Mesoionic Compounds. 43. Ring Annelation Utilizing the Isomeric *anhydro*-2- and 3-Hydroxythiazolo[2,3-*b*]benzothiazolium Hydroxide Mesoionic Systems[1]

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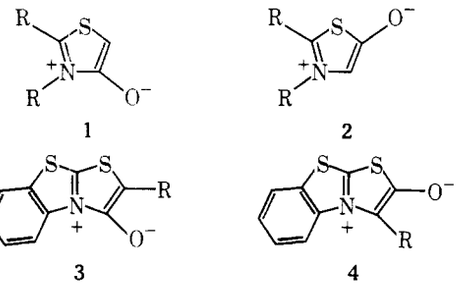
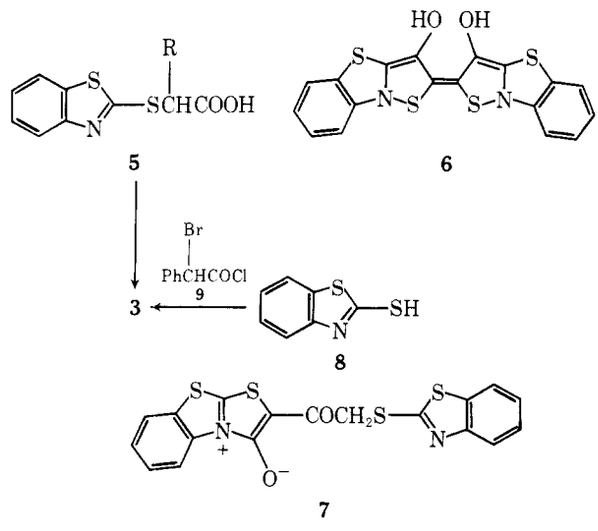
The isomeric *anhydro*-2- and 3-hydroxythiazolo[2,3-*b*]benzothiazolium hydroxides are convenient substrates for annelation of a five- and six-membered ring to benzothiazole, yielding the pyrrolo[2,1-*b*]benzothiazole and the 1*H*-pyrido[2,1-*b*]benzothiazol-1-one ring systems, respectively. The former mesoionic ring system could only be trapped by acetylenic dipolarophiles in situ, whereas the latter was readily available from 2-mercaptobenzothiazole and α-bromophenylacetyl chloride. The latter mesoionic ring system also reacted with *N*-phenyl- and *N*-ethylmaleimide as well as fumaronitrile, affording 1:1 primary cycloadducts.

Annelation of one or more rings to many of the well-characterized five-membered mesoionic ring systems would greatly extend their potential in synthetic applications but relatively few of these fused ring systems have been studied in detail to date.[2] Conspicuously absent are reports of their ability to undergo cycloadditions[3] analogous to those well characterized in five-membered systems containing masked "1,3-dipoles". We now report the synthesis and characterization of the *anhydro*-3-hydroxythiazolo[2,3-*b*]benzothiazolium hydroxide system **3** and the in situ generation and trapping of the isomeric *anhydro*-2-hydroxythiazolo[2,3-*b*]benzothiazolium hydroxide system **4**, the ring-fused analogues of the *anhydro*-4- and 5-hydroxythiazolium hydroxide systems **1** and **2**, respectively.[4,5]



Compounds of type **1** are readily available by cyclodehydration of the corresponding thioglycolic acid or by reaction of the appropriate thioamide with an α-haloacyl chloride derivative.[6] An earlier application[7] of the former procedure to 2-benzothiazolylthioglycolic acid (**5**; R = H) using hot acetic anhydride gave a highly insoluble dye formulated as **6**. The difficulty in obtaining definitive spectral data for this product still leaves the question of its structure in doubt and its physical characteristics indicate that it is most likely a polymer. Treatment of **5** with a 1:1 mixture of Ac_2O–Et_3N at room temperature gave a brick-red solid with ν_{CO} 1595, 1660 cm^{-1} and aromatic protons at δ 8.20–7.21 and a singlet at δ 4.80, integrating in the ratio of 4:1. It was not possible to obtain a molecular ion in the mass spectrum of this product but an ion at *m/e* 180 is consistent with the structure for this product being **7**, obtained by reaction of the initially formed mesoionic ring system with the mixed anhydride of the thioglycolic acid **5** and Ac_2O. Variation of these reaction conditions did not appreciably alter the formation of **7**.



Reaction of **5** with dicyclohexylcarbodiimide also gave a deep-red product whose infrared spectrum was not quite compatible with the mesoionic-type structure **3** (R = H). Attempted purification of this product resulted in decomposition. Reaction of **8** with bromacetyl chloride gave an unstable, greenish crystalline product with ν_{CO} 1595, 1665 cm^{-1}, thought to be **3** (R = $COCH_2Br$). These experiments indicate that the ring system **3** is too reactive for isolation unless a stabilizing substituent such as a phenyl or an electron-withdrawing acyl group is introduced into the 2 position.

Condensation of 2-mercaptobenzothiazole (**8**) with α-bromophenylacetyl chloride (**9**) in $CHCl_3$/$2Et_3N$ occurred readily, affording **3** (R = Ph) in 62% yield. Although several possibilities exist for the initial site of reaction with these reagents, only two final ring-closed products are possible. The isomeric system **4** (R = Ph) was excluded by the synthesis of **3** (R = Ph) from α-phenyl-2-benzothiazolylthioglycolic acid (**5**, R = Ph) and Ac_2O/Et_3N. Reaction of **8** with α-bromo-α-carboethoxyacetyl chloride would be anticipated to yield **3** (R = COOEt). However, the product isolated was identified as 2-benzothiazolyl disulfide, apparently formed by oxidation of **8** by the α-bromo-α-carboethoxyacetyl chloride, such an oxidation not being without precedent.[6]

The mesoionic system **3** contains a "masked" thiocarbonyl ylide dipole, represented by **3** ↔ **3a** ↔ **3b**, and underwent ready reaction with electron-deficient dipolarophiles. With dimethyl acetylenedicarboxylate in refluxing toluene addition to **3** occurred and the product isolated was methyl 1-oxo-2-phenyl-1*H*-pyrido[2,1-*b*]benzothiazole-3,4-dicarboxylate (**11**, R = $COOCH_3$) (80%). This facile extrusion of sulfur from the postulated intermediate **10** (R = $COOCH_3$) is no doubt associated with the presence of the 5,6-double bond in **10**, similar extrusions of sulfur being well established in analogous cycloadducts from monocyclic systems.[5] Dibenzoylacetylene and hexafluoro-2-butyne underwent similar ready cycloaddition to **3** giving the appropriately substituted derivatives of **11** in good yields. These fused pyridones were characterized by analytical and spectral data (Experimental Section).

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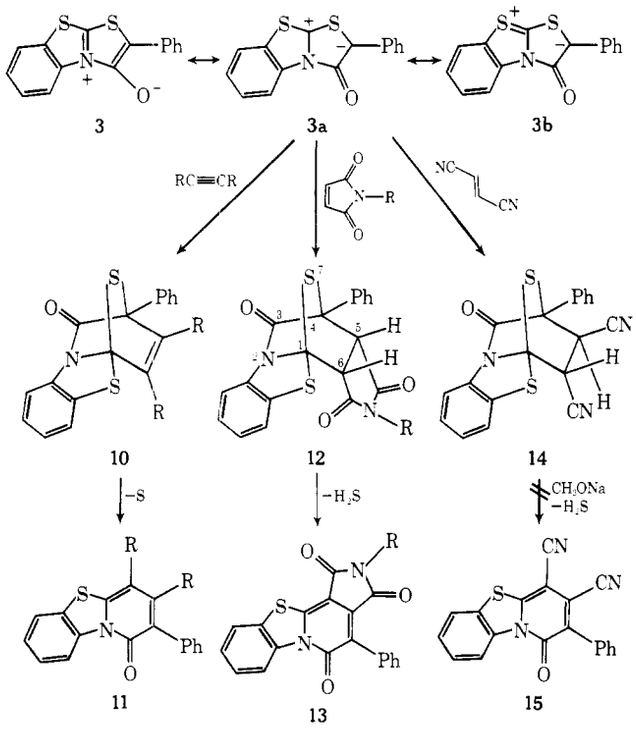
Olefinic dipolarophiles reacted equally as readily with **3**. With *N*-phenylmaleimide in refluxing toluene reaction was complete in 30 min, giving an 84% yield of a product established as the primary cycloadduct **12** (R = Ph). The NMR spectrum, besides aromatic protons, showed two AB doublets at δ 4.33 and 4.10 (J = 7.0 Hz) and the endo configuration for **12** was assigned in analogy with those obtained from the monocyclic *anhydro*-4-hydroxythiazolium hydroxide system and *N*-phenylmaleimide.[4] Efforts to obtain satisfactory analytical data for this compound were unsuccessful. However, both positive and negagive ion CI mass spectra[8] confirmed the assigned molecular weight (456) with ions being observed at $[M + H]^+$ 457, $[M + NH_4]^+$ 474, and $[M - H]^-$ 455. *N*-Ethylmaleimide also reacted readily with **3** giving the cycloadduct **12** (R = Et) (92%) in which the H_5 and H_6 protons of the fused system were again part of an AB doublet at δ 3.99 and 3.86 (J = 6.5 Hz).

These primary cycloadducts were always contaminated by minute amounts of a yellow product, extremely insoluble in most solvents. Complete conversions of the primary 1:1 cycloadducts into this yellow product were readily effected by refluxing **12** (R = Et, Ph) in xylene, H_2S being eliminated. These fused pyridones were readily characterized by their intense molecular ions and analytical data (Experimental Section).

Fumaronitrile also underwent ready cycloaddition with **3** (R = Ph) giving the 1:1 primary cycloadduct **14** in 90% yield. In the NMR spectrum ($CDCl_3$), the protons α to the cyano groups appeared as a singlet at δ 4.11, shifted to δ 5.41 in Me_2SO-d_6, but the exo–endo relationship of these H_5–H_6 protons cannot be determined unambiguously from these data. In contrast to the above adducts, **14** was extremely stable thermally, not losing H_2S on refluxing over 40 h in xylene. Treatment of **14** with sodium methoxide, a process known to cause elimination of H_2S in the cycloadducts obtained from monocyclic systems,[4] only resulted in tar formation, none of the expected pyridone **15** being isolated. In this particular



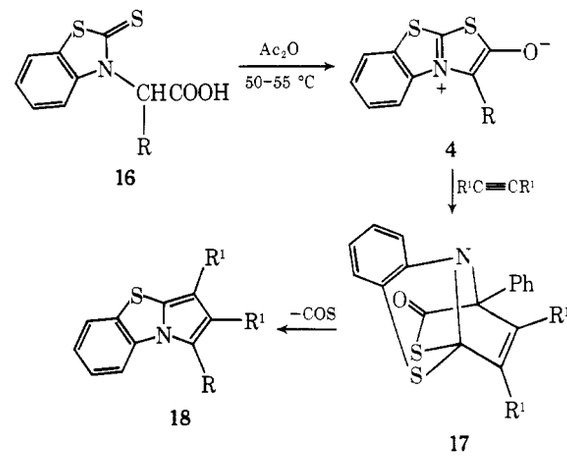
reaction initial removal of a proton from the adduct **14** can result in two C–S bond cleavages: one leads to pyridone formation and with the other a thiophenolate ion would result. This seems to be the most likely cause of tar formation. In the mass spectrum of **14** the most intense ion observed is m/e 327, corresponding to the loss of H_2S from the molecular ion m/e 361 (13), providing confirmation of structure **14**.

These ready cycloadditions to fused five-membered mesoionic ring systems of this general type are the first observed where addition occurs at a bridgehead carbon atom. No doubt influenced by the sulfur atom at the 9 position, formation of the 1:1 primary cycloadducts **10, 12,** and **14** does not result in any loss of benzenoid resonance energy, a factor which may be used to explain the nonreactivity of *anhydro*-3-hydroxythiazolo[3,2-*a*]pyridinium hydroxide in related reactions.[9]

In view of the reactivity of **3,** the isomeric *anhydro*-2-hydroxythiazolo[2,3-*b*]benzothiazolium hydroxide system **4** was of interest as elimination of COS from an initial 1:1 cycloadduct from **4** and acetylenic dipolarophiles would provide a convenient means of annelation of a pyrrole ring to benzothiazole. The most direct synthesis of this ring system would be by cyclodehydration of 2-thioxobenzothiazol-3-ylacetic acid (**16,** R = H), prepared from 2-methylthiobenzothiazole and ethyl bromoacetate followed by hydrolysis.[10] Attempts to achieve ring closure of **16** (R = H) with Ac_2O/Et_3N at room temperature or with *N,N*-dicyclohexylcarbodiimide were unsuccessful, the products obtained apparently being formed by decomposition of the mesoionic system **4** (R = H). However, generation of **4** (R = H) with Ac_2O in the presence of dimethyl acetylenedicarboxylate at 50–55 °C resulted in trapping of this mesoionic system with the ultimate isolation of methyl pyrrolo[2,1-*b*]benzothiazole-2,3-dicarboxylate (**18,** R = H; R^1 = $COOCH_3$) in good yield. The intermediate **17** was presumably involved in the reaction, readily losing COS to form **18.** Analytical and spectral data were in agreement with structure **18,** especially a singlet proton at δ 7.88 (H_1) comparable to the chemical shift δ 7.58 of the analogous proton in methyl indolizine-2,3-dicarboxylate.[11]

Dibenzoylacetylene and hexafluoro-2-butyne also reacted readily with the unstable ring system **4** (R = H) giving the corresponding derivatives of **18** (R = H; R^1 = COPh and R = H; R^1 = CF_3), respectively.

It was anticipated that introduction of a 3-phenyl substituent into **4** would stabilize the ring system sufficiently to allow its isolation. However, attempts to prepare **16** (R = Ph) by



reaction of 2-mercaptobenzothiazole with ethyl α-bromophenylacetate failed.

Experimental Section[12]

2-Mercaptobenzothiazole was purified[13] as follows: The thiol (50.0 g) was dissolved in aqueous sodium hydroxide solution (150 mL of 10% solution) with thorough stirring. After 15 min, the insoluble material was removed by filtration, the cold mother liquor was treated with charcoal, and this mixture was refluxed overnight when the hot reaction mixture was filtered. After cooling, the mother liquor was treated with 15% HCl solution to ca. pH 4 and the snow-white product was collected and dried.

Attempted Preparation of *anhydro*-3-Hydroxythiazolo[2,3-*b*]benzothiazolium Hydroxide (3; R = H). A. By Cyclodehydration of 2-Benzothiazolylthioglycollic Acid. The acid[7] **5** (R = H) (2.0 g) was treated with a mixture of Ac_2O (2 mL) and Et_3N (2 mL) and, after stirring at room temperature for 10 min, anhydrous Et_2O (10 mL) was added. A brick-red solid separated: mp 177–179 °C; IR (KBr) 1660, 1595 cm^{-1} (CO); NMR (Me_2SO-d_6) δ 8.20–7.21 (m, 4, aromatic), 4.80 (s, 1); mass spectrum, *m/e* (rel intensity) 180 (82), 166 (65). This product is best represented by structure **7**.

B. Ring Closure with *N,N*-Dicyclohexylcarbodiimide. A suspension of the acid **5** (R = H) (1.12 g, 5 mmol) in CH_2Cl_2–CH_3CN was treated with *N,N*-dicyclohexylcarbodiimide (1.03 g, 5 mmol), an exothermic reaction occurring with the development of a red coloration. After 3 h the insoluble material was removed and the filtrate was concentrated in vacuo. Addition of anhydrous ether precipitated a red solid of indefinite melting point: IR (KBr) 3400 (CH), 1750, 1715, 1695 cm^{-1} (CO).

Preparation of *anhydro*-3-Hydroxy-2-phenylthiazolo[2,3-*b*]benzothiazolium Hydroxide (3; R = Ph). Method A. A suspension of 2-mercaptobenzothiazole (0.84 g, 5 mmol) in dry $CHCl_3$ (50 mL) was treated dropwise with α-bromophenylacetyl chloride (1.17 g, 5 mmol) at room temperature with rapid stirring. After 10 min Et_3N (1.01 g, 10 mmol) was added dropwise and stirring was continued for a further 30 min. The reaction mixture was washed with cold water (2 × 15 mL), dried (Na_2SO_4), and then concentrated. Addition of a small amount of anhydrous Et_2O gave an orange solid which crystallized from chloroform–ether as orange plates: 0.9 g (63%); mp 180 °C dec; IR (KBr) 1615, 1590 cm^{-1} (CO); λ_{max} (CH_3OH) 420 (log ϵ 4.04), 282 nm (4.21); NMR ($CDCl_3$) δ 7.90–7.05 (m, aromatic); M^+· 283 (62). Anal. Calcd for $C_{15}H_9NOS_2$: C, 63.59; H, 3.20; N, 4.94. Found: C, 63.22; H, 3.11; N, 5.16.

Method B. A stirred mixture of 2-mercaptobenzothiazole (1.68 g, 10 mmol) and α-bromophenylacetic acid (2.16 g, 10 mmol) in anhydrous benzene (70 mL) was treated dropwise with Et_3N (1.01 g, 10 mmol). After stirring for 4 h at room temperature, the product was washed with water (2 × 15 mL) and dried (Na_2SO_4) and the benzene was then evaporated in vacuo. The oily residue was dissolved in anhydrous benzene (2 mL) and treated with a mixture of Ac_2O (2 mL) and Et_3N (2 mL). After 15 min anhydrous ether was added giving an orange solid which crystallized from $CHCl_3$–Et_2O as orange plates: 1.45 g (51%); mp 180 °C dec; identical[14] with the product prepared by A above.

Reaction of *anhydro*-3-Hydroxy-2-phenylthiazolo[2,3-*b*]benzothiazolium Hydroxide (3, R = Ph) with Dipolarophiles. The mesoionic compound and the dipolarophile (equimolar amounts) in toluene were heated under reflux until all the mesoionic compound had reacted (TLC). The toluene was evapoarated in vacuo and the residue was recrystallized from an appropriate solvent.

Methyl 1-Oxo-2-phenyl-1*H*-pyrido[2,1-*b*]benzothiazole-3,4-dicarboxylate (11, R = $COOCH_3$), obtained from **3** (R = Ph) and dimethyl acetylenedicarboxylate after 3 h of reflux, crystallized as colorless needles from $CHCl_3$–EtOH: 80%; mp 245 °C; IR (KBr) 1740, 1695, 1655 cm^{-1} (CO); λ_{max} (CH_3OH) 375 (log ϵ 4.25), 360 (4.18), 310 nm (4.24); NMR ($CDCl_3$) δ 7.82–7.2 (m, 9, aromatic), 3.92 (s, 3, CH_3), 3.58 (s, 3, CH_3); M^+· 393 (100). Anal. Calcd for $C_{21}H_{15}NO_5S$: C, 64.10; H, 3.84; N, 3.56. Found: C, 63.97; H, 3.85; N, 3.52.

3,4-Dibenzoyl-2-phenyl-1*H*-pyrido[2,1-*b*]benzothiazol-1-one (11, R = COPh), from **3** (R = Ph) and dibenzoylacetylene after 3 h, separated as yellow prisms from $CHCl_3$–EtOH: 62%; mp 230 °C; IR (KBr) 1670, 1635 cm^{-1} (CO); λ_{max} (CH_3OH) 370 (log ϵ 4.04), 257 nm (4.25); NMR ($CDCl_3$) δ 7.77–7.22 (m, aromatic); M^+· 485 (78). Anal. Calcd for $C_{31}H_{19}NO_3S$: C, 76.68; H, 3.95; N, 2.88. Found: C, 76.45; H. 3.89; N, 2.69.

3,4-Bis(trifluoromethyl)-2-phenyl-1*H*-pyrido[2,1-*b*]benzothiazol-1-one (11, R = CF_3), from **3** (R = Ph) and hexafluoro-2-butyne after 4 h, formed yellow prisms from acetonitrile: 33%, mp 186–187 °C; IR (KBr) 1670 cm^{-1} (CO); λ_{max} (CH_3OH) 390 (log ϵ 4.23), 372 (4.22), 250 (4.19), 224 nm (4.48); NMR ($CDCl_3$) δ 8.03–7.27 (m, aromatic); M^+· 413 (67). Anal. Calcd for $C_{19}H_9F_6NOS$: C, 55.21; H, 2.20; N, 3.39. Found: C, 54.94; H, 2.20; N, 3.62.

Reaction of 3 (R = Ph) with *N*-Phenylmaleimide. *N*-Phenylmaleimide and **3** (R = Ph) in refluxing toluene for 30 min gave the 1:1 primary cycloadduct **12** (R = Ph) as colorless needles from $CHCl_3$–EtOH: 84%; mp 164–165 °C dec; IR (KBr) 1725, 1720 cm^{-1} (CO); λ_{max} (CH_3OH) 267 nm (log ϵ 4.50); NMR ($CDCl_3$) δ 7.37–7.07 (m, 14, aromatic), 4.33 (ABd, 1, J = 7.0 Hz, H_5), 4.10 (ABd, 1, J = 7.0 Hz, H_6); mass spectrum, *m/e* $[M + H]^+$ 457, $[M + NH_4]^+$ 474, $[M - H]^-$ 455.

The above adduct **12** (R = Ph) was heated in xylene for 30 h affording **13** (R = Ph) as small, yellow needles from DMF–$CHCl_3$: 41%; mp 348–349 °C; IR (KBr) 1730, 1715 cm^{-1} (CO); M^+· 422 (100). Anal. Calcd for $C_{25}H_{14}N_2O_3S$: C, 71.09; H, 3.34; N, 6.33. Found: C, 71.09; H, 3.25; N, 6.51.

Reaction of 3 (R = Ph) with *N*-Ethylmaleimide. Under analogous conditions to those above, the 1:1 primary cycloadduct **12** (R = Et) separated as colorless needles from $CHCl_3$–EtOH: 92%; mp 176 °C dec; IR (KBr) 1725, 1700 cm^{-1} (CO); λ_{max} (CH_3OH) 220 nm (log ϵ 4.63); NMR ($CDCl_3$) δ 7.83–7.03 (m, 9, aromatic), 3.99 (ABd, 1, J = 6.5 Hz, H_5), 3.86 (ABd, 1, J = 6.5 Hz, H_6), 3.53 (qt, 2, J = 7.0 Hz, CH_2CH_3), 1.12 (t, 3, J = 7.0 Hz, CH_2CH_3); M^+· 408 (53). Anal. Calcd for $C_{21}H_{16}N_2O_3S_2$: C,61.73; H, 3.95; N, 6.86. Found: C, 61.95; H. 3.88; N, 6.74.

The above adduct **12** (R = Et), on heating in refluxing xylene for 24 h, gave **13** (R = Et) as yellow needles from $CHCl_3$–EtOH: 51%; mp 246–247 °C; IR (KBr) 1705, 1660 cm^{-1} (CO); λ_{max} (CH_3OH) 417 (log ϵ 3.71), 340 (3.95), 232 nm (3.98); NMR ($CDCl_3$) δ 7.90–7.27 (m, 9, aromatic), 3.71 (qt, 2, J = 7.0 Hz, CH_2CH_3), 1.26 (t, 3, J = 7.0 Hz, CH_2CH_3); M^+· 374 (100). Anal. Calcd for $C_{21}H_{14}N_2O_3S$: C, 67.35; H, 3.77; N, 7.48. Found: C, 65.80; H, 3.85; N, 7.23.

Reaction of 3 (R = Ph) with Fumaronitrile. From **3** (R = Ph) and fumaronitrile after 3 h, the 1:1 primary cycloadduct **14** was obtained as yellow needles from CH_3CN: 90%; mp 201–202 °C; IR (KBr) 2250, 2220 (CN), 1750 cm^{-1} (CO); λ_{max} (CH_3OH) 407 nm (log ϵ 3.55); NMR ($CDCl_3$) δ 7.5 (m, 5, aromatic), 7.17 (m, 4, aromatic), 4.11 (s, 2, CHCN); M^+· 361 (13). Anal. Calcd for $C_{19}H_{11}N_3OS_2$: C, 63.14; H, 3.07; N, 11.62. Found: C, 63.08; H, 2.98; N, 11.69.

Trapping of *anhydro*-2-Hydroxythiazolo[2,3-*b*]benzothiazolium Hydroxide (4, R = H) with Acetylenic Dipolarophiles. 2-Thioxobenzothiazol-3-ylacetic acid (**16**, R = H), Ac_2O (4 mL), the dipolarophile, and dry benzene (5 mL) were stirred at 50–55 °C for 3 h. The reaction mixture was washed with K_2CO_3 (2 × 10 mL of 5% aqueous solution) and water (10 mL) and dried (Na_2SO_4). After evaporation of the benzene, the residue was recrystallized from an appropriate solvent.

Methyl Pyrrolo[2,1-*b*]benzothiazole-2,3-dicarboxylate (18, R = H; R[1] = $COOCH_3$) formed small, colorless needles from EtOH: 43%; mp 152 °C; IR (KBr) 1755 cm^{-1} (CO); λ_{max} (CH_3OH) 290 (log ϵ 4.06), 217 nm (5.30); NMR ($CDCl_3$) δ 7.88 (s, 1, H_1), 7.70–7.21 (m, 4, aromatic), 3.87 (s, 6, CH_3); M^+· 289 (20). Anal. Calcd for $C_{14}H_{11}NO_4S$: C, 58.12; H, 3.83; N, 4.84. Found: C, 57.95; H. 3.81; N, 4.79.

2,3-Dibenzoylpyrrolo[2,1-*b*]benzothiazole (18, R = H; R[1] = COPh) was obtained as cream prisms from $CHCl_3$–EtOH: 57%; mp 214 °C; IR (KBr) 1650 cm^{-1} (CO); λ_{max} (CH_3OH) 335 (log ϵ 4.19), 285 (4.34), 252 (4.56), 205 nm (4.62); NMR ($CDCl_3$) 7.93 (s, 1, H_1), 7.8–7.17 (m, 14, aromatic); M^+· 381 (80). Anal. Calcd for $C_{24}H_{15}NO_2S$: C, 75.58; H, 3.97; N, 3.67. Found: C, 75.77; H, 3.97; N, 3.60.

2,3-Bis(trifluoromethyl)pyrrolo[2,1-*b*]benzothiazole (18, R = H, R[1] = CF_3) required a bath temperature of 70–75 °C for formation from **16** (R = H) and hexafluoro-2-butyne. After chromatography of the crude residue on silica gel using benzene as eluent, the tricyclic system crystallized from *n*-hexane as small, colorless needles: 29%, mp 122 °C; IR (KBr) 1545 cm^{-1} (CF_3); λ_{max} (CH_3OH) 300 (log ϵ 3.77), 292 (3.70), 220 nm (4.84); NMR ($CDCl_3$) δ 7.80–7.23 (m, H_1 and aromatic); M^+· 309 (100). Anal. Calcd for $C_{12}H_5F_6NS$: C, 46.60; H, 1.63; N, 4.53. Found: C, 46.57; H. 1.50; N, 4.35.

Registry No.—**3** (R = H), 66085-19-6; **3** (R = Ph), 66085-20-9; **4** (R = H), 66085-21-0; **5** (R = H), 6295-57-4; **7**, 66085-22-1; **8**, 149-30-4; **9**, 19078-72-9; **11** (R = $COOCH_3$), 66085-23-2; **11** (R = COPh), 66085-24-3; **11** (R = CF_3), 66085-25-4; **12** (R = Ph), 66085-26-5; **12** (R = Et), 66085-27-6; **13** (R = Ph), 66085-28-7; **13** (R = Et), 66085-29-8; **14**, 66085-30-1; **16** (R = H), 59794-34-2; **18** (R = H; R[1] = $COOCH_3$), 66085-31-2; **18** (R = H; R[1] = COPh, 66085-32-3; **18** (R = H; R[1] = CF_3), 66085-33-4; α-bromophenylacetic acid, 4870-65-9; dimethyl acetylenedicarboxylate, 762-42-5; dibenzoylacetylene, 1087-09-8; hexafluoro-2-butyne, 692-50-2; *N*-phenylmaleimide, 941-69-5; *N*-ethylmaleimide, 128-53-0; fumaronitrile, 764-42-1.

References and Notes

(1) Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged. (b) The annelation of pyridinium rings onto nitrogen heterocycles has recently been described: D. D. Chapman, J. K. Elwood, D. W. Heseltine, H. M. Hess, and D. W. Kurtz, *J. Org. Chem.*, **42**, 2474 (1977).

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(8) We are indebted to Dr. B. Pramanik for these data.
(9) K. T. Potts and D. R. Choudhury, *J. Org. Chem.*, following paper in this issue.
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(12) Spectral characterizations and reaction work-up procedures were as described in previous papers in this series. Microanalyses were by Instranal Laboratories, Inc., Rensselaer, N.Y.
(13) We thank Dr. J. J. D'Amico for this procedure which ensures complete elimination of 2-benzothiazolyl disulfide often present as a contaminant.
(14) Criteria for identity were superimposable IR spectra, no depression in mmp, and identical r_f values.

Notes

Mesoionic Compounds. 44. Synthesis and Cycloaddition Reactions of the *anhydro*-1-Hydroxythiazolo[3,2-*a*]quinolinium Hydroxide System[1]

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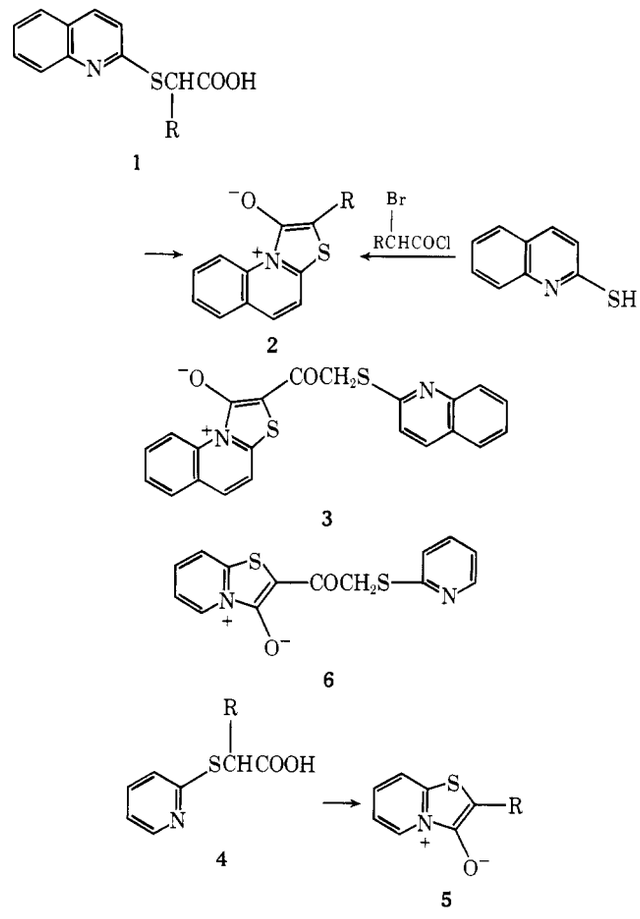
In an accompanying publication,[2] we reported the ready cycloaddition of the isomeric *anhydro*-2- and 3-hydroxythiazolo[2,3-*b*]benzothiazolium hydroxides with acetylenic dipolarophiles to the pyrrolo[2,1-*b*]benzothiazole and the 1*H*-pyrido[2,1-*b*]benzothiazol-1-one ring systems, respectively. As sulfur is isoelectronic with a double bond, we anticipated that the *anhydro*-1-hydroxythiazolo[3,2-*a*]quinolinium hydroxide system **2** should also be of interest as a substrate for cycloaddition reactions. The results obtained with this ring system are described below.

anhydro-1-Hydroxythiazolo[3,2,-*a*]quinolinium hydroxide (**2**, R = H) has been reported earlier,[3] prepared by the cyclodehydration of the 2-quinolinylthioglycolic acid (**1**, R = H) with Ac_2O. On repetition of this procedure, a dark-brown-bronze product was obtained which was difficult to isolate in a pure state despite repeated recrystallizations. However, the observed spectral data were inconsistent with structure **2** (R = H); although infrared carbonyl absorptions at 1610 and 1600 cm^{-1} are compatible with the C_1-carbonyl group, an absorption at 1660 cm^{-1} suggests attachment of a carbonyl group to C_2. The NMR spectrum, in addition to the aromatic multiplet at δ 7.93–7.26, showed a singlet at δ 4.98 which is consistent with structure **3** for this product (vide infra). Similar results were also obtained in the attempted preparation of *anhydro*-3-hydroxythiazolo[3,2-*a*]pyridinium hydroxide (**5**, R = H) from 2-pyridinylthioglycolic acid (**4**, R = H) with Ac_2O under the previously reported conditions.[3] The yellow crystalline product obtained showed ν_{CO} 1680, 1620, and 1600 cm^{-1} and a singlet at δ 4.16 in its NMR spectrum in addition to an aromatic multiplet. Its molecular weight was shown to be 302, and these data require revision of the assigned structure **5** (R = H) to that of **6**, The same product was also obtained from the reaction of bromoacetyl chloride and 2-mercaptopyridine and the formation of **6** is indicative of a high electron density at the 2 position of **5** (R = H). Authentic samples of this ring system have been prepared by the reaction of 2-mercaptopyridine with δ-bromophenylacetyl chloride[4] and 2-bromo-2-ethoxycarbonylacetyl chloride[5] giving **5** (R = Ph) and **5** (R = COOEt), respectively. With a variety of electron-deficient dipolarophiles, no cycloaddition of **5** (R = Ph, COOEt) was observed.

Blocking of the 2 position in **2** with a phenyl substituent proved to be the most effective way of obtaining an authentic example of this ring system and reaction of 2-mercaptoquinoline with α-bromophenylacetyl chloride gave an 82% yield of **2** (R = Ph) as deep-red plates. A carbonyl absorption at 1610 cm^{-1} is consistent with this structure which was confirmed by an alternative synthesis by ring closure of 2-quinolinyl-α-phenylthioglycolic acid (**1**, R = Ph).

Reaction of **2** (R = Ph) with dimethyl acetylenedicarboxylate in refluxing toluene for 6 h gave a yellow crystalline product anticipated to be **8** (R = R^1 = $COOCH_3$). However, the infrared spectrum indicated only ester carbonyl bands at 1725 and 1705 cm^{-1} and no absorption due to the ring carbonyl group was present. The mass spectrum showed M^+· 359



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