

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Reactions of Atoms and Free Radicals in Solution. XXIII. The Peroxide-Induced Addition of Sulfuryl Chloride to 1-Alkenes

BY M. S. KHARASCH AND A. F. ZAVIST¹

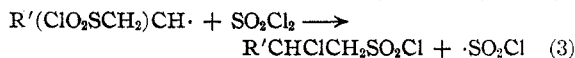
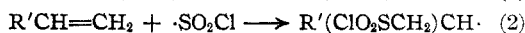
Under properly controlled experimental conditions 1-hexene, 1-heptene, 1-octene and 1-decene undergo peroxide-induced reaction with sulfuryl chloride to yield (in addition to the corresponding 1,2-dichloroalkanes) the corresponding β -chloro-*n*-alkyl sulfones, $(R'CHClCH_2)_2SO_2$. A reaction scheme to account for the products identified is proposed.

Under suitable experimental conditions 1-octene reacts with sulfuryl chloride at room temperature to form a mixture of 1,2-dichlorooctane and a product which is probably 1-chloro-2-octyl chlorosulfite.

The present study supplies cogent evidence of the existence of free chlorosulfonyl ($\cdot SO_2Cl$) radicals and of their ability to react additively with olefin molecules with the formation of carbon-to-sulfur bonds.

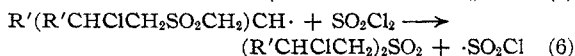
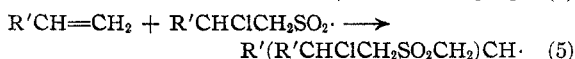
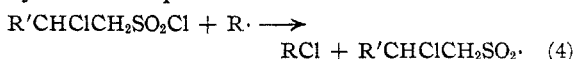
Incidentally to the identification of the addition products described, *n*-hexyl sulfone, *n*-decyl sulfide and *n*-decyl sulfone, of which the authors have located no previous description, have been prepared.

It has previously been shown in this Laboratory that under certain conditions the peroxide-induced reaction of sulfuryl chloride with an olefinic compound results in the addition of chlorine to the olefinic double bond.² The reaction scheme proposed to account for this addition suggested the possibility of effecting, under suitably modified conditions, addition of the elements of sulfuryl chloride to the olefinic double bond.

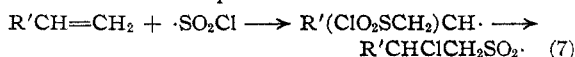


Exploratory experiments with sulfuryl chloride and 1-octene, in which the chloride was present in high dilution, and in which an attempt was made to suppress decomposition of the chlorosulfonyl ($\cdot SO_2Cl$) radical by introducing sulfur dioxide into the reaction system, resulted in the formation of a product comprising two molecules of octene and one molecule of sulfuryl chloride. The analysis of this product and some of its chemical properties were consistent with its characterization as a chlorinated sulfonyl chloride, and it was tentatively so designated in a preliminary report.³ More thorough study has now revealed, however, that this product is in fact the symmetrical β -chloro-*n*-octyl sulfone, $(n-C_6H_{13}CHClCH_2)_2SO_2$.

It may be argued that the expected addition product is in fact formed, but then reacts further by some such process as



However, it also seems possible that the intermediate free radical formed by the addition of the chlorosulfonyl radical to the olefin rearranges to form a new free radical which reacts readily with more of the olefin present in excess.



The postulated rearranged free radical would be identical with that which might be expected to

arise from the attack of a free radical of peroxidic origin on the hypothetical chlorinated sulfonyl chloride, and reaction might continue as suggested in equations 5 and 6.

An attempt to estimate the relative probabilities of the two possible reaction courses here suggested was made by repeating the experiment described with 1-octene and an equimolecular mixture of sulfuryl chloride and ethanesulfonyl chloride. No unsymmetrical sulfones were detected in the reaction mixture; the principal products were 1,2-dichlorooctane and the symmetrical β -chloro-*n*-octyl sulfone; the ethanesulfonyl chloride was recovered nearly quantitatively. Total substitution of ethanesulfonyl chloride for sulfuryl chloride led to no appreciable reaction whatever; the major reactants were recovered unchanged. At the present writing, therefore, it would appear that the second of the two possible reaction schemes suggested is the more probable.

Experiments with 1-octene designed to discover approximately optimum conditions for the addition reaction are summarized in Table II. Under the conditions adopted (described in detail in the experimental part), 1-hexene, 1-heptene, 1-octene and 1-decene all yielded, in addition to the corresponding 1,2-dichloroalkanes, the corresponding β -chloro-*n*-alkyl sulfones, $(R'CHClCH_2)_2SO_2$. For convenient reference and comparison results are summarized in Table I. Yields are calculated on the basis of sulfuryl chloride used.

TABLE I
PRODUCTS OF PEROXIDE-INDUCED REACTIONS OF SULFURYL CHLORIDE WITH 1-ALKENES

Alkene	Amt. SO_2Cl_2 , g.	Yield of product, g. (%)	
		Dichloroalkane	Sulfone
1-Hexene	35.0	31.7 (78.9)	10.4 (13.2)
1-Heptene	32.7	20.3 (49.4)	16.8 (21.0)
1-Octene	75.8	52.4 (51.0)	57.5 (28.4)
1-Decene	33.4	35.9 (68.6)	15.7 (15.2)

Although benzoyl peroxide was used in all the preparations described, supplementary experiments with 1-octene (Table II) showed that the reaction is so peroxide-sensitive that even freshly distilled olefin reacts spontaneously with sulfuryl chloride at 60–65° to yield some of the sulfone. Only when an antiperoxidic inhibitor (*p*-*t*-butylcatechol) was added to the reaction system did the yield of sulfone become negligible ($\approx 1\%$). Such extreme peroxide-sensitivity in an atomic or free-radical chain-

(1) Standard Oil Co. (Indiana) Fellow, 1948–1949.

(2) Kharasch and Brown, *THIS JOURNAL*, **61**, 3432 (1939).

(3) Kharasch and Zavist, *ibid.*, **70**, 3526 (1948).

TABLE II
 REACTION OF SULFURYL CHLORIDE WITH 1-OCTENE UNDER VARIOUS EXPERIMENTAL CONDITIONS

Expt. no.	Activator or inhibitor	Admitted gas	Temp., °C.	Amt. SO ₂ Cl ₂ , g.	Yield dichloroalkane, g. (%)	Yield sulfone, g. (%)
1	Bz ₂ O ₂	None	60	25.0	20.9 (61.4)	10.5 (15.8)
2	Bz ₂ O ₂	N ₂	60	32.0	27.2 (62.6)	1.4 (1.7)
3	Bz ₂ O ₂	SO ₂	60	24.0	13.6 (41.7)	11.5 (18.0)
4	Bz ₂ O ₂	SO ₂	50	17.0	10.7 (44.4)	0.3 (0.7)
5	Bz ₂ O ₂	SO ₂	70	33.8	26.2 (57.2)	7.0 (7.8)
6	Bz ₂ O ₂	SO ₂	80	33.8	25.4 (55.5)	None
7	None	None	60	35.0	18.1 (38.0)	14.2 (15.2)
8	<i>p</i> - <i>t</i> -Butylcatechol	None	60	28.2	6.4 (16.7)	0.8 (1.1)
9	Bz ₂ O ₂	SO ₂	60	75.8	52.4 (51.0)	57.5 (28.4)

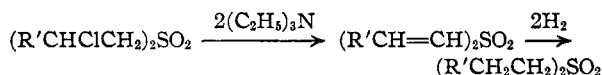
In experiments 1-8, inclusive, undiluted sulfonyl chloride was added slowly to a threefold excess of 1-octene. In experiment 9 the sulfonyl chloride, dissolved in a twofold excess of 1-octene, was added slowly to approximately one equivalent of the olefin. Experiments 7 and 8 were conducted in the dark under an atmosphere of nitrogen; both sulfonyl chloride and 1-octene were freshly distilled under nitrogen, the latter from sodium.

reaction system is by no means unique. For instance it has been found that even the minute traces of peroxides introduced into a reaction system by rinsing the reaction vessels with stock acetone are sufficient to induce the sulfonyl chloride side-chain chlorination of *m*-xylene.⁴

Proof of Structure of Products

The analysis of the 1-octene addition product was consistent with the empirical formulation C₁₈H₃₂Cl₂O₂S. The apparent molecular weight as determined cryoscopically in benzene was 365, and the neutralization equivalent upon titration with standard sodium hydroxide solution was 180. Dehydrohalogenation of the compound with alcoholic alkali proved unsatisfactory because of partial chlorine-ethoxy exchange. Dehydrohalogenation with triethylamine yielded the theoretical amount of amine hydrochloride corresponding to removal of two molecules of hydrogen chloride, and the analysis of the resultant unsaturated compound was consistent with the empirical formulation C₁₆H₃₀O₂S. Ozonolysis of the unsaturated compound yielded no aldehyde—a result in accord with the experience of Rothstein,⁵ who was unable to recover any aldehyde from the ozonolysis of an α,β -unsaturated sulfone (C₆H₅CH₂SO₂CH=CHCH₃).

The method ultimately adopted for the identification of this and the other 1-alkene addition products consisted in dehydrohalogenation of the compound, hydrogenation of the resultant unsaturated compound, and comparison of the *n*-alkyl sulfone so obtained (by means of melting points and mixture melting points) with a specimen of sulfone prepared by an independent method which left no doubt of structure. Details of the



procedure and relevant data are set forth in the experimental part.

Low Temperature Reaction of 1-Octene with Sulfonyl Chloride

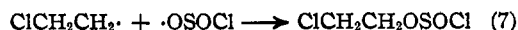
Yakubovich and Zinov'ev⁶ have recently reported that the passage of ethylene into liquid

(4) Kharasch and Brown, *THIS JOURNAL*, **61**, 2142 (1939).

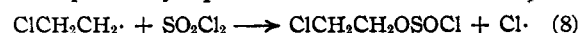
(5) Rothstein, *J. Chem. Soc.*, 687 (1934).

(6) Yakubovich and Zinov'ev, *J. Gen. Chem. (U. S. S. R.)*, **17**, 2028 (1947).

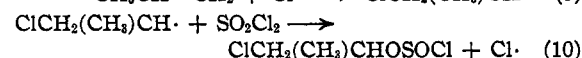
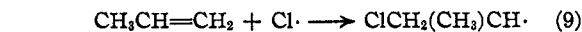
sulfonyl chloride containing a little sulfur chloride at 20° results in a 73% yield of ethylene chloride, together with a 15% yield of β -chloroethyl chlorosulfite. They assume, no doubt correctly, that the addition reaction is initiated by the combination of a chlorine atom with an ethylene molecule, but then proceed to postulate that the chlorosulfite is formed by the combination of a β -chloroethyl radical with a free chlorosulfite radical.



They envision the chlorosulfite (or chlorosulfonyl) radical as a resonance hybrid to which the form $\cdot OSOCl$ makes the principal contribution. In view of the overwhelming improbability that two species of relatively reactive free radicals could survive long enough in the reaction system described to encounter each other in appreciable quantities, it seems more logical to regard the product isolated as evidence that the β -chloroethyl radical (and, by inference, other alkyl radicals) may react with sulfonyl chloride in the manner indicated in equation 8, as well as in the manner exemplified by equations 3 and 6.

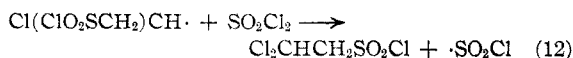


If chlorosulfite formation were indeed a reaction involving chlorine atoms and chlorosulfonyl (or chlorosulfite) radicals, there would, perhaps, be little *a priori* reason to assume that initiation of the addition occurs by combination of an olefin molecule with a chlorine atom rather than with a chlorosulfite radical. However, similar experiments were performed with propylene, and here the constitution of the chlorosulfite clearly indicates the manner in which the addition is initiated.

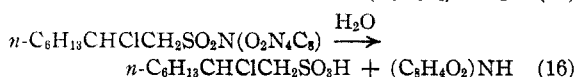
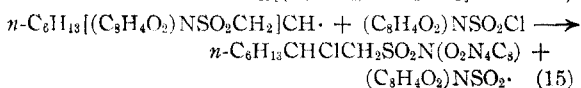
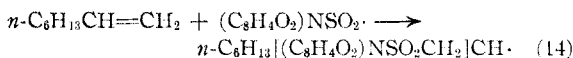
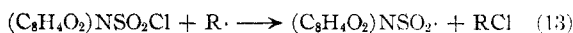


In slightly modified but similar experiments with vinyl chloride (an olefin rather resistant to chlorine attack) the Russian investigators isolated 65% of 1,1,2-trichloroethane and 8% of β,β -dichloroethanesulfonyl chloride. The constitution of this product indicates unmistakably that the addition reaction by which it is formed is initiated by the combination of the olefin with a chlorosulfonyl radical.



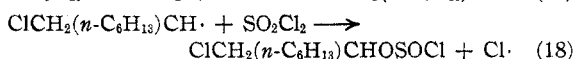
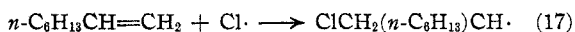


Further evidence, if any be needed, that radicals of the sulfonyl type do indeed react with olefins, forming carbon-to-sulfur, rather than carbon-to-oxygen, bonds is supplied by the peroxide-induced reaction of *N*-phthalimidosulfonyl chloride with 1-octene.⁷



The work of Yakubovich and Zinov'ev suggested the probability that 1-octene might react with sulfonyl chloride at low temperature to form a chlorosulfite. Accordingly, excess 1-octene was added dropwise, over a period of several hours, to sulfonyl chloride containing a trace of sulfur monochloride, while the reaction system was maintained by external cooling at a temperature of 15–25°. 1,2-Dichlorooctane was readily separated from the reaction mixture, but attempts to purify a residual oil containing sulfur and chlorine by subjecting it to "molecular" distillation (50–100°) resulted in its thermal decomposition. Treatment of another sample of this product with glacial acetic acid yielded a mixture of 1,2-dichlorooctane and a compound which is probably 1-chloro-2-octyl acetate.

The 1,2-dichlorooctane could be formed by direct attack on sulfonyl chloride by the free radical formed in reaction (17) or in part by decomposition at higher temperatures of the compound formed in reaction (18). The isolation of the compound indicated in (18) should therefore be possible by working at lower temperatures.



Experiments confirmed this prediction. At this time, it is, therefore, impossible to assess the relative importance of the two possible mechanisms insofar as formation of the 1,2-dichlorooctane is concerned.

Experimental⁸

Materials.—1-Heptene, a student preparation, was distilled through a Podbielniak column (b.p. 92.9°, n_D^{20} 1.3994). The other 1-alkenes, obtained from The Connecticut Hard Rubber Company, were also distilled before use: 1-hexene (b.p. 65.0–65.5°, n_D^{20} 1.3888); 1-octene (b.p. 120–121°, n_D^{20} 1.4090); 1-decene (b.p. 93.8° (60 mm.), n_D^{20} 1.4215). Commercial sulfonyl chloride was distilled (b.p. 68°); commercial benzoyl peroxide and tank nitrogen and sulfur dioxide were used without purification.

Exploratory Experiments.—Experiments designed to discover approximately optimum conditions for the addition reaction were carried out in apparatus identical with, and by procedures similar to, those described for the addition

reactions in general (see following section). Results are summarized in Table II.

Apparatus and Procedure.—Benzoyl peroxide, suspended in about one-fourth to one-third the amount of alkene used, was placed in a 500-ml. (or 250-ml.) three-necked round-bottomed flask equipped with a reflux condenser, gas-inlet tube, and capillary dropping funnel. The mixture was heated to, and maintained at, a temperature of 60–65°, a slow stream of sulfur dioxide was admitted, and sulfonyl chloride, dissolved in the remainder of the alkene, was gradually introduced through the dropping funnel over a period of 5 to 6 hours. Heating was continued for an hour after completion of the addition. Unchanged reactants and sulfur dioxide were then distilled from the reaction mixture under reduced pressure.

1-Hexene and Sulfonyl Chloride.—Benzoyl peroxide (0.2 g., 0.0009 mole), in 17.0 g. (0.20 mole) of 1-hexene, and sulfonyl chloride (35.0 g., 0.26 mole), in 72.0 g. (0.86 mole) of 1-hexene, were combined as described.

Distillation of the reaction product at 59–65° (14 mm.) yielded 31.7 g. (78.9%) of 1,2-dichlorohexane (n_D^{20} 1.4500).

Anal. Calcd. for $\text{C}_6\text{H}_{12}\text{Cl}_2$: Cl, 45.7. Found: Cl, 45.2.

Sublimation of the residue at 90–110° (10^{–5} mm.) yielded a white solid [crude β -chloro-*n*-hexyl sulfone ($n\text{-C}_6\text{H}_{13}\text{CHClCH}_2\text{SO}_2$)] which melted at 41–42° after crystallization from ethanol (10.4 g., 13.2%).

Anal. Calcd. for $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{O}_2\text{S}$: Cl, 23.4; S, 10.6; mol. wt., 303; neut. equiv., 151.6. Found: Cl, 23.4; S, 10.5; mol. wt., 333; neut. equiv., 152.2.

1-Heptene and Sulfonyl Chloride.—Benzoyl peroxide (0.2 g., 0.0009 mole), in 20.0 g. (0.20 mole) of 1-heptene, and sulfonyl chloride (32.7 g., 0.24 mole), in 70.0 g. (0.71 mole) of 1-heptene, were combined as described.

Distillation of the reaction product at 52–57° (4 mm.) yielded 20.3 g. (49.4%) of 1,2-dichloroheptane (n_D^{20} 1.4503).

Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{Cl}_2$: Cl, 41.9. Found: Cl, 41.3.

Sublimation of the residue at 115–135° (10^{–5} mm.) yielded a white solid [crude β -chloro-*n*-heptyl sulfone ($n\text{-C}_7\text{H}_{15}\text{CHClCH}_2\text{SO}_2$)] which melted at 58–59° after crystallization from aqueous ethanol (16.8 g., 21.0%).

Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{Cl}_2\text{O}_2\text{S}$: Cl, 21.4; S, 9.7. Found: Cl, 21.5; S, 9.8.

1-Octene and Sulfonyl Chloride.—Benzoyl peroxide (0.5 g., 0.0021 mole), in 70.2 g. (0.63 mole) of 1-octene, and sulfonyl chloride (75.8 g., 0.56 mole), in 136.8 g. (1.24 mole) of 1-octene, were combined as described.

Distillation of the reaction product at 67–71° (4 mm.) yielded 52.4 g. (51.0%) of 1,2-dichlorooctane (n_D^{20} 1.4531).

Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{Cl}_2$: Cl, 38.8; mol. wt., 183. Found: Cl, 38.4; mol. wt., 183.

Sublimation of the residue at 110–140° (10^{–5} mm.) yielded a white, oil-contaminated crystalline product [crude β -chloro-*n*-octyl sulfone ($n\text{-C}_8\text{H}_{17}\text{CHClCH}_2\text{SO}_2$)] which melted at 57–58° after two recrystallizations from 95% ethanol (57.5 g., 28.4%).

Anal. Calcd. for $\text{C}_{18}\text{H}_{36}\text{Cl}_2\text{O}_2\text{S}$: Cl, 19.7; S, 8.9; mol. wt., 359; neut. equiv., 180. Found: Cl, 19.6; S, 8.6; mol. wt., 365; neut. equiv., 180.

1-Decene and Sulfonyl Chloride.—Benzoyl peroxide (0.2 g., 0.0009 mole), in 20.0 g. (0.14 mole) of 1-decene, and sulfonyl chloride (33.4 g., 0.25 mole), in 44.2 g. (0.32 mole) of 1-decene were combined as described.

Distillation of the reaction product at 56–59° (0.3 mm.) yielded 35.9 g. (68.6%) of 1,2-dichlorodecane (n_D^{20} 1.4564).

Anal. Calcd. for $\text{C}_{10}\text{H}_{20}\text{Cl}_2$: Cl, 33.6. Found: Cl, 34.0.

Sublimation of the residue and crystallization of the sublimate from ethanol yielded 15.7 g. (15.2%) of white crystals melting at 68–69° [β -chloro-*n*-decyl sulfone ($n\text{-C}_{10}\text{H}_{21}\text{CHClCH}_2\text{SO}_2$)].

Anal. Calcd. for $\text{C}_{20}\text{H}_{40}\text{Cl}_2\text{O}_2\text{S}$: Cl, 17.1; S, 7.7. Found: Cl, 17.2; S, 7.9.

1-Octene and Sulfonyl Chloride with Inhibitor.—In a 250-ml. flask equipped as previously described was placed a solution of 1.5 g. (4.3 mole %) of *p*-*t*-butylcatechol in 79.0 g. (0.71 mole) of 1-octene which had been freshly distilled from sodium in an atmosphere of nitrogen. Light was excluded from the apparatus by black paint and opaque wrap-

(7) Kharasch and Mosher, unpublished work.

(8) All reported yields of addition products are based upon the amount of sulfonyl chloride used.

ping. Air was displaced by a stream of nitrogen, which was then discontinued. While the reaction flask was maintained at a temperature of 60–65°, 28.2 g. (0.21 mole) of sulfonyl chloride (freshly distilled in a nitrogen atmosphere) was added dropwise over a period of 4.5 hours. Distillation of the reaction product yielded 6.4 g. (16.7%) of 1,2-dichlorooctane. The relatively non-volatile residue weighed 2.3 g. Assuming that there was no appreciable loss of *p*-*t*-butylcatechol, the maximum yield of sulfone could not exceed 0.8 g. (1.1%).

Other Olefinic Compounds and Sulfonyl Chloride.—Attempts were made to extend the addition reaction as described for the simple 1-alkenes to allyl chloride, 1,3-dichloropropene, α -methallyl chloride, 2-ethyl-1-hexene and 2,4,4-trimethyl-1-pentene. In all cases attempts to dilute sulfonyl chloride with freshly distilled olefin at room temperature led to spontaneous, strongly exothermic reaction. Gradual addition of undiluted sulfonyl chloride to the respective olefins led to good yields of the respective chlorine-addition products (dichloro derivatives). Except in the case of allyl chloride, from which considerable "polymeric" material was formed, these were the only isolable products.

Identification of 1-Hexene Addition Product [β -Chloro-*n*-hexyl Sulfone, (*n*-C₆H₁₃CHClCH₂)₂SO₂].—In the manner described for the corresponding 1-octene product, a sample of the sublimate from the 1-hexene reaction mixture was dehydrohalogenated with the aid of an excess of triethylamine. The pale-yellow oil (*n*_D²⁰ 1.4863) thus obtained was hydrogenated as described for the corresponding 1-octene derivative. The melting point (73–74°) of the resultant white solid was not depressed upon admixture of the material with a sample of *n*-hexyl sulfone prepared as hereinafter described.

Anal. Calcd. for C₁₂H₂₆O₂S: S, 13.7. Found: S, 13.8.

Identification of 1-Heptene Addition Product [β -Chloro-*n*-heptyl Sulfone, (*n*-C₇H₁₅CHClCH₂)₂SO₂].—In the manner described for the corresponding 1-octene product, a sample of the sublimate from the 1-heptene reaction mixture was dehydrohalogenated with the aid of an excess of triethylamine. The colorless oil (*n*_D²⁰ 1.4802) thus obtained was hydrogenated as described for the corresponding 1-octene derivative. The melting point (80–81°) of the resultant white solid was not depressed upon admixture of the material with a sample of *n*-heptyl sulfone prepared as hereinafter described.

Identification of 1-Octene Addition Product [β -Chloro-*n*-octyl Sulfone, (*n*-C₈H₁₇CHClCH₂)₂SO₂].—A 10-g. sample of the sublimate from the 1-octene reaction mixture in 100 ml. of dry benzene was combined with 11.2 g. of triethylamine, and the mixture was allowed to stand for 48 hours at room temperature. Precipitated triethylamine hydrochloride was removed by filtration (yield 7.7 g. 100%; m.p. 253–254°). Benzene was removed from the filtrate under reduced pressure, and the residue was submitted to molecular distillation (130–150° (10⁻⁵ mm.)), yielding 6.0 g. (75%) of colorless oil, *n*_D²⁰ 1.4794 [1-octenyl sulfone, (*n*-C₈H₁₇CH=CH)₂SO₂].

Anal. Calcd. for C₁₈H₃₈O₂S: S, 11.2; mol. wt., 287. Found: S, 11.6; mol. wt., 294.

A 2-g. sample of the dehydrohalogenation product in 150 ml. of absolute ethanol was maintained under a pressure of 2–3 atmospheres of hydrogen in the presence of Raney nickel catalyst for 18 hours. The white crystals obtained upon evaporation of the ethanol and crystallization of the residue from 60° ligroin had a melting point of 78–79°, which was not depressed upon admixture of the material with a sample of *n*-octyl sulfone prepared as hereinafter described.

Anal. Calcd. for C₁₈H₃₄O₂S: C, 66.2; H, 11.8. Found: C, 66.3; H, 11.7.

Identification of the 1-Decene Addition Product [β -Chloro-*n*-decyl Sulfone, (*n*-C₁₀H₂₁CHClCH₂)₂SO₂].—In the manner described for the corresponding 1-octene product, a sample of the sublimate from the 1-decene reaction mixture was dehydrohalogenated with the aid of an excess of triethylamine. The pale-yellow oil (*n*_D²⁰ 1.4789) thus obtained was hydrogenated as described for the corresponding 1-octene derivative. The melting point (88–89°) of the

resultant white solid was not depressed upon admixture of the material with a sample of *n*-decyl sulfone prepared as hereinafter described.

Room-temperature Reaction of 1-Octene with Sulfonyl Chloride.—To 39.5 g. (0.29 mole) of sulfonyl chloride and 0.5 g. of sulfur monochloride, maintained by external cooling at a temperature of 15–25°, 49.3 g. (0.44 mole) of 1-octene was added dropwise over a period of 3 hours. Unchanged reactants were removed under reduced pressure (25–35° (5 mm.)). Acetic acid (100 g.) was added to the remaining mixture, and the combination was refluxed for 5 hours. Unchanged acetic acid was removed under reduced pressure, and the residue was separated by distillation into three fractions: (1) b.p. 33–40° (0.3 mm.), *n*_D²⁰ 1.4516, 32.3 g.; (2) b.p. 40–42° (0.3 mm.), *n*_D²⁰ 1.4452; 7.2 g. (estimated as including acetate equivalent to at least a 7% yield of chlorosulfite); (3) tar, 2.0 g. Fraction 2 was repeatedly refractionated until a 1.0-g. sample with a boiling point of 41° (0.3 mm.) and a refractive index of *n*_D²⁰ 1.4419 was obtained.

Anal. Calcd. for C₈H₁₆Cl₂ (A): C, 52.5; H, 8.8; Cl, 38.8; sapon. equiv., 91.5. *Anal.* Calcd. for C₁₀H₁₈O₂Cl (B): C, 58.1; H, 9.3; Cl, 17.2; sapon. equiv., 103.3. *Anal.* Calcd. for 16% A + 84% B: C, 57.2; H, 9.2; Cl, 20.6; sapon. equiv., 123.

Found: C, 56.9; H, 9.2; Cl, 20.5; S, 0.0; sapon. equiv., 118.

Incidental Preparations. (1) *n*-Alkyl Sulfides.—A simplified version of the sulfide preparation method of Fenton and Ingold⁹ was employed. Slightly less than half of a solution of 12.0 g. of potassium hydroxide in 300 ml. of ethanol was saturated with hydrogen sulfide and then added to the remainder of the solution. After the further addition of ca. 0.1 mole of *n*-alkyl bromide the reaction mixture was allowed to stand at room temperature for 2 days. Potassium bromide was removed by filtration, and most of the ethanol was expelled by steam-bath evaporation. Water was added to the residue, and the aqueous mixture was extracted with ethyl ether. After dehydration of the ethereal extract with anhydrous sodium sulfate, ether was removed under reduced pressure. The crude product remaining was distilled. Data are recorded in Table III.

TABLE III
INCIDENTAL PREPARATIONS

Preparation	Phys. const.	Analyses, S, %		Yield, %, on basis of	
		Calcd.	Found	RBr	R ₂ S
<i>n</i> -Hexyl sulfide	B.p. 73–74° (0.3 mm.)	66.3	..
<i>n</i> -Heptyl sulfide	46.1	..
<i>n</i> -Octyl sulfide	B.p. 172° (7.0 mm.)	55.3	..
<i>n</i> -Decyl sulfide	M.p. 27.0–27.5°	10.5	10.5	74.0	..
<i>n</i> -Hexyl sulfone	M.p. 73–74°	13.7	13.5	60.5	91.5
<i>n</i> -Heptyl sulfone	M.p. 80–81° ^a	39.3	85.2
<i>n</i> -Octyl sulfone	M.p. 78–79° ^b	11.0	11.2
<i>n</i> -Decyl sulfone	M.p. 88–89°	9.1	9.1	59.2	80.0

^a Winssinger, *Jahresbericht*, 1281 (1887), reports a melting point of 80° for this compound. ^b Fenton and Ingold⁹ report a melting point of 76° for this compound.

(2) *n*-Alkyl Sulfones.—A procedure based upon the sulfide-oxidation method of Fuson, *et al.*,¹⁰ was employed. To a stirred solution of 0.035 mole of *n*-alkyl sulfide in 100 ml. of glacial acetic acid 5 ml. of 30% hydrogen peroxide was added dropwise. After the initial heating had subsided, further addition of 10 ml. of 30% hydrogen peroxide was made, the reaction mixture was warmed at 60° for an hour and a half and was then allowed to stand overnight at room temperature. The initial crop of crystalline product was collected by filtration; dilution of the filtrate with water induced the separation of a second crop of crystals. Data are recorded in Table III.

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(9) Fenton and Ingold, *J. Chem. Soc.*, 3130 (1928).

(10) Fuson, Price and Burnes, *J. Org. Chem.*, 11, 478 (1946).