A Facile Method for 2-Thiophenacylidenethiazoline Derivatives

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Received September 15, 1992

The reactions of 2-alkyl-5-phenylisothiazole-3-thiones with 2-chloro-1,3-dicarbonyl compounds in chloroform gave the corresponding isothiazolium chlorides which, upon treatment at room temperature with sodium borohydride in a mixture of chloroform and ethanol, underwent S-N bond cleavage to give 3-alkyl-4,5-disubstituted-2-thiophenacylidenethiazolines. Similarly, treatment of the isothiazolium chlorides with triphenylphosphite in chloroform at 60° afforded the same thiazoline derivatives.

J. Heterocyclic Chem., **30**, 929 (1993).

2-Thiophenacylidenethiazolines **1** have been synthesized basically by three different ways: The first method involves the reactions of 5-phenyl-3-phenylimino-1,2-dithiazoles with propiolic or phenylpropiolic esters [1], which gives **1** with a carbethoxy group at C-5 of the ring. The drawback of this method is twofold: First, esters which are less reactive than dimethyl acetylenedicarboxylate should be used to avoid the formation of diadducts. Secondly, 3-phenylimino-1,2-dithiazoles with bulky groups at the 4 and 5 positions do not give the desired products. The second method involves the reactions of isothiazole-3-thiones **2** with phenacylidenetriphenylphosphorane. For instance, 3-methyl-5-phenyl-2-thiophenacylidenethiazoline and 3-methyl-5-(*p*-tolyl)-2-thiophenacylidenethiazoline were prepared in 36% and 41% yields by the reactions of 2-methyl-5-phenylisothiazole-3-thione (**2a**) with phenacylidenetriphenylphosphorane and *p*-methylphenacylidenetriphenylphosphorane, respectively [2]. The third method is examplified by the preparation of 4-aryl- or 5-aryl-2-thiophenacylidenethiazolines by the thionation of the corresponding 2-phenacylidenethiazolines using phosphorus pentasulfide in 45 to 65% yields [3]. The second and third methods provide 2-thiophenacylidenethiazolines with aryl substituents at C-4 and/or C-5 of the ring. We were interested in developing new synthetic methodology which would afford **1** having substituents other than aryl groups on the thiazoline ring. We envisioned using 3-alkylthioisothiazolium salts **3** as starting materials since **3** are normally synthesized in good to excellent yields from either the reactions of the corresponding isothiazole-3-thiones **2** with simple alkyl halides [4,5], ethyl bromoacetate [4], or phenacyl halides [3], or β-aminopropenone derivatives by thionation, followed by oxidation [6,7]. We have tried the reactions of **3** with 2-chloro-1,3-dicarbonyl compounds followed by treatment with either sodium borohydride or triphenylphosphite. Herein the results are described.

Results and Discussions.

2-Methyl- (**2a**) and 2-ethyl-5-phenylisothiazole-3-thiones (**2b**) were prepared according to the literature method [5]. Stirring of 2-alkyl-5-phenylisothiazole-3-thiones **2** with

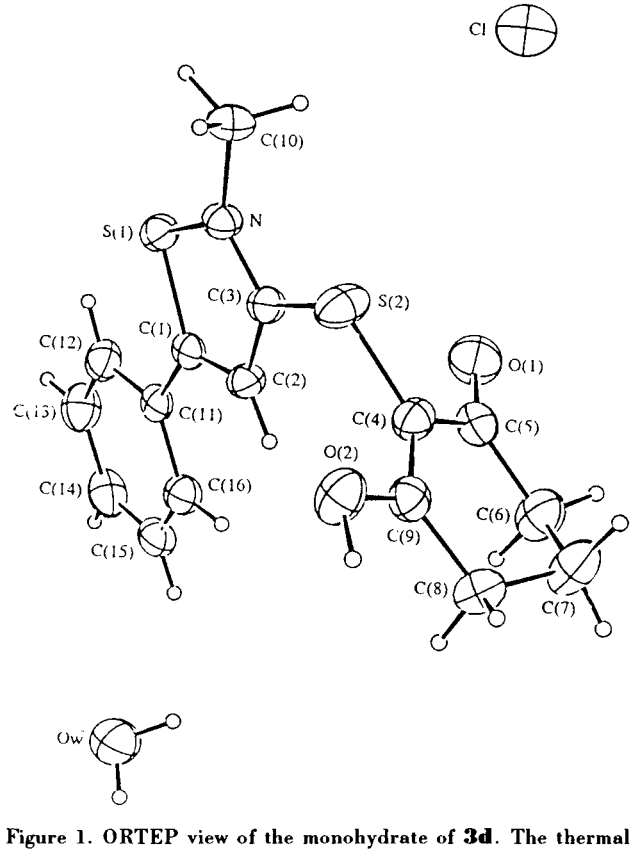
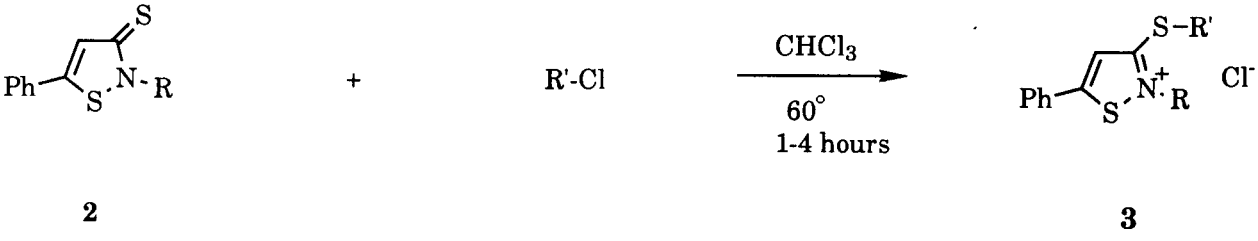


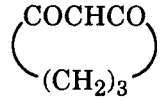
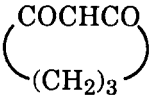
Figure 1. ORTEP view of the monohydrate of 3d. The thermal ecllipsoids are drawn at 50% probability level.

Scheme 1



2 **3**

2	R
a	Me
b	Et

3	R	R'
a	Me	$MeCOCHCO_2Et$
b	Me	$MeCH_2COCHCO_2Me$
c	Me	MeCOCHCOMe
d	Me	
e	Et	$MeCOCHCO_2Et$
f	Et	$MeCH_2COCHCO_2Me$
g	Et	MeCOCHCOMe
h	Et	

various 2-chloro-1,3-dicarbonyl compounds at 60° for 1 to 4 hours, followed by addition of ethyl acetate gave isothiazolium chlorides **3** as shown in Scheme 1.

The structures of **3** were assigned based on the spectroscopic and elemental analyses data. Interestingly the ^1H nmr (300 MHz, deuteriochloroform) of **3** showed a singlet between δ 6.9 and 7.0 ppm originating from a proton at C-4 of the isothiazolium ring. This was in contrast with the same proton signal which appeared at δ 7.45-8.11 ppm in the cases of simple 3-alkylthioisothiazolium salts [1]. In order to identify the bonding position between 1,3-dicarbonyl compounds and **2** in these reactions, **3d** was subjected to single crystal X-ray crystallography. The molecular structure of **3d** is shown in Figure 1 together with the atom-numbering scheme. Atomic coordinates and equivalent isotropic thermal parameters of nonhydrogen atoms are listed in Table 1. Selected bond distances and bond angles of **3d** are tabulated in Table 2 and 3, respectively. The crystal structure clearly shows that the sulfur atom of the thione rather than nitrogen of **2** bonds to C-2 of 1,3-cyclohexanedione.

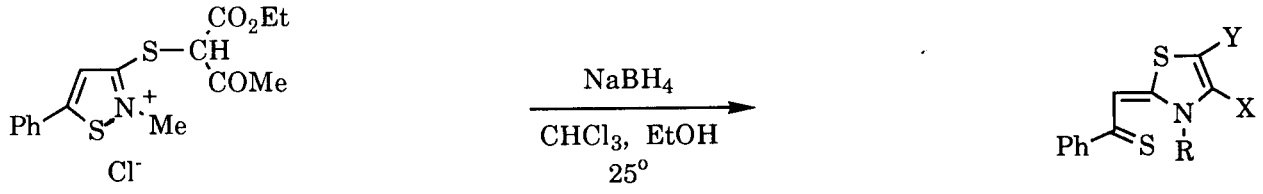
The solution of **3a** in a mixture of chloroform and ethanol (v:v, 5:1) was treated with excess sodium borohydride at 25° to give 5-carbethoxy-4-methyl-2-thiophenacylidenethiazoline (**4a**) in 58% yield as shown in Scheme 2.

By the same treatment, **3b**, **3c**, and **3e-3g** gave 2-thiophenacylidenethiazolines **4b**, **4c**, and **4e-4g** in 48 to 73% yields. The results are summarized in Table 4.

A proposed mechanism for the formation of **4a** is shown in Scheme 3.

The reductive cleavage of the sulfur and nitrogen bond of **3a** by hydride ion affords the ring-opened intermediate **5** which undergoes tautomerization to give thiophenacylketene *S,N*-acetal **6** [8]. This bond cleavage is analogous with *S-N* bond cleavage of 2,3,5-trimethyl-4-substituted isothiazolium tetrafluoroborate by sodium borohydride or lithium aluminum hydride [9]. The amino group of **6** undergoes a nucleophilic attack at the keto carbonyl carbon to form hydroxy-1,3-thiazole **7**, followed by dehydra-

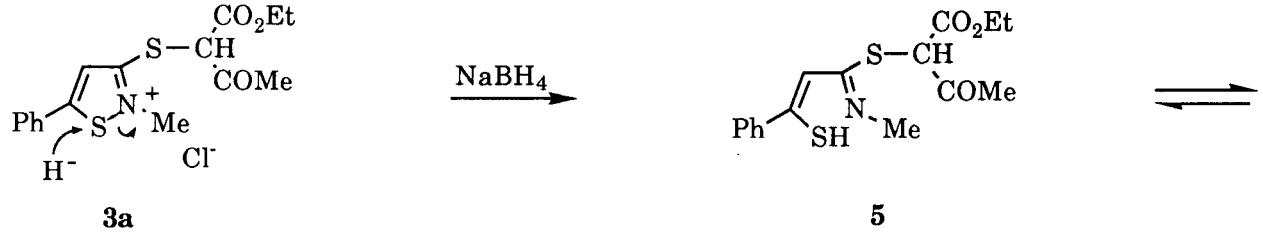
Scheme 2



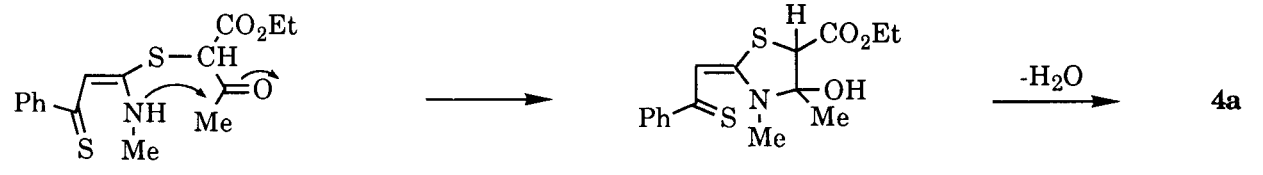
3a **4a**

R= Me , X= Me , Y= CO_2Et

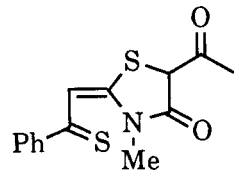
Scheme 3



3a **5**



6 **7**



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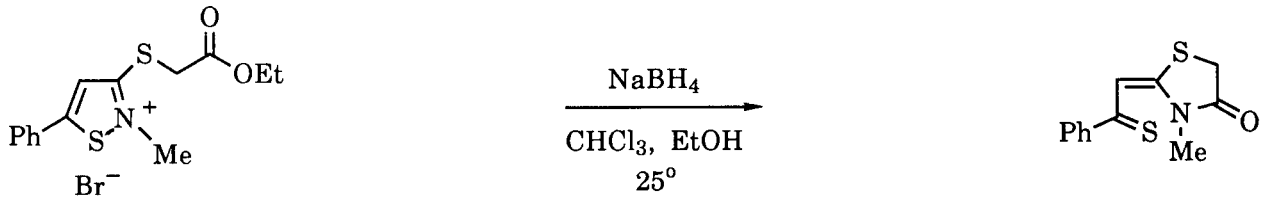
Scheme 4



9 **10**

Table 1

Positional and Equivalent Isotropic Thermal Parameters of Nonhydrogen Atoms for **3d**

Atom	x	y	z	B_{eq}(Å^2)
Cl	0.1848(1)	0.71824(4)	0.40420(3)	3.91(2)
S(1)	0.01827(9)	0.47109(3)	0.24264(2)	2.33(1)
S(2)	0.0041(1)	0.48427(4)	0.41560(3)	3.33(1)
O_w	0.1628(3)	0.0945(1)	0.32417(8)	4.65(5)
O(1)	0.3918(3)	0.4761(1)	0.40123(8)	4.01(5)
O(2)	-0.0733(3)	0.3692(1)	0.49680(8)	3.45(4)
N	-0.0241(3)	0.5024(1)	0.30688(8)	2.21(4)
C(1)	0.1186(3)	0.3944(1)	0.2691(1)	2.00(5)
C(2)	0.1178(3)	0.3956(1)	0.3259(1)	2.19(5)
C(3)	0.0356(3)	0.4584(1)	0.3471(1)	2.15(5)
C(4)	0.1538(4)	0.4278(1)	0.4509(1)	2.60(5)
C(5)	0.3377(4)	0.4366(1)	0.4391(1)	2.89(6)
C(6)	0.4620(4)	0.3911(2)	0.4729(1)	3.66(6)
C(7)	0.3931(4)	0.3734(2)	0.5305(1)	3.97(7)
C(8)	0.2164(4)	0.3374(2)	0.5266(1)	3.13(6)
C(9)	0.0945(4)	0.3794(1)	0.4903(1)	2.59(5)
C(10)	-0.1116(4)	0.5741(1)	0.3151(1)	3.04(6)
C(11)	0.1949(3)	0.3399(1)	0.2311(1)	2.05(5)
C(12)	0.1827(4)	0.3491(2)	0.1735(1)	2.79(5)
C(13)	0.2632(4)	0.2988(2)	0.1384(1)	3.36(6)
C(14)	0.3517(4)	0.2395(2)	0.1603(1)	3.38(6)
C(15)	0.3593(4)	0.2293(1)	0.2174(1)	3.05(6)
C(16)	0.2819(4)	0.2789(1)	0.2528(1)	2.63(5)

$B_{eq} = (1/3)\,\Sigma_i\Sigma_j\beta_{ij}a_ia_j$, Estimated standard deviations are in parenthesis.

Table 2

Selected Bond Distances in Angstroms for **3d**

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	N	1.676(2)	C4	C9	1.370(4)
S1	C1	1.715(2)	C5	C6	1.504(4)
S2	C3	1.728(2)	C6	C7	1.515(4)
S2	C4	1.761(3)	C7	C8	1.513(4)
O1	C5	1.232(3)	C8	C9	1.492(4)
O2	C9	1.316(3)	C11	C12	1.398(3)
N	C3	1.335(3)	C11	C16	1.397(3)
C1	C2	1.366(3)	C12	C13	1.388(4)
C1	C11	1.468(3)	C13	C14	1.380(4)
C2	C3	1.401(3)	C14	C15	1.384(4)
C4	C5	1.455(4)	C15	C16	1.376(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

tion to give **4a**. No 5-acetyl-3-methyl-2-thiophenacylidene-4-thiazolidinone (**8**), which would arise from nucleophilic attack at the ester carbonyl carbon, was detected. However, treatment of 3-carbethoxymethylthio-2-methyl-5-phenylisothiazolium bromide (**9**) with sodium borohydride under the same conditions gave 3-methyl-2-thiophenacylidene-4-thiazolidinone (**10**) in 92% yield as shown in Scheme 4. In the cases of **3d** and **3h**, only **2a** and **2b** were isolated in 90% and 70% yields under the same conditions.

Scheme 5

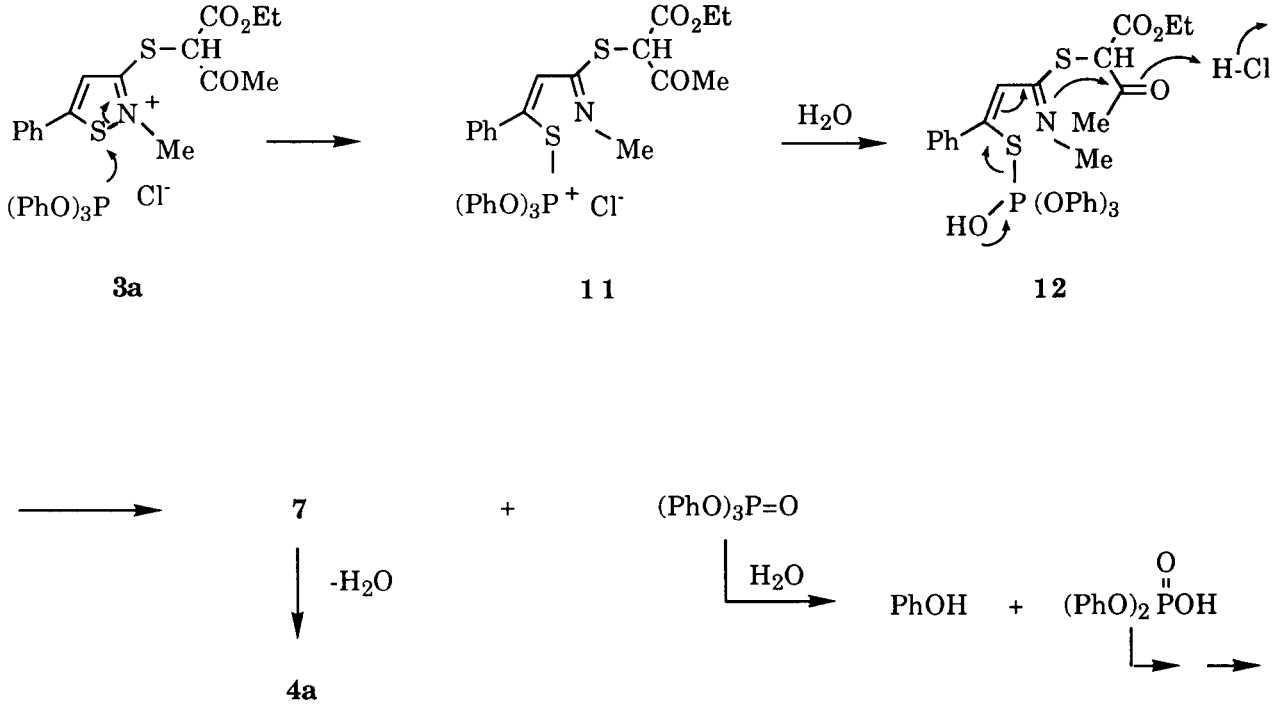


Table 3

Selected Bond Angles in Degrees for **3d**

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N	S1	C1	91.3(1)	C5	C6	C7	112.7(2)
C3	S2	C4	102.0(1)	C4	C5	C6	117.1(2)
C9	O2	H2O	109.0(3)	O1	C5	C4	122.5(3)
S1	N	C3	113.3(2)	O1	C5	C6	120.2(3)
S1	C1	C2	110.8(2)	C6	C7	C8	110.6(2)
S1	C1	C11	119.9(2)	C5	C4	C9	122.0(2)
C2	C1	C11	129.2(2)	N	C3	C2	112.4(2)
C1	C2	C3	112.2(2)	C7	C8	C9	112.5(2)
S2	C3	N	118.5(2)	O2	C9	C4	120.0(2)
S2	C3	C2	129.1(2)	O2	C9	C8	118.5(2)
S2	C4	C5	118.7(2)	C4	C9	C8	121.5(3)
S2	C4	C9	119.2(2)	C1	C11	C12	120.5(2)
				C1	C11	C16	119.7(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4

Yields of 2-Thiophenacylidenethiazoline Derivatives **4**

4	R	X	Y	Yield (%) [a] $NaBH_4$	$(PhO)_3P$	$(MeO)_3P$	$(EtO)_3P$
a	Me	Me	CO_2Et	58	63	30	27
b	Me	Et	CO_2Et	73	49	28	32
c	Me	Me	COMe	66	54	41	31
d	Me	$-(CH_2)_3-$	CO–	[b]	[d]		
e	Et	Me	CO_2Et	48	51	37	33
f	Et	Et	CO_2Et	67	49	23	31
g	Et	Me	COMe	59	59	35	40
h	Et	$-(CH_2)_3-$	CO–	[c]	52		

[a] Isolated yields. [b] Compound **2a** was obtained in 90% yield. [c] Compoound **2b** was obtained in 70% yield. [d] Compound **2a** and phenol were obtained 71% and 98% yields, respectively.

Since the chemical shifts of the protons at C-4 of isothiazolium rings in **3a-h** were very much different from those of simple 3-alkylthioisothiazolium salts, a chemical transformation of **3** with triphenylphosphite was attempted to clear the structural ambiguity before X-ray crystallographic determination. A suspension of **3a-h** in chloroform was treated with equimolar amounts of triphenylphosphite at 60° for an appropriate time. From the reactions were isolated **4**, phenol, and unidentifiable polymeric materials. The results are tabulated in Table 4. Yields of **4** obtained using triphenylphosphite were somewhat lower compared with those obtained using sodium borohydride but chromatographic separations of the reaction mixtures obtained from the former were easy and so pure compounds were readily obtained by recrystallization. The yield of phenol produced increased with the reaction time. The structure of phenol was confirmed by comparison of its ^1H nmr and mass spectral data with those of the authentic sample. In order to test the efficiency of other phosphites, trimethyl- and triethylphosphite were employed. Table 4 shows that the reactions with either trimethyl- or triethylphosphite give **4** in 23 to 41% yields. These results indicate that triphenylphosphite is a better reagent than trimethyl- or triethylphosphite for the transformation of **3** into **4**. Noteworthy was the treatment of **3h** with triphenylphosphite which gave **4h** in 52% yield. Also the reaction with **3d** with triphenylphosphite afforded **2a** and phenol in 71% and 98% yields.

The formation of **4** in the reaction with triphenylphosphite may be explained as shown in Scheme 5.

A bond cleavage between the sulfur and nitrogen atoms by nucleophilic attack of triphenylphosphite at sulfur leads to phosphonium salt **11**, which is attacked by water either present in the incompletely dried solvent at the beginning of the reaction or generated during the course of dehydration step (**7** → **4a**) to give **12**. The intermediate **12**

undergoes decomposition to give **7** and triphenylphosphate. The hydroxy-1,3-thiazole **7** undergoes dehydration to give **4a** and triphenylphosphate is readily hydrolyzed to give phenol and diphenylphosphate [10].

EXPERIMENTAL

Ethyl 2-chloroacetoacetate, 3-chloro-2,4-pentanedione, 1,3-cyclohexandione, sodium borohydride, triphenyl-, trimethyl- and triethylphosphite were obtained from Aldrich Chemical Company, Inc. Column chromatography was performed using aluminum oxide, basic (Merck, 70-230 mesh ASTM), and silica gel (Merck, 230-400 mesh ASTM). Methyl 2-chloro-3-oxopentanoate [11,12] and 2-chloro-1,3-hexanedione [13] were prepared according to the literature procedures. The ^{1}H nmr spectra were recorded on a Varian Gemini-300 300 MHz spectrometer using tetramethylsilane as an internal standard and solvents were specified in each case. Infrared spectra were recorded on a Perkin-Elmer 1310 infrared spectrophotometer. Mass spectra (70 eV, electron impact) were obtained using an HP 5890 A (GC) with an HP 5970 (MSD) mass spectrometer. Melting points were determined with a Thomas capillary melting point apparatus and are uncorrected. Microanalyses were performed by a Perkin-Elmer 240DS and Carlo Erba 1106.

General Procedure for the Reaction of 2-Alkyl-5-phenylisothiazole-3-thiones **2** with 2-Chloro-1,3-dicarbonyl Compounds.

A mixture of **2** and a 2-chloro-1,3-dicarbonyl compound in chloroform (10 ml) was stirred at 60° for 1 to 4 hours. When the spot corresponding to **2** was not observed on a thin layer chromatogram (silica gel, Art 5715, Merck), the solvent was evaporated *in vacuo* and the residue was treated with ethyl acetate to give chloride salts **3**. These salts were readily recrystallized from ethanol.

2-Methyl-5-phenyl-3-(carbethoxyacetylmethylthio)isothiazolium Chloride (**3a**).

Reaction of **2a** (200 mg, 1.035 mmoles) with ethyl 2-chloro-1,3-dioxobutanoate (191 mg, 1.160 mmoles) provided **3a** (310 mg, 0.834 mmole, 81%), mp 137.5-140.5° dec; ^{1}H nmr (deuteriochloroform): δ 1.27 (t, 3H, J = 7.2 Hz, Me), 2.45 (s, 3H, COMe), 4.32 (q, 2H, J = 7.2 Hz, CH_2), 4.52 (s, 3H, N-Me), 6.91 (s, 1H, vinylic H), 7.51-7.70 (m, 6H, ArH); ir (potassium bromide): 3450, 2989, 1697, 1589, 1487, 1383, 1242 cm^{-1}.

Anal. Calcd. for $C_{16}H_{18}ClNO_3S_2$: C, 51.67; H, 4.88; N, 3.77. Found: C, 51.49; H, 4.93; N, 3.86.

2-Methyl-5-phenyl-3-(carbomethoxypropanoylmethylthio)isothiazolium Chloride (**3b**).

Reaction of **2a** (156 mg, 0.807 mmole) with methyl 2-chloro-2,4-dioxopentanoate (165 mg, 1.002 mmoles) provided **3b** (209 mg, 0.562 mmole, 70%), mp 130-131° dec; ^{1}H nmr (deuteriochloroform): δ 1.28 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.77 (q, 2H, J = 7.2 Hz, CH_2CH_3), 3.83 (s, 3H, Me), 4.52 (s, 3H, N-Me), 6.92 (s, 1H, vinylic H), 7.45-7.75 (m, 6H, ArH); ir (potassium bromide): 3190, 2970, 2700, 2460, 1700, 1560, 1515, 1430, 1300, 1052 cm^{-1}.

Anal. Calcd. for $C_{16}H_{18}ClNO_3S_2$: C, 51.67; H, 4.88; N, 3.77. Found: C, 51.75; H, 4.92; N, 3.95.

2-Methyl-5-phenyl-3-(diacetylmethylthio)isothiazolium Chloride (**3c**).

Reaction of **2a** (110 mg, 0.569 mmole) with 3-chloro-2,4-pentanedione (107 mg, 0.795 mmole) for 3 hours provided **3c** (120 mg, 0.351 mmole, 62%), mp 132-133° dec; ^{1}H nmr (deuteriochloroform): δ 2.47 (s, 6H, 2COMe), 4.56 (s, 3H, N-Me), 6.91 (s, 1H, vinylic H), 7.50-7.67 (m, 6H, ArH); ir (potassium bromide): 3200 (s), 1570 (shoulder), 1490, 1440, 1390, 1170, 1100 cm^{-1}.

Anal. Calcd. for $C_{15}H_{16}ClNO_2S_2$: C, 52.70; H, 4.72; N, 4.10. Found: C, 52.84; H, 4.77; N, 4.23.

2-Methyl-5-phenyl-3-(2,6-dioxocyclohexylthio)isothiazolium Chloride (**3d**).

Reaction of **2a** (110 mg, 0.569 mmole) with 2-chloro-1,3-cyclohexanedione (195 mg, 1.330 mmoles) in chloroform (30 ml) for 4 hours at reflux provided **3d** (120 mg, 0.339 mmole, 60%), which was recrystallized from ethanol, mp 171-171.5° dec; ^{1}H nmr (deuteriochloroform): δ 2.06-2.17 (m, 2H, $CH_2CH_2CH_2$), 2.89 (t, 4H, J = 6.3 Hz, $CH_2CH_2CH_2$), 4.16 (s, 3H, N-Me), 6.92 (s, 1H, vinylic H), 7.27-7.56 (m, 5H, ArH), 10.50 (brs, 1H, OH); ir (potassium bromide): 3200, 2850, 1700, 1510, 1480, 1440, 1380, 1200, 1160, 860 cm^{-1}.

Anal. Calcd. for $C_{16}H_{16}ClNO_2S_2$: C, 51.67; H, 4.88; N, 3.77. Found: C, 51.56; H, 4.82; N, 3.89.

2-Ethyl-5-phenyl-3-(carbethoxyacetylmethylthio)isothiazolium Chloride (**3e**).

Reaction of **2b** (85 mg, 0.410 mmole) with ethyl 2-chloro-1,3-dioxobutanoate (63 mg, 0.383 mmole) provided **3e** (112 mg, 0.290 mmole, 71%), mp 97.5-99° dec; ^{1}H nmr (deuteriochloroform): δ 1.27 (t, 3H, J = 7.2 Hz, Me), 1.73 (t, 3H, J = 7.2 Hz, $N\text{-}CH_2CH_3$), 2.48 (s, 3H, COMe), 4.32 (q, 2H, J = 7.2 Hz, OCH_2CH_3), 5.06 (q, 2H, J = 7.2 Hz, $N\text{-}CH_2CH_3$), 7.03 (s, 1H, vinylic H), 7.52-7.76 (m, 6H, ArH); ir (potassium bromide): 3430, 2980, 1690, 1585, 1480, 1380, 1241 cm^{-1}.

Anal. Calcd. for $C_{17}H_{20}ClNO_3S_2$: C, 52.91; H, 5.22; N, 3.63. Found: C, 52.88; H, 5.29; N, 3.58.

2-Ethyl-5-phenyl-3-(carbomethoxypropanoylmethylthio)isothiazolium Chloride (**3f**).

Reaction of **2b** (210 mg, 1.013 mmoles) with methyl 2-chloro-2,4-dioxopentanoate (209 mg, 1.270 mmoles) provided **3f** (250 mg, 0.648 mmole, 64%), mp 115-116° dec; ^{1}H nmr (deuteriochloroform): δ 1.27 (t, 3H, J = 7.2 Hz, CH_2CH_3), 1.71 (t, 3H, J = 7.2 Hz, $N\text{-}CH_2CH_3$), 2.78 (q, 2H, J = 7.2 Hz, CH_2CH_3), 3.84 (s, 3H, OMe), 5.18 (q, 2H, J = 7.2 Hz, $N\text{-}CH_2$), 6.97 (s, 1H, vinylic H), 7.46-7.70 (m, 6H, ArH); ir (potassium bromide): 3185, 2960, 2300, 1700, 1550, 1510, 1290, 1050 cm^{-1}.

Anal. Calcd. for $C_{17}H_{20}ClNO_3S_2$: C, 52.91; H, 5.22; N, 3.63. Found: C, 53.18; H, 5.35; N, 3.69.

2-Ethyl-5-phenyl-3-(diacetylmethylthio)isothiazolium Chloride (**3g**).

Reaction of **2b** (120 mg, 0.579 mmole) with 3-chloro-2,4-pentanedione (278 mg, 2.066 mmoles) for 4 hours provided **3g** (120 mg, 0.337 mmole, 58%), mp 102.5-103.5° dec; ^{1}H nmr (deuteriochloroform): δ 1.67 (t, 3H, J = 7.2 Hz, $N\text{-}CH_2CH_3$), 2.40 (s, 6H, 2COMe), 4.90 (q, 2H, J = 7.2 Hz, $N\text{-}CH_2CH_3$), 7.01 (s, 1H, vinylic H), 7.42-7.64 (m, 6H, ArH); ir (potassium bromide): 3190, 3000, 1700 (shoulder), 1570 (shoulder), 1485, 1380, 1150, 1100, 1020, 920 cm^{-1}.

Anal. Calcd. for $C_{16}H_{18}ClNO_2S_2$: C, 54.00; H, 5.10; N, 3.94. Found: C, 54.12; H, 5.13; N, 3.99.

2-Ethyl-5-phenyl-3-(2,6-dioxocyclohexylthio)isothiazolium Chloride (**3h**).

Reaction of **2b** (115 mg, 0.555 mmole) with 2-chloro-1,3-cyclohexanedione (190 mg, 1.300 mmoles) in chloroform (30 ml) for 4 hours at reflux provided **3h** (130 mg, 0.353 mmole, 64%), recrystallized from ethanol, mp 171.5-172° dec; ^{1}H nmr (deuteriochloroform): δ 1.76 (t, 3H, J = 7.2 Hz, N-CH_2CH_3), 2.06-2.10 (m, 2H, $CH_2CH_2CH_2$), 2.86-2.92 (m, 4H, $CH_2CH_2CH_2$), 4.53 (q, 2H, J = 7.2 Hz, N-CH_2CH_3), 6.92 (s, 1H, vinylic H), 7.54-7.64 (m, 5H, ArH), 10.70 (s, 1H, OH); ir (potassium bromide): 3060 (shoulder), 2200, 1740, 1640, 1550, 1470, 1300, 1180, 960, 900 cm^{-1}.

Anal. Calcd. for $C_{17}H_{18}ClNO_2S_2$: C, 55.5; H, 4.93; N, 3.81. Found: C, 55.2; H, 4.93; N, 3.72.

2-Methyl-5-phenyl-3-(carbethoxymethylthio)isothiazolium Chloride (**9**).

Reaction of **2a** (400 mg, 2.070 mmoles) with ethyl bromoacetate (423 mg, 2.533 mmoles) provided **9** (580 mg, 1.550 mmoles, 75%), mp 177.5-178.5° dec; ^{1}H nmr (deuteriochloroform): δ 1.26 (t, 3H, CH_2CH_3), 2.36 (s, 2H, S-CH_2), 4.20 (q, 2H, CH_2CH_3), 4.74 (s, 3H, N-Me), 7.45-7.49 (m, 3H, ArH), 7.86-7.89 (m, 2H, ArH), 8.39 (s, 1H, vinylic H); ir (potassium bromide): 3010, 1700, 1470, 1420, 1350, 1200, 1140, 748 cm^{-1}.

Anal. Calcd. for $C_{14}H_{16}BrNO_2S_2$: C, 44.92; H, 4.31; N, 3.74. Found: C, 45.09; H, 4.40; N, 3.85.

General Procedure for the Reactions of Isothiazolium Chlorides **3** with Sodium Borohydride.

To a solution of **3** (0.3 mmole) in a mixture of chloroform and ethanol (v:v, 5:1, 10 ml) at room temperature was added excess sodium borohydride. The solution was stirred at 25° until the spot corresponding to **3** had disappeared on the thin layer chromatogram. The solvent was evaporated to dryness *in vacuo*, followed by addition of water (5 ml). The mixture was extracted with methylene chloride (15 ml x 2). The organic layers were dried over (magnesium sulfate), filtered, and evaporation of the solvent gave the crude products, **4**. These compounds were recrystallized from ethanol.

5-Carbethoxy-3,4-dimethyl-2-thiophenacylidenethiazoline (**4a**).

To a solution of **3a** (100 mg, 0.269 mmole) in a mixture of chloroform and ethanol (10 ml) was added portionwise sodium borohydride (15 mg, 0.401 mmole). The solution turned gradually to dark red. After being stirred for 0.5 hour at room temperature, the reaction mixture was worked up as previously described. The residue was chromatographed on aluminum oxide (1 x 1.5 cm). Elution with methylene chloride gave **4a** (50 mg, 0.157 mmole, 58%) as a reddish solid, mp 203-204.5° dec; ^{1}H nmr (deuteriochloroform): δ 1.41 (t, 3H, CH_2CH_3), 2.75 (s, 3H, =C-Me), 3.68 (s, 3H, N-Me), 4.36 (q, 2H, J = 7.2 Hz, CH_2CH_3), 7.27-7.37 (m, 3H, ArH), 7.41 (s, 1H, vinylic H), 7.80-7.84 (m, 2H, ArH); ir (potassium bromide): 2982, 1713, 1609, 1490, 1260, 1275 cm^{-1}; ms: m/z 319 (M$^+$, 100), 286 (39), 258 (58).

Anal. Calcd. for $C_{16}H_{17}NO_2S_2$: C, 60.16; H, 5.36; N, 4.38. Found: C, 60.07; H, 5.29; N, 4.31.

5-Carbomethoxy-4-ethyl-3-methyl-2-thiophenacylidenethiazoline (**4b**).

To a solution of **3b** (156 mg, 0.419 mmole) in a mixture of chloroform and ethanol (15 ml) was added portionwise sodium borohydride (24 mg, 0.642 mmole). The mixture was stirred for 0.5 hour. After chromatography as with **4a**, **4b** (98 mg, 0.307 mmole, 73%) was obtained, mp 223-224° dec; ^{1}H nmr (deuteriochloroform): δ 1.30 (t, 3H, J = 7.2 Hz, CH_2CH_3), 3.27 (q, 2H, J = 7.2 Hz, CH_2CH_3), 3.73 (s, 3H, OMe), 3.91 (s, 3H, N-Me), 7.35-7.38 (m, 3H, ArH), 7.45 (s, 1H, vinylic H), 7.82-7.84 (m, 2H, ArH); ir (potassium bromide): 2940, 1700, 1580, 1470, 1420, 1252, 1151, 1092 cm^{-1}; ms: m/z 319 (M$^+$, 100), 286 (93), 121 (16), 77 (8).

Anal. Calcd. for $C_{16}H_{17}NO_2S_2$: C, 60.16; H, 5.36; N, 4.38. Found: C, 59.90; H, 5.36; N, 4.38.

5-Acetyl-3,4-dimethyl-2-thiophenacylidenethiazoline (**4c**).

To a solution of **3c** (100 mg, 0.293 mmole) in a mixture of chloroform and ethanol (15 ml) was added portionwise sodium borohydride (16 mg, 0.428 mmole). After being worked up as with **4a**, **4c** (56 mg, 0.193 mmole, 66%) was obtained, mp 244-245° dec; ^{1}H nmr (deuteriochloroform): δ 2.56 (s, 3H, COMe), 2.78 (s, 3H, =C-Me), 3.73 (s, 3H, N-Me), 7.38 (m, 3H, ArH), 7.39 (s, 1H, vinylic H), 7.82-7.85 (m, 2H, ArH); ir (potassium bromide): 2920, 1620, 1560, 1465, 1265, 885, 745 cm^{-1}; ms: m/z 289 (M$^+$, 100), 256 (90), 121 (21), 77 (19).

Anal. Calcd. for $C_{15}H_{15}NOS_2$: C, 62.25; H, 5.22; N, 4.84. Found: C, 62.21; H, 5.17; N, 4.68.

5-Carbethoxy-3-ethyl-4-methyl-2-thiophenacylidenethiazoline (**4e**).

To a solution of **3e** (115 mg, 0.298 mmole) in a mixture of chloroform and ethanol (15 ml) was added portionwise sodium borohydride (17 mg, 0.455 mmole). The mixture was stirred for 0.5 hour. After chromatography as with **4a**, **4e** (48 mg, 0.144 mmole, 48%) was obtained. Recrystallization from ethanol gave a deep pinkish needle type crystal, mp 207-208° dec; ^{1}H nmr (deuteriochloroform): δ 1.38-1.49 (m, 6H, OCH_2CH_3, N-CH_2CH_3), 2.77 (s, 3H, =C-Me), 4.22 (q, 2H, J = 7.2 Hz, CH_2CH_3), 4.37 (q, 2H, J = 7.2 Hz, N-CH_2CH_3), 7.35-7.38 (m, 3H, ArH), 7.50 (s, 1H, vinylic H), 7.81-7.83 (m, 2H, ArH); ir (potassium bromide): 3055, 2970, 1703, 1504, 1481, 1265 cm^{-1}; ms: m/z 333 (M$^+$, 61), 300 (95), 272 (59.5), 197 (42.4), 121 (100), 77 (62.7).

Anal. Calcd. for $C_{17}H_{19}NO_2S_2$: C, 61.23; H, 5.74; N, 4.20. Found: C, 61.06; H, 5.59; N, 4.13.

5-Carbomethoxy-3,4-diethyl-2-thiophenacylidenethiazoline (**4f**).

To a solution of **3f** (156 mg, 0.404 mmole) in a mixture of chloroform and ethanol (15 ml) was added portionwise sodium borohydride (24 mg, 0.642 mmole). After being worked up as with **4a**, the reddish residue was chromatographed on silica gel (1 x 2 cm). Elution with chloroform (15 ml) gave **2b** (28 mg, 0.127 mmole, 31%). The next chloroform fraction (25 ml) gave **4f** (90 mg, 0.270 mmole, 67%) as a reddish solid, mp 177-178° dec; ^{1}H nmr (deuteriochloroform): δ 1.30 (t, 3H, J = 7.2 Hz, $=CCH_2CH_3$), 1.50 (t, 3H, J = 7.2 Hz, N-CH_2CH_3), 3.23 (q, 2H, J = 7.2 Hz, $=CCH_2CH_3$), 3.91 (s, 3H, OMe), 4.24 (q, 2H, J = 7.2 Hz, N-CH_2CH_3), 7.37-7.39 (m, 3H, ArH), 7.52 (s, 1H, vinylic H), 7.80-7.83 (m, 2H, ArH); ir (potassium bromide): 2980, 1700, 1580, 1479, 1420, 1260, 1100 cm^{-1}; ms: m/z, 333 (M$^+$, 67), 300 (100), 211 (12), 121 (17), 77 (7).

Anal. Calcd. for $C_{17}H_{19}NO_2S_2$: C, 61.23; H, 5.74; N, 4.20. Found: C, 61.12; H, 5.59; N, 4.15.

5-Acetyl-3-ethyl-4-methyl-2-thiophenacylidenethiazoline (**4g**).

To a solution of **3g** (100 mg, 0.281 mmole) in a mixture of chlo-

roform and ethanol (15 ml) was added portionwise sodium borohydride (16 mg, 0.428 mmole). After being worked up as with **4a**, **4g** (50 mg, 0.165 mmole, 59%) was isolated as a reddish solid, mp 202-203° dec; ^{1}H nmr (deuteriochloroform): δ 1.46 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.57 (s, 3H, COMe), 2.79 (s, 3H, =C-Me), 4.26 (q, 2H, J = 7.2 Hz, CH_2CH_3), 7.38-7.40 (m, 3H, ArH), 7.54 (s, 1H, vinylic H), 7.81-7.84 (m, 2H, ArH); ir (potassium bromide): 2930, 1618, 1550, 1459, 1430 (shoulder), 1340, 1240, 1070, 1000, 860, 780 cm^{-1}; ms: m/z 303 (M^+, 77), 270 (100), 242 (15), 181 (16), 121 (44), 77 (22).

Anal. Calcd. for $C_{16}H_{17}NOS_2$: C, 63.33; H, 5.65; N, 4.62. Found: C, 63.38; H, 5.59; N, 4.75.

Reaction of **3d** with Sodium Borohydride.

To a solution of **3d** (102 mg, 0.288 mmole) in a mixture of chloroform and ethanol (15 ml) was added portionwise sodium borohydride (25 mg, 0.669 mmole). After being worked up as with **4a**, a white solid, **2a**, was isolated in 90% yield.

Reaction of **3h** with Sodium Borohydride.

To a solution of **3h** (114 mg, 0.310 mmole) in a mixture of chloroform and ethanol (10 ml) was added portionwise sodium borohydride (34 mg, 0.910 mmole). After being worked up as with **4a**, a white solid, **2b**, was isolated in 70% yield.

General Procedure for the Reaction of **3** with Triphenylphosphite.

To a suspension of **3** (0.200 mmole) in chloroform (10 ml) was added triphenylphosphite (0.200 mmole), which was stirred for 1 or 2 hours at 60° until the spot of **3** on thin layer chromatogram had disappeared. After the solvent was evaporated *in vacuo*, the red residue was chromatographed on a silica gel column (1 x 3 cm). Elution with methylene chloride gave unreacted triphenylphosphite, phenol, and **4** as a reddish solid, which was recrystallized from ethanol. Further elution with a mixture of methylene chloride and methanol (v:v, 1:5, 30 ml) gave unidentifiable polymeric materials.

Synthesis of **4a**.

(a) To a suspension of **3a** (74 mg, 0.199 mmole) in chloroform (10 ml) was added triphenylphosphite (62 mg, 0.200 mmole) which was stirred for 2 hours at 60°. Chromatography (1 x 3 cm) of the reddish residue using methylene chloride gave phenol (15 mg, 0.192 mmole), and **4a** (40 mg, 0.125 mmole, 63%), mp 204.5-205° dec. Further elution with a mixture of methanol and methylene chloride (v:v, 1:5, 20 ml) gave tar (40 mg). Triturations of the tar with methanol, chloroform, or ethyl acetate failed to give a crystal.

(b) To a suspension of **3a** (50 mg, 0.134 mmole) in chloroform (10 ml) was added trimethylphosphite (17 mg, 0.134 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4a** (13 mg, 0.041 mmole, 30%) as a reddish solid.

(c) To a suspension of **3a** (42 mg, 0.113 mmole) in chloroform (10 ml) was added triethylphosphite (19 mg, 0.114 mmole), which was stirred for 30 minutes at 50°. Chromatography (1 x 2 cm) gave **4a** (10 mg, 0.031 mmole, 27%).

Synthesis of **4b**.

(a) To a suspension of **3b** (48 mg, 0.129 mmole) in chloroform (10 ml) was added triphenylphosphite (40 mg, 0.129 mmole), which was stirred for 1.5 hours at 60°. Chromatography (1 x 2 cm) using methylene chloride (20 ml) as an eluant gave a reddish mixture from which phenol (10 mg, 0.128 mmole) and **4b** (20 mg, 0.063 mmole, 49%) were obtained by washing with diethyl ether, mp of **4b**, 223-224° dec.

(b) To a suspension of **3b** (50 mg, 0.134 mmole) in chloroform (10 ml) was added trimethylphosphite (17 mg, 0.134 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4b** (12 mg, 0.038 mmole, 28%).

(c) To a suspension of **3b** (50 mg, 0.134 mmole) in chloroform (10 ml) was added triethylphosphite (22 mg, 0.134 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4b** (14 mg, 0.044 mmole, 32%).

Synthesis of **4c**.

(a) To a suspension of **3c** (110 mg, 0.322 mmole) in chloroform (15 ml) was added triphenylphosphite (110 mg, 0.355 mmole), which was refluxed for 2 hours. Chromatography (1 x 2 cm) using methylene chloride (10 ml) gave phenol (4 mg, 0.051 mmole). Continuous elution with methylene chloride (30 ml) gave **4c** (50 mg, 0.173 mmole, 54%), mp 244-245° dec.

(b) To a suspension of **3c** (110 mg, 0.322 mmole) in chloroform (20 ml) was added trimethylphosphite (40 mg, 0.321 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2.5 cm) gave **4c** (38 mg, 0.131 mmole, 41%).

(c) To a suspension of **3c** (45 mg, 0.131 mmole) in chloroform (10 ml) was added triethylphosphite (22 mg, 0.131 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4c** (12 mg, 0.041 mmole, 31%).

Reaction of **3d** with Triphenylphosphite.

To a suspension of **3d** (60 mg, 0.170 mmole) in chloroform (10 ml) was added triphenylphosphite (52 mg, 0.168 mmole), which was stirred for 4 hours at 60°, followed by the addition of 5 ml of water. The organic layer was separated and then washed with water three times and dried over magnesium sulfate. After the solvent was evaporated *in vacuo*, the residue was chromatographed on silica gel (1 x 2 cm). Elution with methylene chloride (10 ml) gave phenol (13 mg, 0.166 mmole). The next methylene chloride fraction (20 ml) gave **2a** (25 mg, 0.121 mmole, 71%).

Synthesis of **4e**.

(a) To a suspension of **3e** (50 mg, 0.129 mmole) in chloroform (10 ml) was added triphenylphosphite (40 mg, 0.129 mmole), which was stirred for 1 hour at 55°. Chromatography (1 x 2 cm) using methylene chloride (10 ml) as an eluent gave phenol (12 mg, 0.127 mmole). Next fraction of methylene chloride (15 ml) gave **4e** (22 mg, 0.066 mmole, 51%), mp 207-207.5° dec.

(b) To a suspension of **3e** (110 mg, 0.285 mmole) in chloroform (10 ml) was added trimethylphosphite (37 mg, 0.298 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4e** (35 mg, 0.105 mmole, 37%).

(c) To a suspension of **3e** (70 mg, 0.181 mmole) in chloroform (10 ml) was added triethylphosphite (30 mg, 0.181 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2.5 cm) gave **4e** (20 mg, 0.06 mmole, 33%).

Synthesis of **4f**.

(a) To a suspension of **3f** (50 mg, 0.130 mmole) in chloroform (10 ml) was added triphenylphosphite (40 mg, 0.129 mmole), which was stirred for 1 hour at 60°. Chromatography (1 x 2.5 cm) using methylene chloride (20 ml) as an eluant gave a reddish solid from which phenol (9 mg, 0.115 mmole) and **4f** (21 mg, 0.063

mmole, 49%) were isolated by washing with a mixture of diethyl ether and hexane (v:v, 1:1, 5 ml), mp of **4f**, 177-178° dec.

(b) To a suspension of **3f** (45 mg, 0.117 mmole) in chloroform (10 ml) was added trimethylphosphite (15 mg, 0.121 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4f** (9 mg, 0.027 mmole, 23%).

(c) To a suspension of **3f** (45 mg, 0.117 mmole) in chloroform (10 ml) was added triethylphosphite (20 mg, 0.120 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4f** (12 mg, 0.036 mmole, 31%).

Synthesis of **4g**.

(a) To a suspension of **3g** (60 mg, 0.169 mmole) in chloroform (10 ml) was added triphenylphosphite (58 mg, 0.187 mmole), which was heated at 80° for 5 hours. Elution with methylene chloride (5 ml) gave triphenylphosphite (14 mg, 0.045 mmole, 24%). The next fraction (7 ml) gave phenol (20 mg, 0.256 mmole). The final methylene chloride fraction (15 ml) gave **4g** (30 mg, 0.099 mmole, 59%), mp of **4g**, 202.5-203.5° dec.

(b) To a suspension of **3g** (50 mg, 0.14 mmole) in chloroform (10 ml) was added trimethylphosphite (17 mg, 0.14 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4g** (15 mg, 0.049 mmole, 35%).

(c) To a suspension of **3g** (50 mg, 0.14 mmole) in chloroform (10 ml) was added triethylphosphite (23 mg, 0.14 mmole), which was stirred for 1 hour at 50°. Chromatography (1 x 2 cm) gave **4g** (17 mg, 0.056 mmole, 40%).

3-Ethyl-7-oxo-2-thiophenacylidene-4,5,6,7-tetrahydro-2*H*-benzothiazole (**4h**).

To a suspension of **3h** (40 mg, 0.109 mmole) in chloroform (10 ml) was added triphenylphosphite (47 mg, 0.151 mmole), which was stirred for 1 hour at 60°. Chromatography (1 x 2.5 cm) using methylene chloride (10 ml) gave triphenylphosphite (15 mg, 0.048 mmole). The next methylene chloride fraction (10 ml) gave phenol (10 mg, 0.128 mmole). Finally, elution with ethyl acetate (30 ml) gave **4h** (18 mg, 0.057 mmole, 52%), mp 221.5-223° dec: ^{1}H nmr (deuteriochloroform): δ 1.46 (t, 3H, J = 7.2 Hz, CH_2CH_3), 2.25 (quintet, 2H, $CH_2CH_2CH_2$), 2.53 (t, 2H, J = 6.6 Hz, $=CCH_2$), 2.90 (t, 2H, J = 6.3 Hz, $COCH_2$), 4.16 (q, 2H, J = 7.2 Hz, CH_2CH_3), 7.27-7.39 (m, 3H, ArH), 7.46 (s, 1H, vinylic H), 7.78-7.81 (m, 2H, ArH); ir (potassium bromide): 1640, 1570, 1470, 1410, 1335, 1280, 1070, 920, 745 cm^{-1}; ms: m/z, 315 (M^+, 23), 286 (100), 173 (65), 121 (19).

Anal. Calcd. for $C_{17}H_{17}NOS_2$: C, 64.73; H, 5.43; N, 4.44. Found: C, 64.56; H, 5.39; N, 4.28.

3-Methyl-2-thiophenacylidene-4-thiazolidinone (**10**).

To a solution of **9** (360 mg, 0.962 mmole) in ethanol was added portionwise sodium borohydride (37 mg, 0.978 mmole). After being worked up as with **4a**, the residue was chromatographed on aluminum oxide (basic) (2 x 3 cm). Elution with methylene chloride (20 ml) gave **10** (220 mg, 0.882 mmole, 92%) which was recrystallized from ethanol to give a green crystal, mp 181-182.5°; ^{1}H nmr (deuteriochloroform): δ 3.38 (s, 3H, N-Me), 3.72 (s, 2H, $COCH_2$), 7.39-7.48 (m, 4H, vinylic H, ArH), 7.77-7.80 (m, 2H, ArH); ir (potassium bromide): 1692, 1490, 1450, 1410, 1370, 1330, 1290, 1210, 1190, 1093, 865, 745 cm^{-1}; ms: m/z 249 (M^+), 232, 208, 121, 77.

Anal. Calcd. for $C_{12}H_{11}NOS_2$: C, 57.80; H, 4.45; N, 5.62. Found: C, 57.62; H, 4.43, N, 5.52.

X-ray Crystallographic Analysis of **3d**.

Crystal data for **3d**: $C_{16}H_{16}ClNO_2S_2 \cdot H_2O$, MW = 371.90, orthorhombic, Pbca, a = 7.7073 (7), b = 18.154 (2), c = 23.999 (2) Å, V = 3357.9 (5) Å^3, D_x = 1.467 gcm^{-3}, Z = 8, T = 23°. Colorless rod-like crystals of **3d** were grown from a solution of acetonitrile and chloroform (v:v, 7:3) containing a few drops of diethyl ether stored in a refrigerator. A crystal with dimensions *ca.* 0.25 x 0.25 x 0.48 mm was mounted on an Enraf-Nonium CAD4 diffractometer with graphite-monochromated MoKα radiation (λ(MoKα$_1$) = 0.71073 Å. The unit cell parameters were determined by a least-squares analysis of 25 centered reflections with 23° < 2θ < 30°. Intensity data with 0 ≤ h ≤ 9, 0 ≤ k ≤ 23, 0 ≤ l ≤ 30 up to 2θ = 54° were measured by the ω-scan mode with an ω-scan width (0.65 + 0.35 tanθ)° and a scan speed 2.06/minute. The intensities of three standard refections monitored every 2 hours showed no significant decay during the data collection. The data were corrected for Lorentz and polarization effects. An empirical absorption correction, DIFABS [14] (μ = 4.761 cm^{-1}) was applied at the late stage of refinements, which gave correction factors from 0.782 to 1.266. Structure was solved by direct methods using SHELXS86 [15] and refined by the full-matrix least-squares methods. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from the successive electron density maps and their positions and isotropic thermal parameters were refined with no constraint. Final cycle of refinement converged to R = 0.041, R_w = 0.045 ($R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$; $\sigma(F_o^2) = [\sigma(I(+(pI)^2)]^{1/2}$, p = 0.04) and GOF = 1.356. Of the total 3660 unique reflections, 2481 observed reflections with $I > 3\sigma(I)$ were used for the refinement. All calculations except for the structure solving were performed with Enraf-Nonius MolEN program package [16] on a Micro VAX2000. Atomic scattering factors were from International Tables for X-ray Crystallography [17]. The X-ray structure analysis of the crystal revealed and additional water molecule forming two hydrogen bonds with the carbonyl O and Cl$^-$ ion: ($\angle$ O(1)---H_{wa}-O_w = 171.1(4)°, H_{wa}-O_w = 0.82(4) Å, O(1)---O_w = 2.868(3) Å; $\angle$ O_w-H_{wb}---Cl = 176.4(3)°, O_w-H_{wb} = 0.90(4) Å, O_w---Cl = 3.182(2) Å). The source of the water is not clear but it may originate from a trace amount of water in the solvents.

Acknowledgment.

The authors are grateful for the financial support by the Basic Science Research Institute Program, Ministry of Education, 1992 (B SRI-92-315) and Center for Biofunctional Molecules (CBM). Kimoon Kim thanks Pohang Institute of Science and Technology for partial support of the X-ray analysis.

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