3β,5α-dihydroxy-6β-dimethylaminopregnan-20-one, m.p. 217–221°, $[\alpha]^{26}D$ −9°.

Anal. Calcd. for $C_{23}H_{39}NO_3$: C, 73.16; H, 10.41; N, 3.73. Found: C, 72.90; H, 10.16; N, 3.87.

3β,5α-Dihydroxy-6β-dimethylaminopregnan-20-one 3-Acetate.—3β,5α-Dihydroxy-6β-dimethylaminopregnan-20-one (7.0 g.) and 40 ml. of acetic anhydride were heated at 130° for 0.5 hr. After cooling to 40°, a 3-ml. sample was removed and decomposed with 200 ml. of 10% brine. The solution was neutralized with sodium bicarbonate and extracted with a total of 200 ml. of isopropyl acetate. This was washed twice with water, dried over anhydrous sodium sulfate, and blown to dryness with nitrogen. The residue was crystallized from acetone to give 3β,5α-dihydroxy-6β-dimethylaminopregnan-20-one 3-acetate, m.p. 187–189°, $[\alpha]^{26}D$ −22°.

Anal. Calcd. for $C_{25}H_{41}NO_4$: C, 71.56; H, 9.85; N, 3.34. Found: C, 71.27; H, 9.81; N, 3.62.

3β-Hydroxy-5β-pregnane-6,20-dione 3-Acetate.—With the above solution at 40°, and precipitation beginning, concentrated sulfuric acid was added dropwise until the solution cleared (25 drops). The temperature was maintained at 36–40° with stirring for 15 min. The reaction was poured into 1 l. of 10% brine, allowed to stand for 2 hr., and neutralized with 20% sodium hydroxide solution. The mixture was extracted with a total of 1.2 l. of isopropyl acetate, washed with water until neutral, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum and the residue split into two parts. One part was hydrolyzed and the other part crystallized twice from ethyl acetate to give a product, m.p. 152–154°, which contained no nitrogen. The infrared spectrum showed the presence of three carbonyls. The compound is believed to be 3β-hydroxy-5β-pregnane-6,20-dione 3-acetate, $[\alpha]^{26}D$ +26.5°.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.62; H, 8.83.

3β-Hydroxy-5β-pregnane-6,20-dione.—A solution of 3.1 g. of residue from above in 40 ml. of methanol was treated with 1 g. of potassium carbonate in 10 ml. of water. After standing overnight the solution was poured into 1 l. of water and extracted with a total of 900 ml. of isopropyl acetate. After washing with water, drying over anhydrous sodium sulfate, the solvent was removed by vacuum distillation. The residue was crystallized from ethyl acetate to give 3β-hydroxy-5β-pregnane-6,20-dione, m.p. 186–187°, $[\alpha]D$ + 39.5°.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.50; H, 9.50.

The Oxidative Rearrangement of Vinylic Sulfides[1,2]

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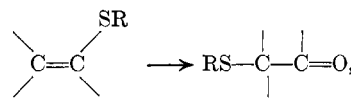
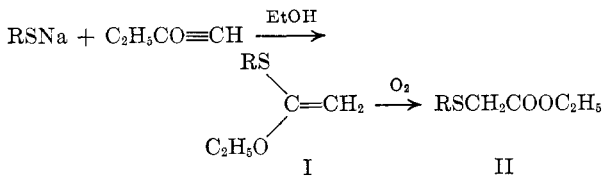
Received March 26, 1962

A variety of vinylic sulfides were prepared and the oxygen-induced rearrangement,  , was investigated. A mechanism for this reaction and facts supporting it are presented.

On investigating the nucleophilic addition of thiols to ethoxyacetylene, the resulting adducts [CH_2=C(OEt)SR, where R is *t*-C_4H_9, C_6H_5, and *p*-$CH_3C_6H_4$] were found to be unstable to air.[3] The major product of this autoxidation was the responding ethyl arylmercapto- or alkylmercaptoacetate (II). Similar oxidative rearrangements[4f]



I II

(1) Presented at the 17th National Organic Chemistry Symposium of the American Chemical Society, June 29, 1961, Bloomington, Indiana.

(2) Abstracted from the Ph.D. thesis of Robert J. Steltenkamp, Purdue University, 1962.

(3) W. E. Truce and R. J. Steltenkamp, *J. Am. Chem. Soc.*, **82**, 6427 (1960).

(4) (a) E. Demole, *Ber.*, **11**, 315, 1302, 1307, 1710 (1878); **12**, 2245 (1879); *Bull. soc. chim.*, [ii] **34**, 201 (1880); (b) F. Swarts, *Bull. acad. roy. Belg.*, [3] **34**, 307–326 (1897); [3] **35**, 849 (1898); [3] **36**, 532 (1898); (c) L. Henry, *ibid.*, [3] **36**, 497 (1899); *Ber.*, **12**, 1839 (1879); (d) J. Foster, *J. Am. Chem. Soc.*, **31**, 596 (1909); (e) R. A. Dickinson and J. A. Leermakers, *ibid.*, **54**, 3852 (1932); (f) G. B. Bachman, *ibid.*, **55**, 4279 (1933); **57**, 1088 (1935); (g) K. L. Muller and H. J. Schumacker, *Z. physik. Chem.*, **B37**, 365 (1937); (h) R. S. Corley, J. Lal, and M. W. Kane, *J. Am. Chem. Soc.*, **78**, 3489 (1956).

have previously been reported only for various halogenated ethylenes and halogenated vinyl ethers,[4] *e.g.*, CH_2=CBr_2 $\xrightarrow{O_2}$ $BrCH_2COBr$.

The autoxidation of the 1,1-adducts[5] (I) proceeded rapidly when oxygen was passed into the pure liquid and the exothermic reaction was generally performed in an ice water bath. In each case the major product, II, was formed in yields of 47 to 54%. Other products isolated were free thiol, the corresponding disulfide, ethoxyacetylene, and the saturated compound, resulting from the addition of mercaptan to the 1,1-adduct.

The autoxidation of 1-ethoxy-1-(phenylmercapto)propene, prepared by the nucleophilic addition of benzenethiol to 1-ethoxy-1-propyne, proceeded readily, affording ethyl α-phenylmercaptopropionate in a 54% yield. The products were examined by vapor phase chromatography and the structure confirmed by independent synthesis.

Ketene mercaptals autoxidize to thiol esters. The reaction occurs with both aromatic and ali-

(5) The nucleophilic addition of thiols to ethoxyacetylene yielded the 1,1-disubstituted ethenes, whereas free radical addition produced the 1,2-adduct. [H. J. Alkema and J. F. Arens, *Rec. trav. chim.*, **79**, 1257 (1960); see also ref. 3.]

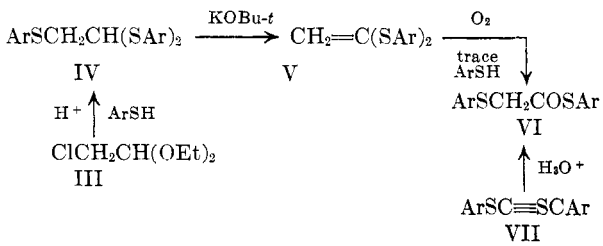
TABLE I

OXIDATIVE REARRANGEMENT OF VINYLIC SULFIDES

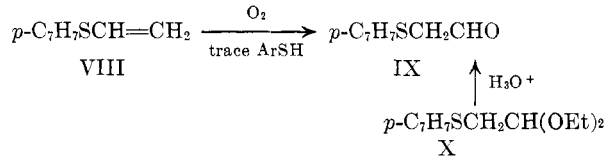
Vinylic sulfide	Major product	V.P.C. analysis[a] Yield, %	V.P.C. analysis[a] Conversion, %	Reaction conditions[b]
$CH_2=C(OC_2H_5)SC_6H_5$	$C_6H_5SCH_2COOC_2H_5$	54	54	0–5°/6 hr.
$CH_2=C(OC_2H_5)SC_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4SCH_2COOC_2H_5$	47	44 (38% by isolation)	0°–r.t./24 hr.
$CH_2=C(OC_2H_5)SC_4H_9$-*t*	*t*-$C_4H_9SCH_2COOC_2H_5$	53	53	0°/4.5 hr.
$CH_3CH=C(OC_2H_5)SC_6H_5$	$C_6H_5SCH(CH_3)COOC_2H_5$	51 54	44 40% 46 36% } by isolation	0°–r.t./48 hr.
$CH_2=C(SC_6H_4CH_3$-*p*$)_2$	*p*-$CH_3C_6H_4SCH_2CO(SC_6H_4CH_3$-*p*$)$	31 (by conversion to carboxylic acid)		50–70°/6 days
$CH_2=C(SC_3H_7$-*i*$)_2$	*i*-$C_3H_7SCH_2CO(SC_3H_7$-*i*$)$	38	36 (19% by conversion to acid)	52–58°/22 hr.
$CH_2=CHSC_6H_4CH_3$-*p*	*p*-$CH_3C_6H_4SCH_2CHO$	33	31	r.t./12 hr.
p-$CH_3C_6H_4SCH=CHSC_6H_4CH_3$-*p*	N.R.			100–135°/4 days
$CCl_2=C(SC_6H_4CH_3$-*p*$)_2$	N.R.			85°/5 days
p-$CH_3C_6H_4SCH=C(SC_6H_4CH_3$-*p*$)_2$	N.R.			60–80°/4 days

[a] See ref. 24. [b] These were the conditions employed to obtain the maximum yields stated.

phatic mercaptals but is generally slower and the yields lower compared to the autoxidation of the ethoxyacetylene adducts. The ketene mercaptals were prepared by the basic elimination of thiol from the corresponding 1,1,2-trisarylmercapto- or alkylmercaptoethanes (IV),[6] which were prepared by the acid-catalyzed reaction of thiol with chloroacetaldehyde diethyl acetal (III). Ketene diisopropylmercaptal and ketene di-*p*-tolymercaptal[7] were autoxidized and the expected thiol esters were obtained in yields of 38 and 31%, respectively. The solid aromatic mercaptal (m.p. 60°) was treated with oxygen in the molten state at 70° and the yield based on the quantity of the corresponding carboxylic acid found on saponification of the thiol ester, VI. An authentic sample of the thiol ester, VI, was prepared by hydration of bis(*p*-tolylmercapto)ethyne (VII)[8] with aqueous acid.



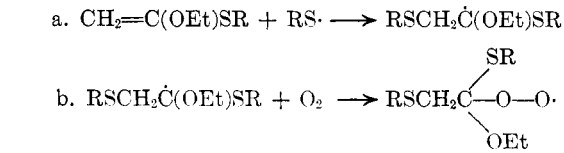
The autoxidation of *p*-tolyl vinyl sulfide (VIII)[9] gave *p*-tolylmercaptoacetaldehyde (IX) as the major product in 33% yield. This aldehyde was independently synthesized by the acid hydrolysis of *p*-tolylmercaptodiethylacetal (X).[10] Maximum



yields were obtained by rapidly bubbling oxygen for twelve hours through the liquid to which a small quantity of thiol had been added. Prolonged autoxidation resulted in a lower yield since the aldehyde reacts slowly with oxygen to give a mixture of several components.

cis-1,2-Bis(*p*-tolylmercapto)ethene,[11] tris(*p*-tolylmercapto)ethene,[12] and 1,1-bis(*p*-tolymercapto)-2,2-dichloroethene failed to undergo this oxidative rearrangement under the conditions employed.[13] A list of the compounds, which have been studied, is found in Table I.

The mechanism may be analogous to that proposed by Walling[14] for the oxidative rearrangement of tetrachloroethylene. Accordingly thiol present in small quantities would be expected to catalyze the rearrangement and in some cases



(6) (a) H. C. Volger and J. F. Arens, *Rec. trav. chim.*, **76**, 848 (1957); (b) H. J. Schneider, J. J. Bagnell, and G. C. Murdoch, *J. Org. Chem.*, **26**, 1987 (1961).

(7) W. E. Truce and B. Groten, *ibid.*, **27**, 128 (1962).

(8) E. Fromm and E. Siebert, *Ber.*, **55B**, 1025 (1922).

(9) W. E. Truce and M. M. Boudakian, *J. Am. Chem. Soc.*, **78**, 2748 (1956).

(10) F. Arndt and C. Martius, *Ann.*, **499**, 228 (1932).

(11) W. E. Truce and R. McManimie, *J. Am. Chem. Soc.*, **76**, 5745 (1954).

(12) W. E. Truce and R. Kassinger, *ibid.*, **80**, 1916, 6450 (1958).

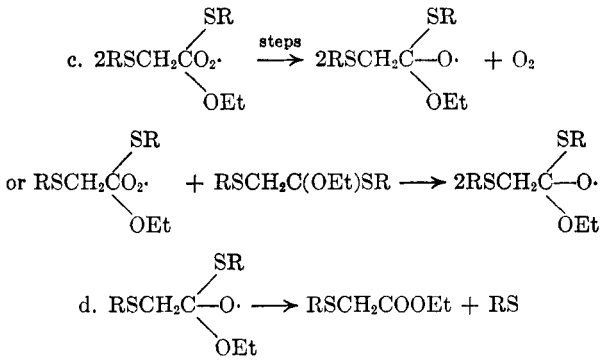
(13) The 1,2-adducts from the free radical addition of thiols to ethoxyacetylene autoxidize to the corresponding acetaldehyde. [J. F. Arens, private communication]. We have found that 1-ethoxy-2-(*p*-tolylmercapto)ethene autoxidized to ethoxy(*p*-tolylmercapto)-acetaldehyde in low yield.

(14) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 448.

TABLE II
1,1-DISUBSTITUTED ETHENES

Adduct	Solvent	B.p. °C.	B.p. Mm.	$n^{25}D$	Yield, %
1-Ethoxy-1-(*p*-tolylmercapto)ethene[a]	Ethanol	107	3.0	1.5500	55
1-Ethoxy-1-(phenylmercapto)ethene	Ethanol	68–72	0.7	1.5520	44
	Ammonia	67–69	0.25–0.40	1.5519	40
		82	2.0		
1-Ethoxy-1-(*t*-butylmercapto)ethene[b]	Ethanol	70–71	18.0	1.4610	10
	Ammonia	71–72	20.0	1.4600	17
1-Ethoxy-1-(phenylmercapto)propene	Ethanol	81.5–82	0.8	1.5500 (not sharp)	63

[a] Lit.,[5] b.p. 95.5–96° (1.5 mm.), $n^{20}D$ 1.5520. *Anal.* Calcd. for $C_{11}H_{14}OS$: C, 67.97; H, 7.26; S, 16.46. Found: C, 68.25; H, 7.50; S, 16.45. [b] This adduct is pyrolyzed at higher temperatures on gas chromatographic analysis. At a block temperature of 250° a clean spectrum was obtained but at 360° (employing the same low column temperature) a more volatile component was predominant.



this was found. Since the reaction proceeds without the addition of thiol, oxygen is believed partially to decompose the adduct producing a small amount of thiol which initiates the rearrangement. In every case, free thiol was produced and in many cases was the second largest component. Step (a) is reasonable since the free radical addition of thiols has been demonstrated[5] and the saturated di-adducts have been found in small amounts in the reaction mixture.

This mechanism is further supported by the exchange of thiol groups when a different thiol is introduced during the autoxidation. Benzenethiol will exchange with the *t*-butylmercapto group in 1-ethoxy-1-(*t*-butylmercapto)ethene (XI) while *t*-butyl mercaptan will exchange with the phenylmercapto group in 1-ethoxy-1-(phenylmercapto)-ethene (XII) during the autoxidation of these adducts. This exchange eliminates an intramolecular process and agrees with the proposed mechanism.

	O_2	$C_6H_5CH_2COOEt$ +	t-$C_4H_9SCH_2COOEt$
CH_2=C(OEt)SC_4H_9-t + C_6H_5SH	→	42%	4%
CH_2=C(OEt)SC_6H_5 + t-C_4H_9SH	→	30%	19%

That benzenethiol gives practically complete exchange whereas *t*-butyl mercaptan gives only partial exchange can be explained by the relative stabilities of the two thiyl radicals. The *t*-butylthiyl radical, being less stable than the resonance stabilized benzenethiyl, may exchange with any benzenethiol present, producing benzenethiyl, *e.g.*, RS· + PhSH → PhS· + RSH. The benzenethiyl then can add to the adduct initiating the rearrangement.

This mechanism also offers an explanation for the behavior of those vinylic sulfides which did not undergo the rearrangement. With these compounds the terminal methylene is absent and the initial addition of the thiyl radical (step a) is sterically hindered.

Experimental[15]

General Procedure for Nucleophilic Addition of Thiols to Ethoxyacetylene (or Ethoxypropyne). (a). Ethanol as Solvent.—To a solution of freshly cut sodium dissolved in absolute ethanol (*ca.* 45 ml. of ethanol per gram of sodium) was added an equimolar amount of thiol. A trace of hydroquinone was added to hinder any radical reaction. An equivalent of ethoxyacetylene[16] (or ethoxypropyne)[17] in an equal volume of absolute ethanol was introduced dropwise to the solution, which was refluxed under a nitrogen atmosphere for 15–24 hr. The solvent was removed under vacuum and the residue treated with water. The mixture was extracted with ether several times, the extracts combined and then shaken with base to remove any thiol. After drying over anhydrous magnesium sulfate, the ether was evaporated and the product purified by distillation.

(b). **Liquid Ammonia as Solvent.**—To a suspension of sodium amide in liquid ammonia, prepared from sodium and ammonia containing a trace of ferric nitrate hexahydrate, was added one third of an equivalent of chloroacetaldehyde diethyl acetal with rapid stirring. To this was slowly added two thirds of an equivalent of thiol. Some difficulty was encountered with aromatic thiols due to crystallization of the ammonium salt in the addition tube. After the addition was completed, the reaction mixture was stirred for several hours (6–8 hr.) and the ammonia was allowed to evaporate overnight under nitrogen. Diethyl ether and sodium hydroxide solution were added, the product was extracted in the ether and dried over magnesium sulfate. The product was purified by vacuum distillation. These adducts could be kept indefinitely in sealed vials under a nitrogen atmosphere. On exposure to the atmosphere they slowly assumed a greenish yellow color and gradually developed a strong carbonyl band in the infrared spectrum.

The structures of the 1,1-adducts were confirmed by the formation of a solid derivative with refluxing aniline.[5] The derivatives were recrystallized from 95% ethanol using activated charcoal. The ethoxyacetylene adducts gave N,N′-diphenylacetamidine, m.p. 131–132.5° (no depression

(15) All boiling and melting points are uncorrected. All microanalyses were performed by C. S. Yeh, I. Groten, and V. Keblys.
(16) W. S. Johnson, *Org. Syn.*, **34**, 46 (1954).
(17) J. F. Arens, *Rec. trav. chim.*, **74**, 275 (1955); see also ref. 5.

TABLE III

1,2-DISUBSTITUTED ETHENES

Adduct	B.P. °C.	B.P. Mm.	$n^{20}D$	Yield, %
1-Ethoxy-2-(*p*-tolylmercapto)ethene[a]	102	0.55	1.5640	61
1-Ethoxy-2-(*t*-butylmercapto)ethene[b]	62–65	5.5	1.4721	60

[a] Lit.,[5] b.p. 108° (1.0 mm.), $n^{20}D$ 1.5683. *Anal.* Calcd. for $C_{11}H_{14}OS$: C, 67.97; H, 7.26; S, 16.46. Found: C, 67.83; H, 7.53; S, 16.32. [b] Lit.,[19] b.p. 60–63° (4.0 mm.), $n^{26.6}D$ 1.4730. *Anal.* Calcd. for $C_6H_{16}OS$: C, 59.95; H, 10.07; S, 19.98. Found: C, 59.79; H, 9.93; S, 19.85.

with an authentic sample[18]) in 50 to 64% yield. The ethoxypropyne adduct gave N,N'-diphenylpropionamidine, m.p. 100–102° (lit.,[5] m.p. 103°), in 45% yield. These adducts, on acid hydrolysis in the presence of 2,4-dinitrophenylhydrazine, gave no derivative.

General Procedure for Free Radical Addition of Thiols to Ethoxyacetylene.—To a mixture consisting of one part thiol dissolved in two to four parts purified dioxane and containing a trace of benzoyl peroxide, was added an equivalent of ethoxyacetylene dissolved in an equal volume of dioxane. After *ca.* one third of the ethoxyacetylene was added dropwise under a nitrogen atmosphere, heat was evolved, and the addition was continued so as to maintain a mild reflux. After the addition the reaction was further refluxed for 7 hr. The dioxane was evaporated and the crude reaction mixture treated with diethyl ether and base to remove the remaining thiol. The aqueous layer was extracted with ether, the ether layers combined and dried over anhydrous magnesium sulfate. After evaporation of the ether, the product was purified by vacuum distillation.

The adduct, 1-ethoxy-2-(*t*-butylmercapto)ethene,[3,5] on gas chromatographic analysis after a single distillation, showed an isomer ratio of 66% *trans* and 34% *cis*. The configurational assignment was based on n.m.r. data[7,20] and infrared absorption analysis. After further heating (65–75° for 20 hr.) an isomer ratio of 85% *trans* and 15% *cis* was obtained; hence it appears that isomerization readily occurs on heating. In fact it appears that the addition of thiols to ethoxyacetylene at lower temperatures (−10°) is a stereospecific *trans* addition since infrared absorption analysis without previous distillation indicated the adduct consisted mainly of the *cis* isomer.[5]

The 1,2-disubstituted ethenes were hydrolyzed in the presence of 2,4-dinitrophenylhydrazine to form the solid hydrazone: *p*-$CH_3C_6H_4SCH_2CHN_2HC_6H_3N_2O_4$, m.p. 111–112°, lit.,[5] 111–111.5°, yield 99%; *t*-$C_4H_9SCH_2CHN_2HC_6H_3N_2O_4$, m.p. 106–107°, lit.,[21] 105.5–106°. No derivative was obtained on refluxing with aniline. Further proof for the configuration of these 1,2-adducts can be found in ref. 3 and 5.

Ketene Mercaptals (V).—The substituted trimercaptoethanes were prepared by treating bromoacetaldehyde diethyl acetal with thiol in ether containing a small amount of concentrated hydrochloric acid[6]: $(p\text{-}CH_3C_6H_4S)_2CHCH_2SC_6H_4CH_3\text{-}p$, m.p. 60–61°, lit.,[6a,8] m.p. 62–63°, yield 88%; $(i\text{-}C_3H_7S)_2CHCH_2SC_3H_7\text{-}i$, b.p. 94–98° (0.5 mm.), $n^{25}D$ 1.5161, yield 51%.

Treatment of these compounds with an equivalent quantity of potassium *t*-butoxide in *t*-butyl alcohol gave the following ketene mercaptal by the elimination of thiol[6]: $CH_2=C(SC_6H_4CH_3\text{-}p)_2$, m.p. 60°, lit.,[7] m.p. 62–63°, mixture m.p. with starting compound 43–52°, yield 65%; $CH_2=C(SC_3H_7\text{-}i)_2$, b.p. 73–76° (0.8 mm.). N,N-Diphenylacetamidine was obtained in 52% by refluxing these compounds with aniline.

1,1-Dichloro-2,2-bis(*p*-tolylmercapto)ethene.[22]—An ethanolic solution of 1,1,1-trichloro-2,2-bis(*p*-tolylmercapto) ethane[23] was added to a solution of potassium hydroxide in ethanol, whereupon an immediate precipitate of potassium chloride formed with mild heat evolution. The salt was filtered and the filtrate cooled, after which a white solid

TABLE IV

AUTOXIDATION OF VINYLIC SULFIDES

Vinylic Sulfide	Amt., g.	Catalyst	Temp., °C.	Time, hrs.	Results[b] % Ester (Conversion)	Results[b] % Starting material
$CH_2=C(OEt)SC_6H_4CH_3\text{-}p$[a]	3.41	None	0	40	33	10
	3.30	Trace *p*-C_7H_7SH	0	24	44	4
	2.23	Trace *p*-C_7H_7SH	r.t.	24	44	6
	4.41	8% *p*-C_7H_7SH	r.t.	24	23	25
$CH_2=C(OEt)(SC_4H_9\text{-}t)$	0.93	0.04 g. *t*-C_4H_9SH	0	...	53	0
	2.74	None	r.t.	12	42	0
	2.00	None	r.t.	4.25	42	0
$CH_2=C(OEt)(SC_6H_5)$	1.23	0.02 g. C_6H_5SH (2%)	0–5	6	54	0
	5.70	0.53 g. C_6H_5SH (8.5%)	r.t.	1–2	46	0
	1.50	None	r.t.	1–2	50	0
	5.21	3.30 C_6H_5SH (39%)	r.t.	1–2	35	0
$CH_3CH=C(OEt)SC_6H_5$	8.74	0.19 C_6H_5SH (2%)	0–r.t.	148	46	15
	6.60	None	0–r.t.	48	44	15
$p\text{-}C_7H_7SCH=CH_2$	1.36	Trace *p*-C_7H_7SH	r.t.	12	31 (33% yield)	
$CH_2=C(SC_3H_7\text{-}i)_2$	2.14	None	52–58	16	N.R.	
	2.14	0.10 *i*-C_3H_7SH	52–58	22	36 (38% yield)	
$CH_2=C(SC_7H_7\text{-}p)_2$	1.25	0.30 *p*-C_7H_7SH (2%)	50–70	144	(31% by isolation of acid from saponification)	
	2.50	None	80	72	(28% by isolation of acid from saponification)	

[a] On exposure to the atmosphere alone, 1-ethoxy-1-(*p*-tolylmercapto)ethene gave a 39% yield of the ester whereas 1-ethoxy-1-(*t*-butylmercapto)ethene gave only an 11% yield of the ester after complete autoxidation (15 hrs.). [b] Yields are based on V.P.C. analyses unless otherwise stated.

(18) M. Sen and J. Ray, *J. Chem. Soc.*, 646 (1926).

(19) W. E. Parham, R. F. Motter, and G. L. O. Mayo, *J. Am. Chem. Soc.*, **81**, 3390 (1959).

(20) W. E. Truce, H. G. Klein, and R. B. Kruse, *ibid.*, **83**, 4636 (1961).

(21) J. F. Arens, *et al.*, *Rec. trav. chim.*, **75**, 1469 (1956).

(22) This compound was prepared by Dr. B. Groten at this laboratory.

(23) G. Schrader, German Patent 1,063,152, August 13, 1959; *Chem. Abstr.*, **55**, 13378 (1961).

crystallized. Recrystallization twice from absolute ethanol gave white needles, m.p. 50.5–51.5°.

Anal. Calcd. for $C_{16}H_{14}Cl_2S_2$: C, 56.32; H, 4.14. Found: C, 56.27; H, 4.27.

Autoxidation Procedure.—The compound to be treated was placed in a 15-ml. round-bottom flask equipped with a reflux condenser and a gas addition tube. A one-hole rubber stopper equipped with a glass capillary to maintain a slight pressure of oxygen was placed on top of the condenser. The oxygen was passed through Drierite to remove any water and dirt particles. The autoxidation was started by initiating the oxygen flow and the reaction was followed by periodic withdrawal of aliquots with a microsyringe for gas chromatographic or infrared analysis. The temperature of the reaction was controlled by immersing the flask into either an ice or heated oil bath.

The autoxidation of the ethoxyacetylene adducts was exothermic and was initiated in an ice bath (see Table I). The ketene mercaptals did not autoxidize as vigorously and in fact had to be heated. The addition of thiol, which served as a catalyst and in a few cases improved the yield, was made with a microsyringe. After the compound completely autoxidized, the material was weighed and analysis made by gas chromatography. The resulting ester was confirmed by comparison with the independently synthesized material. The product of autoxidation of the ethoxyacetylene adducts was a clear yellow, nonviscous liquid. With the ketene mercaptals the product was a darker brown to black. The gas chromatographic[24] results were supported by infrared analyses, isolation yields, saponification yields, increase in the total weight of the reaction material and the percent oxygen increase found by difference in elemental analysis. The saponification of the ester or thiolester was carried out with potassium hydroxide in absolute ethanol. The acid salt, being insoluble in ethanol, was filtered and treated with mineral acid to regenerate the sulfide carboxylic acid. This compound was purified by recrystallization from hot water.

Thiol Exchange.—The exchange during autoxidation was conducted in the manner described above except that during the autoxidation the replacing thiol was added dropwise employing a micro addition funnel. 1-Ethoxy-1-(phenylmercapto)ethene (3.04 g., 0.017 mole) was autoxidized at 0° while *t*-butyl mercaptan (2.10 g., 0.023 mole) was slowly added. After 6 hr. analysis showed 30% ethyl phenylmercaptoacetate and 19% ethyl *t*-butylmercaptoacetate.

The same experiment was conducted using benzenethiol as the exchanging thiol. 1-Ethoxy-1-(*t*-butylmercapto)-ethene (3.08 g., 0.019 mole) was autoxidized at 0° for 12 hr. while benzenethiol (2.15 g., 0.019 mole) was added. Analysis showed 42% ethyl phenylmercaptoacetate and 4% ethyl *t*-butylmercaptoacetate. Both of the pure acetates were treated with the opposite thiol under these autoxidative conditions and no reaction was observed. Thiol exchange, hence, must occur during the formation of the ester and is not a result of a thiol displacement on the ester.

(24) Analyses were performed using the Perkin-Elmer Model 154-C and the F and M, temperature programmed, Model 500 Vapor Fractometer.

Independent Synthesis of the Ethyl Alkylmercapto- or Arylmercaptoacetates.[25]—These sulfide esters were prepared by the reaction of the sodium thiolate with ethyl chloroacetate in absolute ethanol. The inorganic salt was filtered, the solvent was evaporated, and the product purified by vacuum distillation.

TABLE V

ETHYL ALKYLMERCAPTO- OR ARYLMERCAPTOACETATES

Ester	B.P. °C.	B.P. Mm.	$n^{25}D$	Yield, %
Ethyl *p*-tolylmercapto-acetate[a]	112–113	1.2	1.5380	64
Ethyl phenylmercapto-acetate[b]	118	2.7	1.5430	50
Ethyl *t*-butylmercapto-acetate[c]	92 65	13 3.7	1.4549	36
Ethyl α-phenylmer-captopropionate[d]	91–92	0.6	1.5300	69

[a] Lit.,[25] b.p. 179–182° (32 mm.). [b] Lit.,[25] b.p. 276–278°; 144–145° (14 mm.). [c] *Anal.* Calcd. for $C_8H_{16}OS$: C, 54.54; H, 9.09; S, 18.18. Found: C, 54.71; H, 8.81; S, 18.20. [d] Lit.,[25] b.p. 139.5° (15 mm.).

These acetates were stable under the usual autoxidative conditions.

***p*-Tolylmercaptoacetaldehyde (IX).**—Ten grams of *p*-tolylmercapto diethyl acetal[10] (X) was refluxed for 7 hr. with 60 ml. of water containing 3 ml. of sulfuric acid. After cooling, the reaction mixture was extracted with diethyl ether. After drying over anhydrous magnesium sulfate, the ether was evaporated and the product distilled to give a colorless liquid, b.p. 104° (2.0 mm.), $n^{25}D$ 1.5727, yield 4.3 g. (62%).

The compound was autoxidized slowly under the usual conditions to give a complex mixture. After 10 hr., approximately 90% aldehyde remained while after 24 hr., 66% remained.

***p*-Tolyl(*p*-tolylmercapto)thiolacetate (VI).**—Bis(*p*-tolylmercapto)ethyne[8] (VII) (2.0 g., 7.3 mmoles) was dissolved in a solution of 30 ml. of glacial acetic acid and 3 ml. of 50% sulfuric acid and heated to 50–60° for 2 hr. After cooling, the reaction mixture was neutralized with bicarbonate solution and extracted with diethyl ether. The ether extracts were treated with additional sodium bicarbonate to remove all acid and then dried over anhydrous magnesium sulfate. After evaporating the ether, the product was purified by column chromatography employing silica gel as the adsorbent and petroleum ether–5% diethyl ether as the eluent; yield 1.92 g. (6.6 mmoles), 90%.

Acknowledgment.—The authors are indebted to the National Science Foundation (Grant G-9929) and the Gulf Research and Development Company for financial support of this work.

(25) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 2 Chemical Publishing Co., New York, N. Y., 1960, Chap. 3.