3α-Bromo-3β-methyl-4α-methoxy-4β-[((p-nitrobenzoyl)oxy)methyl]-7β-(phenoxyacetamido)cepham (6). This compound was synthesized from 4[2] (0.32 g) as described for **5**. Pure **6** was obtained as an oil after column chromatography on silica gel eluting with 1:1.5 ethyl acetate–hexane: yield, 0.38 g (87%); IR ($CHBr_3$) ν 1776 cm^{-1} (β-lactam C=O); ^1H NMR δ 2.08 (s, 3, CCH_3), 2.80 (d, 1, J = 13.6 Hz, H-2β), 3.51 (s, 3, OCH_3), 4.12 (d, 1, J = 13.6 Hz, H-2α), 5.10 (s, 2, CH_2OCO), 5.06 (d, 1, J = 4.9 Hz, CHS), 5.61 (q, 1, J = 4.9, 9.3 Hz, NHC*H*); ^{13}C NMR δ 62.53 [s, C(3)], 87.98 [s, C(4)]. Anal. Calcd for $C_{24}H_{24}BrN_3O_8S$: C, 48.50; H, 4.04; Br, 13.44; N, 7.07. Found: C, 48.40; H, 4.12; Br, 13.59; N, 6.85.

2β-(Acetoxymethyl)-2α-methyl-3α-methoxy-3β-[((p-nitrobenzoyl)oxy)methyl]-6β-(phenoxyacetamido)penam (7). A solution of **5** (0.93 g, 1.6 mmol) in glacial acetic acid (35 mL) was added under stirring to silver acetate (0.45 g, 2.7 mmol) at room temperature. The resulting stirred mixture was placed in an oil bath at 100 °C and left at the same temperature for 20 min. The suspension was allowed to cool at room temperature, filtered through Celite to remove silver salts, and evaporated to near dryness. The residue was taken up with $CHCl_3$, washed (10% aqueous $NaHCO_3$ and brine), filtered, and evaporated. The solid residue (0.85 g) consisting exclusively of **7** was crystallized from $CHCl_3$–hexane to yield pure **7** (0.65 g, 71%): mp 191–192 °C; IR ($CHBr_3$) ν 1786 cm^{-1} (β-lactam C=O); ^1H NMR δ 1.62 (s, 3, CCH_3), 2.07 (s, 3, $COCH_3$), 3.43 (s, 3, OCH_3), 3.95 and 4.61 (2 d, 2, J = 12.6 Hz, $SCCH_2O$)[3] 4.65 and 5.39 (2 d, 2, J = 14.0 Hz, $NCCH_2O$), 5.29 (d, 1, J = 4.3 Hz, SCH), 5.77 (q, 1, J = 4.3, 10.3 Hz, NHC*H*). Anal. Calcd for $C_{26}H_{27}N_3O_{10}S$: C, 54.46; H, 4.70; N, 7.32. Found: C, 54.38; H, 4.64; N, 7.28.

2α-(Acetoxymethyl)-2β-methyl-3α-methoxy-3β-[((p-nitrobenzoyl)oxy)methyl]-6β-(phenoxyacetamido)penam (8). This compound was prepared from **6** (0.21 g) as described for the preparation of **7**. The crude product was purified by TLC using a 1:3 mixture of ethyl acetate–benzene as the eluent. Pure **8** was obtained as a vitreous product: yield, 0.14 g (70%); IR ($CHBr_3$) ν 1784 cm^{-1} (β-lactam C=O); ^1H NMR δ 1.47 (s, 3, CCH_3), 2.09 (s, 3, $COCH_3$), 3.42 (s, 3, OCH_3), 4.38 and 4.69 (2 d, 2, J = 11.2 Hz, $SCCH_2O$), 4.85 and 5.33 (2 d, 2, J = 13.4 Hz, $NCCH_2O$), 5.28 (d, 1, J = 4.4 Hz, SCH), 5.65 (q, 1, J = 4.4, 9.6 Hz, NHC*H*). Anal. Calcd for $C_{26}H_{27}N_3O_{10}S$: C, 54.46; H, 4.70; N, 7.32. Found: C, 54.63; H, 4.57; N, 7.50.

2β-(Acetoxymethyl)-2α-methyl-3α-methoxy-3β-[((p-nitrobenzoyl)oxy)methyl]-6β-(phenoxyacetamido)penam (*S*)- and (*R*)-Sulfoxide (9 and 10). A stirred solution of **7** (0.46 g, 0.8 mmol) in anhydrous CH_2Cl_2 (25 mL) was cooled at 0 °C and then treated dropwise with a solution of 91% *m*-chloroperoxybenzoic acid (0.15 g, 0.79 mmol) in anhydrous CH_2Cl_2 (10 mL). The resulting solution was stirred 1 h at the same temperature, washed (10% aqueous $NaHCO_3$ and H_2O), filtered, and evaporated to dryness to give an oily residue (0.45 g) consisting of **7** and **8** in a ratio of about 1:4.5. The residue was subjected to preparative TLC using a 3:1 mixture of ethyl acetate and petroleum ether (bp 40–60 °C) as the eluent. Extraction with ethyl acetate at room temperature of the band with the higher R_f gave an oily residue consisting of pure **9** (0.052 g, 11%): IR ($CHBr_3$) ν 1795 (β-lactam C=O); ^1H NMR δ 1.36 (s, 3, CCH_3), 2.14 (s, 3, $OCOCH_3$), 3.50 (s, 3, OCH_3), 4.75 (s, 2, $SCCH_2O$), 4.78 and 5.86 (2 d, 2, J = 13.3 Hz, $NCCH_2$), 5.03 (d, 1, J = 4.6 Hz, SCH), 6.05 (q, 1, J = 4.6, 10.8 Hz, NHC*H*). Anal. Calcd for $C_{26}H_{27}N_3O_{11}S$: C, 52.98; H, 4.61; N, 7.13. Found: C, 53.17; H, 4.71; N, 6.89.

Extraction at room temperature with ethyl acetate of the band with the lower R_f yielded a solid residue (0.25 g) which crystallized from $CHCl_3$–hexane to yield pure **10** (0.20 g, 42%): mp 140–142 °C; IR ($CHBr_3$) ν 1792 (β-lactam C=O); ^1H NMR δ 1.54 (s, 3, CCH_3), 2.09 (s, 3, $OCOCH_3$), 3.47 (s, 3, OCH_3), 4.35 and 4.85 (2 d, 2, J = 12.9 Hz, $SCCH_2O$), 4.63 and 5.50 (2 d, 2, J = 13.8 Hz, $NCCH_2O$), 4.79 (d, 1, J = 4.5 Hz, SCH), 5.97 (q, 1, J = 4.5 and 9.2 Hz, NHC*H*). Anal. Calcd for $C_{26}H_{27}N_3O_{11}S$: C, 52.98; H, 4.61; N, 7.13. Found: C, 52.71; H, 4.55; N, 7.30.

2α-(Acetoxymethyl)-2β-methyl-3α-methoxy-3β-[((p-nitrobenzoyl)oxy)methyl]-6β-(phenoxyacetamido)penam (*S*)- and (*R*)-Sulfoxide (11 and 12). These compounds were synthesized from **8** (0.10 g) as described for **9** and **10**. The crude residue consisting of **11** and **12** in a ratio of about 1:5 was subjected to preparative TLC eluting with 65:35 ethyl acetate–petroleum ether (bp 40–60 °C). Pure **11** was obtained as an oil by extraction with $CHCl_3$ at room temperature of the upper band of the chromatogram: yield, 0.015 g (15%); IR (CHB_3) ν 1791 (β-lactam C=O); ^1H NMR δ 1.70 (s, 3, CCH_3), 2.11 (s, 3, $OCOCH_3$), 3.48 (s, 3, OCH_3), 4.28 and 4.72 (2 d, 2, J = 13.2 Hz, $SCCH_2O$), 4.93 and 5.40 (2 d, 2, J = 14.0 Hz, $NCCH_2O$), 5.19 (d, 1, J = 4.8 Hz, SCH), 6.14 (q, 1, J = 4.8 and 10.2 Hz, NHC*H*). Anal. Calcd for $C_{26}H_{27}N_3O_{11}S$: C, 52.98; H, 4.61; N, 7.13. Found: C, 53.15; H, 4.43; N, 6.92.

Pure **12** was isolated by extraction with $CHCl_3$ at room temperature of the lower band of the chromatogram: yield, 0.055 g (55%); IR ($CHBr_3$) ν 1789 (β-lactam C=O); ^1H NMR δ 1.43 (s, 3, CCH_3), 2.12 (s, 3, $OCOCH_3$), 3.43 (s, 3, OCH_3), 4.57 and 4.98 (2 d, 2, J = 12.2 Hz, $SCCH_2O$), 4.77 and 5.36 (2 d, 2, J = 13.4 Hz, $NCCH_2O$), 4.81 (d, 1, J = 4.8 Hz, SCH), 5.38 (q, 1, J = 4.8 and 10.8 Hz, NHC*H*). Anal. Calcd for $C_{26}H_{27}N_3O_{11}S$: C, 52.98; H, 4.61; N, 7.13. Found: C, 52.79; H, 4.56; N, 6.98.

Thermal Transformation of the *R* Sulfoxide 10. A solution of **10** (0.040 g) in anhydrous benzene (8 mL) was refluxed for 4 h. After the mixture cooled, the solvent was evaporated to yield an oily residue (0.038 g) consisting almost exclusively of **11** (TLC, ^1H NMR). When a solution of **10** in benzene was refluxed for a shorter time (2 h) some starting material was detected (TLC, ^1H NMR) in the reaction mixture.

When the *R* sulfoxide **12** was heated as described above for the **10**, or for longer times, it was recovered unchanged, together with some decomposition material (^1H NMR, TLC).

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Steric Effects of Ortho Substituents on Acid-Catalyzed Cyclization of Thiocyanatoacetophenones

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The synthesis of 2-chlorothiazoles by intramolecular cyclization of thiocyanatoacetophenones with HCl gas is well documented.[1,2] In this paper we report that under the same conditions thiocyanatoacetophenones can also cyclize to give 2-iminio-5-aryl-1,3-oxathiole hydrochlorides; but this mode of cyclization (Scheme I, pathway b) becomes significant only when the benzene ring of the parent compounds have substituents at the ortho positions. This observation was made by analyzing the reaction of HCl gas with thiocyanatoacetopheonones **1**, **3**, **5**, **8**, and **11** (Table I).

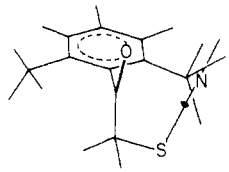
The thiocyanatoacetophenones **1**, **3**, **5**, **8**, and **11** were prepared by following a known sequence of reactions[1,2] outlined in Scheme I. The products obtained by saturating the solutions of these compounds in anhydrous ether with dry HCl gas are listed in Table I. A comparison of the products formed in the five reactions reveals that 2,6-di-

(1) Sharma, G. M.; Sachdev, H. S.; Narang, K. S. *J. Sci. Ind. Res., Sect. B* **1957**, *16*, 411.
(2) Bariana, D. S.; Sachdev, H. S.; Narang, K. S. *J. Indian Chem. Soc.* **1955**, *32*, 427.

0022-3263/86/1951-0543$01.50/0

substituted thiocyanatoacetophenone **11** upon treatment with HCl gas cyclizes to give 1,3-oxathiole ring system **12** exclusively. Under the same conditions, the thiocyanatoacetophenones **5** and **8**, which have only one ortho position substituted by a methyl group, yield an equimolar mixture of 2-chlorothiazoles **6** and **9** and 1,3-oxathiole hydrochlorides **7** and **10**. Thiocyanatoacetophenones **1** and **3** which lack substituents at the ortho positions give 2-chlorothiazoles **2** and **4** as the exclusive product of intramolecular cyclization with HCl.

We propose the following as a working hypothesis to accommodate the effect of ortho substituents on the mode of acid-catalalyzed cyclization of thiocyanatoacetophenones. It seems logical to assume that in the absence of any steric and/or electronic constraints the principal product of intramolecular cyclization of thiocyanatoacetophenones with HCl should be the thermodynamically more stable heteroaromatic thiazole ring rather than the nonaromatic 1,3-oxathiole derivative. Substituents at the ortho positions of thiocyanatoacetophenones appear to block the chlorothiazole pathway by sterically hindering the formation of the transition state **13**. In **13** the carbonyl



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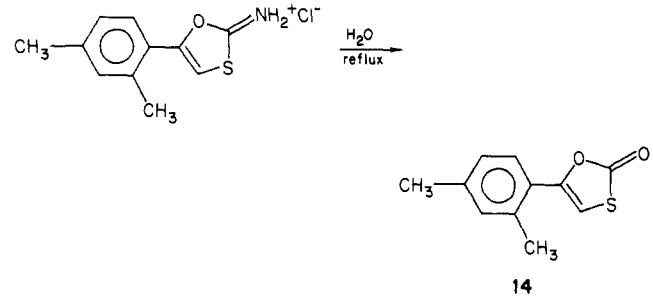
group is perpendicular to the plane of the benzene ring. Molecular models reveal that in this conformation of the transition-state substituents at the two ortho positions of the benzene ring will effectively block the approach of the SCN group to the carbonyl carbon from either of the two available directions. As a result, the pathway leading to the formation of thiazole ring is hindered. the 2,6-disubstituted thiocyanatoacetophenones, therefore, follow the alternate mode of cyclization (Scheme I, pathway b) to give the oxathiole ring system. When only one of the two ortho positions of thiocyanatoacetophenones is occupied by a substituent, then the SCN group may approach the carbonyl carbon from the unhindered side. Consequently, chlorothiazoles as well as oxathioles will form on competitive basis.

In the reactions of thiocyanatoacetophenones with HCl in ether, the oxathiole hydrochlorides, if produced, precipitate out while the 2-chlorothiazoles remain dissolved in the solvent. The products were separated by filteration. The oxathioles were crystallized from glacial acetic acid; liquid thiazoles were purified by vacuum distillation while the solid thiazoles were crystallized from 95% ethanol.

The 1,3-oxathioles **7**, **10**, and **12**, are new compounds. The structures of these compounds were established by elemental analysis and standard spectroscopic techniques including ^{13}C NMR spectroscopy. In the IR spectra of oxathiole hydrochlorides, the $C{=}NH_2^+$ group showed bands around 3300–3000 cm^{-1} (NH_2^+ stretching) and 1685 cm^{-1} ($C{=}N^+$ stretching). The ^1H NMR spectra of these compounds showed olefinic proton resonance at 7.01 ppm (s, 1 H), and the $C{=}NH^+$ proton resonance as a broad D_2O exchangeable band centered at 12 ppm. These data were compared to similar 1,3-oxathiole ring system reported in the literature.[3,4] The ^{13}C NMR spectra exhibited resonances for the 1,3-oxathiole ring system at (Me_2SO-d_6) 180.8 (C2), 149.2 (C5), and 104.2 ppm (C4). The 1,3-oxathioles upon hydrolysis with water should produce the corresponding 5-aryl-1,3-oxathiol-2-ones. This prediction was realized when the imine salt **7** gave the 1,3-oxathiol-2-one **14** in good yield upon refluxing with distilled water for 5 h. The structure of **14** was confirmed by elemental analysis and spectroscopic data.



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Additional work is in progress to study the actual mechanism of the thiocyanation reactions and further application of such cyclizations in the synthesis of larger ring systems.

Experimental Section

Melting points (uncorrected) were taken in open capillary on a Mel-Temp melting point apparatus. Boiling points were determined by microdistillation. The ^1H NMR spectra were measured on JEOL FX-200 and Varian T-60 spectrometers, and the ^{13}C NMR spectra were measured on JEOL FX-200 spectrometer as solutions in $CDCl_3$ or Me_2SO-d_6 depending on solubility. Chemical shifts are reported in parts per million (δ) relative to Me_4Si as internal standard. IR spectra were determined with Beckman TM Acculab or FT Analect FX-6200 spectrometers and absorptions are reported in cm^{-1}. Analytical thin-layer chromatography was performed on precoated silica gel glass plates (0.25 mm, LK5DF Linear-K Whatman), and silica gel (40-140 mesh, 5-3404, J. T. Baker) was used for column chromatography. Microanalyses were performed by the Department of Chemistry, University of Maryland, College Park, MD, and Schwarzkopf Microanalytical Laboratory Inc., Woodside, NY.

General Synthesis of Chloroacetophenones (Scheme I). These compounds were prepared from appropriate alkyl benzenes by reaction with chloroacetyl chloride using Friedel–Crafts conditions as reported in the chemical literature.

Synthesis of Thiocyanatoacetophenones 1, 3, 5, and 8. In general, these compounds are formed by refluxing an ethanolic solution of the requisite phenacyl halide with an excess of potassium thiocyanate.[5,6] 2,4,6-Trimethylthiocyanatoacetophenone (**11**) had not been reported in the literature. This compound was prepared by the following procedure. A solution of 10.00 g of 2,4,6-trimethylchloroacetophenone (5.0 mmol) in 50 mL of acetonitrile was added onto a solution of 6.17 g of KSCN (6.3 mmol, 25% excess) in 80 mL of acetonitrile. The mixture was refluxed for 14 h. The resulting KCl precipitate was filtered, and the filtrate was worked up as follows. Solvent was removed by rotary evaporator to produce a viscous residue. This residue was extracted with dry ether, the extract dried on $MgSO_4$, and the ether removed under vacuum. The residue was crystallized from ethanol: yield, 8.37 g (76%); mp 64–66 °C; IR (Nujol) 2140 ($C{\equiv}N$), 1700, 1610, 1460, 1380, 1280, 1200, 1140, 980, 840 cm^{-1}.

Reaction of Thiocyanatoacetophenones 1, 3, 5, 8, and 11 with HCl Gas. Solutions of 3.19 mmol of thiocyanatoacetophenones in 500 mL of $CaCl_2$-dried ether at −4 °C were saturated by dry HCl gas (3 h). The reaction mixtures were left to stand overnight under dry conditions. During this time, 2-imino-5-aryl-1,3-oxathiole hydrochlorides **7**, **10**, and **12** precipitated out of solution. The oxathiole hydrochlorides were separated by

(3) Hayashi, T. *Bull. Chem. Soc. Jpn.* **1977**, *45*, 1507.
(4) Ueno, Y.; Okawara, M. *Synthesis* **1978**, *3*, 182.
(5) Szekeves, L. *Magy. Kem. Foly.* **1953**, *59*, 228.
(6) Grove, J. F., Borington, H. H. S. *Ann. Appl. Biol.* **1947**, *34*, 113.

Scheme I

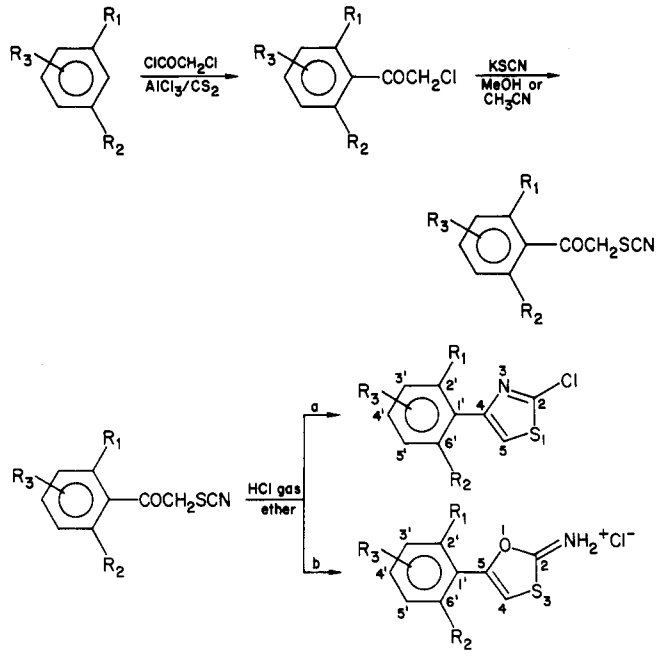
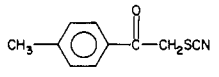
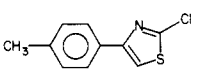
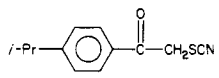
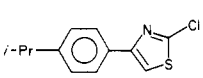
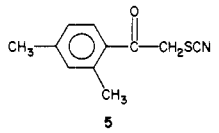
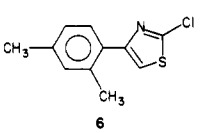
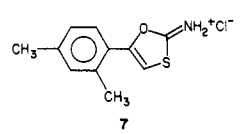
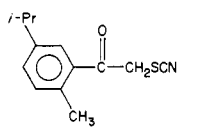
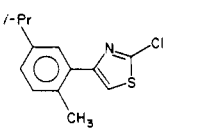
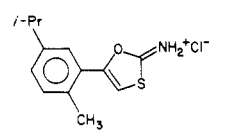
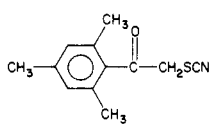
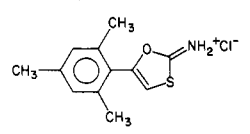


Table I

thiocyanato-aceto-phenones	2-chloro-5-aryl-1,3-thiazoles	2-iminio-5-aryl-1,3-oxathiole hydrochlorides
 1	 2 mp 94-95 °C	none
 3	 4 mp 56-58 °C	none
 5	 6 bp 148-150 °C (3 mm)	 7 mp 193-196 °C
 8	 9 bp 109-111 °C (1 mm)	 10 mp 195-199 °C
 11	none	 12 mp 214-218 °C

suction filtration and purified by crystallization from glacial acetic acid. The filtrates upon evaporation of ether gave 2-chloro-5-aryl-1,3-thiazoles **2**, **4**, **6** and **9**. The liquid thiazoles (**6**, **9**) were purified by vacuum distillation, and the solid thiazoles (**2**, **4**) were crystallized from ethanol.

2-Chloro-4-(4-methylphenyl)-1,3-thiazole (2): yield, 5.95 g (87%); mp 86–88 °C; IR (Nujol) 3120, 2920, 2830, 1460, 1380, 1040, 810, 730 cm^{-1}.

2-Chloro-4-(4-isopropylphenyl)-1,3-thiazole (4): yield 6.00 g (79%; mp 55–58 °C; IR (Nujol) 3100, 1480, 1455, 1410, 1375, 1040, 830, 755 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.7 (d, 2 H, J = 4 Hz), 7.25 (d, 2 H, J = 4 Hz), 2.9 (m, 1 H), 1,3 (d, 6 H).

2-Chloro-4-(2,4-dimethylphenyl)-1,3-thiazole (6): yield 3.0 g (44%); bp 148–150 °C (3.0 mm); IR (neat) 3110, 3010, 2960, 2920, 2880, 1620, 1590, 1495, 1300, 1275, 1230, 1200, 1045 (s), 870, 820, 740, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.42 (d, 1 H), 7.02 (m, 3 H), 2.40 (s, 3 H), 2.32 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 154.47 (C2), 150.20 (C4), 138.26 (C4′), 135.72 (C2′), 131.57 (C5′), 130.55 (C1′), 129.55 (C3′), 126.55 (C6′), 116.89 (C5), 20.9 (d, 2 CH_3).

2-Chloro-4-(2-methyl-4-isopropylphenyl)-1,3-thiazole (9): yield 3.14 g (46%); bp 109–111 °C (1.0 mm); IR (neat) 3110, 2960, 2920, 2880, 1620, 1500, 1440, 1380, 1320, 1270, 1220, 1045 (s), 820, 780, 740, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 7.35 (s, 1 H), 7.1 (m, 3 H), 2.8 (m, 1 H), 2.35 (s, 3 H), 1.2 (d, 6 H).

2-Imino-5-(2,4-dimethylphenyl)-1,3-oxathiole hydrochloride (7): yield 2.7 g (39%); mp 193–196 °C; IR (KBr), 3450, 3040, 2860–2960 (br), 1665 (s, C=N), 1620 (NH_2), 1600, 1540, 1500, 1460, 1385, 1230, 1180, 1160, 1120, 1100, 990, 930, 890, 820, 740, 720, 700 cm^{-1}; ^1H NMR (Me_2SO-d_6, 200 MHz) δ 12.42 (br s, 2 H), 7.45 (d, 1 H), 7.30 (s, 1 H), 7.25 (m, 2 H), 2.40 (s, 3 H), 2.32 (s, 3 H), ^{13}C NMR (Me_2SO-d_6) δ 180.88 (C2), 149.26 (C5), 140.21 (C4′), 136.00 (C2′), 131.92 (C5′), 128.27 (C3′), 126.99 (C6′), 122.72 (C1′), 104.21 (C4), 20.7 (d, 2 CH_3). Anal. Calcd for $C_{11}H_{12}ClNOS$: C, 54.65; H, 5.01; Cl, 14.66; N, 5.80; S, 13.26. Found: C, 54.27; H, 4.99; Cl, 14.50; N, 5.86; S, 13.66.

2-Imino-5-(2-methyl-4-isopropylphenyl)-1,3-oxathiole hydrochloride (10): yield, 3.6 g (52%); mp 195–199 °C; IR (FT, KBr) 3442, 3241, 3096, 2960, 2891, 1657 (s, C=N), 1543, 1501, 1459, 1192, 1162, 1100, 1006, 930, 824, 761, 726 cm^{-1}; ^1H NMR (Me_2SO-d_6, 200 MHz) δ 11.75 (br s, 2 H), 7.40 (s, 1 H), 7.25 (m, 3 H), 2.87 (m 1 H), 2.35 (s, 3 H), 1.17 (s, 3 H), 1.13 (s, 3 H); ^{13}C NMR (Me_2SO-d_6) δ 180.97 (C2), 149.41 (C5), 146.43 (C5′), 133.64 (C2′), 131.36 (C4′), 128.47 (C3′), 126.28 (C6′), 125.34 (C1′), 104.73 (C4), 32.90 (*i*-PrCH), 23.67 (*i*-PrCH$_3$), 20.20 (CH_3). Anal. Calcd for $C_{13}H_{16}ClNOS$: C, 57.87; H, 5.99; Cl 13.14; N, 5.19; S, 11.88. Found: C, 57.99; H, 6.05; Cl, 13.02; N, 5.16; S, 11.92.

2-Imino-5-(2,4,6-Trimethylphenyl)-1,3-oxathiole hydrochloride (12): yield, 6.38 g (93%); mp 214–218 °C; IR (FT, KBr) 3447, 3116, 3042, 2862, 1638 (s, C=N), 1620 (NH_2), 1538, 1461, 1382, 1342, 1228, 1132, 1090, 1032, 982, 951, 892, 859, 795, 742, 705 cm^{-1}; ^1H NMR (Me_2SO-d_6, 200 MHz) δ 11.98, (br s, 2H), 7.22 (s, 1 H), 7.00 (m, 2 H), 2.25 (s, 3 H), 2.22 (s, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 181.35 (C2), 147.94 (C5), 140.44 (C4′), 138.40 (C2′,C6′), 128.53 (C3′,C5′), 122.63 (C1′), 106.57 (C4), 20.75 (p-CH_3), 19.76 (2 *o*-CH_3). Anal. Calcd for $C_{12}H_{14}ClNOS$: C, 56.48; H, 5.53; Cl, 13.89; N, 5.49; S, 12.56. Found: C, 56.77; H, 5.56; Cl, 12.86; N, 5.89; S, 12.42.

The repeated analysis of a highly purified sample did not give satisfactory analysis for chlorine.

Hydrolysis of 2-Imino-5-(2,4-dimethylphenyl)-1,3-oxathiole Hydrochloride (14). A suspension of **7** (530 mg, 2.19 mmol) in distilled water (13 mL) was heated under reflux for 11 h. The resulting yellow solid was dissolved in CH_2Cl_2 and washed twice with distilled water. The methylene chloride solution was dried (Na_2SO_4) and the solvent partially evaporated to 5 mL. This solution was subjected to column chromatography (silica gel) using benzene and benzene–CH_2Cl_2 (50:50) as eluants. The fractions eluted with benzene afforded compound **14** which was crystallized from ethanol: yield, 360 mg (80%); mp 60–62 °C; IR (FT, KBr) 3150, 2936, 1750 (s, C=O), 1614, 1450, 1032, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.45 (d, 1 H), 7.00 (m, 3 H); 6.2 (s, 1 H), 2.45 (s, 3 H), 2.40 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 170.98 (C2), 147.40 (C5), 139.86 (C4′), 135.89 (C2′), 132.01 (C5′), 128.30 (C3′), 126.87 (C6′), 124.71 (C1′), 100.12 (C4), 21.32 (2 CH_3); TLC (benzene) R_f 0.69. Anal. Calcd for $C_{11}H_{10}O_2S$: C, 64.06; H, 4.89; S, 15.55. Found: C, 64.41; H, 4.91; S, 15.40.

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Registry No. **1**, 6097-27-4; **2**, 3884-32-0; **3**, 56430-89-8; **4**, 99797-29-2; **5**, 6097-20-7; **6**, 99797-30-5; **7**, 99797-31-6; **8**, 99797-28-1; **9**, 99797-32-7; **10**, 99797-33-8; **11**, 99797-27-0; **12**, 99797-34-9; **14**, 99797-35-0; 2,4,6-trimethylchloroacetophenone, 50690-12-5.