and closing of five-membered ring. The same on dehydrogenation gave rise to the formation of aromatized indolizine derivatives (**5a-d**, **7a-d**) (Scheme II). The yield of the products ranged between 50 and 61%.

The structures of the compounds were established by microanalysis, physical, and spectra data (Table I).

Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. A Perkin-Elmer infra cord spectrophotometer was used to record the IR spectra. The nuclear magnetic resonance spectra ($CDCl_3$) were run using a Varian A-60 spectrometer with Me_4Si as the internal standard, and chemical shifts are expressed in δ ppm values (Table I). Products were purified by column chromatography over silica gel (60-120 mesh), and then crystallized by appropriate solvents. The purity was checked by TLC.

Preparation of N-(2-Aroylmethyl)picolinium Bromide. Aroylmethyl bromide (0.1 mol) was digested in 20 mL of anhydrous benzene, and 0.1 mol of picoline was added dropwise with constant stirring. After the addition of picoline was complete, the reaction mixture was kept on reflux for about 2 h on a water bath; a pale yellow solid deposited on the inner surface of the flask, and the crude product was recrystallized by methanol/water, to yield a crystalline solid.

Preparation of 1,2-Dicarbomethoxy-3-aroylindolizine and 1,2-Dicarbomethoxy-3-aroylindolizine via 2-Picolinium Ylide and 4-Picolinium Ylide. To the stirred suspension of *N*-(2-aroylmethyl)picolinium bromide (5 mmol) and acetylenic dipolarophile (5 mmol) in anhydrous benzene was added dropwise a solution of 0.7 mL of triethylamine in 10 mL of benzene. After it was stirred for 1 h the whole mass was refluxed on a water bath for 4-6 h. After completion of reaction the resulting mixture was concentrated to 1/10 of its original volume and kept overnight at room temperature. On the next day triethylamine hydrobromide was filtered off and the filtrate was concentrated under reduced pressure to give the reddish brown mass. This product was chromatographed on silica gel with benzene as eluant to give crude product (**5a-d**, **7a-d**) as colored powder and recrystallized from appropriate solvents to obtain the product in pure and crystalline form.

Acknowledgment

We express our thanks to Director, H.B.T.I., Kanpur for providing research facilities.

Registry No. **3a**, 762-42-5; **3b**, 762-21-0; **5a**, 96844-93-8; **5b**, 96844-99-4; **5c**, 96844-94-9; **5d**, 96844-95-0; **7a**, 96826-76-5; **7b**, 96844-96-1; **7c**, 96844-97-2; **7d**, 96844-98-3; *p*-$ClC_6H_4COCH_2Br$, 536-38-9; $C_4H_3SCOCH_2Br$, 63511-54-6; 2-methylpyridine, 109-06-8; 4-methylpyridine, 108-89-4; 2-(bromoacetyl)naphthalene, 613-54-7; (*p*-chlorobenzoylmethyl)-2-picolinium bromide, 82746-43-8; (thienylcarbonylmethyl)-2-picolinium bromide, 96826-74-3; (2-naphthoylmethyl)-2-picolinium bromide, 6276-80-8; (*p*-chlorobenzoylmethyl)-4-picolinium bromide, 25357-43-1; (thienylcarbonylmethyl)-4-picolinium bromide, 96826-75-4; (2-naphthaloylmethyl)-4-picolinium bromide, 6277-78-7.

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Syntheses and Characterization of Some Carbobutoxythio Compounds and Substituted Oxathiazolones

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Eight new carbobutoxythio compounds have been synthesized by reacting *n*-butoxycarbonylsulfenyl chloride with appropriate compounds to test their use as herbicides, fungicides, and insecticides. Three new oxathiazolone derivatives were also synthesized by reacting chlorocarbonylsulfenyl chloride with amides.

A series of carbobutoxythio compounds (**1-8**) was synthesized by reacting *n*-butoxycarbonylsulfenyl chloride (*1*) with substituted amines, bicycloheptanol, and cyclohexene. Table I lists the melting points, the yields, and the proton NMR data of these new compounds. The IR spectra of these compounds have a very strong carbonyl band at 1720-1727 cm^{-1}, characteristic of thiocarbonates.

Three new 5-substituted-1,3,4-oxathiazol-2-ones (**9-11**) were obtained by reaction of chlorocarbonylsulfenyl chloride (*1*) with the appropriate amides according to the literature procedure (*2*, *3*). The physical data of these compounds are listed in Table II.

Experimental Section

All melting points are uncorrected. The proton NMR spectra were recorded on a Perkin-Elmer R-12B spectrometer with

† Deceased, March 31, 1983.

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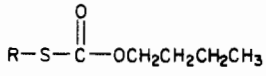
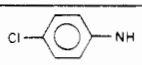
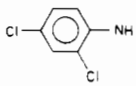
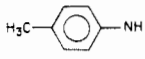
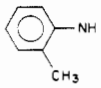
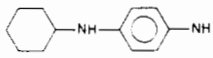
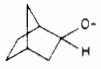
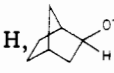
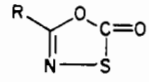
Table I. Data for Carbobutoxythio Compounds

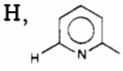
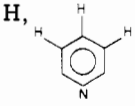


compd	R	mp, °C	yield, %	^{1}H NMR δ[a]
1		57-58	70	0.9 (t, 3 H, CH_3), 1.05-2.05 (m, 4 H, CH_2CH_2), 4.2 (t, 2 H, OCH_2), 5.5 (s, 1 H, NH), 6.75-7.55 (m, 4 H, aromatic)
2		34-35	75	0.9 (t, 3 H, CH_3), 1.05-1.9 (m, 4 H, CH_2CH_2), 4.2 (t, 2 H, OCH_2), 5.8 (s, 1 H, NH), 6.8-7.55 (m, 3 H, aromatic)
3		38	80	0.85 (t, 3 H, CH_3), 1.05-1.8 (m, 4 H, CH_2CH_2), 2.15 (s, 3 H, aromatic CH_3), 4.1 (t, 2 H, OCH_2), 5.8 (s, 1 H, NH), 6.65-7.35 (m, 4 H, aromatic)
4		37	71	0.9 (t, 3 H, CH_3), 1.05-1.75 (m, 4 H, CH_2CH_2), 2.15 (s, 3 H, CH_3), 4.1 (t, 2 H, OCH_2), 5.4 (s, 1 H, NH), 6.45-7.3 (m, 4 H, aromatic)
5		220 dec (grayish green solid)	74	0.9 (t, 3 H, CH_3), 1.1-1.8 (m, 4 H, CH_2CH_2), 4.15 (t, 2 H, OCH_2), 5.6 (broad s, 1 H, NH), 7.1-7.3 (m, 9 H, aromatic)
6		94/0.2 MMhg (colorless liquid)	48	0.75-1.9 (m, 7 H, $CH_3CH_2CH_2$), 3.15-4.4 (m, 10 H, OCH_2 and morpholino CH_2)
7		colorless liquid	40	0.85 (t, 3 H, CH_3), 1.0-2.2 (m, 12 H, CH_2CH_2 and bicyclo CH_2), 2.2-2.5 (m, 2 H, ), 3.5 (m, 1 H, ), 4.2 (t, 2 H, OCH_2)
8		colorless liquid	60	0.75-2.4 (br M, 15 H, $CH_3CH_2CH_2$ and cycloalkyl CH_2), 3.5 (d, 1 H, C*H*S), 4.2-4.4 (m, 3 H, C*H*Cl and OC*H*$_2$)

[a] All NMR were determined in $CDCl_3$ solution. Chemical shifts are parts per million downfield from internal tetramethylsilane symbols: br = broad signal; s = singlet; d = doublet; t = triplet; q = quarlet; m = multiplet.

Table II. Data for Oxathiazolones



compd	R	mp or bp, °C	yield, %	IR ν_{max}, cm^{-1}	mass spectrum *m/e*	^{1}H NMR δ[a]
9	Et	55-56/1.0-1.1 mmHg (colorless liquid)	70	1760 (C=O, film)	131 (M^+)	1.30 (t, 3 H, CH_3), 1.6 (q, 2 H, CH_2)
10		208-210 (acetone)	65	1750 (C=O, Nujol)	180 (M^+)	8.5 (m, 1 H, ), 7.1-7.5 (m, 3 H, )
11		130 (toluene)	50	1760 (C=O, Nujol)	260 (M^+)	1.85 (m, 4 H), 2.70 (m, 4 H)

[a] In $CDCl_3$.

chemical shifts reported in δ (ppm) with reference to tetramethylsilane (δ 0) as internal standard. Infrared spectra were determined by using a Unican-SP-100 spectrometer with reference to polystyrene's frequencies at 1602 and 1583 cm^{-1}. Mass-spectral (MS) data were taken from low-resolution electron-impact spectra determined at 70 eV with a double Du Pont 492B spectrometer; the direct-probe temperature was 20 °C.

***Typical Procedure for the Preparation of Carbobutoxythio Compounds* (1-7).** A 0.1-mol sample of the amine in 100 mL of ether was added to 8 g of Na_2CO_3 in 200 mL of water; 0.1 mol of *n*-butoxycarbonylsulfenyl chloride was then added dropwise with external cooling at 10 °C. After the mixture was stirred for 15 min, the ether layer was separated, washed with water, dried over anhydrous $MgSO_4$, and concentrated. The dark residue was recrystallized from appropriate solvent for **1-5**, distilled at reduced pressure for **6**, and purified by column chromatography for **7**.

***Preparation of* 8.** Excess of cyclohexene (24.6 g, 0.3 mol) was added to *n*-butoxycarbonylsulfenyl chloride (8.429 g, 0.05 mol) in 40 mL of glacial acetic acid with external cooling. The

yellow solution became colorless, and no HCl was evolved. After being stirred for 3 days at room temperature, the reaction mixture was poured into water and extracted with petroleum ether. The organic extract was washed with 10% sodium bicarbonate solution and then with water and dried over anhydrous $MgSO_4$. The dried solution was concentrated and purified by column chromatography.

***Oxathiazolone Derivatives* 9–11.** A 0.365-mol sample of appropriate amide in 150 mL of toluene was heated to reflux and 0.5 mol of chlorocarbonylsulfenyl chloride was added dropwise. After the evolution of HCl stopped (~6 h), the solvent and excess of reagents were distilled off on a water bath and the residue was fractionally distilled at reduced pressure for **9** and recrystallized from appropriate solvent for **10** and **11**.

Registry No. **1**, 94202-34-3; **2**, 94202-35-4; **3**, 94202-36-5; **4**, 94202-37-6; **5**, 94202-38-7; **6**, 94202-39-8; **7**, 94202-40-1; **8**, 94202-41-2; **9**, 94202-42-3; **10**, 94202-43-4; **11**, 94202-44-5; *n*-BuOC(O)SCl, 26555-37-3; *p*-$ClC_6H_4NH_2$, 106-47-8; 2,4-$Cl_2C_6H_3NH_2$, 554-00-7; *p*-$MeC_6H_4NH_2$, 106-49-0; *o*-$MeC_6H_4NH_2$, 95-53-4; $CH_3CH_2C(O)NH_2$, 79-05-0; $NH_2C(O)(CH_2)_4C(O)NH_2$, 628-94-4; *N*-cyclohexyl-1,4-benzenediamine, 13663-13-3; bicyclo[2.2.1]heptan-2-ol, 497-37-0; 2-pyridinecarboxamide, 1452-77-3; cyclohexene, 110-91-8; morpholine, 110-83-8.

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Some Reactions of Trichloromethanesulfenyl Chloride with Alcohols and Thiols

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Four new trichloromethyl disulfides, four alkyl orthocarbonates, and two trithiocarbonates have been synthesized and have been characterized by physical, spectral, and analytical properties.

It was reported that virtually all derivatives of trichloromethanesulfenyl chloride that have been prepared are potential pesticides (*1*). This induced us to prepare some new derivatives in the hope that they may be more active than the known compounds.

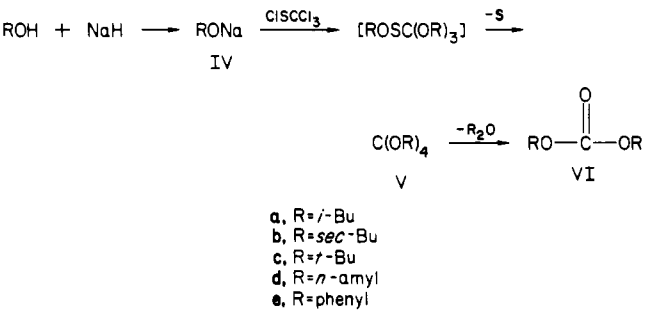
Condensation of thiols with trichloromethanesulfenyl chloride, I, gives trichloromethyl disulfides III (*2*).

$$\underset{\text{II}}{RSH} + \underset{\text{I}}{ClSCCl_3} \rightarrow \underset{\text{III}}{RSSCCl_3} + HCl$$

a, R = *p*-chlorobenzyl
b, R = *n*-hexyl
c, R = *n*-octyl
d, R = norbornyl

Four new asymmetric disulfides, IIIa–d, were prepared from thiols IIa–d and I according to the literature procedure (*3*). The yields and properties of these compounds are listed in Table I.

When the reaction of I with alcohols is carried out in the presence of base, esters of orthocarbonic acids are obtained (*4*). Four new alkyl orthocarbonates, VIa–d, were synthesized



by the reaction of I with sodium alkoxides IVa–d. The orthocarbonates Va and Vb were isolated in the pure state but Vc and Vd were mixed with the normal carbonates VIc and VId. Reaction of I with sodium phenoxide, IVe, gave tetraphenylorthocarbonate, Ve (*5*).

While the reaction of I with alkoxides and phenoxide formed orthocarbonates, entirely different results were obtained when sodium thiophenoxides and mercaptides were used. Backer has reported that the reaction of I with mercaptides gave symmetric disulfides VIII and bis[tris(alkylthio)methyl]disulfides $[(RS)_3CSSC(SR)_3]$; and with thiophenoxides, VIII and bis[tris(arylthio)methyl]trisulfides $[(ArS)_3CSSSC(SAr)_3]$ were formed (*6*). However, we obtained the symmetric disulfides VIII and trithiocarbonates IX with both mercaptides and thiophenoxiddes VIIIa–f. The IR spectra of IX have a strong band at

† Deceased, March 31, 1983.

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