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; $NH_2C(O)C-H_2)_4C(O)NH_2$, 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.

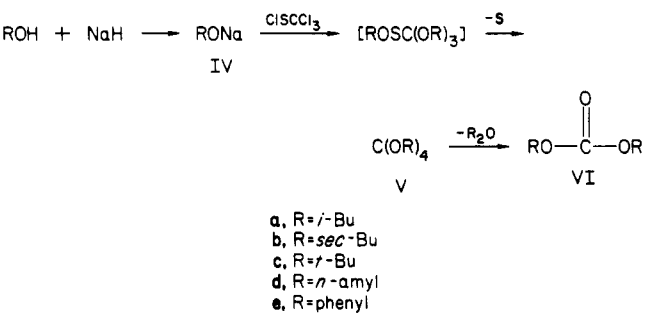
Condensation of thiols with trichloromethanesulfenyl chloride, I, gives trichloromethyl disulfides III (*2*).

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

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

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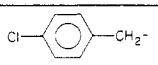
Table I. Products of the Reaction of Trichloromethanesulfenyl Chloride with Mercaptans

$$RSH + ClSCCl_3 \rightarrow \underset{III}{RSSCCl_3}$$

compd	R	bp, °C	yield, %	^{1}H NMR δ[a]
IIIa		136-140/0.25 mmHg	80	3.65 (s, 2 H, CH_2), 6.7 (s, 4 H, aromatic)
IIIb		105-106/0.25 mmHg	59	0.9 (t, 3 H, CH_3), 1.1-2.05 (m, 8 H, CH_2), 3.15 (t, 2 H, CH_2S)
IIIc	$CH_3(CH_2)_7$-	125-126/0.2 mmHg	65	0.85 (t, 3 H, CH_3), 1.0-2.0 (m, 12 H, CH_2), 3.15 (t, 2 H, CH_2S)
IIId		80-85/0.2 mmHg	40	1.0-2.05 (m, 8 H, CH_2), 2.1-2.6 (m, 2 H, CH), 3.2 (broad m, 1 H, CHS)

[a] In $CDCl_3$ solution.

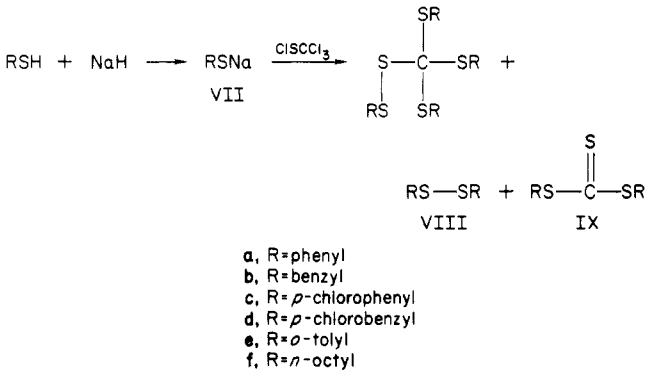
Table II. Products of the Reaction of Trichloromethanesulfenyl Chloride with Sodium Alkoxides and Phenoxides

$$RONa + ClSCCl_3 \longrightarrow \underset{V}{C(OR)_4} \xrightarrow{-R_2O} \underset{VI}{RO-\overset{\overset{O}{\|}}{C}-OR}$$

R	product	yield, %	mp or bp, °C	IR ν,[a] cm^{-1}	^{1}H NMR δ[b]	mass spectrum m/e
$(CH_3)_2CHCH_2$	Va	50	80/0.5 mmHg	1110 (C—O—C)	1.05 (d, 6 H, CH_3C), 1.65-2.4 (m, 1 H, CH), 3.6 (d, 2 H, CH_2O)	230 ($M^+ - C_4H_9O$)
(CH_3CH_2)-$(CH_3)CH$	Vb	72	65-68/2 mmHg	1105 (C—O—C)	0.9 (t, 3 H, CH_3CH_2), 1.2 (d, 3 H, CH_3CH), 1.35 m, 2 H, CH_2), 3.65 (m, 1 H, CH)	190 [$M^+ - 2(CH_3CH_2)$-$(CH_3)CH$]
$(CH_3)_3C$	Vc + VIc (7:3)	60	28-30/0.4 mmHg	1140 (C—O—C), 1740 (C=O)	1.0 (s, CH_3 from Vc), 1.25 (s, CH_3 from VIc)	
n-C_5H_{11}	Vd + VId (6:4)	55	30-32/0.25 mmHg	1220 (C—O—C), 1740 (C=O)	0.9 (t, 3 H, CH_3), 1.2-1.35 (m, 6 H, CH_2), 3.5 (t, CH_2O from Vd), 4.2 (t, CH_2O from VId)	
C_6H_5	Ve	78	95-96 [lit. (5) 97-98] (colorless needles)	1230 (aromatic C—O—C)	7.75 (m, aromatic)	291 ($M^+ - C_6H_5O$)

[a] Compound Ve was run in Nujol; all others were run neat on NaCl. [b] In CCl_4 solution.

1000–1100 cm^{-1} which is characteristic of the C=S stretching mode (*7*). The carbon-13 NMR spectra have chemical shifts



a, R=phenyl
b, R=benzyl
c, R=*p*-chlorophenyl
d, R=*p*-chlorobenzyl
e, R=*o*-tolyl
f, R=*n*-octyl

in the 220–225 ppm region, indicating the presence of —S-(C=S)S— grouping (*8*). Further the trithiocarbonates IX were prepared by the action of VII with thiophosgene (*9*) and were found to be identical with the products of the above reactions. Di(*o*-tolyl) trithiocarbonate, IXe, and di(*n*-octyl) trithiocarbonate, IXf, have so far not appeared in the literature.

Experimental Section

All melting points are uncorrected. The proton NMR spectra were recorded on a Perkin Elmer R-12B spectrometer with 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.[13] ^{13}C NMR spectra were recorded with a Varian Model CFT-20 operating at 20 MHz with tetramethylsilane as an internal standard.

***General Procedure for the Preparation of Trichloromethyl Disulfides* (IIIa–d).** A 0.25-mol sample of thiol was stirred in 200 mL of 2 N NaOH solution and cooled in an ice bath, and 0.25 mol of trichloromethanesulfenyl chloride was added in portions. The resulting mixture was stirred for 2 h and extracted with ether, and the ether extracts were washed with water, dried ($MgSO_4$), concentrated, and fractionally distilled at reduced pressure. The boiling points, yields, and NMR data are listed in Table I.

General Procedure for Reaction of Trichloromethanesulfenyl Chloride (I) with Sodium Alkoxides, Phenoxide, Thiophenoxides, and Mercaptides. A 0.1-mol sample of alcohol (phe-

Table III. Products of the Reaction of Trichloromethanesulfenyl Chloride with Sodium Thiophenoxides and Mercaptides

$$RSNa + ClSCCl_3 \longrightarrow \underset{\text{VIII}}{RSSR} + \underset{\text{IX}}{RS{-}\overset{\overset{S}{\|}}{C}{-}SR}$$

R	product	yield, %	mp, °C	IR ν,[a] cm^{-1}	δ	mass spectrum m/e
C_6H_5	VIIIa	20	61 [lit. (*10*) 62–63] (colorless solid)	680, 735, 1010, 1035, 1340, 1440, 1460	^1H NMR (CCl_4), 7.4 (s, aromatic)	218 (M^+), 109 ($C_6H_5S^+$), 77 ($C_6H_5^+$)
	IXa	40	97–99 [lit. (*11*) 97] (yellow crystals)	1020, 1040 (C=S)	^1H NMR ($CDCl_3$), 7.5 (s, aromatic)	262 (M^+)
$C_6H_5CH_2$	VIIIb	25	71–71 [lit. (*12*) 71–72] (cream solid)		^1H NMR ($CDCl_3$), 3.6 (s, 2 H, CH_2), 7.25 (s, 5 H, aromatic)	246 (M^+)
	IXb	40	72–74 [lit. (*13*) 72–74] (brownish-yellow solid)	1050 (C=S)	^1H NMR (CCl_4), 3.55 (s, 2 H, CH_2), 7.2 (s, 5 H, aromatic)	290 (M^+)
p-ClC_6H_4	VIIIc	20	71 [lit. (*14*) 70–71] (cream solid)		^1H NMR ($CDCl_3$), 7.25 (s, aromatic)	287 (M^+)
	IXc	45	141–143 [lit. (*9*) 128–132] (bright yellow crystals)	(C=S)	^1H NMR n$CDCl_3$), 7.2–7.5 (m, aromatic)	332 ((M + 1)$^+$), 331 (M^+), 187 n($ClC_6H_4SCS)^+$), 108 ([S(C=S)S]$^+$)
p-$ClC_6H_4CH_2$	VIIId	15	58–59 [lit. (*12*) 58–59] (white solid)		^1H NMR ($CDCl_3$), 3.55 (s, 2 H, CH_2), 7.1–7.4 (m, 4 H, aromatic)	315 (M^+)
	IXd	45	64–65 [lit. (*15*) 65] (yellow crystals)	1100 (C=S)	^1H NMR ($CDCl_3$), 4.5 (, 2 H, CH_2S), 7.2 (s, 4 H, aromatic) ^{13}C NMR ($CDCl_3$); 129, 130.5, 133.5, 133.5 (aromatic C's); 40.7 (alkyl C); 221.5 (C=S)	359 (M^+), 315 (M^+ – CS), 283 (M^+ – CS_2), 77 ($C_6H_5^+$)
	VIIIe	15	35 [lit. (*16*) 34.8–35.8] (cream solid)		^1H NMR ($CDCl_3$), 2.24 (s, 3 H, CH_3), 7.05 (s, 4 H, aromatic)	246 (M^+)
o-$(CH_3)C_6H_4$	IXe	25	43–45 (bright yellow crystals)	1050 (C=S)	^1H NMR (CCl_4), 2.35 (s, 3 H, CH_3), 7.05–7.6 (m, 4 H, aromatic)	291 ((M + 1)$^+$)
	VIIIf	15	31–32 [lit. (*17*) 30–31] (cream solid)		^1H NMR (CCl_4), 0.9 (t, 3 H, CH_3), 1.0–2.0 (m, 12 H, CH_2), 2.65 (m, 2 H, CH_2S)	290 (M^+)
n-C_8H_{17}	IXf	25	orange-yellow liquid	1070 (C=S)	^1H NMR (CCl_4), 0.95 (m, 3 H, CH_3), 1.1–2.1 (m, 12 H, CH_2e, 3.35 (m, 2 H, CH_2S) ^{13}C NMR ($CDCl_3$); 14.1 (CH_3); 22.68, 28.57, 28.96, 29.24, 31.84, 36.85, 39.22 (CH_2); 222.2 (C=S)	335 ((M + 1)$^+$), 302 (M^+ – S)

[a] In Nujol over NaCl.

nol, thiophenol, or mercaptan) in 200 mL of dry ether was reacted with NaH (0.2 mol, 57%), added in portions with external cooling under an inert atmosphere of nitrogen. After the initial reaction was over, the temperature was slowly raised and kept at reflux for $^1/_2$ h to ensure the formation of the sodium salt. The resulting mixture was stirred overnight and $ClSCCl_3$ (0.02 mol) in 50 mL of ether was added dropwise to the cold solution. The mixture was stirred overnight, further diluted with ether, and filtered over Celite. The filtrate was dried ($MgSO_4$) and concentrated and the residue distilled at reduced pressure for products from sodium alkoxides IVa–d and recrystallized from appropriate solvents for products from IVe and VIIa–f. The physical property data (boiling and melting points and spectra), structures, and yields are listed in Tables II and III.

Registry No. I, 594-42-3; IIa, 6258-66-8; IIb, 111-31-9; IIc, 111-88-6; IId, 71162-31-7; IIIa, 94137-99-2; IIIb, 94138-00-8; IIIc, 52739-90-9; IIId, 94138-01-9; IVa, 13259-29-5; IVb, 7726-51-4; IVc, 865-48-5; IVd, 1941-84-0; IVe, 139-02-6; Va, 42023-05-2; Vb, 94138-02-0; Vc, 94138-03-1; Vd, 94138-04-2; Ve, 4513-75-1; VIc, 34619-03-9; VId, 2050-94-4; VIIa, 930-69-8; VIIb, 3492-64-6; VIIc, 18803-44-6; VIId, 43170-85-0; VIIe, 34878-60-9; VIIf, 29524-77-4; VIIIa, 882-33-7; VIIIb, 150-60-7; VIIIc, 1142-19-4; VIIId, 23566-17-8; VIIIe, 4032-80-8; VIIIf, 822-27-5; IXa, 2314-54-7; IXb, 26504-29-0; IXc, 24455-29-6; IXd, 54769-04-9; IXe, 94138-05-3; IXf, 89622-57-1.

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Reaction of α,β-Unsaturated Ketones with Urea. Synthesis and Spectral Properties of 2(1*H*)-Pyrimidinone Derivatives

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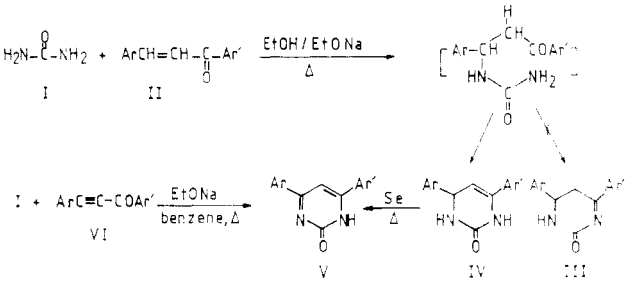
1,3-Diaryl-2-propen-1-ones react with urea to give 4,6-diaryl-3,4-dihydropyrimidinones (IVa–g) that can be further oxidized to the corresponding dehydro analogues (Va–f). The latter compounds are also obtained via interaction of aroylphenylacetylenes with urea. Spectral data, supporting the suggested structures IV and V, are presented.

The reaction of 1,3-diaryl-2-propen-1-ones (II) with urea (I) under acidic or basic conditions has been reported to give 4,6-diaryl-5,6-dihydro-2(1*H*)-pyrimidinones (III) (*1*, *2*). The procedures described therein were rather laborious. Recently we became interested in pyrimidinone syntheses, and this prompted us to reinvestigate the reaction of α,β-unsaturated ketones with urea.

When 1,3-diaryl-2-propen-1-ones (IIa–g) are refluxed with urea in the presence of sodium ethoxide in absolute ethanol for 1 h, they give the corresponding 4,6-diaryl-3,4-dihydro-2(1*H*)-pyrimidinones (IVa–g) (Scheme I), but not 4,6-diaryl-5,6-dihydro-2(1*H*)-pyrimidinones (III) as described previously by Sammour et al. (*2*). Under the same reaction conditions, the α,β-unsaturated ketones (IIh–j) afforded the corresponding 4,6-diaryl-2(1*H*)-pyrimidinone (Vd–f) (Scheme I). Prolonged refluxing (5 h) of IIe–g with urea also gave the corresponding 4,6-diaryl-2(1*H*)-pyrimidinones (Va–c). By analogy to the reaction of α,β-unsaturated ketones (II) with thiourea (*3*) and other nitrogen compounds (*4*), the formation of IV most likely involves initial 1,4-addition of urea to II and subsequent cyclization.

Scheme I



Compounds II and IV

	Ar	Ar′
a	C_6H_5	C_6H_5
b	C_6H_5	m-Cl C_6H_4
c	C_6H_5	p-$CH_3OC_6H_4$
d	C_6H_5	p-BrC_6H_4
e	C_6H_5	p-ClC_6H_4
f	C_6H_5	p-$CH_3C_6H_4$
g	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$
h	p-$CH_3C_6H_4$	p-ClC_6H_4
i	p-$CH_3OC_6H_4$	p-BrC_6H_4
j	p-ClC_6H_4	p-BrC_6H_4

Compounds V

	Ar	Ar′
a	C_6H_5	p-ClC_6H_4
b	C_6H_5	p-$CH_3C_6H_4$
c	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$
d	p-$CH_3C_6H_4$	p-ClC_6H_4
e	p-$CH_3OC_6H_4$	p-BrC_6H_4
f	p-ClC_6H_4	p-BrC_6H_4

Compounds VI

	Ar	Ar′
a	C_6H_5	p-ClC_6H_4
b	C_6H_5	p-$CH_3C_6H_4$
c	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$

Structural Assignments

Spectroscopic data are in accord with structure IV rather than structure III. Thus, the IR spectra of the dihydropyrimidinones (IVa–g) exhibit absorptions at 3235–3215, 3090–3080, and 1685–1675 cm^{-1} which are assigned to the two –NH and the carbonyl groups, respectively (*5*). The ^1H NMR spectra of these compounds (Table I) show a multiplet in the region 5.58–4.77 ppm (2H) which corresponds to the olefinic and methine protons. The two N–H protons appear as two broad singlets in the region 8.70–8.33 and 7.60–7.30 ppm which disappear upon addition of D_2O. Furthermore, the MS data display M^+ together with characteristic peaks at *m/e* (M-

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