1.4462; nmr ($CDCl_3$) τ 6.25 (2 H, septuplet), 8.66 (12 H, doublet); $\nu_{max}^{CCl_4}$ 1815 cm^{-1}; ultraviolet spectrum (heptane) λ_{max} 357 mμ (ϵ 190), 319 (150, shoulder), 306 (230), 294 (250), 285 (210, shoulder), and 230 (670, shoulder).

Anal. Calcd for $C_8H_{14}N_2O_2$: C, 56.5; H, 8.3; N, 16.5. Found: C, 56.6; H, 8.4; N, 16.9.

Acknowledgment.—The author is indebted to Mr. D. P. Wilmes for technical assistance, Dr. J. J. McBrady for infrared and nmr interpretation, Mr. P. B. Olson for analytical determinations, and Mr. J. J. Neumayer for the molecular weight determination.

1-Thioacylaziridines

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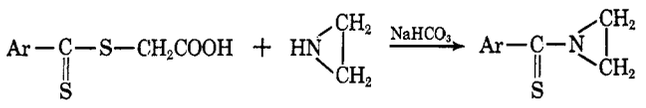
Several 1-acylaziridines are known in the literature. However, 1-thioacylaziridines are not reported except for 1-(N-alkyl- or -arylthiocarbamyl)aziridines.[1] In continuation of the study of aziridine chemistry, it appeared of interest to add new examples of 1-thioacylaziridines.

As an extension of our previous work,[2] several *para*-substituted 1-thiobenzoylaziridines were prepared by the reaction of sodium thiobenzoylthioglycolate with aziridine in water. The purified, crystalline compounds gradually polymerized on standing at room temperature.



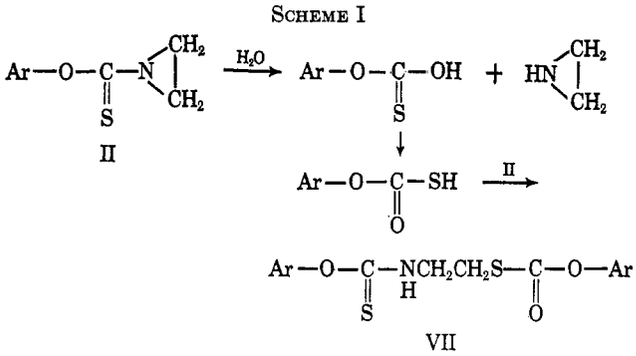
I

Ar = *p*-chlorophenyl (Ia), *p*-tolyl (Ib), and *p*-methoxyphenyl (Ic)

Compounds Ia–c were isomerized to 2-arylthiazolines (IV) by the reaction with picric or *p*-toluenesulfonic acids in refluxing benzene. Under the same conditions, I and thiophenol gave the ring-opened addition products, N-(2-phenylthioethyl)thiobenzamides, along with some thiazolines.

1-(Aryloxythiocarbonyl)aziridines (aryl = *p*-tolyl, IIa; *p*-nitrophenyl, IIb) were obtained from aryl chlorothionformates and aziridine. They were also unstable at room temperature and gave polymers of low molecular weight. Reaction with concentrated hydrochloric acid at room temperature gave 2-aryloxythiazolines (V) along with larger quantities of acid-insoluble substances (VII). The elemental analyses and the infrared and the nmr spectral data of VII all support the structure as it is written, the compounds of which structure might be formed by ring opening of IIa or IIb with thiocarbonic acid aryl esters as shown in Scheme I. *p*-Toluenesulfonic acid also gave a poor yield of 2-(*p*-nitrophenyloxy)thiazoline (Vb) from IIb. Reaction of IIa with thiophenol at

SCHEME I

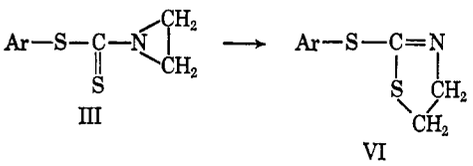


II

Ar = *p*-tolyl (VIIa) and nitrophenyl (VIIb)

room temperature gave the ring-opened addition product, while IIb and thiophenol gave 2-phenylthioethylisothiocyanate under the same condition.

1-(Aryldithiocarbonyl)aziridines (aryl = *p*-chlorophenyl, IIIa; *p*-methoxyphenyl, IIIb) were prepared from chlorodithioformic acid aryl esters and aziridine. They were rapidly polymerized at room temperature, and gradually at about 5°. 1-(*p*-Methoxyphenyldithiocarbonyl)aziridine (IIIb) was converted to 2-(*p*-methoxyphenylthio)thiazoline (VIb) on standing with concentrated hydrochloric acid at room temperature.



III VI

a, Ar = *p*-chlorophenyl
b, Ar = *p*-methoxyphenyl

With thiophenol, IIIb gave the acyclic addition product.

Including 1-(N-phenylthiocarbamyl)aziridine, 1-thioacylaziridines have a great tendency to polymerize in contrast to the corresponding 1-acylaziridines. As to the polymerization reaction of these 1-thioacylaziridines, investigation is in progress, and the results will be reported in the near future.

Experimental Section[3]

Preparation of Thiobenzoylthioglycolic Acids.—*p*-Chlorothiobenzoylthioglycolic acid was prepared from *p*-chlorobenzo trichloride in 50% yield in a same way as described in the preparation of thiobenzoylthioglycolic acid.[4] It melted at 117.5–118.5° (lit.[5] mp 115–117°).

p-Methylthiobenzoylthioglycolic acid, mp 117–118° (lit.[5] mp 118–119°), and *p*-methoxythiobenzoylthioglycolic acid, mp 121–122° (lit.[5] mp 124–125°), were prepared from *p*-chlorotoluene and *p*-chloroanisol in 43 and 46% yield in essentially the same manner as described for the synthesis of thiobenzoylthioglycolic acid from bromobenzene,[6] tetrahydrofuran being used as solvent for the Grignard reaction in these cases.

Preparation of 1-(*p*-Chlorothiobenzoyl)aziridine (Ia).—*p*-Chlorothiobenzoylthioglycolic acid (18.5 g, 0.075 mole) was neutralized with sodium bicarbonate (7 g) in 150 ml of water. Into the aqueous solution, a cold solution of 8 g (0.19 mole) of aziridine in 100 ml of water was added at 0–5°, and the mixture was stirred for 15 min. The yellow crystals were collected on a filter and dissolved in 170 ml of petroleum ether (bp 40–80°) as soon as possible at room temperature. The solution was washed

(1) *E.g.*, (a) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895); (b) Y. Iwakura and A. Nabeya, *Bull. Tokyo Inst. Technol.*, **42**, 69 (1961); (c) M. Tišler, *Arch. Pharm.*, **291**, 457 (1958).

(2) Y. Iwakura, A. Nabeya, T. Nishiguchi, and K. Ohkawa, *J. Org. Chem.*, **31**, 3352 (1966).

(3) Melting points and boiling points are uncorrected. Nmr spectra were measured in a specified solution with tetramethylsilane as the internal standard.

(4) F. Kurzev and A. Lawson, *Org. Syn.*, **42**, 100 (1962).

(5) K. A. Jensen and C. Pedersen, *Acta. Chem. Scand.*, **15**, 1087 (1961).

(6) A. Kjaer, *ibid.*, **4**, 1347 (1950).

TABLE I

1-THIOBENZOYLAZIRIDINES[a]

Compd	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Nmr signals of CH_2[b] (τ), ppm
Ia	43.4–45	C_9H_8ClNS	54.68	4.08	7.09	54.34	3.83	6.81	7.40
Ib	57–59	$C_{10}H_{11}NS$	67.76	6.26	7.90	67.34	6.27	7.63	7.40[c]
Ic	68.5–69	$C_{10}H_{11}NOS$	62.15	5.74	7.25	62.12	5.70	7.04	7.42[d]

[a] The isolation of 1-thiobenzoylaziridine was difficult because of the low melting point (about 5°) and the great tendency to polymerize. [b] Measured in carbon tetrachloride. [c] Another singlet (CH_3) was shown at τ 7.60. [d] Another singlet (CH_3) was at τ 6.20.

TABLE II

THE PICRATES OF 2-ARYLTHIAZOLINES

Picrate of	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IVa	190–191.5	$C_{15}H_{11}ClN_4O_7S$			13.12			12.85
IVb	173–174.5	$C_{16}H_{14}N_4O_7S$			13.79			13.61
IVc	186–188[a,b]	$C_{16}H_{14}N_4O_8S$	45.50	3.34	13.27	45.19	3.43	13.21

[a] Lit. mp 192°: P. Rehländer, *Ber.*, **27**, 2154 (1894). [b] Lit. mp 190–191.5°: G. L. Schmidt, *J. Am. Chem. Soc.*, **87**, 2743 (1965).

TABLE III

2-ARYLTHIAZOLINES

Compd	Mp, °C	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Nmr signals[a] of ring CH_2 (τ), ppm		$\nu_{C=N}$, cm^{-1}
IVa	53.5–55	C_9H_8ClNS	54.68	4.08	7.09	54.75	4.11	6.69	6.65	5.65	1608
IVb	42.5–43.5[b]	$C_{10}H_{11}NS$	67.76	6.26	7.90	67.94	6.40	8.14	6.66	5.58	1610
IVc	54–55[c]	$C_{10}H_{11}NOS$	62.15	5.74	7.25	62.29	6.18	7.06	6.72	5.65	1608

[a] Measured in carbon tetrachloride. Methylene signals were all triplets. [b] Lit. mp 81°: S. Gabriel and Ph. Heymann, *Ber.*, **24**, 783 (1891). Lit. mp 80°: A. Salomon, *ibid.*, **26**, 1321 (1893). [c] Lit. mp 54.5°: see Rehländer, footnote *a*, Table I. Lit. mp 52–54 (crude): see Schmidt, footnote *b*, Table I.

with ice–water several times, filtered from solid impurity, and cooled in a Dry Ice–acetone bath. Crystals were dried under cooling and weighed 12.7 g (86%), mp 43.5–45°.

Ib and c were prepared in the same way in 79 and 70% yield. Analytical data of 1-thiobenzoylaziridines are summarized in Table I.

Isomerization of Ib with Picric Acid.—A mixture of 0.44 g (0.0025 mole) of Ib and 0.57 g (0.0025 mole) of picric acid in 5 ml of benzene was refluxed for 3 hr. Crystals were collected on a filter to give 0.93 g (92%) of IVb picrate, mp 172–174°. The picrate was recrystallized from benzene to give an analytical sample melting at 173–174.5°.

Reaction of Ia or c with picric acid was carried out similarly. Compound IVa or IVc picrate was obtained in 94 or 91% yield, respectively. Analytical data of the picrates are summarized in Table II.

Treatment of IV picrates with alkali gave free thiazolines. The analytical data of the free thiazolines are summarized in Table III.

Isomerization of Ia with *p*-Toluenesulfonic Acid.—A mixture of 0.99 g (0.005 mole) of Ia and 0.86 g (0.005 mole) of *p*-toluenesulfonic acid in 10 ml of benzene was refluxed for 2 hr. Crystals were recrystallized from acetone to give 1.3 g (70%) of IVa *p*-toluenesulfonate melting at 149–150°.

Anal. Calcd for $C_{16}H_{16}ClNO_3S_2$: C, 52.97; H, 4.36; N, 3.79. Found: C, 52.29; H, 4.48; N, 4.10.

Reaction of Ib with Thiophenol.—Thiophenol (0.55 g, 0.005 mole) and Ib (0.89 g, 0.005 mole) were dissolved in 5 ml of benzene, and the solution was refluxed for 2 hr. The benzene solution to which some petroleum ether (bp 40–80°) was added was washed with sodium hydroxide solution to remove thiophenol, and then extracted with dilute hydrochloric acid. Distillation of organic solvents from the organic layer, and recrystallization of the residue with benzene and *n*-hexane gave 1.1 g (73%) of the ring-opened addition product, mp 88–90.5°. Another recrystallization from the same mixed solvent gave an analytical sample melting at 90–91°.

Anal. Calcd for $C_{16}H_{17}NS_2$: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.93; H, 5.74; N, 4.70.

Reaction of *p*-methylthiobenzoylthioglycolic acid with 2-phenylthioethylamine gave the same sample as above.

When equimolar amount of Ib and thiophenol were mixed with outside cooling, and the mixture was left standing at room temperature for 20 days, the yield of the ring-opened addition product increased (82%) and that of the picrate decreased (2%).

Reaction of Ic with thiophenol or Ia with *p*-chlorothiophenol was carried out in a similar way. In every reaction, a mixture of the ring-opened addition product and IV was obtained in both cases when the reaction mixture was refluxed in benzene and when it was left standing at room temperature without solvent.

N-(2-Phenylthioethyl)-*p*-methoxythiobenzamide melted at 76–77°.

Anal. Calcd for $C_{16}H_{17}NOS_2$: C, 63.33; H, 5.65; N, 4.62. Found: C, 63.48; H, 5.44; N, 4.53.

N-[2-(*p*-Chlorophenylthio)ethyl]-*p*-chlorothiobenzamide melted at 63–64°.

Anal. Calcd for $C_{15}H_{13}Cl_2NS_2$: C, 52.63; H, 3.83; N, 4.09. Found: C, 52.95; H, 3.99; N, 3.79.

Preparation of 1-(*p*-Tolyloxythiocarbonyl)aziridine (IIa).—Into a solution of 9.3 g (0.05 mole) of chlorothionformic acid *p*-tolyl ester[2] in 100 ml of ether, a solution of 2.2 g (0.05 mole) of aziridine and 5.0 g (0.05 mole) of triethylamine in 20 ml of ether was added dropwise at −10 to −5°. After the yellow color of the ester disappeared, triethylamine hydrochloride was removed by filtration, while in the receiver of the filtrate ice water was added. The filtrate was washed with ice water several times, and dried over sodium sulfate in a cool place. After ether was evaporated under reduced pressure, the residue was dissolved in petroleum ether at 50°, and the solution was cooled in a Dry Ice–acetone bath. White crystals were obtained. When they were dried at room temperature in a desiccator over calcium chloride, exothermal polymerization took place to give glassy material. In another run where the crystals were dried over silica gel in a cool place, 6.7 g (69%) of IIa, mp *ca.* 65°, was obtained.

Anal. Calcd for $C_{10}H_{11}NOS$: C, 62.15; H, 5.74; N, 7.25. Found: C, 61.94; H, 5.76; N, 7.10.

The nmr spectrum of IIa (in CCl_4) showed two singlets at τ 7.61 (CH_3) and 7.45 (CH_2) with 3:4 area.

Compound IIb was prepared in a similar way and was recrystallized from acetone to give a 44% yield of pure sample melting at 99–101°.

Anal. Calcd for $C_9H_8N_2O_3S$: C, 48.21; H, 3.60; N, 12.50. Found: C, 48.73; H, 4.02; N, 12.83.

The nmr spectrum of IIb (in chloroform) showed a singlet at τ 7.30.

Reaction of IIb with Concentrated Hydrochloric Acid.—Into 5 g of concentrated hydrochloric acid, 1.1 g (0.005 mole) of IIb was added portionwise, and the mixture was allowed to stand at about 30° for 1 day. Dilution of the mixture with water gave a white precipitate. It was collected by suction, and dried to give 0.7 g of white powder melting at 140°. Recrystallization from ethanol raised the melting point to 142°. It had absorption bands at 3330 (NH) and 1727 cm^{-1} (C=O). The nmr spectrum of the sample (in acetone) showed two methylene (triplets at τ 6.55 and 6.01) and two aromatic A_2B_2-type patterns (one is centered at about τ 2.5 and the other 1.6 with J = 9 cps).

Anal. Calcd for $C_{16}H_{13}N_3O_7S_2$ (VIIb): C, 45.39; H, 3.09; N, 9.92. Found: C, 45.72; H, 3.26; N, 9.88.

Neutralization of the acid solution with sodium hydroxide gave 0.1 g (9%) of Vb, mp 65°. Recrystallization from petroleum ether gave a pure sample melting at 67–69°. It had an absorption band at 1643 cm^{-1} (C=N). The nmr spectrum of Vb (in CCl_4) gave triplets at τ 6.43 and 5.90 with equal area.

Anal. Calcd for $C_9H_8N_2O_3S$: C, 48.21; H, 3.60; N, 12.50. Found: C, 48.36; H, 3.69; N, 12.36.

Compound Vb was also prepared from chlorothionformic acid *p*-nitrophenyl ester and 2-bromoethylamine hydrobromide on treatment with alkali.

Reaction of IIa with Concentrated Hydrochloric Acid.—The reaction of IIa (1.9 g, 0.01 mole) with concentrated hydrochloric acid (10 g) was carried out, and the reaction mixture was treated in the same manner as in IIb. From the acid-insoluble part, 0.8 g (28%) of VIIa, melting at about 90°, was obtained. Recrystallization from benzene and petroleum ether raised the melting point to 102–104° after being desiccated at 100° under reduced pressure. It had absorption bands at 3350 (NH) and 1703 cm^{-1} (C=O) in the infrared spectrum. The nmr spectrum (obtained in CCl_4 and at 60°) gave signals at τ 7.57 (singlet, CH_3), 6.69 and 6.05 (both triplets, CH_2), and a group of signals at 3.0–2.5 (aromatic H), the area ratio being 6:4:7 [(CH_3):(two CH_2):(aromatic H, theoretically 8)].

Anal. Calcd for $C_{18}H_{19}NO_3S_2$: C, 59.81; H, 5.30; N, 3.87; S, 17.74. Found: C, 59.43; H, 5.36; N, 3.85; S, 17.78.

Treatment of the acid solution with sodium hydroxide, and the subsequent extraction of the alkaline solution with benzene gave 1.1 g (26%) of Va picrate on addition of picric acid to the benzene solution mp 140°. The picrate was recrystallized from ethanol to give an analytical sample, mp 145°.

Anal. Calcd for $C_{16}H_{14}N_4O_8S$: C, 45.50; H, 3.34; N, 13.26. Found: C, 45.47; H, 3.42; N, 13.27.

On treatment of the picrate with alkali, free Va (liquid) was obtained. The infrared spectrum of Va had a band at 1642 cm^{-1} (C=N). The nmr spectrum of Va (in CCl_4) gave triplets at τ 6.61 and 6.03.

Reaction of IIa with Thiophenol.—A mixture of 1.0 g (0.005 mole) of IIa and 0.55 g (0.005 mole) of thiophenol was allowed to stand at room temperature. The mixture began to solidify in 2 days. The infrared spectrum of the mixture obtained after 10 days of standing had an absorption at 3210 cm^{-1} (NH) and no absorption at 2200-cm^{-1} region. Recrystallization of the crude product from benzene and petroleum ether gave a 67% yield of 2-(phenylthio)ethylthiocarbamic acid *p*-tolyl ester, mp 86–88°.

Anal. Calcd for $C_{16}H_{17}NOS_2$: C, 63.33; H, 5.65; N, 4.62. Found: C, 63.61; H, 5.71; N, 4.90.

An equimolar mixture of IIb and thiophenol was placed in a refrigerator. No crystal appeared after 2 days. The infrared spectrum of the mixture showed a sharp absorption at 2160 cm^{-1} (NCS). On addition of aniline to the reaction mixture, 1-phenyl-3-(2′-phenylthioethyl)thiourea, mp 112–115°, which was identified with an authentic sample,[1b] was obtained (lit.[1b] mp 115–116°).

Preparation of 1-(*p*-Methoxyphenyldithiocarbonyl)aziridine (IIIb).—Chlorodithioformic acid *p*-methoxyphenyl ester was prepared from *p*-methoxythiophenol and thiophosgene in a same manner as described for the *p*-chlorophenyl ester[2] in 51% yield, bp 134° (3 mm).

Condensation reaction of the ester (6.56 g, 0.03 mole) with aziridine (1.7 g, 0.04 mole) was carried out in a similar way as in preparing IIa, with triethylamine (2.7 g, 0.027 mole) as an acid acceptor. The temperature was kept below −15°. After 2 hr, the mixture was treated in quite the same way as in preparing IIa. Ether was evaporated at 0° under reduced pressure, and the residue was dissolved in ether and petroleum ether at room temperature. By cooling the solution in a Dry Ice–acetone bath, 4.3 g (64%) of IIIb, mp *ca.* 45°, was obtained after drying at 0°. The nmr spectrum of IIIb (in CCl_4) showed two singlets at τ 7.53 (CH_2) and 6.15 (CH_3) with 4:3 area.

Anal. Calcd for $C_{10}H_{11}NOS_2$: C, 53.33; H, 4.92; N, 6.22. Found: C, 53.59; H, 5.15; N, 5.78.

1-(*p*-Chlorophenyldithiocarbonyl)aziridine (IIIa) was prepared in quite the same way in 59% yield. It melted at 57° and showed a singlet at τ 7.47 in the nmr spectrum (in CCl_4).

Anal. Calcd for $C_9H_8ClNS_2$: C, 47.05; H, 3.51; N, 6.10. Found: C, 47.14; H, 3.49; N, 6.12.

Reaction of IIIb with Concentrated Hydrochloric Acid.—Into 5 g of concentrated hydrochloric acid, 1.5 g (0.0067 mole) of IIIb was added, and the mixture was allowed to stand at room temperature for 2 days. Treatment of the mixture in a same way as described in the case of IIb gave 1.8 g (61%) of VIb picrate from the acid-soluble part on addition of picric acid. The picrate melted at 178–179° after recrystallization from benzene.

Anal. Calcd for $C_{16}H_{14}N_4O_8S_2$: C, 42.29; H, 3.11; N, 12.33. Found: C, 42.31; H, 3.48; N, 12.07.

Treatment of the picrate with alkali gave free VIb (liquid). It had an absorption band at 1590 cm^{-1} (C=N) in the infrared spectrum. The nmr spectrum of VIb (in CCl_4) showed two triplets at τ 6.83 and 5.88 and a singlet at 6.24 (CH_3). The acid-insoluble portion was oily material containing polymer.

Reaction of IIIb with Thiophenol.—Into 1.00 g (0.009 mole) of thiophenol, 1.90 g (0.0084 mole) of IIIb was added portionwise with cooling, and the mixture was left standing for 20 days. The infrared spectrum of the reaction mixture (not solidified) was identical with that of N-(2-phenylthioethyl)dithiocarbamic acid *p*-methoxyphenyl ester prepared from 2-phenylthioethylamine and dithioformic acid *p*-methoxyphenyl ester (mp 68–69°). Thiophenol was removed by washing the benzene solution of the crude mixture with aqueous sodium hydroxide. Extraction of the benzene solution with dilute hydrochloric acid gave a small quantity (0.05 g, about 1%) of VIb picrate, mp 174–177°, after working up the acidic solution as described in a previous example. Removal of benzene from the benzene solution left an oily product, the infrared spectrum of which showed a band at 2150 cm^{-1} (with a shoulder at 2220 cm^{-1}) (NCS). By heating the product with aniline (1.0 g) at 120° for 2 hr, 1-phenyl-3-(2′-phenylthioethyl)thiourea,[1b] mp 113–116°, was obtained (0.7 g, 35%).

The infrared spectrum of the authentic N-(2-phenylthioethyl)-dithiocarbamic acid *p*-methoxyphenyl ester had a band at 3350 cm^{-1} (NH).

Anal. Calcd for $C_{16}H_{17}NOS_3$: C, 57.31; H, 5.11; N, 4.18. Found: C, 57.55; H, 5.04; N, 4.26, 4.07.

On heating N-(2-phenylthioethyl)dithiocarbamic acid *p*-methoxyphenyl ester in refluxing toluene for 30 min, a band of NCS appeared in the infrared spectrum. In the presence of aniline, the dithiocarbamate gave 1-phenyl-3-(2′-phenylthioethyl)-thiourea, mp 113–115° (39%), on heating at 120° for 2 hr.

Registry No.—Ia, 13094-95-6; Ib, 13084-24-7; Ic, 13084-25-8; IIa, 13084-26-9; IIb, 13084-27-0; IIIa, 13094-96-7; IIIb, 13084-28-1; IVa, 13084-29-2; IVa picrate, 13094-97-8; IVa *p*-toluenesulfonate, 13084-30-5; IVb, 13084-31-6; IVb picrate, 13119-22-7; IVc, 2519-93-9; IVc picrate, 13084-33-8; Va, 13084-34-9; Va picrate, 13084-35-0; Vb, 13084-36-1; VIb, 13094-98-9; VIb picrate, 13084-37-2; VIIa, 13084-38-3; VIIb, 13084-39-4; Ib reaction product with thiophenol, 13084-40-7; N-(2-phenylthioethyl)-*p*-methoxythiobenzamide, 13084-41-8; N-2-(*p*-chlorophenylthioethyl)-*p*-chlorothiobenzamide, 13094-99-0; 2-(phenylthio)ethylthiocarbamic acid *p*-tolyl ester, 13084-42-9; 1-phenyl-3-(2′-phenylthioethyl)thiourea, 13084-43-0; N-(2-phenylthioethyl)dithiocarbamic acid *p*-methoxyphenyl ester, 13084-44-1.

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