melting point of VI was identical with those previously reported.[12]

The nmr spectrum of VIII showed contamination with VI and had absorption at τ 3.85, 6.10, 7.05 and 7.6–8.8. The glpc analysis showed that VIII was contaminated with 14% VI.

Anal. Calcd for $C_7H_8Cl_2$: C, 51.53; H, 4.91. Found: C, 51.67; H, 4.84.

The fraction from the distillation of the reaction mixture was recrystallized from cold pentane and 70 g of VI was isolated. The filtrate from this recrystallization shown by glpc analysis to be enriched in VIII was 65% VIII and 35% VI.

The enriched mixture was subjected to catalytic hydrogenation with PtO_2 according to the method used by Roberts.[13] This mixture yielded two isomeric dichlorides, IX and III, after the uptake of 1 mole of hydrogen. Analysis by nmr and glpc showed the mixture to be 65% III and 35% IX. The products were separated and collected by preparative glpc from a 20 ft × 0.25 in. SF-96 column. Compound IX had an identical mp 71–74° and infrared (CS_2) spectrum as those reported by Roberts.[13]

Compound III, a liquid, was shown by its nmr and microanalysis to be isomeric to IX and was assigned the structure of *exo,cis*-2,3-dichloronorbornane. The nmr spectrum of III was in agreement with that reported for this compound[8] and showed absorption at τ 6.06 (doublet, J = 2 cps), 7.55 (multiplet), and 7.7–8.9 (unresolved multiplet) with intensities of 2.0:2.0:6.0.

Anal. Calcd for $C_7H_{10}Cl_2$: C, 50.90; H, 6.06. Found: C, 51.02; H, 6.01.

Reactions of IBD and Norbornene.—Reactions were carried out in sealed Pyrex ampoules. Reactions which were run in the absence of molecular oxygen were degassed by the freeze–thaw method. The ampoules were continuously shaken during either the thermal or photoinitiated experiments. Photoinitiation was carried out using a Hanovia lamp (model 30620) or two 200-w incandescent light bulbs. The reaction was completed when the solid IBD had all gone into solution and the reaction mixture was clear. The reaction was shown to be complete by iodometric titration.

Typical reaction mixtures were 2–3 ml of 0.15–0.8 *M* norbornene in carbon tetrachloride and 0.13–0.23 mmole/ml of iodobenzene dichloride.

Analysis of Reaction Mixtures.—The product mixtures were analyzed by glpc on both a 10 ft × 0.25 in., 15% SF-96 on firebrick column and a 10 ft × 1/8 in., 5% SE-30 on Chromosorb W column or on a 30 ft × 1/8 in. column consisting of 20-ft 5% SE-30 and 10-ft 5% SE-96 on Chromosorb W. The chromatographic bands were identified by their comparison with the retention times of the authentic samples on the two columns. The products of typical reactions were collected from the SF-96 column and the nmr and infrared spectra were shown to be identical with those of the authentic compounds. Percentages were calculated for the integrated areas of the chromatographic peaks by the method of peak height times peak width at one-half peak height.

Material Balance.—The material balance for typical reactions was obtained, in the usual manner,[9] using Freon 112 as the internal standard. Molar ratios were calculated from calibration curves of Freon 112 and the authentic samples. In the case of the halogenated norbornanes the calibration curve for II was used as a typical curve for all of the halogenated norbornanes.

Registry No.—I, 498-66-8; III, 14627-75-9; IV, 3509-46-4; V, 4660-48-4; VIII, 14627-78-2; *cis*-dichloroethenes, 156-59-2; cyclopentadiene, 542-92-7.

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Intramolecular Alkylation as an Approach to Cyclic Sulfones and Sulfides

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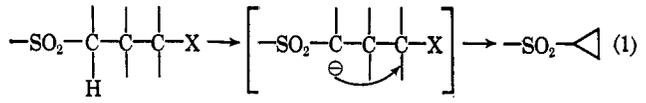
A variety of cyclobutyl, cyclopentyl, and substituted pentamethylene sulfones have been prepared by α,ω-dehydrohalogenation of the corresponding ω-chloroalkyl sulfones. Several aryl cyclopropyl sulfides and 2-phenyltetrahydrothiophenes have also been prepared in this manner from the ω-chloroalkyl sulfides. This approach represents a useful synthesis of these and similar types of compounds.

A previous communication from this laboratory[1] described the preparation of cyclopropyl sufones by α,γ-dehydrohalogenation of various γ-chloropropyl sulfones (eq 1). This approach to cycloalkyl sulfones



(1)

has been extended in the present communication to include the preparation of cyclobutyl and cyclopentyl sulfones and cyclopropyl sulfides. Furthermore, the dehydrohalogenation procedure gives rise to substituted pentamethylene sulfones or 2-phenyltetrahydrothiophenes when permitted by the structures of the precursors.

Cyclobutyl sulfones had not previously been investigated except for the probable preparation of methyl cyclobutyl sulfone,[2] in low yield, from reaction of cyclobutyl bromide with sodium methanesulfinate. The cyclopentyl sulfones, however, have commonly been prepared by oxidizing the corresponding sulfides, by treating cyclopentyl halides with sodium sulfinates, or by treating cyclopentanesulfinates with alkyl halides.[2-7] Variously substituted pentamethylene sulfones are known, prepared by oxidation of the corresponding sulfides.[8]

Cyclopropyl sulfides have been known since 1962, prepared in each case by reaction of chloromethyl sulfides with olefins in the presence of potassium *t*-butoxide, presumably through a carbene intermediate.[9-11] α-Substituted tetrahydrothiophenes have been pre-

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(2) W. E. Truce and J. P. Milionis, *ibid.*, **17**, 1529 (1952).
(3) S. Archer, C. M. Suter, and B. F. Tullar, British Patent 668,562 (March 19, 1952); *Chem. Abstr.*, **47**, 5447 (1953); also U. S. Patent 2,618,640 (Nov 25, 1952).
(4) F. G. Bordwell and R. J. Kern, *J. Am. Chem. Soc.*, **77**, 1141 (1955).
(5) J. Weinstock, R. G. Pearson, and F. G. Bordwell, *ibid.*, **78**, 3473 (1956).
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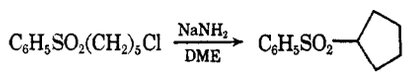
(9) U. Schollkopf, *et al.*, *Tetrahedron Letters*, 165 (1962); *Chem. Ber.*, **97**, 1527 (1964); *ibid.*, **99**, 806 (1966).
(10) H. Reimlinger, *Chem. Ind.* (London), 1682 (1966).
(11) A. M. van Leusen, R. J. Mulder, and J. Strating, *Rec. Trav. Chim.*, **86**, 225 (1967).

pared from the appropriate 1,4-dibromobutanes by treatment with sodium sulfide.[12]

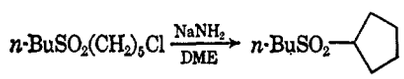
By internal alkylation, we have synthesized phenyl cyclopentyl sulfone from 5-chloropentyl phenyl sulfone and sodium amide in 1,2-dimethoxyethane (DME) (eq 2). The chlorosulfone precursor was obtained by treat-



(2)

ing 1,5-dichloropentane with potassium benzenethiolate and oxidizing the resulting sulfide to the sulfone. In a similar manner 5-chloropentyl *p*-tolyl sulfone was cyclized to *p*-tolyl cyclopentyl sulfone.

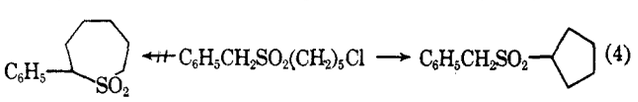
Alkyl cyclopentyl sulfones can also be prepared conveniently by this method. As an example, *n*-butyl 5-chloropentyl sulfone was cyclized to *n*-butyl cyclopentyl sulfone by treatment with $NaNH_2$ in DME (eq 3). The chloro sulfone was not prepared by oxida-



(3)

tion of the chlorosulfide since alkyl 5-chloropentyl sulfides have been shown to undergo ring closure, forming cyclic sulfonium salts under relatively mild conditions.[13] In order to prepare the precursor, 5-chloro-1-pentanol was allowed to react with sodium *n*-butanethiolate to give *n*-butyl 5-hydroxypentyl sulfide, which was oxidized to the corresponding 5-hydroxypentyl sulfone. Treatment of this product with thionyl chloride gave the desired *n*-butyl 5-chloropentyl sulfone.

Cyclization of benzyl 5-chloropentyl sulfone might have been expected to produce some of the seven-membered ring product since the benzylic hydrogen atoms (α') are more acidic than the hydrogens in the α position. However, treatment of this sulfone with $NaNH_2$ in DME led exclusively to the five-membered ring product, benzyl cyclopentyl sulfone (eq 4).

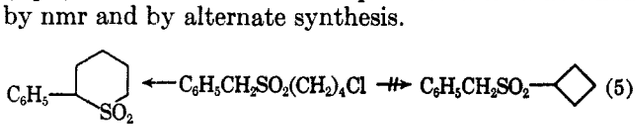


(4)

Each of the cyclopentyl sulfones prepared by the above method was also independently prepared by treating cyclopentyl bromide with the corresponding thiolate and oxidizing the product.

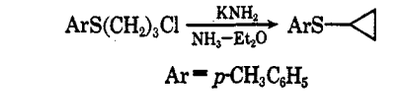
Aryl cyclobutyl sulfones can also be prepared by internal alkylation. For example, *p*-tolyl 4-chlorobutyl sulfone cyclizes cleanly to *p*-tolyl cyclobutyl sulfone when treated with $NaNH_2$ in DME. The product was independently synthesized from cyclobutyl bromide by the same method used for the cyclopentyl sulfones.

Unlike benzyl 5-chloropentyl sulfone, which cyclizes to the five-membered ring instead of to the seven-membered structure, benzyl 4-chlorobutyl sulfone cyclizes to the larger of its two possible cyclic products (eq 5). The structure of the product was established by nmr and by alternate synthesis.



(5)

The internal alkylation approach to cyclic structures has also been extended to the preparation of aryl cyclopropyl sulfides. Sodium amide in 1,2-dimethoxyethane was unsatisfactory for use in these reactions, however, since it reacted with *p*-tolyl 3-chloropropyl sulfide to give the propenyl sulfide by β elimination, instead of the desired cyclopropyl sulfide. Potassium amide in a liquid ammonia–ether solvent system was found to produce aryl cyclopropyl sulfides in good yield (eq 6).

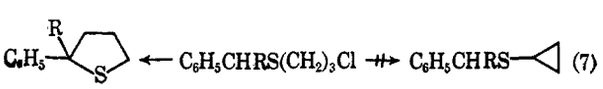


(6)

Ar = *p*-$CH_3C_6H_5$

Other less satisfactory base–solvent systems investigated for this reaction include NaH in DME, KO-*t*-Bu in DMSO, *n*-BuLi in hexane, and the lithium amide of ethylenediamine. Of these, the last reagent gave a 40% yield of cyclic product, KO-*t*-Bu in *t*-BuOH produced the propenyl sulfide, and the remaining systems gave either unreacted sulfide or polymeric material.

Alkyl 3-chloropropyl sulfides usually decomposed to a number of products (detected by vpc) when heated neat or treated with KNH_2 in NH_3–Et_2O. The processes involved probably result from intra and intermolecular sulfonium compounds.[13] However, benzylic 3-chloropropyl sulfides can be cyclized by α,ω-dehydrohalogenation, and in this case the five-membered 2-phenyltetrahydrothiophene structure is formed in preference to the cyclopropyl ring (eq 7). Potassium amide



(7)

R = H (95%), CH_3 (76%)

in ammonia–ether is again the system of choice, since a maximum yield of 38% (R = H) was obtained with sodium amide in 1,2-dimethoxyethane.

An attempt to prepare *p*-tolyl cyclobutyl sulfide from the aryl 4-chlorobutyl sulfide with KNH_2 in NH_3–Et_2O resulted only in decomposition. The reduced acidity of the sulfides as compared to sulfones is apparently an important factor in permitting alternate processes, such as sulfonium salt formation, to compete with proton abstraction and cyclization.

The observed preferences for ring formation, *i.e.*, five- *vs.* three- or seven-membered and six- *vs.* four-membered ring structures, correspond to results found for cyclization or hydrolysis with participation in systems such as ω-haloamines,[14] ω-halo sulfides (to form sulfonium salts),[13,15] and ω-haloalkanoic acids.[16] Ring strain causes the formation of the three- and four-membered ring structures to be thermodynamically unfavorable compared with the five- and six-membered rings. In the relatively strainless five- and seven-membered ring systems, entropy factors favor formation of the smaller ring. The products obtained show that, in the sulfones at least, the relative acidity of the α and α' hydrogens is not a decisive factor in the direction of cyclization. Presumably, if the more acidic benzylic hydrogen is abstracted first, from benzyl 5-chloropentyl sulfone, a fast equilibration to the more basic carbanion

(12) R. D. Obolentsev and V. G. Bukharov, *Chem. Abstr.*, **55**, 25907 (1961).

(13) G. M. Bennett and E. G. Turner, *J. Chem. Soc.*, 813 (1938); W. E. Truce, W. W. Bannister, and R. H. Knospe, *J. Org. Chem.*, **27**, 2821 (1962).

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(15) G. M. Bennett, F. Heathcoat, and A. N. Mossus, *J. Chem. Soc.*, 2567 (1929).

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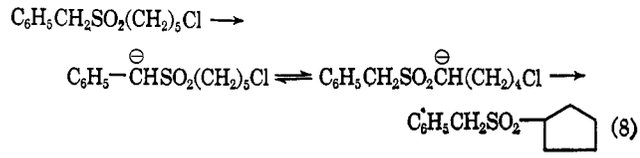
occurs, so that the favored product can be formed in the slow step of the reaction (eq 8).



(8)

Experimental Section[17]

ω-Chloroalkyl Sulfides and Sulfones.—These sulfides, with the exception of *n*-butyl 5-chloropentyl sulfide, were prepared by treating an α,ω-dihaloalkane (dichloro or bromochloro as commercially available) with a thiol in aqueous base to form the ω-chloroalkyl sulfide. The physical constants and yields are listed in Table I. Several of the sulfides were oxidized with hydrogen

TABLE I

ω-HALOALKYL SULFIDES, $RS(CH_2)_nCl$

Compd (no.)	Bp, n_D	% yield
R = phenyl; *n* = 5 (1)	138° (1.2 mm), $n^{29.5}D$ 1.5554[a]	85
R = *p*-tolyl; *n* = 5 (2)	184–186° (10 mm)[b]	68
R = benzyl; *n* = 5 (3)	155–157° (1.7 mm)	44
R = phenyl; *n* = 4 (4)	124–126° (2 mm), $n^{20}D$ 1.5678[c]	60
R = *p*-tolyl; *n* = 4 (5)	141–142° (2 mm), $n^{25}D$ 1.5572	71
R = benzyl; *n* = 4[d] (6)		75
R = phenyl; *n* = 3 (7)	110–111° (1.6 mm), $n^{20}D$ 1.5752[e]	74
R = *p*-tolyl; *n* = 3 (8)	125–127° (3 mm), $n^{21}D$ 1.5850[f]	59
R = benzyl; *n* = 3 (9)	168–169° (19 mm), $n^{20}D$ 1.5622	81
R = 1-phenethyl, *n* = 3[g]		
R = 2-phenethyl, *n* = 3 (10)	128–129° (1.3 mm), $n^{27}D$ 1.5497	91
R = butyl, *n* = 3 (11)	69–71° (2.0 mm), $n^{25}D$ 1.4780	52
R = methyl, *n* = 3 (12)	64–66° (19 mm), $n^{25}D$ 1.4866[h]	63

[a] Lit.[16] bp 140° (1 mm), $n^{20}D$ 1.5604. [b] Mp 34–36°. [c] Lit.[15] bp 155° (12 mm), $n^{20}D$ 1.5683. [d] Used crude. [e] W. R. Kirner and G. H. Richter (*J. Am. Chem. Soc.*, **51**, 3409 (1929)) reported bp 116–117° (4 mm), $n^{20}D$ 1.5752. [f] *Anal.* Calcd: C, 59.84; H, 6.53. Found: C, 59.93; H, 6.49. E. E. Reid ("Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., Inc., New York, N. Y., 1960, p 325) reported bp 127–128° (5 mm). [g] Used crude, over 90% pure by vpc. [h] W. R. Kirner (*J. Am. Chem. Soc.*, **50**, 2446 (1928)) reported bp 71.2° (29 mm), $n^{30}D$ 1.4833.

peroxide to the corresponding sulfones. The results are listed in Table II. All of the sulfone products showed sulfone absorptions in the ranges 7.6–7.8 and 8.8–9.0 μ, and C–Cl absorption near 14 μ in their infrared spectra. As a typical example, phenyl 5-chloropentyl sulfone was prepared in the following manner.

A solution of 70.5 g (0.50 mole) of 1,5-dichloropentane in 200 ml of water containing 33.0 g (0.60 mole) of potassium hydroxide was stirred rapidly as 55.0 g (0.50 mole) of benzenethiol was slowly added. The reaction mixture was refluxed for 6 hr, cooled, and extracted with three 150-ml portions of ether. The combined ether extracts were washed with three 100-ml portions of water and dried over sodium sulfate. After removal of the ether with an aspirator, the residue was distilled: 91.4 g (85.2% yield), bp 138° (1.2 mm), $n^{29.0}D$ 1.5554 (lit.[15] bp 140° (1 mm), $n^{20}D$ 1.5604). A solution of this material in 230 ml of glacial acetic acid was cooled in an ice bath as 69 ml of 30% H_2O_2 was slowly added with continuous stirring. After the addition, the reaction mixture was poured into 300 ml of water and extracted with three 200-ml portions of chloroform. After washing with 200 ml of 1 *N* NaOH and 200 ml of water, the chloroform solution was dried (Na_2SO_4), concentrated, then distilled, yielding 47.1 g (83% yield) of product: bp 193–195° (1.1 mm); infrared λ 7.80, 8.73, 14.8 μ.

(17) Melting points and boiling points are uncorrected. All nmr spectra were run on a Varian A-60 spectrometer operating at 60 Mc/sec, with TMS as an internal standard. Microanalyses were performed by Dr. C. S. Yeh and her staff.

Anal. Calcd for $C_{11}H_{15}ClO_2S$: C, 53.53; H, 6.13; S, 12.99. Found: C, 53.80; H, 6.05; S, 12.83.

***n*-Butyl 5-Chloropentyl Sulfide.**—Sodium metal (5.8 g, 0.25 g-atom) was added to 125 ml of absolute ethanol under N_2 with continuous stirring. After the sodium was dissolved 22.5 g (0.25 mole) of *n*-butanethiol was added. The reaction mixture was cooled in an ice bath as 30.7 g (0.28 mole) of redistilled 4-chloro-1-butanol was slowly added. After addition was complete, the solution was allowed to come slowly to room temperature and was then refluxed 1 hr. Upon cooling, a quantitative yield of NaCl precipitated and was removed. The filtrate was concentrated, then distilled, yielding 37.8 g (86%) of *n*-butyl 5-hydroxypentyl sulfide: bp 122–125° (2.8 mm); infrared λ 2.82, 9.33 μ.

Anal. Calcd for $C_9H_{20}OS$: C, 61.33; H, 11.44; S, 18.15. Found: C, 61.36; H, 11.55; S, 17.90.

The 5-hydroxypentyl sulfide was oxidized to the sulfone as follows: a solution of 34.0 g (0.19 mole) of the sulfide in 100 ml of acetone was cooled in an ice bath as 60 ml of 30% H_2O_2 was slowly added with stirring. After gradually warming to room temperature, the reaction was refluxed for 1 hr. The solvent was removed *in vacuo* and the solid residue recrystallized from ether yielding 32.8 g (83%) of a white solid: mp 53.0–54.5°; infrared λ 2.83, 7.70, 8.84, and 9.40 μ. The nmr spectrum (10% solution in $CDCl_3$) showed multiple absorptions at δ 0.95, 1.60, 3.00, and 3.61, and a singlet at 2.67 with relative areas of 3:10:4:2:1, respectively.

Anal. Calcd for $C_9H_{20}O_3S$: C, 51.79; H, 9.68; S, 15.39. Found: C, 52.00; H, 9.61; S, 15.50.

To obtain the 5-chloropentyl sulfone, a solution of 15.6 g (0.075 mole) of *n*-butyl 5-hydroxypentyl sulfone in 40 ml of dry chloroform was treated slowly with a solution of 10 g (6.5 ml, 0.084 mole) of thionyl chloride (bp 75–76°) in 7 ml of dry chloroform. The mixture was stirred at room temperature for 6 hr, then evaporated *in vacuo*. The solid residue was recrystallized from hexane, yielding 12.0 g (71%) of white crystals: mp 38.0–39.5°; infrared λ 7.68, 8.81, 15.25 μ. The nmr spectrum (10% in $CDCl_3$) showed multiple absorptions at δ 0.92, 1.69, 2.96, and 3.54, with relative areas of 3:10:4:2.

Anal. Calcd for $C_9H_{19}ClO_2S$: C, 47.65; H, 8.44; S, 14.13. Found: C, 47.90; H, 8.43; S, 14.37.

Cycloalkyl Sulfones by Cyclization.—The internal alkylation procedure for preparing cycloalkyl sulfones consisted of treating the ω-chloroalkyl sulfones with excess sodium amide in 1,2-dimethoxyethane (DME). The products summarized in Table III, all showed sulfone absorptions in the ranges 7.6–7.8 and 8.8–9.0 μ in their infrared spectra. All were alternately synthesized and identified by comparison of physical properties and infrared spectra. As a typical example of the internal alkylation reaction, benzyl cyclopentyl sulfone was prepared in the following manner.

Benzyl 5-chloropentyl sulfone (6.5 g, 0.025 mole) was added to a mixture of 1.6 g (0.040 mole) of sodium amide in 25 ml of DME under N_2. After refluxing overnight, the reaction mixture was poured onto ice. The oil which appeared was combined with ether extracts of the remaining aqueous solution and dried (Na_2SO_4). Removal of the solvent and cooling induced crystallization of the residue. Recrystallization from methanol yielded 4.4 g (0.020 mole, 79%) of white crystals: mp 83–85°; infrared λ 7.72, 8.98 μ. Comparison with an independently synthesized sample by melting point, mixture melting point, and infrared spectra established the structure of the product.

Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; S, 14.29. Found: C, 64.41; H, 7.03; S, 14.12.

Cycloalkyl Sulfones by Oxidation.—The sulfones described in Table III, products of cyclization, were independently prepared by formation of the corresponding sulfide from cycloalkyl halides and the appropriate mercaptide, followed by oxidation. The physical properties of these compounds are listed in Table IV. For example, *n*-butyl cyclopentyl sulfone was prepared in the following manner.

Sodium metal (4.6 g, 0.20 g-atom) was added in small pieces to 85 ml of absolute ethanol under N_2. After the sodium was dissolved and the solution cooled, 18.0 g (0.20 mole) of *n*-butanethiol was added. The reaction mixture was cooled in an ice bath as 29.8 g (0.20 mole) of cyclopentyl bromide (MCB, bp 137–138°) was slowly added. After the addition, the ice bath was removed and the reaction stirred at room temperature overnight. After filtration to remove the NaBr, the solvent was removed and the residue distilled, yielding 26.4 g (84%) of the

TABLE II

ω-HALOALKYL SULFONES, $RSO_2(CH_2)_nCl$

Compd (no.)	Mp or bp	% yield	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
R = phenyl, n = 5 (**13**)	193–195° (1.1 mm)	83	53.53	6.13	12.99	53.80	6.05	12.83
R = *p*-tolyl, n = 5 (**14**)	205–207° (1.0 mm)	73	55.27	6.57	12.29	55.50	6.69	12.22
R = benzyl, n = 5 (**15**)	95–98°	81	55.27	6.57	12.29	55.58	6.79	12.00
R = butyl, n = 5 (**16**)	38–39.5°[a]	71	47.65	8.44	14.13	47.90	8.43	14.37
R = *p*-tolyl, n = 4 (**17**)	38–39.5°[b]	80	53.53	6.13	*c*	53.52	5.85	*c*
R = benzyl, n = 4 (**18**)	106–107°	63	53.53	6.13	12.99	53.66	5.90	13.32

[a] Recrystallized from hexane. [b] Recrystallized from methanol. [c] *Anal.* Calcd for Cl: 14.53. Found: 14.23.

TABLE III

CYCLOALKYL SULFONES, $RSO_2CH(CH_2)_n$, BY CYCLIZATION

Compd (no.)	Mp or bp, n_D	% yield	Calcd, % C	Calcd, % H	Calcd, % S	Found, % C	Found, % H	Found, % S
R = phenyl; n = 4 (**19**)	61–63°[a]	85	62.86	6.67		62.99	6.64	
R = *p*-tolyl; n = 4 (**20**)	50.5–52°[a]	82	64.25	7.19	14.29	64.31	7.26	14.02
R = benzyl; n = 4 (**21**)	83–85°	79	64.25	7.19	14.29	64.41	7.03	14.12
R = *n*-butyl; n = 4 (**22**)	127–128° (1.4 mm), $n^{22.5}$ 1.4792[b]	71	56.80	9.53	16.85	57.04	9.75	16.58
R = *p*-tolyl; n = 3 (**23**)	150–155° (0.4 mm), $n^{24}D$ 1.5496[c]	52	62.86	6.67		62.91	6.48	

[a] Recrystallized from methanol. [b] Lit.[2] bp 129° (2 mm); $n^{20}D$ 1.4812; nmr peaks at δ 1.00, 1.77, 2.82, and 3.35, with ratio 3:12:2:1. [c] Mp 45–47°.

TABLE IV

CYCLOALKYL SULFONES, $RSO_2CH(CH_2)_n$, BY OXIDATION

Compd	Mp or bp, n_D	% yield of sulfone	Intermediate sulfides, $RSCH(CH_2)_n$ Bp, n_D	Intermediate sulfides, % yield
R = phenyl; n = 4	61–63°[a]	91	97–99° (2 mm), $n^{25}D$ 1.5747[b]	74
R = *p*-tolyl; n = 4	50–52°[c]	72	91–94° (0.4 mm), $n^{25}D$ 1.5638	69
R = benzyl; n = 4	84–85°[a]	74	*d*	88
R = *n*-butyl; n = 4	126–128° (1.3 mm), $n^{24}D$ 1.4790[e]	74	65–67° (2.5 mm), $n^{23}D$ 1.4797	84
R = *p*-tolyl; n = 3	44.5–46.5°	81	96° (0.7 mm), $n^{25}D$ 1.5662	43

[a] Recrystallized from methanol. [b] A boiling point of 139.5° (13 mm) and an index of refraction of $n^{20}D$ 1.5740 has been reported: I. N. Tits-Skvortsova, S. YaLevina, A. I. Leonova, and T. A. Danilova, *Dokl. Akad. Nauk SSSR*, **74**, 291 (1950); *Chem. Abstr.*, **45**, 9487 (1951). [c] Bp 144–146° (0.3 mm). [d] Crude material shown by vpc to be more than 95% pure; used directly. [e] Lit.[2] bp 129° (2 mm), $n^{25}D$ 1.4812.

cyclopentyl sulfide, bp 65–67° (2.5 mm), $n^{23}D$ 1.4797. A solution of 7.9 g (0.05 mole) of this liquid in 50 ml of acetone was cooled in an ice bath as 15 ml of 30% H_2O_2 was slowly added. When addition was complete the ice bath was removed, and after 0.5 hr the solution was refluxed for 1.5 hr. Upon cooling, the solvent was removed and the residue distilled. Seven grams of sulfone (74% yield) were obtained, bp 126–128° (1.3 mm), $n^{24}D$ 1.4790 (lit.[2] bp 129° (2 mm), $n^{25}D$ 1.4812).

2-Phenyltetrahydrothiapyran 1,1-Dioxide by Cyclization.—Benzyl 4-chlorobutyl sulfone (25 g, 0.10 mole) was added to a mixture of 7.8 g (0.20 mole) of sodium amide in 150 ml of DME. After refluxing overnight, the reaction mixture was poured onto ice yielding a crystalline product. Recrystallization from methanol yielded 12.7 g (60%) of white crystals: mp 182–184.5°; infrared λ 7.60, 8.78 μ. The nmr spectrum contained absorptions at δ 2.17, 3.10, 4.0, and 7.32 with corresponding relative areas of 6:2:1:5.

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 62.52; H, 6.65; S, 15.47.

Alternate Synthesis of 2-Phenyltetrahydrothiapyran 1,1-Dioxide.—This compound was independently prepared by converting 2-phenyltetrahydropyran to 2-phenyltetrahydrothiapyran, and oxidizing this product to the corresponding sulfone. A solution of 63.0 g (0.33 mole) of γ-benzoylbutyric acid[18] in 100 ml of dry ether and 500 ml of dry tetrahydrofuran was slowly added to a rapidly stirred mixture of 25.0 g (0.66 mole) of lithium aluminum hydride in 600 ml of dry tetrahydrofuran under N_2. The reaction mixture was stirred for a total of 4 hr, including time of addition, and then 700 ml of water was added with extreme caution. Following this, 750 ml of 15% H_2SO_4 was added, and the layers were separated. The aqueous layer was extracted with ether, the organic layers combined and dried (K_2CO_3). A reaction occurred with the drying agent and the solution separated into two layers. The top layer was decanted and the solvent removed. The residue was distilled twice, yielding 24.2 g (45%) of 2-phenyltetrahydropyran, bp 82–83° (1.8 mm), $n^{21.2}D$ 1.5267 (lit.[19] bp 105–106° (10 mm), $n^{20}D$ 1.5273). The infrared spectrum contained a strong ether absorption at 9.16 μ, but no hydroxyl peaks. The nmr spectrum (10% solution in CCl_4) shows absorptions at δ 1.6, 3.5, 4.15, and 7.2 with relative areas of 6:1:2:5, respectively.

Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70; mol wt, 162. Found: C, 81.55; H, 8.77; mol wt, 163.

2-Phenyltetrahydrothiapyran was obtained in the following manner. Powdered phosphorus pentasulfide (42 g, 0.19 mole) was added to a rapidly stirred solution of 14.0 g (0.086 mole) of 2-phenyltetrahydropyran in 175 ml of *p*-xylene. After refluxing for 6 hr, the reaction mixture was cooled and the solids were removed. The filtrate, combined with the *p*-xylene washings of the residue, was concentrated and then distilled (bp 90–91° (0.55 mm)). The product crystallized on cooling and was recrystallized from aqueous ethanol, yielding 2.84 g (19%) of white crystals, mp 50–51°. The nmr spectrum contained absorptions at δ 2.0, 2.65, 3.75, and 7.18 with relative areas of 6:2:1:5.

Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.92; S, 17.98. Found: C, 74.12; H, 8.04; S, 18.12.

A solution of 1.1 g (0.006 mole) of 2-phenyltetrahydrothiapyran in 10 ml of glacial acetic acid and 5 ml of acetone was cooled in an ice bath as 2 ml of 30% H_2O_2 was slowly added. After refluxing 1 hr, the reaction mixture was poured onto ice and then extracted with chloroform. After drying (Na_2SO_4), the chloroform was removed and the residue recrystallized from methanol, 0.73 g (58% yield), mp 184–185°, mmp 182–184.5°; the infrared spectrum was identical with that of the cyclization product.

Aryl Cyclopropyl Sulfides by Cyclization.—Phenyl and *p*-tolyl 3-chloropropyl sulfides were cyclized in high yield using potassium amide in liquid ammonia–ether. Alkyl 3-chloropropyl

(18) L. F. Sommerville and C. F. Allen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 82.

(19) F. W. Hayes and D. E. Peterson, *J. Am. Chem. Soc.*, **73**, 5273 (1951).

sulfides, such as methyl, *n*-butyl and 2-phenylethyl, resulted in polymeric decompositions from which no products were isolated.

Potassium metal (8.7 g, 0.2 g-atom) was added in small pieces to a rapidly stirred solution of 0.5 g of ferric nitrate nonahydrate in 250 ml of condensed ammonia. After the blue color was discharged, 19 g (0.10 mole) of phenyl 3-chloropropyl sulfide in 250 ml of dry ether was slowly added. The ammonia was allowed to evaporate slowly from the solution, then the solution was refluxed for 3 hr. Upon cooling, the reaction mixture was hydrolyzed with water and filtered, and the ether layer was separated. The aqueous layer was extracted with ether; the ether solutions were combined, washed with water, dried ($CaCl_2$), and evaporated. The residue was distilled, yielding 11.7 g (79%) of phenyl cyclopropyl sulfide, bp 62–63° (1.0 mm), $n^{25}D$ 1.5801.

Anal. Calcd for $C_9H_{10}S$: C, 71.95; H, 6.71; S, 21.34. Found: C, 72.05; H, 6.75; S, 21.60.

A portion of this sulfide was oxidized to the known sulfone with 30% H_2O_2 in glacial acetic acid. The product melted at 35.5–36.5°, bp 129–131° (1.0 mm) (lit.[1,20] bp 130–135° (0.5 mm), mp 35–36°).

A similar cyclization procedure using *p*-tolyl 3-chloropropyl sulfide gave a 58% yield of *p*-tolyl cyclopropyl sulfide, bp 87° (2.3 mm), $n^{20}D$ 1.5713.

Anal. Calcd for $C_{10}H_{12}S$: C, 73.57; H, 6.79; S, 19.64. Found: C, 73.38; H, 6.54; S, 19.40.

α-Substituted Tetrahydrothiophenes by Cyclization.—Benzylic 3-chloropropyl sulfides undergo intramolecular alkylation to form 2-phenyltetrahydrothiophenes with potassium amide in ammonia–ether. The procedure above for preparation of aryl cyclopropyl sulfides by cyclization was used with the reflux period increased to 16 hr. In this manner 20.9 g of benzyl 3-chloropropyl sulfide was converted to 15.5 g of 2-phenyltetrahydrothiophene (95% yield), bp 118–120° (5 mm), $n^{25}D$ 1.5829 (lit.[12] bp 105–106° (3 mm), $n^{20}D$ 1.5839. A portion of this tetrahydrothiophene was oxidized to 2-phenyltetrahydrothiophene-1,1-dioxide with 30% H_2O_2 in glacial acetic acid, mp (methanol) 65–65.5°.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.12. Found: C, 61.03; H, 5.88.

Similarly 21.5 g (0.10 mole) of 1-phenethyl 3-chloropropyl sulfide was cyclized to give 13.6 g (76% yield) of 2-methyl-2-phenyltetrahydrothiophene, bp 90° (0.5 mm).

Anal. Calcd for $C_{11}H_{14}S$: C, 74.10; H, 7.92; S, 17.99. Found: C, 73.99; H, 7.72; S, 17.98.

(20) H. E. Zimmerman and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **82**, 2505 (1960).

A portion of this 2,2-disubstituted tetrahydrothiophene was oxidized to 2-methyl-2-phenyltetrahydrothiophene-1,1-dioxide using 30% H_2O_2 in glacial acetic acid, mp 54–55°. 2-Phenyltetrahydrothiophene-1,1-dioxide was methylated to give the same compound, as follows: a solution of 0.80 g (0.004 mole) of 2-phenyltetrahydrothiophene-1,1-dioxide in 40 ml of anhydrous dimethylformamide was treated with 3.6 ml (0.008 mole) of sodium hydride–nujol dispersion. After 3.5 hr, 0.84 g (0.006 mole) of purified methyl iodide in anhydrous dimethylformamide was added to the reaction mixture. After 5 hr of additional stirring, the reaction was hydrolyzed with water and extracted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated. The residue was washed with ether, leaving 0.31 g (36% yield) of product, mp 53–55°, mmp 53–55°.

Registry No.—**1**, 14633-28-4; **2**, 14633-29-5; **3**, 14633-30-8; **4**, 14633-31-9; **5**, 14633-32-0; **7**, 4911-65-3; **8**, 3147-30-6; **9**, 14633-35-3; **10**, 14633-36-4; **11**, 14856-63-4; **12**, 13012-59-4; **13**, 14633-38-6; **14**, 14633-39-7; **15**, 14633-40-0; **16**, 14633-41-1; **17**, 14633-42-2; **18**, 14633-43-3; *n*-butyl 5-hydroxypentyl sulfide, 14633-44-4; *n*-butyl 5-hydroxypentyl sulfone, 14633-45-5; **19**, 14633-46-6; **20**, 14633-47-7; **21**, 14633-48-8; **22**, 14633-49-9; **23**, 14633-50-2; cyclopentyl sulfide, 1613-51-0; 2-phenyltetrahydrothiapyran 1,1-dioxide, 14856-64-5; 2-phenyltetrahydropyran, 4203-44-5; 2-phenyltetrahydrothiopyran, 1622-06-6; phenyl cyclopropyl sulfide, 14633-54-6; *p*-tolyl cyclopropyl sulfide, 14633-55-7; 2-phenyltetrahydrothiophene, 2060-65-3; 2-phenyltetrahydrothiophene 1,1-dioxide, 13557-28-3; 2-methyl-2-phenyltetrahydrothiophene, 14856-67-8; 2-methyl-2-phenyltetrahydrothiophene 1,1-dioxide, 14633-57-9.

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Perhydroindan Derivatives. VIII. Bridgehead Alkylation *via* Cyclopropane Intermediates[1a]

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The copper-catalyzed decomposition of ethyl diazoacetate in the presence of enol acetate **1**, allylic acetate **6c**, and olefin **12** has been investigated. The cyclopropyl ester adducts **2** (from **1**) and **7a** (from **6c**) were converted into derivatives of 3a-perhydroindanylacetic acid having a *cis* ring fusion. The reductive cleavage of the adducts **13c** (from **12**) with lithium and ammonia gave a mixture of perhydroindanylacetic acids **11** and **15** in which the isomer **15** with a *trans* ring fusion predominated.

Since the alkylations of the enolate anions (*e.g.*, **1b**) derived from perhydroindan-1-one and several derivatives yield predominantly *cis*-fused perhydroindanone products (*e.g.*, **3b**),[2] we were led to examine other synthetic routes which might be used to introduce a bridgehead substituent into a preformed perhydroindan derivative to form a *trans*-fused product (*e.g.*, **4**). The copper-catalyzed reaction of ethyl diazoacetate with olefins to form cyclopropane derivatives[3] was selected for study with the olefins **1a**, **6c**, and **12** because it seemed probable that each of the initial cyclopropane derivatives **2**, **7**, and **13** could be converted to a perhydroindane with a bridgehead substituent. This paper reports the results of this study and the determination of the stereochemistry for the major alkylated product in each case.

Reaction of the enol acetate **1a** (Scheme I) with

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(2) H. O. House and C. J. Blankley, *J. Org. Chem.*, **32**, 1741 (1967), and references cited therein.

(3) For general reviews of this reaction, see (a) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, pp 108–156; (b) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 95–143; (c) W. Ried and H. Mengler, *Fortschr. Chem. Forsch.*, **5**, 1 (1965).