reproducible amount of SO₂ was formed. The experiments show that oxidation occurs immediately upon contact of the olefin with the acid and not after the olefin is adsorbed. This being the case, it should be possible to obtain more oxidation by a very slow or stepwise addition of olefin to the acid. This was found in an experiment in which five stepwide additions of olefin increased the SO₂ yield four- to fivefold.

A plausible explanation of these results is that the olefin is oxidized at the surface of the acid as it is being adsorbed, but once adsorbed it is converted to a form which is not easily oxidized. We believe that the inert form is mainly that of the t-amyl cation although other processes such as sulfonation or the extensive rearrange-

ments leading to cyclopentadienyl ions, as proposed by Deno,[5] could also lead to a relatively stable species.

Registry No.—Sulfuric acid, 7664-93-9; 3-methylpentane, 96-14-0; 2-methylpentane, 107-83-5; 2,4-dimethylpentane, 108-08-7; 2,3,4-trimethylpentane, 565-75-3; 2,2,4-trimethylpentane, 540-84-1; 2,3-dimethylbutane, 79-29-8; methylcyclopentane, 96-37-7; 2-methyl-2-butene, 513-35-9.

Acknowledgment.—We wish to thank the Esso Research and Engineering Co., for permission to publish these results, and Dr. J. P. Kennedy, for his helpful comments.

(5) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 132 (1964).

The Cleavage of Sulfides and Sulfones by Alkali Metals in Liquid Amines. III. The Cleavage of Alkyl Cycloalkyl and Dicycloalkyl Sulfides and Sulfones by Lithium in Methylamine[1a]

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A series of n-alkyl cycloalkyl sulfides and sulfones and a dicycloalkyl sulfide and sulfone was treated with lithium in methylamine, and the direction of cleavage was determined. The sulfide cleavages may be rationalized in terms of a radical process, whereas sulfone cleavages seem to reflect appreciable carbanion character.

Metal in amine solutions have been employed for the cleavage of many organic compounds, and mechanisms have been proposed involving one-electron (radical) and two-electron transfer (carbanion) processes.[2] Cleavage of ethers with sodium in ammonia has been explained by a carbanion mechanism,[2,3] whereas cleavage of tetraalkylammonium halides has been postulated to involve a gradation of mechanisms in which tertiary and secondary groups cleave as radicals, and primary groups cleave as carbanions.[4] Sulfides are cleaved by calcium hexaammine to give products whose formation can be rationalized on the basis of radical or carbanion processes.[5] Of the systems used for cleaving sulfides and sulfones,[5-8] the most general one was found to be lithium in methylamine, producing a hydrocarbon and a mercaptan or sulfinic acid, respectively, in good yields.[7] Alkyl aryl sulfide cleavages by this system were accounted for in terms of radical processes.[8] On the other hand, dialkyl sulfide fission was explained on the basis of a gradation of mechanisms, e.g., the cleavage of n-butyl sec-butyl sulfide yields equal amounts of n- and sec-butyl mercaptans, and the proposal was made that some factor other than radical or carbanion stability was involved.[8]

In the present work, cleavage has been extended to a series of alkyl cycloalkyl sulfides and their corresponding sulfones and a dicycloalkyl sulfide and its sulfone.

Results

The sulfides shown below (I–IV) were prepared by nucleophilic displacement by mercaptide on a halide or tosylate. Cleavage was accomplished by dropwise addition of lithium dissolved in methylamine to a solution of sulfide in methylamine at the boiling point of the solvent (−7°).[7] After cleavage, the mercaptan fraction was isolated, and its composition was determined by vpc. Details and results of the cleavages are shown in Table I.

$$R^A—S^B—CH(CH_2)_{n-1}$$
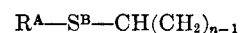
I, R = C₆H₁₁; n = 5
II, R = n-C₇H₁₅; n = 5
III, R = n-C₇H₁₅; n = 6
IV, R = n-C₇H₁₅; n = 4

Cyclohexyl cyclopentyl sulfide (I) cleaved chiefly at bond B (79%), whereas the amount of fission at bond B increased to 87% for cyclopentyl n-heptyl sulfide (II). Cyclohexyl n-heptyl sulfide (III) showed only a slight preference for bond-B breakage (56%), and the direction of cleavage shifted to bond A (62%) for cyclobutyl n-heptyl sulfide (IV).

The corresponding sulfones listed below were prepared by oxidation of the sulfides, and cleaved in the same manner as the sulfides except that the work-up differed. The sulfinic acid fraction was difficult to analyze; therefore the hydrocarbon fraction was analyzed by vpc, and the yield was determined by addition of an internal standard. Since a liquid cyclobutyl portion was desired for vpc analysis, a methyl group was placed in the 3 position of the cyclobutane ring,

(1) (a) Abstracted from the Ph.D. Thesis of F. J. F. (b) To whom inquires should be directed at Illinois Wesleyan University, Bloomington, Ill.

(2) A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

(3) F. J. Sowa, et al., *J. Am. Chem. Soc.*, **59**, 603, 1488 (1937); **60**, 94 (1938).

(4) E. Grovenstein and R. W. Stevenson, *ibid.*, **81**, 4850 (1959).

(5) J. Van Schooten, J. Knotnerus, H. Boer, and Ph. M. Duinker, *Rec. Trav. Chim.*, **77**, 935 (1958).

(6) (a) F. E. Williams and E. Gebauer-Fuelnegg, *J. Am. Chem. Soc.*, **53**, 352 (1931); (b) R. C. Krug and S. Tocker, *J. Org. Chem.*, **20**, 1 (1955); (c) G. K. Hughes and E. P. O. Thompson, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 269 (1949).

(7) W. E. Truce, D. P. Tate, and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960).

(8) W. E. Truce and J. J. Breiter, *ibid.*, **84**, 1621 (1962).

TABLE I

Compd	R'^{A}—S^B—R R'	R	Sulfide, mole	Lithium, g-atom	CH$_3$NH$_2$, ml	Yield, %	RSH, mole %	R'SH, mole %
I	C$_6$H$_{11}$	C$_5$H$_9$	0.025	0.050	50	80	21	79
II	n-C$_7$H$_{15}$	C$_5$H$_9$	0.026	0.053	50	88	13	87
III	n-C$_7$H$_{15}$	C$_6$H$_{11}$	0.027	0.055	50	93	44	56
IV	n-C$_7$H$_{15}$	C$_4$H$_7$	0.026	0.052	50	92	62^a	38

^{a} Identity shown by elemental analysis and infrared spectrum.

TABLE II

Compd	R'^{A}—SO$_2$^{B}—R R'	R	Sulfone, mole	Lithium, g-atom	CH$_3$NH$_2$, ml	Yield, %	RH, mole %	R'H, mole %
V	C$_6$H$_{11}$	C$_5$H$_9$	0.025	0.050	50	96	83	17
VI	n-C$_7$H$_{15}$	C$_5$H$_9$	0.025	0.050	50	78	70	30
VII	n-C$_7$H$_{15}$	C$_6$H$_{11}$	0.015	0.030	30	56	30	70
VIII	n-C$_7$H$_{15}$	3-CH$_3$C$_4$H$_6$	0.010	0.020	30	87	29^a	71

^{a} Authentic sample prepared by reaction of lithium aluminum hydride and cyclobutyl methyl tosylate.

TABLE III

COMPOUNDS PREPARED IN A MANNER SIMILAR TO THAT DESCRIBED

Compd	Yield, %	Bp (mm) or mp, °C	n^{20}D	Lit. Bp (mm) or mp, °C	n^{20}D	Calcd, % C	H	S	Found, % C	H	S
I^{a,b}	54	119–124 (8.5)	1.5118	119–120 (0.3)	1.5118	...	...	...	...	...	...
II	62	84–86 (0.6)	1.4792	...	...	71.95	12.08	15.98	72.10	12.24	15.74
V^c	74	72–73		71–72		...	...	...	...	...	...
VI	40	132–134 (0.4)	1.4770	...	...	62.02	10.41	13.80	62.31	10.53	13.79
VII	39	172–173 (1.5)	1.4873	...	...	63.36	10.66	13.01	63.64	10.45	13.12
VIII	50	137–142 (0.5)	1.4680	...	...	62.02	10.41	13.80	61.78	10.47	14.02

^{a} Cyclopentyl tosylate was used; all other sulfides were prepared from halides. ^{b} I. N. Tits-Skvortsova, A. I. Leonova, and S. Ya. Levina, *Zh. Obshch. Khim.*, **22**, 135 (1952). ^{c} W. E. Truce and J. P. Milionis, *J. Org. Chem.*, **17**, 1529 (1952).

thereby changing the steric environment around the sulfone linkage as little as possible. A Hunsdiecker reaction on 3-methyl-1-cyclobutanecarboxylic acid[9] produced 3-methyl-1-bromocyclobutane[10] from which the sulfone was prepared by nucleophilic displacement by mercaptide and subsequent oxidation. Details of the cleavage appear in Table II.

$$R^A—SO_2^B—CH(CH_2)_{n-1}$$
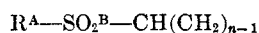
V, R = C$_6$H$_{11}$; n = 5
VI, R = n-C$_7$H$_{15}$; n = 5
VII, R = n-C$_7$H$_{15}$; n = 6
VIII, R = n-C$_7$H$_{15}$; n = 4

Cyclohexyl cyclopentyl sulfone (V) and cyclopentyl n-heptyl sulfone (VI) underwent cleavage chiefly at bond B but in decreasing amounts (83 and 70%, respectively). The direction of fission changed for cyclohexyl n-heptyl sulfone (VII) and cyclobutyl n-heptyl sulfone (VIII) giving approximately equal amounts of fission at bond A (70 and 71%, respectively).

Discussion

Radical stability decreases in the order predicted by the inductive effect: tertiary > secondary > primary;[11] the size of the ring also influences the stability of cycloalkyl radicals. Evidence indicates that the configura-

t'ın of a radical approaches planarity;[12] thus, factors which favor a change in a carbon atom from a tetrahedral to a planar configuration should favor formation of a radical. Likewise, for those ionic reactions which require the above change in configuration, the rate of reaction increases as the ring size varies: cyclobutyl < cyclohexyl < cyclopentyl.[13] This sequence is attributed to internal strain (I strain) arising from bond oppositions in five- and six-membered rings and angle strain in four-membered rings.[13] Decompositions of a series of azobiscycloalkylnitriles by a radical mechanism[14] confirms the same order of reactivity for radical reactions. Carbanion stability is opposite to radical stability, primary > secondary > tertiary,[15] and is not effected by I strain because of the tetrahedral configuration of a carbanion.[16]

The direction of bond fission in the sulfide series seems to reflect radical character. Cyclohexyl cyclopentyl sulfide (I) cleaves predominantly at the cyclopentyl–sulfur bond (79%), presumably reflecting a relief of I strain; the inductive effects cancel. A greater amount of cyclopentyl–sulfur bond breakage (87%) occurs with cyclopentyl n-heptyl sulfide (II), possibly because the inductive effect favors this direction of cleavage. A decrease in ring-sulfur bond fission

(9) B. A. Kazansku and M. Yu Lukina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* **47** (1951); *Chem. Abstr.,* **46**, 4491a (1952).

(10) In a preliminary experiment, Cristol's modification of the Hunsdiecker reaction [S. J. Crystal, *J. Org. Chem.,* **26**, 280 (1961)] was tried on cyclobutanecarboxylic acid, but no cyclobutylbromide was found. A personal communication with Professor Cristol revealed that other workers have had the same experience with cyclobutanecarboxylic acid.

(11) E. T. Butler and M. Polanyi, *Trans. Faraday Soc.,* **39**, 3 (1943); H. V. Hartel, N. Meer, and M. Polanyi, *Z. Physik. Chem.,* **19B**, 139 (1932).

(12) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 380.

(13) Ya. I. Goldfarb and L. I. Belenkü, *Russ. Chem. Rev.,* **29**, 214 (1960); O. H. Wheeler, *J. Am. Chem. Soc.,* **79**, 4191 (1957).

(14) C. G. Overberger, *et al., ibid.,* **75**, 2078 (1953).

(15) R. M. Salinger and R. E. Dessy, *Tetrahedron Letters,* No. 11, 729 (1963); H. Pines, *et al., J. Am. Chem. Soc.,* **78**, 4316, 5946, 5950 (1956).

(16) Reference 12, p 384.

(56%) for cyclohexyl n-heptyl sulfide (III) may result from the operation of the inductive effect and I strain in opposite directions. Production of a cyclohexyl radical would cause an increase in ring strain due to a change from the preferred completely staggered configuration of the sulfide to a less staggered configuration in the nearly planar radical. Cleavage of cyclobutyl n-heptyl sulfide (IV) reveals a shift in bond fission to give chiefly alkyl–sulfur bond breakage (62%), presumably caused by the instability of a cyclobutyl radical due to I strain.

Cleavage in the sulfone series seems to correspond to a process possessing appreciable carbanion character. Cyclopentyl–sulfur bond fission predominates (83%) in cyclohexyl cyclopentyl sulfone (V) and presumably results from relief of steric strain due to loss of the bulky sulfonyl group from the cyclopentyl ring. (The bulky sulfonyl group in four- and five-membered rings causes steric strain due to interaction with eclipsing hydrogens, whereas in six-membered rings the sulfone group occupies an equatorial position in which no strain is produced.) Carbanion character predicts less ring-sulfur bond breakage for cyclopentyl n-heptyl sulfone (VI) because the inductive and steric effects oppose each other; ring-sulfur cleavage is 70%. Cyclohexyl n-heptyl sulfone (VII) cleavage might be expected to be due chiefly to the inductive effect to give predominant heptyl–sulfur bond cleavage; 70% of the bond fission occurs in this direction. Strain in four-membered rings is less than in five-membered rings because the angle between the α-methylene groups in the former is less than in the latter, allowing less contact with the sulfonyl group in four-membered rings. The fact that 71% of the bond breakage occurs at the heptyl–sulfur bond in 3-methyl-1-(n-heptylsulfonyl)cyclobutane (VIII) can be rationalized by attributing the direction of cleavage to the inductive effect.

Experimental Section[17]

Cyclohexyl n-Heptyl Sulfide.—To a solution of 39 g (0.34 mole, Aldrich Chemical Co.) of cyclohexyl mercaptan and sodium ethoxide [prepared from 8 g (0.35 g-atom) of sodium and 100 ml

(17) All melting and boiling points are uncorrected. Microanalyses were performed by C. S. Yeh and M. Hudgens.

of absolute ethanol] under a nitrogen atmosphere was added dropwise 45.1 g (0.34 mole) of n-heptyl chloride. The solution was refluxed overnight, filtered, and poured into 300 ml of water. The organic layer was separated, dried over sodium sulfate, and distilled to give 44.9 g (68%) of sulfide, bp 116–118° (1.5 mm), n^{19}D 1.4840.

Anal. Calcd for $C_{13}H_{26}S$: C, 72.85; H, 12.23; S, 14.93. Found: C, 72.74; H, 12.27; S, 15.20.

Cyclobutyl n-Heptyl Sulfide.—Dry dimethyl sulfoxide (80 ml), n-heptyl mercaptan (21 ml, 0.13 mole), sodium methoxide (7.51 g, 0.14 mole), and cyclobutyl bromide[18] (9.47 g, 0.070 mole) were added, in that order, to a dry flask under nitrogen. The solution was heated at 90° for 2 hr, poured into 300 ml of ice water, and separated. After the aqueous layer was extracted with ether (two 30-ml portions), the combined organic layers were dried over magnesium sulfate. Ether was removed and the remainder was distilled resulting in 8.88 g (69%) of sulfide, bp 124–126° (14 mm), n^{20}D 1.4745.

Anal. Calcd for $C_{11}H_{22}S$: C, 70.90; H, 11.90; S, 17.20. Found: C, 70.91; H, 12.22; S, 16.89.

Preparation of Sulfones.—To a solution of sulfide in glacial acetic acid (0.75 ml of acetic acid per millimole of sulfide) cooled in an ice bath, was added 30% hydrogen peroxide (0.3 ml of peroxide per millimole of sulfide), dropwise. The mixture was allowed to warm to room temperature, heated on a steam bath for 1–3 hr, and poured onto ice. If a solid, the sulfone was filtered, but if a liquid, the sulfone was extracted with ether and the ether layer was washed with 10% sodium bicarbonate. After the ether layer was dried, it was distilled to remove the ether and then the sulfone.

Cleavage of Sulfides and Sulfones.—The procedure for the cleavage of sulfides and sulfones and the work-up of sulfides has been described.[7] Sulfone cleavage mixtures were worked up by cooling the reaction mixture in a Dry Ice–trichloroethylene bath while cold water (one to two times the volume of amine) was added. The flask was allowed to warm to 0°, but Dry Ice was always kept in the condenser. If the small organic layer was visible, the syringe was inserted for samples, but if the insoluble, flocculent lithium sulfinate obscured the small organic layer, n-decane (8 ml) was added to form a visible organic layer. An internal standard was added to determine the yield, and the organic layer was analyzed by vpc as in the sulfide cleavage. (See Table III for data on compounds prepared.)

(18) J. Cason and R. L. Way, *J. Org. Chem.*, **14**, 31 (1949).