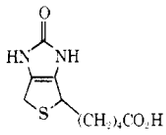

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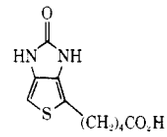

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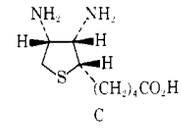

C

of the American Chemical Society, San Francisco, Calif., Aug 29–Sept 3, 1976.

(13) Some material is completely hydrolyzed to the diamino acid (C). Treatment of the mother liquors with phosgene will convert C to biotin, thus affording an additional 10% of the final product.

(14) D. E. Wolf, R. Mozingo, S. A. Harris, R. C. Anderson, and K. Folkers, *J. Am. Chem. Soc.*, **67**, 2100 (1945).

Mesoionic Compounds. 39. Synthesis of Some Functionally Substituted Five-Membered Systems Using 1,2-Bielectrophiles as Cyclization Agents[1a]

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α-Bromoacyl chlorides, functioning as 1,2-bielectrophiles, undergo ready reaction in the presence of Et_3N with several monoprotonic 1,3-binucleophiles to provide an especially convenient synthesis of some five-membered mesoionic ring systems containing diverse functional substituents. The *anhydro*-4-hydroxythiazolium hydroxide system results from N-monosubstituted thioamide derivatives, the *anhydro*-4-hydroxy-1,3-dithiolium hydroxide system from dithiobenzoic acids, and the *anhydro*-5-hydroxy-1,3-oxathiolium hydroxide system from thiobenzoic *S*-acids. These ring systems all undergo ready cycloaddition with dimethyl acetylenedicarboxylate to provide a convenient synthetic procedure for thiophenes containing a variety of substituents in the 2 position.

The majority of five-membered mesoionic ring systems can generally be synthesized[2] by one of five synthetic routes involving either (1) a cyclodehydration; (2) a cyclization via an intermediate isocyanate or isothiocyanate; (3) cyclizations involving nitriles; (4) interconversion of other mesoionic systems; or (5) dealkylation of suitable quaternary heterocycles. The cyclodehydrative process has been widely applied and, as would be anticipated, an extensive variety of cyclodehydration agents has been utilized. The synthesis of the appropriately substituted carboxylic acid precursor often presents difficulties, and in this report we describe a simple and effective route to several of these ring systems that not only overcomes the above disadvantages but also enables functional groups other than the usual alkyl and aryl groups to be introduced into the ring system. These syntheses are now readily accomplished by using a suitable monoprotonic 1,3-binucleophile with a 1,2-bielectrophile such as an α-haloacyl halide, and the following applications illustrate this synthetic approach.

***anhydro*-4-Hydroxythiazolium Hydroxide System.** The usual method of preparation[3a–c] of this system involves the S-alkylation of N-monosubstituted thioamides with an α-halo acid, followed by cyclodehydration of the resulting acid with Ac_2O/Et_3N. This method was often unsuccessful with thioamides containing a variety of substituents attached to the thioxo carbon atom; e.g., attempted alkylation of the thiourea **1** [R = $N(CH_3)_2$] or the dithiocarbamate **1** (R = SR) with α-bromophenylacetic acid (**2**, R^1 = Ph; X = Br; Y = OH) led to hydrolysis products, while the use of ethyl α-bromomalonate (**2**, R^1 = COOEt; X = Br; Y = OH) as an alkylating agent for thiobenzanilide was complicated by concomitant decarboxylation. However, the use of an α-bromoacyl chloride derivative **2** (R^1 = Ph, COOEt; X = Br; Y = Cl) allows the initial alkylation and subsequent ring closure to be accomplished in one step. The intermediate **3** (Y = Cl) is most likely involved, although the ketene derived from it by loss of HCl cannot be definitely excluded. The various substituted derivatives of **4** prepared by this procedure are described in Table I. In this instance the thioamide behaves as a 1,3-binucleophile, resulting in the formation of a five-membered ring on reaction with the 1,2-bielectrophile. In an earlier publication[3d] the reaction of the thioamide with a 1,3-bielectrophile, chlorocarbonylphenylketene, resulted in the ready formation of the six-membered mesoionic system, *anhydro*-6-hydroxy-4-oxo-2,3,5-trisubstituted-4*H*-1,3-thiazinium hydroxide, in excellent yields.

It is possible for four different intermediates to be involved, depending on the site of the initial condensation, but only two isomeric reaction products are possible. If reaction had occurred initially at the acid chloride function to give the intermediate **5**, then ring closure would result in formation of the isomeric *anhydro*-5-hydroxythiazolium hydroxide system **6**. The formation of **6** was excluded in two ways. The intermediate acid **3** (R = *S*-alkyl; R^1 = Ph; Y = OH) was prepared and cyclized with dicyclohexylcarbodiimide to **4** (R = *S*-alkyl;

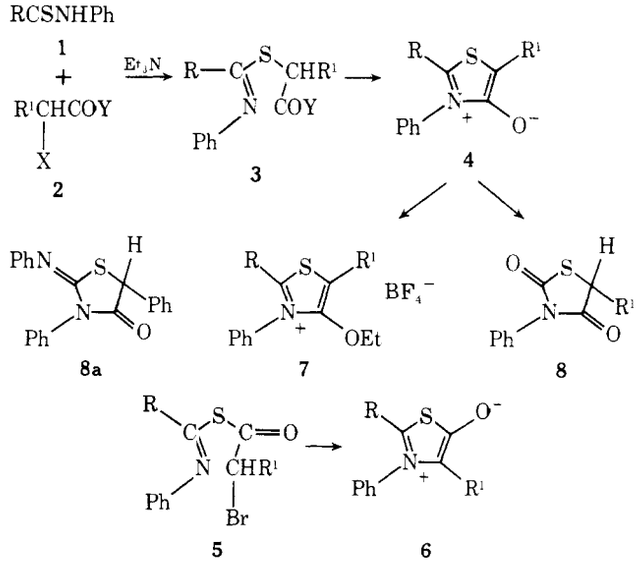
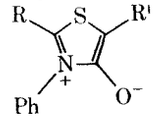


Table I. *anhydro*-4-Hydroxythiazolium Hydroxide Derivatives[j]



Registry no.	Substituents R	Substituents R'	Mp, °C	Yield, %	Crystal habit	Mol formula	M+· (rel int)	λ_{max} (CH_3OH), nm (log ε)	ν_{CO}, cm^{-1}	$\nu_{C=N}$, cm^{-1}	NMR, δ ($CDCl_3$)
61522-15-4	CH_3S	Ph	158–160	78	Golden prisms[a]	$C_{16}H_{13}NOS_2$	299 (30)	243 (4.02), 273 (3.99), 417 (4.04)	1620	1585	7.95–7.00 (m, 10, aromatic), 2.55 (s, 3, SCH_3)
61522-16-5	EtS	Ph	131–133	75	Orange prisms[b]	$C_{17}H_{15}NOS_2$	313 (32)	251 (4.03), 273 (4.01), 421 (4.04)	1630	1590	8.00–7.05 (m, 10, aromatic), 3.00 (q, 2, SCH_2CH_3), 1.37 (t, 3, SCH_2CH_3)
61522-17-6	*n*-PrS	Ph	131–133	76	Orange prisms[b]	$C_{18}H_{17}NOS_2$	327 (38)	241[c] (3.68), 276[c] (3.71), 422 (3.77)	1630	1595	8.00–7.00 (m, 10, aromatic), 2.98 (t, 2, $SCH_2CH_2CH_3$), 1.75 (h, 2, $SCH_2CH_2CH_3$), 1.00 (t, 3, $SCH_2CH_2CH_3$)
61522-18-7	PhS	Ph	166–168	61	Orange prisms[b]	$C_{21}H_{15}NOS_2$	361 (48)	252 (4.05), 270[c] (4.01), 430 (4.00)	1640	1600	7.90–7.10 (m, aromatic)
61522-19-8	EtS	COOEt	168–169.5	57	Yellow prisms[d]	$C_{14}H_{15}NO_3S_2$	309 (29)	247 (4.12), 373 (3.99)	1675, 1645	1595	7.65–7.18 (m, 5, aromatic), 4.30 (q, 2, $CO_2CH_2CH_3$), 3.20 (q, 2, SCH_2CH_3), 1.45 (t, 3, $CO_2CH_2CH_3$), 1.35 (t, 3, SCH_2CH_3)
61522-20-1		Ph	156.6–158.5 dec	64	Golden-yellow prisms[e]	$C_{19}H_{18}N_2O_2S$	338 (31)	237[c] (4.10), 292 (3.96), 392 (3.71)	1640	1590	7.80–6.85 (m, 10, aromatic), 3.60–3.25 (m, 4, OCH_2CH_2N), 3.10–2.78 (m, 4, OCH_2CH_2N)
61522-21-2	$(CH_3)_2N$	Ph	150 dec	58	Gold needles[f]	$C_{17}H_{16}N_2OS$	296 (33)	238 (4.09), 304 (4.04), 408 (3.84)[g]	1640	1630	7.80–7.00 (m, 10, aromatic), 2.70 [s, 6, $(CH_3)_2N$]
61522-22-3	$(CH_3)_2N$	COOEt	198–199.5	25	Cream plates[f]	$C_{14}H_{16}N_2O_3S$	292 (10)	258 (4.00), 345 (3.90)	1680	1620	7.53–7.13 (m, 5, aromatic), 4.22 (q, 2, $CO_2CH_2CH_3$), 2.88 [s, 6, $(CH_3)_2N$], 1.30 (t, 3, $CO_2CH_2CH_3$)
61522-23-4	CN	Ph	188–190 dec	30	Red needles[a]	$C_{16}H_{10}N_2OS$	278 (50)	272 (4.05), 310[c] (3.52), 489 (4.24)[g]	1630	2190 ($\nu_{C\equiv N}$)	8.25–7.25 (m, 10, aromatic)
18100-80-6	Ph	Ph	253–256[h]	76	Red-orange needles[f]	$C_{21}H_{15}NOS$					
61522-24-5	Ph	COOEt	160–161	54	Brilliant yellow needles[i]	$C_{18}H_{15}NO_3S$	325 (12)		1680, 1660		
52730-98-0	*p*-ClC_6H_4	Ph	197–199 dec	71	Red needles[b]	$C_{21}H_{14}ClNOS$	363 (3)	268 (4.31), 449 (4.19)	1625	1590	7.02–6.90 (m, aromatic)
61522-25-6	*p*-ClC_6H_4	COOEt	154–154.5	23	Golden-yellow prisms[e]	$C_{18}H_{14}ClNO_3S$	359 (9)	226[c] (4.23), 247[c] (4.12), 396 (3.76)	1680, 1665	1595	7.57–7.00 (m, 9, aromatic), 4.34 (q, 2, $CO_2CH_2CH_3$), 1.37 (t, 3, $CO_2CH_2CH_3$)
61522-26-7	*p*-$CH_3OC_6H_4$	Ph	187.5–189.5	65	Orange prisms[b]	$C_{22}H_{17}NO_2S$	359 (0.5)	277 (4.12), 297[c] (4.03), 443 (4.12)	1630	1600	7.15–6.65 (m, 14, aromatic), 3.75 (s, 3, OCH_3)
61522-27-8	*p*-$CH_3OC_6H_4$	COOEt	194–195	33	Golden-yellow prisms[e]	$C_{19}H_{17}NO_4S$	355 (13)	227 (4.19), 302 (3.88), 398 (3.06)	1655	1600	7.6–6.7 (m, 9, aromatic), 4.37 (q, 2, $CO_2CH_2CH_3$), 3.8 (s, 3, OCH_3), 1.37 (t, 3, $CO_2CH_2CH_3$)

[a] Crystallized from benzene. [b] Crystallized from benzene–petroleum ether F. [c] Shoulder. [d] Crystallized from $CHCl_3$–petroleum ether F. [e] Crystallized from $CHCl_3$–ether. [f] Crystallized from acetone. [g] $CHCl_3$ solvent. [h] Lit.[3c] mp 251–252 °C. [i] Crystallized from benzene–ether. [j] Satisfactory analytical values (± 0.4% for C, H, N) were reported for all compounds in table.

Table II. Thiophenes Obtained from 4 and Acetylenic Dipolarophiles[f]

Registry no.	Substituent R	Substituent R¹	Substituent R²	Mp, °C	Yield, %	Crystal habit	Mol formula	M⁺· (rel int)	λ_{max} (CH_3OH), nm (log ε)	ν_{CO},[e] cm^{-1}	NMR, δ ($CDCl_3$)
61522-09-6	CH_3S	Ph	$COOCH_3$	130–131	67	Cream prisms[a]	$C_{13}H_{14}O_4S_2$	322 (100)	236 (4.37), 313 (4.16)	1730 1700	7.40 (s, 5, aromatic), 3.85 (s, 3, CO_2CH_3), 3.80 (s, 3, CO_2CH_3), 2.60 (s, 3, SCH_3)
61522-10-9	CH_3S	Ph	COOH	235–237	100	Colorless prisms[b]	$C_{13}H_{10}O_4S_2$	294 (19)	227 (4.16), 309 (3.92)	1730 1675	7.55 (s, 5, aromatic), 2.62 (s, 3, SCH_3)
61522-11-0	EtS	Ph	$COOCH_3$	117–119	63	Colorless prisms[a]	$C_{16}H_{16}O_4S_2$	336 (100)	235 (4.26), 313 (4.02)	1730 1700	7.42 (s, 5, aromatic), 3.90 (s, 3, CO_2CH_3), 3.80 (s, 3, CO_2CH_3), 3.05 (q, 2, SCH_2CH_3), 1.41 (t, 3, SCH_2CH_3)
61522-12-1	*n*-PrS	Ph	$COOCH_3$	74–76	46	Cream prisms[a]	$C_{17}H_{18}O_4S_2$	350 (100)	236 (4.35), 315 (4.11)	1730 1700	7.45 (s, 5, aromatic), 3.90 (s, 3, CO_2CH_3), 3.80 (s, 3, CO_2CH_3), 3.01 (t, 2, $SCH_2CH_2CH_3$), 1.80 (h, 2, $SCH_2CH_2CH_3$), 1.08 (t, 3, $SCH_2CH_2CH_3$)
61522-13-2	$(CH_3)_2N$	Ph	$COOCH_3$	108–109	69	Cream plates[c]	$C_{16}H_{17}NO_4S$	319 (100)	203 (4.33), 227 (4.27), 319 (4.08)	1740 1700	7.24 (m, 5, aromatic), 3.68 (s, 3, CO_2CH_3), 3.63 (s, 3, CO_2CH_3), 2.88 (s, 6, $(CH_3)_2N$)
61522-14-3	$(CH_3)_2N$	COOEt	$COOCH_3$	89–91	16	Colorless needles[c]	$C_{13}H_{17}NO_6S$	315 (100)	215 (4.05), 238 (3.96), 305[d] (3.91), 335 (4.20)	1740 1710 1680	4.28 (q, 2, $CO_2CH_2CH_3$), 3.93 (s, 3, CO_2CH_3), 3.78 (s, 3, CO_2CH_3), 3.07 [s, 6, $(CH_3)_2N$], 1.32 (t, 3, $CO_2CH_2CH_3$)

[a] From benzene–petroleum ether F. [b] From aqueous ethanol. [c] From CH_3OH. [d] Shoulder. [e] KBr. [f] Satisfactory analytical values (±0.4% for C, H, N) were reported for all compounds in table.

R^1 = Ph) giving products identical with those obtained in the direct condensation above. Also on reaction with dimethyl acetylenedicarboxylate substituted thiophenes rather than pyrrole derivatives were obtained, the latter resulting from reaction of the ring system **6** with acetylenic dipolarophiles.[3e] These thiophenes are described in Table II, and, in one instance, hydrolysis to the corresponding dicarboxylic acid was utilized to characterize further the product obtained from the cycloaddition.

The introduction of an alkyl- or arylthio group into the 2 position of **4** was achieved by using the appropriate alkyl or aryl phenyldithiocarbamate **1** (R = SCH_3, SC_2H_5, S-*n*-C_3H_7, and SPh) prepared by treatment of ammonium phenyldithiocarbamate with excess of the appropriate alkyl (or aryl) halide in aqueous solution at room temperature. Modification of the original procedure,[4] as described in the Experimental Section, results in improved yields of products. Addition of α-bromophenylacetyl chloride[5] in an inert solvent such as benzene, ether, or tetrahydrofuran to the alkyl (or aryl) phenyldithiocarbamate in benzene followed by the slow addition of Et_3N resulted in the separation of triethylamine HCl/HBr, and the mesoionic system **4** was obtained by concentration of the filtrate. 2-Bromo-2-ethoxycarbonylacetyl chloride[6] (**2**, R^1 = COOEt; X = Br; Y = Cl) also reacted readily, allowing the introduction of an ethoxycarbonyl substituent into the 5 position of **4**.

The structures of these *anhydro*-4-hydroxythiazolium hydroxides **4** follow from their spectral characteristics (Table I) and their conversion with Meerwein's reagent into the 4-ethoxythiazolium salts **7**. They also underwent ready hydrolysis[7] to the appropriate thiazolidine-2,4-diones **8**. Thus the *anhydro*-2-alkylthio-3,5-diphenyl-4-hydroxythiazolium hydroxides (**4**, R = CH_3S, C_2H_5S, *n*-C_3H_7S; R^1 = Ph) were hydrolyzed in boiling aqueous ethanol (1:2) over 3–4 h giving 3,5-diphenylthiazolidine-2,4-dione[8] (**8**, R^1 = Ph), characterized by two carbonyl absorptions at 171.3 and 169.4 ppm in its ^{13}C NMR spectrum. However, the *anhydro*-2-alkylthio-5-ethoxycarbonyl-4-hydroxy-3-phenylthiazolium hydroxides (**4**, R = *S*-alkyl; R^1 = COOEt) required a 7-h reflux in dilute HCl to effect hydrolysis and in this case hydrolysis of the ester substituent and subsequent decarboxylation occurred as 3-phenylthiazolidine-2,4-dione[9] (**8**, R^1 = H) was obtained.

In the *anhydro*-2-alkylthio-3,5-diphenyl-4-hydroxythiazolium hydroxides (**4**, R = *S*-alkyl; R^1 = Ph) the exocyclic sulfur atom no doubt contributes to the stability of the system by reducing the positive charge on the thioamide portion of the nucleus. This was reflected to some degree by the reduced yields of the thiophenes obtained from their cycloadditions with dimethyl acetylenedicarboxylate. It was also of interest to study the effect of a 2-alkoxyl substituent on the stability of the ring system and use of an *O*-alkyl phenylthiocarbamate (**1**, R = OCH_3, OC_2H_5) in the above reactions should lead to the desired product. Reaction with the acid chloride **2** (R^1 = Ph; X = Br; Y = Cl) always led to an oil from which only the thiazolidine-2,4-dione **8** (R^1 = Ph) could be isolated, indicating a marked susceptibility of the ring system to hydrolysis at the 2 position when a 2-alkoxy substituent is at that position.

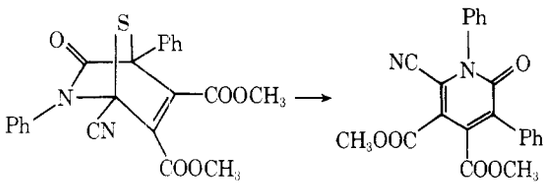
Use of substituted thioureas in the initial condensation provides a convenient method for the introduction of a 2-disubstituted amino substituent. Thus *N*-(*N*-phenylthiocarbamoyl)morpholine (**1**, R = *N*-morpholino) and α-bromophenylacetyl chloride in the presence of Et_3N gave in good yield *anhydro*-3,5-diphenyl-4-hydroxy-2-morpholinothiazolium hydroxide (**4**, R = *N*-morpholino; R^1 = Ph). In addition to its spectral characteristics (Table I), it was characterized by hydrolysis with hot dilute HCl to 3,5-diphenylthiazolidine-2,4-dione (**8**, R^1 = Ph). Other representatives of **4** with 2-amino substituents prepared by this procedure are also described in Table I and the substituted thiophenes obtained

from their cycloaddition with dimethyl acetylenedicarboxylate are reported in Table II.

2-Alkylthiothiazoles undergo reaction with primary and secondary amines such as methylamine, morpholine, and piperidine and the 2-alkylthio substituent is replaced by the amino group.[9] However, in this present study replacement of the 2-alkylthio substituent in 4 with a 2-morpholino group could not be effected under a variety of conditions. It should also be mentioned that reaction of *N*-(*N*-phenylthiocarbamoyl)morpholine (1, R = *N*-morpholino) with α-bromophenylacetic acid did not give the expected intermediate acid 3 (R = *N*-morpholino; R^1 = Ph; Y = OH). Rather ring closure to 4 and concomitant hydrolysis occurred under the reaction conditions so that 3,5-diphenylthiazolidine-2,4-dione (8, R^1 = Ph) was obtained. Similar results were observed with *N,N*-dimethyl-*N'*-phenylthiourea and α-bromophenylacetic acid.

N,N'-Diphenylthiourea (1, R = PhNH) and α-bromophenylacetyl chloride also underwent ready reaction and in this case, as the substituent pattern in 1 precluded formation of the mesoionic system, 3,5-diphenyl-2-phenylimino-4-thiazolidone (8a) was obtained. This was hydrolyzed to 3,5-diphenylthiazolidine-2,4-dione (8, R^1 = Ph) with hot, 40% aqueous H_2SO_4, and its formation provides additional evidence in support of the general reaction pathway described above.

This present procedure allows considerable diversity in the substituents to be introduced into 4. Thus using a variety of thiobenzanilides (1, R = aryl) with α-bromophenylacetyl chloride or 2-bromo-2-ethoxycarbonylacetyl chloride resulted in ready formation of *anhydro*-4-hydroxythiazolium hydroxide derivatives 4 with additional 2 substituents as described in Table I. All these underwent ready cycloaddition with dimethyl acetylenedicarboxylate to form the corresponding thiophene except *anhydro*-2-cyano-3,5-diphenyl-4-hydroxythiazolium hydroxide (4, R = CN; R^1 = Ph), formed from 1-cyanothioformanilide[11] (1, R = CN) and α-bromophenylacetyl chloride. In this case, instead of elimination of phenyl isocyanate from the intermediate 9, sulfur was lost and dimethyl 6-cyano-1,3-diphenyl-2-oxopyridine-4,5-dicarboxylate (10) was formed, although trace amounts of the



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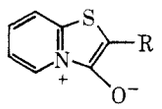

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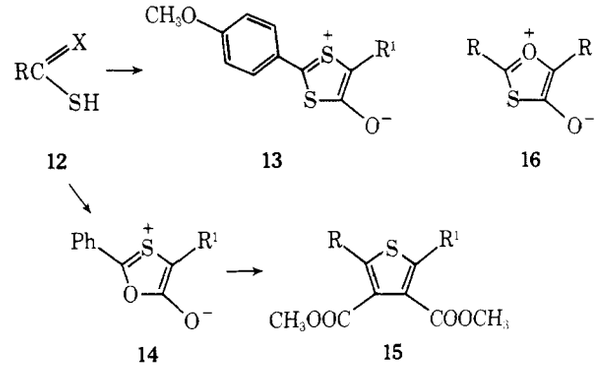
corresponding thiophene were apparently present (TLC) in the crude reaction mixture. This is not unexpected as the reaction of 4 (R = R^1 = Ph) with dicyanoacetylene resulted in a mixture of the corresponding thiophene and pyridone.[3a] The 5-ethoxycarbonyl group apparently reduces the dipolar characteristics of the ring system as 4 (R = Ph; R^1 = COOEt) was recovered in practically quantitative amount from prolonged reflux in xylene in the presence of 2-pyridylacetylene.

This procedure is as equally readily applicable to fused thiazole systems.[12] Thus 2-mercaptopyridine reacted readily with α-bromophenylacetyl chloride in the presence of Et_3N to give *anhydro*-3-hydroxy-2-phenylthiazolo[3,2-*a*]pyridinium hydroxide (11, R = Ph) and the corresponding 2-ethoxycarbonyl derivative (11, R = COOEt) was obtained using 2-bromo-2-ethoxycarbonylacetyl chloride. The ring system 11 did not undergo cycloaddition with dimethyl acetylenedicarboxylate.

***anhydro*-4-Hydroxy-1,3-dithiolium Hydroxide System.** This ring system has been prepared[13] by cyclodehydration of thioaroylthioglycollic acids with Ac_2O/Et_3N and, like the thiazolium system above, is an attractive precursor to substituted thiophenes. Reaction of *p*-methoxydithiobenzoic acid (12, R = *p*-$CH_3OC_6H_4$; X = S) with the above 1,2-bielectrophiles now provides an extremely ready entry into the 1,3-dithiolium system as the dithiobenzoic acids themselves are conveniently prepared[14] from aryl Grignard reagents and CS_2. Thus from 12 (R = *p*-$CH_3OC_6H_4$; X = S) and α-bromophenylacetyl chloride, *anhydro*-4-hydroxy-2-*p*-methoxyphenyl-5-phenyl-1,3-dithiolium hydroxide (13, R^1 = Ph) was obtained



12 13 16

14 15

in satisfactory yield and the corresponding 5-ethoxycarbonyl derivative 13 (R^1 = COOEt) was prepared using 2-bromo-2-ethoxycarbonylacetyl chloride. Although 13 (R^1 = Ph) underwent cycloadditions with dimethyl acetylenedicarboxylate, 13 (R^1 = COOEt) did not, no doubt owing to delocalization of the negative charge over the 5-ethoxycarbonyl substituent which was reflected in the infrared absorptions of the carbonyl groups at 1660 and 1650 cm^{-1}. It also did not form a cycloadduct with 2-pyridylacetylene, a reactive dipolarophile.

***anhydro*-5-Hydroxy-1,3-oxathiolium Hydroxide System.** This ring system has been found to be extremely unstable, with a strong electron-withdrawing substituent in the 4 position of the nucleus being necessary for isolation of the ring system. *anhydro*-2-*p*-Chlorophenyl-5-hydroxy-4-trifluoroacetyl-1,3-oxathiolium hydroxide has been prepared[15] by cyclodehydration of *p*-chlorobenzoylthioglycollic acid with trifluoroacetic anhydride and it was very susceptible to hydrolysis. Reaction of thiobenzoic *S*-acid (12, R = Ph; X = O) with α-bromophenylacetyl chloride/Et_3N gave *anhydro*-5-hydroxy-2,4-diphenyl-1,3-oxathiolium hydroxide (14, R^1 = Ph) which was not isolated but reacted with dimethyl acetylenedicarboxylate to form the thiophene 15 (R = R^1 = Ph). Reaction of 12 (R = Ph; X = O) with 2-bromo-2-ethoxycarbonyl chloride, however, did not result in formation of the ring system. The product obtained was identified as dibenzoyl disulfide, apparently formed by oxidation of 12 (R = Ph; X = O) by the 2-bromo-2-ethoxycarbonylacetyl chloride, similar oxidations having been observed by other reactive bromo compounds.[16] A recent communication[17] describes the preparation of the isomeric system, *anhydro*-4-hydroxy-1,3-oxathiolium hydroxide system 16, by ring closure of a thiocarbonyloxyacetic acid with Ac_2O. Like 14, the isomeric system 16 was too unstable for isolation but could be trapped with acetylenic dipolarophiles, in this case affording a convenient entry into substituted furan systems.

Experimental Section[18]

Reaction of *N,N*-Dimethyl-*N'*-phenylthiourea and α-Bromophenylacetic Acid. Attempted Preparation of *anhydro*-2-

Dimethylamino-3,5-diphenyl-4-hydroxythiazolium Hydroxide. *N,N*-Dimethyl-*N'*-phenylthiourea [**1**, R = $(CH_3)_2N$] (0.54 g, 0.003 mol), α-bromophenylacetic acid (**2**, R^1 = Ph; X = Br; Y = OH) (0.65 g, 0.003 mol), and Et_3N (0.31 g, 0.003 mol) were refluxed in dry benzene (25 mL) for 2 h. Filtration of the Et_3N·HBr and evaporation of the benzene gave 3,5-diphenylthiazolidine-2,4-dione (**8**, R^1 = Ph) as a yellow solid which crystallized from EtOH as colorless, matted needles: 0.18 g (22%); mp 173–175 °C (lit.[8] mp 172.5–173 °C); IR (KBr) 3050 (CH), 1750 (CO), 1680 cm^{-1} (CO); NMR ($CDCl_3$) δ 5.42 (s, 1, H_5), 7.47 (s, 10, aromatic); mass spectrum *m/e* (rel intensity) M^+· 269 (90).

Anal. Calcd for $C_{15}H_{11}NO_2S$: C, 66.89; H, 4.12; N, 5.20. Found: C, 66.52; H, 4.02; N, 5.17.

Similarly 1-morpholinothioformanilide (**1**, R = C_4H_8NO) (0.67 g, 0.003 mol), α-bromophenylacetic acid (0.65 g, 0.003 mol), and Et_3N (0.31 g, 0.003 mol) were refluxed in dry benzene (30 mL) for 2 h. Filtration of the Et_3N·HBr and evaporation of the solvent gave a yellow solid which crystallized from ethanol as colorless, matted needles identical with 3,5-diphenylthiazolidine-2,4-dione: 0.4 g (49%); mp 173–175 °C; mmp 173–175 °C. The dione was also obtained in the reaction of *O*-methyl (or *O*-ethyl) phenylthiocarbamate and α-bromophenylacetic acid.

General Procedure for the Reaction of N-Monosubstituted Thioamides with 1,2-Bielectrophiles. Preparation of *anhydro*-2-Dimethylamino-3,5-diphenyl-4-hydroxythiazolium Hydroxide [4, R = $(CH_3)_2N$; R^1 = Ph]. α-Bromophenylacetyl chloride (**2**, R^1 = Ph; X = Br; Y = Cl) (0.7 g, 0.003 mol) in $CHCl_3$ (10 mL) was added dropwise to a stirred solution of *N,N*-dimethyl-*N'*-phenylthiourea [**1**, R = $(CH_3)_2N$] (0.54 g, 0.003 mol) in dry $CHCl_3$ (10 mL). After 5 min, Et_3N (0.61 g, 0.006 mol) in dry $CHCl_3$ (5 mL) was added dropwise and the resulting yellow solution stirred for 5 min before being washed with two equal portions of H_2O. After separation and drying over Na_2SO_4, the $CHCl_3$ solution was reduced in volume to 2–3 mL and addition of Et_2O and scratching induced a yellow solid to crystallize. Filtration and washing with Et_2O gave yellow, irregular prisms which crystallized from acetone as gold needles, 0.52 g (58%), mp 150 °C dec (Table I). THF or benzene may also be used as the solvent in the above reaction.

General Procedure for the Reaction of *anhydro*-4-Hydroxythiazolium Hydroxides with Acetylenic Dipolarophiles. Preparation of Dimethyl 2-Dimethylamino-5-phenylthiophene-3,4-dicarboxylate [15, R = $(CH_3)_2N$; R^1 = PH]. *anhydro*-2-Dimethylamino-3,5-diphenyl-4-hydroxythiazolium hydroxide (0.12 g, 4×10^{-4} mol) and dimethyl acetylenedicarboxylate (0.1 g, 7×10^{-4} mol) were refluxed in dry benzene (10 mL) under N_2 for 6 h. Evaporation of the solvent gave a yellow oil which when triturated with CH_3OH (~1 mL) deposited a cream solid which was isolated by filtration. Crystallization from CH_3OH gave cream plates, 0.09 g (69%), mp 108–109 °C (Table II).

In the preparation of dimethyl 5-ethoxycarbonyl-2-dimethylaminothiophene-3,4-dicarboxylate the residue after evaporation of the solvent was purified by PLC (1.0 mm, $CHCl_3$/EtOAc, 90:10).

Dimethyl 6-Cyano-1,3-diphenyl-2-oxopyridine-4,5-dicarboxylate (10). *anhydro*-2-Cyano-3,5-diphenyl-4-hydroxythiazolium hydroxide (**4**, R = CN; R^1 = Ph) (0.28 g, 0.001 mol) and dimethyl acetylenedicarboxylate (0.21 g, 0.0015 mol) were refluxed in dry benzene (18 mL) under N_2 for 24 h. Evaporation of the solvent gave an orange oil which upon cooling began to crystallize. Trituration with CH_3OH (~1 mL) and scratching induced further crystllization. Filtration and washing with a small portion of cold CH_3OH gave cream, irregular prisms which, after washing with a small portion of CS_2 to remove elemental sulfur, crystallized from ethanol as tiny, colorless needles: 0.21 g (53%); mp 168–169 °C; IR (KBr) 2950 (CH), 2230 (C≡N), 1740, 1730, 1670 cm^{-1} (CO); λ_{max} (CH_3OH) 345 nm (log ε 4.04), 268 (4.01), 204 (4.54); NMR ($CDCl_3$) δ 3.62 (s, 3, CH_3), 3.96 (s, 3, CH_3), 7.45 (m, 10, aromatic); mass spectrum *m/e* (rel intensity) M^+· 388 (68).

Anal. Calcd for $C_{22}H_{16}N_2O_5$: C, 68.03; H, 4.15; N, 7.21. Found: C, 67.57; H, 4.21; N, 7.21.

Alkyl (or Aryl) Phenyldithiocarbamate.[4] A stirred suspension of ammonium phenyldithiocarbamate in water was treated with an excess of alkyl or aryl halide (CH_3I, EtBr, *n*-PrBr, or C_6H_5Br) and the mixture stirred at room temperature for 6 h. On cooling in a dry ice/acetone bath, crystallization was induced by scratching and the resulting precipitate was separated and washed with H_2O. Recrystallization from benzene or ligroin gave the phenyldithiocarbamate as colorless prisms.

Alternative Preparation of *anhydro*-3,5-Diphenyl-4-hydroxy-2-methylthiothiazolium Hydroxide (4, R = CH_3S; R^1 = Ph). Methyl phenyldithiocarbamate (**1**, R = CH_3S) (18.3 g, 0.1 mol) in benzene (150 mL) was treated with α-bromophenylacetic acid (21.5 g, 0.1 mol) and Et_3N (13.0 g, 0.13 mol). After stirring overnight at room temperature, the precipitate of Et_3N·HBr was separated and the solvent removed in vacuo. The oily residue, dissolved in anhydrous CH_2Cl_2, was treated with an equimolar amount of *N,N'*-dicyclohexylcarbodiimide with stirring at room temperature. The precipitated *N,N'*-dicyclohexylurea was filtered after 12 h and washed with CH_2Cl_2, the combined filtrates concentrated in vacuo, and crystallization induced by triturating the chilled residue with a small amount of anhydrous ether. The orange solid crystallized from benzene forming golden prisms, 17.5 g (50%), mp 158–160 °C (Table I).

Alkylation of *anhydro*-2-Alkylthio-3,5-diphenyl-4-hydroxythiazolium Hydroxide with Meerwein's Reagent. A stirred solution of *anhydro*-3,5-diphenyl-4-hydroxy-2-methylthiothiazolium hydroxide (**4**, R = CH_3S; R^1 = Ph) (0.73 g, 0.0024 mol) in CH_2Cl_2 (10 mL) was treated with a 10% excess of triethyloxonium tetrafluoroborate[19] (0.532 g, 0.0028 mol) and the reaction mixture kept at room temperature for 24 h. On diluting the chilled solution with anhydrous ether the solid that separated was collected and recrystallized from CH_2Cl_2/Et_2O giving 3,5-diphenyl-4-ethoxy-2-methylthiothiazolium tetrafluoroborate (**7**, R = CH_3S; R^1 = Ph) as colorless prisms: 955 mg (92%); mp 199–201 °C; IR (KBr) 3065, 2985, 2910 (CH), 1600 (C=N), 1120–1010 cm^{-1} (BF_4^-); λ_{max} (CH_3OH) 329 nm (log ε 4.16), 263 sh (3.89), 241 sh (4.02); NMR ($CDCl_3$) δ 7.90–7.25 (m, 10, aromatic), 3.98 (q, 2, OCH_2CH_3), 2.83 (s, 3, SCH_3), 0.93 (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{18}H_{18}BF_4NOS_2$: C, 52.05; H, 4.37; N, 3.38. Found: C, 52.06; H, 4.34; N, 3.46.

Similarly 3,5-diphenyl-4-ethoxy-2-ethylthiothiazolium tetrafluoroborate (**7**, R = EtS; R^1 = Ph) crystallized from CH_2Cl_2 as colorless prisms (87%): mp 204–206 °C; IR (KBr) 3065, 2980, 2935 (CH), 1600 (C=N), 1110–1010 cm^{-1} (BF_4^-); λ_{max} (CH_3OH) 330 nm (log ε 4.17), 260 sh (3.91), 240 sh (3.99); NMR ($CDCl_3$) δ 7.85–7.30 (m, 10, aromatic), 3.95 (q, 2, OCH_2CH_3), 3.40 (q, 2, SCH_2CH_3), 1.50 (t, 3, SCH_2CH_3), 0.95 (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{19}H_{20}BF_4NOS_2$: C, 53.14; H, 4.70; N, 3.26. Found: C, 53.09; H, 4.74; N, 3.30.

3,5-Diphenyl-4-ethoxy-2-*n*-propylthiothiazolium tetrafluoroborate (**7**, R = *n*-C_3H_7S; R^1 = Ph) also crystallized from CH_2Cl_2 as cream prisms (77%): mp 133–134.5 °C; IR (KBr) 3070, 2970, 2935 (CH), 1600 (C=N), 1115–1010 cm^{-1} (BF_4^-); λ_{max} (CH_3OH) 330 nm (log ε 4.29), 260 sh (4.04), 240 sh (4.11); NMR ($CDCl_3$) δ 7.90–7.25 (m, 10, aromatic), 3.98 (q, 2, OCH_2CH_3), 3.36 (t, 3, $SCH_2CH_2CH_3$), 1.95 (h, 2, $SCH_2CH_2CH_3$), 1.05 (t, 3, $SCH_2CH_2CH_3$), 0.95 (t, 3, OCH_2CH_3).

Anal. Calcd for $C_{20}H_{22}BF_4NOS_2$: C, 54.18; H, 5.00; N, 3.16. Found: C, 54.35; H, 5.05; N, 3.14.

Alkaline Hydrolysis of Dimethyl 2-Methylthio-5-phenylthiophene-3,4-dicarboxylate (15, R = CH_3S; r^1 = Ph). Dimethyl 2-methylthio-5-phenylthiophene-3,4-dicarboxylate (1.5 g, 0.0015 mol) in a 10% NaOH solution of aqueous methanol (1:1) (14 mL) was heated under reflux for 4 h. The methanol was removed in vacuo and the aqueous solution was acidified with 2 N HCl. Filtration of the precipitate and recrystallization from aqueous ethanol gave the corresponding 2-methylthio-5-phenylthiophene-3,4-dicarboxylic acid as colorless prisms, 0.46 g (100%), mp 235–237 °C (Table II).

3,5-Diphenyl-2-phenyliminothiazolidin-4-one (8a). A solution of α-bromophenylacetyl chloride (0.7 g, 0.003 mol) in benzene (10 mL) was added dropwise to a stirred solution of *N,N'*-diphenylthiourea (**1**, R = PhNH) (0.7 g, 0.003 mol). After 5 min at room temperature Et_3N (0.61 g, 0.006 mol) in benzene (5 mL) was added dropwise, the colorless reaction mixture changing to a red color, and stirring was continued for an additional 10 min. After removal of Et_3N·HX, the solvent was removed under reduced pressure and the oily residue triturated with ethanol giving cream prisms which crystallized from ethanol as colorless prisms of **8a**: 0.63 g (61%); mp 131–132 °C (lit.[8] mp 131–132.5 °C); IR (KBr) 3050 (CH), 1725, 1650 (CO), 1600 cm^{-1} (C=N); NMR (Me_2SO-d_6) δ 7.80–6.90 (m, 15, aromatic), 5.82 (s, 1, CH).

***anhydro*-3-Hydroxy-2-phenylthiazolo[3,2-*a*]pyridinium hydroxide (11, R = C_6H_5)** was obtained from the reaction of 2-mercaptopyridine and α-bromophenylacetyl chloride as described above. It crystallized from chloroform/ether as reddish-yellow prisms: mp 182–184 °C (lit.[12] mp 183–185 °C); IR (KBr) 3100–2950 (CH), 1620 (CO), 1590 cm^{-1} (C=N).

Similarly *anhydro*-2-ethoxycarbonyl-3-hydroxythiazolo[3,2-*a*]pyridinium hydroxide (**11**, R = $COOC_2H_5$) was obtained from the reaction of 2-mercaptopyridine and 2-bromo-2-ethoxycarbonylacetyl chloride. It also crystallized from chloroform/ether as golden prisms (30%): mp 166.5–168 °C; IR (KBr) 3110, 3080, 2975, 2935, 2900 (CH), 1725, 1650 (CO), 1610 cm^{-1} (C=N); λ_{max} (CH_3OH) 249 nm (3.90), 270 (3.76), 401 (4.05); NMR ($CDCl_3$) δ 8.15–7.35 (m, 4, aromatic), 4.40 (q,

2, $CO_2CH_2CH_3$), 1.39 (t, 3, $CO_2CH_2CH_3$); mass spectrum *m/e* (rel intensity) M^+· 223 (79).

Anal. Calcd for $C_{10}H_9NO_3S$: C, 53.80; H, 4.06; N, 6.27. Found: C, 53.79; H, 3.97; N, 6.22.

Hydrolysis of *anhydro*-2-Alkylthio-3,5-diphenyl-4-hydroxythiazolium Hydroxides (4, R = CH_3S, C_2H_5S, *n*-C_3H_7S; R^1 = Ph). The mesoionic thiazole derivative (200 mg) in ethanol/H_2O (1:2) (15 mL) was refluxed for 3–4 h. Upon cooling, the solid precipitate was separated by filtration, washed with water, and recrystallized from ethanol giving colorless prisms of 3,5-diphenylthiazolidine-2,4-dione (**8**, R^1 = Ph) in 58–61% yields.

Hydrolysis of *anhydro*-5-Ethoxycarbonyl-2-ethylthio-4-hydroxy-3-phenylthiazolium Hydroxide (4, R = SC_2H_5; R^1 = COOEt). The mesoionic compound **4** (R = C_2H_5S; R^1 = COOEt) (0.15 g, 0.0005 mol) in H_2O (10 mL) was treated with about 3 drops of concentrated HCl solution and then the reaction mixture was refluxed for 7 h. Upon cooling a precipitate separated and it was recrystallized from aqueous ethanol giving 3-phenylthiazolidine-2,4-dione (**8**, R^1 = H) as colorless prisms with physical constants corresponding to those reported:[9,10b] 0.5 g (56%); mp 146–148 °C; IR (KBr) 3070, 2980, 2930, 1695, 1675, 1600 cm^{-1}; λ_{max} (CH_3OH) 218 nm sh (log ϵ 3.99); NMR ($CDCl_3$) δ 7.65–7.03 (m, 5, aromatic), 4.05 (s, 2, CH_2); mass spectrum *m/e* (rel intensity) M^+· 193 (68) [M − CO], 165 (3) [M − CO, COS], 105 (5).

Hydrolysis of *anhydro*-3,5-Diphenyl-4-hydroxy-2-morpholinothiazolium Hydroxide (4, R = *N*-Morpholino; R^1 = Ph). The mesoionic compound (0.15 g, 0.0004 mol) in ethanol/H_2O (1:3) (8 mL) containing 3 drops of concentrated HCl solution was refluxed for 3 h. Upon cooling, a solid separated and was washed with water. Recrystallization from ethanol gave 3,5-diphenylthiazolidine-2,4-dione as colorless prisms, 70 mg (59%), mp 172–174 °C (lit.[8] mp 172.5–173 °C).

***anhydro*-4-Hydroxy-2-*p*-methoxyphenyl-5-phenyl-1,3-dithiolium Hydroxide.** α-Bromophenylacetyl chloride (0.7 g, 0.003 mol) in benzene (10 mL) was added dropwise to a stirred solution of *p*-methoxydithiobenzoic acid (0.552 g, 0.003 mol) in benzene (10 mL). After 5 min, Et_3N (0.61 g, 0.006 mol) in benzene (5 mL) was added dropwise and the resulting purple solution stirred at room temperature for 10 min. After the separation of the precipitated solid, the filtrate was concentrated in vacuo and the oily residue triturated with ether/petroleum ether F. The crystals which separated were recrystallized from $CHCl_3$/petroleum ether F giving purple prisms: 0.55 g (61%); mp 124–126 °C (lit.[13] mp 125–126 °C); IR (KBr) 1575 cm^{-1} (CO); NMR ($CDCl_3$) δ 3.8 (s, 3, CH_3O), 7.93–6.97 (m, 9, aromatic).

***anhydro*-5-Carboethoxy-4-hydroxy-2-*p*-methoxyphenyl-5-phenyl-1,3-dithiolium Hydroxide.** 2-Bromo-2-ethoxycarbonylacetyl chloride (4.6 g, 0.02 mol) in benzene (30 mL) was added dropwise to a solution of *p*-methoxydithiobenzoic acid (3.7 g, 0.02 mol) in benzene (30 mL) and the reaction mixture was then stirred at room temperature for 10 min. To this stirred mixture was added dropwise a solution of Et_3N (4.1 g, 0.04 mol) in benzene (20 mL). After 10 min, the precipitated Et_3N·HX was filtered and the filtrate concentrated in vacuo. Trituration of the oily residue with petroleum ether F induced a red solid which was separated by filtration. Washing with a small amount of H_2O and crystallization from benzene/petroleum ether F gave red prisms: 2.7 g (45%); mp ca. 148 °C dec; IR (KBr) 1660, 1650 cm^{-1} (CO); λ_{max} (CH_3OH) 495 nm (log ϵ 3.29), 352 (4.50), 252 (4.11); NMR ($CDCl_3$) δ 8.26–6.80 (m, 4, aromatic), 4.36 (q, 2, $CO_2CH_2CH_3$), 3.90 (s, 3, CH_3), 1.35 (t, 3, $CO_2CH_2CH_3$); mass spectrum *m/e* (rel intensity) M^+· 296 (9).

Anal. Calcd for $C_{13}H_{12}O_4S_2$: C, 52.68; H, 4.08. Found: C, 52.48; H, 3.99.

Trapping of *anhydro*-2,4-Diphenyl-5-hydroxy-1,3-oxathiolium Hydroxide with Dimethyl Acetylenedicarboxylate. A solution of thiobenzoic acid (1.38 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in benzene (20 mL) was added dropwise to a stirred solution of α-bromophenylacetyl chloride (2.34 g, 0.01 mol) and benzene (20 mL) over N_2. Dimethyl acetylenedicarboxylate (1.42 g, 0.01 mol) was added and then the reaction mixture was refluxed for 24 h. After cooling, the Et_3N·HX was removed by filtration and the filtrate concentrated in vacuo. Trituration of the oily residue with methanol induced a colorless solid to crystallize. Filtration and crystallization from methanol gave colorless prisms which were identical with authentic dimethyl 2,5-diphenylthiophene-3,4-dicarboxylate, 0.4 g (11%), mp 166–168 °C (lit.[13b] 167–168 °C).

Registry No.—**1** (R = CH_3S), 701-73-5; **1** (R = EtS), 13037-20-2; **1** (R = PrS), 14594-43-0; **1** (R = PhS), 27063-57-6; **1** (R = morpholino), 15093-54-6; **1** (R = $(CH_3)_2N$), 705-62-4; **1** (R = CN), 4955-82-2; **1** (R = Ph), 636-04-4; **1** (R = *p*-ClC_6H_4), 6244-75-3; **1** (R = *p*-$CH_3OC_6H_4$), 26060-23-1; **2** (R′ = Ph; X = Br; Y = OH), 4870-65-9; **2** (R′ = Ph; X = Br; Y = Cl), 19078-72-9; **2** (R′ = COOEt; X = Br; Y = Cl), 41141-81-5; **7** (R = CH_3S; R′ = Ph), 61522-29-0; **7** (R = EtS; R′ = Ph), 61522-31-4; **7** (R = *n*-C_3H_7S; R′ = Ph), 61522-33-6; **8** (R′ = Ph), 4695-03-8; **8** (R′ = H), 1010-53-3; **8a**, 4694-99-9; **10**, 61522-34-7; **11** (R = Ph), 32044-03-4; **11** (R = COOEt), 61522-35-8; **12** (R = *p*-$CH_3OC_6H_4$; X = S), 2168-77-6; **12** (R = Ph; X = O), 98-91-9; **13** (R′ = Ph), 21132-27-4; **13** (R′ = COOEt), 61522-36-9; dimethyl acetylenedicarboxylate, 762-42-5; triethyloxonium tetrafluoroborate, 368-39-8; 2-mercaptopyridine, 2637-34-5.

References and Notes

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