evaporation of the solvent in vacuo, chromatographic workup of the reaction mixture on a preparative plate (silica, 1:2 CH_2Cl_2–petroleum ether) gave the following.

(a) 2-Ethyl-4,4-diphenyl-4*H*-3,1-benzothiazine (**6t**): 0.517 mmol; mp 126–128 °C (from methanol); ^{1}H NMR (CCl_4–C_6D_6, 0.4–0.15 mL) δ 1.00 (t, Me), 2.4 (g, CH_2, $J_{CH_2CH_3}$ = 7.57 Hz), 6.5–7.8 (m, 14 H, arom); mass spectrum, *m/e* 329 (M^+), 300, 166. Anal. Calcd. for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.25. Found: C, 80.13; H, 5.78; N, 4.29.

(b) 2-(Phenylimino)-3-methyl-4,4-diphenylthietane (**3t**): oil, 0.608 mmol; IR (CCl_4) 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 1 H), 5.04 (q, Me, J_{H-CH_3} = 7.3 Hz), 6.9–7.7 (m, 15 H, arom); mass spectrum, *m/e* 329 (M^+), 252, 194, 135, 131. The iminothietane **3t** was heated at 100–110 °C for 30 min in a sealed tube to give the thioamide **4t** *only*: 0.577 mmol; mp 210–213 °C (from methanol); IR (CCl_4) 3395 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.52 (br), 2.27 and 2.31 (Me), 6.58–7.5 (m, 5 H, arom), 8.44 and 9.06 (br, NH); ^{1}H NMR ($CDCl_3$, 100 MHz at 5 and 58 °C) the two sharp signals at δ 2.28 and 2.33 (0.31:1) of Me collapse in a broad signal at 2.30 ppm; mass spectrum, *m/e* 329 (M^+), 296, 252, 237, 193. Anal. Calcd. for $C_{22}H_{19}NS$: C, 80.20; H, 5.81; N, 4.25. Found: C, 80.24; H, 5.77; N, 4.23.

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Supplementary Material Available: Figures 1 (for **1p** and **2a**), 2 (for **1o** and **2a**), and 4 (for **1t** and **2a**) showing the time dependence of the NMR spectra of reaction mixtures and Table III listing the ^{1}H NMR and IR data of ketenimines **1a–k,m–q,t** (4 pages). Ordering information is given on any current masthead page.

Selectivity in Ketenimine–Thioketone Cycloadditions. 2. Kinetic and Theoretical Studies of the Mechanism of the 1,2- and 1,4-Cycloadditions[1]

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The kinetics of the thermal 1,2- and 1,4-cycloadditions of thiobenzophenones to ketenimines to give four-membered adducts, 2-iminothietanes, and six-membered adducts, 4*H*-3,1-benzothiazines, respectively, has been studied with respect to changes of solvents and substituents as well as at different temperatures. Both reactions show the typical features of concerted processes, viz., little change of rate with the polarity of the solvent, small activation energies, and large and negative activation entropies, but have some substantial differences. The results are consistent with a scheme where the products are formed from two site-selective additions of the reactants through independent pathways, very likely by concerted mechanisms. The formation of intermediates such as an open-chain zwitterion or a four-membered cycloadduct involving the C=N bond of the cumulene appears unlikely for both processes. Perturbational molecular reasonings coupled with SCF–MO computations indicate as most probable a [$_\pi 2_s + {}_\pi 2_a$] pericyclic process between the C=S bond of the thione and the C=C of the cumulene for the 1,2-cycloaddition and a [$_\pi 4_s + {}_\pi 2_s$] process between the C=S bond of the thione and the heterodiene system which consists of the C=N bond of the ketenimine and the C=C of the *N*-phenyl ring for the 1,4-cycloaddition.

In a previous article[3] we have described two different reaction modes which take place in the thermal cycloadditions of thioketones to ketenimines, namely, a 1,2-cycloaddition of the C=S bond of the thione across the C=C bond of the cumulene and a 1,4-cycloaddition across the conjugated system consisting of the C=N bond of the cumulene and the C=C of the *N*-aryl group (Scheme I). The extent of substitution at the terminal carbon of the cumulene and the nature of the group R on nitrogen turned out to be the structural factors directing the site of attack by the thione group. However, the intimate electronic factors which determine the outcome of these reactions, namely, their stereochemical course and mechanism(s), remained obscure. The clarification of these

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(3) A. Dondoni, A. Battaglia, and P. Giorgianni, *J. Org. Chem.*, accompanying paper in this issue.

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