Pmr Analysis of Crude Mixture From Acrylamide Reaction.—The reaction was run in the usual manner using 3.55 g (0.050 mol) of acrylamide, 6.81 g (0.108 mol) of ammonium formate, 10.5 ml of acetic acid, and 1.12 ml (0.0250 mol) of sulfur dioxide. The pmr spectrum (in CF_3COOH) showed signals due to acrylamide (m, δ 6.2 and 6.5), the sulfone (t, δ 3.1 and 3.7), and propionamide (s, $J = 7.5$ Hz, δ 1.3). The area ratio was about 6:6:1, respectively. No mercaptan was detected, though it could have been obscured by the methyl signal (s, δ 2.2) of acetic acid.

Registry No.—2a, 13063-92-8; 2b, 6291-88-9; 2c,

3234-31-9; 2d, 5450-67-9; 3a, 1002-19-3; 3b, 1119-62-6; 3c, 15441-06-2; 3d, 25055-41-8.

# Sulfonium Salts. IV. Cleavage–α-Substitution Competition of Dibenzylhalosulfonium Salts

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Benzyl sulfide reacts with chlorine, bromine, NCS, and NBS to provide α-halobenzyl benzyl sulfide, benzyl halide, benzylsulfenyl halide, and, where possible, N-benzylsulfenylsuccinimide. The competitive isotope effects, measured in deuteriochloroform and carbon tetrachloride, are consistent with an E2-type elimination from an initially formed halosulfonium salt. The variation of the ratio of cleavage to α-halogenated products is consistent with a rate-determining step involving halide ion attack on a single intermediate when initial concentrations of halogen and sulfide are low, but involving decomposition of aggregates when initial concentrations above about 0.3 M are used.

Bromination and chlorination of sulfides bearing an α proton at low temperatures in nonpolar aprotic solvents often leads to the formation of metastable adducts[2] (I) which usually decompose upon warming to give α-halo sulfides[3] (III) (Scheme I). Reactions of

SCHEME I
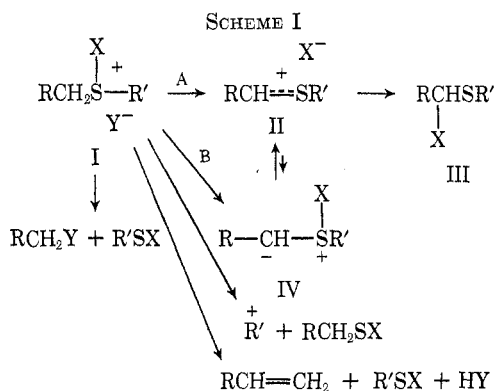
sulfides with chlorine,[3-5] sulfuryl chloride,[5-7] and N-halosuccinimides[8] to produce α-halo sulfides are all considered to proceed through adduct I, generally considered to be a halosulfonium salt.

The largest contributor to the structure of the sulfide–bromine adduct would seem to be ionic on the basis of X-ray,[9] nmr,[9] and conductometric[2d] data. Contributions to the time-averaged structure in solution by the trigonal bipyramidal dihalosulfurane V in analogy with the crystal structure of the adduct of chlorine with bis(p-chlorophenyl) sulfide[10] or the charge transfer type structure[11] VI are not excluded by available data. In fact, the X-ray data[9] is compatible with a much distorted charge transfer structure.

In lieu of reorganizing to α-halo sulfides and HX, possibly by way of ylide IV and sulfocarbonium ion II, halosulfonium salts can undergo carbon–sulfur bond rupture to provide sulfenyl halides and alkyl halides directly either by displacement on carbon[12] or by way of stable carbonium ions.[13] Reactions involving carbon–sulfur fragmentations of halosulfonium salts have also been observed.[14]

Results

The reactions of benzyl sulfide with several halogenating agents such as N-chlorosuccinimide (NCS),

(1) Submitted by M. G. Huang in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(2) (a) F. Runge, E. Profft and R. Drux, *J. Prakt. Chem.*, **2**, 279, (1955); (b) P. Haas, *Biochem. J.*, **29**, 1297 (1935); (c) A. H. Fenselau and J. G. Moffatt, *J. Amer. Chem. Soc.*, **88**, 1762 (1966); (d) H. Böhme and E. Boll, *Z. Anorg. Allg. Chem.*, **290**, 17 (1957).

(3) H. Böhme, H. Fischer and R. Frank, *Justus Liebigs Ann. Chem.*, **563**, 54 (1949).

(4) (a) W. E. Lawson and T. P. Dawson, *J. Amer. Chem. Soc.*, **49**, 3119 (1927); (b) H. Böhme and H. Gran, *Justus Liebigs Ann. Chem.*, **581**, 133 (1953); H. Richtzenhain and B. Alfredsson, *Chem. Ber.*, **86**, 142 (1953).

(5) F. G. Bordwell and B. M. Pitt, *J. Amer. Chem. Soc.*, **77**, 572 (1955).

(6) W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74** 3594 (1952).

(7) L. A. Paquette, *ibid.*, **86**, 4085 (1964).

(8) (a) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969); (b) D. L. Tuleen and V. C. Marcum, *ibid.*, **32**, 204 (1967); (c) D. L. Tuleen, *ibid.*, **32**, 4006 (1967); (d) W. Groebel, *Chem. Ber.*, **92**, 2887 (1959).

(9) G. Allegra, G. E. Wilson, Jr., E. Benedetti, C. Pedone, and R. Albert, *J. Amer. Chem. Soc.*, **92**, 4002 (1970).

(10) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, **91**, 5749 (1969).

(11) C. Rømming, *Quart. Rev. (London)*, **16**, 1 (1962).

(12) J. M. Stewart and H. P. Cordts, *J. Amer. Chem. Soc.*, **74**, 5880 (1952); J. M. Stewart and C. H. Burnside, *ibid*, **75**, 243 (1953); D. S. Tarbell and D. P. Harnish, *Chem. Rev.*, **49**, 1 (1951).

(13) H. Kwart and R. K. Miller, *J. Amer. Chem. Soc.*, **78**, 5008 (1956); H. Kwart and L. J. Miller, *ibid.*, **80**, 884 (1958); H. Kwart and R. W. Body, *J. Org. Chem.*, **30**, 1188 (1965); H. Kwart, R. W. Body, and D. M. Hoffman, *Chem. Commun.*, 765 (1967); H. Kwart and P. S. Strilko, *ibid.*, 767 (1967).

(14) G. E. Wilson, Jr. *J. Amer. Chem. Soc.*, **87** 3785 (1965).

N-bromosuccinimide (NBS), chlorine, and bromine were conducted in carbon tetrachloride and in deuteriochloroform at 35°. All went to completion within 30 min, but it was not possible in all cases to obtain systems which were completely homogeneous throughout the course of the reactions. For the bromine and chlorine reactions, the rate of addition of halogen was maintained such that precipitation of the halosulfonium salt was held to a minimum. Product assignments were confirmed by enhancement of the appropriate peaks in the nmr spectra using authentic samples (Table I). Solid benzylsulfenylsuccinimide was removed by filtration from the NCS and NBS halogenations of benzyl sulfide in carbon tetrachloride, before nmr analyses were performed.

TABLE I

CHEMICAL SHIFTS OF COMPONENTS IN THE REACTIONS
OF BENZYL SULFIDE WITH HALOGENATING AGENTS

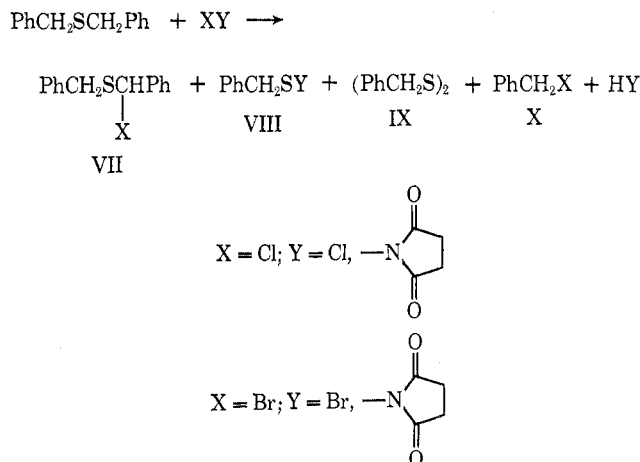| Compound	Protons	δ (CCl$_4$), Hz	δ (CDCl$_3$), Hz
Hexamethylbenzene		130.0	134.0
PhCH$_2$SCH$_2$Ph		208.0	213.0
PhCH$_2$Cl		265.5	268.5
PhCH$_2$Br		264.5	269.5
PhCH$_2$SCl		255.5	
PhCH$_2$SBr		253.5	241.0
PhCHClSCH$_2$Ph	CH$_2$	d, 228.85; d, 240.15	s, 268.5
	CH	343.5	350.0
PhCHBrSCH$_2$Ph	CH$_2$	s, 237.0	s, 240.5
	CH	344.5	353.5
(PhCH$_2$S)$_2$		210.0	215.0
PhCH$_2$SCD$_2$Ph		208.0	213.0
N-Benzylsuccinimide	CH$_2$Ph		275.5
N-Benzylsulfenyl-succinimide	CH$_2$Ph		245.5

NCS and NBS halogenation of benzyl sulfide in carbon tetrachloride gave one major product, α-halobenzyl benzyl sulfide (VII), together with the cleavage products benzyl halide (X), benzylsulfenyl halide (VIII), benzyl disulfide (IX), and solid benzylsulfenylsuccinimide (VIII) (Scheme II). That benzylsuccinimide was not formed could be seen when the reaction was conducted in deuteriochloroform in which solvent all the products remained in solution. Bromination of benzyl sulfide in carbon tetrachloride gave initially a solid yellow adduct which disappeared in 1 to 2 min. The reaction products after 30 min showed one major product, α-bromobenzyl benzyl sulfide, and the cleavage products benzyl bromide, benzylsulfenyl bromide, and benzyl disulfide.

Attempts to isolate the α-halobenzyl benzyl sulfides by distillation resulted in rapid decomposition into benzyl halide and other unidentified materials. Failure to isolate these compounds has been reported in several other cases.[4b,7a,b,15] Chlorination of benzyl sulfide gave solely α-chlorobenzyl benzyl sulfide and α,α-dichlorobenzyl benzyl sulfide. Incorporation of chlorine at the α position was established by oxidation of the sulfide to the corresponding sulfone, the nmr of which showed signals at δ 7.39 (s, 5 H), 5.92 (s, 1 H), and 4.40 (q, J = 14.0 Hz, 2 H) ppm. Polyhalogenation at one carbon atom has been observed as general behavior.[4b,6,16]

(15) K. C. Schreiber and V. P. Fernandez, *J. Org. Chem.* **26**, 2478 (1961).
(16) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4089 (1964).

SCHEME II

PhCH$_2$SCH$_2$Ph + XY ⟶

PhCH$_2$SCHPh + PhCH$_2$SY + (PhCH$_2$S)$_2$ + PhCH$_2$X + HY
    |
    X   VIII   IX   X
VII

$X = Cl; Y = Cl$, —N(succinimide)

$X = Br; Y = Br$, —N(succinimide)

The crystalline bromine adduct of benzyl sulfide was isolated at low temperature. This adduct decomposed slowly at room temperature in the solid state to cleavage and α-substitution products. Prolonged storage at 0° also led to decomposition products. The product distributions for halogenations are given in Table II. In general the per cent cleavage increased slightly with increased solvent polarity, but there was no strong trend. NCS chlorination of benzyl sulfide in carbon tetrachloride provided the best conditions for forming the mono-α-substituted product, and bromination with bromine gave the best yield of cleaved products.

TABLE II

DISTRIBUTION OF HALOGENATION PRODUCTS IN CARBON
TETRACHLORIDE AND IN DEUTERIOCHLOROFORM SOLUTION

	Carbon tetrachloride[a]		Chloroform-d_1[a]	
	% α substitution	% cleavage	% α substitution	% cleavage
Cl$_2$	86[b]	0	c	c
Br$_2$	34.7	64.8	41.5	57.8
NCS	87.2	2.62	77.7	21.6
NBS	60.3	30.4	22.5	77.2

[a] 0.208 M benzyl sulfide at 35° for 30 min. [b] Includes 25% yield of α,α-dichlorobenzyl benzyl sulfide. [c] Quantitative assay was not possible because the internal standard was also chlorinated.

Benzyl sulfide-α-α-d_2 for isotope effect studies was synthesized by a three-step route. Lithium aluminum deuteride reduction of ethyl benzoate and treatment of the product alcohol with thionyl chloride was followed by reaction of the deuterated benzyl chloride with benzyl mercaptide ion to give the desired product. The ir spectrum of this compound shows C–D stretching at 2140 cm^{-1}, and the nmr shows two singlets at δ 3.47 and 7.16 ppm in the ratio of 2:10. From the molecular ions the isotopic composition corrected for ^{13}C, ^{2}H, ^{33}S, and ^{34}S, were calculated to be 0.30% d_0, 1.79 d_1, and 97.9% d_2.

Benzyl sulfide-α,α-d_2 was halogenated at 35° for 30 min in both carbon tetrachloride and deuteriochloroform thus providing α-halobenzyl benzyl sulfides XI and XII. The diastereotopic methylene protons appear as an AB quartet (δ 228.85, 240.15, J = 13.5 Hz) in the case where chlorine is the substituent and as a singlet (δ 237.0 Hz) for the bromine counterpart.
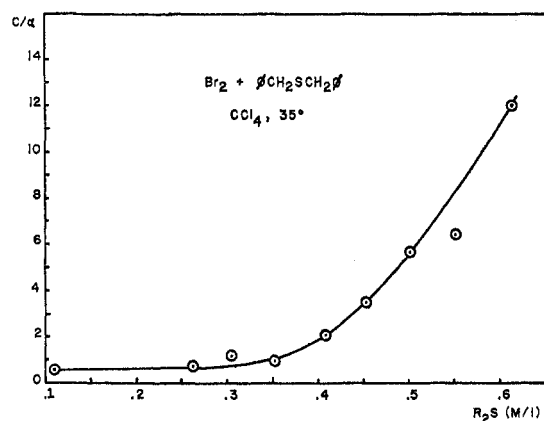
Figure 1.—Concentration dependence of c/α ratio for the halogenation of benzyl sulfide.

PhCHSCD₂Ph   PhCDSCH₂Ph
          | |
          X   X

XI, X = Cl, Br   XII

For calculation of k_H/k_D, an average of at least four integral sweeps of the methylene and methine areas was used. When the nmr signals were too weak to be integrated directly, the reaction mixture was concentrated; the spectra of the concentrated product mixtures showed that no decomposition of the products had taken place. The competitive deuterium isotope effects for halogenation of benzyl sulfide in deuteriochloroform and carbon tetrachloride are shown in Table III.

<div align="center">

TABLE III

KINETIC ISOTOPE EFFECTS IN THE HALOGENATION OF BENZYL
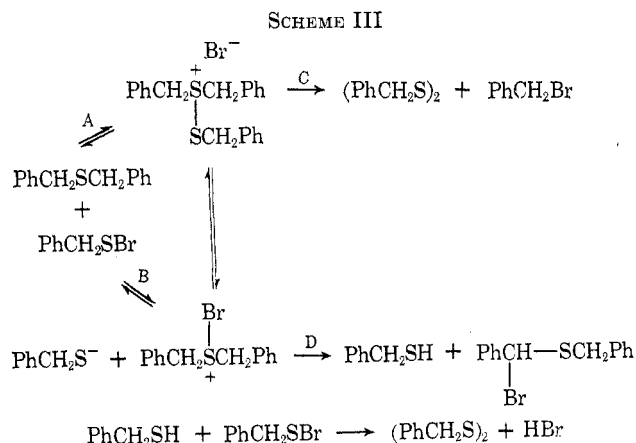SULFIDE AT 35° IN CARBON TETRACHLORIDE AND
DEUTERIOCHLOROFORM

</div>

	CCl₄	CDCl₃
Cl₂	6.55	4.62
Br₂	2.59	2.11
NCS	8.27	5.90
NBS	4.23	3.14

The ratio of cleavage to α-substitution products (c/α) when reaction was complete was examined using equimolar mixtures of bromine and benzyl sulfide over a concentration range of 0.625 to 0.104 M sulfide in carbon tetrachloride. Nmr analysis using hexamethylbenzene as an internal standard was carried out directly on the product mixture after addition of 1 drop of acetone-d_6 to destroy benzylsulfenyl bromide, whose methylene signal interferred with the analysis. The sensitivity of the products to our work-up procedures prevented our obtaining results outside the stated concentration range. Rapid addition of bromide led to instantaneous precipitation of a form of adduct whose rate of dissolution is extremely slow, *ca.* 1 hr for complete disappearance. This could be overcome by addition of bromine over a period of 3–5 min. Slower addition complicates the kinetics as well as the interpretation of the data, but we feel that it is clearly better than the alternative, and that it does not obviate the conclusions. The c/α ratio as a function of initial sulfide concentration is shown in Figure 1.

Discussion

Because both cleavage and Pummerer products are produced in comparable quantities in the halogenation of benzyl sulfide, an opportunity exists in principle to investigate the interrelationship of these two processes. The α-halo sulfide (VII) produced can be rationalized using a generalized Pummerer reaction (Scheme I).[17] Benzyl halide and benzylsulfenyl halide can be considered products of displacement on a halosulfonium salt. Although N-benzylsulfenylsuccinimide could in principle arise through a succinimidylsulfonium salt, we favor the concept of reaction between succinimide and free sulfenyl halide.

The origin of benzyl disulfide, most prominent in the bromination reaction where cleavage is greatest, was not clear. It could arise from direct disproportionation of the displacement product, benzylsulfenyl bromide, or, in one of two ways, from the reaction of the sulfenyl bromide with the sulfide (Scheme III). Although direct disproportionation of benzylsulfenyl bromide cannot definitely be excluded, solutions of this compound were stable with respect to disproportionation for periods longer than the reaction time. Addition of solid benzyl sulfide to a solution of benzylsulfenyl bromide resulted in the formation of α-bromobenzyl benzyl sulfide with only a trace of benzyl bromide. The nmr peaks for the α-bromo sulfide increased in intensity as the reaction proceeded. The absence of benzyl bromide from the products of this reaction excludes the possibility of disulfide formation by way of the thiosulfonium ion intermediate generated from the sulfenyl bromide, pathway C. The alternative, pathway D, explains the data. The halosulfonium salt could, in this case, be generated either directly (pathway B)[18] or by way of the thiosulfonium salt (pathway A).

<div align="center">

SCHEME III

Br⁻
+
PhCH₂ṢCH₂Ph —C→ (PhCH₂S)₂ + PhCH₂Br
      |
A   ṢCH₂Ph

PhCH₂SCH₂Ph
    +
PhCH₂SBr

    B

Br
    |
PhCH₂S⁻ + PhCH₂ṢCH₂Ph —D→ PhCH₂SH + PhCH—SCH₂Ph
              + |
                                             Br

PhCH₂SH + PhCH₂SBr ——→ (PhCH₂S)₂ + HBr

</div>

The absence of N-benzylsuccinimide from the reaction products in NBS and NCS halogenations is significant. We have shown independently that, under the reaction conditions, benzyl bromide and succinimide do not react. It can now be concluded that neither succinimide nor its anion, if formed, is capable of attacking the α-carbon atom of the halosulfonium salt of the sulfocarbonium ion.

(17) G. E. Wilson, Jr., and R. Albert, *Tetrahedron Lett.*, 6271 (1968).

(18) The formation of a bromosulfonium salt by direct displacement by sulfide on benzylsufenyl bromide is in harmony with the suggestion that sulfenyl bromides possess a positive bromine: N. Kharasch, *Org. Sulfur Compounds*, 1, 387 (1961).

Mechanism of Proton Removal.—One theory of the bimolecular elimination mechanism[19] views this process as embracing three types of transition states. All represent concerted processes but differ in the relative extent to which bonds are ruptured. The transition state may resemble a carbonium ion, the olefinic product, or a carbanion. The type of transition state which obtains is determined by the combined demands of substrate, base, and leaving group. As one moves from a central transition state, a decreased k_H/k_D is expected. The magnitudes of the competitive isotope effects (Table III) for halogenation with NCS and chlorine are clearly most compatible with a relatively central E2 elimination to form a sulfocarbonium ion (Scheme I, path A). They are incompatible with an irreversible ElcB mechanism[20] which represents the only alternative. A similar large isotope effect was obtained by Tuleen and Marcum[8] for NCS chlorination of benzyl phenyl sulfide-α-d_1.
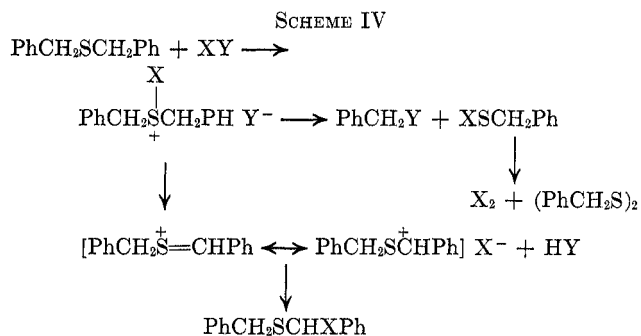
That the methylene protons of chloro sulfide XII are diastereotopically related to each other with a chemical shift between them of 11.3 Hz provides an operational method to examine the possibility of proton exchange at any stage in the reaction. Exchange, if it were to occur to a small extent through an ylide or other route, should provide approximately equal mixtures of two diastereomeric sulfides in which the single methylene protons would lead to a pair of broad singlets located within the quartet of the normal methylene protons of XII. This was rigorously excluded by an experiment in which benzyl sulfide was chlorinated in carbon tetrachloride maintained at saturation with a slow stream of dry deuterium chloride. The nmr of the reaction products at 50-Hz sweep width gave no indication of any deuterium exchange where we estimate that about 5% could have been detected. It is thus clear that exchange does not occur either along the reaction pathway or parallel to it.

The magnitude of k_H/k_D for bromination is somewhat low, but this could be interpreted as arising from a shift to a less synchronous proton removal still lying in the bimolecular region. These results might also be accommodated by an E2S mechanism exactly analogous to the E2C mechanism.[21]

It is interesting that the values of k_H/k_D for the NCS and NBS reactions differ from those with the halogen counterparts. This seems to indicate that the succinimidyl anion is participating to some extent in proton removal.
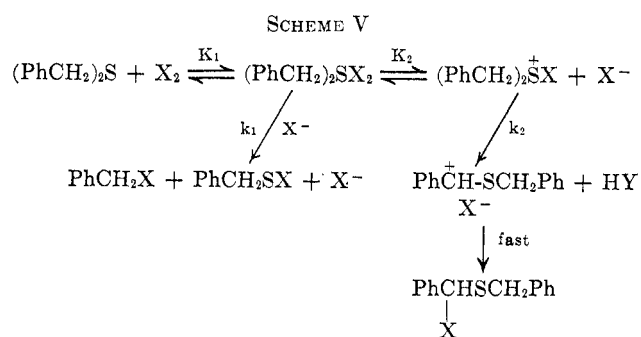
Concentration Dependence of Product Ratios.—Our preliminary studies indicated a general trend toward increased cleavage with all halogenating agents when the equimolar initial concentrations of sulfide and halogenating agent were raised; however, reproducible data could be obtained only for bromination in carbon tetrachloride. The absence of concentration dependence of c/α at low reactant concentrations coupled with the

kinetic isotope effect is consistent with an hypothesis that both cleavage and α-substitution products stem from a common intermediate and that both reactions are first order in both bromosulfonium cation and bromide anion (Scheme IV).[22] It is not consistent with

SCHEME IV

PhCH₂SCH₂Ph + XY ⟶

$$PhCH_2\overset{X}{\underset{+}{\underset{|}{S}}}CH_2PH \ Y^- \longrightarrow PhCH_2Y + XSCH_2Ph$$

$$X_2 + (PhCH_2S)_2$$

$$[PhCH_2\overset{+}{S}{=}CHPh \longleftrightarrow PhCH_2\overset{+}{S}CHPh] \ X^- + HY$$

$$PhCH_2SCHXPh$$

participation by any process, such as rate-determining monomolecular carbon–sulfur cleavage of a halosulfonium cation, which is zero order in bromide ion.

At higher concentrations, the explanation must be more complex. One could assume the intervention of two halosulfonium salts, one largely covalent and the other ionic, which proceed to different products by a transformation involving halide ion (Scheme V). Mak-

SCHEME V

$$(PhCH_2)_2S + X_2 \underset{}{\overset{K_1}{\rightleftharpoons}} (PhCH_2)_2SX_2 \underset{}{\overset{K_2}{\rightleftharpoons}} (PhCH_2)_2\overset{+}{S}X + X^-$$

$$\overset{k_1}{\diagup}X^- \qquad \qquad \overset{}{\diagup}k_2$$

$$PhCH_2X + PhCH_2SX + X^- \qquad Ph\overset{+}{C}H{-}SCH_2Ph + HY$$
$$X^-$$

$$\downarrow \text{fast}$$

$$PhCHSCH_2Ph$$
$$|$$
$$X$$

ing the assumption that K_1 is large, a kinetic scheme based on this mechanism leads to the time-dependent expression

$$\frac{c}{\alpha} = \frac{k_2 X_0}{2k_1 K_2}\left(\frac{2 + \beta t}{2 + \beta t}\right)$$

where X_0 is the initial sulfide concentration and $\beta = -k_1 X_0$. Allowing the reaction to go to completion this derivation predicts c/α to be a linear function of the initial sulfide concentration over the entire concentration range.

$$c/\alpha = k_2 X_0/k_1 k_2$$

Postulation that a salt effect might tend to favor bond cleavage as the reactions proceed at the higher concentrations, appears attractive, but this interpretation may be discarded. Ionization of the hydrogen bromide to any large extent in carbon tetrachloride seems unlikely when one considers that K_{diss} for HCl in nitromethane is only 6.0×10^{-7}.[23]

(19) J. F. Bunnett, *Angew. Chem., Int. Ed. Engl.*, **1**, 225 (1962).

(20) The kinetic isotope effect for an Elcb reaction, which for the case of an irreversible elimination must be identical when measured competitively and by independent runs, is expected to be unity [D. J. McLennan, *Quart. Rev.*, **21**, 490 (1967); Z. Rapopport, *Tetrahedron Lett.*, 3601 (1968)], and has been measured in one case to be 1.2 [D. J. Cram, and A. S. Wingrove, *J. Amer Chem. Soc.*, **86**, 5490 (1964)].

(21) See, for example, A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968); E. C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, **90**, 6447 (1968).

(22) The product ratio does not demand the intervention of free ions in solution nor does it demand that the attacking species be the bromide ion rather than Br₃⁻ or HBr₂⁻. It also does not rule out the possibility that the reactive species are maintained at low concentration by rapid equilibrium processes.

(23) Y. Pocker, K. D. Stevens, and J. J. Champoux, *J. Amer. Chem. Soc.*, **91**, 4199 (1969).

A final alternative exists; namely, that in the nonpolar solvents used, aggregation of halosulfonium salts becomes acute at about 0.3 *M*. The aggregates, in which a charge transfer type structure[9] probably exists, then decompose to a higher proportion of cleavage products than do the monomeric ion pairs. Thus, it appears that most appropriate general formation of these events is that shown in Scheme IV with an hypothesis of aggregation at higher concentrations of reactants.

Experimental Section

Materials and Apparatus for the Halogenation of Benzyl Sulfide.—Benzyl sulfide was obtained commercially and recrystallized from ethanol. Commercially available NCS and NBS were purified by recrystallizing from eight times their weight of water. Reagent grade deuteriochloroform, carbon tetrachloride, bromine, 1 *N* sodium thiosulfate solution, and Matheson anhydrous hydrogen chloride and chlorine were used without further purification. Purified hexamethylbenzene was used as an internal standard for quantitative nmr measurements. Nmr determinations were performed on a Varian Associates, Model A-60, spectrometer. Each integration was repeated at least four times to obtain the average value.

General Procedure for Bromination of Benzyl Sulfide.—A stock solution containing 214.3 mg (1 mmol) of benzyl sulfide and 13.5 mg (0.083 mmol) of hexamethylbenzene in 2.4 ml of carbon tetrachloride was delivered by pipet into a 15-ml round-bottomed flask equipped with a calcium chloride drying tube The solution was stirred and equilibrated for at least 10 min in the kinetic bath. A solution containing 159.8 mg (1 mmol) of bromine in 2.4 ml of carbon tetrachloride maintained at constant temperature in the kinetic bath was then added to the flask all at once. The solid adduct initially formed completely disappeared in less than 2 min, and the brown solution was stirred at 35° for 30 min. At the end of this time, to the red solution was added 1 drop of acetone-d_6 to destroy benzyl sulfenyl bromide. The solution was concentrated to about 2 ml by flushing with nitrogen. This concentrated solution was then used for nmr analysis.

General Procedure for Chlorination of Benzyl Sulfide.—Approximately 0.25 ml (1 mmol) of a solution of chlorine in carbon tetrachloride, whose chlorine content was determined by titration against 1 *N* sodium thiosulfate solution,[24] was then added to 4.55 ml of a thermostated stock solution containing 1 mmol of the sulfide in 4.55 ml of carbon tetrachloride. The reaction was carried out at 35° for 30 min and the final solution was concentrated for nmr analysis.

General Procedure for Halogenation of Benzyl Sulfide with NCS and NBS.—To 4.8 ml of a stock solution containing 1 mmol of the sulfide and the internal standard in carbon tetrachloride was added in one portion 1 mmol of solid NCS or NBS. The reaction proceeded as described above. The solid, benzylsulfenylsuccinimide, was removed by filtration, and the filtrate was concentrated for nmr analysis. When the same reaction was performed in deuteriochloroform, all reaction products remained in solution.

Benzyl Alcohol-α-α-d_2.—To 3 g (0.072 mmol) of lithium aluminum deuteride suspended in 225 ml of freshly distilled ether at reflux was added dropwise during a 50-min period 21.2 g (0.14 mol) of ethyl benzoate in 50 ml of ether. The addition was so adjusted that gentle reflux was maintained. The resulting suspension was maintained under reflux for an additional 3 hr. To the final thick slurry, cooled with ice water, was added slowly 5 ml of water and then it was acidified with concentrated sulfuric acid. The mixture was heated under reflux for 1.5 hr and cooled; the clear layer was removed. Ether (250 ml), followed by 2 ml of water and a few drops of concentrated sulfuric acid, was added and the mixture was refluxed for an additional hour, after which it was cooled and filtered. The residual oil after solvent removal was made neutral to litmus paper and was vacuum distilled. The 15.3 g (99%) of product, bp 91–92° (15 mm), was shown by vpc analysis to be slightly contaminated with ethyl benzoate. Nmr analysis of the α-α-dideuteriobenzyl alcohol showed no detectable protons at the benzylic methylene position.

Benzyl Chloride-α-α-d_2.—The crude benzyl alcohol-α,α-d_2 was dissolved in 100 ml of benzene, and to this solution was added, dropwise with the temperature maintained at 20–25°, 21.5 g (0.18 mol) of thionyl chloride in 50 ml of benzene. The addition was complete in 45 min, and the resulting solution was heated under reflux for 3 hr. The final solution was cooled, and the solvent was removed under vacuum by rotary evaporator. The residual yellow oil was vacuum distilled giving 11.3 g (87.5%) of benzyl chloride-α,α-d_2, bp 60–65° (15 mm). Vpc analysis of the product showed two components, the larger of which was identified as benzyl chloride-α-α-d_2.

Benzyl Sulfide-α-α-d_2.—To sodium benzylmercaptide prepared from 11.0 g (0.0884 mol) of benzyl mercaptan and 4 g (0.1 mol) of sodium hydroxide pellets in 50 ml of ethanol was added 11.3 g of crude benzyl chloride-α-α-d_2. The addition was carried out at 20–25° and was completed in 15 min. The resulting suspension was heated under reflux for 1 hr. The final brown mixture was cooled, and the organic layer was isolated by decantation. The solvent was removed on a rotary evaporator under vacuum leaving a semisolid mass. To the combined solids was added 1 l. of water to precipitate the product which was removed by filtration, washed twice with cold water, and dried. The yellow solid was recrystallized from 200 ml of ethanol giving 10.2 g (34%) of benzyl sulfide-α,α-d_2: mp 49°; ν_{max}^{KBr} 3010, 2910, 2140, 1595, 1575, 1490, 1450, 1410, 1070, 750, 700 cm^{-1}; nmr (CCl$_4$) δ 3.47 (s, 2 H), 7.16 (s, 5 H) ppm; mass spectrum *m/e* at 216 (100), 125 (22.1), 124 (22.9), 123 (55.4), 122 (20.3), 94 (38.5), 93 (56.1), 92 (27.5), 91 (51.8), 77 (21.6), 65 (43.2), 51 (22.2), 46 (31.5), 45 (51.8), 39 (25.4); d_0 0.299%, d_1 1.79%, d_2 97.9%.

α-Chlorobenzyl Benzyl Sulfone.—Benzyl sulfide, 2.14 g (0.01 mol), in carbon tetrachloride was chlorinated with NCS in a manner described in the general procedure. After the reaction was complete and solids had been removed by filtration, the reaction mixture was oxidized with ca. 0.04 mol of monoperphthalic acid in ether. The sulfone, after work-up, recrystallization from ethanol, and drying, was obtained in 78.5% yield: mp 117–118° (lit. 123°[25], 118°); ν_{max}^{KBr} 3010, 2983, 1600, 1580, 1493, 1452, 1410, 1320 (sulfone), 1135, 775, 700 cm^{-1}; nmr (CDCl$_3$) δ 7.39 (s, 5 H), 5.92 (s, 1 H), 4.40 (q, J = 14.0 Hz, 2 H) ppm.

α,α-Dichlorobenzyl Benzyl Sulfide.—To a solution of 3.21 g (0.015 mol) of benzyl sulfide in 20 ml of carbon tetrachloride was added 4.4 g (0.0325 mol) of sulfuryl chloride at room temperature over a 30-min period according to the procedure of Paquette.[16] The solution was then stirred at room temperature for 1 hr, after which it was evaporated to give a thick oil. Nmr analysis was performed without further purification: nmr (CDCl$_3$) δ 7.83 (m, 2 H), 7.16 (m, 8 H), 4.22 (s, 2 H) ppm.

Benzylsulfenyl Chloride.—Into a solution of 2.47 g (0.01 mol) of benzyl disulfide in carbon tetrachloride solution at −15° was bubbled 0.71 g (ca. 0.01 mol) of chlorine during a 10-min period. The resulting red solution was kept at −15° until an nmr measurement was performed. The nmr of this reaction mixture showed no signals for benzyl disulfide. It contained three singlets at δ 7.25, 4.52, and 4.29 ppm.

Benzylsulfenyl Bromide.—To a solution of 739 mg (3 mmol) of benzyl disulfide in carbon tetrachloride at −15° was added 5 ml of carbon tetrachloride containing 480 mg (3 mmol) of bromine. The red solution was stirred at −15° for 20 min before an nmr was taken. The nmr spectrum shows two singlets at 7.30 and 4.24 ppm assignable to the phenyl and methylene protons of benzylsulfenyl bromide, respectively.

To the above mixture at −15° was then added 643 mg (3 mmol) of benzyl sulfide in carbon tetrachloride. The resulting mixture was kept at 35° with constant stirring for 30 min. Nmr analysis at this stage gave, in addition to the weak signal of benzylsulfenyl bromide, the peaks corresponding to α-bromobenzyl sulfide and benzyl disulfide. Nmr analysis after a 1-hr period at 35° gave essentially the same signals except that the intensity of the disulfide peak increased and that of the benzylsulfenyl bromide signal decreased.

N-Benzylsulfenylsuccinimide.—A solution of 14.8 g (0.06 mol) of benzyl disulfide, 10.7 g (0.06 mol) of NBS, and a catalytic amount of benzoyl peroxide in carbon tetrachloride was heated to reflux for 30 min. Work-up followed the published procedure[26] giving a crude solid, recrystallization of which from alcohol gave

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7.0 g (53%) of needles: mp 161–162°, lit.[27] 162°; nmr (CDCl₃) δ 7.30 (s, 5 H), 4.11 (s, 2 H), 2.65 (s, 4 H) ppm; ν_{max}^{KBr} 2920, 2850, 1720, 1555, 1490, 1419, 1305, 1148, 765, and 713 cm⁻¹.

N-Benzylsuccinimide.—This compound was prepared according to the procedure of Argoria.[28]

Chlorination of Benzyl Sulfide with NCS in the Presence of Deuterium Chloride.—A 15-ml round-bottomed flask equipped with magnetic stirrer was charged with 214 mg (1 mmol) of benzyl sulfide in 4.8 ml of carbon tetrachloride. Into this solution kept at 35° was bubbled a stream of dry deuterium chloride at a

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rate of one bubble every 10 sec. A 134-mg (1 mmol) portion of solid NCS was then added, and the resulting mixture was continuously stirred under deuterium chloride flow. Nmr analyses of the filtrate after 30 min of reaction showed four peaks for the methylene protons at δ 219, 232.5, 236.5, and 250 Hz downfield from TMS. There were no detectable signals at δ 243.8 and 228.85 Hz as evidenced by expanding this area at 50-Hz sweep width.

β-Keto Sulfoxides. X. Conversion of Cycloalkanecarboxylic Esters to 1-Cycloalkylpropane-1,2-diones[1]
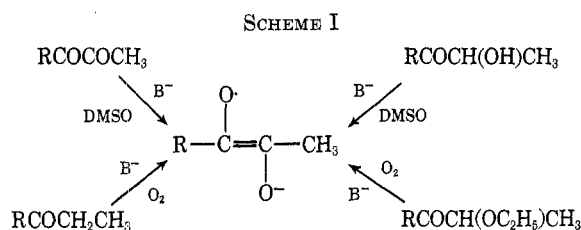
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The conversion of cycloalkylcarboxylic esters to cycloalkyl keto sulfoxides (RCOCH₂SOCH₃) and hence to α diketones (RCOCOCH₃), cycloalkyl ethyl ketones (RCOCH₂CH₃), cycloalkyl vinyl ketones [RCOCH=CH₂, RCOC(CH₃)=CH₂], and α-ethoxy ketones [RCOCH(OC₂H₅)CH₃] is described.

The 1-cycloalkylpropane-1,2-diones, or the corresponding hydroxy ketones, were required for the synthesis of a series of semidione radical anions (Scheme I).[2,3] In addition to the previously known routes to

Scheme I

semidiones,[2] we found during the course of this work that the oxidation of α-alkoxy ketones in basic solution was often an excellent method for the preparation of semidiones. We have developed the synthesis of the diketones from the cycloalkanecarboxylic esters *via* the β-keto sulfoxides,[4,5] as shown in Scheme II.[6,7] The alkylated β-keto sulfoxides[8,9] were also reduced[5,6] to yield the ketones (RCOCH₂CH₃) and α-ethoxy ketones

Scheme II

[RCOCH(OC₂H₅)CH₃] and pyrolyzed[10] to yield the vinyl ketones (Scheme III).

Scheme III
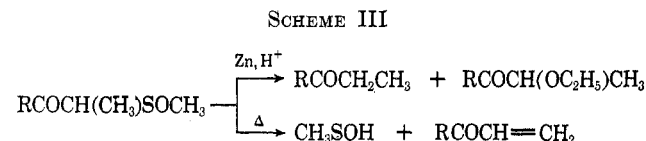
Results and Discussion

Condensation of the cycloalkanecarboxylic esters with the methylsulfinyl carbanion presented no particular problems.[4,5] The reaction with cyclohexanecarboxylic ester has been previously reported.[5] Yields ranged from 41% with R = cyclopropyl to 74% with R = cyclopentyl or cyclohexyl. The β-keto sulfoxides (1) were converted to the enolate anions with sodium hydride in THF and alkylated with methyl iodide to yield RCOCH(CH₃)SOCH₃ (2) and RCOC(CH₃)₂SOCH₃ (3) (a–f, R): a, cyclopropyl; b, 1-methylcyclopropyl; c, cyclobutyl; d, cyclopentyl; e, cyclohexyl; f, 1-methylcyclobutyl.

The cyclopropyl and cyclobutyl compounds were unique in the ease with which dialkylation occurred. Use of a slight excess of methyl iodide and sodium hydride in the alkylation resulted in a mixture of 2a–3a. In 1a the second methyl group entered at the position α to both the carbonyl and sulfoxide functions to form 3a exclusively. The cyclobutyl analog (1c) reacts with 2.3 equiv of sodium hydride and methyl iodide to yield a mixture of the dimethyl (3c) and trimethyl (3f) derivatives. Reaction of 1a with 3.4 equiv of sodium hydride and methyl iodide yielded only 3a. We believe the lack of methylation at the methine position of 1a is due to a stereoelectronic effect which places the methine hydrogen in the nodal plane of the carbonyl group
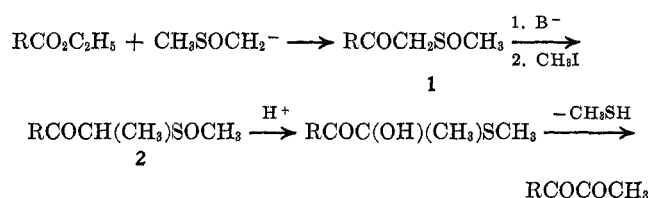
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