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Mesoionic Compounds. XXXI. The Preparation and Cycloaddition Reactions of the *anhydro*-4-Hydroxythiazolium Hydroxide System with Acetylenic Dipolarophiles[1]

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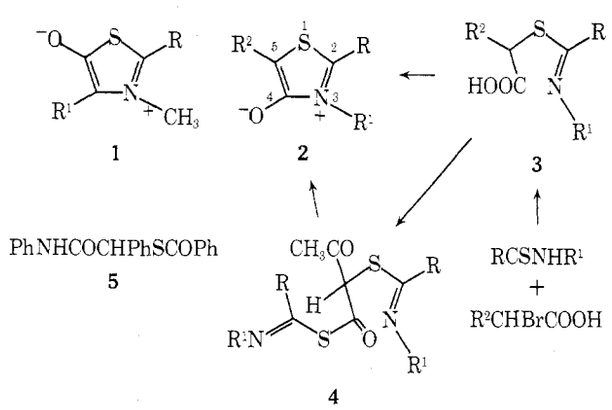
anhydro-2,3-Diphenyl-4-hydroxythiazolium hydroxide has been prepared by Ac_2O/Et_3N cyclization of the condensation product of thiobenzanilide and bromoacetic acid, and the product previously assigned this structure identified as 2-mercapto-1-thioacetoacetic acid, anhydrosulfide with *N*-phenylthiobenzimidic acid, *N*-phenylbenzimidate. Other derivatives of this mesoionic thiazolium system were prepared from the appropriate thiobenzanilide with bromoacetic acid (or α-bromophenylacetic acid). Dimethyl acetylenedicarboxylate, dibenzoylacetylene, dicyanoacetylene, and hexafluoro-2-butyne underwent ready cycloaddition to this thiazolium system, the final product depending on the substitution pattern of the nucleus. With 2,3-diaryl substituents, pyridones were formed with extrusion of sulfur from the initial adduct. With 2,3,5-triphenyl substituents, phenyl isocyanate was eliminated from the initial adduct with the formation of the substituted thiophene in more than 90% yield.

In the preceding publication[2] in our studies of mesoionic ring systems[3] the cycloaddition reactions of the *anhydro*-5-hydroxythiazolium hydroxide system **1**, one of the two[4] possible mesoionic ring systems based on the thiazole nucleus, were described. We now report the synthesis and cycloaddition reactions with acetylenic dipolarophiles of the isomeric *anhydro*-4-hydroxythiazolium hydroxide system **2**, which has an added interest in that there is no opportunity for elimination of carbonyl sulfide from an initial cycloadduct; rather sulfur must be extruded or a retro-Diels–Alder type reaction occur with elimination of phenyl isocyanate.

A synthesis of the mesoionic system **1** had been described[5] earlier, but its reported physical characteristics were inconsistent with those expected for a heterocycle containing a thiocarbonyl ylide structure. Repetition of the Ac_2O/Et_3N cyclization of the intermediate acid (**3**, R = R^1 = Ph; R^2 = H) obtained from thiobenzanilide and bromoacetic acid resulted in the isolation of the product described previously as colorless needles, mp 195–196°. In our preliminary communication this product was shown to have structure **4**. This most likely arises from the reaction of thiobenzanilide with the mixed anhydride derived from the intermediate acid **3** and acetic anhydride, followed by acetylation and, as such, is described as 2-mercapto-1-thioacetoacetic acid, anhydrosulfide with *N*-phenylthiobenzimidic acid, *N*-phenylbenzimidate (**4**, R = R^1 = Ph).



Reaction of thiobenz-*p*-chloroanilide with bromoacetic acid under these conditions gave an analogous product **4** (R = Ph; R^1 = *p*-ClC_6H_4). This product was likewise converted in good yield into the acetyl derivative of **2** (R = Ph; R^1 = *p*-ClC_6H_4; R^2 = $COCH_3$) with hot acetic anhydride.

Minor variation in the proportions of the reactants did not alter appreciably the outcome of the reaction. However, it was possible to have ring closure of the acid **3** to the me-

soionic system **2** favored over its condensation with thiobenzanilide by altering the reaction conditions to increase considerably the amount of Et_3N present while, at the same time, increasing the concentration of the reactants in the cyclization medium.

Treatment of the crude acid **3** (R = R^1 = Ph; R^2 = H), obtained from thiobenzanilide and bromoacetic acid, with the minimum volume for solution to occur of a 1:3 mixture of Ac_2O/Et_3N for 5 min and then inducing the product to crystallize by rapid scratching of the walls of the reaction vessel resulted in the formation of **2** (R = R^1 = Ph; R^2 = H). The intermediate acids **3** obtained from thiobenz-*p*-chloroanilide and also *p*-chlorothiobenzanilide also underwent cyclization to the corresponding substituted derivative of **2**. No acetylation of **2** was observed under these cyclization conditions which were critical,[6] slight variations resulting in decomposition products of **2**. However, the intermediate acid **3** (R = R^1 = R^2 = Ph) formed from thiobenzanilide and α-bromophenylacetic acid underwent ready cyclization to **2** (R = R^1 = R^2 = Ph) with considerable variation in the cyclization conditions being possible. This stabilizing effect of phenyl substituents has been observed in other mesoionic systems.[7]

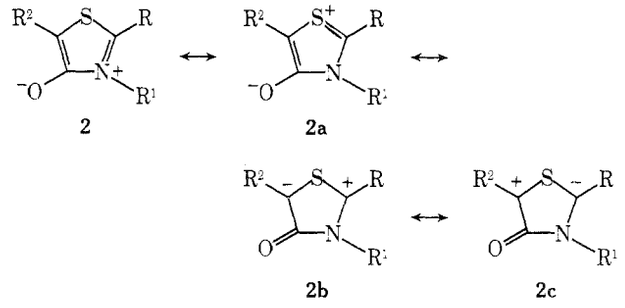
The ring system **2** unsubstituted in the 5 position is susceptible to moisture, undergoing ring opening, and it is advantageous to isolate **2** using "drybox" conditions. In the dry state, **2** is considerably more stable and may be stored without decomposition for several months, the 2-*p*-chlorophenyl analog being especially suitable in this respect.

Controlled hydrolysis of **2** (R = R^1 = Ph; R^2 = H) resulted in the acid **3** (R = R^1 = Ph; R^2 = H) being obtained in a pure state. An alternative mode of hydrolysis induced by the action of water over long periods has been observed for *anhydro*-4-hydroxy-2,3,5-triphenylthiazolium hydroxide (**2**, R = R^1 = R^2 = Ph). In this case α-(benzoylthio)phenylacetanilide (**5**) was obtained, this having been observed previously when 4-acetoxy-2,3,5-triphenylthiazolium perchlorate was treated with sodium bicarbonate.[8]

Treatment of **2** (R = R^1 = Ph; R^2 = H) with cold acetic anhydride readily gave *anhydro*-5-acetyl-2,3-diphenyl-4-hydroxythiazolium hydroxide (**2**, R = R^1 = Ph; R^2 = $COCH_3$). Analogous acetyl derivatives were obtained for the other thiazolium hydroxides used in this study.

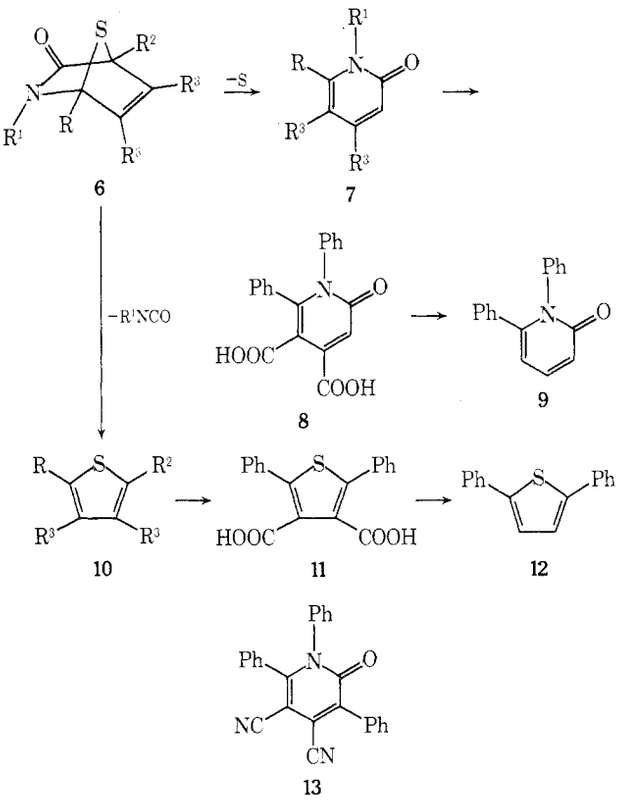
In addition to the above chemical evidence, spectral data are consistent with the assigned structure **2** for these cyclized products. An infrared carbonyl absorption at 1610 cm^{-1}, indicating some degree of single bond character, is analogous to that observed in other mesoionic systems[3,9] and is in contrast to the carbonyl absorption at 1715 cm^{-1} in Δ^2-2-phenyl-4-thiazolone.[10] Similarly the ultraviolet spectrum of **2** (R = R^1 = Ph; R^2 = H) shows a red shift to 350 nm from 330 nm for that of the 4-thiazolone. In the nmr spectrum of **2** a singlet proton was observed at δ 5.57, similar protons in other mesoionic systems usually absorbing in the region δ 8.0–5.5 depending on the nuclear heteroatoms.[2,9,11] It should be noted that this proton resonates at an appreciably higher field than does the corresponding 5-proton in thiazolium salts[12,13] (δ 8.34–7.94) and in thiazoles[13] (δ 6.87). This is most likely the result of delocalization of the exocyclic negative charge to the 5 position of the nucleus, which would be expected to be favored to some degree by interaction of the electrons at this position with the vacant d orbitals on the sulfur atom.

The mesoionic system **2** contains a masked 1,3-dipole system **2a** ↔ **2b** ↔ **2c**, which may formally be regarded as a thiocarbonyl ylide dipole stabilized to some extent by the adjacent nitrogen atom.[14a] This dipole has only very recently been studied in alicyclic systems[14b] and from the reactions of carbonyl ylide dipoles,[15] and from those of the *anhydro*-4-hydroxy-1,3-dithiolium hydroxide mesoionic system[16] and carbonyl-stabilized sulfonium ylides,[17] it was anticipated that the reactions of this ring system would be of considerable interest.



2 **2a** **2b** **2c**

The mesoionic system **2** was found to undergo ready cycloaddition with a variety of acetylenic dipolarophiles in refluxing benzene. The primary 1:1 cycloadduct was not isolated with these acetylenic dipolarophiles, the reaction product being that derived from the primary adduct by extrusion of sulfur or elimination of phenyl isocyanate. The nature of this reaction product was determined by the substituents present in **2**. Thus, *anhydro*-4-hydroxy-2,3-diphenylthiazolium hydroxide (**2**, R = R^1 = Ph; R^2 = H) and dimethyl acetylenedicarboxylate gave, *via* the intermediate **6**, dimethyl 1,6-diphenyl-2-pyridone-4,5-dicarboxylate (**7**, R = R^1 = Ph; R^3 = $COOCH_3$) in 70% yield. This ready



6 **7** **8** **9** **10** **11** **12** **13**

extrusion of sulfur during the course of the reaction is associated with the presence of the double bond in **6** and has also recently been observed in the cycloadducts from acetylenes and tetraphenylthieno[3,4-*c*]thiophene[18] and also thiophenes.[19] In the following publication[20] it will be seen that the primary 1:1 cycloadducts from **2** and olefinic dipolarophiles are quite stable, a behavior associated with bicyclic systems containing sulfur bridges which are only ex-

truded on strong heating.[21] Reaction of **2** (R = Ph, R^1 = *p*-ClC_6H_4 and R = *p*-ClC_6H_4, R^1 = Ph; R^2 = H) with dimethyl acetylenedicarboxylate gave the corresponding pyridones **7**. Similarly dibenzoylacetylene underwent cycloaddition with **2** (R = *p*-ClC_6H_4; R^1 = Ph; R^2 = H) giving 6-*p*-chlorophenyl-4,5-dibenzoyl-1-phenyl-2-pyridone (**7**, R = *p*-ClC_6H_4; R^1 = Ph; R^3 = PhCO). The pyridone structure **7** was assigned on the basis of analytical and spectral data (Experimental Section) together with the alkaline hydrolysis of **7** (R = R^1 = Ph; R^3 = $COOCH_3$) to a product assigned the structure 1,6-diphenyl-2-pyridone-4,5-dicarboxylic acid (**8**). Subsequent decarboxylation yielded a product identified as 1,6-diphenyl-2-pyridone (**9**).

anhydro-4-Hydroxy-2,3,5-triphenylthiazolium hydroxide (**2**, R = R^1 = R^2 = Ph) also underwent cycloaddition with dimethyl acetylenedicarboxylate, though at a slower rate probably caused by the bulky phenyl substituents attached to the thiocarbonyl ylide, a factor which causes sluggish addition of olefinic dipolarophiles. However, in this case dimethyl 2,5-diphenylthiophene-3,4-dicarboxylate (**10**, R = R^2 = Ph; R^3 = $COOCH_3$), identified by spectral data, was formed in 90% yield by elimination of PhNCO (detected by glc) from the primary cycloadduct **6** (R = R^1 = R^2 = Ph; R^3 = $COOCH_3$). Alkaline hydrolysis of **10** (R = R^2 = Ph; R^3 = $COOCH_3$) gave 2,5-diphenylthiophene-3,4-dicarboxylic acid (**11**) which was decarboxylated to 2,5-diphenylthiophene (**12**), previously synthesized from cinnamic acid and sulfur.[22]

The reaction of **2** (R = R^1 = R^2 = Ph) with dibenzoylacetylene likewise gave 3,4-dibenzoyl-2,5-diphenylthiophene (**10**, R = R^2 = Ph; R^3 = COPh), although only obtained in 42% yield. Spectra and analytical data, together with its conversion into tetraphenylthieno[3,4-*c*]thiophene[18] clearly confirm the assigned structure. It has been our experience that diminished yields are often obtained in cycloadditions with dibenzoylacetylene, largely due to decomposition occurring at elevated reaction temperatures. However, it is an extremely versatile dipolarophile which allows the introduction of strategic functional groups into heteroaromatic systems.

Hexafluoro-2-butyne was also found to undergo ready reaction with **2** (R = R^1 = R^2 = Ph) giving 2,5-diphenyl-3,4-di(trifluoromethyl)thiophene (**10**, R = R^2 = Ph; R^3 = CF_3). However, the equally reactive dicyanoacetylene did not give exclusive thiophene formation with the mesoionic system **2** (R = R^1 = R^2 = Ph). In this case a mixture of 4,5-dicyano-1,3,6-triphenyl-2-pyridone (**13**) (4.4%) and 3,4-dicyano-2,5-diphenylthiophene (**10**, R = R^2 = Ph; R^3 = CN) (95.2%) was obtained.

These results suggest that the thermal decomposition of the primary 1:1 cycloadduct **6** is controlled more by steric effects than by electronic effects. Both retro-cycloadditions generate a thermodynamically stable, small fragment and a heteroaromatic system. Extrusion of sulfur from **6** (R = R^1 = R^2 = Ph) would result in a pyridone with every peripheral position substituted with bulky substituents, whereas elimination of phenyl isocyanate provides a thiophene in which this steric overcrowding is largely eliminated. Isolation of a small amount of the pyridone **13** together with the thiophene **10** (R = R^2 = Ph; R^3 = CN) from dicyanoacetylene and the mesoionic system **2** (R = R^1 = R^2 = Ph) is consistent with this rationalization. The spatial requirements of the linear cyano group are considerably less than the carbomethoxy, benzoyl, or trifluoromethyl groups and, consequently, the steric overcrowding in **13** is reduced.

In other cycloadducts analogous to **6** from which sulfur is extruded,[18,19] product formation involves aromatization to a benzene nucleus even though considerable steric overcrowding results. However, in these systems there is no alternative possibility for bond fission as exists in the case of **6**. Though it has not been realized in practice, it is conceivable to derive **6** from a thiophene and phenyl isocyanate and, as both these fragments are particularly stable, it is not surprising that the retro-Diels–Alder reaction is observed.

These cycloadditions are particularly noteworthy for the ease with which they occur and for the mild conditions under which sulfur is extruded. This is in contrast to the usual bridge-sulfur extrusion which requires more vigorous conditions.[21] They provide an extremely facile synthetic route to pyridones and thiophenes, limited only by the restraints imposed by the synthesis of **2** and the requisite acetylenic dipolarophiles. In conjunction with our study of the *anhydro*-2-aryl-4-hydroxy-1,3-dithiolium system, a variety of tri- and tetrasubstituted thiophenes are readily available. However, there are limitations to the choice of the acetylenic dipolarophile. Diphenylacetylene did not yield a well-defined product, nor did *N,N,N′,N′*-tetramethyl-2-butyne-1,4-diamine, 2-methyl-1-buten-3-yne, 1-methoxy-1-buten-3-yne, and 3-hydroxy-1-hexyne. Electron-rich acetylenes such as the ynamines also resulted in intractable tarry mixtures.

Experimental Section[23]

2-Mercapto-1-thioacetoacetic Acid, Anhydrosulfide with *N*-Phenylthiobenzimidic Acid, *N*-Phenylbenzimidate (4, R = R^1 = Ph). Thiobenzanilide (10.0 g), bromoacetic acid (6.5 g), and Et_3N (19 g) were dissolved in benzene (50 ml), and the solution was stirred at room temperature for 4 hr. $Et_3N \cdot HBr$ was filtered off and the benzene and excess Et_3N were removed under vacuum yielding an unstable yellow oil which was used without further purification. This was treated with a mixture of Et_3N (15 ml) and Ac_2O (15 ml) and the solution left at room temperature for 7 days. The precipitate which separated was collected and recrystallized from chloroform–ether forming colorless needles: 4.0 g (33%); mp 192–194° (lit.[5] mp 195–196°); ir (KBr) 1725 (CO), 1680 (CO), 1590 (C=N) cm^{-1}; λ_{max} (CH_3OH) 201 nm (log ϵ 4.83), 240 sh (4.10), 267 sh (3.58); nmr ($CDCl_3$) δ 1.79 (s, 3, $COCH_3$), 4.70 (s, 1, –CH), 7.54 (m, 20, aromatic); $M \cdot^+$ 508.

Anal. Calcd for $C_{30}H_{24}N_2O_2S_2$: C, 70.85; H, 4.76; N, 5.51. Found: C, 70.67; H, 5.14; N, 5.26.

In a similar fashion *p*-chlorobenzanilide gave rise to 2-mercapto-1-thioacetoacetic acid, anhydrosulfide with *N*-*p*-chlorophenylthiobenzimidic acid, *N*-*p*-chlorophenylbenzimidate (4, R = Ph; R^1 = *p*-ClC_6H_4) and, in this case, anhydrous ether was added to effect complete precipitation of the product which crystallized from chloroform–ether as colorless needles: 3.8 g (30%); mp 190–192° (lit.[5] mp 165–166°); ir (KBr) 1720 (CO), 1660 (CO), 1590 (C=N) cm^{-1}; λ_{max} (CH_3OH) 202 nm (log ϵ 4.84), 246 sh (4.22); nmr ($CDCl_3$) δ 1.80 (s, 3, $COCH_3$), 4.75 (s, 1, –CH), 7.40 (m, 18, aromatic); $M \cdot^+$ 542.

Anal. Calcd for $C_{30}H_{22}Cl_2N_2O_2O_2S_2$: C, 62.40; H, 3.82; N, 4.86. Found: C, 62.40; H, 3.88; N, 4.84.

***anhydro*-4-Hydroxy-2,3-diphenylthiazolium Hydroxide (2, R = R^1 = Ph; R^2 = H).** Thiobenzanilide (10.0 g), bromoacetic acid (6 .5 g), and Et_3N (30 g) were dissolved in benzene (200 ml), and the solution was stirred at room temperature for 4 hr. After filtration of the $Et_3N \cdot HBr$, the excess Et_3N, and benzene were evaporated, and the residual, unstable yellow oil was then treated with a mixture of Et_3N (9 ml) and Ac_2O (3 ml) using a drybox. Upon scratching the walls of the flask a yellow precipitate formed in a few minutes. After addition of anhydrous ether the product was collected and washed with ether. The product was extremely sensitive to moisture and undergoes decomposition on standing in the atmosphere. It was obtained as orange-yellow needles: 4.5 g (38%); mp 113–115° dec; ir (KBr) 1610 (CO) cm^{-1}; λ_{max} (CH_3OH) 240 nm (log ϵ 4.27), 350 (2.62); nmr ($CDCl_3$) δ 4.57 (s, 1, 5-H), 7.28 (m, 10, aromatic); $M \cdot^+$ 235 (29).

Anal. Calcd for $C_{15}H_{11}NOS$: C, 71.14 H, 4.37. Found: C, 71.20; H, 4.66.

Using the appropriate thiobenzanilide, the following were prepared by the above general procedure.

1. ***anhydro*-3-*p*-Chlorophenyl-4-hydroxy-2-phenylthiazoli-**

um Hydroxide (2, R = Ph; R^1 = p-ClC_6H_4; R^2 = H): orange-yellow needles; 4.0 g (35%); mp 115–116° dec; ir (KBr) 1620 cm^{-1}; λ_{max} (CH_3OH) 220 nm sh (log ϵ 3.87), 242 (3.66), 385 (3.46); nmr ($CDCl_3$) δ 5.57 (s, 1, 5-H), 7.32 (m, 9, aromatic); M·+ 287 (25).

Anal. Calcd for $C_{15}H_{10}ClNOS$: C, 62.22; H, 3.48. Found: C, 62.37; H, 3.57.

2. *anhydro*-2-*p*-Chlorophenyl-4-hydroxy-3-phenylthiazolium Hydroxide (2, R = p-ClC_6H_4; R^1 = Ph; R^2 = H): orange-yellow needles; 6.5 g (52%); mp 125–130° dec; ir (KBr) 1650 (CO) cm^{-1}; nmr ($CDCl_3$) δ 5.60 (s, 1, 5-H), 7.25 (m, 9, aromatic); M·+ 287 (28).

Anal. Calcd for $C_{15}H_{10}ClNOS$: C, 62.61; H, 3.48; N, 4.87. Found: C, 62.23; H, 3.79; N, 4.71.

Reaction with Acetylenic Dipolarophiles. A. *anhydro*-2,3-Diaryl-4-hydroxythiazolium Hydroxides (2, R = R^1 = aryl; R^2 = H). The mesoionic compound **2** (R = R^1 = Ph; R^2 = H) (2.53 g, 0.01 mol) in benzene (50 ml) and redistilled dimethyl acetylenedicarboxylate (1.5 g, 0.011 mol) were mixed together and an immediate, exothermic reaction with darkening of the reaction mixture occurred. After heating at 80° for 3 hr, the benzene was evaporated and the residue chromatographed on Kieselgel g using chloroform as eluent. Dimethyl 1,6-diphenyl-2-pyridone-4,5-dicarboxylate (**7**, R = R^1 = Ph; R^3 = $COOCH_3$) formed colorless needles from chloroform–petroleum ether (bp 40–60°): 2.45 g (70%); mp 180–181°; ir (KBr) 1710 ($COOCH_3$), 1660 (CO–N) cm^{-1}; λ_{max} (CH_3OH) 205 nm (log ϵ 4.65), 250 (3.99), 355 (3.82); nmr ($CDCl_3$) δ 3.47 (s, 3, 4-$COOCH_3$), 3.92 (s, 3, 5-$COOCH_3$), 7.17 (m, 11, aromatic); mass M·+ 363 (100).

Anal. Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.86. Found: C, 69.43; H, 4.74; N, 3.84.

Similarly, dimethyl 1-*p*-chlorophenyl-6-phenyl-2-pyridone-4,5-dicarboxylate (**7**, R = Ph; R^1 = p-ClC_6H_4; R^3 = $COOCH_3$) was obtained from **2** (R = Ph; R^1 = p-ClC_6H_4; R^2 = H) as colorless needles from chloroform–petroleum ether; 1.95 g (70%), mp 234–235°.

Anal. Calcd for $C_{21}H_{16}ClNO_5$: C, 63.14; H, 4.02; N, 3.52. Found: C, 62.99; H, 4.09; N, 3.38.

With dibenzoylacetylene the following reaction conditions were used. The mesoionic compound **2** (R = p-ClC_6H_4; R^1 = Ph; R^2 = H) (0.7 g, 0.025 mol) in dry benzene (50 ml) was treated with dibenzoylacetylene (0.69 g, 0.025 mol) at room temperature with stirring for 18 hr. After 1 hr a product had started to separate and this was finally collected. 6-*p*-Chlorophenyl-4,5-dibenzoyl-1-phenyl-2-pyridone (**7**; R = p-ClC_6H_4, R^1 = Ph; R^3 = COPh) crystallized from chloroform–petroleum ether as colorless needles: 0.45 g (37%); mp 251–253°; ir (KBr) 1670 (COPh), 1610 (CON<) cm^{-1}; λ_{max} (CH_3OH) 258 nm (log ϵ 4.29), 330 (3.73); nmr ($CDCl_3$) δ 8.1–6.9 (m, aromatic); M·+ 489 (39).

Anal. Calcd for $C_{31}H_{20}ClNO_3$: C, 76.00; H, 4.11; N, 2.86. Found: C, 75.18; H, 4.07; N, 2.82.

4,5-Dibenzoyl-1,6-diphenyl-2-pyridone (7, R = R^1 = Ph; R^3 = COPh) was prepared[24] in a similar manner from **2** (R = R^1 = Ph; R^2 = H). It crystallized from ethanol as colorless, matted needles: 61%, mp 236–238°; ir (KBr) 3080, 3050 (CH), 1670 (CO) cm^{-1}; nmr ($CDCl_3$) δ 8.32–8.02 (m, 2, aromatic), 7.84–6.95 (m, 19, aromatic), M·+ 455 (92).

Anal. Calcd for $C_{31}H_{21}NO_3$: C, 81.74; H, 4.65; N, 3.08. Found: C, 82.00; H, 4.82; N, 3.15.

B. *anhydro*-4-Hydroxy-2,3,5-triphenylthiazolium Hydroxide (2, R = R^1 = R^2 = Ph). The above mesoionic compound[5] (3.3 g, 0.01 mol) in dry benzene (100 ml) and dimethyl acetylenedicarboxylate (1.5 g, 0.011 mol) were refluxed together overnight. Solution of **2** gradually occurred and the reaction color changed from deep red to yellow during this period. The benzene was evaporated and the residue chromatographed on Kieselgel g using chloroform as eluent. Dimethyl 2,5-diphenylthiophene 3,4-dicarboxylate (**10**; R = R^2 = Ph; R^3 = $COOCH_3$) crystallized from chloroform–petroleum ether as colorless needles: 3.10 g (90%); mp 167–168° (lit.[7b] mp 166–167.5°); ir (KBr) 1710 cm^{-1}; λ_{max} (CH_3OH) 206 nm (log ϵ 4.49), 240 (4.34), 295 (4.12); nmr ($CDCl_3$) δ 3.78 (s, 6, $COOCH_3$), 7.50 (m, 10, aromatic); M·+ 352 (100).

3,4-Dibenzoyl-2,5-diphenylthiophene (10, R = R^2 = Ph; R^3 = COPh) was prepared[24] from **2** (R = R^1 = R^2 = Ph) (2.0 g, 0.006 mol) in benzene (50 ml) and dibenzoylacetylene (1.42 g, 0.006 mol) using a 30-hr reflux period. Chromatography was on florisil using chloroform as eluent. It crystallized from 95% ethanol as cream, irregular prisms: 1.2 g (42%); mp 139–140°; ir (KBr) 1660, 1640, (CO) cm^{-1}; λ_{max} (CH_3OH) 198 nm (log ϵ 4.81), 262 (4.66); nmr ($CDCl_3$) δ 7.85–7.62 (m, 4, aromatic), 7.60–7.18 (m, 16, aromatic); M·+ 444 (100).

Anal. Calcd for $C_{30}H_{20}O_2S$: C, 81.06; H, 4.54. Found: C, 80.86; H, 4.49.

2,5-Diphenyl-3,4-di(trifluoromethyl)thiophene (10, R = R^2 = Ph; R^3 = CF_3), prepared from **2** (R = R^1 = R^2 = Ph) and hexafluoro-2-butyne formed yellow, irregular prisms sublimed at 100° (0.01 mm): 2.5 g (90%); mp 98–99°; nmr ($CDCl_3$) δ 7.43 (s, aromatic).

Anal. Calcd for $C_{18}H_{10}F_6S$: C, 58.06; H, 2.68. Found: C, 57.95; H, 2.63.

3,4-Dicyano-2,5-diphenylthiophene (10, R = R^2 = Ph; R^3 = CN). The mesoionic compound **2** (R = R^1 = R^2 = Ph) (1.0 g) and dicyanoacetylene (0.25 g) were refluxed in benzene for 3 hr. After reaction workup and chromatography as above, the thiophene was eluted from the column first and crystallized from chloroform–petroleum ether as colorless needles: 0.80 g (95.2%); mp 181–182°; ir (KBr) 2250 (CN) cm^{-1}; nmr ($CDCl_3$) δ 7.76 (m, aromatic).

Anal. Calcd for $C_{18}H_{10}N_2S$: C, 75.51; H, 3.52; N, 9.79. Found: C, 75.18; H, 3.46; N, 9.72.

The second fraction eluted from the column was 4,5-dicyano-1,3,6-triphenyl-2-pyridone (**13**). It crystallized from chloroform–petroleum ether as colorless needles: 0.05 g (4.4%); mp 252–254°; ir (KBr) 2290 (CN), 1700 (CO) cm^{-1}; M·+ ~500 (<1).

Anal. Calcd for $C_{25}H_{15}N_3O$: C, 80.41; H, 4.05. Found: C, 80.26; H, 4.10.

Acetylation of the Mesoionic System 2 (R = R^1 = Ph; R^2 = H). The mesoionic compound (2.0 g) in chloroform (100 ml) and Ac_2O (10 ml) was kept overnight at room temperature. After evaporation of the solvent the residue was chromatographed on Kieselgel g using $CHCl_3$: 5% EtOH as eluent. The acetyl compound (**2**, R = R^1 = Ph; R^2 = $COCH_3$) crystallized from chloroform–ether, and ethanol, as orange plates: 0.95 g (20%); mp 250° (lit.[5] mp 250°); ir (KBr) 1650 ($COCH_3$), 1600 (CO) cm^{-1}; λ_{max} (CH_3OH) 237 nm sh (log ϵ 3.98), 263 (4.10), 401 (4.04); nmr ($CDCl_3$) δ 2.63 (s, 3, $COCH_3$), 7.37 (m, 10, aromatic); M·+ 295 (29).

When the condensation product **4** (R = R^1 = Ph) was refluxed with Ac_2O for 10 hr and the solvent evaporated, orange plates (86%), mp 250–252° of the above acetyl compound **2** (R = R^1 = Ph; R^2 = $COCH_3$) were obtained.

***anhydro*-5-Acetyl-4-hydroxy-3-*p*-chlorophenyl-2-phenylthiazolium Hydroxide (2, R = Ph; R^1 = p-ClC_6H_4; R^2 = $COCH_3$)** was obtained from **2** (R = Ph; R^1 = p-ClC_6H_4; R^2 = H) (2.0 g) and Ac_2O as above. It crystallized from chloroform–ether as orange needles: 0.5 g (22%); mp 240–242°; ir (KBr) 1660 ($COCH_3$), 1600 (CO) cm^{-1}; λ_{max} (CH_3OH) 225 nm (log ϵ 4.14), 263 (4.02), 403 (3.92); nmr ($CDCl_3$) δ 2.65 (s, 3, $COCH_3$), 7.45 (m, 9, aromatic); M·+ 330 (20).

Anal. Calcd for $C_{17}H_{12}ClNO_2S$: C, 61.90; H, 3.64; N, 4.25. Found: C, 61.75; H, 3.86; N, 4.44.

The same acetyl derivative was obtained when the condensation product **4** (R = Ph; R^1 = p-ClC_6H_4) was refluxed with Ac_2O as above.

Hydrolysis of Dimethyl 1,6-Diphenyl-2-pyridone-4,5-dicarboxylate (7, R = R^1 = Ph; R^3 = $COOCH_3$). Dimethyl 1,6-diphenyl-2-pyridone-4,5-dicarboxylate (2.0 g) was refluxed with a 10% NaOH solution of aqueous methanol (1:1) (50 ml). The methanol was removed *in vacuo* and the aqueous solution was acidified with 2 *N* HCl. The pyridone dicarboxylic acid **8** crystallized and after filtration was obtained from aqueous ethanol as colorless prisms: 1.3 g (72%), mp 256–257°; ir (KBr) 3320 (OH), 1700 1625 (CO) cm^{-1}.

Anal. Calcd for $C_{19}H_{13}NO_5$: C, 68.06; H, 3.91; N, 4.18. Found: C, 67.86; H, 4.01; N, 4.01.

Registry No.—**2** (R = R^1 = Ph, R^2 = H), 13288-67-0; **2** (R = Ph, R^1 = p-ClC_6H_4, R^2 = H), 26245-44-3; **2** (R = p-ClC_6H_4, R^1 = Ph, R^2 = H), 52730-97-9; **2** (R = R^1 = R^2 = Ph), 18100-80-6; **2** (R = R^1 = Ph, R^2 = $COCH_3$), 13288-62-5; **2** (R = Ph, R^1 = p-ClC_6H_4, R^2 = $COCH_3$), 52718-80-6; **4** (R = R^1 = Ph), 26245-40-9; **4** (R = Ph, R^1 = p-ClC_6H_4), 26245-42-1; **7** (R = R^1 = Ph, R^3 = $COOCH_3$), 24562-71-8; **7** (R = Ph, R^1 = p-ClC_6H_4, R^3 = $COOCH_3$), 52718-81-7; **7** (R = p-ClC_6H_4, R^1 = Ph, R^3 = COPh), 52718-82-8; **7** (R = R^1 = Ph, R^3 = COPh), 52718-83-9; **8**, 24562-72-9; **10** (R = R^2 = Ph, R^3 = $COOCH_3$), 20851-13-2; **10** (R = R^2 = Ph, R^3 = COPh), 40953-25-1; **10** (R = R^2 = Ph, R^3 = CF_3), 52718-84-0; **10** (R = R^2 = Ph, R^3 = CN), 52718-85-1; **13**, 52718-86-2; thiobenzanilide, 636-04-4; bromoacetic acid, 79-08-3; *p*-chlorobenzanilide, 6833-15-4; dimethyl acetylenedicarboxylate, 762-42-5; dibenzoylacetylene, 1087-09-8; hexafluoro-2-butyne, 692-50-2; dicyanoacetylene, 1071-98-3.

References and Notes

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Mesoionic Compounds. XXXII. Cycloaddition Reactions of the *anhydro*-4-Hydroxythiazolium Hydroxide System with Olefinic Dipolarophiles[1]

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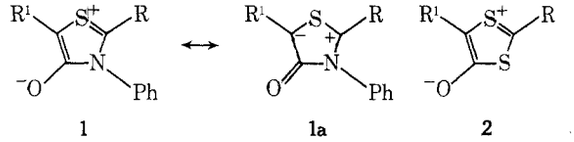
Di- and trisubstituted derivatives of the mesoionic *anhydro*-4-hydroxythiazolium hydroxide system underwent 1,3-dipolar cycloadditions *via* their thiocarbonyl ylide dipole giving stable 1:1 adducts of the substituted 1,2,3,4,5,6-hexahydro-3-oxo-1α,4α-epithiopyridine system with a wide variety of electron-deficient dipolarophiles. The stereochemistry of each adduct was determined by extensive nmr analysis and also by chemical methods. Several adducts lost the elements of H_2S upon treatment with sodium methoxide forming 4,5-disubstituted 1,3,6-triphenylpyrid-2-ones, and with *m*-chloroperbenzoic acid gave sulfoxide derivatives.

The title mesoionic ring system **1** has been shown[2] to undergo ready cycloaddition of acetylenic dipolarophiles to yield substituted 2-pyridones and thiophenes in good yields. The ring system contains a "masked" thiocarbonyl ylide dipole **1a** stabilized to some extent by an adjacent nitrogen atom. The same ylide is present in the *anhydro*-4-hydroxy-1,3-dithiolium hydroxide system **2** which has also



1 **1a** **2**

been shown to undergo cycloaddition of acetylenic dipolarophiles[3] to yield substituted thiophenes with elimination of carbonyl sulfide, as well as forming stable 1:1 cycloadducts with olefinic dipolarophiles.[4]

A study of the cycloaddition reactions of **1** was thus of particular interest. It would enable the effect of replacing the 3-sulfur atom in **2** with a nitrogen atom to be evaluated, as well as providing a novel series of bridged sulfur, bicyclic adducts incorporating a hexahydro-3-oxo-1α,4α-epithiopyridine system.

Electron-deficient olefins such as dimethyl maleate and fumarate, *N*-phenylmaleimide, maleic anhydride, methyl vinyl ketone, *trans*-dibenzoylethylene, ethyl acrylate, ethyl methacrylate, ethyl crotonate, acrylonitrile, and fumaronitrile all formed stable, 1:1 cycloadducts with di- and trisubstituted derivatives of **1** with relative ease. However, no major product was isolated from the reaction of **1** with norbornene, norbornadiene, tetracyanoethylene, 4-cyanopyridine, and chalcone, either in refluxing benzene or at room temperature. Similarly electron-rich olefins such as ethyl vinyl ether resulted in multi-component reaction mixtures from which no single product could be isolated.

The gross structural features of the 1:1 cycloadducts obtained from **1** and the dipolarophiles listed above were established from analytical, mass spectral, and other spectral data (Tables I–IV). All were consistent with the formation of a 1:1 adduct with the thiocarbonyl ylide dipole, and the stereochemistry of these adducts was established from their nmr spectra considered below in increasing order of complexity.

Cycloadducts from *anhydro*-2,3-Diaryl-4-hydroxythiazolium Hydroxide. *N*-Phenylmaleimide Adducts. Reaction of **1** (R = *p*-ClC_6H_4; R^1 = H) with *N*-phenyl-