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Mesoionic Compounds. XXX. Cycloaddition Reactions of the *anhydro*-2-Aryl-5-hydroxy-3-methylthiazolium Hydroxide System[1]

K. T. Potts,* J. Baum,[1d] E. Houghton, D. N. Roy, and U. P. Singh

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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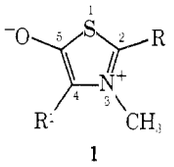
The title mesoionic ring system underwent cycloaddition of dimethyl acetylenedicarboxylate with elimination of carbonyl sulfide from the initial 1:1 adduct forming substituted pyrroles. *N*-Thiobenzoylsarcosine, the precursor to this mesoionic system, acetic anhydride, and dimethyl acetylenedicarboxylate also gave the substituted pyrrole, and this convenient procedure has been extended to the precursors to the mesoionic oxazole and sydnone systems. *N*-Phenylmaleimide and dimethyl fumarate readily gave 1:1 adducts and the endo isomer of the former product was readily isomerized to the exo isomer. Complex reaction mixtures were obtained from other olefinic dipolarophiles. With tetracyanoethylene no cycloadduct was formed but rather an "ene"-type product was isolated, in which substitution had occurred at the 4 position of the thiazole nucleus. With phenyl isothiocyanate at elevated temperatures, *anhydro*-2-aryl-4-mercapto-1-methyl-3-phenylimidazolium hydroxide and its 1:1 adduct with the heterocumulene were formed, whereas with phenyl isocyanate, 1:1 adducts of the heterocumulene with the thiazole and imidazole mesoionic systems were isolated. Activated isocyanates readily reacted at room temperature giving stable 1:1 cycloadducts.

In the thiazole ring system two isomeric mesoionic systems,[2] represented by the *anhydro*-2,4-disubstituted 5-hydroxy-3-methylthiazolium hydroxide (**1**) and the *anhydro*-2,3,5-trisubstituted 4-hydroxythiazolium hydroxide (**2**) are possible. The number of potential products is increased by possible variation of the exocyclic substituent between oxygen, sulfur, and nitrogen and, as has been shown recently in the *s*-triazole system,[3] with carbon substituents containing electron-delocalizing groups. In this publication we describe the cycloaddition reactions of **1** and its conversion into mesoionic imidazole derivatives and, in those following, the synthesis of **2** and its reactions with a wide variety of dipolarophiles.



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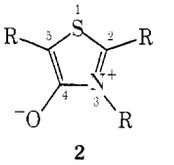

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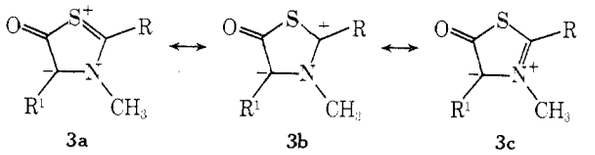


3a **3b** **3c**

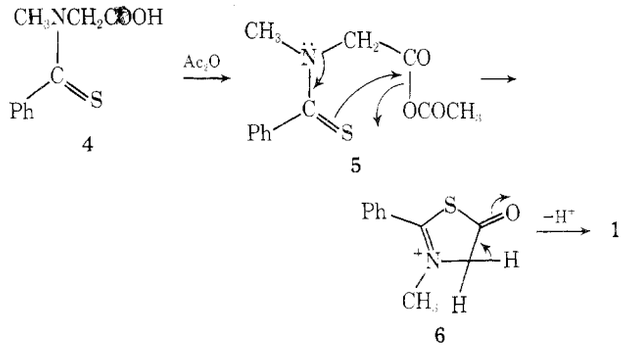
Inherent in the mesoionic concept[2b] are contributions to **1** from dipolar forms **3a–c**. This "masked" 1,3-dipole is an azomethine ylide stabilized by the sulfur atom and **1** would be expected to undergo analogous 1,3-dipolar cycloaddition reactions[4] to those observed with the mesoionic 1,2,3-oxadiazole (sydnone) system,[5] the 1,3,4-oxadiazole system,[5a] and the oxazole system.[6] In this present system it was anticipated that COS would be eliminated from cycloadducts with acetylenic dipolarophiles giving pyrroles and that the adducts with olefinic dipolarophiles would be sufficiently stable for isolation. This present system is particularly interesting as it completes the series oxazole, thiazole, and imidazole in which the azomethine ylide is stabilized by adjacent oxygen, sulfur, and nitrogen atoms, respectively.

Synthesis. The mesoionic system **1** was first synthesized[7] in 1957 as its acetyl derivative (**1**; R = Ph; R^1 = $COCH_3$) from *N*-thiobenzoylsarcosine (**4**) and hot acetic anhydride. However, a cold mixture of acetic anhydride and triethylamine resulted[8] in the formation of *anhydro*-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide (**1**; R = Ph; R^1 = H), and *N*-phenyl-*N*-thiobenzoylglycine gave the corresponding 2,3-diphenyl product. Variation of this latter procedure was found to be excellent for the preparation in greater than 80% yield of the derivatives of **1** (R = Ph, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$; R^1 = H) used in this study. These were all stable, pale-yellow, crystalline products which partially decomposed after storing over several months. The corresponding acetyl compounds (**1**; R^1 = $COCH_3$) were quite stable, a property reflected in their being completely unreactive in cycloaddition reactions, and were prepared from **1** and hot acetic anhydride.

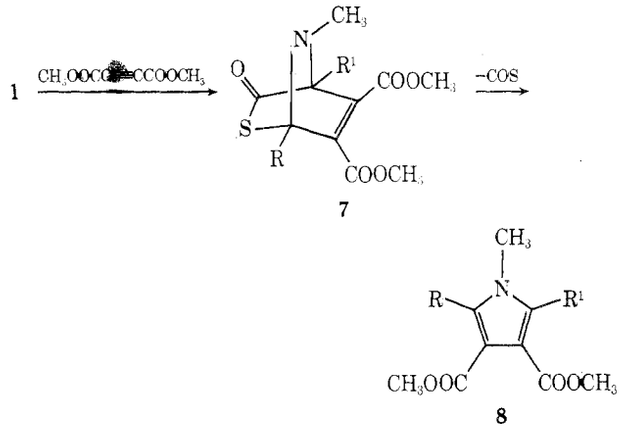
The Ac_2O/Et_3N cyclization mixture is also effective in similar ring closures to other mesoionic systems where acetylation or other reactions occur in the absence of Et_3N.[9] It is thought that an initial mixed anhydride **5** undergoes ring closure to **6** with subsequent removal of a proton by acetate ion. The latter would be a slow and relatively unfavorable process and, accordingly, these cyclizations with Ac_2O require moderately high temperatures and under these reaction conditions acetylation of **1** readily occurs. However, in the presence of Et_3N (pK_a = 11.4), removal of the proton from **6** would be fast and this is reflected in the

extremely mild conditions required for cyclization with the mixed reagent. Pyridine (pK_a = 5.2) was ineffective in the cyclization mixture, the acetyl product (1; R^1 = $COCH_3$) only being obtained in poor yield.

anhydro 2,4-Disubstituted 5-hydroxy-3-methyloxazolium hydroxide has also recently been converted into 1 and its exocyclic sulfur derivative[6b] by reaction with carbonyl sulfide and carbon disulfide, respectively.



Cycloaddition Reactions with Acetylenic Dipolarophiles. The *anhydro*-2-aryl-5-hydroxy-3-methylthiazolium hydroxides (1; R = Ph, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$; R^1 = H) underwent ready cycloaddition of dimethyl acetylenedicarboxylate in hot benzene. Elimination of carbonyl sulfide from the initial 1:1 adduct 7 occurred with formation of a substituted pyrrole 8 (R = Ph, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$; R^1 = H) with yields in excess of 80%. This is the first instance in which carbonyl sulfide was eliminated from a primary 1:1 adduct, although later experiments have shown that a variety of fragments may be eliminated from initial cycloadducts in reactions with mesoionic systems.

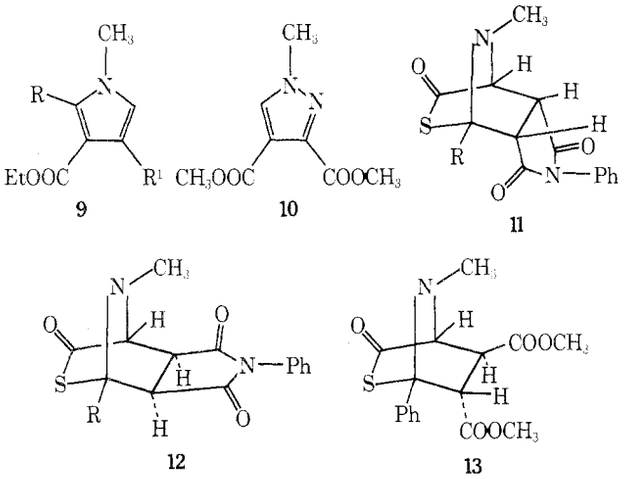


Cycloadditions Utilizing Precursors to the Mesoionic System 1. A modification of the above procedure provides an attractive route to the preparation of various derivatives of 8, and it may be extended to the synthesis of other five-membered heterocycles.[10] The precursor to the mesoionic system 1, *N*-thiobenzoylsarcosine (4), when heated with Ac_2O and dimethyl acetylenedicarboxylate gave, as the final product, the pyrrole (8; R = Ph; R^1 = H) in 78% yield. Carbonyl sulfide was identified as the effluent gas, indicating that cyclization to the mesoionic system (1; R = Ph, R^1 = H) had occurred. These reaction conditions are analogous to those under which the acetyl derivatives of 1 (R^1 = $COCH_3$) were obtained and the 1,3-dipolar addition of the dipolarophile must have occurred considerably faster than any acetylation of the nucleus. The presence of Et_3N had no effect on the overall yield of the reaction product.

This *in situ* cycloaddition procedure avoids the need for isolating the mesoionic ring system which may, in some instances, present experimental difficulties.

A variety of acetylenic dipolarophiles, such as ethyl propiolate and ethyl phenylpropiolate, gave the pyrroles 9 (R = Ph, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$; R^1 = H) and 9 (R = Ph, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$; R^1 = Ph), respectively. The same pyrroles may also be obtained in comparable yields by utilizing the *N*-benzoylsarcosine precursors to the corresponding oxazolium mesoionic systems[10a] (Experimental Section).

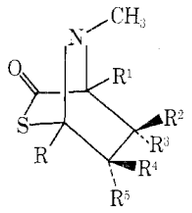
Similarly, *N*-nitrososarcosine, the precursor to *N*-methylsydnone, underwent reaction with dimethyl acetylenedicarboxylate under analogous conditions forming dimethyl 1-methylpyrazole-3,4-dicarboxylate (10) in good yield.



Cycloaddition Reactions with Olefinic Dipolarophiles. The reaction of 1 (R = Ph; R^1 = H) with *N*-phenylmaleimide in benzene proceeded smoothly at room temperature with the precipitation of a colorless solid, which was isolated and characterized as the 1:1 primary cycloadduct, N,6-diphenyl-2-oxo-3,4,5,6-tetrahydro-3α,6α-epi-*N*-methylimino-2*H*-thiapyran-4β,5β-dicarboximide[10b] (11; R = Ph), on the basis of the following evidence. Carbonyl absorptions were observed under a broad band centered at 1730 cm^{-1} in the infrared spectrum and no ultraviolet absorption maxima occurred above 203 nm. Besides the aromatic protons at δ 7.08–7.58, a doublet of doublets ($J_{4,5}$ = 1.5 Hz, $J_{5,6}$ = 5.5 Hz) at δ 4.30 was assigned to H-5. A doublet containing the small coupling at δ 3.87 was assigned to the bridgehead proton H-4, and H-6 occurred as a cis-coupled doublet at δ 3.83. The bridgehead *N*-methyl protons resonated at δ 2.28 (Table I). These data indicate that the endo configuration 11 is more plausible, in analogy with cycloadducts of the 4-hydroxythiazolium system[11] and the isomeric adduct described below. Rapid decomposition of 11 was observed in the mass spectrometer indicative of thermal instability and a marked tendency for expulsion of COS from the molecule.

In an attempt to oxidize 11 with *m*-chloroperbenzoic acid, a product was obtained from normal work-up (Experimental Section) whose analytical data corresponded to that of an isomeric product. The mass spectrum of this compound showed a fragment ion M − 60 at *m/e* 304 (7%), which indicated that the COS bridge remained intact in this product. The nmr spectrum showed three aliphatic multiplets (Table I) with the same coupling patterns as in the endo adduct 11. The resonance at δ 4.35 (d, J = 0.5 Hz) may be assigned to the bridgehead proton H-4, the doublet at δ 3.93 (J = 7.5 Hz) to H-6, and the doublet of doublets at δ 3.38 to H-5. The most likely structure for this product is 12, the exo adduct, formed possibly by acid-catalyzed rearrangement of 11. Any dissociation–reassociation process would appear to be excluded by the known instability of the initial mesoionic structure 1 to hydrolytic conditions.

Table I
Nmr Spectral Data of Cycloadducts of *anhydro*-2-Aryl-5-hydroxy-3-methylthiazolium Hydroxide and Olefinic Dipolarophiles



Compd[a]	Chemical shift (δ)[b] R¹	R²	R³	R⁴	R⁵	N–CH₃
11, R = Ph R¹ = R² = R⁴ = H R³ = R⁵ = CONPhCO	3.87, d $J_{1,2}$ = 1.5; $J_{2,4}$ = 5.5 Hz	4.30, dd		3.83, d		*2.28*,[c] s
12, R = Ph R¹ = R³ = R⁵ = H R² = R⁴ = CONPhCO	4.35, d $J_{1,3}$ = 0.5; $J_{3,5}$ = 7.5 Hz		3.38, dd		3.93, d	*2.40*, s
11, R = *p*-ClC_6H_4 R¹ = R² = R⁴ = H R³ = R⁵ = CONPhCO	3.83, d $J_{1,2}$ = 2.0; $J_{2,4}$ = 4.0 Hz	4.30, dd		3.80, d		*2.32*, s
12, R = *p*-ClC_6H_4 R¹ = R³ = R⁵ = H R² = R⁴ = CONPhCO	4.33, bs $J_{1,3}$ = ~0–0.5; $J_{3,5}$ = 7.5 Hz		3.40, bd		3.92, d	*2.37*, s
13, Ar = Ph R¹ = R³ = R⁴ = H R² = R⁵ = $COOCH_3$[b]	4.20, d $J_{1,3}$ = 6.0; $J_{3,4}$ = 5.25 Hz	*3.74*, s	3.90, dd	4.11, d	*3.15*, s	*2.34*, s

[a] Spectra determined in $CDCl_3$ at 100 MHz. [b] Aromatic protons usually occurred in the range δ 7.1–7.5. [c] Methyl resonances in italics.

In comparing the nmr data for **11** and **12**, it is seen that the H-4 proton is deshielded in the exo adduct **12** due to the effects of the imide carbonyl group. Similarly H-5 was found at higher field in **12** relative to **11** due to either a greater deshielding effect of the *N*-methylimino bridge or a shielding effect of the β-carbonyl group. Although the coupling constants do not compare exactly with the stereochemical assignments in the 4-hydroxythiazolium cycloadducts, this may be due to a slightly different geometry within the bicyclic ring system.[11]

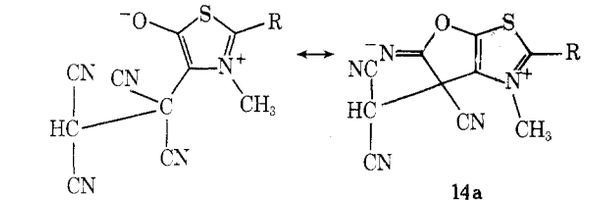
With dimethyl fumarate and **1** (R = Ph; R¹ = H) in benzene at room temperature an adduct represented by **13** was isolated, showing three carbonyl absorptions at 1740, 1730, and 1710 cm^{-1} within a broad band. Absorption maxima were observed at 313 nm (log ε 3.51) and 248 (3.63) in the ultraviolet spectrum and nmr data (Table I) showed three coupled aliphatic protons at δ 4.20 (d, J = 6.0 Hz), δ 4.11 (d, J = 5.3 Hz), and δ 3.90 (dd) assigned to H-4, H-6, and H-5, respectively. Methyl resonances were observed at δ 3.74, 3.15, and 2.34 assigned to the C-5 $COOCH_3$, C-6 $COOCH_3$, and the N–CH_3 protons respectively. The 4-5 coupling (J = 6.0 Hz) is quite large and may be indicative of a bridgehead-endo coupling in comparison with the cycloadducts from the 4-hydroxythiazolium system.[11] The major fragmentation of the molecular ion of **13** involved the formation of an M − 60 ion, corresponding to the elimination of COS.

The mesoionic compound **1** (R = *p*-ClC_6H_4; R¹ = H) similarly underwent cycloaddition with *N*-phenylmaleimide yielding a primary cycloadduct **11** (R = *p*-ClC_6H_4) similar in properties to the adduct **11** (R = Ph) described above. Also in an analogous fashion, treatment of **11** (R = *p*-ClC_6H_4) with *m*-chloroperbenzoic acid afforded an isomeric product given the exo structure **12** (R = *p*-ClC_6H_4). The nmr data for these compounds are listed in Table I. This formation of 1:1 adducts with these olefinic systems is in direct contrast to the reactions of the analogous oxazolium systems where the primary adducts break down with loss of CO_2.

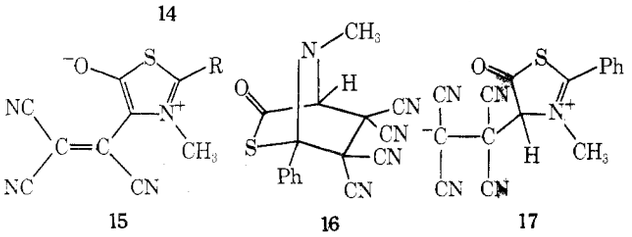
It should be noted that the reactions of **1** with the dipolarophiles, methyl vinyl ketone, *trans*-dibenzoylethylene, and fumaronitrile gave complex reaction mixtures from which no solid derivatives could be isolated.

Tetracyanoethylene was also found to undergo reaction with the thiazolium system **1** on gentle warming in benzene solution. In one instance from **1** (R = Ph; R¹ = H), two products were isolated from an initial deep-red mass which separated from the reaction mixture after a few minutes.

The following considerations led to the assignment of structures **14** and **15**, respectively, to these two products.



14 **14a**



15 **16** **17**

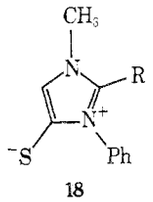
Analytical and mass spectral data showed the products differed from each other by the elements of HCN. The first product was apparently a simple 1:1 adduct of **1** and tetracyanoethylene but representation of this as a 1,3-dipolar cycloadduct in the manner of those described above may be disregarded. Such an adduct would not be expected to have a visible absorption spectrum and also it would not lose

HCN, as the double bond would then be introduced at the bridgehead unless some accompanying ring opening occurred. Thermal ring opening of the mesoionic oxazolium system has been shown[6d] to yield a transient ketene and, if such a valence bond isomerization were occurring with **1**, the anticipated product would be a tetracyanocyclobutanone. This is excluded on the basis of the carbonyl absorption of the product (ν_{CO} 1560 cm^{-1}). Though this value for the carbonyl absorption is *ca.* 50 cm^{-1} lower than anticipated, it may indicate some interaction of the oxygen atom with an adjacent cyano group as in **14a**, so that some contribution from a C=N absorption is actually being observed as well.

The second product had a ν_{CO} 1610 cm^{-1}, comparable to that of **1** (R = Ph; R^1 = H), and there as an increase in intensity of the ν_{CN} absorption at 2200 cm^{-1} compared to that in **14** (ν_{CN} 2205 cm^{-1}). These data are consistent with structure **15**.

Under the above reaction conditions **1** (R = *p*-ClC_6H_4; R^1 = H) and tetracyanoethylene gave only the product corresponding to **15**. Similar products have been observed with other mesoionic ring systems and tetracyanoethylene,[12,13] and several possible ways of forming products of type **15** are feasible but no data are available which allow a distinction to be made between an intermediate such as the "normal" 1:1 adduct **16** or whether an "ene" type process involving **17** is operative. The opportunity for stabilizing the negative charge by the cyano groups in **17** tends to favor a dipolar process which would be consistent with the ionic character of numerous tetracyanoethylene cycloadditions.[14]

Cycloaddition Reactions with Heterocumulenes. An alternative procedure to the direct synthesis of a mesoionic ring system by a cyclodehydration route is a cycloaddition reaction with a heterocumulene. Phenyl isothiocyanate is particularly effective in this respect and, on reaction with **1** (R = Ph, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$; R^1 = H) in hot benzene, the corresponding *anhydro*-2-aryl-4-mercapto-1-methyl-3-phenylimidazolium hydroxide (**18**) was obtained. In the absence of solvent, in addition to **18**, the cycloaddition product **19** of **18** with phenyl isothiocyanate was also isolated. These structures were assigned on the basis of analytical data and the chemical and spectral evidence described below.



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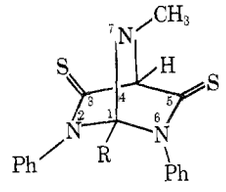

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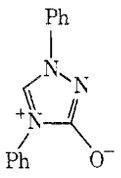
N-Phenylsydnone underwent[15] reaction with phenyl isocyanate in the absence of solvent to give *anhydro*-1,4-diphenyl-3-hydroxy-*s*-triazolium hydroxide (**20**), rather than the anticipated *anhydro*-1,3-diphenyl-4-hydroxy-1,2,3-triazolium hydroxide (**21**). A similar, reverse mode of addition can be excluded for the thiazolium system on the basis of the nmr spectrum of the *anhydro*-2-aryl-4-mercapto-1-methyl-3-phenylimidazolium hydroxide (**18**). A singlet proton resonating at δ 6.91 is more consistent with structure **18** than with structure **22**, the product from the reverse mode of addition. In the latter, the single proton at position 2 is of the formamidinium type and, in compounds related to **20**, this proton has been observed at δ 10.41–9.51, depending on the solvent.[16]

The imidazolium mesoionic derivatives readily formed methiodides and, in these salts, the 5 proton was observed at δ 8.0, consistent with the formulation of the salts as **23**. These salts also enable addition across the C=S of phenyl isothiocyanate to be excluded as such an addition, contrary to the usual mode of reaction of phenyl isothiocyanate,[17] would give *anhydro*-2-aryl-3-methyl-5-phenyliminothiazolium hydroxides (**24**). These, on reaction with methyl iodide, would form the thiazolium salts **25**. The chemical



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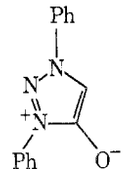

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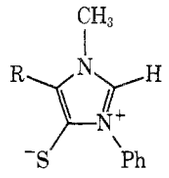

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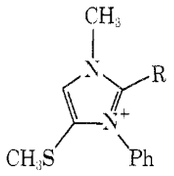

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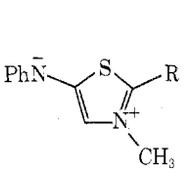

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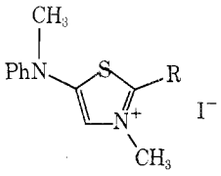

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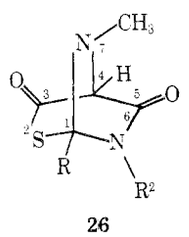
shifts of the added methyl groups in these salts were δ 2.5–2.4, clearly establishing them as SCH_3 groups rather than NCH_3 groups.[18]

Reaction of *anhydro*-2-aryl-4-mercapto-1-methyl-3-phenylimidazolium hydroxide (**18**) with phenyl isothiocyanate gave the same product **19** that was isolated from the reaction of **1** with phenyl isothiocyanate. Similar considerations regarding the mode of addition of phenyl isothiocyanate to **18** as were discussed for its addition to **1** need to be taken into account. Poor solubility precluded definitive nmr data but a consideration of the products obtained with phenyl isocyanate strongly support structure **19** (see below).

A more highly substituted member of this imidazolium system **18** has also been obtained from the reaction of *anhydro*-4-mercapto-3-methyl-2,4-diphenyloxazolium hydroxide with phenyl isothiocyanate.[19] However, in this case the additional phenyl substituent in the 5 position apparently deactivates the nucleus as no 1:1 adduct with phenyl isothiocyanate was observed. In this connection it is also of interest to note that the exocyclic sulfur system corresponding to **1** has greatly reduced 1,3-dipolar addition characteristics, a thiophenetetracarboxylic ester being obtained on prolonged reaction with dimethyl acetylenedicarboxylate.[6b]

Reaction of **1** (R = Ph; R^1 = H) with phenyl isocyanate gave two products, the primary 1:1 adduct of **1** and phenyl isocyanate represented by **26** (R = R^2 = Ph), and the 1:1 adduct **28** (R = Ph) formed from *anhydro*-2,3-diphenyl-4-



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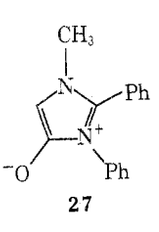

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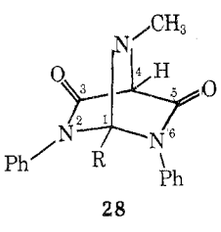
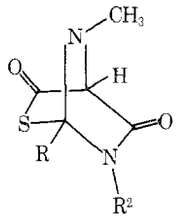


28

hydroxy-1-methylimidazolium hydroxide (**27**) and phenyl isocyanate. Elimination of carbonyl sulfide from **26** (R = R^2 = Ph) most likely accounts for the formation of **27** in the reaction medium. It is not surprising that **27** itself was not isolated from the reaction as it has been shown that this is an extremely reactive ring system[12] and that the 5 position is one of high electron density.[20] Structures **26** (R

Table II
1:1 Primary Cycloadducts Derived from *anhydro*-2-Aryl-5-hydroxy-3-methylthiazolium Hydroxides (1) and Activated Isocyanates



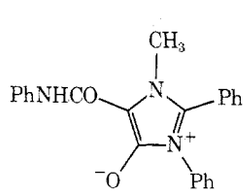
R	R^2	Mp, °C, dec	Yield, %	Crystal habit	Spectral data[a] ν_{CO}, cm^{-1}	λ_{max}, nm (log ε)	M·+	Nmr data[b]
Ph	p-$CH_3C_6H_4SO_2$	200–204	79	Colorless prisms[c]	1675, 1600	344 (4.08) 275 (4.04) 228 (4.27)	388 (8)	δ 11.55 (bs, 1, C_4-H, D_2O exchanged), 7.18–8.12 (m, 9, aromatic), 4.08 (s, 3, NCH_3), 2.45 (s, 3, CCH_3)
p-ClC_6H_4	p-$CH_3C_6H_4SO_2$	215–218	78	Yellow prisms[c]	1660, 1600	350 (4.09) 273 (4.08) 226 (4.27)		δ 11.43 (bs, 1, C_4-H, D_2O exchanged), 7.13–8.10 (m, 8, aromatic), 4.07 (s, 3, NCH_3), 2.43 (s, 3, CCH_3)
Ph	COPh	165–167	82	Light-yellow needles[c]	1730, 1680, 1610	348 (4.29) 290 (3.92) 241 (4.49)	338 (6)	δ 12.37 (bs, 1, C_4-H, D_2O exchanged), 7.38–8.13 (m, 10, aromatic), 4.25 (s, 3, NCH_3)
p-ClC_6H_4	COPh	238–240	72	Yellow needles[d]	1730, 1675, 1620	352 (4.21) 288 sh (3.80) 242 (4.37)	372 (40)	δ 12.28 (bs, 1, C_4-H, D_2O exchanged), 7.08–8.25 (m, 9, aromatic), 4.23 (s, 3, NCH_3)
Ph	p-ClC_6H_4CO	232–235	80	Light-yellow needles[d]	1725, 1680, 1610	348 (4.26) 293 (3.83) 247 (4.47)	372 (35)	δ 12.35 (bs, 1, C_4-H, D_2O exchanged), 7.27–8.10 (m, 9, aromatic), 4.25 (s, 3, NCH_3)
p-ClC_6H_4	p-ClC_6H_4CO	250–253	77	Light-yellow needles[d]	1720, 1680, 1620	353 (4.30) 292 sh (3.86) 249 (4.52)	406 (23)	δ 7.47–8.13 (m, aromatic), 4.33 (s, 3, NCH_3)

[a] Ir (KBr), uv (CH_3OH). [b] All $CDCl_3$ except R = p-ClC_6H_4, R^1 = p-ClC_6H_4CO. [c] Solvent: 1,2-dichloroethane–ether. [d] Solvent: 1,2-dichloroethane. [e] Satisfactory analytical values (±0.4% for C, H, N) were reported for all compounds in table: Ed.

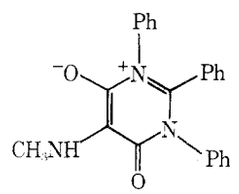
= R^2 = Ph) and **28** (R = Ph) were assigned on the basis of analytical and spectral data and because of a striking consistency in their physical characteristics with those of analogous products obtained from related mesoionic systems.

The molecular formula of **26** (R = R^2 = Ph) was established from mass spectral data, with a strong molecular ion at *m/e* 310 (28%). The proton at the 4 position in **26** was observed at δ 10.64, this extremely low value being attributed to the proton being in the deshielding zones of the adjacent carbonyl groups in the 3 and 5 positions. Carbonyl absorptions in the infrared spectrum at 1660 and 1600 cm^{-1}, and the absence of any OH or NH absorptions, exclude structures containing an OH or NH group, a structural feature usually associated with such a low chemical shift. Moreover, the formation of **28** *via* **27** cannot be readily explained unless an intermediate **26** is involved in the reaction.

Similarly **28**, the adduct from **27** and phenyl isocyanate, gave a strong molecular ion, *m/e* 369 (30%), in its mass spectrum. The corresponding 4 proton was observed at δ 10.58 and again, carbonyl absorption at 1670 and 1640 cm^{-1} and the absence of any OH or NH absorption favor a 1:1 adduct of this type. Structures such as **29** and **30** to



29



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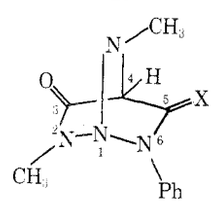
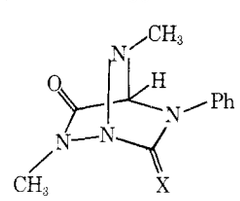


31

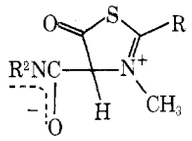


32

which rational transformations from the initial reactants may be devised are not consistent with the above spectral data.

This low-field chemical shift of the 4 proton in these 1:1 adducts has also been observed in the 1:1 adducts formed from the isomeric *anhydro*-2,3-diaryl-4-hydroxythiazolium hydroxide and phenyl isocyanate and phenyl isothiocyanate.[9] Analogous to the present system are the adducts formed from *anhydro*-1,3-dimethyl-4-hydroxy-1,2,3-triazolium hydroxide and these heterocumulenes.[21] Represented by structures **31** (X = O and S, respectively), the 4 proton was observed at δ 10.23 in the former and at δ 12.5 in the latter. The downfield shift of the 4 proton in the latter was attributed to the known extra deshielding of the thiocarbonyl group in the 5 position of **31** (X = S) and eliminates from consideration the isomeric product (**32**) formed by addition of phenyl isothiocyanate in the reverse manner. Similar arguments apply to the structures discussed above.

A similar series of cycloadducts were obtained from **1** (R = Ph, *p*-ClC_6H_4; R^1 = H) and the activated isocyanates, *p*-toluenesulfonyl, benzoyl, and *p*-chlorobenzoyl isocyanate. These all reacted readily at room temperature in contrast to the high reaction temperatures involved in the above reactions, and the adducts were isolated in excellent yields. In all cases 1:1 adducts were obtained and elimination of COS was not observed under the reaction conditions (Table II). In analogy with the reactions described above, the bicyclic structure **26** is preferred for these cycloadducts although the ylide structure **33** cannot be rigorously excluded with the present data.[22a]



33

The properties of these compounds proved uncharacteristic of ylides. For example, **26** (R = Ph; R^2 = *p*-$CH_3C_6H_4SO_2$), the adduct derived from **1** (R = Ph; R^1 = H) and *p*-toluenesulfonyl isocyanate, did not form a salt with perchloric and picric acid, methyl iodide, Meerwein's reagent, methyl *p*-toluenesulfonate, and acetyl chloride, and was stable to hot 10% NaOH. Refluxing **26** with isopropenyl acetate gave a complex reaction mixture from which no homogeneous compound could be isolated. The other cycloadducts within this series behaved in an analogous fashion.

Spectral characteristics, however, are ambiguous. The proton assigned C-4 in all compounds [excepting **26** (R = Ph, R = *p*-ClC_6H_4; R^2 = *p*-ClC_6H_4CO), only soluble in CF_3COOD] resonated in a chemical shift range of δ 9.80–12.37, and was exchanged with D_2O, although at varying rates depending on the solubility of the compounds in $CDCl_3$. This low-field resonance suggests either an NH, an aldehydic type proton, or an α-proton in a β-diketone. The first is excluded on the basis of the infrared spectra, and the other two from the observance in the mass spectrometer of a retro Diels–Alder reaction into the respective mesoionic and isocyanate fragment ions. However, in the mass spectrum of **26** (R = Ph; R^2 = *p*-$CH_3C_6H_4SO_2$), besides the retro Diels–Alder reaction, a rearrangement was observed with the formation of an [M − 107] ion at *m/e* 281. The intensity of the isotope peak at *m/e* 283 (5.4%) strongly suggests the presence of sulfur with the ^{34}S isotope contributing *ca.* 4.5% to this ion intensity. Formation of *m/e* 281 requires the loss of *p*-$CH_3C_6H_4O\cdot$, a process well documented for arylsulfonamides,[22b] and though more conveniently accommodated by structure **33,** it is conceivable that **33** is formed in the primary ionization process. This behavior can only arise from an initial simple association of the mesoionic compound and the appropriate isocyanates, also precluding any rearrangement to an aldehyde moiety. The chemical shift of the N–CH_3 protons in the isolated products was noted between δ 4.07–4.27 ($CDCl_3$) and in one instance δ 4.33 for **26** (R = *p*-ClC_6H_4; R^2 = *p*-ClC_6H_4CO) in CF_3COOD, consistent with a methyl group bonded to a quaternary nitrogen.

Experimental Section[23]

N-p-**Methoxythiobenzoylsarcosine.** *p*-Methoxythiobenzoylthioglycollic acid[24] (2.5 g) and sarcosine (0.9 g) were dissolved in 10% NaOH solution and the pH adjusted to 8–9. After 4 days at room temperature the deep pink color of the dithioglycollic acid had disappeared and, on addition of dilute HCl, a solid product (2.3 g) separated. It crystallized from chloroform–petroleum ether (bp 35–60°) as pale yellow needles: mp 132–133°; $M^{\cdot+}$ 239.

Anal. Calcd for $C_{11}H_{13}NO_3S$: C, 55.23; H, 5.44; N, 5.85. Found: C, 55.01; H, 5.51; N, 6.07.

anhydro-**5-Hydroxy-2-*p*-methoxyphenyl-3-methylthiazolium Hydroxide (1; R = *p*-$CH_3OC_6H_4$; R^1 = H).** *N-p*-Methoxythiobenzoylsarcosine[24] when treated at room temperature for several hours with a 1:3 mixture of Ac_2O/Et_3N gave the above product which crystallized from dry acetone as yellow needles: mp 155–156° dec.; 80%; ir (KBr) 1615 cm^{-1} (CO); λ_{max} (CH_3OH) 215 nm sh (log ϵ 4.12), 255 (3.67), 272 (3.65), 357 (3.97); nmr ($CDCl_3$) δ 3.73 (s, 3, OCH_3), 3.88 (s, 3, NCH_3), 6.23 (s, 1, 4-H), 6.91, 7.07 (ABd, 2, J = 9.0 Hz, aromatic), 7.31, 7.47 (ABd, 2, J = 9.0 Hz, aromatic); $M^{\cdot+}$ 221 (100).

Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.73; H, 4.93; N, 6.33. Found: C, 59.67; H, 5.03; N, 6.35.

The physical characteristic of *anhydro*-5-hydroxy-3-methyl-2-phenyl- (and 2-*p*-chlorophenyl-) thiazolium hydroxide have been described previously.[1b]

Dimethyl 1-Methyl-2-*p*-methoxyphenylpyrrole-3,4-dicarboxylate (8; R = *p*-$CH_3OC_6H_4$; R^1 = H). *anhydro*-5-Hydroxy-2-*p*-methoxyphenyl-3-methylthiazolium hydroxide and excess dimethyl acetylenedicarboxylate were heated under reflux in anhydrous benzene for 15 hr. After chromatography on neutral alumina using benzene as eluent, the product crystallized from benzene–petroleum ether (bp 35–60°) as pale yellow needles: mp 155–156°; 80%; ir (Nujol) 1710 cm^{-1} (CO); λ_{max} (CH_3OH) 226 nm (log ϵ 4.46), 265 (4.20); nmr ($CDCl_3$) δ 3.47 (s, 3, 4-$COOCH_3$), 3.68 (s, 3, 3-$COOCH_3$), 3.81 (s, 3, OCH_3), 3.85 (s, 3, NCH_3), 6.87, 7.01 (ABd, 2, J = 9.0 Hz, aromatic), 7.22, 7.37 (ABd, 2, J = 9.0 Hz, aromatic), 7.25 (s, 1, 5-H); $M^{\cdot+}$ 303 (75).

Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.37; H, 5.61; N, 4.61. Found: C, 63.51; H, 5.74; N, 4.55.

The corresponding 2-phenyl and 2-*p*-chlorophenyl products have been characterized previously.[1b]

Cycloaddition Reactions Utilizing Precursors to Mesoionic Compounds. Preparation. A. Dimethyl 1-Methyl-2-phenylpyrrole-3,4-dicarboxylate (8; R = Ph; R^1 = H). *N*-Benzoylsarcosine[25] (1.93 g) in acetic anhydride (20 ml) was treated with dimethyl acetylenedicarboxylate (1.42 g) and, after the initial exothermic reaction had subsided, the reaction mixture was warmed at 125–130° for 1 hr. It was poured into cold water and the product extracted with chloroform which was then washed with $NaHCO_3$ solution (10%), water, and dried (anhydrous Na_2SO_4). After evaporation of the chloroform, the residue was chromatographed on neutral alumina using benzene as eluent. The pyrrole crystallized from benzene–petroleum ether (bp 35–60°) as colorless needles: 1.9 g (65%); mp 118–119°. Its spectral characteristics have been described previously.[1b]

When *N*-thiobenzoylsarcosine[24] was used in this reaction, the pyrrole was obtained in 78% yield and the corresponding *N-p*-chlorothiobenzoylsarcosine[24] and *N-p*-methoxythiobenzoylsarcosine[24] resulted in an 88 and 75% yield of the corresponding pyrroles, respectively.

B. Ethyl 1-Methyl-2-phenylpyrrole-3-carboxylate (9; R = Ph; R^1 = H). *N*-Benzoylsarcosine (0.96 g), acetic anhydride (10 ml), and ethyl propiolate (0.49 g) reacted together as above and, after reaction workup, the product was obtained as a colorless oil which, on distillation, bp 105–110° (0.02 mm), crystallized. It

formed colorless plates from benzene–petroleum ether (bp 35–60°): 0.36 g (30%); mp 49–50°; ir (Nujol) 1710 cm^{-1} (CO); λ_{max} (CH_3OH) 220 nm (log ϵ 4.07), 273 (3.79); nmr ($CDCl_3$) δ 0.98, 1.10, 1.22 (t, 3, J = 7.0 Hz, CH_2CH_3), 3.35 (s, 3, NCH_3), 3.95, 4.07, 4.18, 4.30 (qt, 2, J = 7.0 Hz, CH_2CH_3), 6.61, 6.66 (ABd, 1, J = 2.25 Hz, 4-H), 6.70, 6.75 (ABd, 1, J = 2.25 Hz, 5-H), 7.41 (s, 5, phenyl); $M^{\cdot+}$ 229 (33).

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.53; H, 6.53; N, 6.09.

Use of *N*-thiobenzoylsarcosine in the above reaction gave the pyrrole in 38% yield.

C. Ethyl 2,4-Diphenyl-1-methylpyrrole-3-carboxylate (9; R = R¹ = Ph). *N*-Benzoylsarcosine (1.92 g), acetic anhydride (20 ml), and ethyl phenylpropiolate (1.74 g) were heated at 130° for 1 hr as above. Chromatography of the residue, obtained from evaporation of the chloroform extract, on neutral alumina using benzene as eluent gave the pyrrole as a pale yellow oil. After distillation [bp 155–160° (0.2 mm)] it crystallized as colorless needles: 0.96 g (31%); mp 84–85°; ir (Nujol) 1700 cm^{-1} (CO); λ_{max} (CH_3OH) 222 nm (log ϵ 5.34), 280 (3.98); nmr ($CDCl_3$) δ 0.73, 0.85, 0.97 (t, 3, J = 7.0 Hz, CH_2CH_3), 3.43 (s, 3, NCH_3), 3.78, 3.89, 4.01, 4.14 (qt, 2, J = 7.0 Hz, CH_2CH_3), 6.66 (s, 1, 5-H), 7.40 (s, 10, phenyl); $M^{\cdot+}$ 305 (100).

Anal. Calcd for $C_{20}H_{19}NO_2$: C, 78.70; H, 6.23; N, 4.60. Found: C, 78.51; H, 6.33; N, 4.43.

This was also the sole product (33%) when *N*-thiobenzoylsarcosine was used in the above reaction.

Dimethyl 1-Methylpyrazole-3,4-dicarboxylate (10). *N*-Nitrososarcosine[26] (2.36 g), dimethyl acetylenedicarboxylate (2.84 g), and acetic anhydride (20 ml) reacted together as above. After chromatography of the crude product on neutral alumina using benzene–petroleum ether (bp 35–60°) (1:2), the pyrazole was obtained as colorless crystals. It separated from benzene–petroleum ether as colorless needles: 2.30 g (60%); mp 68–69°; ir (Nujol) 1745 cm^{-1} (CO); λ_{max} (CH_3OH) 224 nm (log ϵ 4.06); nmr ($CDCl_3$) δ 3.87 (s, 3, NCH_3), 3.97 (s, 3, 4-$COOCH_3$), 4.00 (s, 3, 3-$COOCH_3$), 7.91 (s, 1, 5-H); $M^{\cdot+}$ 198 (90).

Anal. Calcd for $C_8H_{10}N_2O_4$: C, 48.48; H, 5.09; N, 14.40. Found: C, 48.27; H, 4.96; N, 13.87.

Reaction of *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium Hydroxide with *N*-Phenylmaleimide. The mesoionic compound 1 (R = Ph; R¹ = H) (1.3 g, 0.0068 mol), *N*-phenylmaleimide (1.2 g, 0.0068 mol), and dry benzene (30 ml) were stirred together at room temperature. Filtration of the precipitated solid and recrystallization from ethanol gave the endo isomer, *N*,6-diphenyl-2-oxo-3,4,5,6-tetrahydro-3α,6α-epi-*N*-methylimino-2*H*-thiapyran-4β,5β-dicarboximide (**11**; R = Ph) as colorless needles: 1.45 g (58.5%), mp 146–148° dec (with gas evolution); ir (KBr) 1730 (broad, CO) cm^{-1}.

Anal. Calcd for $C_{20}H_{16}N_2O_3S$: C, 65.91; H, 4.43; N, 7.69. Found: C, 65.79; H, 4.48; N, 7.67.

Isomerization of 11 (R = Ph). To **11** (R = Ph) (0.5 g, 0.0014 mol) in methylene chloride (20 ml) was added in small portions *m*-chloroperbenzoic acid (0.28 g, 0.0014 mol) with stirring for 1 hr at room temperature. Extraction of the CH_2Cl_2 layer with 10% sodium bicarbonate, water, drying over sodium sulfate, and evaporation of the solvent *in vacuo*, followed by recrystallization of the residue from ethanol afforded the exo isomer, *N*,6-diphenyl-2-oxo-3,4,5,6-tetrahydro-3α,6α-epi-*N*-methylimino-2*H*-thiapyran-4α,-5α-dicarboximide (**12**; R = Ph) as yellow needles: 0.2 g (38%); mp 151–153° dec (with gas evolution); ir (KBr) 1720 (broad, CO) cm^{-1}; mass spectrum *m/e* (rel intensity) ($M^{\cdot+}$ − COS) 304 (7), 184 (18), 157 (22), 156 (31), 60 (100), 45 (10), 42 (13), 32 (33).

Anal. Calcd for $C_{20}H_{16}N_2O_3S$: C, 65.91; H, 4.43; N, 7.69. Found: C, 65.92; H, 4.45; N, 7.58.

Reaction of *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium Hydroxide with Dimethyl Fumarate. The mesoionic compound 1 (R = Ph; R¹ = H) (1.3 g, 0.0068 mol), dimethyl fumarate (0.98 g, 0.0068 mol), and dry benzene (30 ml) were stirred together at room temperature overnight. Solvent was removed under reduced pressure and the residue was chromatographed on preparative Silica gel (chloroform) followed by recrystallization from ethanol affording dimethyl 6-phenyl-2-oxo-3,4,5,6-tetrahydro-3α,6α-epi-*N*-methylimino-2*H*-thiapyran-4α,5β-dicarboxylate (**13**) as colorless prisms: 1.05 g (46%); mp 129–131° dec (with gas evolution); ir (KBr) 3000, 2950 (CH), 1740, 1730, 1710 (CO) cm^{-1}; λ_{max} (CH_3OH) 248 nm (log ϵ 3.63), 313 (3.51); $M^{\cdot+}$ 335 (2).

Anal. Calcd for $C_{16}H_{17}NO_5S$: C, 57.30; H, 5.11; N, 4.18. Found: C, 57.57; H, 5.23; N, 3.99.

Reaction of *anhydro*-2-*p*-Chlorophenyl-5-hydroxy-3-methylthiazolium Hydroxide with *N*-Phenylmaleimide. Equimolar amounts of the mesoionic compound 1 (R = *p*-ClC_6H_4; R¹ = H) and *N*-phenylmaleimide in dry benzene were stirred together at room temperature. The endo adduct, 6-*p*-chlorophenyl-2-oxo-*N*-phenyl-3,4,5,6-tetrahydro-3α,6α-epi-*N*-methylimino-2*H*-thiapyran-4β,5β-dicarboximide (**11**, R = *p*-ClC_6H_4) was isolated as small, colorless needles from ethanol: yield 68%; mp 134–136° dec (with gas evolution); ir (KBr) 1710 (broad, CO) cm^{-1}; λ_{max} (CH_3OH) 222 nm (log ϵ 4.30); mass spectrum *m/e* (rel intensity) (M − COS) 338 (1), 60 (49), 46 (96), 45 (50), 43 (43), 32 (54), 31 (100).

Anal. Calcd for $C_{20}H_{15}N_2ClO_3S$: C, 60.22; H, 3.79; N, 7.02. Found: C, 60.48; H, 3.92; N, 6.89.

Isomerization of 11 (R = *p*-ClC_6H_4). Treatment with an equimolar amount of *m*-chloroperbenzoic acid in methylene chloride at room temperature yielded, after extraction in the usual manner, the exo isomer 6-*p*-chlorophenyl-2-oxo-*N*-phenyl-3,4,5,6-tetrahydro-3α,6α-epi-*N*-methylimino-2*H*-thiapyran-4α,5α-dicarboximide (**12**, R = *p*-ClC_6H_4) as cream prisms from acetonitrile: yield 20%; mp 161–164° dec (with gas evolution); ir (KBr) 1710 (broad, CO) cm^{-1}; λ_{max} (CH_3OH) 223 nm (log ϵ 4.38), 341 (3.51); mass spectrum (rel intensity) *m/e* 350 (4), 60 (100).

Anal. Calcd for $C_{20}H_{15}N_2ClO_3S$: C, 60.22; H, 3.79; N, 7.02. Found: C, 60.37; H, 3.93; N, 7.11.

Reaction of *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium Hydroxide with Tetracyanoethylene. The above mesoionic compound (**1**, R = Ph; R¹ = H) (0.57 g, 0.003 mol) in dry benzene (30 ml) was treated with tetracyanoethylene (0.38 g, 0.003 mol) and a deep red solution was formed immediately. After warming on the water bath for a few min, a deep red product separated. After 1 hr at room temperature the product was collected (0.5 g, 53%) and was then boiled with methanol and the insoluble product **14** (R = Ph) filtered and washed with dry ether: mp 230–232°; ir (Nujol) 2205 (CN), 1560 (CO) cm^{-1}; λ_{max} (CH_3OH) 201 nm (log ϵ 4.37), 297 (3.83), 488 (4.24); $M^{\cdot+}$ 320.

Anal. Calcd for $C_{16}H_9N_5OS$; C, 60.19; H, 2.84; N, 21.94. Found: C, 60.41; H, 2.83; N, 21.71.

The above methanolic filtrate was diluted with dry ether and, on standing, a bright red crystalline product separated: 0.05 g, mp 275–277°; ir (Nujol) 2200 (CN), 1612 (CO) cm^{-1}; λ_{max} (CH_3OH) 293 nm (log ϵ 3.94), 346 (3.34), 485 (4.35); $M^{\cdot+}$ 292 (32).

Anal. Calcd for $C_{15}H_8N_4OS$: C, 61.81; H, 2.74; N, 19.23. Found: C, 61.34; H, 2.62; N, 19.13.

The structure of this product was established as *anhydro*-5-hydroxy-3-methyl-2-phenyl-4-tricyanoethenylthiazolium hydroxide (**15**, R = Ph).

Similarly from *anhydro*-2-*p*-chlorophenyl-5-hydroxy-3-methylthiazolium hydroxide (**1**; R = *p*-ClC_6H_4; R¹ = H) (0.45 g, 0.002 mol) and tetracyanoethylene (0.26 g, 0.002 mol) a deep red solid was obtained (0.49 g, 94%), mp 210–215°. This methanol-insoluble product was chromatographed on silica gel and eluted with a chloroform–ethanol (9.5:0.5) mixture. The deep red band was collected and the product recrystallized from methanol, separating as bright red flakes of *anhydro*-2-*p*-chlorophenyl-5-hydroxy-3-methyl-4-tricyanoethenylthiazolium hydroxide (**15**, R = *p*-ClC_6H_4): mp 283–285°; ir (Nujol) 2205 (CN), 1695 (CO) cm^{-1}; λ_{max} (CH_3OH) 222 nm (log ϵ 4.08), 237 (4.01), 298 (3.74), 480 (3.97); $M^{\cdot+}$ 326 (15).

Anal. Calcd for $C_{15}H_7N_4ClOS$: C, 55.08; H, 2.14; N, 17.14. Found: C, 55.08; H, 2.14; N, 16.49.

Reaction of *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium Hydroxide with Phenyl Isothiocyanate. The above mesoionic compound (**1**, R = Ph; R¹ = H) (1.9 g) and phenyl isothiocyanate (4 ml) were warmed at 80° for 30 min in a nitrogen atmosphere. On cooling the reaction mixture solidified. Anhydrous ether was added; the product was collected and then chromatographed on Kieselgel g using chloroform as eluent. 7-Methyl-1,2,6-triphenyl-2,6,7-triazabicyclo[2.2.1]heptane-3,5-dithione (**19**; R = Ph) was eluted first using chloroform. It crystallized from chloroform–ether as yellow needles: 0.5 g (12%); mp 266–268°; ir (KBr) 1640 (w), 1600 (w), 1560 (w), 1500, 1360, 770, 700 cm^{-1}; λ_{max} (CH_3OH) 233 nm (log ϵ 4.53), 325 (4.18), 378 (4.21); nmr ($CHCl_3$) δ 4.2 (s, 3, N–CH_3), 14.6 (s, 1, 4-H), 7.9-7.2 (m, 15, aromatic); $M^{\cdot+}$ 401 (28).

Anal. Calcd for $C_{23}H_{19}N_3S_2$: C, 68.81; H, 4.77; N, 10.47. Found: C, 68.67; H, 4.77; N, 10.40.

Further development of the column with chloroform–10% methanol gave *anhydro*-2,3-diphenyl-4-mercapto-1-methylimidazolium hydroxide (**18**, R = Ph) which crystallized from chloroform–ether as yellow flakes; 1.7 g (64%), mp 231–232°. The physical characteristics of this product have been reported previously.[1b]

Reaction of *anhydro*-2,3-Diphenyl-4-mercapto-1-methylimidazolium Hydroxide (18, R = Ph) with Phenyl Isothiocyanate. The mesoionic compound (0.5 g) and phenyl isothiocyanate (2 ml) were heated at 100° under nitrogen for 5 hr. On cooling anhydrous ether was added, and the yellow solid which separated was then chromatographed on Kieselgel g using chloroform as eluent. The adduct (**19**, R = Ph) crystallized from chloroform–ether as yellow needles, mp 266–268°. This product was identical in all respects with that isolated above.[27]

Further development of the column with chloroform–10% methanol gave the mesoionic compound **18** (0.4 g).

In a similar fashion 2,6-diphenyl-1-*p*-methoxyphenyl-7-methyl-2,6,7-triazabicyclo[2.2.1]heptane-3,5-dithione (**19**, R = *p*-$CH_3OC_6H_4$) was obtained from *anhydro*-5-hydroxy-2-*p*-methoxyphenyl-3-methylthiazolium hydroxide (**1**, R = *p*-$CH_3OC_6H_4$; R^1 = H) (2.4 g) and phenyl isothiocyanate (5 ml). It crystallized from chloroform–ether as yellow needles: 1.4 g (30%); mp 250°; λ_{max} (CH_3OH) 225 nm sh (log ϵ 4.34), 265 (4.23), 323 (4.13), 377 (4.20).

Anal. Calcd for $C_{24}H_{21}N_3OS_2$: C, 66.81; H, 4.91; N, 9.74. Found: C, 66.60; H, 5.06; N, 9.47.

Further development of the column with chloroform–10% methanol gave *anhydro*-4-mercapto-2-*p*-methoxyphenyl-1-methyl-3-phenylimidazolium hydroxide (**18**, R = *p*-$CH_3OC_6H_4$) as pale yellow needles from chloroform–ether: 1.3 g (38%); mp 204–206°; ir (KBr) 1610, 1580, 1510, 1260, 1200, 845, 765, 710 cm^{-1}; λ_{max} (CH_3OH) 246 nm (log ϵ 4.18), 320 (3.91); nmr ($CDCl_3$) δ 3.63 (s, 3, NCH_3), 3.77 (s, 3, OCH_3), 6.83 (ABd, 2, J = 9.0 Hz, aromatic), 6.91 (s, 1, 5-H), 7.12 (ABd, 2, J = 9.0 Hz, aromatic), 7.33 (s, 5, aromatic); $M^{\cdot+}$ 296 (4). This product decomposed on standing and was characterized as its methiodide (**23**, R = *p*-$CH_3OC_6H_4$). This crystallized from ethanol as colorless prisms: mp 210–212°; ir (KBr) 1610, 1500, 1480, 1310, 1290, 1200, 850, 765, 710 cm^{-1}; λ_{max} (CH_3OH) 208 nm (log ϵ 4.48), 268 (4.09); nmr ($CDCl_3$) δ 2.40 (s, 3, SCH_3), 3.79 (s, 3, NCH_3), 4.00 (s, 3, OCH_3), 6.90 (ABd, 2, J = 9.0 Hz, aromatic), 7.5 (broad, s, 5, aromatic), 7.63 (ABd, 2, J = 9.0 Hz, aromatic), 7.99 (s, 1, 5-H).

Anal. Calcd for $C_{18}H_{19}IN_2OS$: C, 49.33; H, 4.37; N, 6.40. Found: C, 49.31; H, 4.39; N, 6.27.

The corresponding 2,3-diphenyl-1-methyl-4-methylthioimidazolium iodide (**23**, R = Ph) and 2-*p*-chlorophenyl-1-methyl-4-methylthio-3-phenylimidazolium iodide (**23**, R = *p*-ClC_6H_4) were prepared in a similar fashion and their physical characteristics have been described earlier.[1b]

Reaction of *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium Hydroxide with Phenyl Isocyanate. The above mesoionic compound (**1**, R = Ph; R^1 = H) (1.91 g) and phenyl isocyanate (3.0 g) were stirred at 100° in an atmosphere of nitrogen for 5 min. On cooling the reaction mixture solidified to a yellow, crystalline mass which was triturated with dry ether and collected. It was chromatographed on Kieselgel g using chloroform–10% ethyl acetate as eluent, 1,6-diphenyl-7-methyl-6,7-diaza-2-thiabicyclo[2.2.1]heptane-3,5-dione (**26**, R = R^2 = Ph) being eluted first. It crystallized from chloroform as pale yellow needles: mp 158–159°, 11%; ir (KBr) 1660, 1600, 1550 cm^{-1}; λ_{max} (CH_3OH) 238 nm (log ϵ 4.16), 283 (4.14), 354 (4.21); nmr ($CDCl_3$) δ 4.17 (s, 3, NCH_3), 7.7–6.9 (m, 10, aromatic), 10.64 (s, 1, 4-H); $M^{\cdot+}$ 310 (28).

Anal. Calcd for $C_{17}H_{14}N_2O_2S$: C, 65.80; H, 4.55; N, 9.03. Found: C, 66.00; H, 4.57; N, 9.11.

Further development of the chromatogram with chloroform–10% ethyl acetate gave 7-methyl-1,2,6-triphenyl-2,6,7-triazabicyclo[2.2.1]heptane-3,5-dione (**28**, R = Ph) which crystallized from chloroform–ether as colorless needles: mp 249–250°; 48%; ir (KBr) 1670, 1640, 1590, 1550, 1500 cm^{-1}; λ_{max} (CH_3OH) 222 nm sh (log ϵ 4.37), 320 (4.46); nmr ($CDCl_3$) δ 4.03 (s, 3, NCH_3), 7.8–6.9 (m, 15, aromatic), 10.58 (s, 1, 4-H); $M^{\cdot+}$ 369 (30).

Anal. Calcd for $C_{23}H_{19}N_3O_2$: C, 74.78; H, 5.18; N, 11.38. Found: C, 74.89; H, 5.28; N, 11.35.

In a similar fashion, *anhydro*-5-hydroxy-2-*p*-methoxyphenyl-3-methylthiazolium hydroxide (**1**, R = *p*-$CH_3OC_6H_4$; R^1 = H) and phenyl isocyanate gave rise to 1-*p*-methoxyphenyl-7-methyl-6-phenyl-6,7-diaza-2-thiabicyclo[2.2.1]heptane-3,5-dione (**26**, R = *p*-$CH_3OC_6H_4$; R^2 = Ph) which crystallized from chloroform–ether as yellow needles: mp 190–191°; 12%; ir (KBr) 1650, 1600, 1570, 1550, 1520 cm^{-1}; λ_{max} (CH_3OH) 222 nm (log ϵ 4.14), 243 (4.05), 286 (4.24), 357 (4.32); nmr ($CDCl_3$) δ 3.89 (s, 3, OCH_3), 4.24 (s, 3, NCH_3), 7.8–6.9 (m, 9, aromatic), 10.66 (s, 1, 4-H); $M^{\cdot+}$ 340 (52).

Anal. Calcd for $C_{18}H_{16}N_2O_3S$: C, 63.52; H, 4.74; N, 8.23. Found: C, 63.80; H, 4.61; N, 8.32.

2,6-Diphenyl-1-*p*-methoxyphenyl-7-methyl-2,6,7-triazabicyclo[2.2.1]heptane-3,5-dione (28; R = *p*-$CH_3OC_6H_4$) was likewise eluted as the second fraction and it crystallized from chloroform–ether as colorless prisms: mp 255–256°; 50%; ir (KBr) 1670, 1640, 1610, 1590, 1550 cm^{-1}; λ_{max} (CH_3OH) 248 nm (log ϵ 4.17), 320 (4.46); nmr ($CDCl_3$) δ 3.75 (s, 3, OCH_3), 4.02 (s, 3, NCH_3), 7.8–6.7 (m, 14, aromatic), 10.54 (s, 1, 4-H); $M^{\cdot+}$ 399 (42).

Anal. Calcd for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.39; H, 5.26; N, 10.58.

General Procedure for the Reaction of 1 with Activated Isocyanates. Reaction with *p*-Toluenesulfonyl Isocyanate. To the mesoionic compound 1 (R = Ph; R^1 = H) (1.0 g, 0.0052 mol) in dry benzene (30 ml) was added dropwise a solution of *p*-toluenesulfonyl isocyanate (1.1 g, 0.0056 mol) in dry benzene (5 ml) at room temperature with stirring for 6 hr. Addition of anhydrous ether precipitated a colorless solid that crystallized from 1,2-dichloroethane–ether as colorless prisms of 7-methyl-1-phenyl-6-*p*-toluenesulfonyl-2-thia-6,7-diazabicyclo[2.2.1]heptanō-dione (**26**, R = Ph; R^2 = *p*-$CH_3C_6H_4SO_2$): 1.6 g (79%), mp 200–204° dec (with gas evolution) (Table II).

Registry No.—1 (R = *p*-$CH_3OC_6H_4$, R^1 = H), 40727-16-0; **1** (R = Ph, R^1 = H), 52052-19-4; **1** (R = *p*-ClC_6H_4, R^1 = H), 51787-62-3; **8** (R = *p*-$CH_3OC_6H_4$, R^1 = H), 52705-21-2; **8** (R = Ph, R^1 = H), 19611-52-0; **9** (R = Ph, R^1 = H), 22050-30-2; **9** (R = R^1 = Ph), 22050-79-9; **10**, 22050-80-2; **11** (R = Ph), 52705-22-3; **11** (R = *p*-ClC_6H_4), 52705-23-4; **12** (R = Ph), 52745-41-2; **12** (R = *p*-ClC_6H_4), 52745-42-3; **13**, 52705-24-5; **14** (R = Ph), 52705-25-6; **15** (R = Ph), 52705-26-7; **15** (R = *p*-ClC_6H_4), 52705-27-8; **18** (R = Ph), 19950-84-6; **18** (R = *p*-$CH_3OC_6H_4$), 52705-28-9; **19** (R = Ph), 52705-29-0; **19** (R = *p*-$CH_3OC_6H_4$), 52705-30-3; **23** (R = *p*-$CH_3OC_6H_4$), 52705-31-4; **26** (R = R^2 = Ph), 52705-32-5; **26** (R = *p*-$CH_3OC_6H_4$, R^2 = Ph), 52705-33-6; **26** (R = Ph, R^2-*p*-$CH_3C_6H_4SO_2$), 52705-34-7; **26** (R = *p*-ClC_6H_4, R^2 = *p*-$CH_3C_6H_4SO_2$), 52748-19-3; **26** (R = Ph, R^2 = COPh), 52705-35-8; **26** (R = *p*-ClC_6H_4, R^2 = COPh), 52705-36-9; **26** (R = Ph, R^2-*p*-ClC_6H_4CO), 52705-37-0; **26** (R = *p*-ClC_6H_4, R^2 = *p*-ClC_6H_4CO), 52705-38-1; **28** (R = Ph), 52705-39-2; **28** (R = *p*-$CH_3OC_6H_4$), 52705-40-5; *N*-*p*-methoxythiobenzoylsarcosine, 52705-41-6; *p*-methoxythiobenzoylthioglycollic acid, 52705-42-7; dimethylacetylenedicarboxylate, 762-42-5; *N*-benzoylsarcosine, 2568-34-5; ethyl propiolate, 623-47-2; ethyl phenylpropiolate, 2216-94-6; *N*-nitrososarcosine, 13256-22-9; *N*-phenylmaleimide, 941-69-5; dimethyl fumarate, 624-49-7; tetracyanoethylene, 670-54-2; phenyl isocyanate, 103-71-9; phenyl isothiocyanate, 103-72-0; *p*-toluenesulfonylisocyanate, 4083-64-1; benzoyl isocyanate, 4461-33-0; *p*-chlorobenzoyl isocyanate, 4461-36-3; sarcosine, 107-97-1.

References and Notes

(1) (a) Support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) presented in part in Preliminary Communications: K. T. Potts and D. N. Roy, *Chem. Commun.*, 1061, 1062 (1968); (c) K. T. Potts and U. P. Singh, *Ibid.*, 66 (1969); (d) abstracted in part from the Ph.D. Thesis of J.B. (1973); NSF Trainee, 1969–1971.

(2) (a) A recent review which summarizes earlier concepts and references is M. Ohta and H. Kato in "Nonbenzenoid Aromatics," J. P. Snyder, Ed., Academic Press, New York, N.Y., 1969, Chapter 4; (b) W. Baker and W. D. Ollis, *Quart. Rev., Chem. Soc.*, **11**, 15 (1957).

(3) G. V. Boyd and A. J. H. Summers, *J. Chem. Soc. B*, 1648 (1971); R. Grashey and M. Baumann, *Angew. Chem., Int. Ed., Engl.*, **8**, 133 (1969).

(4) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **2**, 565 (1963).

(5) (a) R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, **101**, 536 (1968); (b) H. Gotthardt and R. Huisgen, *ibid.*, **101**, 552 (1968); (c) R. Huisgen and H. Gotthardt, *ibid.*, **101**, 1059 (1968); (d) R. Huisgen, R. Grashey, and H. Gotthardt, *ibid.*, **101**, 829 (1968); (e) J. K. Stille, F. W. Harris, and M. A. Bedford, *J. Heterocycl. Chem.*, **3**, 155 (1966); (g) I. G. Kolokol'tseva, V. N. Chistokletov, M. D. Stadnichuk, and A. A. Petrov, *Zh. Obshch. Khim.*, **38**, 1820 (1968); (h) H. Gotthardt, R. Huisgen, and R. Knoir, *Chem. Ber.*, **101**, 1056 (1968); (i) A. Ya Lazaris, *Zh. Org. Khim.*, **2**, 1322, 1719 (1966); (j) D. Ll. Hammick and D. J. Voaden, *J. Chem. Soc.*, 5871 (1965); (k) L. K. Vagina, V. N. Christokletov, and A. A. Petrov, *Zh. Org. Khim.*, **1**, 1700 (1965).

(6) (a) R. Huisgen, E. Funke, H. Gotthardt, and H.-L Panke, *Chem. Ber.*, **104**, 1532 (1971); (b) E. Funke, R. Huisgen, and F. C. Schaefer, *ibid.*, **104**, 1550 (1971); (c) E. Brunn, E. Funke, H. Gotthardt, and R. Huisgen, *ibid.*, **104**, 1562 (1971); (d) H. O. Bayer, R. Huisgen, R. Knorr, and F. C. Schaefer, *ibid.*, **103**, 2581 (1970).

(7) A. Lawson and C. E. Searle, *J. Chem. Soc.*, 1556 (1957).

(8) M. Ohta and C. C. Shin, *Bull. Chem. Soc. Jap.*, **38**, 704 (1965).

(9) K. T. Potts, E. Houghton, and U. P. Singh, *J. Org. Chem.*, **39**, 3627 (1974); unpublished results.

(10) (a) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **96**, 4268, 4276 (1974). (b) The α and β nomenclature used here refers to the orientation of the substituents with respect to the *N*-methylimino bridge. In compounds **11–13**, the peripheral numbering used for discussing the nmr data places the bridgehead atoms at positions 1 and 4 for conve-

nience in comparing data from related adducts in other papers in this series.
(11) K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, **39**, 3631 (1974).
(12) (a) K. T. Potts and S. Husain, *J. Org. Chem.*, **36**, 3368 (1971); (b) A. Chinone, S. Sato, and M. Ohta, *Bull. Chem. Soc. Jap.*, **44**, 826 (1971).
(13) K. T. Potts and M. Sorm, *J. Org. Chem.*, **36**, 8 (1971).
(14) J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *J. Amer. Chem. Soc.*, **94**, 2904 (1972), and references listed therein; P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).
(15) H. Kato, S. Sato, and M. Ohta, *Tetrahedron Lett.*, 4261 (1967).
(16) K. T. Potts, S. K. Roy, and D. P. Jones, *J. Org. Chem.*, **32**, 2245 (1967); R. F. Smith, J. L. Deutsch, P. A. Almeter, D. S. Johnson, S. M. Roblyler, and T. C. Rosenthal, *J. Heterocycl. Chem.*, **7**, 671 (1970).
(17) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N.Y., 1967.
(18) L. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969.
(19) R. Huisgen, E. Funke, F. C. Schaefer, H. Gotthardt, and E. Brunn, *Tetrahedron Lett.*, 1809 (1967).
(20) E. B. Roche and D. W. Stansloski, *J. Heterocycl. Chem.*, **7**, 139 (1970).
(21) K. T. Potts and S. Husain, *J. Org. Chem.*, **37**, 2049 (1972).
(22) (a) R. Appel and H. Rittersbacher, *Chem. Ber.*, **97**, 852 (1964); (b) G. Spiteller and R. Kaschnitz, *Monatsh.*, **94**, 964 (1963); E. Dyneson, S. O. Lawesson, G. Schroll, J. H. Bowie, and R. G. Cooks, *J. Chem. Soc. B*, 15 (1968).
(23) Spectral characterizations were carried out with the following instrumentations; ir, Perkin-Elmer Model 421 and 137 infrared spectrophotometers; uv, Cary Model 14 spectrophotometer; nmr, Varian A-60, T-60 and HA-100 spectrometers using TMS as internal standard; mass spectra, Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV using the direct insertion probe at a temperature of *ca.* 150°. Evaporations were done under reduced pressure using a rotavap apparatus and melting points were determined in capillaries. Analyses are by Galbraith Laboratories Inc., Knoxville, Tenn.
(24) K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1087 (1961).
(25) J. O'Brien and C. Niemann, *J. Amer. Chem. Soc.*, **79**, 84 (1957).
(26) D. L. Hammick, *J. Chem. Soc.*, 3303 (1961).
(27) Criteria for product equivalency were superimposable infrared spectra, no depression in mixture melting point, and identical R_f values.

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

K. T. Potts,* E. Houghton, and U. P. Singh

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

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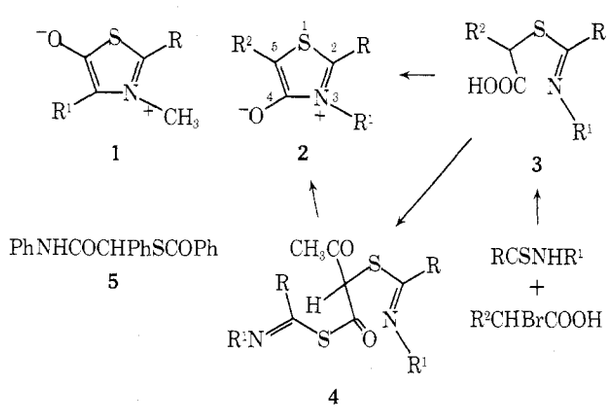
anhydro-2,3-Diphenyl-4-hydroxythiazolium hydroxide has been prepared by Ac_2O/Et_3N cyclization of the condensation product of thiobenzanilide and bromoacetic acid, and the product previously assigned this structure identified as 2-mercapto-1-thioacetoacetic acid, anhydrosulfide with *N*-phenylthiobenzimidic 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-