Table II. Crystallography Data for Compound 7

formula	$C_{15}H_{15}O_5N_3$	V, Å^3	1487.8 (5)
M_r	317.3	Z	4
space group	$P2_1/c$	d(calcd), g cm^{-3}	1.42
a, Å	9.158 (1)	μ (Mo Kα), cm^{-1}	0.68
b, Å	14.214 (2)	no. of unique data	2579
c, Å	11.498 (2)	no. of data ($I \geq 3\sigma(I)$)	1897
β, deg	96.25 (4)	R	0.052
		R_w	0.070

ethyl acetate to give pure 6-(methoxycarbonyl)-5-phenylpyrrolo[1,2-*a*]-1,3,5-triazine-2,4-dione (8; 0.12 g, 12%); mp 279–280 °C dec; IR 3370 (NH), 1770, 1730, 1690 cm^{-1} (C=O). NMR, see Table I. Anal. Calcd for $C_{14}H_{11}N_3O_4$: C, 58.95; H, 3.89; N, 14.73. Found: C, 58.98; H, 4.16; N, 14.87.

The filtrate was evaporated and the residue chromatographed on silica gel (30 g). Elution with chloroform–petroleum ether and with chloroform gave small oily fractions which were not identified. Chloroform–ethyl acetate (8:2) eluted a solid which was crystallized from methanol to give 6,9-dihydro-6-methoxy-9-(methoxycarbonyl)-3-phenylpyrrolo[1,2-*a*]-1,3,5-triazine-2,4-dione (7): 0.39 g (35%); mp 173–174 °C; IR 3240 (NH), 1750, 1725, 1665 cm^{-1} (C=O). NMR [$(CD_3)_2SO$] δ 3.54, 3.80 (s, 3 H each, OCH_3), 5.73 (d J = 6.2 Hz, 1 H), 5.92 (d, J = 1.6 Hz, 1 H), 6.04 (dd, 1 H), 7.24–7.47 (m, 5 H), 7.42 (s, 1 H, exchangeable with D_2O); mass spectrum, m/e (relative intensity) 258 (100, $M^+ - CH_3COO$), 226 (10), 139 (65), 119 (30), 107 (27), 96 (27). Anal. Calcd for $C_{15}H_{15}N_3O_5$: C, 56.78; H, 4.77; N, 13.24. Found: C, 56.86; H, 4.88; N, 12.89.

(b) In Dichloromethane. Irradiation of a solution of 1 g of **3** in 450 mL of dichloromethane was nearly complete after 8 h (UV monitoring). The solution was evaporated, and chloroform (50 mL) was added. Filtration and trituration with ethyl acetate yielded 8-(methoxycarbonyl)-3-phenylpyrrolo[1,2-*a*]-1,3,5-triazine-2,4-dione (**10**): 0.4 g (40%); mp 299–300 °C dec; IR 3200 (NH), 1750, 1700, 1680 cm^{-1} (C=O); NMR, see Table I; mass spectrum, m/e (relative intensity) 285 (100, M^+), 254 (8), 166 (17), 135 (15), 124 (7), 119 (25), 107 (9), 91 (17). Anal. Calcd for $C_{14}H_{11}N_3O_4$: C, 58.95; H, 3.89; N, 14.73. Found: C, 58.85; H, 4.01; N, 14.42. Chromatography of the filtrate did not give identifiable products.

X-ray Crystal Structure Analysis.[16] Data were measured on a PW1100/20 Philips four-circle computer-controlled diffractometer. Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by at least-squares fit of 24 centered reflections in the range of $10 \leq \theta \leq 13°$. Intensity data were collected by using the ω–2θ technique to a maximum 2θ of 50°. The scan width, $\Delta\omega$, for each reflection was 1° with a scan time of 20 s. Background measurements were made for other 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All nonhydrogen atoms were found by using the results of the MULTAN direct method analysis.[17] After several cycles of refinements[18] the positions of the hydrogen atoms were calculated and added with a constant isotropic temperature factor of 0.5 Å^2 to the refinement process. Refinement proceeded to converge by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight, w, is $\sigma(|F_o|)^{-2}$. A final difference fourier synthesis map showed several peaks less than 0.1 e Å^{-3} scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum||F_o| - |F_c||\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]1/2$, are presented with other pertinent crystallographic data in Table II.

Registry No. 1, 25991-27-9; 2, 4233-33-4; 3, 88180-59-0; 4, 88200-31-1; 5, 88180-60-3; 7, 88180-61-4; 8, 88180-62-5; 9, 88180-63-6; 10, 88180-64-7.

Supplementary Material Available: Complete X-ray data of compound 7, including atomic positional and thermal parameters, bond distances, and angles (5 pages). Ordering information is given on any current masthead page.

(16) We thank Dr. S. Cohen for his help with this analysis.

(17) Main, P.; Hull, S. W.; Lessinger, L.; Germain, G.; DeClercq, J. P.; Woolfson, M. M. "MULTAN 78. A System of Computer Programs for The Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and Louvain, Belgium; 1978.

(18) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University of Jerusalem by using the SHELX 1977 structure-determination package.

Additions and Cycloadditions of Ketenes to 1,3-Thiazole and Its Alkyl Derivatives

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1,3-Thiazole and its 4-methyl and 5-methyl derivatives react with *tert*-butylcyanoketene (TBCK) and dichloroketene (DCK), affording Michael-type addition products at C_2, viz., 2-acylthiazoles, and 2:1 cycloadducts (with TBCK only) which proved by X-ray analysis to be bicyclic systems constituted by a thiazoline and a piperidine-1,3-dione ring condensed across the C–N bond. 2-Ethyl- and 2-isopropyl-1,3-thiazole undergo acylation by DCK at the C_α of the alkyl chain. The latter thiazole gives also a 2:1 cycloadduct, which X-ray analysis showed to be a bicyclic system constituted by a thiazoline and an oxazinone ring condensed across the C–N bond. A mechanism is envisaged involving the quaternization of the thiazole nitrogen by the ketene to give an *N*-thiazolium enolate system which owing to proton exchange between the C_2 of the ring or the C_α of the 2-alkyl chain and its enolate portion is in equilibrium with an *N*-acylthiazolium ylide or zwitterion, respectively. Subsequent reactions of these active intermediates with the ketene lead to the final products.

Relatively few examples of synthetically valuable reactions leading to carbon–carbon bond formation at the thiazole ring are to be found in the literature.[1] We have recently reported reactions of thiazoles with various C-

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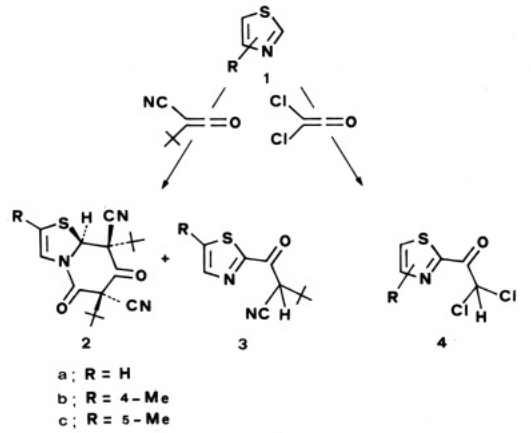
Table I. Reactions of Ketenes with 1,3-Thiazoles 1

thiazole	ketene[a]	molar ratio of ketene/1	reaction conditions time (h)/temp (°C)/solvent[b]	products (yield %)[c]
1a (R = H)	TBCK	2	3/rt/Bz	2a (15)
1a	TBCK	3	3/rt/Bz	2a (50)
1a	TBCK	2	24/reflux/Bz	3a (47)
1a	TBCK	4	20/reflux/Bz	3a (50)
1a	DCK	2	5/rt/He	4a (43)
1b (R = 4-Me)	DCK	2	5/rt/He	4b (42)
1c (R = 5-Me)	TBCK	3	3/rt/Bz	2c (35)
1c	TBCK	2	20/reflux/Bz	3c (36)
1c	DCK	2	3/rt/He	4c (40)
1d (R = 2-C_2H_5)	DCK	2	5/rt/He	12 (95)
1e (R = 2-*i*-C_3H_7)	DCK	2	3.5/rt/He	13 (45), 14 (10)

[a] TBCK = *tert*-butylcyanoketene; DCK = dichloroketene. [b] rt = room temperature; Bz = benzene; He = *n*-hexane. [c] Yields refer to products isolated and are calculated with respect to thiazole.

Scheme I



electrophiles[2] and observed that ketenes are efficient reactants for the above purpose. Reactions were based on the directing and activating effect of the dimethylamino group[2a] or the mobility of the silyl group[2c] in the thiazole ring. We have now observed other facile reactions between thiazoles and ketenes which appear to involve the initial activation of the heterocycle by quaternization of its nitrogen by the ketene.

Results and Discussion

(a) Reactions of 1,3-Thiazole (1a) and 4-Methyl- (1b) and 5-Methyl-1,3-thiazole (1c). Addition of 1,3-thiazole (**1a**) to an excess of *tert*-butylcyanoketene (TBCK) in benzene at room temperature gave the 2:1 cycloadduct **2a** (Scheme I) in different yields depending on the molar ratio of the reactants[3] (Table I). Compound **2a** slowly decomposed in solution[4] but showed enough stability in the solid state for full characterization by X-ray diffraction analysis (Figure 1). This showed that **2a** is a bicyclic system constituted by a six-membered 1,3-dione ring condensed across the C–N bond of a thiazoline ring. Formation of **2a** appeared to involve TBCK as a monomer since treatment of **1a** with the dimer of TBCK (generated in situ[5] from the ketene and triethylamine) gave 1,3-di-*tert*-butyl-1,3-dicyanoallene, viz, the product of the thermal fragmentation of the dimer of TBCK.[2a] The regioselectivity of the addition of TBCK across the C=N bond of **1a** affording a 1,3-dione system constitutes an unusual mode of ring closure of this ketene since δ-lactone systems are normally obtained in additions across the C=C bond of another thiazole[2a] and across the C=N bond of thiazolines[6,7] and thiazines.[7] When **1a** and excess TBCK were reacted in refluxing benzene (Table I) and the reaction mixture quenched with diluted HCl, the only isolated product in ca. 47% yield was the Michael-type 1:1 adduct 2-acylthiazole **3a**. The yield of **3a** was substantially unaffected by the molar ratio of the reactants. Identical reactions were observed between 5-methyl-1,3-thiazole (**1c**) and TBCK (Table I) whereas the 4-methyl derivative **1b** is unreactive both at room temperature and in refluxing benzene.

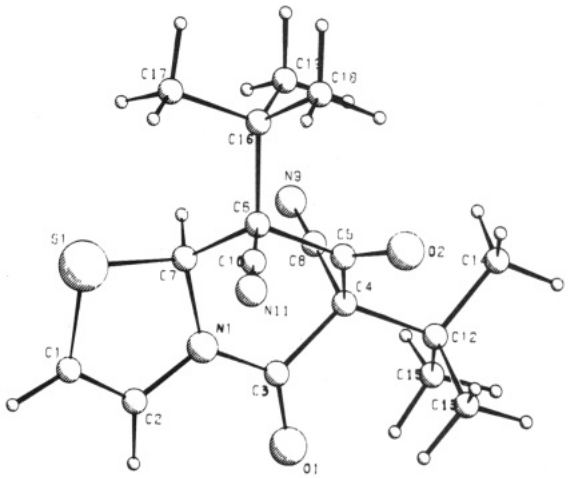


Figure 1. Perspective view of cycloadduct **2a**.

Dichloroketene (DCK) reacted with all three thiazoles **1a**, **1b**, and **1c**[8] whereas chlorocyanoketene and diphenylketene were inert. DCK reacted smoothly at room temperature to give exclusively the corresponding 2-acylthiazoles **4** in satisfactory yields (Scheme I, Table I).

(1) "The Chemistry of Heterocyclic Compounds—Thiazole and its Derivatives"; Metzger, J., Ed.; Wiley: New York, 1979; Vol. 34.

(2) (a) Dondoni, A.; Medici, A.; Venturoli, C.; Forlani, L.; Bertolasi, V. *J. Org. Chem.* **1980**, *45*, 621. (b) Medici, A.; Pedrini, P.; Venturoli, C.; Dondoni, A. *Ibid.* **1981**, *46*, 2790. (c) Medici, A.; Pedrini, P.; Dondoni, A. *J. Chem. Soc. Chem. Commun.* **1981**, 655.

(3) A molar ratio of [TBCK]:[1a] = 4 gave a 40% yield of **2a** and 6% of **3a**, thus indicating a dependence of product distribution on reactant concentrations.

(4) The yield of **2a** isolated in an experiment (molar ratio of [TBCK]:[1a] = 2) where the reaction time was prolonged to 24 h was only 8%.

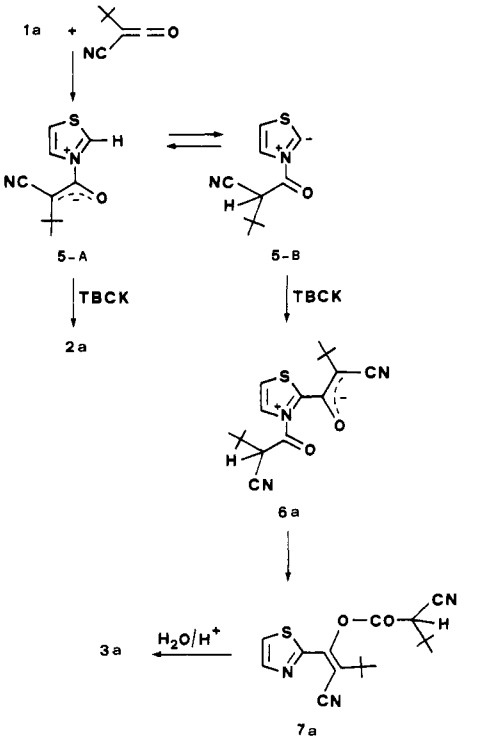
(5) Moore, H. W.; Duncan, W. G. *J. Org. Chem.* **1973**, *38*, 156.

(6) Moore, H. W.; Hernandez, L., Jr.; Kunert, D. M.; Mercer, F.; Sing, A. *J. Am. Chem. Soc.* **1981**, *103*, 1769.

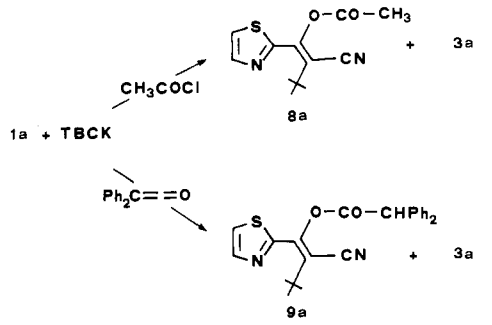
(7) Schaumann, E.; Mrotzek, H.; Assmann, F. *Liebigs Ann. Chem.* **1979**, 334.

(8) DCK was formed by the in situ dehydrohalogenation of dichloroacetyl chloride by triethylamine. Details on the order of reactants addition are given in the Experimental Section. Generation of DCK from trichloroacetyl chloride and Zn did not produce appreciable amounts of products but thiazole precipitated as a complex with $ZnCl_2$.

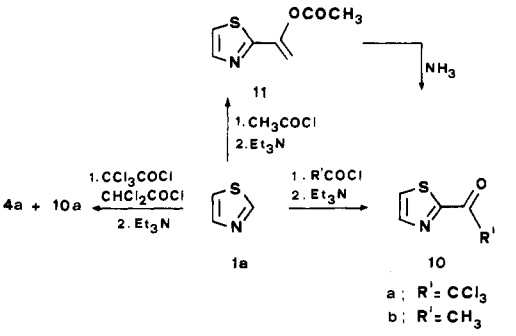
Scheme II



Scheme III



Scheme IV



Cycloadducts analogous to **2** could not be isolated from reactions of DCK with the above thiazoles.

A consistent interpretation of these observations is given in Scheme II which for simplicity refers to the TBCK–**1a** system. The reaction initiates with the quaternization of the nitrogen of the thiazole by the ketene[9] to give the zwitterion **5-A** which equilibrates with the *N*-acylthiazolium ylide **5-B**. The driving force for the hydrogen migration from the C_2 of the ring to the enolate portion of **5-A** is the stability of the ylide **5-B**.[10] The *N*-thiazolium ylide structure has been involved in the H/D exchange of thiazolium ions[11] and in their catalytic activity of the umpolung nucleophilic additions of carbonyl compounds to olefins[12] and is well-known to be responsible for biochemical properties of thiamin.[13] The attack by a second molecule of ketene at the enolate portion of **5-A** and cyclization give the bicyclic system **2a** (route A) whereas attack at the negative center of the ylide **5-B** leads to another zwitterion **6a** (route B) that evolves into the enol ester **7a**, a rather unstable species which was detected by the NMR spectrum of the reaction mixture. On acid hydrolysis, **7a** gives the ketone **3a** as a stable and isolable product. The positioning between the two concurrent pathways appears temperature dependent[14] as Route A was followed at low temperature and Route B at high temperature. The enol ester **7a** can be viewed to arise from the zwitterion **6a** through exchange of the acyl group between the ring nitrogen and the C_2 enolate group. The conversion **6** → **7** appeared to be very rapid and probably intramolecular since incorporation of deuterium was not detected in **7a** or in **3a** on quenching the reaction with D_2O. However, evidence for the formation of **6a** came from reactions carried out in the presence of appropriate trapping agents such as acetyl chloride and diphenylketene (Scheme III) since, in addition to the ketone **3a**, the 2-thiazolyl enol esters **8a** and **9a** were obtained as stable products.

Very likely reactions of DCK also fit in Scheme II although the presence of triethylamine employed for the ketene generation may give rise to a more complex system. For instance, the base may catalyze the conversion of the *N*-thiazolium enolate system into the *N*-acylthiazolium ylide and favor the former over the latter to an extent that the 2:1 cycloadduct across the C=N bond is not formed. Moreover, a rapid base-catalyzed deacylation of a zwitterion intermediate analogous to **6a** would give directly the 2-acylthiazole **4** without the intervention of an enol ester of type **7a**. In fact, NMR spectra revealed that ketone **4** was already present in the reaction mixture before its treatment with dilute hydrochloric acid.

The peculiarity of the thiazole–ketene system became more evident when reactions of 1,3-thiazole (**1a**) with acyl chlorides were examined (Scheme IV). Trichloroacetyl chloride reacted only after addition of triethylamine to give the corresponding 2-acylthiazole **10**, whereas acetyl chloride under identical conditions gave the 2-thiazolyl enol ester **11**. A 1:1 mixture of trichloro- and dichloroacetyl chloride gave the ketones **10a** and **4a**. The formation of **10a** and **10b** can be viewed as a *base-catalyzed* electrophilic substitution at C_2 of the thiazole ring. This should involve the initial quaternization of nitrogen by the acyl chloride

(9) Molecular orbital calculations show that the formation of **5-A** is consistent with the total charge distribution on the reactants, since the central carbon of the ketene bears the largest positive charge (ref 2) and the nitrogen of the thiazole bears the largest negative charge (M. Guerra, private communication). On the other hand a direct electrophilic attack of ketene on C_2 is not consistent with both an orbital and charge-density control.

(10) The high stability of the C_2 thiazolium ylides has been interpreted to be due to the ability of sulfur to estabilize the negative charge by d-π overlap. (Breslow, R. *Ann. N. Y. Acad. Sci.* **1962**, *98*, 445. Haake, P.; Bausher, L. P.; Miller, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1113). This belongs to the general problem on the stability of α-thioanions. For a recent work, see: Wolfe, S.; Schirlin, D. *Tetrahedron Lett.* **1980**, *21* 827 and references cited therein.

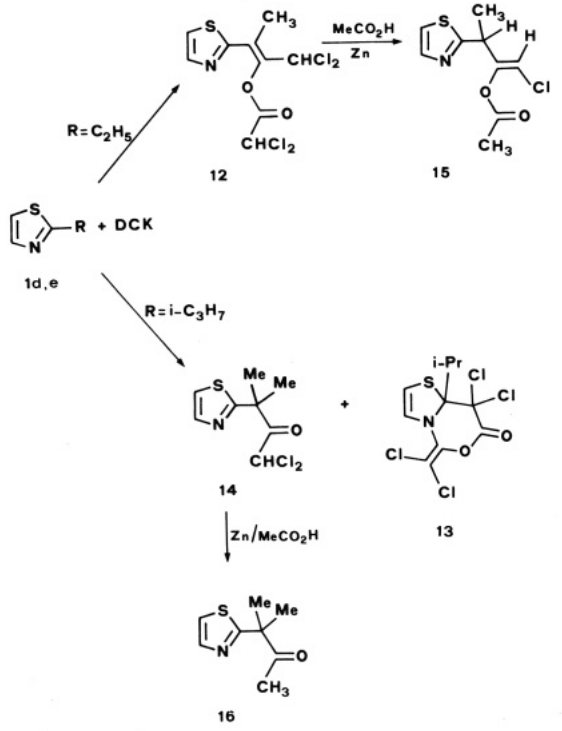
(11) Haake, P. *Tetrahedron Lett.* **1981**, *22*, 2939.

(12) Stetter, H.; Mertens, A. *Chem. Ber.* **1981**, *114*, 2497. Stetter, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 81. *Ibid.* **1976**, *15*, 639.

(13) Breslow, R.; McNelis, E. *J. Am. Chem. Soc.* **1959**, *81*, 3080 and earlier papers.

(14) Reactions followed by NMR showed that at 25 °C the 2:1 cycloadduct **2a** was the exclusive product, at 48.7 °C **2a** and the enol ester **7a** were formed in ca. 6:1 ratio, and at 80 °C compound **7a** was the only detectable product.

Scheme V



and deprotonation of C_2 to give the *N*-acylthiazolium ylide as a reactive intermediate. The presence of a base is a prerequisite for this reaction to occur. On the other hand, the formation of **11** and **4a** appears to involve the initial dehydrohalogenation of the acyl chloride to ketene and therefore it falls in the Scheme of the ketene–thiazole reaction.

(b) Reactions of 2-Ethyl-1,3-thiazole (1d) and 2-Isopropyl-1,3-thiazole (1e). TBCK was inert toward 2-alkylthiazoles **1d** and **1e**, whereas DCK reacted smootly at room temperature at the alkyl chain R to give different adducts depending on R (Scheme V). From the reaction of DCK with 2-ethyl-1,3-thiazole (**1d**), the product isolated in almost quantitative yield (Table I) was the 2-thiazolyl enol ester **12**, whereas with the 2-isopropyl derivative **1e** the products were the 2:1 cycloadduct **13** and the ketone **14** in ca. a 4.5:1 ratio. The structures of adducts **12** and **14** were consistent with their spectroscopic characteristics and their conversion into products **15** and **16**, respectively, by reductive dechlorination with Zn/CH_3COOH. The structure of cycloadduct **13**, whose δ-lactone ring was supported by a strong IR band at 1800 cm^{-1} (O–CO), was assigned from X-ray single-crystal analysis (Figure 2). This structural elucidation was necessary since chemical transformations of **13**, such as opening reactions of the lactone ring, could be ambiguous.[15] Moreover, this mode of cyclization of DCK is quite rare as it has the only precedent in the reaction with 2-aryloxazolines.[16] This regiochemistry appears characteristic of additions of DCK to heterocyclic C=N bonds since with acyclic imines the products were the four-membered ring azetidinones.[17]

Also the formation of products **12–14** can be explained in the light of an autocatalytic process which initiates with the quaternization of the thiazole nitrogen by the ketene (Scheme VI). This leads to the zwitterion **17-A** which equilibrates with **17-B** by removal of the hydrogen from

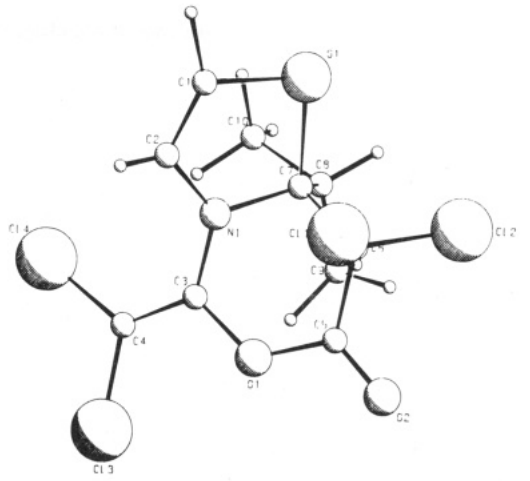
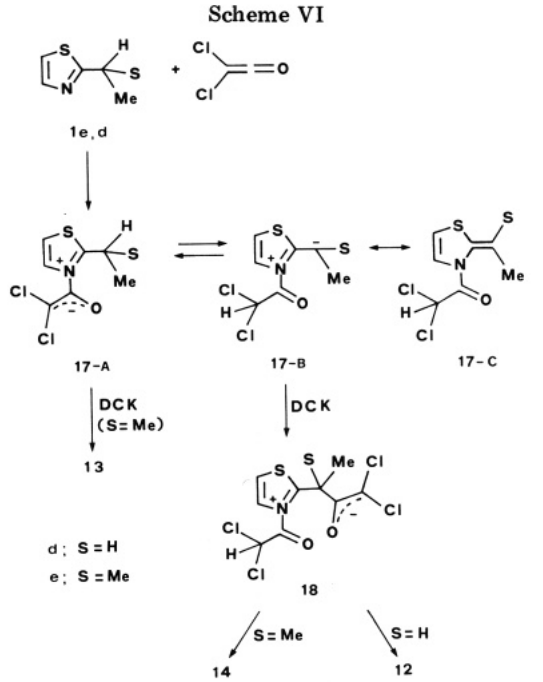


Figure 2. Perspective view of cycloadduct **13**.

Scheme VI



C_α of the alkyl chain.[18] The high energy content of **17-B** due to the separation of charges would be diminished in structure **17-C**, thus providing a stabilization of the system. Attack of a second molecule of DCK at the N-enolate portion of **17-A** and regioselective ring closure leads to the 2:1 cycloadduct **13**. On the other hand, attack on the carbanion centre of **17-B** gives an assumed intermediate **18** which depending on the substituent S evolves toward **14** and **12**. In fact for S = H, the intermediate **18d**, owing to the contribution of tautomeric forms, is stable enough to undergo the conversion of the enolate group into the enol ester probably via intramolecular migration of the *N*-acyl group, whereas for S = Me the corresponding intermediate **18e** does not survive enough and gives the ketone **14** through removal of the *N*-acyl group by action of triethylamine. Finally, the group S appears to control the product distribution at a level which preceeds the formation of **18**. The exclusive formation of **12** from 2-ethylthiazole **1d** and by contrast the overwhelming amount of **13** over **14** from 2-isopropyl derivative **1e** suggest a

(15) It has already been pointed out (ref 16) that ring opening by $MeO^-/MeOH$ of a 1,3-dione or a δ-lactone system could give in principle the same product.

(16) Johnson, P.; Caldwell, J. W. *J. Org. Chem.* **1973**, *38*, 4465.

(17) Duran, F.; Ghosez, L. *Tetrahedron Lett.* **1970**, 245.

(18) Very likely, also in this case, the generation of the carbanionic center as well as other tautomeric processes are catalyzed by triethylamine used for the in situ generation of the ketene.

considerable destabilization of 17-B–17-C when hydrogen is replaced by methyl.

Conclusions

The reactions of 1,3-thiazole (**1a**) and some alkyl derivatives with two representative ketenes such as TBCK and DCK lead to open-chain and cyclic adducts which bear functionalities suitable for further synthetic elaborations. It is suggested that the common feature of these reactions is the quaternization of the thiazole nitrogen by the ketene. This results in the formation of an *N*-thiazolium enolate system which by deprotonation of the C_2 of the ring or of the C_α of the 2-alkyl chain is in equilibrium with an *N*-acylthiazolium ylide or zwitterion. This behavior is unlike that of other thiazolium systems which require the assistance of an external base for the generation of the carbanionic centre.[11,12] On the other hand, it shows some similarity with thiamin pyrophosphate, the coenzyme (Vitamin B_1) for α-ketoacid decarboxylase and transketolase, which has been suggested[19] to display its activity through a *N*-thiazolium ylide structure and the participation of the *N*-methyleneaminopyrimidine portion in proton migration steps.

Experimental Section

General Comments. All melting points are uncorrected. ^1H and ^{13}C NMR spectra (in $CDCl_3$) were obtained on a 80-MHz WP80 Bruker spectrometer. Chemical shifts are given in ppm from Me_4Si. Mass spectra were recorded at 70 eV on a Varian Mat 112 high-resolution mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 297 grating spectrometer. All experiments were carried out under N_2 and with freshly distilled and dried solvents.

Starting Materials. 1,3-Thiazole (**1a**), 4-methyl-1,3-thiazole (**1b**), and acyl chlorides were commercially available. 5-Methyl-1,3-thiazole[20] (**1c**) (bp 141–142 °C), 2-ethyl-1,3-thiazole[21] (**1d**) (bp 158 °C), and 2-isopropyl-1,3-thiazole[22] (**1e**) (bp 44–45 °C (12 mmHg)) were prepared by literature methods. *tert*-Butylcyanoketene (TBCK) was generated in situ before each experiment by thermal decomposition of the proper azido quinone.[23] Dichloroketene (DCK) was generated in situ by dehydrochlorination of dichloroacetyl chloride with triethylamine.[24] Diphenylketene (DPK) was prepared according to the literature procedure.[25]

Reaction of 1,3-Thiazole (1a) with TBCK. (A) At Room Temperature. A solution of 340 mg (4 mmol) of thiazole **1a** in 40 mL of benzene was added with stirring to 2 equiv of TBCK in the same amount of solvent. After 3 h the solvent was removed under vacuum and diethyl ether was added to the oily residue to induce the crystallization of the cycloadduct **2a** (198 mg, 15%): mp 152–154 °C (from *n*-hexane); IR (KBr) 2230 (C≡N), 1745 (C=O), 1690 (N—C=O), 1355 cm^{-1}; ^1H NMR δ 6.82 (d, 1, =CH, J = 5 Hz), 6.75 (s, 1, >CH), 5.90 (d, 1, =CH, J = 5 Hz), 1.38 (s, 9, CMe_3), 1.30 (s, 9, CMe_3); ^{13}C NMR δ 188.5 (s), 154.4 (s), 121.4 (d), 114.4 (s), 112.8 (s), 108.7 (d), 66.4 (s), 63.2 (s), 62.4 (d), 38.9 (s), 38.7 (s), 27.9 (q), 26.5 (q); mass spectrum, m/e (relative intensity) 331 (M^+, 8), 275 (10), 260 (6), 246 (8), 208 (35), 193 (20), 123 (20), 108 (50), 86 (100), 57 (50).

Anal. Calcd for $C_{17}H_{21}N_3O_2S$: C, 61.61; H, 6.39; N, 12.68; S, 9.67. Found: C, 61.48; H, 6.35; N, 12.60; S, 9.70.

(B) In Refluxing Benzene. A solution of 340 mg (4 mmol) of thiazole **1a** in 40 mL of benzene was added to a refluxing solution of TBCK (8 mmol) in 40 mL of the same solvent. After 20 h the solvent was removed under vacuum and the crude mixture was chromatographed (silica, 7:3 cyclohexane:ethyl ether) to give 391 mg (47%) of the 2-acylthiazole **3a**: mp 36–37 °C (from *n*-hexane); IR (KBr) 2230 (C≡N), 1695 (C=O), 1470, 1380 cm^{-1}; ^1H NMR δ 8.1 (d, 1, =CH, J = 2.9 Hz), 7.85 (d, 1, =CH, J = 2.9 Hz), 5.1 (s, 1, >CH), 1.18 (s, 9, CMe_3); mass spectrum, m/e (relative intensity) 208 (M^+, 2), 193 (6), 152 (46), 124 (10), 112 (100), 84 (16).

Anal. Calcd for $C_{10}H_{12}N_2OS$: C, 57.67; H, 5.81; N, 13.45; S, 15.39. Found: C, 57.60; H, 5.84; N, 13.41; S, 15.43.

Reaction of 5-Methyl-1,3-thiazole (1c) with TBCK. (A) At Room Temperature. A solution of 396 mg (4 mmol) of the thiazole (**1c**) in 40 mL of benzene was added with stirring to a 3-fold excess of TBCK in the same amount of solvent. After 3 h the solvent was removed under vacuum and diethyl ether was added to the oily residue to induce the crystallization of the cycloadduct **2c** (483 mg, 35%): mp 157–159 °C (from *n*-hexane); IR (KBr) 2220 (C≡N), 1745 (C=O), 1685 (N—C=O), 1360 cm^{-1}; ^1H NMR δ 6.74 (s, 1, >CH), 6.58 (q, 1, =CH, J = 1.25 Hz), 1.97 (d, 3, CH_3, J = 1.25 Hz), 1.37 (s, 9, CMe_3), 1.29 (s, 9, CMe_3).

Anal. Calcd for $C_{18}H_{23}N_3O_2S$: C, 62.58; H, 6.71; N, 12.16; S, 9.28. Found: C, 62.51; H, 6.68; N, 12.20; S, 9.32.

(B) In Refluxing Benzene. A solution of 340 mg (4 mmol) of **1c** in 40 mL of benzene was added to a refluxing solution of TBCK (8 mmol) in 40 mL of the same solvent. After 20 h the solvent was removed under vacuum and the mixture was chromatographed (silica, 7:3 cyclohexane:ethyl ether) to give 320 mg (36%) of the 2-acylthiazole **3c**: colorless oil; IR (film) 2220 (C≡N), 1690 (C=O), 1400 cm^{-1}; H NMR δ 7.72 (q, 1, =CH, J = 0.7 Hz), 5.01 (s, 1, >CH), 2.6 (d, 3, CH_3, J = 0.7 Hz), 1.16 (s, 9, CMe_3).

Anal. Calcd for $C_{11}H_{14}N_2OS$: C, 59.43; H, 6.35; N, 12.60; S, 14.42. Found: C, 59.40; H, 6.37; N, 12.62; S, 14.39.

Reactions of 1,3-Thiazole (1a), 4-Methyl-1,3-thiazole (1b), and 5-Methyl-1,3-thiazole (1c) with DCK. General Procedure. A solution of 2 equiv of dichloroacetyl chloride in 150 mL of *n*-hexane was slowly added over 4 h at room temperature to a stirred solution of the proper thiazole (1 equiv) and triethylamine (2 equiv) in 200 mL of *n*-hexane. Workup of the reaction mixture (aqueous $NaHCO_3$, anhydrous Na_2SO_4, evaporation of the solvent) and chromatography (silica, 7:3 cyclohexane:ethyl ether) gave the 2-acylthiazoles **4** showing the following.

2-(Dichloroacetyl)-1,3-thiazole (**4a**) (43%): mp 55–56 °C (from *n*-hexane); IR (KBr) 1710 (C=O) cm^{-1}; ^1H NMR δ 8.12 (d, 1, =CH, J = 3.12 Hz), 7.87 (d, 1, =CH, J = 3.12 Hz), 7.28 (s, 1, >CH); mass spectrum, m/e (relative intensity) 195 (M^+, 8), 112 (100), 84 (21).

Anal. Calcd for $C_5H_3Cl_2NOS$: C, 30.64; H, 1.54; N, 7.15; S, 16.35. Found: C, 30.66; H, 1.55; N, 7.10; S, 16.37.

2-(Dichloroacetyl)-4-methyl-1,3-thiazole (**4b**) (42%): oil; IR (film) 1710 (C=O) cm^{-1}; ^1H NMR δ 7.45 (q, 1, =CH, J = 0.8 Hz), 7.29 (s, 1, >CH), 2.56 (d, 3, CH_3, J = 0.8 Hz); mass spectrum, m/e (relative intensity) 209 (M^+, 10), 126 (100), 98 (10).

Anal. Cald for $C_6H_5Cl_2NOS$: C, 34.31; H, 2.40; N, 6.67; S, 15.26. Found: C, 34.29; H, 2.44; N, 6.68; S, 15.23.

2-(Dichloroacetyl)-5-methyl-1,3-thiazole (**4c**) (40%): mp 47–49 °C (from *n*-hexane); IR (KBr) 1700 (C=O) cm^{-1}; ^1H NMR δ 7.78 (q, 1, =CH, J = 1.1 Hz), 7.27 (s, 1, >CH), 2.64 (d, 3, CH_3, J = 1.1 Hz); mass spectrum, m/e (relative intensity) 209 (M^+, 9), 126 (100), 98 (13).

Anal. Calcd for $C_6H_5Cl_2NOS$: C, 34.31; H, 2.40; N, 6.67; S, 15.26. Found: C, 34.35; H, 2.39; N, 6.62; S, 15.28.

Reaction of 1,3-Thiazole (1a) with TBCK and Acetyl Chloride. A solution of 340 mg (4 mmol) of the thiazole **1a** in 40 mL of benzene was added to a refluxing solution of TBCK (8 mmol) and acetyl chloride (8 mmol) in the same amount of solvent. After 20 h the solvent was removed under vacuum and the crude mixture was chromatographed (silica, 7:3 cyclohexane:ethyl ether) to give 25 mg (3%) of 2-acylthiazole **3a** and 45 mg (4.5%) of 2-thiazolyl enol ester **8a**. The enol ester **8a** showed the following: mp 86–88 °C (from *n*-hexane); IR (KBr) 2200 (C≡N), 1775 (C=O), 1585 (C=C) 1370, 1190 cm^{-1}; ^1H NMR δ 7.9 (d, 1, =CH, J = 3.2 Hz), 7.5 (d, 1, =CH, J = 3.2 Hz), 2.34 (s, 3, $COCH_3$), 1.38 (s, 9, CMe_3); mass spectrum, m/e (relative intensity) 208 (M^+ –

(19) Schellenberger, A. *Ann. N. Y. Acad. Sci.* **1982**, *378*, 51. Schmidt, R. R. *Lect. Heterocycl. Chem.* **1978**, *4*, 97. Suppl. J. Heterocycl. Chem. 1978, 15.
(20) Poite, M.; Metzger, J. *Bull. Soc. Chim. Fr.* **1962**, 2078.
(21) Collet, R.; Gallo, R.; Metzger, J. *Bull. Soc. Chim. Fr.* **1967**, 4499.
(22) Dubs, P.; Pesaro, M. *Synthesis* **1974**, 294.
(23) Weyler, W. Jr.; Duncan, W. G.; Liewen, M. B.; Moore, H. W. *Org. Synth.* **1976**, *55*, 32.
(24) Stevens, H. C.; Reich, D. A.; Brandt, D. R.; Fountain, K. R.; Gaughan, E. J. *J. Am. Chem. Soc.* **1965**, *87*, 5257.
(25) Taylor, E. C.; McKillop, A.; Hawks, G. H. *Org. Synth.* **1973**, *52*, 36.

42, 23), 193 (60), 142 (50), 126 (77), 112 (50), 110 (40), 43 (100).

Anal. Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19; S, 12.81. Found: C, 57.55; H, 5.67; N, 11.21; S, 12.83.

Reaction of 1,3-Thiazole (1a) with TBCK and DPK. A solution of 340 mg (4 mmol) of **1a** in 40 mL of benzene was added to a refluxing solution of TBCK (8 mmol) and DPK (8 mmol) in the same amount of benzene. After 20 h the solvent was distilled under vacuum and the crude mixture was chromatographed (silica, 7:3 cyclohexane:ethyl ether) to give 386 mg (24%) of **9a** and 183 mg (22%) of **3a**. The enol ester **9a** showed the following: mp 110–111 °C (from *n*-hexane); IR (KBr) 2200 (C≡N), 1775 (C=O), 1600, 1120, 1080 cm^{-1}; ^1H NMR δ 7.85 (d, 1, =CH, J = 3.2 Hz), 7.4 (d, 1, =CH, J = 3.2 Hz), 7.34 (m, 10, ArH), 5.32 (s, 1, >CH), 1.16 (s, 9, CMe_3); mass spectrum, m/e (relative intensity) 208 (M^+ – 194, 14), 194 (19), 167 (100), 165 (50), 152 (31), 126 (22), 112 (45), 85 (45), 83 (45).

Anal. Calcd for $C_{24}H_{22}N_2O_2S$: C, 71.61; H, 5.51; N, 6.96; S, 7.96. Found: C, 71.66; H, 5.53; N, 6.90; S, 7.91.

Reaction of 2-Ethyl-1,3-thiazole (1d) with DCK. A solution of 1.19 g (8 mmol) of dichloroacetyl chloride in 150 mL of *n*-hexane was added over 5 h to a stirred solution of 452 mg (4 mmol) of **1d** and 808 mg (8 mmol) of triethylamine in 200 mL of the same solvent. The reaction mixture was washed with aqueous $NaHCO_3$, the organic layer was dried over Na_2SO_4, and the solvent was evaporated under vacuum. After treating the oily residue with *n*-hexane, the solution was stored in the refrigerator overnight to induce the crystallization of the adduct **12** (1.06 g, 80%): mp 94–95 °C (from *n*-hexane); IR (KBr) 1780 (C=O), 1630, 1300, 1130 cm^{-1}; ^1H NMR δ 7.9 (d, 1, =CH, J = 3.3 Hz), 7.45 (d, 1, =CH, J = 3.3 Hz), 6.8 (s, 1, >CH), 6.35 (s, 1, >CH), 2.45 (s, 3, =C—CH_3); ^{13}C NMR δ 163 (s), 162.1 (s), 143.8 (d), 140.0 (s), 121.1 (d), 120.8 (s), 66.0 (d), 64.5 (d), 17.1 (q); mass spectrum, m/e (relative intensity) 333 (M^+, 25), 298 (28), 250 (60), 223 (85), 140 (100), 123 (80), 110 (45), 84 (60), 83 (65), 58 (60).

Anal. Calcd for $C_9H_7Cl_4NO_2S$: C, 32.27; H, 2.11; N, 4.18; S, 9.57. Found: C, 32.25; H, 2.13; N, 4.22; S, 9.60.

Reaction of 2-Isopropyl-1,3-thiazole (1e) with DCK. A solution of 1.19 g (8 mmol) of dichloroacetyl chloride in 150 mL of *n*-hexane was slowly added over 4 h to a stirred solution of 508 mg (4 mmol) of **1e** and 808 mg (8 mmol) of triethylamine in 200 mL of the same solvent. The reaction mixture was washed with aqueous $NaHCO_3$, the organic layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under vacuum. The residue was chromatographed (Florisil, 7:3 cyclohexane:ethyl ether) to give 624 mg (45%) of the 2:1 cycloadduct **13**, 66 mg (7%) of the ketone **14**, and 101 mg (20%) of the unreacted thiazole **1e**.

The compound **13** showed the following: mp 84–86 °C (from *n*-hexane); IR (KBr) 1800 (C=O), 1650, 1350, 1170 cm^{-1}; ^1H NMR δ 6.35 (d, 1, =CH, J = 4.8 Hz), 5.5 (d, 1, =CH, J = 4.8 Hz), 2.4 (m, 1, $CH(CH_3)_2$, J = 6.8 Hz), 1.35 (d, 3, CH_3, J = 6.8 Hz), 1.1 (d, 3, CH_3, J = 6.8 Hz); mass spectrum, m/e (relative intensity) 347 (M^+, 3), 304 (6), 269 (3), 237 (7), 202 (26), 126 (100), 112 (71), 85 (24), 83 (26).

Anal. Calcd for $C_{10}H_9Cl_4NO_2S$: C, 34.41; H, 2.60; N, 4.01; S, 9.19. Found: C, 34.37; H, 2.62; N, 4.03; S, 9.17.

,The ketone **14** showed the following: oil; IR (film) 1740 (C=O), 1490, 1060, 1025, 790 cm^{-1}; ^1H NMR δ 7.85 (d, 1, =CH, J = 3.2 Hz), 7.4 (d, 1, =CH, J = 3.2 Hz), 6.6 (s, 1, >CH), 1.8 (s, 6, $2CH_3$); ^{13}C NMR δ 196.5 (s), 172.0 (s), 143.3 (d), 120.2 (d), 65.2 (d), 52.7 (s), 25.9 (q); mass spectrum, m/e (relative intensity) 237 (M^+, 3), 202 (3), 142 (11), 126 (100), 112 (9), 59 (34), 58 (23).

Anal. Calcd for $C_8H_9Cl_2NOS$: C, 40.35; H, 3.81; N, 5.88; S, 13.46. Found: C, 40.40; H, 3.78; N, 5.92; S, 13.47.

Reaction of 1,3-Thiazole (1a) with Acetyl Chloride in the Presence of Et_3N. Freshly distilled acetyl chloride (0.51 mL, 7.1 mmol) was added in one portion to a stirred solution of 0.3 g (3.5 mmol) of **1a** in 30 mL of benzene. After 30 min 0.98 mL (7.1 mmol) of Et_3N in 10 mL of benzene were slowly added over 2 h. The reaction mixture was stirred for 2 days, washed with aqueous $NaHCO_3$, and extracted with benzene. The organic layer was dried (Na_2SO_4) and the solvent was removed under reduced pressure. Chromatography (silica, 7:3 cyclohexane:ethyl ether) of the residue gave 20 mg (3.6%) of the enol ester **11**: oil; IR (film) 1780 (C=O), 1645, 1620 cm^{-1}; ^1H NMR δ 7.8 (d, 1, =CH, J = 3.2 Hz), 7.4 (d, 1, =CH, J = 3.2 Hz), 6.0 (d, 1, =CH, J = 2.6 Hz), 5.3 (d, 1, =CH, J = 2.6 Hz), 2.3 (s, 3, $COCH_3$).

Anal. Calcd for $C_7H_7NO_2S$: C, 49.69; H, 4.17; N, 8.28; S, 18.95. Found: C, 49.67; H, 4.16; N, 8.30; S, 18.96.

Reaction of 1,3-Thiazole (1a) with Trichloroacetyl Chloride in the Presence of Et_3N. Freshly distilled trichloroacetyl chloride (0.79 mL, 7.1 mmol) was added in one portion to a stirred solution of 0.3 g (3.5 mmol) of **1a** in 30 mL of benzene. After 30 min 0.98 mL (7.1 mmol) of Et_3N in 10 mL of benzene were added dropwise over 2 h. The reaction mixture was stirred for 2 days and worked up as detailed above to give 360 mg (45%) of 2-trichloroacetyl-1,3-thiazole (**10a**): mp 61–63 °C (from *n*-hexane); IR (KBr) 1710 (C=O), 1480, 1380 cm^{-1}; ^1H NMR δ 8.2 (d, 1, =CH, J = 3.1 Hz), 7.85 (d, 1, =CH, J = 3.1 Hz); mass spectrum, m/e (relative intensity) 229 (M^+, 3), 158 (6), 112 (100), 85 (22).

Anal. Calcd for $C_5H_2Cl_3NOS$: C, 26.06; H, 0.87; N, 6.08; S, 13.91. Found: C, 26.10; H, 0.88; N, 6.05; S, 13.88.

Hydrolysis of Enol Ester 11. To a solution of 100 mg (0.5 mmol) of **11** in 20 mL of THF was added 1 mL of aqueous NH_3 (ca. 40%). After 20 min, ethyl ether was added and the reaction mixture was washed with aqeuous $NaHCO_3$. The organic layer was dried (Na_2SO_4), the solvent was removed under vacuum, and the residue was chromatographed (silica, 7:3 cyclohexane:ethyl ether) to give 50 mg (78%) of 2-acetylthiazole (**10b**): oil; IR (film) 1690 (C=O), 1480 cm^{-1}; ^1H NMR δ 8.02 (d, 1, =CH, J = 3.2 Hz), 7.68 (d, 1, =CH, J = 3.2 Hz), 2.7 (s, 3, $COCH_3$); mass spectrum, m/e (relative intensity) 127 (M^+, 87), 112 (70), 99 (85), 85 (50), 84 (50), 58 (100).

Anal. Calcd for C_5H_5NOS: C, 47.23; H, 3.96; N, 11.01; S, 25.21. Found: C, 47.20; H, 3.97; N, 10.99; S, 25.25.

Reductive Dehalogenation of Ketone 14. A mixture of 200 mg (0.8 mmol) of **14** and 0.3 g of Zn powder in 10 mL of acetic acid was stirred for 1 h at room temperature. The reaction mixture was filtered and the acetic acid evaporated under vacuum. After addition of ethyl ether, the solution was washed with aqueous $NaHCO_3$, the organic layer was dried (Na_2SO_4), and the solvent was removed under vacuum. Chromatography of the residue (silica, 7:3 cyclohexane:ethyl ether) gave 124 mg (92%) of the ketone **16**: oil; IR (film) 1710 (C=O) cm^{-1}; ^1H NMR δ 7.85 (d, 1, =CH, J = 3.2 Hz), 7.39 (d, 1, =CH, J = 3.2 Hz), 2.1 (s, 3, $COCH_3$), 1.67 (s, 6, $2CH_3$).

Anal. Calcd for $C_8H_{11}NOS$: C, 56.77; H, 6.55; N, 8.28; S, 18.94. Found: C, 56.78; H, 6.54; N, 8.29; S, 18.96.

Reductive Dehalogenation of Enol Ester 12. A solution of 1 g (3.13 mmol) of **12** in 10 mL of acetic acid was added dropwise to a stirred suspension of 2 g of Zn powder in 10 mL of the same solvent. The reaction mixture was stirred for 12 h and filtered, and the acetic acid was evaporated under vacuum. The residue was treated with ethyl ether, washed with aqeuous $NaHCO_3$, and dried (Na_2SO_4). After evaporation of the solvent under vacuum, the crude mixture was chromatographed (silica, 9:1 dichloromethane:ethyl acetate) to give 500 mg (69%) of the adduct **15**: oil; IR (film) 1770 (C=O) cm^{-1}; ^1H NMR δ 7.75 (d, 1, =CH, J = 3.2 Hz), 7.32 (d, 1, =CH, J = 3.2 Hz), 6.1 (d, 1, =CH, J = 1 Hz), 4.2 (dq, 1, >CH, J = 1 Hz, J = 7.4 Hz), 2.2 (s, 3, CH_3), 1.6 (d, 3, CH_3, J = 7.4 Hz); mass spectrum, m/e (relative intensity) 189 (M^+ – 43, 31), 154 (31), 149 (9), 113 (100), 112 (45), 43 (13).

Anal. Calcd for $C_9H_{10}ClNO_2S$: C, 46.66; H, 4.35; N, 6.05; S, 13.84. Found: C, 46.62; H, 4.37; N, 6.04; S, 13.85.

^1H NMR Study of the Reaction between 1,3-Thiazole (1a) and TBCK. A solution of TBCK (4.7 mmol) in C_6D_6 (ca. 1 mL) and 2.35 mmol of **1a** were mixed in a NMR tube and the reaction mixture was maintained at constant temperature for each experiment (25 °C, 48.7 °C, 80 °C) by a thermostatted bath. NMR spectra were recorded at intervals following the disappearance of the thiazole from signals at δ 8.7, 7.84, and 7.22 and the formation of the cycloadduct **2a** at δ 6.6, 6.33, and 4.97 and of the open-chain enol ester **7a** at δ 7.4, 6.6, and 3.14.

X-ray Crystal Structure Analysis of 2a. Crystal data: $C_{17}H_{21}N_3O_2S$, M_r = 331.4, orthorombic, a = 19.830 (11) Å, b = 13.123 (8), Å, c = 13.197 (8) Å, Z = 8, D_c = 1.07 g cm^{-3}, space group *Pbcn*. Intensity diffraction data were collected up to ϑ 30° by using the $\omega - 2\vartheta$ step-scanning mode with Zr-filtered Mo Kα radiation (λ = 0.7107 Å). The reflection profiles were analyzed with the Lehmann–Larsen algorithm.[26] A total of 4636 reflections

(26) Blessing, R. H.; Coppens, P.; Becker, P. *J. Appl. Crystallogr.* 1974, 7, 488.

was collected, 1720 of them [$I > 3\sigma(I)$] were considered observed and used in structure analysis and refinement. The structure was solved by direct methods and refined by full-matrix anisotropic least-squares techniques. Hydrogen atoms were refined with the constraint C-H = 1.08 Å. The final R index was 0.074 (R_ω = 0.082, $\omega = 1/\sigma^2(F)$.

X-ray Crystal Structure Analysis of 13. Crystal data: $C_{10}H_9Cl_4NO_2S$, M = 349.1, monoclinic, a = 14.264 (8) Å, b = 8.128 (6) Å, c = 12.356 (7) Å, β = 106.76 (7)°, Z = 4, D_c = 1.69 g cm^{-3}, space group $P2_1/n$. Intensity data were measured up to 70° by the $\omega - 2\vartheta$ step-scanning mode with Ni-filtered Cu Kα radiation (λ = 1.5418 Å). A total of 2912 reflections was collected and 2230 with $I > 2\sigma(I)$ were used in the analysis. The structure was solved by direct methods and refined by full-matrix anisotropic least-squares techniques. Hydrogen atoms were refined with the constraint C-H = 1.08 Å. The final R index was 0.054 (R_w = 0.063, $w = 1/\sigma^2(F)$.

Registry No. **1a**, 288-47-1; **1b**, 693-95-8; **1c**, 3581-89-3; **1d**, 15679-09-1; **1e**, 15679-10-4; **2a**, 87830-79-3; **2c**, 87830-80-6; **3a**, 79265-40-0; **3c**, 87830-81-7; **4a**, 79265-41-1; **4b**, 87830-82-8; **4c**, 87830-83-9; **7a**, 87830-84-0; **8a**, 87830-85-1; **9a**, 87830-86-2; **10a**, 87636-20-2; **10b**, 24295-03-2; **11**, 87830-87-3; **12**, 87830-88-4; **13**, 87841-56-3; **14**, 87830-89-5; **15**, 87830-90-8; **16**, 87830-91-9; TBCK, 29342-22-1; DCK, 4591-28-0; DPK, 525-06-4.

Supplementary Material Available: Tables of atomic coordinates, bond distances, and bond angles of cycloadducts **2a** and **13** (5 pages). Ordering information is given on any current masthead page.

(*Z*)- and (*E*)-1,2-Bis(phenylsulfonyl)ethylenes as Synthetic Equivalents to Acetylene as Dienophile

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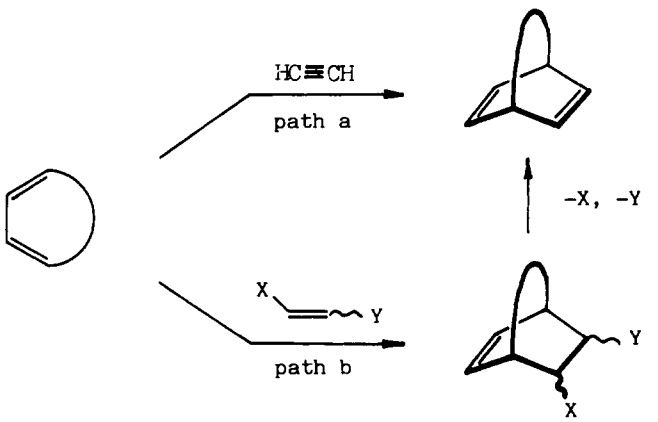
A new method for introducing an ethylenic bridge via a cycloaddition reaction has been developed. It makes use of either (*Z*)- or (*E*)-1,2-bis(phenylsulfonyl)ethylene (**5** or **6**) as synthetic equivalents of acetylene. The high activation due to the two sulfonyl groups promotes cycloaddition even to very unreactive dienes. The removal of the two sulfonyl groups for the required formation of the carbon–carbon double bond is promoted by reduction with metal amalgams in high yields. These properties, associated with the stability of the reagents and the ease of performance of the reactions, make this method a very useful synthetic tool for the preparation of polycyclic dienes and a valid alternative to the commonly available reagents that largely depend upon oxidative methods.

The synthesis of cyclic and polycyclic 1,4-dienes has been attracting the attention of several research groups for many years as they are important building blocks for the preparation of complex molecules. In fact the reactivity of these homodienes is of practical and theoretical interest in view of the forced conformation imposed by the cyclic or polycyclic arrangement. Depending upon the degree of conjugation of the two carbon–carbon double bonds, this class of dienes can experience [2 + 2] intramolecular, photochemical cycloaddition, di-π-methane (Zimmerman) rearrangement, complexation with metals, and a variety of structural rearrangements.

As shown in Scheme I, the most direct approach to the synthesis of these 1,4-dienes is the [4 + 2] cycloaddition of acetylene to 1,3-dienes. However, due to the low dienophilic reactivity of the triple bond as well as the hazards involved in handling acetylene under pressure and at high temperatures, this direct route can be used only with the most reactive dienes. As a consequence, several alternative procedures have been devised that are based on the use of acetylene equivalents (path b in Scheme I). These are characterized by a high dienophilic reactivity and by the fact that the activating groups can be readily removed to introduce the second carbon–carbon double bond in the molecule. Indeed, it is this second property that limits the scope of this synthetic approach.

According to the Hendrickson model,[1] the activating groups can be eliminated through oxidative, isohypsic, or reductive processes. The most common acetylene equivalents (maleic anhydride, fumaric and maleic acid derivatives, etc.) belong to the first class, but most of the several oxidation methods available[2-5] present intrinsic drawbacks. Isohypsic acetylene equivalents[6-8] (acrylic acid derivatives,

Scheme I



(1) Hendrickson, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 6847.

(2) von Doering, W. E.; Farber, M.; Sayigh, A. *J. Am. Chem. Soc.* **1952**, *74*, 4370.

(3) Criegee, R. "Oxidation in Organic Chemistry"; Wiberg, K. B. Ed.; Academic Press: New York, 1965; Part A, p 278. Rubottom, G. M. "Oxidation in Organic Chemistry"; Trahanovsky, W. S. Ed.; Academic Press: New York, 1982; Part D, pp 81-89.

(4) Radlick, P.; Klem, R.; Spurlock, S.; Sims, J. J.; van Tamelen, E. E.; Whitesides, T. *Tetrahedron Lett.* **1968**, 5117. Westberg, H. H.; Dauben, Jr., H. J. *Ibid.* **1968**, 5123.

(5) Trost, B. M.; Chen, F. *Tetrahedron Lett.* **1971**, 2603.

(6) Snow, R. A.; Dagenhardt, C. R.; Paquette, L. A. *Tetrahedron Lett.* **1976**, 4447.

0022-3263/84/1949-0596$01.50/0