# Mesoionic Compounds. XXXV. Cycloaddition Reactions of the *anhydro*-4-Hydroxythiazolium Hydroxide and *anhydro*-5-Hydroxyoxazolium Hydroxide Systems with Heterocumulenes[1]

K. T. Potts,* J. Baum, S. K. Datta, and E. Houghton

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

*Received June 3, 1975*

Activated isocyanates underwent ready reaction at room temperature with *anhydro*-2-*p*-chlorophenyl-4-hydroxy-3-phenylthiazolium hydroxide yielding 1:1 primary cycloadducts assigned a 2,6-diaza-7-thiabicyclo[2.2.1]-heptane structure. Analogous adducts were also obtained with *anhydro*-5-hydroxy-3-methyl-2-phenyloxazolium hydroxide. Phenyl isocyanate and phenyl isothiocyanate, however, required elevated temperatures (80 °C) for the formation of 1:1 adducts with the former system.

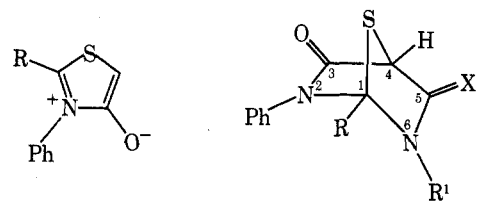
Heterocumulenes have been shown to undergo a variety of cycloaddition reactions[2] and, with the mesoionic *anhydro*-5-hydroxythiazolium hydroxide system, provided several interesting 1:1 cycloadducts as well as a convenient route to the *anhydro*-4-mercaptoimidazolium hydroxide system.[3] We now describe the reactions of several isocyanates and isothiocyanates with the isomeric *anhydro*-4-hydroxythiazolium hydroxide system **1** and with the *anhydro*-5-hydroxyoxazolium hydroxide system **10**, the adducts from the latter being particularly interesting in that they retain the elements of carbon dioxide, an unusual feature in products derived from this ring system.[4]

Phenyl isothiocyanate, phenyl isocyanate, benzoyl isocyanate, *p*-chlorobenzoyl isocyanate, trichloroacetyl isocyanate, *p*-toluenesulfonyl isocyanate, and *N*-chlorosulfonyl isocyanate all underwent ready reaction with *anhydro*-2-aryl-4-hydroxy-3-phenylthiazolium hydroxide[5] (**1**, R = Ph and *p*-$ClC_6H_4$) forming crystalline cycloadducts. Analytical and mass spectral data (Table I) established that these were 1:1 adducts, and structural formulas have been assigned on the basis of the following considerations.

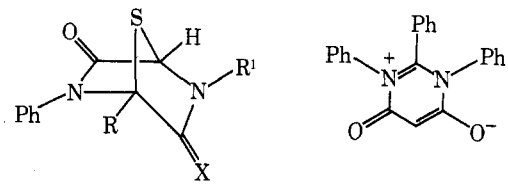
With phenyl isothiocyanate and **1** (R = Ph) an orange-yellow, crystalline product (Table I) separated from the hot benzene reaction mixture after 15 min. Its molecular formula, $C_{22}H_{16}N_2OS_2$, corresponded to a simple 1:1 adduct but the spectral data excluded any substitution into the 5 position of **1**. Its infrared spectrum, devoid of OH, SH, or NH absorptions, showed $\nu_{CO}$ 1630 $cm^{-1}$ and $\nu_{C=S}$ 1135 $cm^{-1}$, and the ultraviolet spectrum [203 nm (log $\epsilon$ 4.65), 277 (4.10), 306 sh (3.85), 424 (4.06)] showed a considerable shift to longer wavelength from that of **1** (R = Ph), and also from the absorption of an *N*-phenylthioamide such as *N*-phenylthioacetamide[6] [218 nm (log $\epsilon$ 4.15), 301 (4.01)]. The NMR spectrum was very simple, consisting of aromatic protons (15) at $\delta$ 7.63 and a singlet proton at an exceptionally low chemical shift, $\delta$ 12.06.

Several structural representations for an adduct of this composition are possible, including those containing an SH or OH group, but all may be excluded on the basis of the above spectral data except **2** and **3** (R = $R^1$ = Ph; X = S), representing different modes of addition of phenyl isothiocyanate to the thiocarbonyl ylide dipole of **1**. Structure **3** can be discarded, as in the corresponding adduct from **1** (R = Ph) and phenyl isocyanate, the singlet proton moved upfield, albeit still at an exceptionally low value, to $\delta$ 10.27. This indicates that the bridgehead proton at C-4 is being strongly deshielded by the C=O and the C=S groups at the 3 and 5 positions, respectively, being in the deshielding zone of both groups. As the C=S group is known[7] to exert a stronger deshielding influence than the C=O group, such a shift is consistent with structure **2**, 3-oxo-1,2,6-triphenyl-2,6-diaza-7-thiabicyclo[2.2.1]heptane-5-thione (R = $R^1$ = Ph; X = S).

A low chemical shift in the region of $\delta$ 12.06 is usually associated with a proton attached to an electronegative element such as oxygen, nitrogen, or sulfur, or to an aldehydic proton. In **2**, the 4 proton is not readily exchanged with deuterium, requiring base catalysis for exchange to occur.



**1** **2**



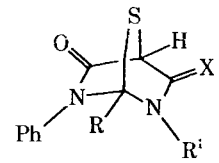
**3** **4**

The inductive effects exerted by the carbonyl groups and thiocarbonyl groups, as well as the bridgehead sulfur atom, alone cannot account for this low chemical shift. In similar cycloadducts obtained from heterocumulenes and *anhydro*-1,3-dimethyl-4-hydroxy-1,2,3-triazolium hydroxide,[8] *anhydro*-2,3-diphenyl-4-hydroxy-1-methylimidazolium hydroxide,[3] and *anhydro*-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide,[3] similar chemical shifts were observed for the analogous bridgehead hydrogen atoms.

The ultraviolet spectrum of **2** (R = $R^1$ = Ph; X = S) is also consistent with this structure. Interaction between a $\beta$-thio group and a carbonyl group has been shown[9] and in $\beta$-keto sulfides causes a shift of the perturbed CO absorption to 300 nm,[10] and interaction between the bridge sulfur atom and the thiocarbonyl group also explains unsuccessful attempts to remove cleanly the sulfur bridge (see below).

Phenyl isocyanate and **1** (R = Ph) readily formed a yellow 1:1 cycloadduct (Table I) over 1 hr in refluxing benzene. Its spectral characteristics are consistent with structure **2** (R = $R^1$ = Ph; X = O). The infrared spectrum showed $\nu_{CO}$ 1650 and 1625 $cm^{-1}$, the latter most likely the result of interaction of the sulfur bridge with one of the carbonyl groups, an effect which is also reflected in the ultraviolet spectrum having a long wavelength absorption at 400 nm. The NMR spectrum, in addition to the aromatic

Table I. Cycloadducts Obtained from Heterocumulenes and the *anhydro*-4-Hydroxythiazolium Hydroxide System[a]

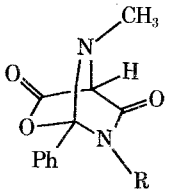


| Registry no. | R | R' | X | Yield, % | Mp,[b] °C | Molecular formula | Anal., % Calcd C | Calcd H | Calcd N | Found C | Found H | Found N | Spectral data: M·+ (rel intensity) | Ir (KBr), cm⁻¹ | λmax (CH3OH), nm (log ε) | NMR, δ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57513-19-6 | Ph | Ph | S | 88 | 230[c] | $C_{22}H_{16}N_2OS_2$ | 68.03 | 4.15 | 7.21 | 67.99 | 3.99 | 7.19 | 388 (65) | 1630 (CO), 1135 (CS) | 203 (4.65), 277 (4.10), 306[d] (3.85), 424 (4.06) | 12.06 (s, 1, $H_4$), 7.63 (m, 15, aromatic)[e] |
| 57513-20-9 | Ph | Ph | O | 73 | 215–216[f] | $C_{22}H_{16}N_2O_2S$ | 70.96 | 4.33 | 7.52 | 71.24 | 4.33 | 7.69 | 372 (17) | 1650, 1625 (CO) | 203 (4.58), 234 (4.20), 268 (4.15), 400 (4.20) | 10.27 (s, 1, $H_4$), 7.40 (m, 15, aromatic)[e] |
| 57513-21-0 | *p*-$ClC_6H_4$ | PhCO | O | 74 | 273–276 | $C_{23}H_{15}ClN_2O_3S$ | 63.52 | 3.48 | 6.44 | 62.57 | 3.52 | 6.18 | 434 (6) | 1740, 1690, 1640 (CO) | 225 (4.33), 245[d] (4.25), 399 (4.04) | 8.3–7.2 (m, $H_4$ and aromatic)[g] |
| 57513-22-1 | *p*-$ClC_6H_4$ | $SO_3Et$ | O | 61 | 184–187 | $C_{18}H_{15}ClN_2O_5S_2$ | 49.25 | 3.44 | 6.38 | 49.14 | 3.43 | 6.38 | | 1700, 1650 (CO) | 260 (4.15), 285[d] (3.86), 411 (4.13) | 1.3 (t, 3, $SO_3CH_2CH_3$), 4.3–4.4 (dq, 2, $SO_3CH_2$-$CH_3$), 7.4–7.5 (bs, 9, aromatic), 9.8 (s, 1, $H_4$)[h] |
| 57513-23-2 | *p*-$ClC_6H_4$ | *p*-$CH_3C_6H_4SO_2$ | O | 36 | 252–257 | $C_{27}H_{17}ClN_2O_4S_2$ | 56.96 | 3.53 | 5.78 | 57.05 | 3.47 | 5.66 | 485 (3) | 1660, 1640 (CO), 1350, 1170 ($SO_2$) | 223 (3.82), 259 (3.79), 395 (3.75) | 2.4 (s, 3, $CH_3$), 7.0–8.1 (m, 13, aromatic), 10.8 (s, 1, $H_4$)[e] |
| 57513-24-3 | *p*-$ClC_6H_4$ | *p*-$ClC_6H_4CO$ | O | 74 | 273–275 | $C_{23}H_{14}Cl_2N_2O_3S$ | 58.85 | 3.01 | 5.97 | 59.15 | 2.94 | 5.84 | 469 (9) | 1730, 1680, 1630 (CO) | 232 (4.32), 254 (4.32), 399 (4.16) | 7.00–8.17 (m, $H_4$ and aromatic)[g] |
| 57513-25-4 | *p*-$ClC_6H_4$ | $Cl_3CCO$ | O | 92 | 250[i] | $C_{18}H_{10}Cl_4N_2SO_3$ | 45.38 | 2.11 | 5.88 | 45.02 | 2.21 | 5.69 | | 1760, 1680, 1625 (CO) | | 12.43 (s, 1, $H_4$), 7.60–7.22 (m, 9, aromatic)[j] |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57513-26-5 | *p*-$ClC_6H_4$ | H | O | 80 | 279–280[k] | $C_{16}H_{11}ClN_2SO_2$ | 58.08 | 3.35 | 8.47 | 57.99 | 3.34 | 8.50 | 330 (20) | 3375 (NH), 1640, 1575 (CO) | 7.54–7.30 (m, aromatic)[h] |
| 57513-27-6 | *p*-$ClC_6H_4$ | $CH_3CO$ | S | 90 | 217–218[l] | $C_{18}H_{13}ClN_2S_2O_2$ | 55.59 | 3.34 | 7.20 | 55.47 | 3.37 | 7.22 | 338 (45) | 1720, 1650 (CO) | 12.0 (broad s, 1, $H_4$), 7.8–7.1 (m, 9, aromatic), 2.4 (s, 3, $CH_3$)[e] |

[a] All crystallized from chloroform–ether as yellow needles except *c*, orange yellow needles, and *i*, bright yellow irregular prisms from 1,2-dichloroethane, *k*, orange prisms from ethanol, and *l*, lustrous red prisms from chloroform–ether. [b] Decomposition. [d] Shoulder. [e] $CDCl_3$. [f] Chromatography on Kieselgel g using $CHCl_3$. as eluent was needed for purification. [g] $CF_3CO_2D$. [h] $Me_2SO$-$d_6$. [i] $CF_3COOH$.

**Table II. 1:1 Primary Cycloadducts Derived from *anhydro*-5-Hydroxy-3-methyl-2-phenyloxazolium Hydroxide and Activated Isocyanates[a]**




| | | | | | | Anal., % | | | | | | Spectral data | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calcd | | | Found | | | | | |
| Registry no. | R | Mp, °C (dec) | Yield, % | Habit | Formula | C | H | N | C | H | N | $\nu_{CO}$, $cm^{-1}$ (KBr) | $\lambda_{max}$ ($CH_3OH$), nm (log $\epsilon$) | NMR ($CDCl_3$), $\delta$ |
| 57513-28-7 | PhCO | 193–196 | 16 | Yellow irreg prisms | $C_{18}H_{14}N_2O_4$[b] | 67.07 | 4.38 | 8.69 | 67.01 | 4.35 | 8.62 | 1720, 1700–1690 | 323 (3.75), 259[c] (4.05), 240 (4.42) | 10.95 (bs, 1, $C_4$ H, exchanged with $D_2O$), 7.27–8.13 (m, 10, aromatic), 4.27 (s, 3, $NCH_3$) |
| 57513-29-8 | *p*-$ClC_6H_4CO$ | 209–211 | 60 | Yellow needles | $C_{18}H_{13}ClN_2O_4$ | 60.60 | 3.67 | 7.85 | 60.39 | 3.64 | 7.82 | 1720, 1700 (b) | 330 (3.76), 263[c] (4.21), 246 (4.42) | 10.90 (bs, 1, $C_4$ H, exchanged with $D_2O$), 7.27–8.02 (m, 9, aromatic), 4.27 (s, 3, $NCH_3$) |
| 57513-30-1 | *p*-$CH_3C_6H_4SO_2$ | 189–192 | 68 | Colorless prisms | $C_{18}H_{16}N_2O_5S$ | 58.05 | 4.33 | 7.52 | 58.18 | 4.24 | 7.51 | 1710, 1680 | 230 (4.23) | 9.80 (bs, 1, $C_4$ H, exchanged with $D_2O$), 7.27–8.10 (m, 9, aromatic), 4.13 (s, 3, $NCH_3$), 2.45 (s, 3, aryl $CH_3$) |

[a] All recrystallized from 1,2-dichloroethane. [b] $M^{\cdot+}$322 (3). [c] Shoulder.

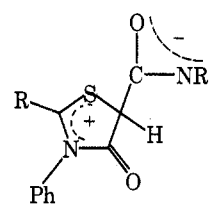
protons at δ 7.40, consisted of a sharp singlet at δ 10.27 which required base catalysis for deuterium exchange.

An immediate reaction was observed when benzoyl isocyanate and 1 (R = $p$-$ClC_6H_4$) were mixed in dry benzene at room temperature, a 1:1 cycloadduct being obtained as yellow needles (Table I). The infrared spectrum showed carbonyl absorptions at 1740 (COPh), 1690 (CON<), and 1640 $cm^{-1}$ (CON<), the ultraviolet spectrum a long-wavelength absorption at 399 nm, but in this case the chemical shift of the bridgehead proton, characteristic of the above adducts, was not observed owing to use of $CF_3CO_2H$ as the NMR solvent. These data are best accommodated by structure 2 (R = Ph; $R^1$ = COPh; X = O).

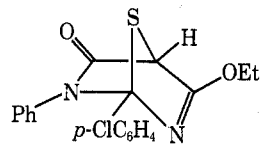
An equally ready reaction was observed between 1 (R = $p$-$ClC_6H_4$) and $N$-chlorosulfonyl isocyanate. This adduct, obtained as an unstable, hygroscopic, greenish solid, was converted into the corresponding ethyl ester which was isolated as yellow needles (Table I). Two carbonyl absorptions at 1700 and 1650 $cm^{-1}$, and a long-wavelength ultraviolet absorption at 411 nm, are consistent with the spectral parameters associated with the structure 1-$p$-chlorophenyl-6-ethoxysulfonyl-2-phenyl-2,6-diaza-7-thiabicyclo-[2.2.1]heptane-3,5-dione (2, R = $p$-$ClC_6H_4$; $R^1$ = $SO_2Et$; X = O). The NMR spectrum, in addition to the aromatic protons and those of an OEt group, showed a singlet at δ 9.8, assignable to the C-4 bridgehead proton.

$p$-Toluenesulfonyl isocyanate also readily formed a 1:1 cycloadduct with 1 (R = $p$-$ClC_6H_4$) in dry benzene at room temperature within 5 min. This yellow product's spectral characteristics (Table I) are fully in accord with its representation as 1-$p$-chlorophenyl-2-phenyl-6-$p$-tolylsulfonyl-2,6-diaza-7-thiabicyclo[2.2.1]heptane-2,5-dione (2, R = $p$-$ClC_6H_4$; $R^1$ = $p$-$CH_3C_6H_4SO_2$; X = O).

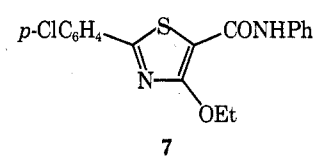
The data described above indicate 2 as the structure for these cycloadducts, a possible alternative ylidic structure 5 that cannot be definitely excluded on the basis of these data being eliminated on the basis of $^{13}C$ NMR and chemical data. The ylide 5 is plausible for the 1:1 adduct, being



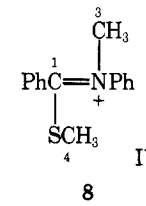
5



6



7



8

analogous to a similar type betaine 1:1 complex postulated[11] in the reaction of pyridine $N$-oxide with sulfonyl diisocyanate, and it should readily undergo protonation with perchloric acid, or alkylation with suitable reagents, in analogy with similar $N$-imines and $C$-ylides derived from 1,2,4-triazole[12] and other such systems. The adducts described above were remarkably inert to protonation and alkylation. In particular the $p$-toluenesulfonyl isocyanate adduct did not react with perchloric acid, methyl iodide, triethyloxonium fluoroborate, and methyl trifluoromethanesulfonate and on the basis of these results the ylide structure 5 must be discarded.

The $p$-toluenesulfonyl derivative was inert to $m$-chloroperbenzoic acid, sulfoxide formation not being observed, although it would be expected that in structure 2 (R = $p$-$ClC_6H_4$; $R^1$ = $p$-$CH_3C_6H_4SO_2$) with a sulfide bridge, oxidation would occur readily as has been observed with the 1:1 adducts derived from these mesoionic systems and several olefins.[13] The spectral data for these compounds described above, however, reflect the unusual nature of the adducts in that the lone pair electrons on the bridge sulfur atom are not readily available for reaction with oxidizing agents.

A major premise in our structural arguments is that the bridgehead proton at C-4 is strongly deshielded by the C-3 carbonyl group and the C-5 carbonyl or thiocarbonyl group. Accordingly, change in the nature of the group at C-5 should have a pronounced effect on the chemical shift of this bridgehead proton as well as on the properties of the system, and it was found that the 1:1 cycloadduct obtained from 1 (R = $p$-$ClC_6H_4$) and trichloroacetyl isocyanate was a particularly useful substrate upon which to bring about the desired transformations.

Hydrolysis of the adduct 2 (R = $p$-$ClC_6H_4$; $R^1$ = $COCCl_3$; X = O), formed at room temperature in 92% yield, with hot aqueous sodium carbonate solution over 15 min gave a product 2 (R = $p$-$ClC_6H_4$; $R^1$ = H; X = O) in 80% yield which, with Meerwein's reagent, afforded 1-$p$-chlorophenyl-3-ethoxy-6-phenyl-2,6-diaza-7-thiabicyclo[2.2.1]-hept-2-en-5-one (6). Thermolysis of 6 at 170 °C (0.5 mm) could have resulted in extrusion of sulfur or elimination of phenyl isocyanate, the latter being anticipated on the basis of the behavior of the initial cycloadducts of this ring system with acetylenic dipolarophiles.[5] Two products were isolated from the thermolysis, identified as 2 (R = $p$-$ClC_6H_4$; $R^1$ = H; X = O) and 2-$p$-chlorophenyl-4-ethoxythiazole-5-carboxanilide (7). Analytical and spectral data substantiating the above structures are shown in Table I and the Experimental Section. The trichloroacetyl group in 2 (R = $p$-$ClC_6H_4$; X = O) was necessary for this facile hydrolysis to occur. The adduct 2 (R = $p$-$ClC_6H_4$; $R^1$ = $COCH_3$; X = S), obtained from 1 (R = $p$-$ClC_6H_4$) and acetyl isothiocyanate, could not be hydrolyzed except under conditions that resulted in a more deep-seated degradation of the adduct.

The variation of the chemical shift of the bridgehead proton at C-4 in this series of products is particularly informative. In 2 (R = $p$-$ClC_6H_4$; $R^1$ = $COCCl_3$; X = O) a singlet proton at δ 12.43 may be attributed to the bridgehead proton; conversion of this adduct into 2 (R = $p$-$ClC_6H_4$; $R^1$ = H; X = O) resulted in this proton being obscured by the aromatic protons (δ 7.5–7.3), there being a complete absence of a signal at lower field. This large chemical shift may be due in part to an appreciable contribution from the enolic form of the newly generated amide. A further upfield shift occurs on formation of 6. No signal was found in the region δ 18–10 but a one-proton singlet occurred at δ 7.10. Although this signal cannot be assigned with absolute certainty, there are strong indications that it can be assigned to the bridgehead proton at C-4. The NMR spectrum of the thermolysis product 7 also showed an interesting feature. The 4-ethyl group gave rise to two quartets at δ 3.8 and 3.1 ($J$ = 8.0 Hz) that collapsed to two singlets on irradiation of the triplet resonance, and this nonequivalency of the methylene protons was no doubt due to a steric interaction with the neighboring 5-carboxanilide group.

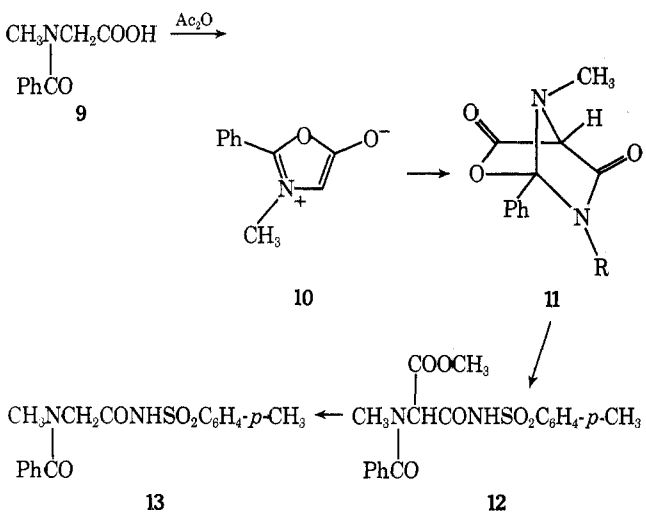
The $^{13}C$ NMR spectra of several of these products were also helpful in these structural studies, particularly in providing additional evidence for the elimination of the ylide structure 5 for these cycloadducts. The ylide structure requires the presence of a >C=N⁺< entity with the carbon being attached to an aromatic ring and a sulfur atom. Such a partial structure is present in the $S$-methylthioamide[14] derivative 8 and the carbon chemical shift in this product

Table III. $^{13}C$ Chemical Shifts for Several Heterocumulene Cycloadducts (ppm Downfield from $Me_4Si$)

| Compd | Carbon atom number | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 3 | 4 | 5 | 8 | 9 |
| 2, R = *p*-$ClC_6H_4$; $R^1 = COCH_3$; X = S | 125.78 | 156.83 | 110.34 | 184.52 | 169.41 | 25.87 |
| 6 | 125.96 | 137.62 | 88.72 | 156.83 | 60.48 | 14.04 |
| 11, R = *p*-$ClC_6H_4CO$ | 120.61 | 161.75 | 92.85 | 163.63 | 36.43 | 157.35 |
| 8 | 194.04 | 48.74 | 18.10 | | | |

was observed at 194.04 ppm. In *anhydro*-5-hydroxy-3-methyl-2-phenylthiazolium hydroxide the analogous carbon atom (C-2) was observed at 141.3 ppm and in *anhydro*-2-ethyl-5-mercapto-3-phenyl-1,3,4-thiadiazolium hydroxide the analogous carbon had shifted to 173.8 ppm.[15] These spectral data, as well as the chemical transformations above, clearly establish the bicyclic structure **2** for these heterocumulene cycloadducts.

In the reaction of *anhydro*-5-hydroxy-3-methyl-2-phenyloxazolium hydroxide (**10**) with *p*-toluenesulfonyl, benzoyl, and *p*-chlorobenzoyl isocyanate, the mesoionic system[3,4] was generated in situ from *N*-benzoylsarcosine (**9**) and acetic anhydride at 40 °C. These all formed 1:1 cycloadducts,




described in Table II, and assigned structure **11** (R = *p*-$CH_3SO_2C_6H_4$, COPh, and *p*-$ClC_6H_4CO$) on the basis of the spectral data and by analogy with the adducts discussed above. A similar product has been obtained from *anhydro*-2,4-diphenyl-5-hydroxy-3-methyloxazolium hydroxide and phenyl isocyanate.[16]

The above adducts (Table II) decomposed with gas evolution at their melting points and on electron impact the predominant fragmentation pathway was a disassociation process. Refluxing **11** (R = *p*-$CH_3SO_2C_6H_4$) with methanol resulted in an hydrolysis product **12** and use of warm 10% sodium hydroxide solution as the hydrolysis medium gave **13**, which was also obtained from **12** and 10% sodium hydroxide solution.

Just as some five-membered mesoionic systems can be converted into other representatives of this class of compounds by reaction with phenyl isothiocyanate,[8] removal of the sulfur bridge in **2** (R = $R^1$ = Ph; X = O) would provide a simple route to *anhydro*-4-hydroxy-6-oxo-1,2,3-triphenylpyrimidinium hydroxide[17] (**4**). However, all attempts to remove the sulfur with reagents such as triphenylphosphine, tris(dimethylamino)phosphine, Raney nickel, etc., were unsuccessful, probably reflecting the interaction of the sulfur with the C-3 or C-5 carbonyl groups. Oxidation with peracetic acid was successful, but, in this case, the product obtained was PhNHCOCHOHCOPhCOPh, formed by hydrolysis of **4** under the reaction conditions.[18]

## Experimental Section[19]

Reaction of ***anhydro*-4-Hydroxy-2,3-diphenylthiazolium Hydroxide with Phenyl Isothiocyanate (and Phenyl Isocyanate).** The mesoionic compound[5] **1** (R = Ph) (2.2 g, 0.087 mol) and phenyl isothiocyanate (1.5 g, 0.011 mol) in dry benzene (100 ml) were heated together under reflux and, within 15 min, product started to separate. After an additional 1 h, the reaction mixture was cooled, anhydrous ether added, and the product collected. 3-Oxo-1,2,6-triphenyl-2,6-diaza-7-thiabicyclo[2.2.1]heptane-5-thione (**2**, R = $R^1$ = Ph; X = S) crystallized from chloroform–ether as orange-yellow needles, 88%, mp 230 °C dec (Table I). Acetyl isothiocyanate[20] and **1** (R = *p*-$ClC_6H_4$) required a 3-h reflux period and, on cooling, red prisms of the adduct separated, mp 217–218 °C.

**General Procedure for the Reaction of *anhydro*-2-*p*-Chlorophenyl-4-hydroxy-3-phenylthiazolium Hydroxide (1, R = *p*-$ClC_6H_4$) and Activated Isocyanates.** The mesoionic compound and a slight excess of the isocyanate were mixed in benzene with stirring at room temperature. After several minutes the products separated and were collected and recrystallized from chloroform–ether (Table I).

With *N*-chlorosulfonyl isocyanate the precipitated product was extremely unstable and it was converted into the corresponding ester by the addition of excess ethanol.

**Hydrolysis of 1-*p*-Chlorophenyl-2-phenyl-6-trichloroacetyl-2,6-diaza-7-thiabicyclo[2.2.1]heptane-3,5-dione (2, R = *p*-$ClC_6H_4$; $R^1$ = $COCCl_3$; X = O).** The adduct (4.76 g, 0.01 mol) was heated under reflux with aqueous sodium carbonate (4 g in 40 ml of $H_2O$) for 15 min. On cooling, an orange solid separated that crystallized from absolute ethanol as orange prisms and was identified as **2** (R = *p*-$ClC_6H_4$; $R^1$ = H; X = O), 2.7 g (80%), mp 279–280 °C dec (Table I).

**1-*p*-Chlorophenyl-3-ethoxy-6-phenyl-2,6-diaza-7-thiabicyclo[2.2.1]hept-2-en-5-one (6).** A slurry of **2** (R = *p*-$ClC_6H_4$; $R^1$ = H; X = O) (3.30 g, 0.01 mol) in dry methylene chloride (100 ml) was treated with triethyloxonium fluoroborate[21] (1.90 g, 0.01 mol) added in one portion and, after 2 h, a homogeneous solution had formed. After addition of aqueous potassium carbonate (5.6 g of 50% solution), the organic portion was separated and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo afforded an orange oil that crystallized from ether–pentane as orange prisms: 2.25 g (62%); mp 88°; ir (KBr) 1650 (CO), 1600 $cm^{-1}$ (C=N); NMR ($CDCl_3$, 100 MHz) δ 7.5–7.2 (m, 8, aromatic), 7.1 (s, 1, $H_4$), 4.5 (qt, 2, $CH_2CH_3$, $J$ = 7.0 Hz), 1.4 (t, 3, $CH_2CH_3$); $M^+$· 358 (20).

Anal. Calcd for $C_{18}H_{15}ClN_2SO_2$: C, 60.21; H, 4.21; N, 7.80. Found: C, 59, 99; H, 4.30; N, 7.69.

**Thermolysis of 6.** The above 3-ethoxy compound (400 mg) was heated at 170 °C (0.5 mm). On cooling, the crude melt was dissolved in acetone and purified by chromatography on preparative silica gel (0.5 mm) using ethyl acetate. Crystallization of the first band from 1,2-dichloroethane afforded 1-*p*-chlorophenyl-2-phenyl-2,6-diaza-7-thiabicyclo[2.2.1]heptane-3,5-dione (**2**, R = *p*-$ClC_6H_4$; $R^1$ = H; X = O) as yellow prisms, 100 mg (ca. 10%), mp 280 °C. The second major band crystallized from ether–pentane as orange prisms and was identified as 2-*p*-chlorophenyl-4-ethoxythiazole-5-carboxanilide (**7**): 210 mg (50%); mp 222°; ir (KBr) 3325 (NH), 2975 (aromatic CH), and 1625 $cm^{-1}$ (CO); NMR ($CDCl_3$) δ 8.0 (broad s, 1, NH), 7.5–7.0 (m, 9, aromatic), 3.7–3.1 (two qt, 2, $CH_2CH_3$), 1.2 (t, 3, $CH_2CH_3$, $J$ = 8.0 Hz); $M^+$· 358 (62).

Anal. Calcd for $C_{18}H_{15}ClN_2SO_2$: C, 60.21; H, 4.21; N, 7.80. Found: C, 60.34; H, 4.08; N, 7.80.

**General Procedure for Reaction of *N*-Benzoylsarcosine with Activated Isocyanates. Reaction with *p*-Toluenesulfonyl Isocyanate.** *N*-Benzoylsarcosine[22] (1.93 g, 0.01 mol) in acetic anhydride (30 ml) at 40 °C was stirred and *p*-toluenesulfonyl isocyanate (1.97 g, 0.01 mol) added in small portions. Within 5 min a light yellow product had separated. Recrystallization from 1,2-dichloroethane afforded 7-methyl-1-phenyl-6-*p*-toluenesulfonyl-6,7-diaza-2-oxabicyclo[2.2.1]heptane-3,5-dione (**11**, R = *p*-

$CH_3C_6H_4SO_2$) as colorless prisms, 1.0 g (68%), mp 189–192 °C dec (with gas evolution).

**Hydrolysis of 11 (R = p-$CH_3C_6H_4SO_2$). A. With Methanol.** The adduct (0.7 g, 0.0019 mol) was refluxed in dry methanol for 4 h. Solvent was removed in vacuo and the residue recrystallized from ethanol, affording 2-methoxycarbonyl-2-(*N*-benzoyl-*N*-methylamino)acet-*p*-toluenesulfonamide (**12**) as small, colorless, clustered needles: 0.55 g (57%); mp 157–159 °C; ir (KBr) 3000 (broad, CH), 1750, 1720 $cm^{-1}$ (CO); $\lambda_{max}$ ($CH_3OH$) 226 nm (log $\epsilon$ 4.45); NMR ($CDCl_3$) $\delta$ 10.93 (bs, 1, NH, exchanged with $D_2O$), 7.17–7.97 (m, 9, aromatic), 5.33 (s, 1, $C_2$ H, exchanged with $D_2O$), 3.73 (s, 3, $OCH_3$), 3.00 (s, 3, $NCH_3$), 2.42 (s, 3, aryl $CH_3$); $M^+$· 403 (2).

Anal. Calcd for $C_{19}H_{20}N_2O_6S$: C, 56.56; H, 4.75; N, 6.95. Found: C, 56.45; H, 4.73; N, 6.83.

**B. With 10% Sodium Hydroxide Solution.** The adduct (1.0 g, 0.0027 mol) was heated on a steam bath with 10% sodium hydroxide (15 ml) for 5 min. The reaction mixture was cooled, neutralized with 3 N HCl, and extracted with chloroform. The chloroform layer was separated, dried over sodium sulfate, and evaporated in vacuo, leaving a colorless, crystalline residue which recrystallized from 1,2-dichloroethane–anhydrous ether yielding 2-(*N*-benzoyl-*N*-methylamino)acet-*p*-toluenesulfonamide (**13**) as colorless prisms: 0.2 g (20%); mp 156–157°; ir (KBr) 3000 (broad), 1710, 1625 $cm^{-1}$; $\lambda_{max}$ ($CH_3OH$) 226 nm (log $\epsilon$ 4.32); NMR ($CDCl_3$) $\delta$ 7.17–7.92 (m, 9, aromatic), 4.13 (bs, 2, $CH_2$), 3.02 (s, 3, $NCH_3$), 2.43 (s, 3, aryl $CH_3$); $M^+$· 346 (6).

Anal. Calcd for $C_{17}H_{18}N_2O_4S$: C, 58.94; H, 5.24; N, 8.09. Found: C, 58.86; H, 5.13; N, 8.25.

**Hydrolysis of 12.** Treatment of **12** with 10% sodium hydroxide on a steam bath for 15 min, extraction of the reaction with chloroform, and evaporation of the chloroform extract afforded a colorless, crystalline solid identical[23] with **13** above.

**Acknowledgments.** It is a pleasure to acknowledge the assistance of Dr. E. Williams, G. E. Corporate R & D Center, Schenectady, N.Y., in the determination of the $^{13}C$ NMR data.

**Registry No.**—**1** (R = Ph), 13288-67-0; **1** (R = p-$ClC_6H_4$), 52730-97-9; **6**, 57513-31-2; **7**, 57513-32-3; **8**, 57513-33-4; **9**, 2568-34-5; **12**, 57513-34-5; **13**, 57513-35-6; phenyl isothiocyanate, 103-72-0; phenyl isocyanate, 103-71-9; benzoyl isocyanate, 4461-33-0; *p*-chlorobenzoyl isocyanate, 4461-36-3; trichloroacetyl isocyanate, 3019-71-4; *p*-toluenesulfonyl isocyanate, 4083-64-1; *N*-chlorosulfonyl isocyanate, 1189-71-5; acetyl isothiocyanate, 13250-46-9.

## 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) abstracted in part from the Ph.D. Thesis of J.B., 1973; (c) NSF Trainee.
(2) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes", Academic Press, New York, N.Y., 1967.
(3) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, **39**, 3619 (1974).
(4) H. Gotthardt and R. Huisgen, *Chem. Ber.*, **103**, 2625 (1970); R. Knorr, R. Huisgen and G. K. Staudinger, *ibid.*, **103**, 2639 (1970).
(5) K. T. Potts, E. Houghton, and U. P. Singh, *J. Org. Chem.*, **39**, 3627 (1974).
(6) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 3492 (1963).
(7) K. T. Potts and R. Armbruster, *J. Org. Chem.*, **36**, 1846 (1971); R. Hull, *J. Chem. Soc. C*, 1777 (1968).
(8) K. T. Potts and S. Husain, *J. Org. Chem.*, **37**, 2049 (1972).
(9) N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960).
(10) G. Bergson and A. L. Delin, *Ark. Kemi*, **18**, 489 (1962).
(11) R. Appel and H. Rittersbacher, *Chem. Ber.*, **97**, 852 (1964).
(12) G. V. Boyd and A. J. H. Summers, *J. Chem. Soc. B*, 1648 (1971); H. J. Timpe, *Adv. Heterocycl. Chem.*, **17**, 213 (1975).
(13) K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, **39**, 3631 (1974).
(14) D. A. Peak and F. Stansfield, *J. Chem. Soc.*, 4067 (1952).
(15) M. T. W. Hearn and K. T. Potts, *J. Chem. Soc., Perkin Trans. 2*, 875 (1974).
(16) T. Shiba and H. Kato, *Bull. Chem. Soc. Jpn.*, **43**, 3941 (1970).
(17) K. T. Potts and M. Sorm, *J. Org. Chem.*, **37**, 1422 (1972).
(18) We are indebted to Dr. U. P. Singh for this experiment.
(19) Spectral characterizations were carried out with the following instrumentation: ir, Perkin Elmer Model 337 infrared spectrophotometer; uv, Cary Model 14 spectrophotometer; NMR, Varian A-60, T-60, and HA-100 spectrometers using $Me_4Si$ 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, Knoxville, Tenn., and Instranal Laboratories, Inc., Rensselaer, N.Y.
(20) A. Takamizawa, K. Hirai, and K. Matsui, *Bull. Chem. Soc. Jpn.*, **36**, 1214 (1963).
(21) H. Meerwein, *Org. Synth.*, **46**, 113 (1966).
(22) J. O'Brien and C. Niemann, *J. Am. Chem. Soc.*, **79**, 84 (1957).
(23) Criteria used for establishing identity were superimposable infrared spectra, no depression in mixture melting point, and identical $R_f$ values.

# Mesoionic Compounds. XXXVI. Reaction of Mesoionic Systems with Diphenylcyclopropene Derivatives[1]

K. T. Potts,* J. Baum, and E. Houghton

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

*Received June 3, 1975*

*anhydro*-2,3-Diphenyl-4-hydroxythiazolium hydroxide and diphenylcyclopropenone at 80° gave a 1:1 cycloadduct shown to be 2,3,5,6-tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4,7-dione which, on thermolysis, lost the elements of COS forming 1,4,5,6-tetraphenyl-2(1*H*)-pyridone. With diphenylcyclopropenethione at room temperature the corresponding 7-oxo-2,3,5,6-tetraphenyl-6-aza-8-thiabicyclo[3.2.1]oct-2-ene-4-thione was formed which, on thermolysis, gave 3,4,6-triphenyl-2*H*-thiopyran-2-thione and 4-oxo-2,3,6,7-tetraphenyl-2*H*-1,3-thiazocinium 8-thiolate. *anhydro*-2-*p*-Chlorophenyl-4-hydroxy-3-phenylthiazolium hydroxide gave an analogous series of *p*-chlorophenyl substituted products. *anhydro*-2,4-Diphenyl-5-hydroxy-3-methyl-1,3-oxazolium hydroxide, generated in situ from *N*-benzoyl-*N*-methyl-*C*-phenylglycine and $Ac_2O$, and diphenylcyclopropenone gave 1-methyl-2,3,5,6-tetraphenyl-4(1*H*)-pyridone, and the corresponding thione was formed with diphenylcyclopropenethione. Reaction with 1,2,3-triphenylcyclopropene gave 1-methyl-2,3,4,5,6-pentaphenyl-1,4-dihydropyridine. *anhydro*-5-Hydroxy-3-methyl-2-phenylthiazolium hydroxide and diphenylcyclopropenethione underwent reaction at room temperature giving 1-methyl-2,3,5-triphenyl-4(1*H*)-pyridinethione, whereas with diphenylcyclopropenone no reaction occurred. Chemical and spectral evidence used to establish these structures is described.

In the short time since the initial synthesis[2] of diphenylcyclopropenone, it has found applications as a versatile intermediate in organic synthesis.[3] As would be anticipated from its physical characteristics, it is a particularly interesting substrate in cycloaddition reactions and this property is shared to some degree by its thio analogue. Cycloadducts have been formed with carbonyl ylides,[4] heteroaromatic ring systems such as pyridine, pyridazine, etc.,[5] some 1,3-dipolar systems,[6] and also with enamines and other electron-rich olefinic systems.[7] Recently 1-azirines were