1,3-Dipolar Cycloaddition of 5,6-Dihydroimidazo[2,1-*b*]thiazolium Betaines

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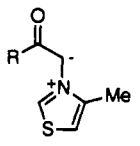
5,6-Dihydroimidazo[2,1-*b*]thiazolium betaines were generated in situ from 3,7-disubstituted 5,6-dihydroimidazo[2,1-*b*]thiazolium bromides and triethylamine. The reaction of these imidazothiazolium betaines with acetylenic dipolarophiles, such as ethyl propiolate, dimethyl acetylenedicarboxylate, and dibenzoylacetylene, provided geometric cis,trans isomers containing 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazole. We have proposed a mechanism of this reaction that involves 1,3-dipolar cycloaddition, isomeric rearrangement, and then nucleophilic addition successively. The ratio of trans and cis isomers depended on the temperature and solvents. The stereoselectivity of trans isomers increased with increasing temperature and decreasing polarity of solvents.

Introduction

We have been interested in the reaction of *N*-bridged heterobicyclic systems. Imidazo[2,1-*b*]thiazoles reacted with electrophiles such as isothiocyanates, isocyanates and carbon disulfide to yield the corresponding betaines.[1-3] In our previous work,[4] we reported a 1,4-dipolar cycloaddition of 5,6-dihydro-3-phenyl-7-(*N*-phenylcarbamoyl)imidazo-[2,1-*b*]thiazolium betaine with 2-bromoacetophenone. Potts et al.[5] reported that 4-methylthiazolium betaines **1** undergo condensation with acetylenic dipolarophiles, giving 1:1 or 1:2 rearranged adducts with a variety of dipolarophiles. Recently, Musicki also reported on the synthesis of pyrrolo[1,2-*c*]imidazole mesomeric betaines **2** and their cycloaddition reaction with several kind of dipolarophiles.[6,7]



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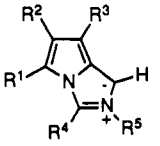

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3-Substituted 5,6-dihydroimidazo[2,1-*b*]thiazoles **3** reacted readily with 2-bromoacetophenones or ethyl bromoacetate in acetone at room temperature, providing the corresponding 3,7-disubstituted 5,6-dihydroimidazo[2,1-*b*]thiazolium bromides **4** (Scheme I).

Now, we wish to describe the 1,3-dipolar cycloaddition of 3,7-disubstituted 5,6-dihydroimidazo[2,1-*b*]thiazolium betaines **5**, which are generated in situ from the salts **4** and triethylamine, with acetylenic dipolarophiles.[5,8,9]

Results and Discussion

Isomeric Rearranged 1:2 Adducts. Imidazothiazolium betaines **5** reacted readily with ethyl propiolate to give two 1:2 cis,trans adducts **6** and **7** which were isolated by column chromatography (Scheme I) (Table I). The products obtained in this reaction might be not the simple cycloaddition adducts but rather some isomeric

Scheme I

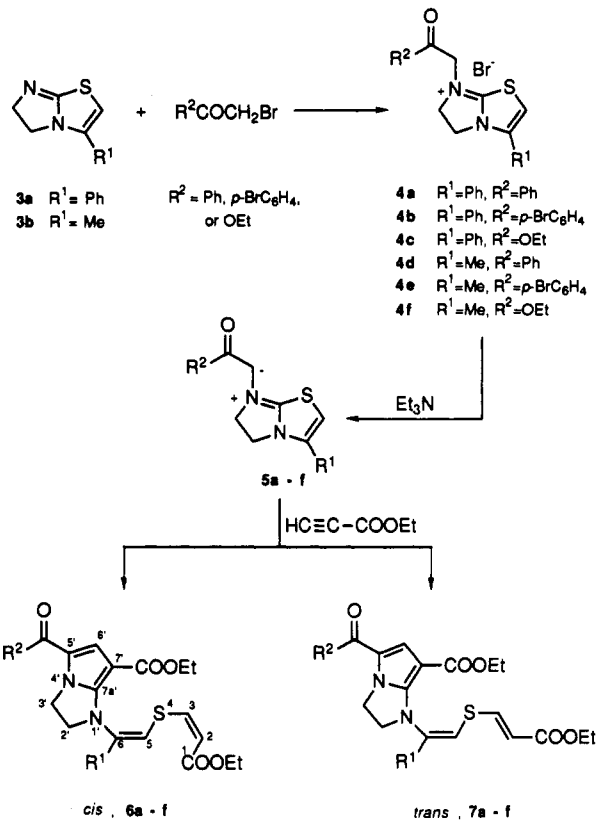

Table I. Reaction of Imidazothiazolium Betaines 5 and Ethyl Propiolate at 20 °C in MeCN

betaines	R^1	R^2	yield,[a] %	*cis*-6/*trans*-7[b]
5a	Ph	Ph	85	48/52
5b	Ph	*p*-BrC_6H_4	82	46/54
5c	Ph	EtO	63	34/66
5d	Me	Ph	48	43/57
5e	Me	*p*-BrC_6H_4	46	36/64
5f	Me	EtO	50	29/71

[a] Isolated yields. [b] The ratio was determined by HPLC.

rearranged products by their analytical and spectral data. ^{1}H NMR spectral data of these products showed typical coupling constants of the AB system of vinyl protons (J = 10.0–10.1 Hz for cis adducts, J = 15.1–15.2 Hz for trans adducts). In the case of compounds **6d** and **7d** (R^1 = Me, R^2 = Ph), all 26 hydrogen and 24 carbon atoms were resolved by HETCOR and DEPT NMR experiments (3 × CH_3, 4 × CH_2, 9 × CH, 8 × C). The ^{1}H NMR spectrum of cis isomer **6d** showed two doublets at δ 7.18 (C_3 H) and

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(8) Ogura, H.; Kikuchi, K. *J. Org. Chem.* **1972**, *37*, 2679.
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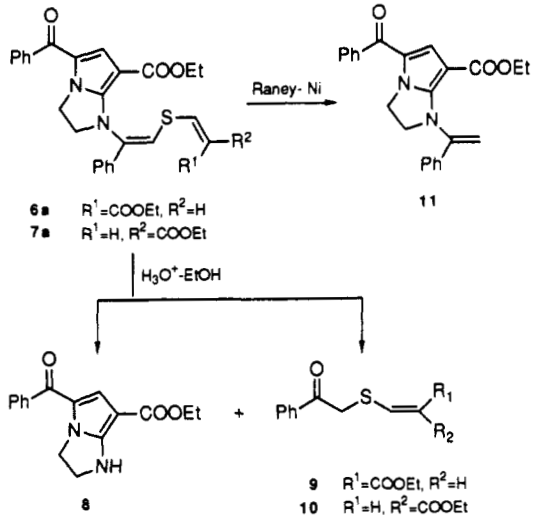
Scheme II



δ 5.86 (C_2 H) with vicinal coupling constants, J = 10.1 Hz, slightly broadened singlets at δ 5.90 (C_5 H) and δ 1.94 (C_7 H) that were recognized as a quartet and a doublet, respectively (J = 1 Hz), and a singlet at δ 7.06 (C_6 H). On the other hand, in the case of trans isomer **7d**, the signal of C_3 H appeared at δ 7.60 in lower field than the analogous proton in cis isomer **6d**, and the value of C_2 H–C_3 H vicinal coupling constants was 15.1 Hz. The mass spectra of **6d** and **7d** were also characterized by m/z = 454 (M^+), 284, due to the loss of 1'-substituent of pyrroloimidazole ring from a molecular ion and protonation, 171, based on a 1'-substituent fragment of pyrroloimidazole ring, and 105 as a base peak.

The stereochemistry of the C_5=C_6 double bond was determined by NOE difference spectra. On irradiation of C_7 H of **6d** or **7d**, a positive NOE enhancement for the C_5 H was observed (1.3% for both **6d** and **7d**). This result indicates that C_7 and C_5 H are on the same side of the C_5=C_6 double bond.

Chemical Evidence in Support of Structures Assigned. Isomers **6a** or **7a** were decomposed to **8** and **9** or **10**, respectively, under aqueous acidic conditions (Scheme II). Structural elucidation of **8**, **9**, and **10** were accomplished on the basis of spectral data and microanalyses. The IR spectra of **9** showed absorption in the NH stretching region of 3335 cm^{-1}. The ^1H NMR spectra of **8** were characterized by a D_2O-exchangeable broad singlet at δ 5.13 assigned to the NH proton and a singlet at δ 6.98 assigned to the C_6 proton. Also, the mass spectrum of **8** showed a molecular ion peak at m/z = 284 and a base peak at m/z = 238 due to the loss of EtOH from the molecular ion. The ^1H NMR spectra of **9** and **10** proved that their stereochemistry was retained in this reaction. The ^1H NMR spectrum of cis isomer **9** showed two doublets at δ 7.18 (C_3 H) and δ 5.88 (C_2 H) with vicinal coupling constants, J = 10.0 Hz, and a singlet at δ 4.01 (C_5 H). On the other hand, in case of trans isomer **10**, chemical shifts of C_3 H and C_5 H were observed at δ 7.64 and δ 4.25, respectively, in lower field than the analogous protons in cis isomer **9**, and the coupling constant of C_2 H–C_3 H was 15.2 Hz higher value than that of cis isomer **9**. The mass spectra of **9** and **10** showed an identical pattern, a molecular ion peak at m/z = 250 and a benzoyl ion peak at m/z = 105 as a base peak.

Fortunately, the treatment of **6a** or **7a** with Raney nickel resulted in desulfurization to give a styrene product **11** (Scheme II), characterized by its ^1H NMR spectrum of two singlet at δ 5.23 and δ 4.94 based on its two styrene protons and by a molecular ion peak at m/z = 386.

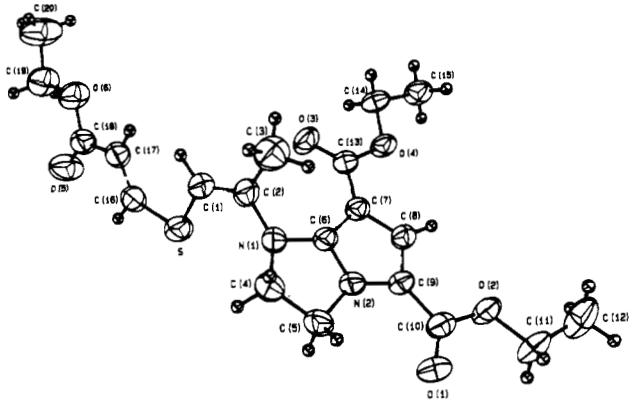
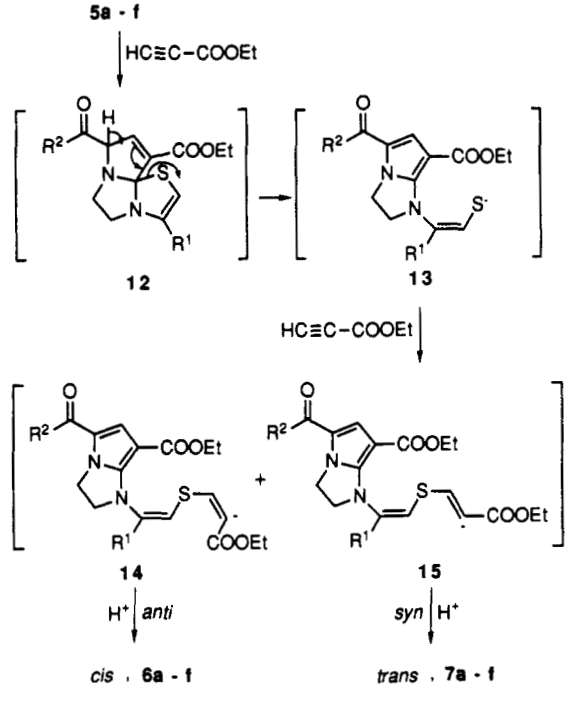


Figure 1. Crystal structure of **7f**.

Scheme III



X-ray Crystal Diffraction Analysis. In order to confirm the structures assigned, we tried to prepare the single crystals of all the products **6** and **7** for X-ray crystallography. Eventually, in the case of **7f**, we were able to obtain a good crystal, and the X-ray crystal diffraction analysis of **7f** confirmed the pyrroloimidazole ring system with the trans configuration, as depicted in Figure 1.

Mechanism. A plausible mechanism for the reaction of 3,7-disubstituted 5,6-dihydroimidazo[2,1-*b*]thiazolium betaines **5** with ethyl propiolate to give isomeric rearranged 1:2 adducts may be represented by the sequence as shown in Scheme III. First, the betaines **5** may undergo normal 1,3-dipolar cycloaddition with one molecule of ethyl propiolate to give tricyclic intermediates **12**,[10] then, ring opening of thiazole may be proceeded by cleavage of C_{11}–S bond. It seems that a rearrangement to the formation of the aromatic pyrrole provides the driving force for the C_{11}–S bond breaking. Several papers have mentioned this similar type of bond breaking between carbon and het-

(10) Our unpublished result; this kind of tricyclic adduct was isolated from the 1,3-cycloaddition reaction of 3-phenyl-6,7-dihydro-5*H*-thiazolo[3,2-*a*]pyrimidine and ethyl propiolate.

Table II. Product Ratio in Reaction of Betaine 5a and Ethyl Propiolate at Various Temperatures in MeCN

T, °C	*cis*-6a/*trans*-7a[a]	T, °C	*cis*-6a/*trans*-7a[a]
40	42/58	-10	56/44
20	48/52	-20	57/43
10	51/49	-30	61/39
0	53/47		

[a] The ratio was determined by HPLC.

Table III. Product Ratio in Reaction of Betaine 5a and Ethyl Propiolate in Various Solvents at 20 °C

solvents	reactn time, h	conversn rate, %	yield,[a] %	*cis*-6a/*trans*-7a[b]
benzene	8	72	77	4/96
dichloromethane	8	85	82	6/94
dioxane	8	42	84	8/92
acetone	8	91	76	22/78
acetonitrile	2	100	85	48/52
DMF	2	100	80	55/45
DMSO	2	100	74	58/42

[a] Isolated yields. [b] The ratio was determined by HPLC.

eroatoms in the heterocyclic systems.[5,6,9,11] The final stage may be nucleophilic attack of vinyl sulfide anion **13** toward another molecule of ethyl propiolate and protonation. There are two possible attacks for nucleophilic addition on ethyl propiolate, anti and syn attacks. If anti attack is favored, then cis isomer **6** will be produced via a transition state of cis vinyl anion **14**. In the other case, trans isomer **7** will be produced via a transition state of trans vinyl anion **15**. The rate of this nucleophilic addition of vinyl sulfide anion **13** toward ethyl propiolate seems to be faster than that of tautomerization of vinyl sulfide anion **13**. So, cycloadducts **6a–f** and **7a–f** with *Z* geometry of the C_5=C_6 double bond were produced exclusively.

Temperature and Solvent Effects. In Table II, the temperature effect in the reaction of imidazothiazolium betaine **5a** and ethyl propiolate appears. It was shown that the ratio of trans isomer increased with increasing temperature. Thus, the trans isomer seems to be the thermodynamically controlled product, while the cis isomer is the kinetically controlled product. Actually, the cis isomer is sterically much hindered in its molecular model. Also, Table III shows that the solvent plays an important role in the nucleophilic addition to ethyl propiolate. In polar solvents, more effective solvation and more facile charge separation probably provide the necessary rationale for anti addition. On the other hand, in nonpolar solvents anionic nucleophiles are more likely to be paired with a proton, and now syn addition may become more favorable. It seems to be accepted that activation energy for charge separation should be reduced with increasing polarity. But in polar solvent, stereoselectivity is decreased as compared with that in nonpolar solvent. It may be due to the relative instability of cis isomer produced via anti attack.

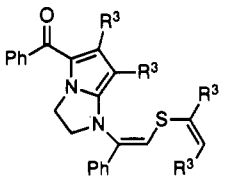
The lower solubility of the starting salts **4** in nonpolar solvent probably leads to the lower generation rate of the betaines **5** from the salts **4** and triethylamine. In nonpolar solvent, considerable amounts of unreacted starting salts **4** were recovered even after being allowed to react at room temperature for 8 h.

Reaction with Other Acetylenic Dipolarophiles. The reaction of imidazothiazolium betaine **5a** with dimethyl acetylenedicarboxylate (DMAD) or dibenzoylacetylene gave analogous 1:2 adducts **16a** and **17a**, **18a** and **19a**, respectively, to **6a** and **7a**, which were difficult to separate by column chromatography (Table IV). But each isomer was able to be identified by ^{1}H NMR spectra of the mixture.

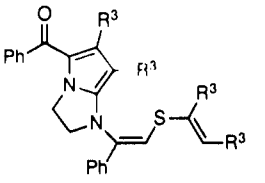
Table IV. Reaction of Imidazothiazolium Betaine 5a with Other Acetylenic Dipolarophiles at 20 °C in DMF

betaine	dipolarophile	yield,[a] %	cis/trans[b]
5a	DMAD	78	54/46
5a	dibenzoylacetylene	81	35/65

[a] Isolated yields. [b] The ratio was determined by ^{1}H NMR.



16a *cis*, R^3 = COOMe
18a *cis*, R^3 = COPh



17a *trans*, R^3 = COOMe
19a *trans*, R^3 = COPh

In the ^{1}H NMR spectra of **6** and **7**, the chemical shifts of C_5 protons showed characteristic trends. The peaks of C_5 protons of cis isomers were observed downfield relative to those of trans isomers. A similar trend was also anticipated in the cases of **16a** and **17a**, **18a** and **19a** because they are located in similar environments.

In the ^{1}H NMR spectrum of the mixture of **16a** and **17a**, eight singlets observed in the range δ 3.20–3.90 were attributable to four CH_3 groups of the mixture. Two singlets at δ 6.00 and δ 6.59 were assigned to C_5 H and C_2 H, respectively, of trans isomer **17**. And two singlets at δ 6.25 and 6.48 were assigned to C_5 H and C_2 H, respectively, of the cis adduct **16a**. The mass spectra of **16a** and **17a** showed an identical pattern, a molecular ion peak at m/z = 604.

In the ^{1}H NMR spectrum of the mixture of **18a** and **19a**, two singlets at δ 6.00 and 5.89 were assigned to C_5 H of cis isomer **18a** and trans isomer **19a**, respectively. The mass spectra of **18a** and **19a** were characterized by an identical molecular ion peak at m/z = 788.

Conclusion

5,6-Dihydroimidazo[2,1-*b*]thiazolium betaines with a 1,3-dipolar structure are prepared by treatment of corresponding thiazolium salts with triethylamine. These imidazothiazolium betaines react readily with acetylenic dipolarophiles to form geometric cis,trans 1:2 adducts with 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazole structure. This reaction seems to be proceeded through three steps, 1,3-dipolar cycloaddition, isomeric rearrangement, and then nucleophilic addition. The stereochemistry of the resulting cis and trans adducts is controlled by the solvent and temperature. The stereoselectivity of trans isomers increase with increasing temperature and decreasing polarity of solvents.

Experimental Section

General. All melting points were determined on a Thomas-Hoover capillary melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin-Elmer Model 1310 infrared spectrophotometer. NMR spectra were obtained on a Varian Gemini 300 spectrometer and a Brucker AC 300P spectrometer. All chemical shift values were reported in the δ scale from internal tetramethylsilane. Mass spectra were recorded on a Hewlett-Packard Model 5985B spectrometer. Microanalyses were determined with a Perkin-Elmer 240 DS element analyzer. Analytical liquid chromatograms were obtained with Varian Star LC (9010 solvent delivery system and 9050 UV detector) using a

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Merck LiChrosorb RP-18 column (4 × 250 mm, 10 μm) with 85/15 MeOH/H_2O as eluent, at 254 nm. Preparative liquid chromatography was performed on a Buchi B-680 MPLC system, using a column packed with Merck Kieselgel 60 (230–400 mesh).

3-Phenyl-5,6-dihydroimidazo[2,1-*b*]thiazole (**3a**) and 3-methyl-5,6-dihydroimidazo[2,1-*b*]thiazole (**3b**) were prepared by condensing 2-imidazolidinethione with 2-bromoacetophenone and chloroacetone, respectively, as reported in the literature.[12-15]

General Procedure for Preparation of 3,7-Disubstituted 5,6-Dihydroimidazo[2,1-*b*]thiazolium Salts 4. 3-Substituted 5,6-dihydroimidazo[2,1-*b*]thiazole **3** (100 mmol) and bromoacetophenones (100 mmol) or ethyl bromoacetate (100 mmol) were stirred in dry acetone at room temperature for 5 h. After cooling, the formed salts were filtered and recrystallized.

3-Phenyl-7-(2-phenyl-2-oxoethyl)-5,6-dihydroimidazo[2,1-*b*]thiazolium bromide (4a): 97%; mp 262–265 °C dec (EtOH–H_2O (3:2)), cream crystals; IR (KBr) 1692, 1595, 1439, 1302, 1224, 767 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.04 (d, 2, *J* = 7.2 Hz, Ar H), 7.75–7.56 (m, 8, Ar H), 7.15 (s, 1, C_2 H), 5.49 (s, 2, CH_2CO), 4.69 (t, 2, *J* = 9.5 Hz, C_6 H), 4.38 (t, 2, *J* = 9.5 Hz, C_5 H); ^{13}C NMR (Me_2SO-d_6) δ 192.30, 172.30, 137.70, 134.32, 134.05, 130.27, 129.24, 128.91, 128.28, 127.56, 127.44, 108.59, 56.08, 54.01, 47.47.

Anal. Calcd for $C_{19}H_{17}BrN_2OS$: C, 56.86; H, 4.27; N, 6.98. Found: C, 56.70; H, 4.23; N, 6.97.

3-Phenyl-7-[2-(4′-bromophenyl)-2-oxoethyl]-5,6-dihydroimidazo[2,1-*b*]thiazolium bromide (4b): 95%; mp 252–255 °C dec (EtOH–H_2O (3:2)), cream crystals; IR (KBr) 1696, 1588, 1371, 1286, 1218, 982 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.97 (d, 2, *J* = 8.5 Hz, Ar H), 7.83 (d, 2, *J* = 8.5 Hz, Ar H), 7.72–7.69 (m, 2, Ar H), 7.57–7.55 (m, 3, Ar H), 7.19 (s, 1, C_2 H), 5.53 (s, 2, CH_2CO), 4.70 (t, 2, *J* = 9.5 Hz, C_6 H), 4.39 (t, 2, *J* = 9.5 Hz, C_5 H); ^{13}C NMR (Me_2SO-d_6) δ 191.79, 172.16, 137.57, 133.10, 131.96, 130.28, 129.23, 128.38, 127.54, 127.41, 108.94, 56.07, 54.21, 47.54.

Anal. Calcd for $C_{19}H_{16}Br_2N_2OS$: C, 47.52; H, 3.36; N, 5.83. Found: C, 47.34; H, 3.30; N, 5.89.

3-Phenyl-7-(2-ethoxy-2-oxoethyl)-5,6-dihydroimidazo[2,1-*b*]thiazolium bromide (4c): 93%; mp 145–147 °C (acetone–EtOH (2:1)), colorless crystals; IR (KBr) 1726, 1580, 1370, 1291, 1239 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.69–7.66 (m, 2, Ar H), 7.55–7.53 (m, 3, Ar H), 7.21 (s, 1, C_2 H), 4.67 (s, 2, CH_2CO), 4.65 (t, 2, *J* = 9.3 Hz, C_6 H), 4.37 (t, 2, *J* = 9.3 Hz, C_5 H), 4.20 (q, 2, *J* = 7.1 Hz, CH_2CH_3), 1.24 (t, 3, *J* = 7.1 Hz, CH_2CH_3); ^{13}C NMR (Me_2SO-d_6) δ 171.80, 167.16, 137.64, 130.26, 129.22, 127.53, 127.30, 109.11, 61.58, 55.75, 48.80, 47.54, 14.00.

Anal. Calcd for $C_{13}H_{17}BrN_2O_2S$: C, 48.79; H, 4.64; N, 7.59. Found: C, 48.50; H, 4.57; N, 7.48.

3-Methyl-7-(2-phenyl-2-oxoethyl)-5,6-dihydroimidazo-[2,1-*b*]thiazolium bromide (4d): 87%; mp 180–182 °C (acetone–EtOH (3:2)), colorless crystals; IR (KBr) 1694, 1595, 1576, 1447, 1381, 1302, 1237 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 8.01 (d, 2, *J* = 7.4 Hz, Ar H), 7.73 (t, 1, *J* = 7.3 Hz, Ar H), 7.62–7.57 (m, 2, Ar H), 6.73 (s, 1, C_2 H), 5.47 (s, 2, CH_2CO), 4.56 (t, 2, *J* = 9.6 Hz, C_6 H), 4.34 (t, 2, *J* = 9.6 Hz, C_5 H), 2.28 (s, 3, CH_3); ^{13}C NMR (Me_2SO-d_6) δ 192.53, 171.29, 134.82, 134.28, 134.02, 128.89, 128.25, 106.77, 55.95, 53.98, 45.52, 12.12.

Anal. Calcd for $C_{14}H_{15}BrN_2OS$: C, 49.57; H, 4.46; N, 8.26. Found: C, 49.30; H, 4.40; N, 8.19.

3-Methyl-7-[2-(4′-bromophenyl)-2-oxoethyl]-5,6-dihydroimidazo[2,1-*b*]thiazolium bromide (4e): 89%; mp 246–248 °C dec (acetone–EtOH (3:2)), cream crystals; IR (KBr) 1699, 1572, 1395, 1296, 1228, 989 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 7.93 (d, 2, *J* = 8.3 Hz, Ar H), 7.83 (d, 2, *J* = 8.3 Hz, Ar H), 6.69 (s, 1, C_2 H), 5.40 (s, 2, CH_2CO), 4.53 (t, 2, *J* = 9.6 Hz, C_6 H), 4.32 (t, 2, *J* = 9.6 Hz, C_5 H), 2.27 (s, 3, CH_3); ^{13}C NMR (Me_2SO-d_6) δ 191.88, 171.29, 134.91, 133.09, 131.95, 130.21, 128.34, 105.61, 55.91, 53.87, 45.46, 12.05.

Anal. Calcd for $C_{14}H_{14}Br_2N_2OS$: C, 40.21; H, 3.37; N, 6.70. Found: C, 40.02; H, 3.28; N, 6.79.

3-Methyl-7-(2-ethoxy-2-oxoethyl)-5,6-dihydroimidazo[2,1-*b*]thiazolium bromide (4f): 90%; mp 146–149 °C (acetone–EtOH (2:1)), colorless crystals; IR (KBr) 1738. 1574, 1379, 1299, 1215, 1023 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 6.79 (s, 1, C_2 H), 4.63 (s, 2, CH_2CO), 4.55 (t, 2, *J* = 9.3 Hz, C_6 H), 4.33 (t, 2, *J* = 9.3 Hz, C_5 H), 4.15 (q, 2, *J* = 7.1 Hz, CH_2CH_3), 2.25 (s, 3, CH_3), 1.20 (t, 3, *J* = 7.1 Hz, CH_2CH_3); ^{13}C NMR (Me_2SO-d_6) δ 170.67, 167.29, 134.81, 107.45, 61.50, 55.59, 48.69, 45.65, 14.00, 12.18.

Anal. Calcd for $C_{10}H_{15}BrN_2OS$: C, 39.10; H, 4.92; N, 9.12. Found: C, 38.85; H, 4.84; N, 8.99.

General Procedure for the Reaction of 3,7-Disubstituted 5,6-Dihydroimidazo[2,1-*b*]thiazolium Betaines 5 with Ethyl Propiolate. A stirred solution of the appropriate imidazothiazolium salt **4** and 2 molar equiv ethyl propiolate in dry acetonitrile was treated dropwise with an equimolar amount of triethylamine. A deep brown color developed with proceeding reaction. After the solution was stirred for 2 h at 20 °C, removal of solvent from the reaction mixture and preparative liquid chromatography (hexane/EtOAc (5:1)) gave cis and trans adducts **6** and **7** (Table I).

Ethyl (2*Z*,5*Z*)-6-[5-benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoate (6a): cream powder; mp 157–158 °C; IR (KBr) 1700, 1609, 1565, 1509, 1331, 1266, 1220, 1168 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (d, 2, *J* = 6.8 Hz, Ar H), 7.53–7.42 (m, 3, Ar H), 7.33–7.27 (m, 5, Ar H), 7.28 (d, 1, *J* = 10.0 Hz, C_3 H), 7.03 (s, 1, $C_{6'}$ H), 6.54 (s, 1, C_5 H), 5.95 (d, 1, *J* = 10.0 Hz, C_2 H), 4.74 (br s, 1, one of CH_2CH_3), 4.68–4.54 (m, 2, $C_{3'}$ H), 4.21 (q, 2, *J* = 7.1 Hz, CH_2CH_3), 4.17 (br s, 1, one of CH_2CH_3), 4.03–3.88 (m, 2, $C_{2'}$ H), 1.29 (t, 3, *J* = 7.1 Hz, CH_2CH_3), 1.06 (t, 3, *J* = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 184.03, 166.28, 162.71, 150.36, 146.09, 139.66, 138.83, 135.67, 131.43, 128.71, 128.65, 128.60, 128.28, 126.93, 125.68, 122.95, 120.89, 114.39, 97.38, 60.48, 59.44, 55.51, 45.57, 14.41, 14.31; mass spectrum *m*/*z* (rel intensity) 77 (41), 105 (100), 121 (24), 210 (10), 237 (26), 283 (19), 373 (9), 443 (11), 516 (57, M^+).

Anal. Calcd for $C_{29}H_{28}N_2O_5S$: C, 67.42; H, 5.46; N, 5.42. Found: C, 67.40; H, 5.46; N, 5.47.

Ethyl (2*E*,5*Z*)-6-[5-benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoate (7a): cream powder; mp 131–133 °C; IR (KBr) 1702, 1614, 1584, 1513, 1334, 1262, 1165 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82 (d, 2, *J* = 6.8 Hz, Ar H), 7.68 (d, 1, *J* = 15.2 Hz, C_3 H) 7.53–7.32 (m, 8, Ar H), 7.06 (s, 1, $C_{6'}$ H), 6.43 (s, 1, C_5 H), 5.96 (d, 1, *J* = 15.2 Hz, C_2 H), 4.66 (br s, 2, $C_{3'}$ H), 4.34 (br s, 1, one of CH_2CH_3), 4.23 (br s, 1, one of CH_2CH_3), 4.18 (q, 2, *J* = 7.1 Hz, CH_2CH_3), 3.97 (br s, 2, $C_{2'}$ H), 1.27 (t, 3, *J* = 7.1 Hz, CH_2CH_3), 1.05 (t, 3, *J* = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 184.08, 164.94, 162.65, 149.84, 143.18, 142.85, 138.69, 135.68, 131.54, 129.15, 128.70, 128.31, 126.55, 126.29, 123.04, 116:26, 116.23, 112.76, 97.70, 60.50, 59.58, 56.00, 45.55, 14.28; mass spectrum *m*/*z* (rel intensity) 77 (49), 105 (100), 121 (32), 207 (17), 237 (21), 283 (17), 373 (14), 411 (14), 443 (13), 516 (42, M^+).

Anal. Calcd for $C_{29}H_{28}N_2O_5S$: C, 67.42; H, 5.46; N, 5.42. Found: C, 67.22; H, 5.46; N, 5.32.

Ethyl (2*Z*,5*Z*)-6-[5-(4′-bromobenzoyl)-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoate (6b): cream powder; mp 139–141 °C; IR (KBr) 1701, 1607, 1565, 1510, 1334, 1268, 1226, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70 (d, 2, *J* = 8.3 Hz, Ar H), 7.60 (d, 2, *J* = 8.3 Hz, Ar H), 7.33–7.31 (m, 5, Ar H), 7.27 (d, 1, *J* = 10.0 Hz, C_3H), 7.00 (s, 1, $C_{6'}$H), 6.55 (s, 1, C_5 H), 5.96 (d, 1, *J* = 10.0 Hz, C_2 H), 4.72 (br s, 1, one of CH_2CH_3), 4.67–4.53 (m, 2, $C_{3'}$H), 4.21 (q, 2, *J* = 7.1 Hz, CH_2CH_3), 4.17 (br s, 1, one of CH_2CH_3), 4.04–3.90 (m, 2, $C_{2'}$H), 1.29 (t, 3, *J* = 7.1 Hz, CH_2CH_3), 1.06 (t, 3, *J* = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 182.60, 166.29, 162.58, 150.56, 146.00, 139.39, 137.59, 135.62, 131.55, 130.26, 128.68, 128.63, 127.00, 126.15, 125.64, 122.61, 121.17, 114.44, 97.56, 60.49, 59.52, 55.46, 45.45, 14.32; mass spectrum *m*/*z* (rel intensity) 103 (89), 105 (56), 121 (92), 183 (77), 185 (100), 193 (54), 207 (61), 283 (50), 315 (54), 317 (52), 355 (50), 365 (61), 411 (59), 594 (82, M^+), 596 (84, M^+).

Anal. Calcd for $C_{29}H_{27}BrN_2O_5S$: C, 58.49; H, 4.57; N, 4.70. Found: C, 58.24; H, 4.55; N, 4.64.

Ethyl (2*E*,5*Z*)-6-[5-(4′-bromobenzoyl)-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoate (7b): cream powder; mp 121–123 °C; IR (KBr) 1700, 1613, 1587, 1510, 1330, 1259, 1162 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70 (d, 2, *J* = 8.2 Hz, Ar H), 7.68 (d, 1, *J* = 15.2 Hz, C_3 H), 7.60 (d, 2, *J* = 8.2 Hz, Ar H), 7.41–7.33 (m, 5, Ar H), 7.03 (s, 1, C_6, H), 6.45 (s, 1, C_5 H), 5.95 (d, 1, *J* = 15.2 Hz, C_2 H), 4.65

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(br s, 2, $C_{3'}$ H), 4.34 (br s, 1, one of CH_2CH_3), 4.23 (br s, 1, one of CH_2CH_3), 4.19 (q, 2, J = 7.1 Hz, CH_2CH_3), 3.98 (br s, 2, $C_{2'}$ H), 1.28 (t, 3, J = 7.1 Hz, CH_2CH_3), 1.06 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 182.67, 164.92, 162.53, 150.06, 143.07, 142.63, 137.46, 135.61, 131.59, 130.25, 129.20, 128.76, 126.62, 126.26, 122.69, 116.45, 116.32, 113.02, 97.89, 60.53, 59.67, 55.95, 45.52, 14.28; mass spectrum m/z (rel intensity) 103 (85), 105 (61), 121 (94), 183 (85), 185 (100), 193 (54), 207 (57), 283 (61), 315 (52), 317 (50), 355 (50), 365 (63), 411 (51), 594 (83, M^+), 596 (85, M^+).

Anal. Calcd for $C_{29}H_{27}BrN_2O_5S$: C, 58.49; H, 4.57; N, 4.70. Found: C, 58.24; H, 4.44; N, 4.61.

Ethyl (2*Z*,5*Z*)-6-[5,7-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoate (6c): colorless powder; mp 116–118 °C; IR (KBr) 1680, 1561, 1509, 1248, 1214, 1164, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.28 (s, 5, Ar H), 7.27 (d, 1, J = 10.1 Hz, C_3 H), 7.11 (s, 1, $C_{6'}$ H), 6.45 (s, 1, C_5 H), 5.93 (d, 1, J = 10.1 Hz, C_2 H), 4.48 (br s, 3, $C_{3'}$ H and one of CH_2CH_3), 4.28 (q, 2, J = 7.1 Hz, CH_2CH_3), 4.21 (q, 2, J = 7.1 Hz, CH_2CH_3), 4.09 (br s, 1, one of CH_2CH_3), 3.97 (br s, 2, $C_{2'}$ H), 1.35 (t, 3, J = 7.1 Hz, CH_2CH_3), 1.29 (t, 3, J = 7.1 Hz, CH_2CH_3), 1.08 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 166.30, 162.72, 160.81, 148.71, 146.43, 140.37, 135.82, 128.51, 125.81, 121.63, 119.87, 114.63, 114.18, 96.52, 69.43, 60.01, 59.24, 55.39, 45.08, 14.49, 14.32; mass spectrum m/z (rel intensity) 77 (28), 103 (43), 121 (89), 202 (77), 206 (82), 251 (89), 267 (23), 341 (45), 411 (41), 484 (100, M^+).

Anal. Calcd for $C_{25}H_{28}N_2O_6S$: C, 61.97; H, 5.82; N, 5.78. Found: C, 61.90; H, 5.70; N, 5.74.

Ethyl (2*E*,5*Z*)-6-[5,7-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoate (7c): colorless powder; mp 79–82 °C; IR (KBr) 1687, 1569, 1515, 1305, 1251, 1160, 1098 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.63 (d, 1, J = 15.1 Hz, C_3 H), 7.34–7.24 (m, 5, Ar H), 7.09 (s, 1, $C_{6'}$ H), 6.31 (s, 1, C_5 H), 5.89 (d, 1, J = 15.1 Hz, C_2 H), 4.40 (t, 2, J = 8.0 Hz, $C_{3'}$ H), 4.24 (br s, 1, one of CH_2CH_3), 4.22 (q, 2, J = 7.1 Hz, CH_2CH_3), 4.13 (br s, 1, one of CH_2CH_3), 4.12 (q, 2, J = 7.1 Hz, CH_2CH_3), 3.92 (br s, 2, $C_{2'}$ H), 1.29 (t, 3, J = 7.1 Hz, CH_2CH_3), 1.21 (t, 3, J = 7.1 Hz, CH_2CH_3), 1.02 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 164.90, 162.58, 160.65, 148.17, 143.56, 143.42, 135.83, 128.99, 128.54, 126.37, 121.24, 115.93, 114.67, 111.61, 96.85, 60.37, 60.02, 59.30, 55.86, 45.16, 14.44, 14.27; mass spectrum m/z (rel intensity) 77 (20), 103 (93), 121 (87), 202 (48), 206 (47), 251 (46), 267 (16), 341 (41), 411 (26), 484 (100, M^+).

Anal. Calcd for $C_{25}H_{28}N_2O_6S$; C, 61.97; H, 5.82; N, 5.78. Found: C, 61.63; H, 5.70; N, 5.67.

Ethyl (2*Z*,5*Z*)-6-[5-benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-4-thiahepta-2,5-dienoate (6d): cream powder; mp 154–155 °C; IR (KBr) 1684, 1604, 1570, 1500, 1321, 1285, 1267, 1222, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78 (d, 2, J = 6.8 Hz, Ar H), 7.54–7.41 (m, 3, Ar H), 7.18 (d, 1, J = 10.1 Hz, C_3 H), 7.06 (s, 1, $C_{6'}$ H), 5.90 (s, 1, C_5 H), 5.86 (d, 1, J = 10.1 Hz, C_2 H), 4.51 (t, 2, J = 8.5 Hz, $C_{3'}$ H), 4.21–4.13 (m, 6, 2 × CH_2CH_3 and $C_{2'}$ H), 1.94 (s, 3, C_7 H), 1.26 (t, 3, J = 7.1 Hz, CH_2CH_3), 1.24 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 183.88, 166.26, 162.96, 150.36, 146.98, 138.83, 138.45, 131.31, 128.46, 128.10, 126.58, 122.82, 119.06, 113.07, 97.23, 60.09, 59.56, 54.64, 45.02, 18.85, 14.27, 14.13; mass spectrum m/z (rel intensity) 77 (44), 105 (100), 171 (18), 210 (15), 238 (19), 284 (12), 295 (13), 323 (18), 381 (16), 454 (40, M^+).

Anal. Calcd for $C_{24}H_{26}N_2O_5S$: C, 63.24; H, 5.77; N, 6.16. Found: C, 63.20; H, 5.73; N, 5.98.

Ethyl (2*E*,5*Z*)-6-[5-benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-4-thiahepta-2,5-dienoate (7d): cream powder; mp 104–105 °C; IR (KBr) 1682, 1615, 1580, 1509, 1490, 1297, 1269, 1242, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.76 (d, 2, J = 6.8 Hz, Ar H), 7.60 (d, 1, J = 15.1 Hz, C_3 H), 7.49–7.39 (m, 3, Ar H), 7.05 (s, 1, $C_{6'}$ H), 5.86 (d, 1, J = 15.1 Hz, C_2 H), 5.81 (s, 1, C_5 H), 4.49 (t, 2, J = 8.5 Hz, $C_{3'}$ H), 4.20–4.10 (m, 6, 2 × CH_2CH_3 and $C_{2'}$ H), 1.99 (s, 3, C_7 H), 1.23 (t, 6, 2 × CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 183.95, 164.93, 162.96, 149.92, 143.80, 143.37, 138.60, 131.43, 128.56, 128.21, 126.36, 123.14, 115.33, 111.03, 97.71, 60.22, 59.70, 55.59, 45.26, 19.77, 14.37, 14.20; mass spectrum m/z (rel intensity) 77 (49), 105 (100), 171 (21), 210 (17), 238 (33), 284 (12), 295 (11), 311 (15), 323 (14), 381 (22), 454 (42, M^+).

Anal. Calcd for $C_{24}H_{26}N_2O_5S$: C, 63.42; H, 5.77; N, 6.16. Found: C, 63.30; H, 5.90; N, 6.01.

Ethyl (2*Z*,5*Z*)-6-[5-(4′-bromobenzoyl)-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-4-thiahepta-2,5-dienoate (6e): pale yellow needles; mp 121–123 °C; IR (KBr) 1690, 1614, 1574, 1506, 1488, 1479, 1337, 1260, 1212, 1159, 1099 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59 (d, 2, J = 8.3 Hz, Ar H), 7.51 (d, 2, J = 8.3 Hz, Ar H), 7.13 (d, 1, J = 10.1 Hz, C_3 H), 6.97 (s, 1, $C_{6'}$ H), 5.87 (s, 1, C_5 H), 5.80 (d, 1, J = 10.1 Hz, C_2 H), 4.43 (t, 2, J = 8.7 Hz, $C_{3'}$ H), 4.14–4.07 (m, 6, 2 × CH_2CH_3 and $C_{2'}$ H), 1.87 (s, 3, C_7 H), 1.18 (t, 6, J = 7.1 Hz, 2 × CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 182.38, 166.34, 162.94, 150.69, 147.04, 138.75, 137.44, 131.51, 130.19, 126.72, 126.14, 122.66, 119.42, 113.29, 97.57, 60.23, 59.76, 54.84, 45.22, 19.09, 14.46, 14.32; mass spectrum m/z (rel intensity) 155 (36), 157 (36), 171 (60), 183 (100), 184 (95), 317 (43), 318 (42), 373 (45), 401 (32), 459 (37), 461 (30), 532 (65, M^+), 534 (60, M^+).

Anal. Calcd for $C_{24}H_{25}BrN_2O_5S$: C, 54.04; H, 4.72; N, 5.25. Found: C, 54.14; H, 4.75; N, 5.20.

Ethyl (2*E*,5*Z*)-6-[5-(4′-bromobenzoyl)-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-4-thiahepta-2,5-dienoate (7e): pale yellow needles; mp 128–130 °C; IR (KBr) 1704, 1620, 1583, 1505, 1483, 1308, 1270, 1163 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.67 (d, 2, J = 8.6 Hz, Ar H), 7.63 (d, 1, J = 15.1 Hz, C_3 H), 7.59 (d, 2, J = 8.6 Hz, Ar H), 7.05 (s, 1, $C_{6'}$ H), 5.88 (d, 1, J = 15.1 Hz, C_2 H), 5.85 (s, 1, C_5 H), 4.52 (t, 2, J = 8.7 Hz, $C_{3'}$ H), 4.24–4.14 (m, 6, 2 × CH_2CH_3 and $C_{2'}$ H), 2.03 (s, 3, C_7 H), 1.27 (t, 6, J = 7.1 Hz, 2 × CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 182.71, 165.08, 162.98, 150.26, 143.87, 143.20, 137.37, 131.62, 130.22, 126.62, 126.36, 122.84, 115.38, 111.43, 97.96, 60.40, 59.95, 55.60, 45.32, 19.93, 14.49, 14.33; mass spectrum m/z (rel intensity) 155 (41), 157 (40), 171 (56), 183 (100), 185 (95), 317 (40), 318 (45), 373 (45), 401 (30), 459 (36), 461 (32), 532 (63, M^+), 534 (60, M^+).

Anal. Calcd for $C_{24}H_{25}BrN_2O_5S$: C, 54.04; H, 4.72; N, 5.25. Found: C, 54.03; H, 4.68; N, 5.23.

Ethyl (2*Z*,5*Z*)-6-[5,7-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-4-thiahepta-2,5-dienoate (6f): colorless powder; mp 126–127 °C; IR (KBr) 1680, 1573, 1517, 1254, 1235, 1180, 1154, 1006 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (d, 1, J = 10.0 Hz, C_3 H), 7.17 (s, 1, $C_{6'}$ H), 5.85 (d, 1, J = 10.0 Hz, C_2 H), 5.84 (s, 1, C_5 H), 4.34–4.07 (m, 10, $C_{3'}$ H, $C_{2'}$ H and 3 × CH_2CH_3), 1.91 (s, 3, C_7 H), 1.34–1.24 (m, 9, 3 × CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 166.50, 163.29, 160.67, 149.03, 147.51, 139.99, 121.63, 118.03, 114.79, 113.17, 96.77, 60.27, 60.06, 59.60, 54.83, 44.87, 18.83, 14.47, 14.34; mass spectrum m/z (rel intensity) 45 (22), 103 (36), 140 (30), 171 (43), 206 (100), 279 (29), 291 (35), 349 (20), 422 (66, M^+).

Anal. Calcd for $C_{20}H_{26}N_2O_6S$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.64; H, 6.13; N, 6.53.

Ethyl (2*E*,5*Z*)-6-[5,7-bis(ethoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-4-thiahepta-2,5-dienoate (7f): colorless crystals; mp 91–93 °C; IR (KBr) 1682, 1588, 1509, 1312, 1238, 1163, 1138, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.58 (d, 1, J = 15.1 Hz, C_3 H), 7.12 (s, 1, $C_{6'}$ H), 5.83 (d, 1, J = 15.1 Hz, C_2 H), 5.72 (s, 1, C_5 H), 4.28–4.08 (m, 10, $C_{3'}$ H, $C_{2'}$ H and 3 × CH_2CH_3), 1.95 (s, 3, C_7 H), 1.30–1.19 (m, 9, 3 × CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 165.07, 163.12, 160.53, 148.39, 144.41, 144.17, 121.34, 115.01, 109.63, 109.58, 97.12, 60.26, 60.05, 59.62, 55.65, 44.92, 19.65, 14.43, 14.28; mass spectrum m/z (rel intensity) 45 (29), 140 (39), 171 (56), 206 (100), 279 (31), 291 (31), 349 (23), 422 (59, M^+).

Anal. Calcd for $C_{20}H_{26}N_2O_6S$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.61; H, 6.19; N, 6.57.

Decomposition of Ethyl 6-[5-Benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoates (6a or 7a) in Aqueous Acidic Ethanol. The cis or trans adduct, **6a** or **7a** (0.5 g, 0.97 mmol), a few drops of concd hydrochloric acid, and 95% ethanol (70 mL) were stirred at 45 °C for 2 h. Removal of solvent from the reaction mixture and preparative liquid chromatography (hexane–EtOAc (3:1)) gave **8** and **9** or **10**, respectively.

5-Benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazole (8): yellow crystals; mp 180–182 °C; IR (KBr) 3335, 1674, 1613, 1530, 1489, 1308, 1164 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.78–7.75 (m, 2, Ar H), 7.52–7.40 (m, 3, Ar H), 6.98 (s, 1, C_6 H), 5.13 (br s, 1, N_1 H), 4.49 (t, 3, J = 8.5 Hz, C_3 H), 4.22 (q, 2, J = 7.1 Hz, CH_2CH_3), 4.06 (td, 2, J = 8.5 Hz, 1.3 Hz, C_2 H), 1.29 (t, 3, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 183.87, 164.21, 155.40, 138.85, 131.34, 128.60, 128.25, 125.43, 123.00, 94.31, 59.73, 49.68, 46.35, 14.62; mass spectrum m/z (rel intensity) 52 (14), 77 (51), 105 (61),

154 (5), 183 (10), 210 (85), 238 (100), 284 (81, M^+).

Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.35; H, 5.70; N, 9.78.

Ethyl (2*Z*)-5-benzoyl-4-thiapent-2-enoate (9): colorless crystals; mp 95–97 °C; IR (KBr) 1661, 1561, 1453, 1375, 1352, 1280, 1224, 1167 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.97–7.94 (m, 2, Ar H), 7.60–7.43 (m, 3, Ar H), 7.18 (d, 1, J = 10.0 Hz, C_3 H), 5.88 (d, 1, J = 10.0 Hz, C_2 H), 4.16 (q, 2, J = 7.1 Hz, CH_2CH_3), 4.01 (s, 2, C_5 H), 1.25 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 194.04, 166.62, 147.07, 134.96, 134.00, 128.85, 128.59, 114.55, 60.31, 39.74, 14.31; mass spectrum m/z (rel intensity) 51 (30), 77 (80), 105 (100), 204 (27), 250 (17, M^+).

Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.19; H, 5.50; N, <0.3.

Ethyl (2*E*)-5-benzoyl-4-thiapent-2-enoate (10): colorless oil; IR (neat) 1695, 1583, 1451, 1388, 1372, 1306, 1255, 1202, 1171, 1038 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.96–7.93 (m, 2, Ar H), 7.64 (d, 1, J = 15.2 Hz, C_3 H), 7.61–7.44 (m, 3, Ar H), 5.81 (d, 1, J = 15.2 Hz, C_2 H), 4.25 (s, 2, C_5 H), 4.14 (q, 2, J = 7.1 Hz, CH_2CH_3), 1.24 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 192.41, 164.97, 144.20, 135.04, 134.00, 128.91, 128.58, 115.53, 60.38, 38.99, 14.31; mass spectrum m/z (rel intensity) 51 (35), 77 (75), 105 (100), 204 (31), 250 (20, M^+).

Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.30; H, 5.53; N, <0.3.

Desulfurization of Ethyl 6-[5-Benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-6-phenyl-4-thiahexa-2,5-dienoates (6a and 7a) with Raney Nickel. The compound **6a** or **7a** (0.5 g, 0.97 mmol) and freshly prepared Raney nickel (W-2)[16] (4 g) were stirred in absolute ethanol (20 mL) at 50 °C for 1.5 h. Nickel was filtered off, and the filtrate was concentrated. On cooling in refrigerator, a yellow solid, 5-benzoyl-2,3-dihydro-7-(ethoxycarbonyl)-1-(1-phenylvinyl)-1*H*-pyrrolo[1,2-*a*]imidazole (**11**), was formed and separated: 0.25 g (67%); mp 154–156 °C; IR (KBr) 1704, 1611, 1570, 1519, 1332, 1277, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84–7.81 (m, 2, Ar H), 7.56–7.45 (m, 5, Ar H), 7.44–7.33 (m, 3, Ar H), 7.15 (s, 1, C_6 H), 5.23 (s, 1, $C_{2'}$ H), 4.94 (s, 1, $C_{2'}$ H), 4.60 (t, 2, J = 8.6 Hz, C_3 H), 4.15 (t, 2, J = 8.6 Hz, C_2 H), 4.05 (q, 2, J = 7.1 Hz, CH_2CH_3), 1.08 (t, 3, J = 7.1 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 184.08, 162.82, 150.59, 147.99, 138.76, 136.83, 131.53, 128.80, 128.72, 128.49, 128.33, 126.99, 126.63, 122.97, 103.13, 97.76, 59.70, 57.46, 45.47, 14.32; mass spectrum m/z (rel intensity) 77 (16), 105 (15), 210 (9), 238 (20), 341 (9), 386 (100, M^+).

Anal. Calcd for $C_{24}H_{22}N_2O_3$: C, 74.59; H, 5.74; N, 7.25. Found: C, 74.33; H, 5.61; N, 7.18.

General Procedure for the Reaction of 3-Phenyl-7-(2-phenyl-2-oxoethyl)-5,6-dihydroimidazo[2,1-*b*]thiazolium Betaine (5a) with DMAD or Dibenzoylacetylene. A stirred solution of imidazothiazolium salt **4a** and 2 molar equiv of DMAD or dibenzoylacetylene in dry DMF were treated dropwise with an equimolar amount of triethylamine. A deep brown color developed with proceeding reaction. After being stirred for 2 h at 20 °C, the reaction mixture was poured into ice–water. Filtering the formed solid and purification with preparative liquid chromatography (hexane/EtOAC (2:1)) gave the mixture of cis and trans adducts.

Methyl (2*Z*,5*Z*)- and (2*E*,5*Z*)-6-[5-benzoyl-6,7-bis(methoxycarbonyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl]-3-(methoxycarbonyl)-6-phenyl-4-thiahexa-2,5-dienoate (16a and 17a): 78%; yellow solid; ^1H NMR ($CDCl_3$) δ 7.68–7.65 (m, 2, Ar H), 7.50–7.29 (m, 8, Ar H), 6.59 and 6.48 (s, 1, C_2 H of trans and cis isomers, respectively), 6.25 and 6.00 (s, 1, C_5 H of cis and trans isomers, respectively), 4.60 (br s, 2, $C_{3'}$ H), 4.32 (br s, 2, $C_{2'}$ H), 3.90 and 3.85 (s, 3, CH_3), 3.77 and 3.71 (s, 3, CH_3), 3.43 and 3.40 (s, 3, CH_3), 3.21 and 3.20 (s, 3, CH_3); mass spectrum m/z (rel intensity) 265 (9), 390 (30), 469 (100), 604 (10, M^+).

(2*Z*,5*Z*)- and (2*E*,5*Z*)-6-(5,6,7-tribenzoyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]imidazol-1-yl)-3-benzoyl-1-oxo-1,6-diphenyl-4-thiahexa-2,5-diene (18a and 19a): 81%; orange solid; ^1H NMR ($CDCl_3$) δ 7.98–7.87 (m, 4, Ar H), 7.64–6.86 (m, 27, Ar H and C_2 H), 6.00 and 5.89 (s, 1, C_5 H of cis and trans isomers, respectively), 4.75–4.66 (m, 2, $C_{3'}$ H), 4.39 (br s, 2, $C_{2'}$ H); mass spectrum m/z (rel intensity) 236 (100), 350 (17), 419 (31), 553 (41), 788 (13, M^+).

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Supplementary Material Available: X-ray crystallographic data for **7f**, several types of NMR spectra of **6d** and **7d**, and ^1H NMR spectra of the two mixtures **16a/17a** and **18a/19a** (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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