Methanesulfenyl Chloride. VI.
A Stereochemical Study of Certain Organosulfur Reactions[1]

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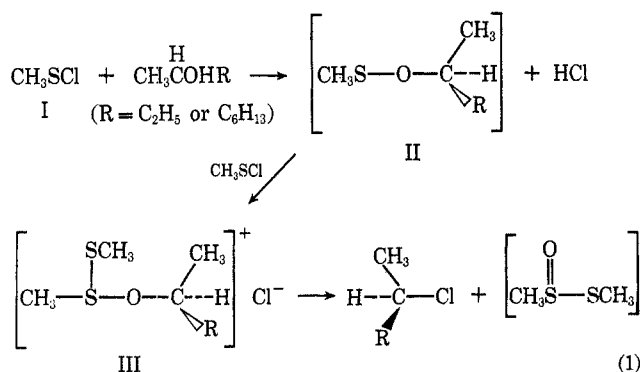*Department of Chemistry, University of Maine, Orono, Maine 04473*

The reaction of methanesulfenyl chloride (I) with optically active 2-octanol or 2-butanol, and with the methyl xanthates, $CH_3SC(S)OR$, or methanesulfinate esters, $CH_3S(O)OR$, containing these optically active groups resulted in the formation of 2-octyl or 2-butyl chlorides of predominantly inverted configuration. The reaction of methylsulfur trichloride with the same optically active alcohols produced alkyl chlorides with a high degree of inversion. The alkyl chlorides formed when chlorine reacts with the 2-octyl or 2-butyl methanesulfinate esters showed a lower degree of inversion (greater racemization) than those formed in the other reaction. Evidence is presented that in the reaction of I with sulfinate esters, $RS(O)OR'$, electrophilic attack can occur at either the alkoxide or sulfoxide oxygen atoms or at the sulfur atom. When R' is methyl, reaction appears to occur chiefly at the alkoxide oxygen but as R' becomes more bulky attack at the alkoxide oxygen is inhibited and the predominant reaction is at the sulfur atom.

In previous papers from this laboratory we reported that methyl chloride is formed when methanesulfenyl chloride, CH_3SCl (I), reacts with S-alkyl O-methyl-xanthate[2] or with methanol,[3,4] when methylsulfur trichloride reacts with methanol,[5] and when chlorine reacts with methyl methanesulfinate.[6] It seemed of interest to reexamine these reactions using optically active 2-octanol and 2-butanol, and optically active compounds containing octyl and butyl groups, to determine if the results would shed light on the mechanism by which the alkyl halide is formed.

In most cases the reactions took place with predominant inversion of the optically active groups, suggesting typical nucleophilic displacement at carbon by chloride ion in the product-forming step. A higher degree of racemization in some cases can be explained in terms of inductive effects which weaken the carbon–oxygen bond and facilitate the separation of a carbonium ion.

The reaction of methanesulfenyl chloride (I) with methanol was reported earlier to yield a complex mixture of six different organic compounds, the formation of which has been explained by a sequence of reactions,[4] the correctness of which has been supported by additional work in our laboratory. On the basis of the previously postulated reaction steps and the inverted configuration of the alkyl chlorides isolated (2-butyl, 89–95%, and 2-octyl, 55–72%), the formation of alkyl chlorides in the reaction of I with 2-butanol and 2-octanol appears chiefly to proceed as shown in eq 1.

$$\qquad\qquad (1)$$

The alcoholysis of methylsulfur trichloride to produce methanesulfinyl chloride and alkyl chlorides[5] produced the latter with high degrees of inversion (2-butyl, 92%, and 2-octyl, 61–73%). Following the previously proposed mechanistic pathway,[7] eq 2 shows how this reaction is believed to occur.

$$\qquad\qquad (2)$$
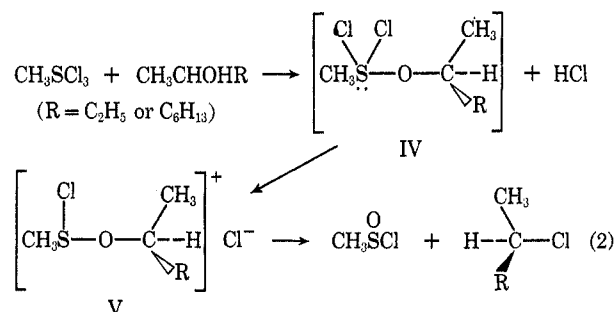
The reaction of I with S-methyl O-alkyl dithiocarbonates (xanthates) showed predominant inversion of the alkyl group but also gave some evidence for a solvent effect. The sequence of reactions previously postulated[3] and supported in the present study, together with the stereochemical explanation for the inversion (2-butyl, 66–81%, and 2-octyl, 57–89%) is shown in eq 3.

$$\qquad\qquad (3)$$
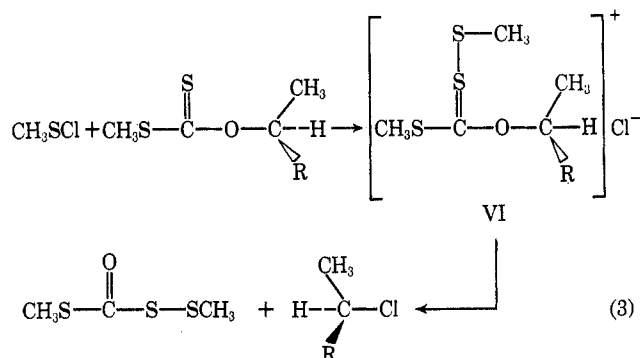
The degree of inversion appeared to be somewhat solvent dependent in the reaction of I with methyl 2-butylxanthate. When the reaction was carried out in carbon tetrachloride the 2-butyl chloride formed

(1) Taken from the M.S. and Ph.D. Theses of R. V. Norton, University of Maine, 1965 and 1967, and D. A. Koop, University of Maine, 1969 and 1962; M.S. Thesis of P. M. Cocanour, University of Maine, 1969.

(2) I. B. Douglass and W. J. Evers, *J. Org. Chem.,* **29,** 419 (1964).

(3) I. B. Douglass, *ibid.,* **24,** 2004 (1959).

(4) I. B. Douglass and D. A. Koop, *ibid.,* **27,** 1398 (1962).

(5) I. B. Douglass and D. R. Poole, *ibid.,* **22,** 536 (1957).

(6) I. B. Douglass, *ibid.,* **30,** 633 (1965).

(7) I. B. Douglass and R. V. Norton, *ibid.,* **33,** 2104 (1968).

showed 66–69% inversion. In dioxane the inversion was 80–81%. These results suggest that dioxane, the more polar solvent, has a stabilizing influence on the ionic intermediate VI retarding its tendency to dissociate into a carbonium ion and holding the ion intact until the 2-butyl group is removed in an S_N2 type of reaction.

Dr. Harold Kwart, in a private communication, has suggested that the different degrees of inversion obtained in nonionizing and polar solvents may be due to different transition states resulting from the covalent and ionic forms of intermediate VI (eq 3a). No such


(3a)
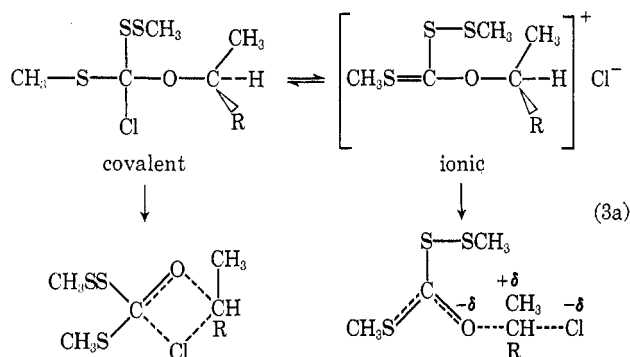
favored in nonionizing media   favored in high dielectric media

solvent effect could be detected in the case of methyl 2-octylxanthate. Although the reaction was carried out in dioxane, ether, chloroform, and carbon tetrachloride using different solvent volumes and molar ratios of reactants, the variation in degree of inversion (50–89%) showed no significant pattern and seemed to result from some unidentified and uncontrolled factor.

The reaction of I with alkyl methanesulfinates has special interest. The formation of methyl methanesulfinate, $CH_3S(O)OCH_3$ (VII), was reported earlier[4] to be part of the sequence of reactions taking place when I and methanol are brought together. In a previous paper[4] we reported that, when I and VII are caused to react in the absence of other reagents, the products include methyl chloride (26 mol %), methyl disulfide (29 mol %), methanesulfonyl chloride (17 mol %), methanesulfinyl chloride (23 mol %), and methyl methanethiolsulfonate, $CH_3SO_2SCH_3$ (5 mol %), with all products representing a total yield of 71%. In our previous paper we referred to the initial reaction as resulting in an "addition complex." We are now convinced that the "addition complex" may have several forms depending on where in the sulfinate ester molecule the initial attack by I occurs.
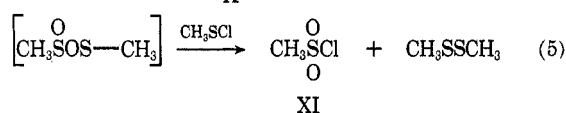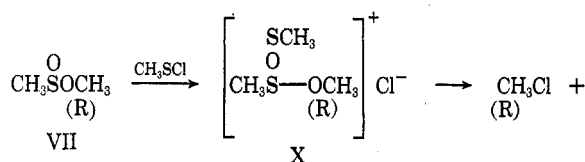
The sulfinate ester
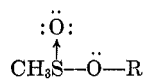
contains three types of unshared electron pairs, one type on the sulfur atom, another type on the sulfoxide oxygen atom, and a third type on the alkoxide oxygen. Since I is an electrophilic reagent it may be expected to attack the unshared pair most available.

If attack occurs on the alkoxide moiety, the reaction would proceed as shown in eq 4 with 2 mol of methanesulfinyl chloride (VIII) being formed as 3 mol of I are

consumed in the reaction sequence. If attack occurs
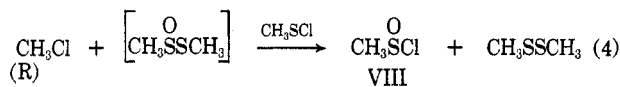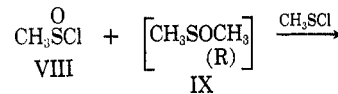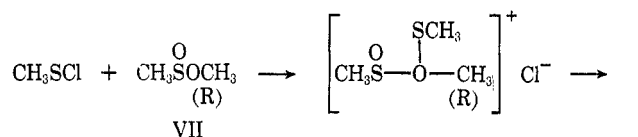
at the sulfoxide oxygen, however, the reaction might take place as shown in eq 5 with 1 mol of methanesulfonyl chloride (XI) being formed with simultaneous consumption of 2 mol of I.

If electrophilic attack by I occurred at the sulfur atom, the products would be methyl methanethiolsulfonate as shown in eq 6. When the reaction of I with
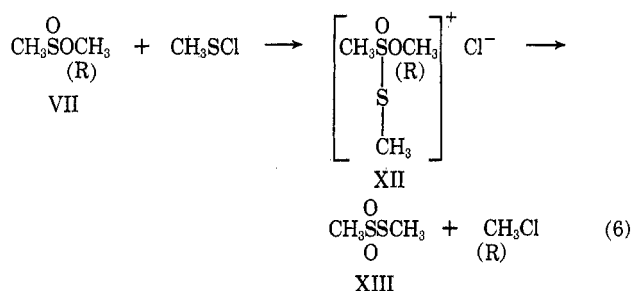
sulfinate esters was first studied[3] it was anticipated that electrophilic attack would occur primarily at the sulfur. The finding of a sulfonyl chloride instead of a thiolsulfonate, however, led us to believe that reaction occurred at an oxygen atom.

In the study referred to above[4] we observed that the reaction of various esters with different sulfenyl chlorides gave varying proportions of sulfinyl and sulfonyl chlorides. One of us[8] attempted, with only partial success because of the experimental problems involved, to demonstrate the steric influence of R and R' groups of different sizes in the reaction of I with esters R'O-S(O)R. Table I shows the results obtained. The only conclusion which could be drawn was that with bulky groups there was greater tendency for the reaction to favor sulfonyl chloride formation and, presumably, sulfoxide attack.

More recently we have found that nuclear magnetic resonance (nmr) spectroscopy affords a convenient

(8) D. A. Koop, Ph.D. Thesis, University of Maine, 1962.

TABLE I

THE REACTION OF CH₃SCl WITH SULFINATE ESTERS RSOR'
$$\text{RSOR'}$$
(molar ratio of CH₃SCl/ester = 2)

| R	R'	Mol of RSO₂Cl formed	Mol of RSOOR' used	Molar ratio[a] of RSO₂Cl/ RS(O)OR'
Me	Me	0.04	0.12	0.3
Me	Et	0.03	0.11	0.3
Me	Pr	0.06	0.25	0.2
Et	Me	0.04	0.17	0.2
Et	Et	0.05	0.12	0.4
Et	Pr	0.08	0.17	0.5
2-Pr	Et	0.07	0.11	0.6
2-Pr	Pr	0.12	0.14	0.9

[a] The ratios listed are equivalent to the per cent of the ester which reacts by attack at the sulfoxide oxygen. The results are not entirely consistent with the more accurately determined values shown in Table II, partly as a result of the inherent difficulty of determining the sulfonyl chloride content in a mixture of disulfide, sulfinyl chloride, thiolsulfonate, alkyl halide, unreacted ester, and spontaneous decomposition products of methanesulfenyl chloride.

means for identifying individual components of complex mixtures of organosulfur compounds. The chemical shift for CH₃SOCl (VIII) is a sharp singlet at δ 3.37, that for CH₃SO₂Cl (XI) is at δ 3.61, that for CH₃SO₂SCH₃ is at δ 3.28, and that for CH₃SO₂SCH₃ is at δ 2.69 with no interference from other signals in the mixtures studied. Table II shows the results obtained when various alkyl methanesulfinates were treated with I. The molar ratio of products formed was obtained by integrating the relative δ responses of the different types of methyl groups in the nmr spectra of the crude reaction mixtures.

The nmr spectra used in obtaining the data for Table II clearly showed that CH₃SO₂Cl, CH₃SOCl, and CH₃SO₂SCH₃ are all formed. On the assumption that the mechanisms outlined in eq 4, 5, and 6 are correct, the results indicate that electrophilic attack by I occurs to varying degrees at all available electron pairs. As the group R in the ester CH₃S(O)OR becomes more bulky, electrophilic attack at the alkoxide oxygen is inhibited. The available data do not indicate what factors influence preferential attack at the sulfoxide oxygen or at the sulfur. We can offer no explanation for the fact that in the case of the ethyl ester, attack t the sulfoxide oxygen is greatly favored.

Other stereochemical effects were observed in the reactions of I with 2-butyl methanesulfinate. In duplicate experiments the 2-butyl chloride formed was found to have 80% inversion, a value lower than that obtained when I reacts with 2-butanol. Although an examination of eq 1 and 4 would suggest that the 2-butyl chloride produced in each should have the same degree of rotation (intermediates II and IX are identical), it must be realized that the reaction of I with a sulfinate ester also involved eq 5 and 6. The 2-butyl chloride isolated, therefore, has been formed in three different ways and the observed rotation is a net effect.

The reaction of sulfinate esters with chlorine produced alkyl halides significantly lower in their degree of inversion than any of the reactions described above, 54–56% in the case of 2-butyl and 19–37% in the case of 2-octyl. The postulated course of the reaction is shown in eq 7.
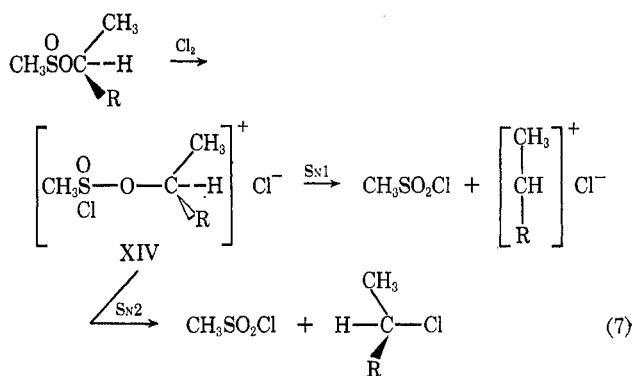
The relatively high degree of racemization suggests that inductive forces in the ionic intermediate XIV facilitate the separation of a carbonium ion which, on combining with chloride ion, formed racemized alkyl halide.

Without clearer evidence for the existence of the postulated ionic intermediates which decompose in the alkyl chloride-forming steps, one is not justified in attempting a full explanation for the differences in degree of inversion observed in the different reactions. If one compares the structures of III, V, X, and XIV, however, interesting structural differences appear. All the structures are alike except for different atoms or groups attached to the common sulfur atom of the CH₃-S-O-C chain (III, SCH₃; V, Cl; X, O-SCH₃; XIV, O and Cl). If one assumes that these intermediates actually exist and react to form the alkyl halides, one is tempted to compare their structures for indications of inductive forces which could account for carbonium ion separation and racemization of the alkyl chloride. The experimental results do not show any consistent and outstanding differences in racemization of alkyl chlorides formed from III, V, and X. In the case of XIV, however, the presence of both oxygen and chlorine atoms on the sulfur, each held by a semipolar bond, leads one to expect an unusually strong inductive force which might weaken the oxygen–carbon bond facilitating carbonium ion separation. The high degree of racemization found in both the butyl chloride (44–46% racemized) and octyl chloride (63–81% racemized) is consistent with this view.

Experimental Section

All boiling points are uncorrected. Microanalyses were performed by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. Optical rotations were determined in the early part of the study by means of an antiquated Franz Schmidt and Haensch polarimeter using a 1-dm D. C. Rudolph and Son's water-jacketed micropolarimeter cell at 25 ± 0.1°. In repeating part of the 2-octyl work and in all of the 2-butyl study, a precision polarimeter, PEPOL 60 manufactured by Bellingham and Stanley Ltd. of London, England, was employed. No serious disagreement between the values obtained with the two instruments was observed.

The resolution of 2-octanol was accomplished using the procedure developed by Kenyon.[9] After fractional crystallization of the brucine salt of 2-octyl hydrogen phthalate from acetone, the fractions were hydrolyzed and the recovered 2-octanol was distilled. In this manner (S)-(+)-2-octanol having [α]²⁵D +9.34 ± 0.18° (91% optical purity) and (R)-(−)-2-octanol having [α]²⁵D −9.21 ± 0.07° and [α]²⁵D −9.42 ± 0.05° (90

(9) H. Gilman and A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p 418.

TABLE II

REACTION OF CH₃SCl WITH ALKYL METHANESULFINATES, CH₃S(O)OR

(0.10 mol of ester, 0.02 mol of CH₃SCl)

Sulfinate ester CH₃S(O)OR	Products,[a] mol %			% of attack[b] by CH₃SCl at		
	CH₃SOCl eq 4	CH₃SO₂Cl eq 5	CH₃SO₂SCH₃ eq 6	Alkoxide oxygen eq 4	Sulfoxide oxygen eq 5	Sulfur sulfur eq 6
Methyl	58.1	13.9	28.0	41.0	19.6	39.4
	63.5	13.5	23.0	46.5	19.8	33.7
Ethyl	42.5	36.0	21.8	26.8	45.5	27.7
	42.7	34.8	22.5	27.3	44.1	28.6
	40.5	38.1	21.4	25.3	47.8	26.9
2-Propyl	17.8	28.9	53.3	9.8	31.7	58.5
	15.4	30.8	53.8	8.3	33.3	58.4
2-Butyl	6.5	35.0	58.5	3.4	36.2	60.4
	5.7	34.1	60.2	2.9	35.1	62.0
2-Octyl	0	40.0	60.0	0	40.0	60.0
	0	38.2	61.8	0	38.2	61.8

[a] The molar ratios of these three compounds were obtained by integrating the nmr spectra of crude reaction mixtures obtained on a Varian A-60 analytical spectrometer at ambient probe temperature. [b] Assuming that the moles of ester reacting at the alkoxide oxygen are equal to 0.5 of the moles of sulfinyl chloride formed (eq 4), at the sulfoxide oxygen are equal to the moles of sulfonyl chloride formed (eq 5), and at the sulfur atom are equal to the moles of thiolsulfonate formed (eq 6), the per cent reacting in each way can be calculated from the mole per cents of products as follows.

$$\% \text{ attack} = \frac{100 \times \text{mol } \% \text{ of } (0.5\text{CH}_3\text{SOCl or CH}_3\text{SO}_2\text{Cl or CH}_3\text{SO}_2\text{SCH}_3)}{\text{mol } \% \text{ of } (0.5\text{CH}_3\text{SOCl} + \text{CH}_3\text{SO}_2\text{Cl} + \text{CH}_3\text{SO}_2\text{SCH}_3)}$$

and 92% optical purity, respectively, based on a maximum rotation of [α]²⁵D ±10.3°)[10] were obtained.

The preparation of (S)-(+)-2-butanol was carried out by the procedure of Brown.[11,12] After purification by preparative gas chromatogaphy using a Varian Aerograph Model 700 Autoprep, 2-butanol was obtained having [α]²⁵D +11.24° (83% optically pure) and [α]²⁵D 9.37° (69% optically pure) compared with [α]²⁵D ±13.51°.[13]

Methanesulfenyl chloride[3] and methylsulfur trichloride[14] were prepared by methods previously described. Methanesulfinyl chloride was prepared in 88% yield by the modification of previous methods recently described.[7]

(S)-2-Octyl methanesulfinate was prepared by allowing 2-octanol (4.95 g, 0.038 mol, [α]²⁵D +9.21 ± 0.07°) to react with freshly distilled methanesulfinyl chloride (4.36 g, 0.0043 mol) at −30° under an atmosphere of dry nitrogen. After a stirring period of 1 hr at the reduced temperature the solution was allowed to stand at room temperature for several hours and then was distilled through a 9-in. Vigreux column. The resulting ester, obtained in 84% yield, boiled at 72° (0.75 mm) and had n²⁵D 1.4443 and [α]²⁵D −31.04 ± 0.37°. It was assumed to have the same optical purity as the 2-octanol used (90%).

Anal. Calcd for C₉H₂₀O₂S: C, 56.29; H, 10.50; S, 16.70. Found: C, 56.48; H, 10.50; S, 16.21.

(S)-(+)-2-Butyl methanesulfinate was prepared in an analogous manner. Starting with 0.1 mol each of alcohol and sulfinyl chloride the product was obtained in 74% yield, boiled at 56° (11 mm), and had n²⁵D 1.4214 and [α]²⁵D +17.87.

Anal. Calcd for C₅H₁₂O₂S: C, 43.19; H, 8.70; S, 23.06. Found: C, 43.54; H, 8.71; S, 23.33.

The S-methyl O-alkyl xanthates were prepared by adding sodium hydride (10.00 g, 0.262 mol) to a solution of the optically active alcohol (0.23 mol) in 50 ml of anhydrous ether contained in a three-neck flask equipped with stirrer, reflux condenser, and nitrogen-flushing system at such a rate as to maintain boiling. After 1 hr, carbon disulfide (35.2 g, 0.25 mol) was added at such a rate that the reaction could be controlled and stirring was continued an additional hour. Methyl iodide (35.2 g, 0.25 mol) was then cautiously added and gentle refluxing continued for 10 hr, following which the mixture was added to 50 ml of water. Separation of the ethereal layer, drying, and distillation at reduced pressure yielded the following product: O-(S)-(+)-2-butyl S-methyl dithiocarbonate, prepared from 2-butanol of 83% optical purity (81% yield), boiled at 78° (11 mm) and had n²⁵D 1.5124 and [α]²⁵D +5.6.

Anal. Calcd for C₆H₁₂OS₂: C, 43.87; H, 7.36; S, 39.03. Found: C, 43.74; H, 7.55; S, 39.25.

O-(S)-(+)-2-Octanol S-methyl dithiocarbonate, prepared from 2-octanol of 91% optical purity (89% yield), boiled at 102° (0.4 mm) and had n²⁵D 1.5065, d²⁴₄ 0.988, [α]²⁵D −6.75.

Anal. Calcd for C₁₀H₂₀OS₂: C, 54.50; H, 9.15; S, 29.09. Found: C, 55.04; H, 9.20; S, 29.24.

Neither of the two compounds showed any infrared absorption in the carbonyl region and thus were free from any S,S-dialkyl isomers.

Reaction of I with Sulfinate Esters.—The reactions reported in Table II were carried out by mixing 0.01 mol of the ester to be tested with 0.02 mol of I in a test tube held at the temperature of solid carbon dioxide. Each mixture was then allowed to warm to room temperature and a small portion was diluted to a 10% concentration with spectral grade carbon tetrachloride containing 1% of tetramethylsilane. The nmr spectra of the diluted samples were determined without delay. The spectra showed proton δ signals for the alkyl halides and methyl disulfide but these signals did not interfere with those for the critical products: CH₃SOCl, δ 3.37 ppm; CH₃SO₂Cl, δ 3.61 ppm; CH₃SO₂SCH₃, δ 3.28 ppm; CH₃SO₂SCH₃, δ 2.69 ppm.

Procedure for Obtaining Optically Active Alkyl Chlorides (Table III).—In carrying out reactions with I, the optically active compound was placed in a three-necked 25-ml flask equipped with a Teflon stirrer assembly, a nitrogen-flushing system, and a septum adapter. After cooling of the stirring liquid to −20° or lower, freshly prepared I was added in one portion through the septum adapter and the mixture was stirred for 15 min.

The reactions with methylsulfur trichloride were carried out by slowly adding the alcohols to well-stirred slurries of freshly prepared methylsulfur trichloride in 25 ml of methylene chloride at approximately −30°. After the solid disappeared the reaction mixture was kept at 0° for several hours.

In the chorination experiments the optically active sulfinate esters were treated with chlorine at −50° in the absence of solvent under a nitrogen atmosphere.

The 2-octyl chloride samples were isolated by chromatographing the crude reaction mixtures on a column of Mallinckrodt 250 mesh silica gel with hexane as the initial developer, using 50 g of adsorbent per 1.5 g of reaction mixture. The 2-octyl chloride was eluted in the first 100 ml of hexane. After removal of the solvent, the residual 2-octyl chloride was identified by comparing its ir and pmr spectra with those of authentic samples.

The 2-butyl chloride was recovered by heating the crude reaction mixtures, with continued stirring to 75°, while flushing with a stream of dry nitrogen and collecting all volatile material driven off in a liquid nitrogen trap. After the volatile product was washed with water, and dried, the 2-butyl chloride was isolated by preparative gas chromatography using a Varian-Aerograph Model 700 Autoprep with 20 ft × ³/₈ in. stainless steel

(10) N. Kornblum, L. Fishbein, and R. A. Smiley, *J. Amer. Chem. Soc.*, 77, 6261 (1955).
(11) H. C. Brown and G. Zweifel, *ibid.*, 83, 486 (1961).
(12) H. C. Brown, in *Org. React.* 13, (1963).
(13) P. J. Leroux and H. S. Lucas, *J. Amer. Chem. Soc.*, 73, 41 (1951).
(14) I. B. Douglass, K. R. Brower, and F. T. Martin, *ibid.*, 74, 5770 (1952).

TABLE III
STERIC COURSE OF VARIOUS ORGANOSULFUR REACTIONS

Optically active reagent	% optical purity	Reactant	Molar ratio, reagent/ reactant	% yield, alkyl chloride	% optical purity	% inversion
S-Methyl O-(S)-(+)-2-octylxanthate	91	CH₃SCl	1:1	51	63	69
S-Methyl O-(S)-(+)-2-octylxanthate	81	CH₃SCl	4:3	26	46	57
(R)-(−)-2-Octanol	92	CH₃SCl	1:2	20	51	55
(S)-(+)-2-Octanol	91	CH₃SCl	5:4	17	66	72
(R)-(−)-2-Octanol	92	CH₃SCl₃	1:1	26	67	73
(S)-(+)-2-Octanol	91	CH₃SCl₃	1:1	31	55	61
(S)-(+)-2-Octyl methanesulfinate (RS)	91	Cl₂	1:1.3	56	17	19
(R)-(−)-2-Octyl methanesulfinate (RS)	90	Cl₂	1:1.2	43	33	37
S-Methyl O-(S)-(+)-2-butylxanthate (6 g, 10 ml of CCl₄)	82.2	CH₃SCl in 10 ml of CCl₄	2:3	40	54	66
S-Methyl O-(S)-(+)-2-butylxanthate (6 g, 10 ml of CCl₄)	82.2	CH₃SCl in 10 ml of CCl₄	2:3	35	56	69
S-Methyl O-(S)-(+)-2-butylxanthate (6 g, 10 ml of dioxane)	82.2	CH₃SCl in 10 ml of dioxane	2:3	20	67	81
S-Methyl O-(S)-(+)-2-butylxanthate (6 g, 10 ml of dioxane)	82.2	CH₃SCl in 10 ml of dioxane	2:3	20	66	80
(S)-(+)-2-Butanol	68.0	CH₃SCl	1:3	32	60	89
(S)-(+)-2-Butanol	82.2	CH₃SCl	1:3		78	95
(S)-(+)-2-Butyl methanesulfinate (RS)	68	CH₃SCl	1:1	2	54	80
(S)-(+)-2-Butyl methanesulfinate (RS)	68	CH₃SCl	1:1	5	54	80
(S)-(+)-2-Butanol	68	CH₃SCl₃	3:4	9	62	92
(S)-(+)-2-Butanol	68	CH₃SCl₃	3:4	48	63	92
(S)-(+)-2-Butyl methanesulfinate (RS)	68	Cl₂	1:1		38	56
(S)-(+)-2-Butyl methanesulfinate (RS)	68	Cl₂	1:1		37	54

column packed with 30% SE-30 on Chromosorb P and operated at 130° with a helium carrier flow rate of 150 ml/min. The exit tip was modified by fastening to it a hypodermic needle which was inserted through the septum of a sealed trap cooled in liquid nitrogen. This arrangement made it possible to collect the low-boiling 2-butyl chloride with minimal loss.

The stoichiometry of the various reactions has been discussed previously[2,4,6] and all expected products were identified in the present study. Because of the problems involved in recovering pure alkyl chlorides for polarometric analysis, the yield data reported in Table III represent only the pure material isolated rather than the maximum amount formed in the reaction. In some cases when enough alkyl chloride had been separated to determine the optical rotation no further attempt was made to isolate additional product.

Determining the Degree of Inversion.—Values for the optically pure reference compounds used in this study were as follows: 2-butanol, [α]²⁵D 13.51°;[18] 2-octanol, [α]²⁵D 10.3°;[10] 2-butyl chloride, [α]²⁵D 33.8°[15]; and 2-octyl chloride, [α]²⁵D 41.2°, the latter obtained by extrapolating data reported by Gerrard and Hudson.[16] This value for 2-octyl chloride is somewhat lower than the average of values which could be obtained by extrapolating more recent data,[17] but there is sufficient uncertainty in the actual value to make the difference insignificant.

The optical purity of the alcohols used as starting materials was determined by dividing their observed specific rotations by the values for optically pure material given above. The xanthate and methanesulfinate intermediates were assumed to have the same optical purity as the alcohols from which they were prepared. It was also assumed that the optical purity of the original alcohol set an upper limit on the optical purity of the alkyl chloride produced. Thus, multiplication of the specific rotation of optically pure 2-butyl or 2-octyl chloride by the fractional purity of the alcohol from which it was derived gave a maximum specific rotation which the chloride might have. The degree of inversion was then determined as the ratio of the observed rotation to the calculated theoretical maximum value.

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Chemistry of a Cumulated Double-Bond Compound.   X.
Reactions of Isocyanates and Carbodiimide with Acetylenic Compounds

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In the reaction of phenyl isocyanate with phenylacetylene in the presence of $Fe(CO)_5$, 4-benzylidene-1,3-diphenylhydantoin (1a) was obtained in 85% yield by the addition reaction and hydrogen shift. Oxidation of 1a gave diphenylparabanic acid. The hydrogen transfer of acetylenic hydrogen was identified with phenyl-acetylene-1-d. The reaction of diphenylcarbodiimide with phenylacetylene in the presence of $Fe(CO)_5$ gave 4-benzylidene-1,3-diphenyl-2,5-bis(phenylimino)imidazolidine and 4-benzylidene-1,3-diphenyl-2-phenylimino-imidazolidin-5-one in 78 and 17% yields, respectively. 1,3,4-Triphenylpyrroline-2,5-dione and 1,3,4-triphenyl-5-phenyliminopyrrolin-2-one were obtained in 42 and 15% yields, respectively, in the reaction using phenyl isocyanate, diphenylacetylene, and $Fe(CO)_5$. In this reaction, hydantoin and imidazolidine were not obtained. Reaction mechanisms are discussed.

Cycloaddition reactions of heterocumulenes to olefins have been investigated in detail for a long time.[1] On the other hand, the reaction between heterocumulene and acetylenic compound has been dealt with in a few papers,[2-5] but there is no information regarding a reaction between isocyanate (or carbodiimide) and phenylacetylenes without the reaction between metal phenylacetylide and aryl isocyanates.[6-8] It was recognized in our preliminary experiments that isocyanates and carbodiimides were unreactive to acetylenic compounds without a catalyst.

It is well known that acetylenic compounds[9] and heterocumulenes[10-14] form numerous organometallic complexes with metal carbonyls. Consequently, we can expect some reaction between heterocumulenes, such as isocyanates or carbodiimides, and acetylenic compounds in the presence of metal carbonyls *via* metal complex intermediate formation.

In this paper, reactions of isocyanates and carbodiimides with acetylenic compounds in the presence of iron carbonyls are studied and some interesting results are obtained.

Results and Discussion

Reactions with Phenylacetylene.—In the reaction of phenyl isocyanate with phenylacetylene in the presence

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of iron pentacarbonyl at 150–160°, 4-benzylidene-1,3-diphenylhydantoin (1a) was obtained in 85% yield. This product seemed to be formed with 2 mol of phenyl isocyanate and 1 mol of phenylacetylene by an addition reaction and hydrogen shift. The structure of 1a was confirmed by ir, nmr, and mass spectra, and furthermore, by oxidation of 1a which gave diphenyl-parabanic acid (2) and benzoic acid.
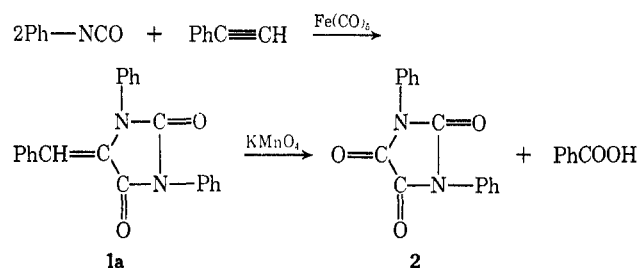
The ir spectrum of 1a in a Nujol mull indicated peaks at 1775, 1725, and 1650 cm^{-1}. The former two peaks were assigned to C=O stretching vibration of –CO–NR–CO– group in a five-membered ring and the latter to a C=C stretching vibration. In the mass spectrum of 1a, the molecular ion was found at m/e 340 (calcd for $C_{22}H_{16}N_2O_2$: 340), and the major fragment was found at 193 which corresponded to PhCH=C=NPh resulting from 1a by losing the –CO–NR–CO– group (calcd for $C_{14}H_{11}N$: 193). The pattern of fragmentation well explained the structure of 1a.

The hydantoin 1a had been prepared through different processes,[6-8] and fair agreements between the observed and reported values were obtained by melting point and ir, nmr, and mass spectra.

The hydrogen transfer of the acetylenic hydrogen of phenylacetylene was identified by the following results. The reaction using phenylacetylene-1-d in place of phenylacetylene gave 4-(benzylidene-α-d)-1,3-diphenylhydantoin (1'a) in 60% yield. The melting point of 1'a was identical with that of hydantoin 1a, 200°; the mixture melting point of the hydantoin 1a and 1'a was not depressed. The ir spectrum of the hydantoin 1'a was identical with that of hydantoin 1a