h for 1 or 2). The reaction mixtures were cooled, taken up in methanol, and filtered to remove copper salts. Internal standard (*N*-nitrosodipropylamine) was added, and the solutions were made up to volume for GC analysis. Products were identified by GLC/MS and positive spike experiments. Results are given in Table IV.

Carbamates were synthesized by literature methods.[15] Boiling points for all compounds were in reasonable agreement with those in the literature. Identity with carbamates found in thermolysis reaction mixtures was established by GC/MS and positive spike experiments.

Methyl *N*,*N*-dimethylcarbamate (5): bp 126–128 °C (lit.[16] bp 131 °C); NMR ($CDCl_3$) δ 2.90 (s, 6 H, N-CH_3), 3.68 (s, 3 H, OCH_3).

Methyl *N*,*N*-Diethylcarbamate (10): bp 156–157 °C (lit.[16] 155 °C) NMR ($CDCl_3$) 1.07 (t, 6 H, NCH_2CH_3), 3.15 (q, 4 H, NCH_2CH_3), 3.61 (s, 3 H, OCH_3).

Ethyl *N*,*N*-dimethylcarbamate (12): bp 145–147 °C (lit.[16] bp 147 °C); NMR ($CDCl_3$) δ 1.13 (t, 3 H, CH_2CH_3), 2.97 (s, 6 H, NCH_3), 4.06 (q, 2 H, CH_2CH_3).

Ethyl *N*,*N*-diethylcarbamate (8): bp 164–167 °C (lit.[16] bp 169–172 °C); NMR ($CDCl_3$) δ 1.15 (overlapping triplets, 9 H, OCH_2CH_3 and NCH_2CH_3), 3.28 (q, 4 H, NCH_2CH_3), 4.15 (q, 2 H, OCH_2CH_3).

N,N-Disubstituted alanine and glycine esters were synthesized by standard literature procedures from the appropriate bromo esters and dialkylamines. Boiling points were comparable to those reported in the literature, and appropriate NMR and mass spectral data were obtained. Identity with the alanine and glycine derivatives found in thermolysis reaction mixtures was established by GLC/MS and positive spike experiments.

Methyl *N*,*N*-dimethylglycine: bp 94–96 °C [kut,[17] bp 50–53 °C (30 mmHg)]; NMR ($CDCl_3$) δ 2.35 (s, 6H, NCH_3), 3.18 (s, 2 H, CH_2), 3.73 (s, 3 H, OCH_3).

Methyl *N*,*N*-diethylglycine (11): bp 122–123 °C [lit.[17] bp 84.5–85.5 °C (57 mmHg)]; NMR ($CDCl_3$) δ 1.05 (t, 6 H, CH_2CH_3), 2.65 (q, 4 H, CH_2CH_3), 3.33 (s, 2 H, CH_2), 3.70 (s, 3 H, OCH_3).

Ethyl *N*,*N*-dimethylalanine (13): bp 70–72 °C (500 mmHg) (lit.[14] bp 154–157 °C); NMR ($CDCl_3$) δ 1.35 (overlapping triplets, 6 H, CH_2CH_3 and $CHCH_3$), 2.36 (s, 6 H, NCH_3), 3.25 (q, 1 H, $CHCH_3$), 4.23 (q, 2 H, CH_2CH_3).

Ethyl *N*,*N*-diethylalanine (9): bp 93-96 °C (500 mmHg) (lit.[18] bp 172–477 °C); NMR ($CDCl_3$) δ 1.05 and 1.30 (overlapping triplets, 12 H, CH_2CH_3 and $CHCH_3$), 2.62 (overlapping quartets, 4 H, NCH_2CH_3), 3.54 (q, 1 H, $CHCH_3$), 4.18 (q, 2 H, OCH_2CH_3).

Isolation of Ethyl *N*,*N*-Diethylalanine from a Large-Scale Thermolysis Reaction Mixture. Triethylnitrosourea (0.54 g) was heated at 95 °C under a water-cooled condenser. A vigorous evolution of gas was observed. The reaction mixture was heated for 17 h, and the yellow-brown oil remaining in the reaction vial was analyzed by GLC (Ultrabond 20 M, ft 10 × 2 mm, 20 mL/min He, 4 min at 80 °C, 8 °C/min to 130 °C). The pot residue contained **9** and **8** in a 4:1 ratio, accounting for 80% of the starting material. Column chromatography of the pot residue on silica gel with hexane/ethyl acetate (0–10%) as eluant gave a sample of **9** that was identical by IR, NMR, and mass spectrum with that synthesized (vide supra).

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Registry No. 1, 3475-63-6; 2, 50285-72-8; 3, 50285-71-7; 4, 50285-70-6; 5, 7541-16-4; 8, 3553-80-8; 9, 82614-48-0; 10, 4652-44-2; 11, 30280-35-4; 12, 687-48-9; 13, 82614-49-1; CuCl, 7758-89-6; methyl-*N*,*N*-dimethylglycine, 7148-06-3.

(15) Hartman, W. W.; Brethen, M. R. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 278.
(16) Barker, M.; Hunter, L.; Reynolds, N. G. *J. Chem. Soc.* **1948**, 874.
(17) Tarakawa, T. *J. Pharm. Sci.* **1954**, *74*, 287.
(18) Burnett, W. B.; Jenkins, R. L.; Peet, C. H.; Dreger, E. E.; Adams, R. *J. Am. Chem. Soc.* **1937**, *59*, 2248.

Regioselective Aluminum Chloride Catalyzed Reactions of Unsaturated Electrophiles with Thiazoles

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Aluminum chloride promotes reactions of α,β-unsaturated esters and nitriles with 1,3-thiazoles to give 1:1 and 2:1 adducts, the nature and distribution of which depend on the substituent R at C_2 of the heterocycle and the nucleophile QN employed as a quencher of the reaction mixture. With 2-bromothiazole, ethyl propiolate, and dimethyl acetylenedicarboxylate give substituted (*E*)- and (*Z*)-*N*-vinylthiazolin-2-ones (QN, aqueous sodium bicarbonate) and 2-imino-*N*-vinylthiazolines (QN, benzylamine), while ethyl acrylate and acrylonitrile afford substituted *N*-propanoylthiazolin-2-ones (QN, aqueous sodium bicarbonate). With 1,3-thiazole and 2-ethylthiazole, ethyl propiolate gives (QN, aqueous sodium bicarbonate) *N*-formyl- and *N*-propanoylthiazolines, respectively, together with 2:1 open-chain adducts containing 2 mol of acetylene and 1 mol of thiazole. A plausible scheme accounting for the formation of the observed products involves a regioselective attack by C_β of the multiple bond of the ester or nitrile coordinated with $AlCl_3$ on the nitrogen of the thiazole ring to give a zwitterion with allenic structure which by action of the QN undergoes C_2–R (R = Br) or C_2–S (R = H, C_2H_5) bond fission and forms the observed products.

The functionalization of the 1,3-thiazole ring through reactions with unsaturated electrophiles, viz., π systems activated by electron-withdrawing groups, constitutes an attractive entry to direct synthesis of derivatives of this important heterocyclic system, the core of numerous natural and synthetic compounds with biological activity.[1] Unfortunately, because of its aza-aromatic character, the thiazole ring is little inclined to react with π acceptors,[2] and thus very few reactions of that type have been so far described. For instance, thiazoles have been reported to react with dimethyl acetylenedicarboxylate[3] to give various cycloadducts from secondary processes, thus considerably

(1) (a) Metzger, J. V., Ed. "Thiazole and Its Derivatives"; Wiley: New York, 1979. (b) Iddon, B.; Lowe, P. A. *Org. Compd. Sulphur, Selenium, Tellurium* **1979**, *5*, 358.
(2) Reinhoudt, D. N. *Adv. Heterocycl. Chem.* **1977**, *21*, 253.
(3) Abbott, P. J.; Acheson, R. M.; Watkin, D. J.; Carruthers, J. R. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1269 and references cited therein.

0022-3263/82/1947-3844$01.25/0

Table I. Reactions of Thiazoles 1 with Acetylenic Esters–$AlCl_3$ Complexes

thiazole	acetylene[a]	run	reactants (molar ratio)[b]	conditions[c] (solv; reac time, h)	quencher	overall yield,[d] %	products (molar ratio)
1a (R = Br)	EP	1	1:1:1	ether, 72	H_2O/OH^-	16	3a (4.8), 4a (1)
	EP	2	1:1:2	ether, 72	H_2O/OH^-	48	3a (5.9), 4a (1), 5a (0.1)
	EP	3	1:2:2	ether, 72	H_2O/OH^-	49	3a (11.2), 4a (1), 5a (2.3)
	EP	4	5:1:5[e]	ether, 72	H_2O/OH^-	72	3a (2.7), 4a (1), 5a (1.1)
	EP	5	1:2:2	ether, 72	$PhCH_2NH_2$	36	6a (31), 7a (1)
	DMAD	6	1:2:2	ether, 48	H_2O/OH^-	48	3b (3.8), 4b (1), 5b (0.48)
1b (R = H)	EP	7	1:2:2	benzene,[f] 120	H_2O/OH^-	35	9b (1), 10b (8), 8b (1.8)
1c (R = C_2H_5)	EP	8	1:2:2	ether, 144	H_2O/OH^-	16	9c (1), 10c (4.4), 8c (6)

[a] EP = ethyl propiolate; DMAD = dimethyl acetylenedicarboxylate. [b] Thiazole/acetylene/$AlCl_3$. [c] Addition of acetylene–$AlCl_3$ complex to thiazole at room temperature unless otherwise stated. [d] Calculated with respect to thiazole 1 unless otherwise stated and determined on isolated products after workup of the reaction mixture. [e] Yields calculated with respect to EP. [f] Addition of thiazole to acetylene–$AlCl_3$ complex.

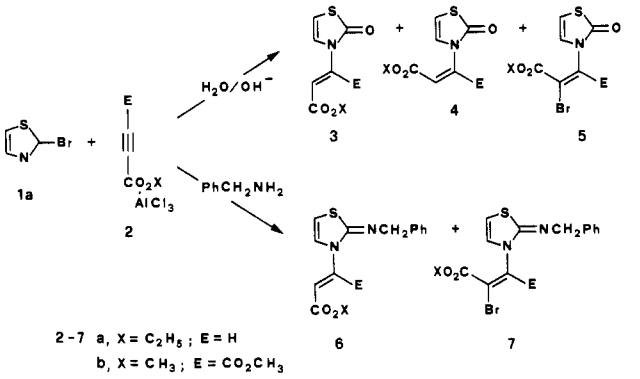
limiting the synthetic utility of these reactions. On the other hand, we have described recently[4] some reactions of thiazoles with highly reactive heterocumulenes (ketenes and tosyl isocyanate) as well as with isolated double bond systems activated by electron-withdrawing groups (tetracyanoethene and diethyl azodicarboxylate) which occur regioselectively under very mild conditions owing to the directing and activating effects of appropriate substituents (dimethylamino and trimethylsilyl) in the heterocyclic ring.

Along the lines of the well-known activation by Lewis acids on reactivity and selectivity of α,β-unsaturated esters and nitriles in Diels–Alder reactions,[5] [2 + 2] cycloadditions,[6,7] and ene reactions,[7] we have turned our attention to these catalysts in order to promote reactions of acetylenes and alkenes with thiazoles. Since the activation of the double or triple bond arises from coordination of the catalyst with the ester or nitrile function which enhances the electrophilicity of the β-carbon,[7,8] the choice of the thiazoles has been somewhat conditioned by the requirement that their basicity had to be low enough to give little interference with the above complex. Following a partial report on this subject,[9] we describe here the results from the $AlCl_3$-catalyzed reactions of three thiazoles with acetylenic and ethylenic esters and a nitrile,[10] these systems, on the other hand, being practically unreactive in the absence of the catalyst.

Results and Discussion

Reactions of Thiazoles 1 with Acetylenic Esters. Reactions of 2-bromothiazole (**1a**) with ethyl propiolate–$AlCl_3$ complex (**2a**, Scheme I), prepared in situ from equivalent amounts of ethyl propiolate (EP) and $AlCl_3$ followed by quenching with aqueous sodium bicarbonate, gave the (*E*)- and (*Z*)-*N*-vinylthiazolin-2-ones **3a** and **4a**,

Scheme I



the latter prevailing over the former (Table I, run 1). The overall yield of the reaction considerably increased when 2 equiv of EP and $AlCl_3$ were used with respect to thiazole **1a** (run 2 and 3), and in addition to products **3a** and **4a** the bromovinyl derivative **5a** was also isolated. Quenching the reaction mixture in an excess of benzylamine (run 5) gave 2-(benzylamino)-(*E*)-*N*-vinylthiazoline (**6a**) and the bromovinyl derivative **7a** in a 31:1 ratio. All products **3a**–**7a** were recovered unaltered from their solutions in ethyl ether in the presence of 1 or 2 equiv of $AlCl_3$, this indicating their stereochemical stability under the reaction conditions.

The structures of the *N*-vinylthiazolines **3a**–**7a** were assigned on the basis of their NMR spectra. The *Z* configuration about the *N*-vinyl group of **4a** stemmed from the smaller coupling constant (J_{HH} = 10.9 Hz) between the corresponding vicinal protons with respect to those of *E* isomers **3a** and **6a** (J_{HH} ca. 15 Hz), while the conformation about the N–C(vinyl) single bond in **4a** was suggested by the very-low-field resonance (δ 8.0) of the C_4 proton which was attributed to deshielding by the vicinal β-ethoxycarbonyl group. The latter spectroscopic feature was employed for the assignment of the stereochemistry at the *N*-vinyl group in the bromovinyl derivatives **5a** and **7a** whose C_4 protons showed resonances at ca. 8.0 ppm. Furthermore, simple chemical transformations provided information on the structural relation between some of the above products. In fact, irradiation of pure samples of either **3a** or **4a** produced mixtures of both isomers with prevalence of the former over the latter, while the (bromovinyl)thiazolin-2-one **5a** was readily debrominated by Bu_3SnH to give **3a** and **4a**.

The complex **2b** prepared from dimethyl acetylenedicarboxylate (DMAD) and $AlCl_3$[11] (Table I, run 6) reacted

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

(5) Inukai, T.; Kojima, T. **1967**, *32*, 869, 872; Sauer, J.; Kredel, J. *Tetrahedron Lett.* **1966**, 731. Trong Anh, N.; Seyden-Penne, J. *Tetrahedron* **1973**, *29*, 3259.

(6) Reinhoudt, D. N.; Volger, H. C.; Kouwenhoven, C. G.; Wynberg, H.; Helder, R. *Tetrahedron Lett.* **1972**, 5269.

(7) Snider, B. B.; Rodini, J. D.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283. Snider, B. B.; Roush, D. M.; Rodini, J. D.; Gonzales, D.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773. Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. Fienemann, H.; Hoffmann, H. M. R. *J. Org. Chem.* **1979**, *44*, 2802.

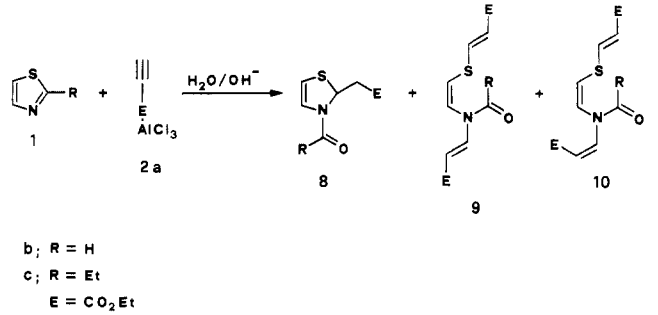
(8) An equivalent explanation in terms of the MO theory is based on a "lowering of the energies of π orbitals as well as redistribution of the orbital electron densities", see: Houk, N. K.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094.

(9) Medici, A.; Pedrini, P.; Fogagnolo, M.; Dondoni, A. *J. Chem. Soc., Chem. Commun.* **1980**, 1077.

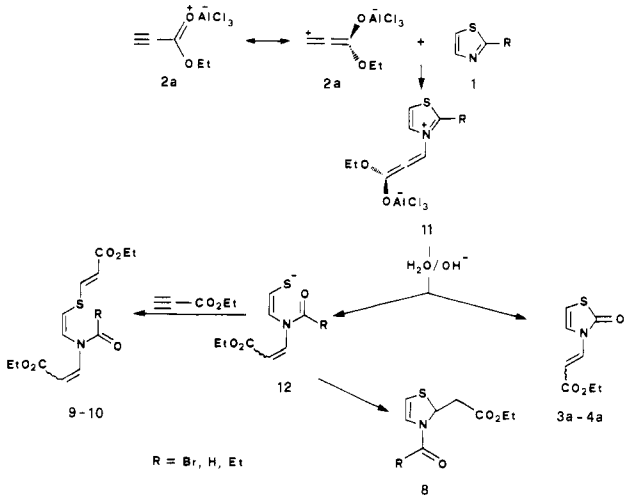
(10) Experiments with other Lewis acids revealed that BF_3 was practically unefficient and that $TiCl_4$ gave lower yields and large amounts of tars.

(11) No reaction was observed between DMAD and **1a** in DMF, CH_3CN, and CH_3OH after 4 days at room temperature.

Scheme II



Scheme III



with 2-bromothiazole (**1a**) to give, after quenching with aqueous sodium bicarbonate, disubstituted (*E*)- and (*Z*)-*N*-vinylthiazolin-2-ones **3b** and **4b** and the bromovinyl derivative **5b** (Scheme I). On the other hand, quenching the reaction mixture with benzylamine did not afford any 2-imino-*N*-vinylthiazolines **6b** or **7b**, while 2-bromothiazole (**1a**) was recovered together with tarry material. The configuration about the *N*-vinyl group in compounds **3b** and **4b**, which constituted an unseparable 3.8:1 mixture, was assigned on the basis of the long-range coupling constants J_{CCH} which were smaller (less than 2.0 Hz from the 134-ppm signal)[12] in the most abundant isomer **3b** than in **4b** (4.5 Hz from the 139.4-ppm signal). These values compare quite well with those reported[13] for diethyl maleate (J_{CCH} = 1.5 Hz) and diethyl fumarate (J_{CCH} = 4.5 Hz) and therefore may be taken as an indication of the relative positions of the two ester groups, viz., cis in **3b** and trans in **4b**. Whereas this assignment confirmed the one in our preliminary report,[9] the conformation about the N–C(vinyl) single bond remained undefined since the observation of almost identical high-field chemical shifts for the proton at C_4 in both **3b** (δ 6.6) and **4b** (δ 6.7) did not allow us to draw any stereochemical conclusions in the manner applied to **3a** and **4a**. Therefore, the assumed conformation for compounds **3b–5b** in Scheme I is arbitrary. Finally, the configuration about the *N*-vinyl group of the bromovinyl derivative **5b** could also not be assigned because of the lack of conclusive spectroscopic features or conclusive chemical transformations. For instance, the debromination by Bu_3SnH, which in this case gave only one stereoisomer, viz., **4b**, is not instructive because the stereochemistry of this reaction is unknown.

The scope of the reaction of acetylenic ester–$AlCl_3$ complexes **2** was extended to some thiazoles bearing substituents other than bromine at C_2. Reactions of 1,3-thiazole (**1b**) and 2-ethylthiazole (**1c**) with EP–$AlCl_3$ (**2a**, Scheme II) followed by the usual treatment with aqueous $NaHCO_3$ gave modest yields (Table I) of three products which were identified as the *N*-acylthiazolines **8** and the isomeric open-chain 2:1 adducts **9** and **10** (from 2 mol of acetylene and 1 mol of thiazole). On the other hand, no reaction was observed between either **1b** or **1c** with DMAD–$AlCl_3$ (**2b**) after 4 days at room temperature. The stereochemistry about the carbon–carbon double bonds of **9** and **10** was assigned on the basis of ^1H NMR spectra and decoupling experiments. In both pairs of adducts **9b–10b** (R = H) and **9c–10c** (R = C_2H_5) almost identical coupling constants were observed for the vicinal protons in the *S*-vinyl group (J_{HH} ca. 14 Hz) and in the central carbon–carbon double bond (J_{HH} ca. 7.0 Hz), thus indicating the same configuration about these bonds in all four compounds, namely, *E* and *Z*, respectively, as inferred from the relative values of these parameters. Similarly, the coupling constants in the *N*-vinyl group for compounds **9b,c** (J_{HH} = 15.5 Hz) and **10b,c** (J_{HH} = 10 Hz) pointed to the *E* and *Z* configurations, respectively.

A reasonable scheme which accommodates the results from the reactions of the various thiazoles **1** is illustrated for their reactions with EP–$AlCl_3$ complex (**2a**) followed by quenching with alkaline water (Scheme III). This involves initially a regioselective attack on the nitrogen of the thiazole[14] **1** by the electrophilic C_β of the complex **2a** resulting from coordination of $AlCl_3$ with the ester group of EP.[7] This leads to the zwitterion **11** which maintains the allenic structure in the unsaturated chain attached to nitrogen, owing to the extended conjugation. The mode of evolution of **11** on quenching with a nucleophile depends on the substituent at C_2 of the thiazole ring; namely, attack by water or OH^- determines C_2–R bond fission when R is a good leaving group such as Br^- or C_2–S bond fission, viz., ring opening, when R is H or C_2H_5. In the former case, the removal of $AlCl_3$ from the coordinating ester group and protonation at the central carbon of the allenic system gives the *N*-vinylthiazolin-2-ones **3a** and **4a** whereas in the latter case it leads to an open-chain intermediate, **12**, which either recyclizes to the *N*-acylthiazoline **8** via nucleophilic attack by sulfur at C_α of the *N*-vinyl group[15] or adds to a second molecule of EP to give the 2:1 adducts **9** and **10**. Evidently, when the reaction mixture is quenched with benzylamine instead of alkaline water, the intermediate **11a** (R = Br) would produce the 2-(benzylimino)thiazoline **6a**.

Scheme III can be reasonably extended to the reaction of DMAD–$AlCl_3$ complex (**2b**) with 2-bromothiazole (**1a**). In this case the key intermediate would be the *N*-allenylthiazolium derivative **13a** which on treatment with alkaline water is transformed into the disubstituted *N*-vinylthiazolin-2-ones **3b** and **4b**. Attack of benzylamine at C_α of the *N*-allenyl chain of **13a** and displacement of

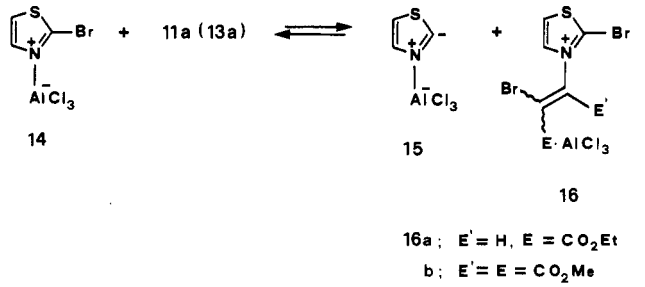
(12) From the comparison of the line width (ca. 3 Hz) of the 134-ppm signal with that of sharp singlets (1.5 Hz), the J_{CCH} value is expected not to exceed 2 Hz.

(13) Muller, N. *J. Chem. Phys.* **1962**, *35*, 2792.

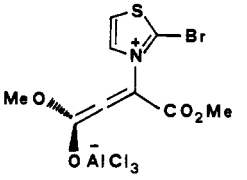
(14) The regioselectivity of the reaction is consistent with molecular orbital charge distributions (CNDO/2) which indicate for all compounds **1** the largest charge density on nitrogen.

(15) Intermediate **12** is formally similar to that suggested for the reactions of benzothiazoles with DMAD to give benzothiazine derivatives: McKillop, A.; Sayer, T. S. B.; Bellinger, G. C. A. *J. Org. Chem.* **1976**, *41*, 1328. Cyclization of **12** to a five-membered-ring thiazoline **8** rather than to a six-membered-ring dihydrothiazine is consistent with the regiochemistry of the addition at C_β by nucleophiles to α,β-unsaturated monoesters.

Scheme IV



1a instead of attack at C_2 of the thiazole ring would account for the lack of formation of 2-(benzylimino)thiazoline derivatives.



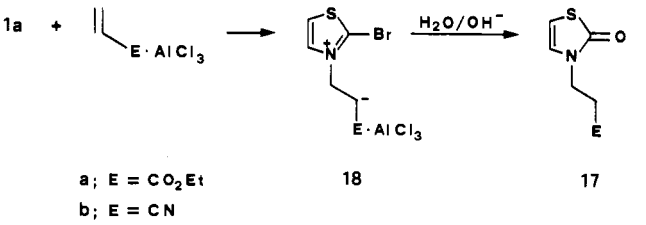
13a

The low stereoselectivity of the addition across the triple bond of the acetylenic esters EP and DMAD as shown by the formation of both π diastereomers *E* and *Z* can be accounted for on the basis of the allenic structure of the zwitterions **11** and **13** since protonation at the central carbon of the *N*-allenyl group can equally occur from one side of the thiazole ring or from the other. The preference for syn over anti addition (see **3**, **4**, and **6a**) may be related to the internal proton transfer from the nucleophile already bonded to C_2 of the thiazole ring, whereas the opposite selectivity (see **9** and **10**) may arise from control by steric factors. Moreover, zwitterions **11a** and **13a** account also for the formation of the *N*-(bromovinyl)thiazolines **5a**, **7a**, and **5b** if it is assumed that some exchange of bromine as Br^+ (Scheme IV) takes place between these zwitterions and the thiazolium–$AlCl_3$ complex **14** which is likely to be present together with the acetylenic ester–$AlCl_3$ complex in the reaction mixture. The high stability[16] of the thiazolium ylide **15** is probably the driving force of this exchange process. In agreement with this hypothesis, the excess of both thiazole **1a** and $AlCl_3$ with respect to the acetylenic ester (Table I, run 4), which ensured a larger concentration of **14** with respect to other experiments, increased the amount of *N*-(bromovinyl)thiazolin-2-one **5a** at expenses of the (*E*)-*N*-vinylthiazolin-2-one **3a**.

Reactions of 2-Bromothiazole (1a) with Alkenes. In order to extend the scope of the reaction to double bond systems, we reacted 2-bromothiazole (**1a**) with ethyl acrylate and acrylonitrile in the presence of $AlCl_3$ (Scheme V). These alkenes were less reactive than the acetylenic esters EP and DMAD and required 4 or 5 days in refluxing benzene to give, after quenching with alkaline water, *N*-propanoylthiazolin-2-ones **17** in very modest yields (ca. 35%). These reactions can also be formulated as arising from regiospecific attack of the nitrogen of **1a** on C_β of the double bond whose electrophilicity is enhanced by the coordination of the ester or nitrile function with $AlCl_3$.[5] This would lead to the zwitterion **18** which, similarly to **11a** and **13a**, is converted into product **17** by the action of alkaline water.

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

Scheme V



Conclusions

This study shows that acetylenes and ethylenes bearing an ester or nitrile function are activated by $AlCl_3$ in reactions with 1,3-thiazoles to give adducts which arise from one-bond formation between the nitrogen of the thiazole and C_β of the unsaturated moiety. The observed reactions constitute a new method for regioselective functionalization of the thiazole ring. Their synthetic value is evident when considering that the resulting N-substituted thiazolinones[17] and thiazolinimines are compounds related to thiazolidinones,[18] a class of heterocycles endowed with a large spectrum of biological activity. These adducts, moreover, appear not to be readily accessible by other routes. In fact, while they can be viewed as formal adducts from 2-hydroxythiazole or 2-(benzylamino)thiazole to alkenes and acetylenes, reactions between these compounds are likely to follow other routes as shown by 2-aminothiazole and α,β-unsaturated esters,[19] which in fact give mainly six-membered-ring cycloadducts, viz., condensed pyrimidinones.

Experimental Section

General Comments. All melting points are uncorrected. ^1H and ^{13}C NMR spectra (in $CDCl_3$) were obtained on an 80-MHz WP80 Bruker spectrometer. Chemicals shifts are given in parts per million 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 (**1b**), ethyl propiolate (**EP**), dimethyl acetylenedicarboxylate (**DMAD**), acrylonitrile, and ethyl acrylate were commercially available. 2-Bromo-1,3-thiazole[20] [**1a**, bp 70–71 °C (20 mmHg)] and 2-ethyl-1,3-thiazole[21] (**1c**, bp 148 °C) were prepared as described.

General Procedure for Preparation of Electrophile-$AlCl_3$ Complexes. To a stirred solution of the electrophile (ca. 10 mmol) in dry solvent (ca. 150 mL) was added the appropriate number of equivalents of $AlCl_3$, and stirring was continued for at least 1 h.

General Procedure for Reaction of Thiazoles 1 with Electrophile–$AlCl_3$ Complexes. To a stirred solution of thiazole **1** in the selected solvent was added dropwise a solution of electrophile–$AlCl_3$ complex, and stirring was continued as required (Table I). After the reaction was quenched with an aqueous solution of $NaHCO_3$ or with 3–4 equiv of benzylamine, the mixture was filtered through Celite. The organic layer was washed with water to pH 7 and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum, and the residue was chromatographed on Silica. Selected reactions are described in detail.

Reaction of 2-Bromo-1,3-thiazole (1a) with Ethyl Propiolate–$AlCl_3$ Complex (Run 3, Table I). The thiazole **1a** (0.82 g, 5 mmol) in 50 mL of ethyl ether was treated with EP–$AlCl_3$

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complex (10 mmol) according to the general procedure. After 72 h, quenching with aqueous $NaHCO_3$ afforded the crude mixture which was chromatographed (silica, 7:3 petroleum ether/ethyl ether) to give, in order, 50 mg (6%) of **1a**, 33 mg (3.3%) of **4a**, 110 mg (7.8%) of **5a**, and 380 mg (38.2%) of **3a**.

Ethyl 3-(2-oxo-*N*-thiazolyl)-(*Z*)-propenoate (**4a**) showed the following: mp 42–44 °C (from *n*-hexane); IR (CCl_4) 1720, 1695, 1645, 1630 cm^{-1}; ^1H NMR δ 7.99 (d, 1, =CHN, J = 5.7 Hz), 7.06 (d, 1, =CHN, J = 10.9 Hz), 6.20 (d, 1, =CHS, J = 5.7 Hz), 5.5 (d, 1, =CHCOOEt, J = 10.9 Hz), 4.22 (q, 2, OCH_2), 1.3 (t, 3, CH_3); ^{13}C NMR δ 173.0 (s), 165.5 (s), 132.2 (d), 125.8 (d), 105.4 (d), 101.8 (d), 61.1 (t), 14.2 (q); mass spectrum, m/e (relative intensity) 199 (M^+, 43), 154 (35), 126 (100), 98 (70).

Anal. Calcd for $C_8H_9NO_3S$: C, 48.23; H, 4.55; N, 7.03; S, 16.09. Found: C, 48.00; H, 4.49; N, 7.02; S, 15.95.

Ethyl 2-bromo-3-(2-oxo-*N*-thiazolyl)-(*E*)-propenoate (**5a**) showed the following: mp 64–66 °C (from *n*-hexane); IR (CCl_4) 1725, 1700, 1630 cm^{-1}; ^1H NMR δ 8.5 (s, 1, =CHN), 7.99 (d, 1, =CHN, J = 5.8 Hz), 6.36 (d, 1, =CHS, J = 5.8 Hz), 4.35 (q, 2, OCH_2), 1.35 (t, 3, CH_3); ^{13}C NMR δ 171.7 (s), 162.7 (s), 132.7 (d), 121.0 (d), 103.1 (d), 101.1 (s), 63.11 (t), 14.2 (q); mass spectrum, m/e (relative intensity) 277 (M^+, 11), 232 (6), 198 (100), 170 (65), 142 (31), 126 (15), 98 (17).

Anal. Calcd for $C_8H_8BrNO_3S$: C, 34.54; H, 2.89; N, 5.03; S, 11.52; Br, 28.73. Found: C, 34.64; H, 2.79; N, 5.09; S, 11.56; Br, 30.01.

Ethyl 3-(2-oxo-*N*-thiazolyl)-(*E*)-propenoate (**3a**) showed the following: mp 93–95 °C (from *n*-hexane); IR (CCl_4) 1725, 1640 cm^{-1}; ^1H NMR δ 7.94 (d, 1, =CHN, J = 14.5 Hz), 6.93 (d, 1, =CHN, J = 5.7 Hz), 6.39 (d, 1, =CHS, J = 5.7 Hz), 5.95 (d, 1, =CHCOOEt, J = 14.5 Hz), 4.24 (q, 2, OCH_2), 1.3 (t, 3, CH_3); ^{13}C NMR δ 171.0 (s), 166.3 (s), 135.3 (d), 120.4 (d), 105.8 (d), 105.2 (d), 60.7 (t), 14.3 (q); mass spectrum, m/e (relative intensity) 199 (M^+, 50), 154 (43), 126 (100), 98 (72).

Anal. Calcd for $C_8H_9NO_3S$: C, 48.23; H, 4.55; N, 7.03; S, 16.09. Found: C, 47.99; H, 4.50; N, 7.10; S, 16.20.

Reaction of 2-Bromo-1,3-thiazole (1a) with Ethyl Propiolate–$AlCl_3$ Complex (Run 5, Table I). The thiazole **1a** (0.82 g, 5 mmol) in 50 mL of ethyl ether was treated with EP–$AlCl_3$ complex (10 mmol) according to the general procedure. After 72 h, quenching with 3.21 g (30 mmol) of benzylamine in 100 mL of ether afforded the crude mixture which was chromatographed (silica, 95:5 benzene/ethyl ether) to give, in order, 20 mg (1.1%) of **7a**, 490 mg (34%) of **6a**, and 50 mg (5%) of **3a**.

Ethyl 2-bromo-3-[2-(benzylimino)-*N*-thiazolyl]-(*E*)-propenoate (**7a**) showed the following: mp 68–71 °C (from *n*-pentane); IR (KBr) 1700, 1645, 1610 cm^{-1}; ^1H NMR δ 8.86 (s, 1, =CHN), 7.97 (d, 1, =CHN, J = 5.28 Hz), 7.35 (m, 5, Ar H), 6.14 (d, 1, =CHS, J = 5.28 Hz), 4.38 (s, 2, $=NCH_2Ph$), 4.30 (q, 2, OCH_2), 1.34 (t, 3, CH_3); mass spectrum, m/e (relative intensity) 366 (M^+, 13), 287 (100), 259 (10), 215 (16), 213 (10), 187 (17), 181 (17).

Anal. Calcd for $C_{15}H_{15}BrN_2O_2S$: C, 49.05; H, 4.12; N, 7.63; S, 8.73; Br, 21.76. Found: C, 49.12; H, 4.10; N, 7.59; S, 8.69; Br, 21.85.

Ethyl 3-[2-(benzylimino)-*N*-thiazolyl]-(*E*)-propenoate (**6a**) showed the following: mp 64–66 °C (from *n*-hexane); IR (KBr) 1700, 1640, 1610 cm^{-1}; ^1H NMR δ 8.25 (d, 1, =CHN, J = 14.8 Hz), 7.35 (m, 5, Ar H), 6.77 (d, 1, =CHN, J = 5.08 Hz), 6.13 (d, 1, =CHS, J = 5.08 Hz), 5.96 (d, 1, =CHCOOEt, J = 14.8 Hz), 4.37 (s, 2, $=NCH_2Ph$), 4.22 (q, 2, OCH_2), 1.29 (t, 3, CH_3); ^{13}C NMR δ 167.2 (s), 154.5 (s), 139.5 (s), 137.3 (d), 128.4 (d), 127.6 (d), 126.9 (d), 122.6 (d), 102.3 (d), 101.8 (d), 60.2 (t), 58.5 (t), 14.4 (q); mass spectrum, m/e (relative intensity) 288 (M^+, 3), 205 (34), 91 (100), 65 (19).

Anal. Calcd for $C_{15}H_{16}N_2O_2S$: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.40; H, 5.60; N, 9.77; S, 11.15.

Reaction of 2-Bromo-1,3-thiazole (1a) with Dimethyl Acetylenedicarboxylate–$AlCl_3$ Complex (Run 6, Table I). The thiazole **1a** (0.82 g, 5 mmol) in 50 mL of ethyl ether was treated with DMAD–$AlCl_3$ complex (10 mmol) according to the general procedure. After 48 h, quenching with aqueous $NaHCO_3$ afforded the crude mixture which was chromatographed (silica, 1:1 cyclohexane/ethyl ether) to give, in order, 760 mg of a mixture of unreacted **1a** and DMAD, 70 mg (4.4%) of **5b** and 530 mg of a mixture of **3b** and **4b** (43.6%) in a 3.8:1 molar ratio (from NMR).

Dimethyl 2-bromo-3-(2-oxo-*N*-thiazolyl)-butenedioate (**5b**) showed the following: mp 89–91 °C (from *n*-pentane); IR (KBr) 1740, 1720, 1670, 1610 cm^{-1}; ^1H NMR δ 6.63 (d, 1, =CHN, J = 5.8 Hz), 6.31 (d, 1, =CHS, J = 5.8 Hz), 3.92 (s, 3, CH_3), 3.81 (s, 3, CH_3); mass spectrum, m/e (relative intensity) 321 (M^+, 12), 290 (10), 242 (100), 112 (17), 99 (25).

Anal. Calcd for $C_9H_8BrNO_5S$: C, 33.55; H, 2.50; N, 4.35; S, 9.95; Br, 24.81. Found: C, 33.59; H, 2.52; N, 4.30; S, 9.90; Br, 24.86.

The mixture of dimethyl 3-(2-oxo-*N*-thiazolyl)butenedioates **3b** and **4b** showed the following: yellow oil; IR (film) 1735, 1680, 1570 cm^{-1}; mass spectrum, m/e (relative intensity) 243 (M^+, 21), 212 (7), 184 (81), 156 (16), 115 (100), 111 (19), 86 (38). The NMR characteristics of each compound were derived from the spectrum of the mixture.

Dimethyl 3-(2-oxo-*N*-thiazolyl)-(*E*)butenedioate (**3b**) showed the following: ^1H NMR δ 7.04 (s, 1, MeOOCCH=C), 6.58 (d, 1, =CHN, J = 5.6 Hz), 6.23 (d, 1, =CHS, J = 5.6 Hz), 3.87 (s, 3, OCH_3), 3.77 (s, 3, OCH_3); ^1H NMR (C_6D_6) δ 6.86 (s, 1, MeOOCCH=C), 6.07 (d, 1, =CHN, J = 5.6 Hz), 5.44 (d, 1, =CHS, J = 5.6 Hz), 3.30 (s, 3, OCH_3), 3.26 (s, 3, OCH_3); ^{13}C NMR δ 171.0 (s), 163.2 (2), 162.6 (s), 134.9 (s), 127.0 (d), 124.4 (d), 101.9 (d), 53.6 (q), 52.5 (q).

Dimethyl 3-(2-oxo-*N*-thiazolyl)-(*Z*)-butenedioate (**4b**) showed the following: ^1H NMR δ 6.67 (d, 1, =CHN, J = 5.6 Hz), 6.42 (s, 1, MeOOCCH=C), 6.31 (d, 1, =CHS, J = 5.6), 3.91 (s, 3, OCH_3), 3.77 (s, 3, OCH_3); ^1H NMR (C_6D_6) δ 6.09 (s, 1, MeOOCCH=C), 5.85 (d, 1, =CHN, J = 5.6 Hz), 5.29 (d, 1, =CHS, J = 5.6 Hz), 3.6 (s, 3, OCH_3), 3.35 (s, 3, OCH_3); ^{13}C NMR δ 170.0 (s), 164.9 (s), 162.9 (s), 139.4 (s), 122.2 (d), 112.7 (d), 104.7 (d), 53.4 (q), 52.3 (q).

Debromination of *N*-(Bromovinyl)thiazolin-2-one (5a). To a stirred solution of **5a** (0.1 g, 0.36 mmol) in dry THF (50 mL) was added tributyltin hydride (0.99 g, 3.4 mmol). After 72 h, the mixture was treated with a saturated solution of KF in water and extracted with ethyl ether. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude mixture was chromatographed (silica, 7:3 cyclohexane/ethyl ether) to give, in order, 4 mg (5.5%) of **4a**, 5 mg (5%) of **5a**, and 22 mg (30.5%) of **3a**.

Photolysis of *N*-Vinylthiazolin-2-ones 3a and 4a. A solution of 10 mg (0.052 mmol) of **3a** in CH_2Cl_2 (10 mL) was irradiated in a photochemical reactor (Rayonet Model RMR-400) by using a 3000-Å lamp. After 4 h, the solution was evaporated and chromatographed on a preparative silica plate (7:3 cyclohexane/ethyl ether as eluent) to give 6.4 mg (61.5%) of **3a** and 2.2 mg (21.2%) of **4a**.

Irradiation of **4a** (same amount of **3a** and conditions) gave 4.8 mg (46.2%) of **3a** and 3.2 mg (30.8%) of **4a**.

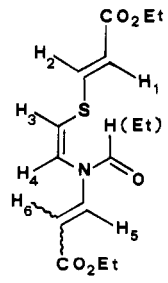
Debromination of *N*-(Bromovinyl)thiazolin-2-one (5b). To a stirred solution of **5b** (0.1 g, 0.31 mmol) in dry THF (50 mL) was added tributyltin hydride (0.99 g, 3.4 mmol). After 72 h, the mixture was treated with a saturated solution of KF in water and extracted with ethyl ether. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under vacuum. The crude mixture was chromatographed (silica, 7:3 cyclohexane/ethyl ether) to give 40 mg (53%) of **4b**.

Reaction of 1,3-Thiazole (1b) with Ethyl Propiolate–$AlCl_3$ Complex (Run 7, Table I). To a solution of EP–$AlCl_3$ complex (10 mmol) in dry benzene (100 mL) was added dropwise a solution of **1b** (0.425 g, 5 mmol) in the same solvent (100 mL). After 120 h, the reaction mixture was quenched with aqueous $NaHCO_3$ and chromatographed (silica, 7:3 cyclohexane/ethyl acetate) to give 47 mg (3.2%) of **9b**, 59 mg (5.8%) of **8b**, and 382 mg (25.6%) of **10b**.

An arbitrary numbering system is adopted for the identification of the various protons and the corresponding signals of compounds **9** and **10**.

The adduct **9b** showed the following: mp 69–71 °C (from *n*-hexane); IR (KBr) 1700, 1630, 1590 cm^{-1}; ^1H NMR δ 8.4 (s, 1, HC=O), 8.0 (br, 1, H_2), 7.6 (d, 1, H_5, $J_{5,6}$ = 15.6 Hz), 6.65 (d, 1, H_4, $J_{3,4}$ = 7.2 Hz), 6.25 (d, 1, H_3, $J_{3,4}$ = 7.2 Hz), 5.95 (d, 1, H_6, $J_{6,5}$ = 15.6 Hz), 5.45 (d, 1, H_1, $J_{1,2}$ = 14.6 Hz), 4.25 (q, 2, CH_2O), 4.23 (q, 2, CH_2O), 1.3 (t, 6, CH_3); mass spectrum, m/e (relative intensity) 299 (M^+, 5), 271 (10), 225 (21), 179 (54), 168 (76), 152 (90), 114 (100). Anal. Calcd for $C_{13}H_{17}NO_5S$: C, 52.16; H, 5.72; N, 4.68; S, 10.71. Found: C, 52.11; H, 5.69; N, 4.72; S, 10.75.

The adduct **10b** showed the following: mp 67–69 °C (from *n*-hexane); IR (KBr) 1725, 1700, 1640, 1620 cm^{-1}; ^1H NMR δ 8.4



9-10

(s, 1, HC=O), 8.0 (br, 1, H_2), 7.08 (d, 1, H_5, $J_{5,6}$ = 10.1 Hz), 6.65 (d, 1, H_4, $J_{4,3}$ = 7.3 Hz), 6.18 (d, 1, H_3, $J_{3,4}$ = 7.3 Hz), 5.95 (d, 1, H_6, $J_{6,5}$ = 10.1 Hz), 5.4 (d, 1, H_1, $J_{1,2}$ = 14.1 Hz), 4.19 (q, 4, OCH_2), 1.28 (t, 6, CH_3); mass spectrum, *m/e* (relative intensity) 299 (M^+, 7), 271 (23), 225 (23), 179 (59), 168 (82), 152 (100).

Anal. Calcd for $C_{13}H_{17}NO_5S$: C, 52.16; H, 5.72; N, 4.68; S, 10.71. Found: C, 52.17; H, 5.66; N, 4.62; S, 10.83.

2-[(Ethyloxycarbonyl)methyl]-3-formyl-Δ^4-thiazoline (**8b**) showed the following: oil, IR (film) 1720, 1670, 1600 cm^{-1}; ^1H NMR δ 8.4 (s, 1, HC=O), 6.38 (d, 1, =CHN, J = 4.6 Hz), 6.1 (dd, 1, J = 4 Hz, J = 9.6 Hz), 5.75 (d, 1, =CHS, J = 4.6 Hz), 4.2 (q, 2, OCH_2), 3.22 (dd, 1, J = 4 Hz, J = 16 Hz), 2.8 (dd, 1, J = 9.6 Hz, J = 16 Hz), 1.27 (t, 3, CH_3); ^{13}C NMR δ 169.5 (s), 158.9 (d), 119.6 (d), 107.5 (d), 61.0 (t), 59.4 (d), 40.5 (t), 14.1 (q); mass spectrum (CI, methane), *m/e* (relative intensity) 202 (M^+ + 1, 60), 174 (42), 173 (35), 114 (55), 86 (100).

Anal. Calcd for $C_8H_{11}NO_3S$: C, 47.75; H, 5.51; N, 6.96; S, 15.93. Found: C, 47.62; H, 5.54; N, 6.70; S, 15.97.

Reaction of 2-Ethyl-1,3-thiazole (1c) with Ethyl Propiolate–$AlCl_3$ Complex (Run 8, Table I). To a solution of EP–$AlCl_3$ complex (10 mmol) in dry ether (100 mL) was added dropwise a solution of **1c** (0.53 g, 5 mmol) in the same solvent (100 mL). After 144 h, the reaction mixture was quenched with aqueous $NaHCO_3$ and the crude mixture was chromatographed (silica, 7:3 *n*-hexane/ethyl acetate) to give, in order, 148 mg (26.2%) of **1c**, 27 mg (1.6%) of **9c**, 97 mg (8.4%) of **8c**, and 101 mg (6.2%) of **10c**.

The adduct **9c** showed the following: oil; IR (film), 1720, 1630 cm^{-1}; ^1H NMR δ 8.28 (d, 1, H_2, $J_{2,1}$ = 14.3 Hz), 7.6 (d, 1, H_5, $J_{5,6}$ = 15.3 Hz), 6.68 (d, 1, H_4, $J_{4,3}$ = 7 Hz), 6.33 (d, 1, H_3, $J_{3,4}$ = 7 Hz), 5.85 (d, 1, H_6, $J_{6,5}$ = 15.3 Hz), 5.25 (d, 1, H_1, $J_{1,2}$ = 14.3 Hz).

Anal. Calcd for $C_{15}H_{21}NO_5S$: C, 55.03; H, 6.46; N, 4.28 S, 9.79. Found: C, 54.91; H, 6.40; N, 4.25; S, 9.75.

The adduct **10c** showed the following: mp 106–107 °C (from cyclohexane); IR (KBr) 1715, 1695, 1610 cm^{-1}; ^1H NMR δ 8.3 (d, 1, H_2, $J_{2,1}$ = 14.2 Hz), 7.09 (d, 1, H_5, $J_{5,6}$ = 10.1 Hz), 6.63 (d, 1, H_4, $J_{4,3}$ = 7 Hz), 6.2 (d, 1, H_3, $J_{3,4}$ = 7 Hz), 5.98 (d, 1, H_6, $J_{6,5}$ = 10.1 Hz), 5.27 (d, 1, H_1, $J_{1,2}$ = 14.2 Hz), 4.2 (q, 2, OCH_2), 4.18 (q, 2, OCH_2), 2.50 (q, 2, CH_2—C=O), 1.28 (t, 6, CH_3), 1.17 (t, 3, CH_3); mass spectrum, *m/e* (relative intensity) 327 (M^+, 18), 270 (25), 225 (15), 196 (100), 179 (50), 152 (68), 86 (27).

Anal. Calcd for $C_{15}H_{21}NO_5S$: C, 55.03; H, 6.46; N, 4.28; S, 9.79. Found: C, 55.11; H, 6.40; N, 4.32; S, 9.81.

2-[(Ethoxycarbonyl)methyl]-3-propanoyl-Δ^4-thiazoline (**8c**) showed the following: oil; IR (film) 1730, 1660 cm^{-1}; ^1H NMR δ 6.35 (d, 1, =CHN, J = 4.8 Hz), 6.18 (dd, 1, J = 4.4 Hz, J = 9.4 Hz), 5.72 (d, 1, =CHS, J = 4.8 Hz), 4.17 (q, 2, OCH_2), 3.12 (dd, 1, J = 4.4 Hz, J = 16 Hz), 2.75 (dd, 1, J = 9.4 Hz, J = 16 Hz), 2.37 (q, 2, CH_2—C=O), 1.2 (t, 6, CH_3).

Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.36; H, 6.60; N, 6.11; S, 13.99. Found: C, 52.41; H, 6.65; N, 6.20; S, 13.83.

Reaction of 2-Bromo-1,3-thiazole (1a) with Ethyl Acrylate–$AlCl_3$ Complex. To a solution of ethyl acrylate–$AlCl_3$ complex (3.6 mmol) in dry benzene (50 mL) was added dropwise a solution of **1a** (0.3 g, 1.8 mmol) in the same solvent (50 mL). The solution was refluxed for 72 h and quenched with aqueous $NaHCO_3$. The crude mixture was chromatographed (silica, 95:5 dichloromethane/ethyl acetate) to give 130 mg (36.1%) of ethyl-3-(2-oxo-*N*-thiazolyl)propanoate (**17a**) as a yellow oil; IR (film) 1730, 1650 cm^{-1}; ^1H NMR δ 6.62 (d, 1, =CHN, J = 5.3 Hz), 6.02 (d, 1, =CHS, J = 5.3 Hz), 4.07 (q, 2, OCH_2), 3.91 (t, 2 N–CH_2, J = 6.5 Hz), 2.65 (t, 2, CH_2COOEt, J = 6.5 Hz), 1.17 (t, 3, CH_3); ^{13}C NMR δ 171.9 (s), 171.1 (s), 125.4 (d), 100.8 (d), 60.9 (t), 41.3 (t), 33.5 (t), 14.1 (q); mass spectrum, *m/e* (relative intensity) 201 (M^+, 66), 156 (36), 128 (40), 127 (46), 101 (73), 86 (40), 73 (76), 55 (100).

Anal. Calcd for $C_8H_{11}NO_3S$: C, 47.75; H, 5.51; N, 6.96; S, 15.93. Found: C, 47.66; H, 5.47; N, 6.89; S, 15.87.

Reaction of 2-Bromo-1,3-thiazole (1a) with Acrylonitrile–$AlCl_3$ Complex. To a solution of acrylonitrile–$AlCl_3$ complex (3.6 mmol) in dry benzene (50 mL) was added dropwise a solution of **1a** (0.3 g, 1.0 mmol) in the same solvent (50 mL). The solution was refluxed for 72 h and quenched with aqueous $NaHCO_3$. The crude mixture was chromatographed (silica, 95:5 dichloromethane: ethyl acetate) to give 100 mg (36.1%) of 3-(2-oxo-*N*-thiazolyl)propionitrile (**17b**): mp 59–61 °C (from *n*-hexane); IR (KBr) 2240, 1650 cm^{-1}; ^1H NMR δ 6.73 (d, 1, =CHN, J = 5.3 Hz), 6.21 (d, 1, =CHS, J = 5.3 Hz), 4.02 (t, 2, N–CH_2, J = 6.4 Hz), 2.8 (t, 2, CH_2CN, J = 6.4 Hz); ^{13}C NMR δ 172.0 (s), 124.2 (d), 117.0 (s), 102.3 (d), 41.5 (t), 17.8 (t); mass spectrum, *m/e* (relative intensity) 154 (M^+, 96), 126 (100), 114 (59), 101 (79), 98 (87), 86 (100), 81 (50).

Anal. Calcd for $C_6H_6N_2OS$: C, 46.74; H, 3.92; N, 18.17; S, 20.79. Found: C, 46.81; H, 3.95; N, 18.19; S, 20.83.

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Registry No. **1a**, 3034-53-5; **1b**, 288-47-1; **1c**, 15679-09-1; **3a**, 76885-35-3; **3b**, 76885-40-0; **4a**, 76885-36-4; **4b**, 82134-85-8; **5a**, 76885-37-5; **5b**, 82134-86-9; **6a**, 76885-38-6; **7a**, 82134-87-0; **8b**, 82134-88-1; **8c**, 82134-89-2; **9b**, 82134-90-5; **9c**, 82134-91-6; **10b**, 82134-92-7; **10c**, 82134-93-8; **17a**, 82134-94-9; **17b**, 82134-95-0; EP, 623-47-2; DMAD, 762-42-5; $AlCl_3$, 7446-70-0; acrylonitrile, 107-13-1; ethyl acrylate, 140-88-5.