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Studies on Mesoionic Compounds. XIII.[1] Synthesis of Mesoionic 1,2,3-Thiadiazolium-4-thiolates[2]

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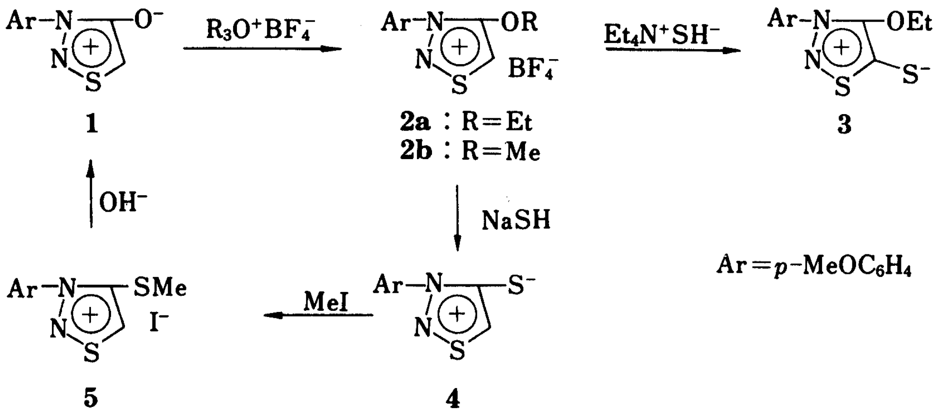
New mesoionic heterocycles, 3-aryl- and 3-alkyl-1,2,3-thiadiazolium-4-thiolates (**4** and **8**), were synthesized by two different procedures. Some of the *S*-methyl derivatives of these compounds gave the corresponding mesoionic 4-olate derivatives on alkaline hydrolysis.

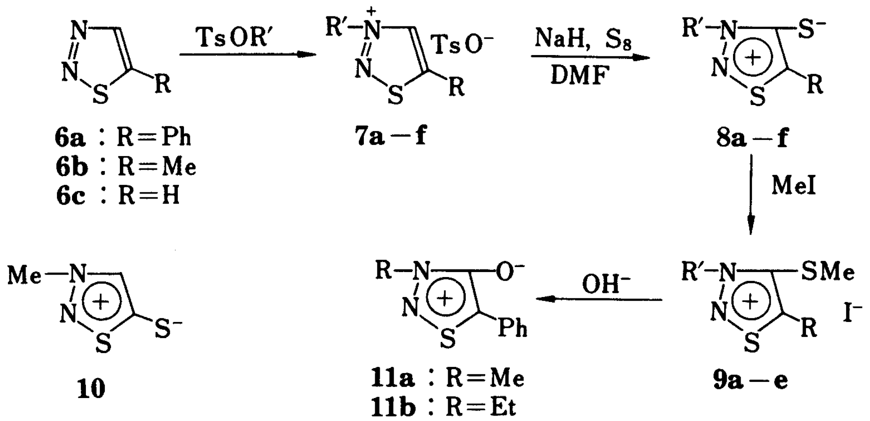
Keywords——mesoionic compound; 1,2,3-thiadiazole; *N*-alkylation; alkyl *p*-toluenesulfonate; direct thiation; hydrolysis

The synthesis and chemical properties of mesoionic compounds have been widely studied, and the pharmacological activities of these compounds have also been examined.[3] Since 1,2,3-thiadiazolium-4-olates, *e.g.* compound (**1**), were first synthesized by Duffin and Kendall,[4] their chemical properties[5] and monoamine oxidase inhibitory activity[6] have been reported. We recently found that mesoionic 1,2,3-thiadiazolium-4-aminides could be obtained by alkylation of the corresponding 4-amino-1,2,3-thiadiazole derivatives.[1] In connection with our synthetic studies on mesoionic compounds, we now report the synthesis of an analogue of the 1,2,3-thiadiazole system possessing an exocyclic sulfur atom; such a system has not previously been described.

According to our procedure for the conversion of an exocyclic oxygen atom into a sulfur atom in mesoionic heterocycles,[7] 4-ethoxy-1,2,3-thiadiazolium fluoroborate (**2a**) was submitted to the reaction with sodium hydrosulfide. However, this reaction gave complex materials. Furthermore, treatment of **2a** with tetraethylammonium hydrosulfide[8] gave only a trace of the 5-thiolate compound (**3**). The structure **3** was deduced from the spectral features; the infrared (IR) spectrum showed an absorption band of ether at 1310 cm^{-1}, the nuclear magnetic resonance (NMR) spectrum revealed the presence of an ethoxyl group and high resolution mass spectrum (MS) showed the formula $C_{11}H_{12}N_2O_2S_2$. Thus, compound (**2a**) could not be converted to the desired compound (**4**), probably due to steric factors. We next examined the reaction of the 4-methoxy derivative (**2b**). When **2b** was treated with sodium hydrosulfide at -70°C, the 4-thiolate compound (**4**) was obtained as red crystals in 24% yield. Its NMR and ultraviolet (UV) spectral data were very similar to those of the 4-olate derivative (**1**). The MS and elemental analysis were consistent with the expected composition of **4**. The presence of the exocyclic sulfur atom in **4** was further confirmed by reaction with methyl iodide to give the *S*-methyl compound (**5**) in high yield. This new mesoionic compound (**4**) was apparently stable to acid and alkali. Although the electrophilic reactions of the 4-olate compound (**1**) exemplified by halogenation, Vilsmeier–Haack reaction and Mannich reaction occurred smoothly to yield the corresponding 5-substituted derivatives in high yields,[5b] these reactions of **4** did not occur at all. Treatment of **5** with ethanolic methylamine solution gave the 4-olate compound (**1**) in 19% yield instead of the 4-methylaminide derivative.[7] Treatment of **5** with 5% sodium hydroxide and 5% sodium carbonate at room temperature also afforded **1** in 18% and 31% yields, respectively.

On the other hand, an alternate procedure is required for the preparation of 3-alkyl derivatives of this system, because the corresponding 4-oxo compounds could not be obtained by





7,8,9; a : R=Ph, R'=Me; **b** : R=Ph, R'=Et; **c** : R=Ph, R'=PhCH$_2$;
d : R=R'=Me; **e** : R=Me, R'=PhCH$_2$; **f** : R=H, R'=Me

Duffin and Kendall's method using diazonium compounds.[4] Begtrup[9] reported an interesting synthesis of mesoionic 1,2,3-triazole derivative by direct thiation of a cyclic ylid derived from the corresponding triazolium salt. We attempted to extend this method to the present thiadiazole system. 5-Phenyl-1,2,3-thiadiazole (**6a**) was heated with methyl *p*-toluenesulfonate at 100°C to give 3-methyl-5-phenyl-1,2,3-thiadiazolium *p*-toluenesulfonate (**7a**) quantitatively. It is known that *N*-alkylation of 1,2,3-thiadiazoles with various alkylation agents such as alkyl halide, alkyl fluorosulfonate, dimethyl sulfate, *etc.* occurs exclusively or predominantly at *N*-3.[1,10,11] Treatment of **7a** with sodium hydride and sulfur in dimethylformamide at 0°C afforded the desired compound, 3-methyl-5-phenyl-1,2,3-thiadiazolium-4-thiolate (**8a**), as orange crystals in 47% yield. The NMR spectrum of **8a** showed signals due to the *N*-methyl and phenyl groups and lacked the C-4 proton signal. High resolution MS indicated the formula $C_9H_8N_2S_2$. Reaction of **8a** with methyl iodide yielded the 4-methylthio derivative (**9a**) in high yield. These results supported the mesoionic formulation of **8a**. Similarly, treatment of **6a** with ethyl and benzyl *p*-toluenesulfonates followed by sodium hydride and sulfur yielded the corresponding 4-thiolates (**8b** and **8c**) in 54% and 73% yields, respectively. 5-Methyl-1,2,3-thiadiazole (**6b**) also gave the mesoionic compounds (**8d** and **8e**) in the same way as above. In the case of the unsubstituted thiadiazole (**6c**), the 4-thiolate (**8f**) and the 5-thiolate (**10**) were obtained in 3% and 48% yields, respectively. High resolution MS of these two products (**8f** and **10**) showed the formula $C_3H_4N_2S_2$, and the IR and UV spectra of the two compounds were very similar. We deduced their formulations by comparing the MS; a fragment ion at *m/e* 42 (base peak) which was attributed to $\mathrm{Me\overset{+}{N}{\equiv}CH}$ was observed in the spectrum of **10**, while it was absent in that of **8f**. Predominant formation of **10** in this reaction is understandable, since 1,2,3-thiadiazole is deuterated easily at C-5.[12)]

We next investigated the hydrolysis of the *S*-methyl derivatives (**9**), which were obtained from **8**, as well as **5**. Treatment of **9a** and **9b** with dilute alkali afforded the 4-olates (**11a** and **11b**) in 59% and 42% yields, respectively. The present method improves our previous procedure to obtain **11a** from a 1,2,3-thiadiazolium-4-aminide derivative *via* *N*-nitrosation.[1)] However, in the case of **9c**, debenzylation occurred to yield 4-methylthio-5-phenyl-1,2,3-thiadiazole. Furthermore, similar reactions of the 5-methyl derivatives (**9d** and **9e**) resulted in the formation of resinous products. These results suggest that the stability of the mesoionic 1,2,3-thiadiazole ring system is enhanced by conjugation with an aromatic substituent.

Experimental

All melting points were determined with a Yanagimoto hot-stage apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 spectrophotometer, and UV spectra were measured with a Hitachi model 200-10 spectrophotometer. NMR spectra were recorded on a JEOL JNM-PMX-60 spectrometer with tetramethylsilane as an internal standard. MS were obtained with a JEOL JMS-D200 instrument.

4-Ethoxy-3-*p*-methoxyphenyl-1,2,3-thiadiazolium-5-thiolate (3)——To a solution of 4-ethoxy-3-*p*-methoxyphenyl-1,2,3-thiadiazolium fluoroborate (**2a**)[5b)] (972 mg) in MeCN (24 ml) was added tetraethylammonium hydrosulfide[8)] (978 mg) at -78°C, and the mixture was stirred at the same temperature for 1 h then at room temperature for 30 min. After concentration of the mixture *in vacuo*, the residue was chromatographed on silica gel (20 g). Elution with $CHCl_3$ gave crystals, which were recrystallized from iso-PrOH to afford 32 mg (4%) of **3** as red needles, mp 110°C. UV λ_{max}^{EtOH} nm (log ε): 245 (3.87), 303 (3.18). NMR ($CDCl_3$) δ: 1.53 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 3.88 (3H, s, OMe), 4.52 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 7.00, 7.43 (4H, AB-q, $J=9$ Hz, arom.). High resolution MS, Calcd for $C_{11}H_{12}N_2O_2S_2$ (M^+): 268.0339. Found: 268.0298.

4-Methoxy-3-*p*-methoxyphenyl-1,2,3-thiadiazolium Fluoroborate (2b)——A mixture of 3-*p*-methoxyphenyl-1,2,3-thiadiazolium-4-olate[4)] (1) (2.08 g) and trimethyloxonium fluoroborate[13)] (2.96 g) in CH_2Cl_2 (50 ml) was stirred at room temperature for 12 h. After evaporation of the CH_2Cl_2, the residue was washed with ether and recrystallized from EtOH to give 2.49 g (80%) of **2b**, colorless needles, mp 188—189°C. NMR (DMSO-d_6) δ: 3.93 (3H, s, OMe), 4.35 (3H, s, OMe), 7.29, 7.85 (4H, AB-q, $J=9$ Hz, arom.), 9.33 (1H, s, C-5H). *Anal.* Calcd for $C_{10}H_{11}BF_4N_2O_2S$: C, 38.73; H, 3.58; N, 9.03. Found: C, 38.79; H, 3.41; N, 9.28.

3-*p*-Methoxyphenyl-1,2,3-thiadiazolium-4-thiolate (4)——A solution of NaSH (504 mg) in MeOH (9 ml) was added to a suspension of **2b** (1.86 g) in MeOH (18 ml) at -70°C with stirring. The mixture was stirred at the same temperature for 1 h then at 0°C for 3 h. After evaporation of the MeOH *in vacuo*, the residue was dissolved in $CHCl_3$. The solution was washed with water, dried over $MgSO_4$, and concentrated. Recrystallization of the residue from MeOH gave 325 mg (24%) of **4** as red needles, mp 193—194°C. UV λ_{max}^{EtOH} nm (log ε): 252 (3.77), 343 (3.77). NMR ($CDCl_3$) δ: 3.93 (3H, s, OMe), 7.10, 7.90 (4H, AB-q, $J=9$ Hz, arom.), 8.45 (1H, s, C-5H). MS *m/e*: 224 (M^+). *Anal.* Calcd for $C_9H_8N_2OS_2$: C, 48.19; H, 3.60; N, 12.49. Found: C, 48.06; H, 3.59; N, 12.75.

3-*p*-Methoxyphenyl-4-methylthio-1,2,3-thiadiazolium Iodide (5)——A mixture of **4** (224 mg) and MeI (2 ml) in $CHCl_3$ (6 ml) was stirred at room temperature for 10 min. Concentration of the mixture *in vacuo*, and recrystallization of the residue from EtOH gave 358 mg (98%) of **5**, orange prisms, mp 159—163°C. NMR (CD_3OD) δ: 2.93 (3H, s, SMe), 4.02 (3H, s, OMe), 7.25, 7.83 (4H, AB-q, $J=9$ Hz, arom.), 9.82 (1H, s, C-5H). *Anal.* Calcd for $C_{10}H_{11}IN_2OS_2$: C, 32.79; H, 3.03; N, 7.65. Found: C, 32.77; H, 3.03; N, 7.65.

Hydrolysis of 5——A mixture of **5** (50 mg) and 5% Na_2CO_3 (0.5 ml) in MeOH (3 ml) was stirred at room temperature for 48 h. Extraction with $CHCl_3$, and usual work-up of the extract gave a brown oil. The major product was separated by preparative TLC (SiO_2, $CHCl_3$–MeOH (9: 1)) to give 9 mg (31%) of yellow crystals, mp 145—150°C. This product was identical with an authentic sample of **1**[4)] (mp 148—150°C) by comparison of IR and NMR spectra.

3-Alkyl-1,2,3-thiadiazolium *p*-Toluenesulfonate (7)——5-Phenyl-1,2,3-thiadiazole[14)] (**6a**) (4.05 g) and methyl *p*-toluenesulfonate (7.5 ml) were heated together at 100°C with stirring for 3 h. After cooling, the mixture was washed thoroughly with ether and dried to give 10.2 g (quantitative) of **7a**, mp 65—72°C. NMR ($CDCl_3$) δ: 2.27 (3H, s, Ar–$C\underline{H}_3$), 4.77 (3H, s, NMe), 7.00, 7.63 (4H, AB-q, $J=8.5$ Hz, arom.), 7.47—7.92 (5H, m, Ph), 10.32 (1H, s, C-4H).

The following thiadiazolium *p*-toluenesulfonates were prepared in a similar manner.[15)]

7b: Yield 80%, colorless needles, mp 108°C (ether–iso-PrOH). NMR ($CDCl_3$) δ: 1.67 (3H, t, $J=7$ Hz, $CH_2C\underline{H}_3$), 2.23 (3H, s, Ar–$C\underline{H}_3$), 5.10 (2H, q, $J=7$ Hz, $C\underline{H}_2CH_3$), 7.00, 7.63 (4H, AB-q, $J=8.5$ Hz, arom.), 7.26—7.91 (5H, m, Ph), 10.76 (1H, s, C-4H).

7c: Yield 97%, colorless sticks, mp 191—193°C (EtOH). NMR (DMSO-d_6) δ: 2.30 (3H, s, Ar–$C\underline{H}_3$), 6.30 (2H, s, $PhC\underline{H}_2$), 7.00—8.13 (14H, m, arom.), 10.63 (1H, s, C-4H).

7d: Yield 90%, brown oil. NMR ($CDCl_3$) δ: 2.30 (3H, s, Ar–C$\underline{\mathrm{H}}_3$), 2.73 (3H, s, C-5Me), 4.52 (3H, s, NMe), 7.05, 7.56 (4H, AB-q, J=8.5 Hz, arom.), 9.57 (1H, s, C-4 H).

7e: Yield 97%, brown oil. NMR ($CDCl_3$) δ: 2.28 (3H, s, Ar–C$\underline{\mathrm{H}}_3$), 2.76 (3H, s, C-5 Me), 6.03 (2H, s, PhC$\underline{\mathrm{H}}_2$), 7.13, 7.74 (4H, AB-q, J=8.5 Hz, arom.), 7.36 (5H, m, Ph), 9.96 (1H, s, C-4 H).

7f: Yield 99%, colorless plates, mp 117—118°C ($CHCl_3$). NMR ($CDCl_3$) δ: 2.32 (3H, s, Ar–C$\underline{\mathrm{H}}_3$), 4.63 (3H, s, NMe), 7.15, 7.70 (4H, AB-q, J=9 Hz, arom.), 9.98 (1H, d, J=3 Hz), 10.23 (1H, d, J=3 Hz).

3-Alkyl-1,2,3-thiadiazolium-4-thiolates (8)——DMF (5.5 ml) was added dropwise to a cooled mixture of **7a** (1.044 g), sulfur (768 mg) and 53% NaH dispersed in mineral oil (272 mg) under a nitrogen atmosphere at 0—2°C with stirring. After being stirred at the same temperature for 1 h, then at room temperature for 1 h, the mixture was concentrated *in vacuo*. MeOH was added to the residue and the solution was filtered. The filtrate was concentrated, and the residue was dissolved in AcOEt. The solution was washed with water, dried over $MgSO_4$, and concentrated. The crude product was washed with hexane and recrystallized from iso-PrOH to give 293 mg (47%) of **8a**, orange needles, mp 141—142°C. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 298 (4.10), 459 (3.49). NMR ($CDCl_3$) δ: 4.43 (3H, s, NMe), 7.57 (3H, m, arom.), 8.33 (2H, m, arom.). High resolution MS, Calcd for $C_9H_8N_2S_2$ (M^+): 208.0128. Found: 208.0116.

The following derivatives were obtained similarly.

8b: Yield 54%, orange needles, mp 106—107°C (iso-PrOH). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 300 (4.06), 459 (3.41). NMR ($CDCl_3$) δ: 1.67 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 4.95 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 7.43—7.77 (3H, m, arom.), 8.13—8.46 (2H, m, arom.). MS *m/e*: 222 (M^+). *Anal.* Calcd for $C_{10}H_{10}N_2S_2$: C, 54.02; H, 4.53; N, 12.60. Found: C, 53.71; H, 4.55; N, 12.90.

8c: Yield 73%, red needles, mp 98—100°C (EtOH). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 303 (4.07), 470 (3.44). NMR ($CDCl_3$) δ: 6.10 (2H, s, PhC$\underline{\mathrm{H}}_2$), 7.20—7.73 (8H, m, arom.), 8.08—8.35 (2H, m, arom.). MS *m/e*: 284 (M^+). *Anal.* Calcd for $C_{15}H_{12}N_2S_2$: C, 63.35; H, 4.25; N, 9.85. Found: C, 63.69; H, 4.31; N, 10.14.

8d: Yield 51%, red needles, mp 133—135°C (iso-PrOH). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 254 (4.27), 418 (3.46). NMR ($CDCl_3$) δ: 2.57 (3H, s, C-5 Me), 4.30 (3H, s, NMe). MS *m/e*: 146 (M^+). *Anal.* Calcd for $C_4H_6N_2S_2$: C, 32.85; H, 4.14; N, 19.16. Found: C, 32.84; H, 4.20; N, 19.41.

8e: Yield 28%, red needles, mp 118—120°C (cyclohexane). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 257 (4.00), 430 (3.22). NMR ($CDCl_3$) δ: 2.59 (3H, s, C-5 Me), 6.03 (2H, s, PhC$\underline{\mathrm{H}}_2$), 7.17—7.83 (5H, m, Ph). High resolution MS, Calcd for $C_{10}H_{10}N_2S_2$ (M^+): 222.0285. Found: 222.0306.

3-Methyl-1,2,3-thiadiazolium-4-thiolate (8f) and -5-thiolate (10)——In the same manner as above, treatment of **7f** (816 mg) with sulfur (768 mg), 60% NaH in mineral oil (240 mg) and *N*,*N*-dimethylformamide (DMF) (4 ml) gave an oily mixture of products, which was then chromatographed on SiO_2 (21 g). Elution with benzene gave 11 mg (3%) of **8f**, yellow needles, mp 139—141°C (iso-PrOH). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 256 (3.48), 404 (3.98). NMR ($CDCl_3$) δ: 4.00 (3H, s, NMe), 7.74 (1H, s, C-5 H). MS *m/e*: 132 (M^+, base peak), 117, 56, 43, 28. High resolution MS, Calcd for $C_3H_4N_2S_2$ (M^+): 131.9816. Found: 131.9808.

Further elution with benzene gave 190 mg (48%) of **10**, yellow needles, mp 106—107°C (iso-PrOH). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 266 (3.82), 414 (3.85). NMR ($CDCl_3$) δ: 4.33 (3H, s, NMe), 8.26 (1H, s, C-4 H). MS *m/e*: 132 (M^+), 86, 57, 42 (base peak), 28. *Anal.* Calcd for $C_3H_4N_2S_2$: C, 27.26; H, 3.05; N, 21.19. Found: C, 27.11; H, 3.07; N, 21.25.

3-Alkyl-4-methylthio-1,2,3-thiadiazolium Iodides (9)——A mixture of **8a**—**e** (1 mmol) and MeI (1 ml) in $CHCl_3$ (3 ml) was stirred at room temperature for 1 h. Concentration of the mixture *in vacuo* gave **9a**—**e**.

9a: Yield 100%, red oil. NMR ($CDCl_3$) δ: 2.55 (3H, s, SMe), 4.87 (3H, s, NMe), 7.60—8.20 (5H, m, Ph).

9b: Yield 91%, yellow leaflets, mp 149—150°C (acetone). NMR ($CDCl_3$) δ: 1.85 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 2.58 (3H, s, SMe), 5.13 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 7.40—7.70 (3H, m, arom.), 7.73—8.00 (2H, m, arom.).

9c: Yield 99%, red oil. NMR ($CDCl_3$) δ: 2.43 (3H, s, SMe), 6.38 (2H, s, PhC$\underline{\mathrm{H}}_2$), 7.37—7.80 (8H, m, arom.), 7.93—8.13 (2H, m, arom.).

9d: Yield 90%, yellow leaflets, mp 149—150°C (iso-PrOH). NMR (DMSO-d_6) δ: 2.70 (3H, s, SMe), 3.01 (3H, s, C-5 Me), 4.70 (3H, s, NMe).

9e: Yield 98%, red oil. NMR ($CDCl_3$) δ: 2.61 (3H, s, SMe), 3.04 (3H, s, C-5 Me), 6.21 (2H, s, PhC$\underline{\mathrm{H}}_2$), 7.03 (5H, s, Ph).

3-Alkyl-1,2,3-thiadiazolium-4-olates (11)——A mixture of **9a** (178 mg) and 5% NaOH (0.1 ml) in MeOH (2 ml) was stirred at room temperature for 10 min. After dilution with water, the mixture was extracted with $CHCl_3$. Usual work-up of the extract gave 27 mg (59%) of **11a**, yellow plates, mp 155—156°C (iso-PrOH). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1600 (CO). UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 256 (3.97), 395 (4.04). NMR ($CDCl_3$) δ: 4.05 (3H, s, NMe), 7.20—8.10 (5H, m, Ph). MS *m/e*: 192 (M^+). *Anal.* Calcd for $C_9H_8N_2OS$: C, 56.22; H, 4.19; N, 14.57. Found: C, 56.38; H, 4.28; N, 14.78. This product was identical with the authentic sample obtained previously.[1)]

In a manner similar to that described above, reaction of **9b** (150 mg) with 5% Na_2CO_3 (0.1 ml) in MeOH (2 ml) for 12 h gave 36 mg (42%) of **11b**, yellow needles, mp 102—103°C (cyclohexane). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 1610 (CO). NMR ($CDCl_3$) δ: 1.52 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 4.38 (2H, q, J=7 Hz, $C\underline{H}_2CH_3$), 7.17—7.50 (3H, m, arom.), 7.80—8.03 (2H, m, arom.). MS *m/e*: 206 (M^+). *Anal.* Calcd for $C_{10}H_{10}N_2OS$: C, 58.23; H, 4.89; N, 13.58. Found: C, 58.35; H, 4.88; N, 13.87.

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