Anal. Calcd. for $C_{20}H_{22}N_2O_2\cdot HCl$: C, 66.93; H, 6.46. Found: C, 66.77; H, 6.08.

1-Acetylcarbazole.—A solution of 1.02 g. (0.0285 mole) of IV hydrochloride (see above) dissolved in 100 ml. of water was treated with 4 ml. of 1 *N* aqueous sodium hydroxide and the base was filtered off and washed with water. It was then dissolved in 50 ml. of ethanol and treated with 10 ml. of 6.5 *N* aqueous sodium hydroxide. The solution, which turned yellow immediately, was heated under reflux for 4 hr., water was added to incipient turbidity, and the solution was filtered and cooled. The resulting long yellow needles weighed 510 mg. (86%) and had m.p. 128°. Two recrystallizations from ethanol-water gave material of m.p. 134–136° (lit.,[12] m.p. 133–134°).

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.36; H, 5.30. Found: C, 80.30; H, 5.60.

Acknowledgment.—We wish to thank Dr. Samuel W. Blackman and Mr. Charles Marr of these laboratories for the elemental analyses for carbon and hydrogen. The nitrogen and sulfur analyses were done by Schwarzkopf Microanalytical Laboratory.

Preparation and Polymerization of S-, O-, and N-Vinyl Derivatives of Carbonic Acid.[1] Unsaturated Carbonic Acid Derivatives. II

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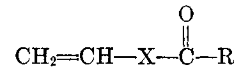
This paper describes the preparation, physical properties, and homopolymerization of several vinyl carbamates, vinyl thiolcarbamates, and vinyl thiolcarbonates. These monomers were prepared by the dehydrochlorination of the corresponding β-chloroethyl compounds which were prepared by the reaction of (A) β-chloroethyl chloroformate or β-chloroethyl chlorothiolformate with amines, alcohols, or mercaptans; (B) ethylene sulfide with chloroformates or chlorothiolformates; or (C) chlorothiolformates with β-chloroethylamines or N-substituted ethyleneimines.

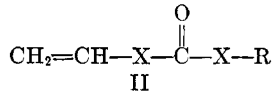
S-, O-, and N-vinyl derivatives of carboxylic acids (I) are well known and are of scientific as well as commercial interest.[3,4]



$CH_2{=}CH{-}X{-}\overset{\overset{O}{\|}}{C}{-}R$

I

X = S, O, NR



$CH_2{=}CH{-}X{-}\overset{\overset{O}{\|}}{C}{-}X{-}R$

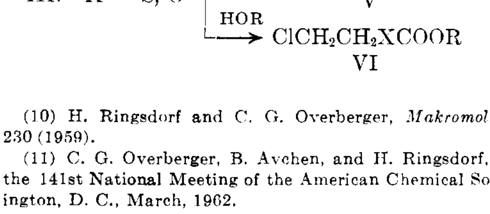
II

Surprisingly, the analogous derivatives of carbonic acid (II) have not yet been carefully investigated. The literature describes a series of N-unsaturated carbonic acid derivatives, prepared by the reaction of vinyl- and isopropenylisocyanate with alcohols, mercaptans, and amines.[5-8] Little work has been done in the field of vinyl thiolcarbonates and vinyl thiolcarbamates. Sauer published the synthesis of vinyl N,N-dialkyldithiocarbamates[9] and the cyclicpolymerization of divinyl dithiolcarbonate was studied in this institute.[10]

In connection with our investigation concerning the preparation of nitrogen- and sulfur-containing polymers as potential radiation prophylactics,[11] we have been interested in S-, O-, and N-vinyl compounds. This paper describes the preparation and homopolymerization of new vinyl carbamates, thiolcarbamates, and thiolcarbonates.

Several unsuccessful attempts were made to prepare these monomers either by dehydration of β-hydroxyethyl carbamates, thiolcarbamates, and thiolcarbonates or by cracking the corresponding β-acetoxyethyl compounds. A convenient synthesis was found to be the dehydrochlorination of the corresponding β-chloroethyl compounds.

For the preparation of these new S-, O-, and N-β-chloroethyl carbonic acid derivatives, three principal procedures were used: (A) reaction of β-chloroethyl chloroformate (III) and β-chloroethyl chlorothiolformate (III) with amines, alcohols, and mercaptans.[10,12]



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[1] This is the 24th in a series of papers concerned with the preparation and properties of new monomers and polymers; for the previous paper in this series see C. G. Overberger and J. J. Ferraro, *J. Org. Chem.*, **27**, 3539 (1962); for the first paper in the subseries see ref. 10.

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[3] W. Reppe, *Experientia*, **5**, 93 (1949).

[4] H. Hopff and B. Mühlethaler, *Kunststoffe*, **4**, 257 (1957).

[5] Y. Iwakura, M. Sato, T. Tamikado, and T. Mizoguchi, *Chem. High Polymers* (Japan), **13**, 390 (1956).

[6] (a) R. Hart and A. van Dormael, *Bull. soc. chim. Belges*, **65**, 571 (1956); (b) R. Hart and D. Timmerman, *Makromol. Chem.*, **31**, 223 (1959); (c) R. Hart and D. Timmerman, *Bull. soc. chim. Belges*, **67**, 123 (1958); (d) L. Ghosez and G. Smetz, *J. Polymer Sci.*, **35**, 215 (1959).

[7] G. Welzel and G. Greber, *Makromol. Chem.*, **31**, 230 (1959).

[8] R. C. Schulz and H. Hartman, *Monatsh.*, **92**, 303 (1961).

[9] J. C. Sauer, *J. Org. Chem.*, **24**, 1592 (1959).

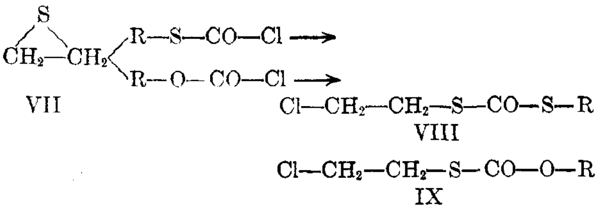
[10] H. Ringsdorf and C. G. Overberger, *Makromol. Chem.*, **31**, 230 (1959).

[11] C. G. Overberger, B. Avchen, and H. Ringsdorf, Abstract of the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

[12] J. I. Jones, *J. Chem. Soc.*, 2735 (1957).

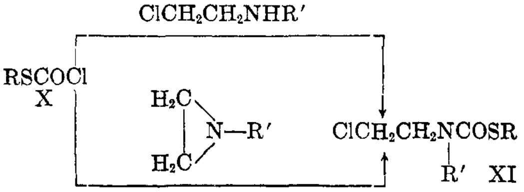
The reactions were carried out either in ether with one equivalent of triethylamine or under interfacial conditions (water–ether) with one equivalent of sodium hydroxide.

(B) Reaction of ethylene sulfide (VII) with chloroformates and chlorothiolformates.



Ethylene sulfide is highly reactive[13] and the ring opening with chloroformates occurs readily.[10] In most cases the reaction is exothermic and cooling or the use of an inert solvent (ether) is necessary, particularly if a catalyst (*e.g.* tertiary amines) is added.

(C) Reaction of chlorothiolformates with β-chloroethyl amines or N-substituted ethyleneimines.[14]

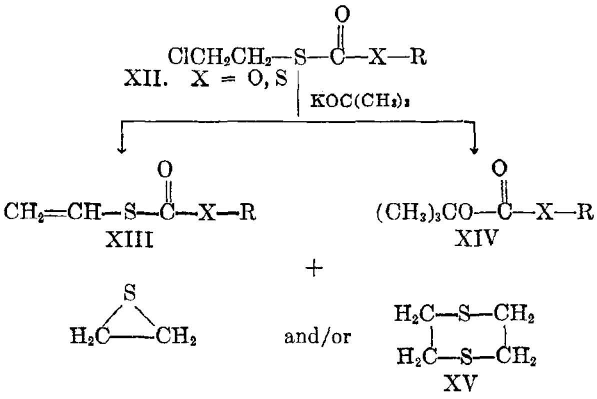


The chlorothiolformates (X) react vigorously with cyclic imines. An ether solution of the imines was usually added to the acid chlorides in ether. The β-chloroethylamines and the chlorothiolformates reacted under interfacial conditions.

The methods of preparation, yields, and physical properties of the β-chloroethyl compounds are given in Tables I, II, III, and IV. The β-chloroethyl dithiolcarbonates are vesicants and should be handled with care.

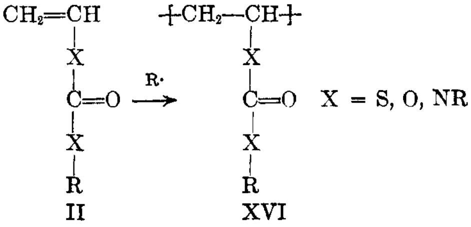
The β-chloroethyl compounds were dehydrohalogenated with potassium *t*-butoxide in absolute *t*-butyl alcohol or in tetrahydrofuran at 50–80°. Side products obtained in dehydrochlorination were O-*t*-butyl carbonates (XIV), ethylene sulfide, dithiane (XV),[15] and polyethylene sulfide.[16] These side products were due to partial transesterification and were most frequently obtained in the reaction of thiol- and dithiolcarbonates (XII).

The highest yields were found in the case of vinyl N,N-dialkylthiolcarbamates. Attempts to use tertiary amines as dehydrohalogenation agents failed.



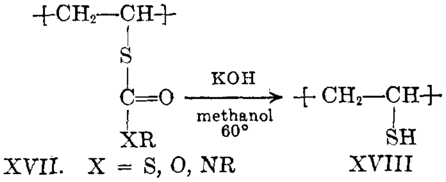
Reactions with sodium methoxide and ethoxide yielded the saturated esters exclusively. The yields and physical properties of these vinyl compounds are given in Tables V, VI, and VII.

The polymerization of the unsaturated carbonic acid derivatives led to a series of new polymers.



All monomers were successfully polymerized in bulk at 60–65° with 2,2'-azobisisobutyronitrile or benzoyl peroxide as catalyst. Attempts to initiate the reaction with Friedel–Crafts catalyst failed. The polymers prepared by radical initiation are white solids; a few are fiber-forming. The softening points (taken on a Fisher-Johns melting block), viscosities and solubilities of the polymers prepared under comparable conditions are given in Tables VIII and IX.

The poly(S-vinyl thiolcarbamates) (XVII. X = NR) as well as the poly(S-vinyl thiolcarbonates) and the poly(S-vinyl dithiolcarbonates) (XVII. X=S, O) were hydrolyzed to yield polyvinyl mercaptans (XVIII).[17] The poly(S-vinyl carbamates) hydrolyze slower than the other polymers studied or poly(vinyl thiolacetate).[18] The hydrolysis of β-chloroethyl carbonate derivatives as a side reaction in the monomer preparation also followed this order.



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[13] A. Schönberg, "Houben-Weyl, Methoden der Organischen Chemie," Vol. 9, E. Muller, ed., Georg Thieme Verlag, Stuttgart, 1955, p. 149.

[14] H. Bestian, "Houben-Weyl, Methoden der Organischen Chemie," Vol. 9, Pt. 2, E. Muller, ed., George Thieme Verlag, Stuttgart, 1958, p. 249.

[15] M. Delepine, *Compt. rend.*, **171**, 36 (1920).

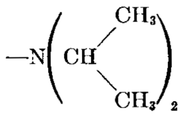
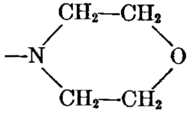
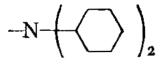
[16] G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, **127**, 910 (1925).

[17] M. M. Brubaker, U. S. Patents 2,378,535 and 2,378,536 (1945).

[18] C. G. Overberger, J. J. Ferraro, and F. W. Orttung, *J. Org. Chem.*, **26**, 3458 (1961).

TABLE I

β-CHLOROETHYL THIOLCARBAMATE, $Cl—CH_2—CH_2—S—CO—R$

Compound	R	Prepared by method	Yield, %	B.p., °C./mm.	M.p., °C.	n_D/°C.	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. S	Calcd. Cl	Found C	Found H	Found N	Found S	Found Cl
1	$—N(CH_3)_2$	A	84	88–89/2.0	...	1.5132/19	$C_5H_{10}ClNOS$	35.81	6.01	8.36	19.13	21.15	36.18	6.13	8.21	18.82	21.26
2	$—N(C_2H_5)_2$	A	97	64/0.3	...	1.5036/23	$C_7H_{14}ClNOS$	42.95	7.21	7.16	16.39	18.12	43.04	7.20	7.09	16.32	18.30
3[a]		A	60	...	24–25	...	$C_9H_{16}ClNOS$	48.91	7.30	6.34	...	16.05	49.13	7.26	6.14	...	15.79
4[b]		A	82	...	53–54	...	$C_7H_{12}ClNO_2S$	40.09	5.77	6.68	15.29	16.41	39.82	5.74	6.97	15.32	16.75
5[c]		A	38	...	85–86	...	$C_{15}H_{26}ClNOS$	59.45	8.64	4.62	10.58	11.69	59.01	8.05	4.69	10.64	11.70

[a] Recrystallized from ether. [b] Recrystallized from pentane. [c] Recrystallized from methanol.

TABLE II

S-β-CHLOROETHYL ALKYL DITHIOLCARBONATES, $Cl—CH_2—CH_2—S—CO—S—R$

Compound	R	Prepared by method	Yield, %	B.p., °C./mm.	M.p., °C.	n_D/°C.	Formula	Calcd. C	Calcd. H	Calcd. S	Calcd. Cl	Found C	Found H	Found S	Found Cl
6[a]	$—CH_2CH_2Cl$	B	76	96–97/0.1	40–41	...	$C_5H_8Cl_2OS_2$	27.40	3.68	29.26	32.36	27.11	3.64	28.85	35.52
7	$—CH_2CH_2CH_3$	B	47	73/0.3	...	1.5341/25	$C_6H_{11}ClOS_2$	36.26	5.58	32.24	17.84	36.25	5.59	32.06	17.99
8	$—CH(CH_3)_2$	A	63	83/1.0	...	1.5251/29	$C_6H_{11}ClOS_2$	36.26	5.58	32.24	17.84	36.47	5.49	32.20	17.67
9	$—C_6H_5$	B	64	114/0.2	...	1.6119/28	$C_9H_9ClOS_2$	46.44	3.90	27.55	15.24	46.13	3.89	27.58	14.95

[a] Ref. 10.

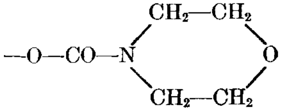
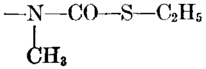
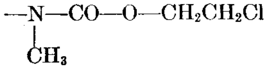
TABLE III

S-β-CHLOROETHYL ALKYL THIOLCARBONATES, $Cl—CH_2—CH_2—S—CO—R$

Compound	R	Prepared by method	Yield, %	B.p., °C./mm.	n^{21}_D	Formula	Calcd. C	Calcd. H	Calcd. S	Calcd. Cl	Found C	Found H	Found S	Found Cl
10	$—Cl$	B	70	59–60/3.5	...	$C_5H_9ClO_2S$								
11	$—CC_2H_5$	B	52	52/2.0	1.4759	$C_5H_9ClO_2S$	35.61	5.38	19.01	21.03	36.68	5.50	15.41	21.30
12	$—OC(CH_3)_3$	A	56	51–52/0.8	1.4693	$C_7H_{13}ClO_2S$	42.74	6.66	18.03	16.30	42.80	6.63	18.02	16.21

TABLE IV

O- AND N-β-CHLOROETHYL CARBAMATES AND N-β-CHLOROETHYL THIOLCARBAMATES, Cl—CH$_2$—CH$_2$R

Compound	R	Prepared by method	Yield, %	B.p., °C./mm.	M.p., °C.	n^{21}D	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. Cl	Calcd. S	Found C	Found H	Found N	Found Cl	Found S
13[a]	—O—CO—N(C$_2$H$_5$)$_2$	A	91	60–61/0.8	...	1.4464	—$C_7H_{14}ClNO_2$	46.68	7.85	7.80	19.74	...	46.63	8.39	7.62	19.91	...
14[b]		A	97	91–92/0.7	38–39	...	—$C_7H_{12}ClNO_3$	43.40	6.25	7.28	18.30	...	43.64	6.50	7.54	13.31	...
15	 $-N(CH_3)-CO-S-C_2H_5$	C	74	71–72/0.3	...	1.5210	—$C_6H_{12}ClNOS$	39.66	6.66	7.72	19.54	17.65	39.46	6.69	7.88	19.24	17.51
16	 $-N(CH_3)-CO-O-CH_2CH_2Cl$	C	84	84–85/0.4	...	1.4733	—$C_6H_{11}Cl_2NO_2$	36.02	5.59	7.00	35.39	...	35.88	5.63	7.05	35.60	...

[a] Ref. 12. [b] Recrystallized from pentane.

TABLE V

VINYL THIOLCARBAMATES, CH$_2$=CH—S—CO—R

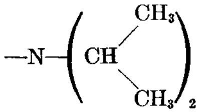
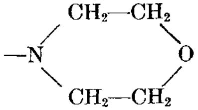
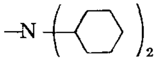
Compound	R	Yield, %	B.p., °C./mm.	M.p., °C.	n^{25}D	d_0^{25}	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. S	Found C	Found H	Found N	Found S
17	—N(CH$_3$)$_2$	61	54–55/1.5	...	1.5197	1.0741	C_5H_9NOS	45.77	6.91	10.68	24.44	45.96	6.72	10.62	24.25
18	—N(C$_2$H$_5$)$_2$	83	58–59/1.2	...	1.5043	1.0174	$C_7H_{13}NOS$	52.79	8.23	8.80	20.14	52.95	8.29	8.80	19.92
19		63	75–76/0.7	...	..	...	$C_9H_{17}NOS$	37.75	9.14	7.47	17.12	37.55	9.35	7.43	16.87
20		41	96/1.0	56–58	...	...	$C_7H_{11}NO_2S$	48.53	6.41	8.09	18.51	48.58	6.39	8.23	18.39
21		96	...	73	...	...	$C_{15}H_{25}NOS$	...	...	5.26	12.01	...	...	5.39	11.62

TABLE VI

S-VINYL THIOLCARBONATES AND S-VINYL DITHIOLCARBONATES, CH$_2$=CH—S—CO—R

Compound	R	Yield, %	B.p., °C./mm.	M.p., °C.	n^{25}D	d_0^{25}	Formula	Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
22[a]	—OC(CH$_3$)$_3$	5	50/6.0		1.4607	...	$C_7H_{12}O_2S$	52.47	7.55	20.01	52.66	7.83	19.97
23	—SCH(CH$_3$)$_2$	62	62/2.0		1.5238	1.0662	$C_6H_{10}OS_2$	44.40	6.20	39.70	44.26	6.48	39.41

[a] This compound was also isolated as a side product of bis-β-chloroethyl dithiolcarbonate. See ref. 10.

Table VII

Vinyl Carbamates and N-Vinyl Thiolcarbamates, $CH_2{=}CH{-}R$

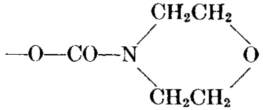
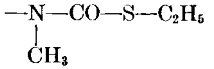
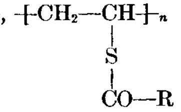
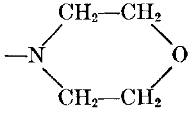
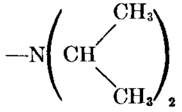
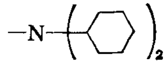
Compound	R	Yield, %	B.p. °C./mm.	$n^{25}D$	d_0^{25}	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. S	Found C	Found H	Found N	Found S
24	$-O-CO-N(C_2H_5)_2$	45	49/4.8	1.4345	0.9444	$C_7H_{13}NO_2$	58.72	9.15	9.78	...	58.84	9.37	9.53	...
25		24	61-62/0.8	1.4756	1.1326	$C_7H_{11}NO_3$	53.49	7.06	8.91	...	53.35	7.34	8.86	...
26	 $-N(CH_3)-CO-S-C_2H_5$	62	47/0.7	1.5299	1.0436	$C_6H_{11}NOS$	49.62	7.58	9.65	22.09	49.34	7.53	9.86	22.08

Table VIII

Poly(vinylthiolcarbamates),  $-[CH_2-CH(S-CO-R)]_n-$

Polymerization temperature: 63–66°
Initiator: 0.3 wt. % azobisisobutyronitrile
Conversion: 7–80%

Polymer	R	Softening point, °C.	$[\eta]^a$ at 29.2°	Soluble in	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. S	Found C	Found H	Found N	Found S
27	$-N(CH_3)_2$	115-130	0.49	Chloroform Acetic acid	C_5H_9NOS	45.77	6.91	10.68	24.44	45.55	7.09	10.41	24.56
28	$-N(C_2H_5)_2$	100-115	0.10	Tetrahydrofuran Ethanol	$C_7H_{13}NOS$	52.79	8.23	8.80	20.14	53.32	8.45	8.37	18.90
29		155-170	0.15	Benzene Acetic acid	$C_7H_{11}NO_2S$	48.53	6.41	8.09	18.51	48.02	6.49	8.33	18.43
30		110-130	0.12	Chloroform Benzene	$C_9H_{17}NOS$	57.75	9.14	7.47	17.12	57.60	9.23	7.01	17.31
31		105-115	0.13	Benzene Tetrahydrofuran	$C_{15}H_{25}NOS$	67.48	9.44	5.26	12.01	67.39	9.56	5.48	11.02

[a] In benzene.

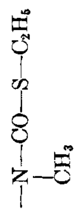
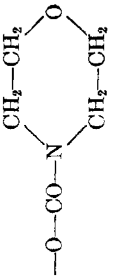
Copolymers of S- and N-vinylcarbonic acid derivatives have been prepared. The copolymers, which may hydrolyze under physiological conditions to release amino and thiol groups, will be tested as potential radiation prophylactics. These investigations as well as the copolymerization studies will be reported elsewhere.

TABLE IX

POLYMERIC S-, N- AND O-VINYL DERIVATIVES OF CARBONIC ACID

$$-[CH_2-\underset{R}{\overset{|}{CH}}]_n-$$

Polymerization temperature: 63–70°
Initiator: 0.3 Wt. % Azobisisobutyronitrile
Conversion: 55–75%

Polymer	R	Softening point, °C.	$[\eta]^a$ at 29.2°	Soluble in	Formula	Calcd. C	Calcd. H	Calcd. N	Calcd. S	Found C	Found H	Found N	Found S
32	$-S-CO-S-CH(CH_3)_2$	60–80	1.02	Benzene Tetrahydrofuran	$C_6H_{10}OS_2$	44.40	6.20	...	39.70	44.57	6.11	...	39.33
33	$-S-CO-O-C(CH_3)_3$	105–120	0.33	Benzene Chloroform	$C_7H_{12}O_2S$	52.47	7.55	...	20.01	52.38	7.80	...	19.97
34	 $-\underset{CH_3}{\underset{\mid}{N}}-CO-S-C_2H_5$	135–175	1.09	Benzene Tetrahydrofuran	$C_6H_{11}NOS$	49.62	7.58	9.65	22.09	49.79	7.58	9.96	22.32
35		115–135	0.14	Benzene Tetrahydrofuran	$C_7H_{11}NO_3$	53.49	7.06	8.91	...	53.26	7.17	8.76	...

^{a} In benzene.

Experimental[19]

Materials.—The N-alkylaziridines were purchased from the Borden Chemical Corp., Philadelphia 24, Pennsylvania; the alkyl chloroformates from the Matheson Co., Inc., East Rutherford, New Jersey; and the alkyl chlorothiolformates from Stauffer Chemical Co., New York 17, N. Y.

Ethylene Sulfide.[20]—The cyclic sulfide was prepared by reaction of ethylene oxide with potassium thiocyanate in water; yield 50–70%, b.p. 53–56 (b.p. 55–56°).

S-β-Chloroethyl Chlorothiolformate.[10]—To a stirred solution of 99.1 g. (1 mole) of phosgene and a few drops of pyridine in a flask fitted with a thermometer and a Dry Ice condenser there was added dropwise 60.1 g. (1 mole) of ethylene sulfide while maintaining the temperature at 0–5°. It is advisable to make sure that the exothermic reaction has started before larger quantities of the cyclic sulfide are added. After the addition was completed (1–2 hr.), the solution was gradually heated to 50° and kept at this temperature for 2 hr. After cooling, the Dry Ice–acetone condenser was removed and nitrogen was bubbled through the product until the weight was constant. On fractional distillation the mixture afforded S-β-chloroethyl chlorothiolformate 105 g. (66%) b.p. 59–60°/5 mm., and 21 g. (11%) of S,S-bis-β-chloroethyl dithiolcarbonate,[10] b.p. 96–97°/0.8 mm. The chlorothiolformate is a lachrymator and a vesicant.

General Procedures. S- and O-β-Chloroethyl Carbamates (Tables I and IV).—To a stirred solution of 2 moles of the dialkylamine in 200 ml. of ether at 0°, a solution of 1 mole of S-β-chloroethyl chlorothiolformate or O-β-chloroethyl chloroformate in 100 ml. of ether was added over a period of 30–60 min. The white precipitate of the amine salt was formed immediately. After completion of the addition, the slurry was stirred at 30–40° for 2 hr. The amine salt was filtered; the ether solution was washed with dilute sulfuric acid and water, and dried over magnesium sulfate. The ether was removed and the residue vacuum distilled or recrystallized. The infrared spectra of these compounds show absorption maximum characteristic of the carbonyl group between 1640 cm.$^{-1}$ and 1660 cm.$^{-1}$.[21] The yields, boiling points, indices of refraction, and analysis of these compounds are given in Tables I and IV.

S-β-Chloroethyl S-Isopropyl Dithiolcarbonate.—S-β-Chloroethyl chlorothiolformate, 104.0 g. (0.657 mole), in 100 ml. of ether was added to 50 g. (0.657 mole) of isopropyl mercaptan and 67.4 g. (0.657 mole) of triethylamine in 400 ml. of ether at such a rate as to maintain moderate refluxing. After the addition was completed, the slurry was stirred and refluxed for 2 hr. The salt was filtered and the ether layer was washed with dilute sulfuric acid and water. The ether was removed and the residue vacuum distilled. The yield, physical properties, and analysis appear in Table II. The same procedure was used for the preparation of S-β-chloroethyl O-*t*-butyl thiolcarbonate. The yield, physical properties, and analysis of this compound appear in Table III.

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[19] All melting points are uncorrected; Analysis by Alfred Bernhardt, Mikroanalytisches Laboratorium in Max-Planck-Institut für Kohlenforschung, Mulheim (Ruhr), West Germany.

[20] Ref. 13, p. 154.

[21] R. A. Nyquist and W. J. Potts, *Spectrochim. Acta*, **17**, 679 (1961).

β-Chloroethyl Carbonates and S-β-Chloroethyl Thiolcarbonates (Tables II and III).—Ethylene sulfide (1 mole) was slowly added to 1 mole of alkyl chloroformate or alkyl chlorothiolformate containing a few drops of pyridine while maintaining the reaction mixture at 10–20°. After the addition was completed, the temperature was slowly raised to 80° and the solution was stirred for 2 hr. The crude products were vacuum distilled. The infrared spectra showed carbonyl absorption between 1640 cm.$^{-1}$ and 1670 cm.$^{-1}$ (—S—CO—S—)[21] and between 1720 cm.$^{-1}$ and 1740 cm.$^{-1}$ (—O—CO—S—).[21] The yields, analysis, boiling points, and the indices of refraction of these compounds are given in Tables II and III.

S-Ethyl N-β-Chloroethyl-N-methyl Thiolcarbamate (Table IV).—A solution of 50 g. (0.875 mole) of N-methylaziridine in 150 ml. of ether was added to a solution of 111.5 g. (0.875 mole) of ethyl chlorothiolformate in 250 ml. of ether at a rate sufficient to maintain moderate refluxing. After the addition was complete, the turbid solution was refluxed for 2 hr. The reaction mixture was filtered and washed with dilute sulfuric acid and water. The ether was removed and the residue vacuum distilled. The same procedure was used to prepare β-chloroethyl N-β-chloroethyl-N-methylcarbamate. The yield, physical properties, and analysis of these compounds (15) and (16), respectively, appear in Table IV.

S-, O-, and N-Vinyl Carbonic Acid Derivatives.—The β-chloroethyl compounds (0.5 mole) were dissolved in 100 ml. of absolute *t*-butyl alcohol and added dropwise to a freshly prepared solution of 0.5 mole of potassium *t*-butoxide in 300–400 ml. of absolute *t*-butyl alcohol. The temperature was kept at 50–70° during the reaction. After the addition was completed, the slurry was stirred for at least 1–2 hr., usually until the reaction mixture was neutral or only weakly basic. The reaction mixture was cooled, neutralized with glacial acetic acid, and 100 ml. of ether were added to complete the precipitation of the salt. The slurry was filtered, the solvent evaporated, and the residue vacuum distilled. The analysis, yields, and physical properties of the monomers are reported in Tables V, VI, and VII.

Polyethylene sulfide[15] and/or 1,4-dithiane[16] were isolated as side products in dehydrohalogenation reactions. Both compounds were identified by analysis, infrared spectrum, and melting point. 1,4-Dithiane, m.p. 112–113 (m.p. 113), usually complicated the vacuum distillation by its tendency to sublime.

Anal. Calcd. for polyethylene sulfide $(C_2H_4S)_n$; C, 40.01; H, 6.61; S, 53.38. Found: C, 39.98; H, 6.80; S, 53.37.

Polymerization of the Monomers.—The monomers were polymerized in bulk with 0.3 wt. % of 2,2′-azobisisobutyronitrile as initiator in glass tubes sealed under nitrogen. The polymers were isolated by precipitation from pentane or methanol and purified by reprecipitation from tetrahydrofuran and pentane. The polymerization conditions, the viscosities, the softening points, and the solubilities of the polymer are given in Tables VIII and IX.

Hydrolysis of Poly(S-vinyl Thiolcarbamates) and Poly(S-vinyl Thiolcarbonates).—The polymers were hydrolyzed by heating under reflux in an atmosphere of prepurified nitrogen with 10% sodium hydroxide in water–alcohol until a clear solution was obtained.[18] For the case of poly(S-vinyl S-isopropyl dithiolcarbonates) the hydrolysis was completed after 5 hr. The polyvinylmercaptan was precipitated with 2 *N* hydrochloric acid, filtered, washed with water, and dried. After isolation, the polymer was insoluble in base due to oxidative cross-linking. The infrared spectrum of the polymer did not show any carbonyl absorption. Contrary to this poly(S-vinyl N,N-diethyl thiolcarbonate) did not go into solution before 20 hr. of refluxing. The infrared spectrum of the precipitated polyvinyl mercaptan still showed a weak carbonyl absorption at 1655 cm.$^{-1}$.

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Dihydroisocoumarins. IV. Reaction with N-Bromosuccinimide. A New Route to Some Isocoumarin Syntheses

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Starting from appropriate homophthalates, 6,7-dimethoxy-, 5-methoxy-7-methyl-, 5,6-dimethoxy-, and 6,7-methylenedioxyisochroman were synthesized and oxidized to the corresponding dihydroisocoumarins. These were converted into the isocoumarins with the aid of *N*-bromosuccinimide.

Previous studies[1–3] from this laboratory on the syntheses of dihydroisocoumarins involve the formation of the hetero ring from appropriate *o*-aminophenethyl alcohols; the amino group is transformed into carboxyl which lactonizes with the *o*-hydroxyethyl group to form the dihydroisocoumarins. This route, however, depends on the availability of such starting materials as *o*-nitrophenylacetates and *o*-nitrophenethyl alcohols, very few of which are readily accessible. Therefore, the alternative method based on the oxidation[4] of isochromans with selenium dioxide was adopted for the preparation of the dihydroisocoumarins. The oxidation with selenium dioxide, though proceeding normally in one case, gave dark gummy products in the other instances which required extensive purification for the isolation of the dihydroisocoumarins and consequently the yields were lowered. Subsequently, chromium trioxide proved to be a superior reagent for oxidation as the products were purer and the yields were higher.

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(1) P. K. Banerjee and D. N. Chaudhury, *J. Org. Chem.*, **26**, 4344 (1961).

(2) J. N. Srivastava and D. N. Chaudhury, *J. Indian. Chem. Soc.*, **38**, 998 (1961).

(3) P. K. Banerjee and D. N. Chaudhury, *ibid.*, **39**, 243 (1962).

(4) P. Maitte, *Ann. Chim.*, (xii), **9**, 473 (1954).