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Registry No.—Diiron nonacarbonyl, 15321-51-4; iron pentacarbonyl, 13463-40-6; dicobalt octacarbonyl, 10210-68-1; methanesulfonyl azide, 1516-70-7; methanesulfonyl azide iron complex, 51779-40-9; methanesulfonyl azide cobalt complex, 51898-91-0; benzenesulfonyl azide, 938-10-3; benzenesulfonyl azide iron complex, 51779-42-1; *p*-toluenesulfonyl azide, 941-55-9; *p*-toluenesulfonyl isocyanate, 4083-64-1; *o*-aminophenyl methyl sulfone, 2987-49-7; *o*-azidophenyl methyl sulfone, 51779-31-8; *N,N'*-bis(*o*-methanesulfonylphenyl)urea, 51806-01-0; *tert*-butyl azidoformate, 1070-19-5; di-*tert*-butyl iminodicarboxylate, 51779-32-9; *tert*-butyl carbamate, 4248-19-5; *N,N'*-bis(*tert*-butoxycarbonyl)urea, 51779-33-0; *N*-*tert*-butoxycarbonylurea, 31598-86-4.

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Synthesis of Dihalomethyl and α-Haloalkyl Sulfones by the Halogenative Decarboxylation of α-Aryl- and α-Alkylsulfonylalkanecarboxylic Acids

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The synthesis by brominative decarboxylation of meta- and para-substituted bromomethyl and α-bromobenzyl benzyl sulfones is described. Included are nine $ArCH_2SO_2CH_2Br$, four $PhCHBrSO_2CH_2Ar$, and five $ArCHBrSO_2CH_2Ph$ types. The nine bromomethyl benzyl sulfones were prepared from the dibromomethyl benzyl sulfones by reduction. Halogenative decarboxylations of α-cyclopropylsulfonyl-α-phenylacetic acid and phenylsulfonylacetic acid in refluxing carbon tetrachloride using *N*-halosuccinimides are described. Phenylthioacetic acid with *N*-chlorosuccinimide in CCl_4 gave mainly phenylthio-α-chloroacetic acid at 25° and mainly phenyl chloromethyl sulfide at 77°. Mechanisms for these reactions are discussed.

The halogenative decarboxylation of α-carboxyalkyl sulfones has been used as a preparative method for haloalkyl and dihalomethyl sulfones since before the turn of the century.[1] Sulfone carboxylic acids of the type $ArSO_2CH_2CO_2H$ give aryl dihalomethyl sulfones, $ArSO_2CHX_2$ (X = Cl, Br, or I), whereas $ArSO_2CHRCO_2H$ types give $ArSO_2CHXR$.[1] Since the corresponding sulfides, $ArSCH_2CO_2H$, $ArSCHRCO_2H$, $RSCH_2CO_2H$, and $RSCHR'CO_2H$, are readily available from reactions of ArSNa or RSNa with $ClCH_2CO_2H$ or $ClCHRCO_2H$ or from reactions of RX with $HSCH_2CO_2Na$ or $HSCHRCO_2Na$, these provide convenient starting materials. The corresponding sulfone carboxylic acids are obtained in high yield by oxidation. The latter react readily with halogens in aqueous acetic acid solution to give good yields, *e.g.*, of dihalomethyl aryl or alkyl sulfones.[1,2] It is often convenient to carry out the preparation of the sulfide, oxidation, bromination, and decarboxylation all in a single reaction vessel, as in the preparation of bis-α-bromobenzyl sulfone.[3] In the present study this method has been extended to the preparation of a number of other α-halo sulfones, *e.g.*

$$ArCH_2X \xrightarrow[\text{2. excess } 30\%\ H_2O_2 \\ \text{3. NaBr}]{\text{1. } HSCH_2CO_2Na} ArCH_2SO_2CHBr_2$$

Use of excess hydrogen peroxide in step 2 ensures complete oxidation of the sulfide and serves to generate bromine in the halogenation step.

This method can also serve as a route to bromomethyl alkyl or aryl sulfones, since the dibromomethyl sulfones are readily reduced to bromomethyl sulfones by sulfite ion[2] (see Experimental Section).

$$ArCH_2SO_2CHBr_2 + SO_3^{2-} + 2H_2O \xrightarrow{H_2O-EtOH} ArCH_2SO_2CH_2Br + SO_4^{2-} + Br^- + H_3O^+$$

A number of types of α-bromobenzyl benzyl sulfones have now been prepared by this general route.

Table I
Halogenative Decarboxylations of Sulfone Carboxylic Acids by *N*-Halosuccinimides (1 Equiv) in Refluxing Carbon Tetrachloride

Substrate	Halogen source	Time, hr	Product	Yield,[a] %
$PhSO_2CH_2CO_2H$ (1)	NCS[b]	12	$PhSO_2CHCl_2$	73
			$PhSO_2CH_2Cl$	15
c-$PrSO_2CH(Ph)CO_2H$ (2)	NCS[b]	5.5	c-$PrSO_2CHClPh$	80
			c-$PrSO_2CCl_2Ph$	20
c-$PrSO_2CH(Ph)CO_2H$ (2)	NBS[c]	5.5	c-$PrSO_2CHBrPh$	87 (63)[d]
c-$PrSO_2CH(Ph)CO_2H$ (2)	NIS[e]	6	c-$PrSO_2CHIPh$	32
$PhSO_2C(Me)(Ph)CO_2H$ (3)	NCS[b]	18	None	
$PhSO_2C(Me)(Ph)CO_2H$ (3)	NCS[b]	19[f]	$PhSO_2CH(Me)Ph$	Low
$PhSCH_2CO_2H$	NCS[b]	4	$PhSCH_2Cl$	(80)[g]
$PhSCH_2CO_2H$	NCS[b]	18[h]	$PhSCHClCO_2H$	71

[a] By nmr. [b] *N*-Chlorosuccinimide. [c] *N*-Bromosuccinimide. [d] Isolated yield. [e] *N*-Iodosuccinimide. [f] In chlorobenzene at 140°. [g] Isolated as the sulfone after oxidation; nmr analysis showed 84% of $PhSCH_2Cl$ and 16% of $PhSCH(Cl)CO_2H$. [h] At 25°.

We also report an alternative procedure for carrying out halogenative decarboxylations using *N*-halosuccinimides as the halogen source and comment on the mechanism and possible extension of the reaction to related systems.

Results

Examples of brominative decarboxylations used in the preparation of bromo sulfones of the types $ArSO_2CHBr_2$, $ArCH_2SO_2CHBr_2$, $ArCHBrSO_2R$, $PhCHBrSO_2CH_2Ar$, and $ArCHBrSO_2CH_2Ph$ are given in the Experimental Section.

The halogenative decarboxylations using *N*-halosuccinimides (NCS, NBS, and NIS) as a source of halogen were carried out in refluxing carbon tetrachloride solution. Phenylsulfonylacetic acid ($PhSO_2CH_2CO_2H$, 1), α-cyclopropylsulfonyl-α-phenylacetic acid [c-$PrSO_2CH(Ph)CO_2H$, 2], and α-phenyl-α-methyl-α-phenylsulfonylacetic acid [$PhSO_2C(Me)(Ph)CO_2H$, 3] were used as typical substrates containing two, one, and zero enolizable hydrogen atoms, respectively. The results are summarized in Table I.

Examination of Table I shows that halogenative decarboxylation is successful when either one or two enolizable hydrogen atoms is present, but fails when an enolizable hydrogen atom is absent.

It seems likely that electrophilic reagents other than halogens may be used in electrophile decarboxylations. Attempts to substitute a PhS group into $PhSO_2CH_2CO_2H$ under the halogenative decarboxylation conditions using PhSCl, $PhSSO_2C_6H_4Me$-*p*, *N*-PhS-phthalimide, or *N*-PhS-phthalimide and F_3CCO_2H have thus far been unsuccessful, however.

Discussion

It is significant that in all the preparative halogenative decarboxylations of sulfone carboxylic acids reported to date one or two hydrogen atoms are present on the carbon atom bearing the RSO_2 and CO_2H groups.[1-3] The failure of $PhSO_2C(Me)(Ph)CO_2H$ (3) to undergo halogenative decarboxylation, even under strenuous conditions (Table I), emphasizes the requirement of the presence of at least one enolizable hydrogen atom. Judging from these preparative studies and earlier kinetic studies on the decarboxylation of sulfone carboxylic acids and halo sulfone carboxylic acids, a mechanism involving rate-limiting enolization followed by rapid halogenation and subsequent rapid decarboxylation becomes highly probable, *e.g.*[4]

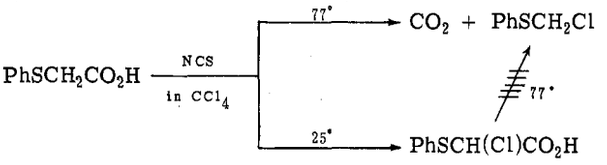
$$PhSO_2CHRCO_2H \xrightarrow{slow} PhSO_2CH{=}C(OH)_2 \xrightarrow{fast}$$

$$PhSO_2C(X)(R)CO_2H \xrightarrow{fast} PhSO_2CHXR + CO_2$$

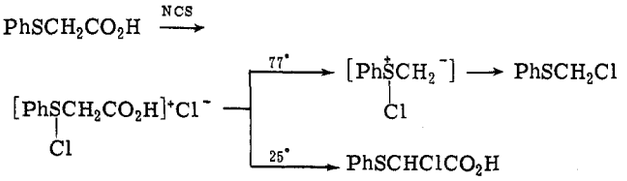
N-Halosuccinimides no doubt serve merely as a convenient source of low concentrations of X_2, a role that has been demonstrated in other types of halogenations, including allylic halogenation.[6] If two enolizable hydrogen atoms are present, enolization of the intermediate halo sulfone carboxylic acid, *e.g.*, $PhSO_2CHXCO_2H$, competes favorably with decarboxylation, and the major product is the dihalomethyl sulfone, *e.g.*, $PhSO_2CHX_2$.

Evidence for rate-limiting enolization in the bromination of α-sulfonylcarboxylic acids comes from the early work of Ramberg and his students, who demonstrated, using several optically active systems, *e.g.*, $EtSO_2\overset{*}{C}H(Me)CO_2H$ and $PhSO_2\overset{*}{C}H(Me)CO_2H$, that in acidic solutions in the presence of excess bromine the (pseudo-first-order) rates of bromination and racemization were essentially identical.[7] The order of ease of decarboxylation rates $RSO_2CX_2CO_2H > RSO_2CHXCO_2H > RSO_2CH_2CO_2H$ was established in early preparative studies,[1] as was the more rapid decarboxylation of the carboxylate salts as compared to the free acids.[1,9]

It is clear from the above discussion that halo or dihalo sulfone carboxylic acids are intermediates in the halogenative decarboxylation of α-alkylsulfonyl- or α-arylsulfonylcarboxylic acids. A different route is followed, however, in the conversion of α-phenylthioacetic acid to phenyl chloromethyl sulfide by the action of NCS in refluxing CCl_4. Here phenylthiochloroacetic acid can be isolated from a chlorination run at 25°, but it does not decarboxylate to phenyl chloromethyl sulfide under the reaction conditions (Table I).



A chlorosulfonium salt is probably formed as the initial product. At 25° it rearranges to phenylthiochloroacetic acid,[11] but at higher temperatures decarboxylation of the sulfonium salt competes favorably with rearrangement.[12]



It seems likely from these mechanistic considerations that halogenative decarboxylations will be successful in general for systems of the type $EWGCH_2CO_2H$ and $EWGCH(R)CO_2H$, where EWG is a strongly electron-withdrawing group ($ArSO_2$, RSO_2, CN, NO_2, COR, CO_2R, SR_2^+, NR_3^+, and the like) and R is either an alkyl or an aryl group.

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Experimental Section

Nmr spectra were run on Varian T60 and Perkin-Elmer-Hitachi R-20B spectrometers (60 MHz). Chemical shifts are reported in δ units (parts per million downfield from TMS) and were determined in chloroform solution. Melting points are uncorrected. Microanalyses are by Micro-Tech, Skokie, Illinois.

Dibromomethyl Benzyl and Aryl Sulfones. The preparation of dibromomethyl 3-nitrobenzyl sulfone starting from 3-nitrobenzyl chloride and mercaptoacetic acid is typical of the preparations of dibromomethyl benzyl sulfones (Table II).[14] Dibromomethyl aryl sulfones can be prepared by a similar procedure starting with arenethiols and chloroacetic acid.[2]

Table II. Melting Points and Carbon and Hydrogen Analyses for Dibromomethyl Benzyl Sulfones, $ArCH_2SO_2CHBr_2$.

Substituent	MP °C[a]	Molecular Formula	Calcd. C	Calcd. H	Found C	Found H
3-NO_2	138-140.2	$C_8H_7Br_2NO_4S$	25.76	1.89	25.90	2.04
4-Me	122-123.8	$C_9H_{10}Br_2O_2S$	31.60	2.95	31.79	3.01
4-Cl	121.2-122.5	$C_8H_7Br_2ClO_2S$	26.51	1.95	26.69	2.05
3-Me	145-146	$C_9H_{10}Br_2O_2S$	31.60	2.95	31.55	2.95
3-F	100.8-101.3	$C_8H_7Br_2FO_2S$	27.77	2.04	27.82	2.16
4-NO_2	149-149.5	$C_8H_7Br_2NO_4S$				
3-Br	148.8-150.2	$C_8H_7Br_3O_2S$	23.61	1.73	23.87	1.82
4-MeO	140-141.2	$C_9H_9Br_3O_3S$	24.74	2.08	25.02	2.17

[a]Uncorrected.

In a 250-ml flask equipped with a condenser and stirrer was placed 8.60 g (0.0802 mole) of 3-nitrobenzyl chloride (Eastman) dissolved in 75 ml of 95% EtOH. A solution prepared from 6 ml (0.052 mole) of an 80% aqueous solution of mercaptoacetic acid (Eastman) and 50 ml of aqueous sodium hydroxide (0.15 mole) was added in one portion. After the initial reaction had subsided, the solution was heated at reflux for 1 hr and stirred overnight at room temperature. Most of the ethanol was removed by rotary evaporation and the residue was diluted with 125 ml of water. The solution was acidified to Congo Red paper with 3 N HCl, and the oily layer taken up in ether(2 125-ml extracts). After washing with water the combined ethereal extracts were

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evaporated to give crude 3-nitrobenzylthioacetic acid. To a solution of the crude acid in 75 ml of glacial acetic acid was added 30 ml (0.26 mole) of 30% H_2O_2 over a 30 min period. After a 15 min reflux the solution was allowed to come to room temperature (1 hr) and an aqueous solution of potassium bromide was added until the evolution of bromine ceased. Rapid decolorization of bromine occurred and carbon dioxide was evolved. An additional 6 ml of Br_2 was added to complete the reaction. (If sufficient H_2O_2 and KBr are used this is unnecessary.) The reaction mixture was diluted with water and washed with aqueous bisulfite to remove excess bromine. The solid was collected on a filter and then recrystallized from 95% ethanol: pale yellow crystals, mp 138.8-140.2°; nmr 7.3-8.4 (m, 4H), 6.13 (s, 1H), 4.84 (s 2H). The other dibromomethyl benzyl sulfones for which analytical data are reported in Table II had similar nmr spectra. The sample of dibromomethyl 3-bromo-4-methoxybenzyl sulfone was obtained in a reaction where p-methoxybenzyl alcohol (anisyl alcohol) was the starting material. (Bromination of the benzene ring occurred during the reaction.)

Bromomethyl Benzyl Sulfones. These were prepared from the dibromomethyl benzyl sulfones in average yields of about 75% by reduction with a slight excess of potassium sulfite in aqueous ethanol (7 hr reflux). The nmr spectrum for bromomethyl 3-nitrobenzyl sulfone is typical:[14] 7.6-8.4 (m, 4H); 4.62 (s, 2H); 4.30 (s, 2H).

Table III. Melting Points and Carbon and Hydrogen Analyses for Bromomethyl Benzyl Sulfones, $ArCH_2SO_2CH_2Br$.

Substituent	MP °C[a]	Molecular Formula	Calcd. C	Calcd. H	Found C	Found H
3-NO_2	114-115	$C_8H_8BrNO_4S$	32.67	2.72	32.62	2.76
4-Me	1.69.5-170.5	$C_9H_{11}BrO_2S$	41.08	4.21	41.00	4.42
4-Cl	195.5-198	$C_8H_8BrClO_2S$				
3-Me	90-90.5	$C_9H_{11}BrO_2S$	41.08	4.21	41.27	4.14
3-F	95-95.8	$C_8H_8BrFO_2S$	35.97	3.02	35.73	3.04
4-NO_2	214-215.8	$C_8H_8BrNO_4S$	32.67	2.72	33.08	2.88
3-Br						
4-MeO	146.5-147.2	$C_9H_{11}Br_2O_3S$	30.19	2.82	30.30	2.16
3-Br	117-117.9	$C_8H_8Br_2O_2S$	29.29	2.46	29.40	2.48

[a]Uncorrected

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α-Bromobenzyl Methyl Sulfone. The procedure was similar to that described for dibromomethyl 3-nitrobenzyl sulfone except that no additional bromine was added. α-Bromophenylacetic acid, 6.7 g (0.0312 mole) in MeOH was treated with a methanol solution containing 0.0312 mole of methanethiol. Oxidation of the sulfide was effected with 20 ml (0.176 mole) of 30% H_2O_2. The yield of sulfone was 88%; mp 96-97°; nmr: 7.3-7.7 (m, 5H); 5.73 (s, 1H); 3.00 (s, 3H). Anal. Calcd for $C_8H_8BrO_2S$: C, 38.37; H, 3.64. Found: C, 38.53; H, 3.60.

α-Bromobenzyl Benzyl Sulfones. Arylmethanethiols were prepared in situ by the action of m- or p-substituted benzyl chlorides with thiourea in 95% ethanol and subsequent treatment with aqueous sodium hydroxide. The crude thiols were condensed with α-bromophenylacetic acid and the resulting α-carboxybenzyl substituted benzyl sulfides were oxidized and subjected to brominative decarboxylation, as above.[14]

Table IV. Melting Points and Carbon and Hydrogen Analyses for α-Bromobenzyl Benzyl Sulfones, $PhCHBrSO_2CH_2Ar$.

Substituent	MP °C[a]	Molecular Formula	Calcd C	Calcd H	Found C	Found H
4-Me	129-129.5	$C_{15}H_{15}BrO_2S$	53.11	4.46	53.03	4.69
4-Cl	175.9-176.1	$C_{14}H_{12}BrClO_2S$	46.75	3.36	47.05	3.67
3-F	110.6-111.3	$C_{14}H_{12}BrFO_2S$	48.99	3.52	48.92	3.52
3-Me	120.4-121.1	$C_{15}H_{15}BrO_2S$	53.11	4.46	53.22	4.58

[a]Uncorrected

The isomeric m- and p-substituted α-bromobenzyl benzyl sulfones were prepared starting from m- and p-substituted mandelic acids. Treatment with PBr_3 followed by methanol gave the bromo esters, $ArCHBrCO_2Me$, which were condensed with phenylmethanethiol to give the sulfides; the latter were subjected to hydrolysis, oxidation and brominative decarboxylation, as above.[14]

Table V. Melting Points and Carbon and Hydrogen Analyses for α-Bromobenzyl Benzyl Sulfones, $ArCHBrSO_2CH_2Ph$.

Substituent	MP °C	Molecular Formula	Calcd C	Calcd H	Found C	Found H
4-Me	124.8-125.2	$C_{15}H_{15}BrO_2S$	53.11	4.46	53.22	4.58
4-Cl	140.2-140.7	$C_{14}H_{12}BrClO_2S$	46.75	3.36	46.76	3.57

Continued...

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3-Cl	117-117.3	$C_{14}H_{12}BrClO_2S$	46.75	3.36	47.00	3.63
4-F	115-115.3	$C_{14}H_{12}BrFO_2S$	48.99	3.52	49.16	3.81
3-Me	83-84	$C_{15}H_{15}BrO_2S$	53.11	4.46	53.08	4.47

[a]Uncorrected

α-Cyclopropylsulfonyl-α-phenylacetic Acid (2). Benzyl cyclopropyl sulfone[18] (1.0 g, 5.1 mmol) was dissolved under nitrogen in 100 ml of anhydrous ethyl ether. Butyllithium (2.61 ml of 2.1 M in hexane) was added with a syringe while the mixture was maintained at 0°. The mixture was warmed to 32° for ½ hr, then dry carbon dioxide (5 g) was bubbled in. The salt precipitated. Ether was removed by rotary evaporation, 100 ml of water was added, and the water extracted with 2 50 ml portions of ether. The solution was acidified to Congo Red, then extracted with 3 30 ml portions of chloroform. The chloroform was dried with sodium sulfate and the solvent removed to give 920 mg (75% yield) of a clear colorless oil which solidified on standing. Recrystallization from chloroform/hexane gave white crystals, mp 133-135°. Nmr: 0.84-1.31 (m, 4H); 2.57 (m, 1H); 5.10 (s, 1H); 7.16-7.60 (m, 5H); 8.57 (s, 1H). Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.96; H, 5.04. Found: C, 55.03; H, 5.15.

Cyclopropylsulfonylphenylacetic acid was recovered unchanged after refluxing in carbon tetrachloride solution for 6.5 hr.

Treatment of α-Cyclopropylsulfonyl-α-phenylacetic Acid (2) with NBS and NCS in CCl_4. A 666 mg (2.38 mmol) portion of 2 was added to 6.55 mg (3.67 mmol) of NBS in 10 ml of carbon tetrachloride and the mixture refluxed for 5.5 hr. Removal of solvent gave a mixture of oil and solid. Nmr analysis indicated the presence of α-bromobenzyl cyclopropyl sulfone, succinimide and NBS. Chromatography of the mixture on 20 g of acidic alumina, grade II, with column dimensions 2 x 20 cm using 20% ether hexane eluent (changing to 25% ether hexane after 500 ml of solvent was used) collecting 50 ml fractions gave 410 mg (63%) of α-bromobenzyl cyclopropyl sulfone in fractions 4-6. Recrystallization from hexane gave the analytical sample, mp 67-68°. Nmr: 1.11 (m, 4H); 2.63 (m, 1H); 5.71 (s, 1H); 7.43 (m, 5H). Ir (max): 7.85, 8.81. Anal. Calcd for $C_{12}H_{13}BrO_2S$: C, 43.64; H, 4.03. Found: C, 43.70; H, 4.05.

This procedure is representative of those carried out in the other halogenative decarboxylations. (See Table I for a summary of the results.)

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α-Cyclopropylsulfonyl-α-phenylacetic acid (2.6 g, 0.0108 mole crude) was refluxed for 4 hr in 100 ml of CCl_4 containing 2.0 g NCS and a crystal of benzoyl peroxide. After standing overnight, 50 ml of water was added and the organic phase washed twice with $NaHCO_3$. Drying and removal of solvent gave 1.83 g of oil, by nmr analysis 80% $PhCH(Cl)SO_2CH(CH_2)_2$ and 20% $PhC(Cl)_2SO_2CH(CH_2)_2$. Evaporative distillation (0.05 mm, 120°) did not change the composition. Chromatography of 520 mg of this material was done on 30 g silica gel. Elution with 15% ether/hexane gave, in the early fractions, 84 mg of α,α-dichlorobenzyl cyclopropyl sulfone; 0.96-1.30 (m, 4H); 2.43-2.92 (m, 1H); 7.31-7.81 (m, 3H); 7.76-8.13 (m, 2H). Anal. Calcd for $C_{12}H_{12}Cl_2O_2S$: C, 45.29; H, 3.80. Found: C, 45.23; H, 3.77.

Elution with 20% ether/hexane gave 480 mg of α-chlorobenzyl cyclopropyl sulfone, which was contaminated with the dichloride. Nmr: 0.92-1.35 (m, 4H); 2.26-2.74 (m, 1H); 5.70 (s, 1H); 7.30-7.78 (m, 5H). With the exception of the chemical shift of the benzyl proton, the nmr spectrum of this material is the same as that of the bromo compound prepared analogously. Analysis indicated the presence of about 20% of the dichloride. Anal. Calcd for $C_{12}H_{13}ClO_2S$: C, 52.05; H, 4.80. Found: C, 50.85; H, 4.65.

Treatment of Phenylthioacetic Acid with NCS in CCl_4 at Reflux. Phenylthioacetic acid (167 mg, 1 mmol) was added to 10 ml of carbon tetrachloride containing NCS (138 mg, 1 mmol). The mixture was refluxed for 4 hr, cooled, filtered and solvent removed to give an oil. The nmr of this material showed it to be a mixture of chloromethyl phenyl sulfide (identified by comparison with the spectrum of the known compound) and phenylthiochloroacetic acid (nmr: 5.50, CH; 7.35, aromatic; 10.61, OH) in a 6 to 1 ratio respectively. This material was not characterized further but was oxidized by dissolving in 10 ml of dichloromethane and adding m-chloroperoxybenzoic acid (500 mg) and refluxing for 1 hr. The dichloromethane solution was washed with sodium sulfite, then sodium bicarbonate. Drying and removal of solvent gave 153 mg of oil which solidified on seeding with chloromethyl phenyl sulfone. The nmr was identical to that of chloromethyl phenyl sulfone; yield: 80.3%.

Treatment of Phenylthioacetic acid with NCS in CCl_4 at 25°. Phenylthioacetic acid (1 mmol) was stirred for 18 hr at 25° with NCS (1 mmol). (Succinimide was floating on top after 3 hr.) The mixture was filtered and the solvent removed to give 247 mg of an oil. Nmr analysis showed phenylthio-

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chloroacetic acid (71%) and starting material (7%). Integration of the acid proton relative to the aromatic protons was 1:5, indicating that the remainder of the material was a phenyl-substituted carboxylic acid, presumably phenylthiodichloroacetic acid. A sample of this mixture was heated at reflux in CCl_4. Although some decomposition occurred, no chloromethyl phenyl sulfide was detected in the nmr spectrum. The remainder of the material was oxidized with 2 equiv. of m-chloroperoxybenzoic acid in dichloromethane at 25° for 24 hr. After washing with bicarbonate, drying and removal of the solvent, 20 mg of product was obtained. Nmr analysis showed it to be a mixture of chloromethyl phenyl sulfone and dichloromethyl phenyl sulfone in a 1 to 3 ratio. Acidification of the bicarbonate washes led only to the recovery of m-chlorobenzoic acid. No other carboxylic acids remained.

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Registry No.—**1**, 3959-23-7; **2**, 51416-85-4; **3**, 51416-86-5; $PhSCH_2CO_2H$, 103-04-8; NCS, 128-09-6; NBS, 128-08-5; NIS, 516-12-1; $PhSO_2CHCl_2$, 7205-98-3; c-$PrSO_2CHClPh$, 51416-87-6; c-$PrSO_2CCl_2Ph$, 51416-88-7; c-$PrSO_2CHBrPh$, 51416-89-8; c-$PrSO_2CHIPh$, 51416-90-1; $PhSO_2CH(Me)Ph$, 24422-78-4; $PhSCH_2Cl$, 7205-91-6; $PhSCHClCO_2H$, 51416-91-2; 3-$NO_2C_6H_4CH_2SO_2CHBr_2$, 51416-92-3; 4-$MeC_6H_4CH_2SO_2CHBr_2$, 31355-33-6; 4-$ClC_6H_4CH_2SO_2CHBr_2$, 51416-93-4; 3-$MeC_6H_4CH_2SO_2CHBr_2$, 31355-35-8; 3-$FC_6H_4CH_2SO_2CHBr_2$, 51416-94-5; 4-$NO_2C_6H_4CH_2SO_2CHBr_2$, 31355-36-9; 3-$BrC_6H_4CH_2SO_2CHBr_2$, 31355-30-3; 4-$MeOC_6H_4CH_2SO_2CHBr_2$, 31355-37-0; 3-$NO_2C_6H_4CH_2SO_2CH_2Br$, 51416-95-6; 4-$MeC_6H_4CH_2SO_2CH_2Br$, 51416-96-7; 4-$ClC_6H_4CH_2SO_2CH_2Br$, 51416-97-8; 3-$MeC_6H_4CH_2SO_2CH_2Br$, 51416-98-9; 3-$FC_6H_4CH_2SO_2CH_2Br$, 51416-99-0; 4-$NO_2C_6H_4CH_2SO_2CH_2Br$, 51417-00-6; 4-$MeOC_6H_4CH_2SO_2CH_2Br$, 51417-01-7; 3-$BrC_6H_4CH_2SO_2CH_2Br$, 51417-02-8; 4-$MeC_6H_4CHBrSO_2Ar$, 51417-03-9; 4-$ClC_6H_4CHBrSO_2Ar$, 51417-04-0; 3-$FC_6H_4CHBrSO_2Ar$, 51417-05-1; 3-$MeC_6H_4CHBrSO_2Ar$, 51417-06-2; 4-$MeC_6H_4CHBrSO_2CH_2Ph$, 51417-07-3; 4-$ClC_6H_4CHBrSO_2CH_2Ph$, 51417-08-3; 3-$ClC_6H_4CHBrSO_2CH_2Ph$, 51417-09-5; 4-$FC_6H_4CHBrSO_2CH_2Ph$, 51417-10-8; 3-$MeC_6H_4CHBrSO_2CH_2Ph$, 51417-11-9; 3-nitrobenzyl chloride, 619-23-8; mercaptoacetic acid, 68-11-1; α-bromobenzyl methyl sulfone, 23211-69-0; α-bromophenylacetic acid, 4870-65-9; methanethiol, 74-93-1; benzyl cyclopropyl sulfone, 51417-12-0.

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Facilitation of Deuterium Exchange in a Sulfone by a γ-Halogen Atom in a Ramberg–Bäcklund Reaction

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Observation of deuterium exchange occurring during 1,3-dehydrobromination of $Me_2CHSO_2CHBrPh$ in NaOMe–MeOD and of a low k^H/k^D isotope effect (1.2) for 1,3-dehydrobromination in 40% aqueous dioxane shows that this reaction is occurring by a two-stage, carbanion mechanism, rather than a one-stage, concerted mechanism. Deuterium exchange at the methine position of $Me_2CHSO_2CHClPh$ was found to be over 1000 times as rapid as that in the parent sulfone, $Me_2CHSO_2CH_2Ph$. It is postulated that the chlorine atom accelerates exchange not only by an inductive effect but also by facilitating solvent exchange at the initially formed singly solvated carbanion.

In a previous paper we reported some surprising differences for the effect of methyl substitution on deuterium exchange α to a sulfonyl group *vs.* removal of a similarly situated proton in a Ramberg–Bäcklund reaction. Each substitution of a methyl group in the series $PhCH_2SO_2CH_3$ (1), $PhCH_2SO_2CH_2Me$ (2), $PhCH_2SO_2CHMe_2$ (3) caused a decrease in methoxide-catalyzed deuterium exchange rate of about 100-fold.[1] The rate-limiting step in such exchanges has been shown by Cram to be the rate of solvent exchange between the initially solvated carbanion and bulk solvent (k_s).[2]

$$MeO^- + HCR_2SO_2CH_2Ph \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MeOH\cdots{}^-CR_2SO_2CH_2Ph$$

$$MeOH\cdots{}^-CR_2SO_2CH_2Ph \xrightarrow{MeOD} MeOD\cdots{}^-CR_2SO_2CH_2Ph \quad (k_s)$$

Methyl substitution probably decreases k_1 by an inductive effect, and may also decrease k_s. Since k_{-1} (internal return) is extremely fast—perhaps even faster than a diffusion-controlled rate—it will be affected to a much lesser extent. Let us assume that the 10^4 rate decrease from 1 to 3 results from a tenfold decrease in k_1 and also in k_s for each methyl substitution. An overall decrease in rate of ~100-fold would then be expected in analogous Ramberg–Bäcklund reactions in the series $PhCHBrSO_2CH_3$ (4), $PhCHBrSO_2CH_2Me$ (5), $PhCHBrSO_2CHMe_2$ (6), since a tenfold retardation in k_1 should be observed on each methyl substitution.

$$MeO^- + HCR_2SO_2CHBrPh \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

4, 5, 6
(R = H or Me)

$$MeOH\cdots{}^-CR_2(\text{S}O_2)CHBrPh \xrightarrow{k_2} R_2C(\text{S}O_2)CHPh + Br^-$$

Instead, the overall rate is affected but little by methyl substitution, the relative rates for **4:5:6** being (1.0):1.7:0.62.[1] One way to account for these results is to assume that competition between k_2 and k_{-1} has decreased the relative amount of internal return.[1] Another possibility is that there is a change in mechanism along the series; for example, the reaction of 4 (R = R = H) might occur in two stages, as indicated by the equations, whereas the reaction of 6 (R = R = Me) might occur in one stage (concerted mechanism). Additional experiments have now been carried out in an attempt to choose between these two possibilities.

Ordinarily, because of internal return, one observes low or even inverse k^H/k^D isotope effects for exchange of protons α to sulfonyl groups.[2] On the other hand, in a concerted reaction one might expect to observe a sizable k^H/k^D isotope effect. The isotope effect for 6 was therefore examined. Since the two-stage Ramberg–Bäcklund reaction is known to have a large k^{Br}/k^{Cl} leaving-group effect,[3] it was also of interest to examine the behavior of the chloro analog of 6, $PhCHClSO_2CHMe_2$ (7).

Results

The desired α-bromobenzyl isopropyl sulfone and its deuterated analog were obtained by methods reported in the literature. The rates of hydroxide- or methoxide-initiated dehydrobromination were measured spectrophotometrically in 40% aqueous dioxane and methanol solutions, respectively (Table I).

The k^H/k^D of 1.0 in methanol indicated that prior exchange was occurring, and this was supported by quenching experiments. In an experiment run with 6 at 25° in methanol-*O*-*d* the starting material was 37% deuterated at the methine position after the reaction was only 18% complete. Some exchange at the methine position occurred also in 40% aqueous dioxane, but the amount was not sufficient to affect the rate data, as may be judged by the high correlation coefficients obtained from a least-squares plot in the rate calculations (r = 0.9992 for the deuterium compound and 0.9999 for the hydrogen compound). We believe, therefore, that the k^H/k^D of 1.2 at 50° is reasonably accurate; at 25° one would expect the ratio to increase slightly.