References and Notes

(1) (a) Partial support of this work by USPHS Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) abstracted from the Ph.D. Thesis of S. J. Chen, 1976.
(2) K. T. Potts, S. J. Chen, J. Kane, and J. L. Marshall, *J. Org. Chem.*, preceding paper in this issue.
(3) (a) A. Lawson and D. H. Miles, *J. Chem. Soc.*, 2865 (1959); (b) E. B. Roche and D. W. Stansloski, *J. Heterocycl. Chem.*, **7**, 139 (1970). See also M. J. S. Dewar and I. J. Turchi, *J. Chem. Soc., Perkin Trans. 2*, 548 (1976).
(4) K. T. Potts and S. Husain, *J. Org. Chem.*, **36**, 3368 (1971).
(5) R. Huisgen, E. Funke, F. C. Schaefer, H. Gotthardt, and E. Brunn, *Tetrahedron Lett.*, 1809 (1967).
(6) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, **39**, 3619 (1974).
(7) T. Shiba and H. Kato, *Bull. Chem. Soc. Jpn.*, **43**, 3941 (1970).
(8) G. Singh and P. S. Pande, *Tetrahedron Lett.*, 2169 (1974).
(9) M. Hamaguchi and T. Ibata, *Chem. Lett.*, 169 (1975).
(10) (a) E. Fischer and J. Schmidlin, *Justus Liebigs Ann. Chem.*, **340**, 19 (1905); (b) H. Staudinger and H. Becker, *Ber.*, **50**, 1076 (1917); D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 2186 (1944); G. T. Morgan and E. Walton, *J. Chem. Soc.*, 1744 (1931).
(11) H. Meerwein, *Org. Synth.*, **46**, 113 (1966).
(12) G. A. Holmberg, *Fin. Kemistsam. Medd.*, **59**, 25 (1950); *Chem. Abstr.*, **46**, 8651 (1952).
(13) P. Ruggli and R. Grand, *Helv. Chim. Acta*, **20**, 373 (1937).
(14) W. Reeve and E. Barron, *J. Org. Chem.*, **34**, 1005 (1969).
(15) (a) J. Nematollahi and R. Ketcham, *J. Org. Chem.*, **28**, 2378 (1963); (b) J. F. Klebe and H. Finkbeiner, *J. Am. Chem. Soc.*, **90**, 7255 (1968). We would like to express our thanks to Dr. H. Finkbeiner, General Electric Corporate Research and Development Center, for an authentic sample of this compound.
(16) A. C. Hontz and E. C. Wagner, *Org. Synth.*, **31**, 48 (1951).
(17) M. S. Saettone, *J. Org. Chem.*, **31**, 1959 (1966).
(18) H. Finkbeiner, *J. Org. Chem.*, **30**, 3414 (1965).
(19) H. Bredereck and K. Bredereck, *Chem. Ber.*, **94**, 2278 (1961).
(20) K. T. Potts and S. J. Chen, unpublished results.
(21) For a recent summary of this topic see M. P. Cava and M. V. Lakshmikantham, *Acc. Chem. Res.*, **8**, 139 (1975).
(22) Spectral characterizations were carried out as in preceding papers in this series.
(23) J. N. Baxter, J. Cymerman-Craig, M. Moyle, and R. A. White, *J. Chem. Soc.*, 659 (1956); W. G. Finnegan, F. A. Henry, and E. Lieber, *J. Org. Chem.*, **18**, 779 (1953).

Mesoionic Compounds. 41. *anhydro*-4-Hydroxy-2,3,5-trisubstituted-1,3-selenazolium Hydroxides and *anhydro*-4-Hydroxy-6-oxo-2,3,5-trisubstituted-4*H*-1,3-selenazinium Hydroxides

Kevin T. Potts,* Frank Huang, and Rangin K. Khattak

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

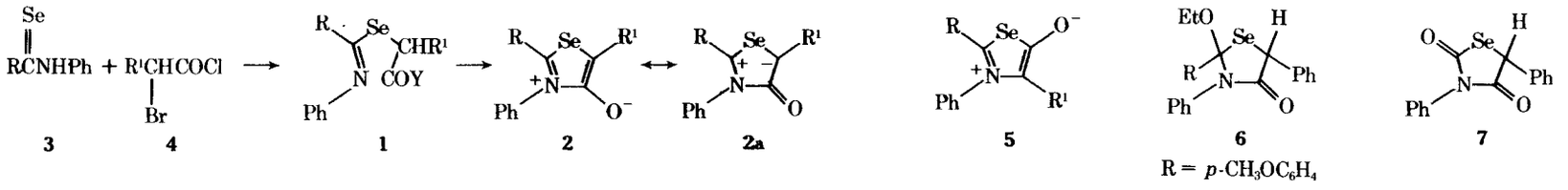
Received July 27, 1976

Reaction of a variety of monoprotonic selenoamide derivatives with 1,2-bielectrophiles such as α-bromophenylacetyl chloride and 2-bromo-2-ethoxycarbonylacetyl chloride gave representatives of the *anhydro*-4-hydroxy-1,3-selenazolium hydroxide mesoionic ring system possessing varying degrees of stability. These reacted with dimethyl acetylenedicarboxylate giving the corresponding pyridones with extrusion of selenium from the initial 1:1 adduct, a reaction pathway in contrast to the correspondingly substituted sulfur system where thiophene derivatives were usually formed. With phenyl isothiocyanate, selenium was also extruded from the initial 1:1 adduct leading to the *anhydro*-4-mercapto-6-oxopyrimidinium hydroxide system, the first example of the conversion of a five-membered mesoionic ring system into a six-membered mesoionic system. With chlorocarbonylphenylketene, the selenoamides readily formed the *anhydro*-4-hydroxy-6-oxo-4*H*-1,3-selenazinium hydroxide system.

In the two preceding papers in this series,[2] the introduction of various functional groups into several five-membered mesoionic ring systems was readily achieved by variation of both the 1,3-binucleophilic component of the reaction system and its 1,2-bielectrophilic counterpart, making this general procedure the one of choice for the synthesis of these ring systems. Extension of this method to selenium-containing 1,3-binucleophiles now provides a convenient synthesis of several endocyclic selenium mesoionic systems whose physical and chemical characteristics are described below.

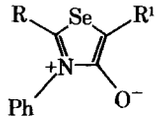
The only example of a selenium-containing mesoionic ring system with an endocyclic selenium atom is *anhydro*-4-hydroxy-2,3,5-triphenyl-1,3-selenazolium hydroxide (**2**, R = R^1 = Ph), which was prepared[3] recently by dehydrative cyclization of the appropriate α-seleno acid (**1**, R = R^1 = Ph; Y = OH) with Ac_2O/Et_3N. Our studies, commenced prior to this report, have also focused in part on this ring system as the selenocarbonyl dipole represented by **2a** would be expected to influence the ability of the ring system to undergo a variety of 1,3-dipolar cycloadditions with dipolarophiles and a comprehensive study of the synthesis and reactions of this ring system is thus of particular interest. The utility of the corresponding sulfur-containing ring system in cycloadditions and as a source of other heterocycles is now well established[4] and the lesser stability of the C–Se bond compared to the C–S bond[5] suggested that the reactions of the ring system **2** would show a surprising individuality.

Synthesis. The requisite selenium-containing 1,3-binucleophiles have all been described in the literature[6] and, by the use of the appropriate selenoamide derivatives, it was possible to introduce aryl, alkylthio, and disubstituted amino substituents into the 2 position of **2**. Thus selenoanisanilide (**3**, R = *p*-$CH_3OC_6H_4$), prepared from *N*-phenylanisimidoyl chloride and sodium hydroselenide,[7] and α-bromophenylacetyl chloride (**4**, R^1 = Ph) in anhydrous benzene in the presence of Et_3N gave *anhydro*-3,5-diphenyl-4-hydroxy-2-*p*-methoxyphenyl-1,3-selenazolium hydroxide (**2**, R = *p*-$CH_3OC_6H_4$; R^1 = Ph) as deep-red needles (Table I). It is logical to assume that the intermediate **1** (R = *p*-$CH_3OC_6H_4$; R^1 = Ph; Y = Cl), or the ketene derived from it, was involved in the reaction and that the product formed was not the isomeric system **5**. This was confirmed by ring closure of the acid **1** (R = *p*-$CH_3OC_6H_4$; R^1 = Ph; Y = OH), prepared[3] from selenoanisanilide and α-bromophenylacetic acid, with Ac_2O/Et_3N. Attempted recrystallization of **2** (R = *p*-$CH_3OC_6H_4$; R^1 = Ph) resulted in decomposition and, on warming with ethanol, addition of a molecule of ethanol occurred across the 2,5 positions of the system giving 3,5-diphenyl-2-ethoxy-2-*p*-methoxyphenylselenazolidin-4-one (**6**). This reaction is similar to that occurring when 1,3,4-oxadiazolium salts are treated



3 4 1 2 2a 5 6 7

Table I. *anhydro*-2,5-Disubstituted-4-hydroxy-3-phenyl-1,3-selenazolium Hydroxides[e]



Substituents			Yield,			$M^{+\cdot}$	Spectral data		
R	R^1	Mp, °C	%	Crystal habit[a]	Mol formula	(rel int)	λ_{max}, nm (log ϵ)	ν_{CO} (KBr)	NMR, δ ($CDCl_3$)
p-$CH_3OC_6H_4$	Ph	195–197[b]	80	Deep-red needles: A	$C_{22}H_{17}NO_2Se$		510 (4.07), 290 (4.19)[c]	1610	3.7 (s, 3, OCH_3), 6.6–8.1 (m, 4, aromatic)
EtS	Ph	136–138	31	Yellow-orange irreg prisms: A	$C_{17}H_{15}NOSSe$		480 (3.82), 283 (4.05)[d]	1620	1.4 (t, 3, CH_3), 3.1 (q, 2, CH_2), 7.2–7.8 (m, 10, aromatic)
CH_3S	Ph	129–131[b]	43	Red prisms: A	$C_{16}H_{13}NOSSe$	347 (0.5)	480 (3.84), 283 (4.08)[d]	1685	2.63 (s, 3, CH_3), 6.97–8.87 (m, 10, aromatic)
CH_3S	COOEt	153–155	33	Yellow, irreg prisms: B	$C_{13}H_{13}NO_3SSe$	343 (2)	408 (3.78), 245 (4.11)[d]	1700 1625	1.32 (t, 3, CH_2CH_3), 2.70 (s, 3, CH_3), 4.27 (q, 2, CH_2CH_3), 7.10–7.70 (m, 5, aromatic)
EtS	COOEt	154–156[b]	56	Yellow needles: C	$C_{14}H_{15}NO_3SSe$	357 (0.1)	410 (4.85), 243 (4.11)[d]	1670 1620	1.25 (t, 3, SCH_2CH_3), 1.50 (t, 2, $CO_2CH_2CH_3$), 3.22 (q, 2, SCH_2CH_3), 4.30 (q, 2, CO_2CH_2-CH_3), 7.12–7.67 (m, 5, aromatic)
$(CH_3)_2N$	Ph	145–150	22	Yellow, irreg prisms: A	$C_{17}H_{16}N_2OSe$			1625	2.7 [s, 6, $(CH_3)_2N$], 6.8–7.7 (s, 10, aromatic)

[a] Recrystallization solvents: A, not recrystallized; B, $CHCl_3/Et_2O$; C, benzene. [b] Decomposition. [c] CH_3CN. [d] $CHCl_3$. [e] Satisfactory analytical values (±0.4% for C, H, N) were reported for all compounds in table.

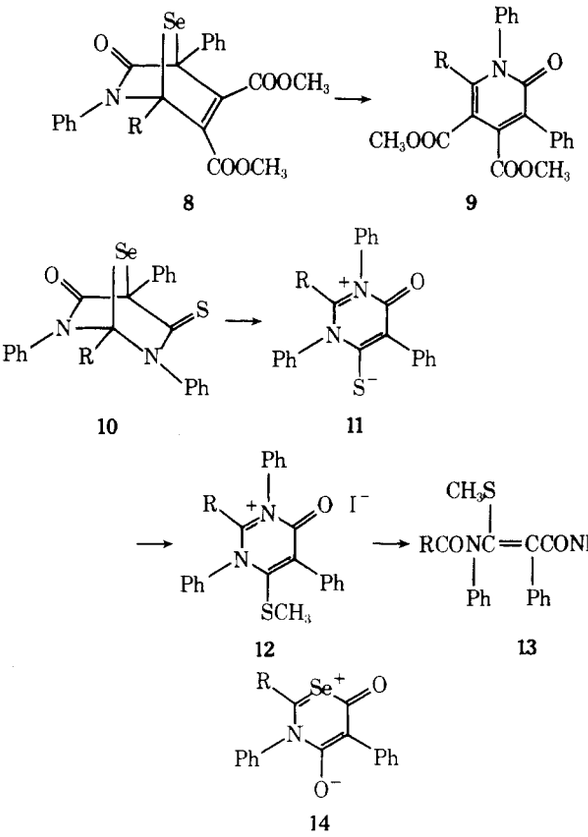
with nucleophiles such as sodium ethoxide.[8] Similarly reaction of *S*-methyl-*N*-phenylselenothiocarbamate[9] (**3**, R = CH_3S) with α-bromophenylacetyl chloride (**4**, R^1 = Ph) in anhydrous ether in the presence of Et_3N (2 mol) gave the corresponding 2-methylthio product **2** (R = CH_3S; R^1 = Ph). This product was sensitive to moisture and underwent decomposition on standing over several days; in water ready hydrolysis occurred giving 3,5-diphenyl-1,3-selenazolidine-2,4-dione (**7**). Use of 2-bromo-2-ethoxycarbonylacetyl chloride (**4**, R^1 = COOEt) in the reaction with **3** (R = CH_3S) gave *anhydro*-5-ethoxycarbonyl-4-hydroxy-2-methylthio-3-phenyl-1,3-selenazolium hydroxide (**2**, R = CH_3S; R^1 = COOEt). The introduction of the 5-ethoxycarbonyl substituent resulted in a considerably more stable product that did not undergo decomposition on standing.

The preparation of the corresponding 2-ethylthio derivative of **2** (R = EtS; R^1 = Ph) was more satisfactorily accomplished by Ac_2O/Et_3N (1:1) cyclization of **1** (R = EtS; R^1 = Ph; Y = OH), prepared from **3** (R = EtS) and α-bromophenylacetic acid. Although the 2-ethylthio product decomposed on attempted recrystallization, it was sufficiently stable to be handled conveniently, and underwent cycloaddition with dimethyl acetylenedicarboxylate as described below. Reaction of **3** (R = EtS) with 2-bromo-2-ethoxycarbonylacetyl chloride (**4**, R^1 = COOEt) gave the corresponding 5-ethoxycarbonyl derivative **2** (R = EtS; R^1 = COOEt) directly, the 5-ethoxycarbonyl substituent again imparting stability to the system.

Reaction of 1,1-dimethylamino-3-phenyl-2-selenourea[9] [**3**, R = $(CH_3)_2N$] and α-bromophenylacetyl chloride in benzene/Et_3N readily gave the corresponding *anhydro*-2-dimethylamino-3,5-diphenyl-4-hydroxy-1,3-selenazolium hydroxide [**2**, R = $(CH_3)_2N$; R^1 = Ph] which was sufficiently stable to moisture for isolation but which underwent decomposition on standing and heating.

The spectral characteristics shown in Table I, together with the syntheses described above, strongly support the assigned structure **2**. It was possible to eliminate structure **5** from consideration by studying the reaction of these selenazolium derivatives with dimethyl acetylenedicarboxylate and phenyl isothiocyanate. With the former, the selenazolium hydroxide **2** (R = *p*-$CH_3OC_6H_4$; R^1 = Ph) in refluxing benzene over 10 h in the dark gave dimethyl 1,3-diphenyl-6-(*p*-methoxyphenyl)-2-oxopyridine-4,5-dicarboxylate (**9**, R = *p*-$CH_3OC_6H_4$), the intermediate **8** (R = *p*-$CH_3OC_6H_4$) decomposing by elimination of selenium. This is in contrast[4a] to the corresponding sulfur-containing mesoionic system in which the corresponding intermediate **8** undergoes elimination of phenyl isocyanate with the formation of a tetrasubstituted thiophene. No doubt the ease of elimination of selenium is the guiding force in this present reaction. A similar ready loss of selenium was also reported[3] in the reaction of **2** (R = R^1 = Ph) with dimethyl acetylenedicarboxylate. Similarly **2** (R = EtS; R^1 = Ph) and dimethyl acetylenedicarboxylate in boiling benzene gave dimethyl 1,3-diphenyl-2-oxo-6-ethylthiopyridine-4,5-dicarboxylate (**9**, R = EtS). In several other representatives of **2** studied, the thermal stability of the ring system was such that decomposition occurred before significant cycloaddition was realized. Should the structure of these derivatives be represented by the ring system **5**, then under these reaction conditions pyrrole derivatives would be anticipated, formed by elimination of COSe from the initial 1:1 cycloadduct.[10]

Interconversions of five-membered mesoionic ring systems are now well established, thermal,[11] hydrolytic,[12] and reactions of the mesoionic system with heterocumulenes[10,13] having all been reported. Conversion of a five-membered mesoionic system into a six-membered mesoionic system has not yet been accomplished and the ready loss of selenium from the



intermediate **8** suggested that it would also be readily extruded from **10** (R = *p*-$CH_3OC_6H_4$), the 1:1 adduct formed from **2** (R = *p*-$CH_3OC_6H_4$; R^1 = Ph) and phenyl isothiocyanate. This was found to be the case when **2** (R = *p*-$CH_3OC_6H_4$; R^1 = Ph) and phenyl isothiocyanate were refluxed in xylene over 72 h, *anhydro*-1,3-diphenyl-4-mercapto-2-*p*-methoxyphenyl-6-oxopyrimidinium hydroxide (**11**, R = *p*-$CH_3OC_6H_4$) being obtained in 66% yield. This pyrimidinium derivative reacted with methyl iodide giving the corresponding salt **12** (R = *p*-$CH_3OC_6H_4$) and on heating the iodide with aqueous ethanol, hydrolytic ring opening occurred giving **13** (R = *p*-$CH_3OC_6H_4$). This represents a very convenient synthesis of the mesoionic ring system **11** which cannot be made easily by direct synthesis. The corresponding *anhydro*-4-hydroxy-6-oxopyrimidinium hydroxide system is readily available by reaction of monoprotonic amidines with carbon suboxide or chlorocarbonylphenylketene but its reaction with phenyl isothiocyanate resulted in thermal rearrangement occurring under the high temperatures involved.[14]

Replacement of the 1,2-bielectrophile in the reaction with selenoamide derivatives with a 1,3-bielectrophile such as chlorocarbonylphenylketene should provide a convenient synthesis of six-membered mesoionic systems containing selenium. This reaction, analogous to the formation of the *anhydro*-4-hydroxy-6-oxo-4*H*-1,3-thiazinium hydroxide system[15] from thioamides and chlorocarbonylphenylketene,[16] occurred readily when the ketene and *N*-phenyl *S*-methylselenothiocarbamate (**3**, R = CH_3S) were mixed in anhydrous ether at room temperature, *anhydro*-3,5-diphenyl-4-hydroxy-2-methylthio-6-oxo-4*H*-1,3-selenazinium hydroxide (**14**, R = CH_3S) being obtained in 53% yield. The corresponding 2-ethylthio product (**14**, R = EtS) was similarly formed from **3** (R = EtS) and the ketene. Both products decomposed on attempted recrystallization but could be obtained in an analytical pure form as described in the Experimental Section. They were considerably less stable than their corresponding sulfur analogues and decomposed on standing over several weeks.

Experimental Section[17]

General Procedures for the Preparation of 2. A. Formation of *anhydro*-3,5-Diphenyl-4-hydroxy-2-*p*-methoxyphenyl-1,3-selenazolium Hydroxide (2, R = *p*-$CH_3OC_6H_4$; R^1 = Ph). A mixture of selenoanisanilide (0.258 g, 0.0009 mol) in dry benzene (35 mL) and α-bromophenylacetyl chloride[18] (0.21 g, 0.0009 mol) was stirred together for 30 min. The yellow precipitate was suspended in anhydrous Et_2O (30 mL) and Et_3N (0.18 g, 0.002 mol) was added, the color of the reaction mixture turning violet and deep-red crystals soon separating. These were collected, washed with H_2O, EtOH, and Et_2O, and dried in vacuo; an additional crop of deep-red needles separated from the filtrate, 0.30 g (90%), mp 195–197 °C dec (Table I).

B. *anhydro*-5-Ethoxycarbonyl-4-hydroxy-2-methylthio-3-phenyl-1,3-selenazolium Hydroxide (2, R = CH_3S; R^1 = COOEt). A solution of 2-bromo-2-ethoxycarbonylacetyl chloride[19] (0.46 g, 0.002 mol) in anhydrous ether (10 mL) was added to a solution of *S*-methyl *N*-phenylselenothiocarbamate[9] (0.46 g, 0.002 mol) in anhydrous ether (25 mL) and the mixture stirred at room temperature under N_2 for 10 min. Et_3N (0.202 g, 0.002 mol) was added and stirring continued for an additional 1.5 h. The resulting mixture was extracted with hot benzene and, after concentration and cooling, yellow needles separated, 0.8 g (56%), mp 154–156 °C dec. Alternatively the initial yellow precipitate may be separated and resuspended in anhydrous Et_2O before addition of Et_3N (Table I).

Cycloaddition with Dimethyl Acetylenedicarboxylate. Preparation of Dimethyl 1,3-Diphenyl-2-oxo-6-ethylthiopyridine-4,5-dicarboxylate (9, R = EtS). *anhydro*-3,5-Diphenyl-4-hydroxy-2-ethylthio-1,3-selenazolium hydroxide (0.5 g, 0.0012 mol) and the ester (0.4 g, 0.003 mol) in dry benzene (25 mL) were refluxed for 72 h, the initial orange-red color of the reaction mixture disappearing in 10 h. After filtration of the reaction mixture, the solvent was concentrated in vacuo and the initial precipitate of amorphous selenium (0.1 g, 90%) was removed. Complete evaporation of the solvent gave a solid residue which was washed with hexane and then recrystallized from $CHCl_3$/hexane forming off-white coral-shaped crystals: mp 128–129 °C; IR (KBr) ν_{CO} 1760, 1730, 1655 cm^{-1}; NMR ($CDCl_3$) δ 1.06 (t, 3, SCH_2CH_3), 2.6 (q, 2, SCH_2CH_3), 3.65 (s, 3, OCH_3), 3.8 (s, 3, OCH_3), 7.35 (m, 10, aromatic); mass spectrum *m/e* (rel intensity) M^+· 423 (70).

Anal. Calcd for $C_{23}H_{21}NSO_5$: C, 65.25; H, 4.96; N, 3.31. Found: C, 64.90; H, 4.97; N, 3.42.

In the preparation of the corresponding 5-*p*-methoxyphenylpyridone (9, R = *p*-$CH_3OC_6H_4$), purification was effected by chromatography on silica gel after removal of the selenium. Dimethyl 1,3-diphenyl-6-*p*-methoxyphenyl-2-oxopyridine-4,5-dicarboxylate (9, R = *p*-$CH_3OC_6H_4$) crystallized from chloroform/hexane as colorless needles: 35%; mp 230–231 °C; λ_{max} ($CHCl_3$) 355 nm (log ε 3.51); IR (KBr) ν_{CO} 1740, 1730, 1660, 1610 cm^{-1}; NMR ($CDCl_3$) δ 3.45 (s, 3, CO_2CH_3), 3.6 (s, 3, CO_2CH_3), 3.7 (s, 3, OCH_3), 6.8–7.5 (m, 14, aromatic); mass spectrum *m/e* (rel intensity) M^+· 469 (40).

Anal. Calcd for $C_{28}H_{23}NO_6$: C, 71.63; H, 4.94; N, 2.98. Found: C, 71.27; H, 4.83; N, 2.95.

3,5-Diphenyl-2-ethoxy-2-*p*-methoxyphenyl-1,3-selenazolidin-4-one (6). The mesoionic system 2 (R = *p*-$CH_3OC_6H_4$; R^1 = Ph) (0.10 g, 0.0003 mol) was refluxed in ethanol (25 mL) for 1 h. After concentrating to 10 mL and standing at 0 °C overnight, a pink product was obtained. It crystallized from ethanol/petroleum ether (bp 40–60 °C) as needles with a slight pink color: 0.32 g (28%); mp 190–191 °C; IR (KBr) ν_{CO} 1675 cm^{-1}.

Anal. Calcd for $C_{24}H_{23}NSeO_3$: C, 63.86; H, 5.10; N, 3.10. Found: C, 63.68; H, 5.14; N, 3.01.

Hydrolysis of *anhydro*-3,5-Diphenyl-4-hydroxy-2-methylthio-1,3-selenazolium Hydroxide (2, R = CH_3S; R^1 = Ph). *S*-Methyl *N*-phenylselenothiocarbamate (0.690 g, 0.003 mol) in $CHCl_3$ (25 mL) was treated with α-bromophenylacetyl chloride (0.704 g, 0.003 mol). After 10 min at room temperature, Et_3N (0.61 g, 0.006 mol) was added and the reaction mixture stirred for an additional 10 min. The reaction mixture was washed twice with H_2O (25 mL) and the $CHCl_3$ solution dried ($MgSO_4$). On concentration of the solvent a product separated and 3,5-diphenyl-1,3-selenazolidine-2,4-dione crystallized from $CHCl_3$/Et_2O as colorless needles: 0.31 g (33%); mp 168–170 °C; IR (KBr) ν_{CO} 1740, 1675 cm^{-1}; λ_{max} (CH_3OH) 265 nm (log ε 3.54), 220 (3.84); NMR ($CDCl_3$) δ 5.63 (s, 1, CH), 7.33–7.57 (m, 10, aromatic); mass spectrum *m/e* (rel intensity) M^+· 317 (29).

Anal. Calcd for $C_{15}H_{11}NO_2Se$: C, 56.97; H, 3.51; N, 4.43. Found: C, 56.78; H, 3.58; N, 4.39.

***anhydro*-1,3-Diphenyl-4-mercapto-2-*p*-methoxyphenyl-6-oxopyrimidinium Hydroxide (11, R = *p*-$CH_3OC_6H_4$).** A mixture of *anhydro*-3,5-diphenyl-4-hydroxy-2-*p*-methoxyphenyl-1,3-selenazolium hydroxide (2, R = *p*-$CH_3OC_6H_4$; R^1 = Ph) (1.0 g, 0.003 mol) and phenyl isothiocyanate (0.54 g, 0.004 mol) in dry xylene (30 mL) was refluxed for 72 h, the initial violet color of the reaction mixture turning brown during this time. On cooling a yellow, crystalline product mixed with selenium separated. This was dissolved in $CHCl_3$, the selenium separated, and, after removal of the $CHCl_3$, the residue was recrystallized from benzene forming yellow needles: 0.75 g (66%); mp 275–276 °C; IR (KBr) ν_{CO} 1675 cm^{-1}; λ_{max} (CH_3CN) 325 nm (log ε 4.02), 270 (4.09); NMR ($CDCl_3$) δ 3.6 (s, 3, OCH_3), 6.5–7.6 (m, 19, aromatic); mass spectrum *m/e* (rel intensity) M^+· 462 (22).

Anal. Calcd for $C_{29}H_{22}N_2O_2S$: C, 75.31; H, 4.80; N, 6.06. Found: C, 75.41; H, 4.85; N, 6.00.

The methiodide of 11 (R = *p*-$CH_3OC_6H_4$; R^1 = Ph) was prepared by refluxing with an excess of CH_3I in dry benzene for 3 h. The product separated from the cooled solution and crystallized from acetone as yellow needles: 0.15 g (62%); mp 272–274 °C; IR (KBr) ν_{CO} 1725 cm^{-1}; NMR ($CDCl_3$) δ 1.9 (s, 3, SCH_3), 3.64 (s, 3, OCH_3), 6.5–8.3 (m, 19, aromatic).

Anal. Calcd for $C_{30}H_{25}IN_2O_2S$: C, 59.60; H, 4.14; N, 4.63. Found: C, 59.53; H, 4.10; N, 4.52.

Hydrolysis of 2-*p*-Methoxyphenyl-4-methylthio-6-oxo-1,3,5-triphenylpyrimidinium Iodide (12, R = *p*-$CH_3OC_6H_4$). The iodide was refluxed in 95% EtOH for 1 h. The product that separated on cooling crystallized from EtOH as colorless prisms: mp 154–155 °C; IR (KBr) ν_{NH} 3340, ν_{CO} 1670 cm^{-1}; NMR ($CDCl_3$) δ 2.19 (s, 3, SCH_3), 3.7 (s, 3, OCH_3), 6.5–7.7 (m, 20, aromatic and NH).

Anal. Calcd for $C_{30}H_{26}N_2O_3S$: C, 72.87; H, 5.26; N, 5.66. Found: C, 72.93; H, 5.45; N, 5.51.

***anhydro*-3,5-Diphenyl-4-hydroxy-2-methylthio-6-oxo-4*H*-1,3-selenazinium Hydroxide (14, R = CH_3S).** Chlorocarbonylphenylketene (0.18 g, 0.001 mol) in anhydrous Et_2O (5 ml) was added to *S*-methyl *N*-phenylselenothiocarbamate (3, R = CH_3S) (0.23 g, 0.001 mol) in anhydrous Et_2O (25 mL). After stirring at room temperature under N_2 for 1 h, the product was collected and washed with anhydrous Et_2O, giving orange, irregular prisms: 0.2 g (53%); mp 96–98 °C dec; IR (KBr) ν_{CO} 1675, 1615 cm^{-1}; λ_{max} ($CHCl_3$) 325 nm (log ε 4.02), 247 sh (4.12); NMR ($CDCl_3$) δ 2.58 (s, 3, CH_3), 7.10–7.70 (m, 10, aromatic).

Anal. Calcd for $C_{17}H_{13}NO_2SSe$: C, 54.55; H, 3.50; N, 3.74. Found: C, 54.15; H, 3.66; N, 3.75.

The corresponding 2-ethylthio product (14, R = EtS) was also obtained as orange, irregular prisms: 62%; mp 128–130 °C dec; IR (KBr) ν_{CO} 1670, 1610 cm^{-1}; λ_{max} ($CHCl_3$) 332 nm (log ε 3.85), 270 (3.89); NMR ($CDCl_3$) δ 1.27 (t, 3, CH_3), 2.95 (q, 2, CH_2), 7.03–7.66 (m, 10, aromatic).

Anal. Calcd for $C_{18}H_{15}NO_2SSe$: C, 55.52; H, 3.88; N, 3.60. Found: C, 55.45; H, 4.10; N, 3.85.

Registry No.—**2** (R = *p*-$CH_3OC_6H_4$; R′ = Ph), 61521-79-7; **2** (R = EtS; R′ = Ph), 61521-80-0; **2** (R = CH_3S; R′ = Ph), 61521-81-1; **2** (R = CH_3S; R′ = COOEt), 61521-82-2; **2** (R = EtS; R′ = COOEt), 61521-83-3; **2** (R = $(CH_3)_2N$; R′ = Ph), 61521-84-4; **3** (R = *p*-$CH_3OC_6H_4$), 61521-85-5; **3** (R = CH_3S), 21347-34-2; **3** (R = $(CH_3)_2N$), 21347-32-0; **3** (R = EtS), 61521-86-6; **4** (R′ = Ph), 19078-72-9; **4** (R′ = COOEt), 41141-81-5; **6** (R = *p*-$CH_3OC_6H_4$), 61521-87-7; **7**, 61521-88-8; **9** (R = EtS), 61521-89-9; **9** (R = *p*-$CH_3OC_6H_4$), 61521-90-2; **11** (R = *p*-$CH_3OC_6H_4$), 61521-91-3; **12** (R = *p*-$CH_3OC_6H_4$), 61521-92-4; **13** (R = *p*-$CH_3OC_6H_4$), 61521-93-5; **14** (R = CH_3S), 61521-94-6; **14** (R = EtS), 61521-95-7; phenyl isothiocyanate, 103-72-0; CH_3I, 74-88-4; chlorocarbonylphenylketene, 17118-70-6.

References and Notes

(1) Partial support of this work by U.S. public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged.
(2) K. T. Potts and S. J. Chen, *J. Org. Chem.*, preceding paper in this issue; K. T. Potts, S. C. Chen, J. Kane, and J. L. Marshall, *ibid.*, accompanying paper is this issue.
(3) M. P. Cava and L. E. Saris, *J. Chem. Soc., Chem. Commun.*, 617 (1975).
(4) (a) K. T. Potts, E. Houghton, and U. P. Singh, *J. Org. Chem.*, **39**, 3627 (1974); (b) K. T. Potts, J. Baum, and E. Houghton, *ibid.*, **39**, 3631 (1974); (c) K. T. Potts, J. Baum, S. K. Datta, and E. Houghton, *ibid.*, **41**, 813 (1976).
(5) See, e.g., D. L. Klayman and W. H. H. Gunther, Ed., "Organic Selenium Compounds: Their Chemistry and Biology", Wiley-Interscience, New York, N.Y., 1973.
(6) Reference 5, Chapter VIII, contains a survey of this general area.
(7) E. L. Holljes and E. C. Wagner, *J. Org. Chem.*, **9**, 43 (1944); E. Bennett and R. Zingaro, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 359.
(8) G. V. Boyd and A. J. H. Summers, *Chem. Commun.*, 549 (1968).
(9) D. L. Klayman and R. J. Shine, *J. Org. Chem.*, **34**, 3549 (1969).
(10) Cf. with, e.g., K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, **39**, 3619 (1974).
(11) P. N. Preston, K. K. Tiwari, K. Turnbull, and T. J. King, *J. Chem. Soc., Chem.*

Commun., 343 (1976).
(12) A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 627 (1974); W. D. Ollis and C. A. Ramsden, *Ibid.*, 638 (1974); R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *J. Chem. Soc. Chem. Commun.*, 406, 307 (1976).
(13) H. Kato, S. Sato and M. Ohta, *Tetrahedron Lett.*, 4261 (1967); R. Huisgen, E. Funke, F. C. Schaefer, H. Gotthardt, and E. Brunn, *Ibid.*, 1809 (1967); W. D. Ollis and C. A. Ramsden, *J. Chem. Soc., Perkin Trans. 1*, 633 (1974).
(14) T. Kappe and R. K. Zadeh, *Synthesis*, 247 (1975).
(15) K. T. Potts, R. Ehlinger, and W. M. Nichols, *J. Org. Chem.*, **40**, 2596 (1975).
(16) S. Nakamshi and K. Butler, *Org. Prep. Proced. Int.*, **7**, 155 (1975).
(17) Spectral characterization of products obtained and experimental parameters used are the same as those described in the preceding papers.
(18) E. Fischer and J. Schmidlin, *Justus Liebigs Ann. Chem.*, **340**, 191 (1905).
(19) H. Staudinger and H. Becker, *Ber.*, **50**, 1016 (1917); D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1286 (1944); G. T. Morgan and E. Walton, *J. Chem. Soc.*, 1743 (1931).

Notes

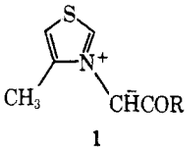
Cycloaddition of *N*-Iminothiazolium Ylides with Acetylenic Dipolarophiles. Formation of Pyrazoles[1]

Kevin T. Potts* and Dilip R. Choudhury

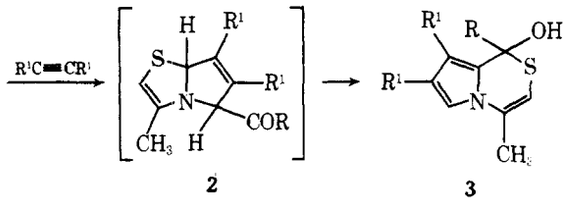
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12181

Received October 25, 1976

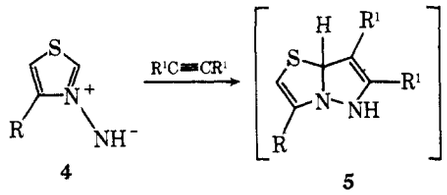
The cycloaddition of ylides derived from suitable heterocycles[2] with acetylenic dipolarophiles provides a convenient method of annelation of a second ring. We have shown[3] recently that in the reaction of the thiazolium ylide **1** with acetylenic dipolarophiles, the initial cycloadduct **2** underwent ready transformation to the 1*H*-pyrrolo[2,1-*c*][1,4]thiazine **3**. The reaction of the corresponding *N*-imino ylide **4** (R = H) with dimethyl acetylenedicarboxylate has been reported[4] to give the 7,9a-dihydrothiazolo[3,2-*b*][1,2]diazepine (**7**, R^1 = $COOCH_3$), a 1:2 adduct whose structure was assigned on the basis of spectral data. However, we have now found that although the data indicate that a 1:2 adduct was formed, rearrangement had occurred during the reaction and the product is the pyrazole **6**.



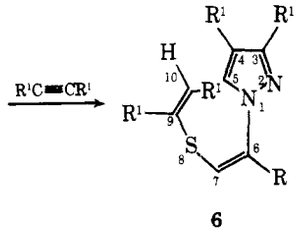
1



2 **3**

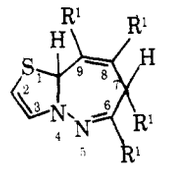


4 **5**

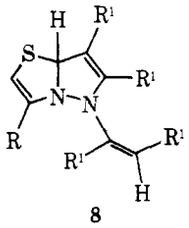


a, R = H; R^1 = $COOCH_3$
b, R = CH_3; R^1 = $COOCH_3$
c, R = CH_3; R^1 = COPh

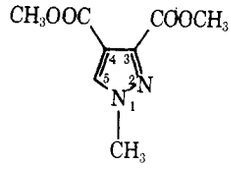
6



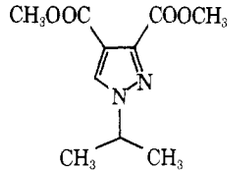
7



8



9



10

The ylide **4** (R = H, CH_3), generated in situ from the corresponding 3-aminothiazolium mesitylsulfonate[4] and NEt_3 (1 equiv) in DMF at room temperature, reacted readily with dimethyl acetylenedicarboxylate (2 equiv). After quenching the reaction from **4** (R = H) with ice–water and purification of the separated product by chromatography on silica gel, colorless needles of the pyrazole **6a** were obtained. Analytical and mass spectral data established the 1:2 composition of this product, and the ^1H NMR (100 MHz) data (Experimental Section) are consistent with this structure. These data are in agreement with those reported earlier for **7** but, rather than being definitive for structure **7**, they are also consistent with both structures **6a** and **8**. In terms of structure **7**, the observed coupling constant (8.0 Hz) between H_2 and H_3 is too large for these protons in a thiazoline ring, this coupling constant normally being ca. 5 Hz.[5] Similarly the chemical shift δ 8.08 of the proton assigned to the bridgehead H_{9a} is at too low a field compared to those observed for protons in an analogous environment.[3] However, structure **6a** readily accommodates the chemical shifts at δ 8.08, 7.02, 6.18, and 6.10 by protons at positions 5, 6, 7, and 10, respectively. The coupling constant $J_{6,7}$ = 8.0 Hz is consistent with maintaining a cis stereochemistry in the intermediate vinyl sulfide formed by fission of the C–S bond in **5**. The chemical shift of H_5 at δ 8.08 is also in agreement with that observed (δ 7.88) for H_5 in dimethyl 1-methylpyrazole-3,4-dicarboxylate (**9**) synthesized[6] from *N*-methylsydnone and dimethyl acetylenedicarboxylate.

^{13}C NMR data[7] provided decisive evidence in support of structure **6** (Table I). The absence of a resonance assignable to an sp^3 bridgehead carbon atom excludes structures **7** and **8**, and the seven sp^2 carbon atoms observed are readily accounted for by structure **6**. Off-resonance decoupling established that four of these carbon atoms bear a hydrogen atom,