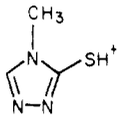
IR (KBr) 1680 (br, s, CO) cm^{-1}; NMR (CF_3COOH) 3.90 (s, 3, NCH_3), 5.72 (s, 1, CH), 7.50 (s, 5, Ph), 9.60 (s, 1, C_5 H); mass spectrum, *m/e* (rel intensity) 249 ($M^{+\cdot}$, 14), 205 ($M^{+\cdot} - CO_2$, 46), 121 ($PhCS^+$, 100).

Anal. Calcd for $C_{11}H_{11}N_3O_2S$: C, 53.01; H, 4.45; N, 16.86. Found: C, 53.14; H, 4.46; N, 16.74.

Under analogous conditions 4,5-dimethyl-3(4*H*)-triazolethione[11] (**18**; R = CH_3) gave *S*-(4,5-dimethyl-1,2,4-triazol-3-yl)phenylthioglycolic acid (**19b**) as colorless prisms (77%). It formed colorless prisms from methanol: mp 187 °C dec; IR (Nujol) 1680 (br, s, CO) cm^{-1}; NMR (CF_3COOH) δ 2.78 (s, 3, CCH_3), 3.73 (s, 3, NCH_3), 5.67 (s, 1, CH), 7.48 (s, 5, Ph); mass spectrum, *m/e* (rel intensity) 263 ($M^{+\cdot}$, 8), 219 ($M^{+\cdot} - CO$, 54), 121 ($PhCS^+$, 45).

Anal. Calcd for $C_{12}H_{13}N_3O_2S$: C, 54.75; H, 4.98; N, 15.96. Found: C, 54.82; H, 4.90; N, 15.61.

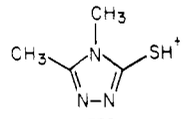
***anhydro*-3-Hydroxy-7-methyl-2-phenylthiazolo[3,2-*b*]-[1,2,4]triazolium Hydroxide (20a).** A mixture of the thioglycolic acid (**19a**; 1.7 g, 6.8 mmol) and Ac_2O (5 mL) was warmed on a steam bath at 70–80 °C for 10 min, during which time the reaction mixture assumed a yellow color. When the mixture was cooled at 0 °C, yellow crystals of **20** (R = H) separated. These were collected, washed with anhydrous Et_2O, dried at 80 °C for 3 h, and finally recrystallized from CH_3NO_2 containing a few drops of Ac_2O, giving yellow needles: 1.40 g (89%); mp 175–176 °C dec; IR (KBr) 1610 (CO) cm^{-1}; NMR [CF_3COOH + $(CF_3CO)_2O$] δ 4.25 (s, 3, NCH_3), 7.58 (s, 5, Ph), 8.82 (s, 1, C_6 H); mass spectrum, *m/e* (rel intensity) 231 ($M^{+\cdot}$, 27), 121 ($PhCS^+$, 69), 115 (III, 100).



III

Anal. Calcd for $C_{11}H_9N_3OS$: C, 57.14; H, 3.92; N, 18.18. Found: C, 56.83; H, 3.93; N, 17.89.

Similarly, a mixture of **19b** and Ac_2O afforded a 94% yield of *anhydro*-6,7-dimethyl-3-hydroxy-2-phenylthiazolo[3,2-*b*][1,-2,4]triazolium hydroxide (**20b**), likewise obtained as yellow needles from CH_3NO_2 and a few drops of Ac_2O: mp 210 °C dec; IR (KBr) 1620 (CO) cm^{-1}; NMR [CF_3COOH + $(CF_3CO)_2O$] δ 2.80 (s, 3, CCH_3), 4.07 (s, 3, NCH_3), 7.53 (s, 5, Ph); mass spectrum, *m/e* (rel intensity) 245 ($M^{+\cdot}$, 16), 129 (IV, 100), 121 ($PhCS^+$, 39).



IV

Anal. Calcd for $C_{12}H_{11}N_3OS$: C, 58.77; H, 4.52; N, 17.14. Found: C, 58.95; H, 4.40; N, 17.27.

General Procedure for Reaction of 20. A. With Acetylenic Dipolarophiles. The mesoionic system (**20a**) (0.46 g, 2 mmol) and dimethyl acetylenedicarboxylate (0.3 g, slight excess) in dry xylene (10 mL) were heated under reflux for 1 h. After the mixture was cooled to ca. 5 °C, the beige precipitate which separated was collected and washed with methanol; 0.23 g (34%). Products obtained in this way are described in Table III.

B. With Olefinic Dipolarophiles. The mesoionic system (**20b** 0.02 mol), *N*-ethylmaleimide (0.25 g, 0.02 mol), and dry xylene (10 mL) were heated together under reflux for 16 h. When the mixture was cooled, the yellow crystalline product was filtered and washed with Et_2O; 0.45 g (67%). Use of a lower reaction temperature (80 °C) or a shorter reaction time always resulted in a mixture of the cycloadduct and the initial mesoionic ring system.

Registry No. 4, 60-56-0; **5a**, 71370-34-8; **9** (R^1 = R^2 = $COOCH_3$), 71370-35-9; **9** (R^1 = R^2 = COPh), 71370-36-0; **9** (R^1, R^2 = –CON(Et)CO–), 71370-37-1; **9** (R^1, R^2 = –CON(Ph)CO–), 71370-38-2; **9** (R^1, R^2 = –COOCO–), 71370-39-3; **9** (R^1 = R^2 = CN), 71370-40-6; **9** (R = CN), 71371-25-0; **9** (R = COOEt), 71371-26-1; **11**, 71370-41-7; **12**, 71370-42-8; **15a**, 71370-43-9; **15b**, 71370-44-0; **17** (R = CH_3), 71370-45-1; **17** (R = *p*-$CH_3OC_6H_4$), 71370-46-2; **17** (R = *p*-$CH_3C_6H_4$), 71370-47-3; **18** (R = H), 24854-43-1; **18** (R = CH_3), 38942-50-6; **19a**, 71370-48-4; **19b**, 71370-49-5; **20a**, 71370-50-8; **20b**, 71370-51-9; **22** (R = H; R^1 = $COOCH_3$), 71370-52-0; **22** (R = CH_3; R^1 = $COOCH_3$), 71370-53-1; **22** (R = CH_3; R^1 = COPh), 71370-54-2; **22** (R = H; R^1, R^1 = –CON(Et)CO–), 71370-55-3; **22** (R = CH_3; R^1, R^1 = –CON(Et)CO–), 71370-56-4; **22** (R = CH_3; R^1, R^1 = –CON(Ph)CO–), 71370-57-5; **22** (R = CH_3; R^1, R^1 = –COOCO–), 71370-58-6; α-bromophenylacetyl chloride, 19078-72-9; bromacetyl bromide, 598-21-0; bromoacetic acid, 79-08-3; acrylonitrile, 107-13-1; ethyl acrylate, 140-88-5; methyl isocyanate, 624-83-9; *p*-methoxyphenyl isocyanate, 5416-93-3; *p*-tolyl isocyanate, 622-58-2; α-bromophenylacetic acid, 4870-65-9; dimethyl acetylenedicarboxylate, 762-42-5; dibenzoylacetylene, 1087-09-8; *N*-ethylmaleimide, 128-53-0; *N*-phenylmaleimide, 941-69-5; maleic anhydride, 108-31-6; fumaronitrile, 764-42-1.

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Ring Annulation with Heterocyclic Ylides. Annulation of Pyridinones to the Thiazole and 1,3,4-Thiadiazole Systems[1a]

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2(3*H*)-Thiazolethione and its 4-methyl derivative and α-bromophenylacetyl chloride/NEt_3 readily gave *anhydro*-3-hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium hydroxide and its 5-methyl derivative. This ring-fused mesoionic system underwent cycloaddition in refluxing toluene with acetylenic and olefinic dipolarophiles to form substituted 5*H*-thiazolo[3,2-*a*]pyridin-5-ones. α-Bromophenylacetyl chloride also reacted readily with 5-methyl-2(3*H*)-1,3,4-thiadiazolethione to form the *anhydro*-5-hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,-3,4]thiadiazolium hydroxide system. In this instance cycloaddition with olefinic and acetylenic dipolarophiles occurred in refluxing benzene, a variety of substituted 5*H*-1,3,4-thiadiazolo[3,2-*a*]pyridin-5-ones being obtained.

In the preceding paper,[2] use was made of cycloaddition reactions with the *anhydro*-3-hydroxyimidazo[2,1-*b*]thiazolium hydroxide and the *anhydro*-3-hydroxythiazolo-[3,2-*b*][1,2,4]triazolium hydroxide ring systems formed from the corresponding cyclic thiones to effect annulation of the pyridinone ring to the imidazole and 1,2,4-triazole

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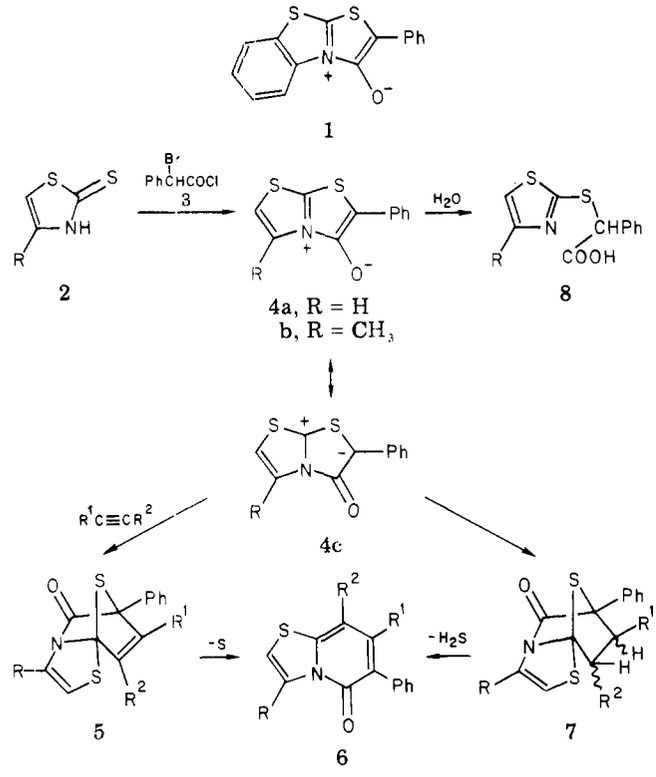
systems. This paper describes the synthesis and cycloadditions of the *anhydro*-3-hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium hydroxide and the *anhydro*-5-hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,3,4]thiadiazolium hydroxide ring systems.

***anhydro*-3-Hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium Hydroxide (4).** Earlier experiments[3] with the mesoionic system 1 derived from 2(3*H*)-benzothiazolethione showed 1 to be a very reactive system in cycloadditions, the thiocarbonyl ylide dipole undergoing reaction with a variety of electron-deficient dipolarophiles. To evaluate the importance of the benzene ring on the stability and reactivity of 1, we have prepared the corresponding thiazole analogue 4 by reaction of the 2-(3*H*)-thiazolethiones 2 with α-bromophenylacetyl chloride (3). This mesoionic system underwent cycloaddition with

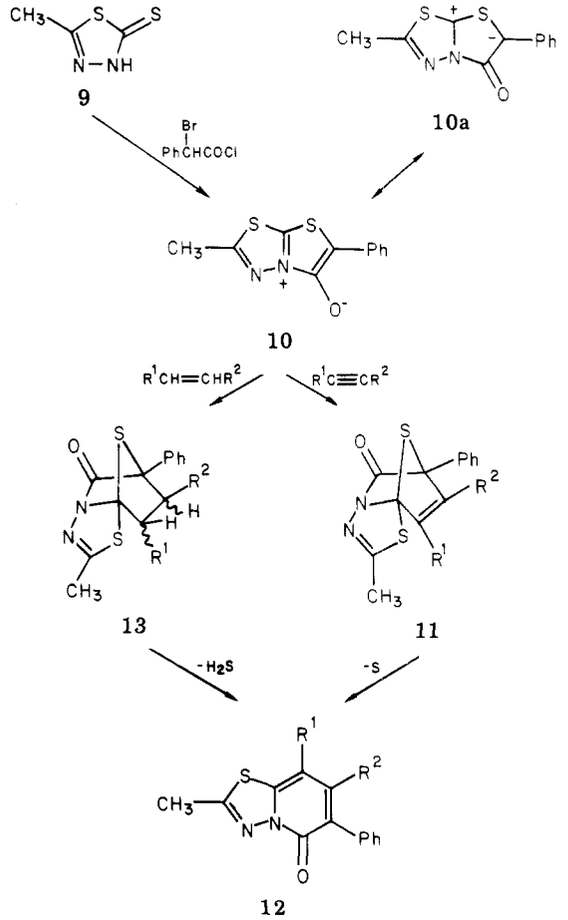


electron-deficient olefinic and acetylenic dipolarophiles across the thiocarbonyl ylide dipole presented by **4c**. In refluxing toluene (105 °C) reaction was complete with dimethyl acetylenedicarboxylate in 2–4 h, but with the olefinic dipolarophiles a reaction period of 16–17 h was required. With the former, sulfur was extruded from the postulated, initial 1:1 cycloadduct **5**, giving the fused pyridinone **6**. With the latter, H_2S was eliminated from the postulated, initial 1:1 cycloadduct **7**, again forming **6** in variable yields. In the case of acrylonitrile and ethyl acrylate the cycloaddition always occurred[2] to give the isomer anticipated by electronic effects, i.e., acrylonitrile gave 8-cyano-3-methyl-6-phenyl-5*H*-thiazolo[3,2-*a*]-pyridin-5-one (**6**, R = CH_3; R^1 = H; R^2 = CN). The structures of these thiazolo[3,2-*a*]pyridin-5-ones were apparent from the analytical and spectral data described in Table I, and their formation in these cycloadditions excludes formation of the isomeric *anhydro*-2-hydroxy-3-phenylthiazolo[2,3-*b*]thiazolium hydroxide in the condensation of **2** and **3**.

Both *anhydro*-3-hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium hydroxide (**4a**) and its 5-methyl derivative **4b** were hydrolyzed by water, reverting to the precursor acids **8**. Although more stable than their monocyclic counterparts with 2-alkylthio substituents,[5] they were appreciably less stable to hydrolysis than their benzo analogue, *anhydro*-3-hydroxy-2-phenylthiazolo[2,3-*b*]benzothiazolium hydroxide (**1**). Cycloaddition of **4a** and **4b** with both olefinic and acetylenic dipolarophiles required refluxing toluene for the cycloaddition to proceed cleanly whereas with the benzo analogue comparable cycloadditions occurred in refluxing benzene with noticeably reduced reaction times.

***anhydro*-5-Hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,3,4]thiadiazolium Hydroxide (10).** The introduction of an additional nitrogen atom into the 5-position of **4** resulted in enhanced resistance to hydrolysis, *anhydro*-5-hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,3,4]thiadiazolium hydroxide (**10**) being noticeably more stable to hydrolysis than **4**. It was prepared from 5-methyl-2(3*H*)-1,3,4-thiadiazolethione (**9**) and α-bromophenylacetyl chloride/NEt_3 and obtained as yellow plates, characterized by well-defined spectral and analytical data (Experimental Section). In its mass spectrum, its molecular ion was the most intense ion, and a similar relationship was also observed in the mass spectrum of **4b**.

The ring-fused mesoionic system **10** underwent cycloaddition with olefinic and acetylenic dipolarophiles, but usually prolonged reaction times (18–26 h) were required for complete conversion of **10** into the final cycloadducts.



Olefinic dipolarophiles underwent cycloaddition in refluxing benzene (80 °C) except for ethyl acrylate which

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(5) Potts, K. T.; Chen, S. J.; Kane, J.; Marshall, J. L. *J. Org. Chem.* **1977**, *42*, 1633.

Table I. 5*H*-Thiazolo[3,2-*a*]pyridin-5-ones 6 Formed from *anhydro*-3-Hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium Hydroxides (4) and Acetylenic and Olefinic Dipolarophiles

R	dipolarophile used	yield, %	mp, °C	crystal form	cryst. solvent	formula[b,c]	IR (KBr) ν_{CO}, cm^{-1}	NMR ($CDCl_3$), δ
H	$CH_3OOCC{\equiv}CCOOCH_3$[d]	79	165.5-166	pale yellow prisms	A	$C_{17}H_{13}NO_5S$	1730 w, 1680 m, 1630 s	3.60 (s, 3, OCH_3), 3.92 (s, 3, OCH_3), 7.18 (d, 1, J = 4.5 Hz, C_2H), 7.38 (s, 5, Ph), 8.28 (d, 1, J = 4.5 Hz, C_3H)
CH_3	$CH_3OOCC{\equiv}CCOOCH_3$[e]	49	197.5-198	cream prisms	A	$C_{18}H_{15}NO_5S$	1730 w, 1690 w, 1640 s	2.83 (d, 3, J = 1.0 Hz, C_3CH_3), 3.55 (s, 3, OCH_3), 3.87 (s, 3, OCH_3), 6.62 (q, 1, J = 1.0 Hz, C_3H), 7.32 (s, 5, Ph)
CH_3	*N*-ethylmaleimide	37	192-193	yellow needles	A	$C_{18}H_{14}N_2O_3S$	1750 w, 1700 s, 1640 s	1.22 (t, 3, J = 6.9 Hz, CH_2CH_3), 2.97 (d, 3, J = 1.0 Hz, C_3CH_3), 3.65 (q, 2, J = 6.9 Hz, CH_2CH_3), 6.63 (q, 1, J = 1.0 Hz, C_2H), 7.45 (s, 5, Ph)
H	*N*-phenylmaleimide	65	263-264	yellow needles	B	$C_{21}H_{12}N_2O_3S$	1760 w, 1720 s, 1670 s	7.2-7.6 (m, aromatic and thiazolyl H)
CH_3	*N*-phenylmaleimide	44	295	yellow prisms	B or C	$C_{22}H_{14}N_2O_3S$	1750 w, 1660 s, 1600 s	2.90 (d, 3, J = 1.0 Hz, C_3CH_3), 6.68 (q, 1, J = 1.0 Hz, C_2H), 7.42 (s, 5, Ph), 7.47 (s, 5, Ph)
CH_3	$CH_2{=}CHCOOEt$	51	170-171	pale yellow prisms	B	$C_{17}H_{15}NO_3S$	1640 s, 1680 s	1.40 (t, 3, J = 6.7 Hz, CH_2CH_3), 2.88 (d, 3, J = 1.0 Hz, C_3CH_3), 4.37 (q, 2, J = 6.7 Hz, CH_2CH_3), 6.57 (q, 1, J = 1.0 Hz, C_2H), 7.2-7.4 (m, 3, aromatic), 7.5-7.8 (m, 2, aromatic), 8.07 (s, 1, C_7H)
CH_3	$CH_2{=}CHCN$	56	176.5	yellow needles	B	$C_{15}H_{10}N_2OS$	2200 (CN), 1650 s	2.88 (d, 3, J = 1.0 Hz, C_3CH_3), 6.58 (q, 1, J = 1.0 Hz, C_2H), 7.2-7.6 (m, 5, Ph), 7.58 (s, 1, C_7H)

[a] A = CH_3OH; B = CH_3COCH_3; C = CH_3NO_2. [b] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table. [c] All products gave M^+ (100%). [d] Reaction time 2 h. [e] Reaction time 4 h.

Table II. 5*H*-1,3,4-Thiadiazolo[3,2-*a*]pyridin-5-ones (12) Formed from *anhydro*-5-Hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,3,4]thiadiazolium Hydroxide (10) and Acetylenic and Olefinic Dipolarophiles

dipolarophile used	solvent[a]	reaction time, h	yield, %	mp, °C	crystal habit[b]	cryst. solvent	formula[c]	*m/e* (rel intens)	IR (KBr) ν_{CO}, cm^{-1}	NMR ($CDCl_3$), δ
$CH_3OOCC{\equiv}CCOOCH_3$	T	18	76	233.5	A	CH_3OH	$C_{17}H_{14}N_2O_5S$	358 (95)	1740 m, 1710 s	2.73 (s, 3, C_2CH_3), 3.57 (s, 3, OCH_3), 3.87 (s, 3, OCH_3), 7.33 (s, 5, Ph)
PhCOC≡CCOPh	T	26	52	287 dec	B	xylene	$C_{27}H_{18}N_2O_3S$	450 (84)	1640 br, s	2.77 (s, 3, C_2CH_3), 7.0-7.4 (m, 15, aromatic)
N-ethylmaleimide	Bz	22	49	237-237.5	B	CH_3OH	$C_{17}H_{13}N_3O_3S$	339 (100)	1760 w, 1700 s, 1660 s	1.23 (t, 3, J = 7.0 Hz, CH_2CH_3), 2.80 (s, 3, C_2CH_3), 3.67 (q, 2, J = 7.0 Hz, CH_2CH_3), 7.47 (s, 5, Ph)
N-phenylmaleimide	Bz	22	70	265-266	B	CH_3COCH_3	$C_{21}H_{13}N_3O_3S$	387 (100)	1760 w, 1700 s, 1670 s, 1640 s	2.85 (s, 3, C_2H_3), 7.3-7.6 (m, 10, aromatic)
maleic anhydride	T	22	51	278	B	CH_3NO_2	$C_{15}H_8N_2O_4S$	312 (100)	1830 s, 1760 s, 1670 s, 1600 s	2.85 (s, 3, C_2CH_3), 7.47 (s, 5, Ph)
$CH_2{=}CHCOOEt$	T	20	21	210-211	C	$CH_3CHOHCH_3$	$C_{16}H_{14}N_2O_3S$	314 (100)	1700 sh, 1650 s	1.42 (t, 3, J = 6.8 Hz, CH_2CH_3), 2.78 (s, 2, C_2CH_3), 4.43 (q, 2, J = 6.8 Hz, CH_2CH_3), 7.2-7.5 (m, 3, aromatic), 7.6-7.8 (m, 2, aromatic), 8.20 (s, 1, C_7H)

[a] Bz = benzene; T = toluene. [b] A = colorless needles; B = yellow needles; C = cream needles. [c] Satisfactory analytical data (±0.4% for C, H, N) were reported for all new compounds listed in the table.

required refluxing toluene (105 °C) as solvent for addition to occur, no addition being observed in benzene even over 24 h. Although dimethyl acetylenedicarboxylate and dibenzoylacetylene added to **10** in refluxing toluene, ethyl propiolate, and ethyl phenylpropiolate did not undergo cycloaddition to **10**, a quantitative recovery of the mesoionic system was obtained in both cases. It appears that two electron-withdrawing groups attached to the acetylene are required for cycloaddition to occur as, in addition to imparting hydrolytic stability to **10**, the additional nitrogen atom has also slightly reduced its reactivity in cycloadditions. In all cases, no intermediate product **11** or **13** was isolated. Extrusion of sulfur or elimination of H_2S occurred under the thermal reaction conditions, the final products isolated being the 5*H*-1,3,4-thiadiazolo[3,2-*a*]-pyridin-5-ones **12** described in Table II. *p*-Methoxyphenyl isocyanate also did not undergo cycloaddition to **10** in refluxing benzene, a quantitative recovery of the mesoionic system being obtained.

Discussion

Sufficient evidence is now available to draw some qualitative conclusions about factors affecting the stability and reactivity of the thiocarbonyl ylide dipole contained in mesoionic ring systems incorporating the thiazole nucleus. In monocyclic systems aromatic substituents in the 2- and 3-positions stabilize the ring systems but do not affect its cycloaddition capabilities.[4] An additional aromatic substituent in the 5-position imparts appreciable stability but also reduces its reactivity due to delocalization of the negative charge over this substituent.[4] An electron-donating 2-substituent such as an alkylthio group results[5] in a much less stable moelcule but an appreciably more reactive thiocarbonyl ylide dipole. Incorporating the sulfur atom at the 2-position into a five-membered ring results in a ring-fused system considerably more stable than its monocyclic analogue, and the fused system also contains a reactive thiocarbonyl ylide dipole. Fusion of a benzene ring to the bicyclic mesoionic system imparts[3] stability to the tricyclic system **1** and also enhances the reactivity of the thiocarbonyl ylide dipole. Introduction of an additional nitrogen atom into the ring-fused system stabilizes the system appreciably. Moreover, it is still sufficiently reactive to take part in cycloadditions, longer reaction times being required.

Experimental Section[6]

***anhydro*-3-Hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium Hydroxide (4a).** α-Bromophenylacetyl chloride[7] (**3**) (2.6 g, 0.011 mol) was added dropwise to a suspension of 2(3*H*)-thiazolethione[8] (**2**, R = H; 1.3 g, 0.011 mol) in anhydrous ether (20 mL). After 5 min, excess of NEt_3 (2.5 g) was added slowly at room temperature and the reaction mixture stirred for 1 h. The yellow crystalline product which separated was collected and washed with water, followed by ether; 2.3 g (89%). Recrystallization from chloroform–petroleum ether (bp 40–60 °C) afforded yellow prisms: mp 208 °C dec, turning dark at ca. 190 °C; IR (KBr) 1600 (sh), 1580 (CO) cm^{-1}; NMR (CF_3COOH) δ 7.57 (br s, 5, Ph), 8.03 (d, 1, J = 4.0 Hz, C_6 H), 8.35 (d, 1, J = 4.0 Hz, C_5 H); mass spectrum, m/e (rel intensity) 233 ($M^{+\cdot}$, 40), 121 ($PhCS^+$, 100).

Anal. Calcd for $C_{11}H_7NOS_2$: C, 56.66; H, 3.03; N, 6.01. Found: C, 55.74; H, 2.93; N, 6.09.

In a similar manner 4-methyl-2(3*H*)-thiazolethione[9] (5.4 g, 0.043 mol), α-bromophenylacetyl chloride (9.98 g, 0.043 mol), and NEt_3 (10.0 g) gave **4b**, 9.6 g (91%). It crystallized from acetone as yellow prisms, the analytical sample being washed further with $CHCl_3$: mp 171–172 °C dec; IR (KBr) 1600 (CO) cm^{-1}; NMR (CF_3COOH) δ 2.85 (d, 3, J = 1.0 Hz, CH_3), 7.63 (s, 5, Ph), 7.73 (q, 1, J = 1.0 Hz, C_6H); mass spectrum, m/e (rel intensity) 247 ($M^{+\cdot}$, 100), 121 ($PhCS^+$, 83).

Anal. Calcd for $C_{12}H_9NOS_2$: C, 58.30; H, 3.67; N, 5.67. Found: C, 58.15; H, 3.60; N, 5.50.

General Procedure for the Reaction of *anhydro*-3-Hydroxy-2-phenylthiazolo[2,3-*b*]thiazolium Hydroxide with Dipolarophiles. A. Acetylenic Dipolarophiles. The mesoionic system **4b** (0.49 g, 2 mmol) and dimethyl acetylenedicarboxylate (0.3 mL) in dry toluene (10 mL) were heated under reflux for 4 h. Removal of the toluene left a dark residue which was chromatographed on neutral alumina (Merck) with benzene as eluent. The first fraction was obtained finally as a viscous oil which crystallized on trituration with ether. It crystallized from methanol as cream prisms: 0.35 g (49%), mp 197.5–198 °C. Fused pyridinones prepared in this way are described in Table I.

B. Olefinic Dipolarophiles. The mesoionic compound **4b** (0.49 g, 2 mmol), *N*-ethylmaleimide (0.25 g, 2 mmol), and dry toluene (10 mL) were heated together under reflux for 17 h, the reaction being monitored by TLC. The toluene was removed under reduced pressure, leaving a dark colored residue which solidified on trituration with ether. Recrystallization from methanol afforded yellow needles: 0.25 g (37%), mp 192–193 °C. The other products were purified by recrystallization from the solvents listed in Table I.

***anhydro*-5-Hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*]-[1,3,4]thiadiazolium Hydroxide (10).** 5-Methyl-2(3*H*)-1,3,4-thiadiazolethione[10] (**9**; 2.64 g, 0.02 mol) suspended in anhydrous ether (20 mL) was treated dropwise with α-bromophenylacetyl chloride (4.68 g, 0.02 mol), the addition being made at room temperature. After 5 min Et_3N (4.5 g, 0.045 mol) was added dropwise and the resulting yellow colored reaction mixture stirred at room temperature for 20 min. The yellow crystalline product that separated was collected and washed several times with water and then ether; 4.8 g (97%). It crystallized from nitromethane as yellow plates: mp 220.5–221 °C dec; IR (KBr) 1610 (CO) cm^{-1}; NMR (CF_3COOH) δ 3.03 (s, 3, C_6 CH_3), 7.4–7.8 (m, 5, aromatic); mass spectrum, m/e (rel intensity) 248 ($M^{+\cdot}$, 100).

Anal. Calcd for $C_{11}H_8N_2OS_2$: C, 53.23; H, 3.25; N, 11.29. Found: C, 52.98; H, 3.19; N, 11.31.

General Procedure for the Reaction of *anhydro*-5-Hydroxy-2-methyl-6-phenylthiazolo[2,3-*b*][1,3,4]thiadiazolium Hydroxide (10) with Dipolarophiles. The mesoionic system **10** (0.496 g, 0.02 mol) and *N*-ethylmaleimide (0.25 g, 0.02 mol) were refluxed in the solvent shown in Table II. If no precipitate was obtained on cooling the reaction mixture, the solvent was evaporated under reduced pressure and the residue triturated with the recrystallization solvent listed in Table II.

Registry No. 2 (R = H), 5685-05-2; **2** (R = CH_3), 5685-06-3; **3**, 19078-72-9; **4a**, 71371-09-0; **4b**, 71371-10-3; **6** (R = H; R^1 = R^2 = $COOCH_3$), 71371-11-4; **6** (R = CH_3; R^1 = R^2 = $COOCH_3$), 71371-12-5; **6** (R = CH_3; R^1, R^2 = –CON(Et)CO–), 71371-13-6; **6** (R = H; R^1, R^2 = –CON(Ph)CO–), 71371-14-7; **6** (R = CH_3; R^1, R^2 = –CON(Ph)-CO–), 71371-15-8; **6** (R = CH_3; R^1 = H; R^2 = COOEt), 71371-16-9; **6** (R = CH_3; R^1 = H; R^2 = CN), 71371-17-0; **9**, 29490-19-5; **10**, 71371-18-1; **12** (R^1 = R^2 = $COOCH_3$), 71371-19-2; **12** (R^1 = R^2 = COPh), 71371-20-5; **12** (R^1, R^2 = –CON(Et)CO–), 71371-21-6; **12** (R^1, R^2 = –CON(Ph)CO–), 71371-22-7; **12** (R^1, R^2 = –COCO–), 71371-23-8; **12** (R^1 = H; R^2 = COOEt), 71371-24-9; dimethyl acetylenedicarboxylate, 762-42-5; *N*-ethylmaleimide, 128-53-0; *N*-phenylmaleimide, 941-69-5; ethyl 2-propenoate, 140-88-5; 2-propenecarbonitrile, 107-13-1; 1,4-diphenyl-2-butyne-1,4-dione, 1087-09-8; maleic anhydride, 108-31-6.

(6) Reaction workup procedures and spectral characterizations were as in the preceding paper.[2]

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