The percentage isotope effect per atom deuterium (Table III) was calculated as for ethanolysis.

t-Test for the hypothesis that the isotope effect for IIIb is the same in acetolysis and in ethanolysis gives $t = 2.31$, with 5 degrees of freedom, $P = 8\%$.

t-Test for the hypothesis that the isotope effect per atom deuterium for Vb is the same in acetolysis and ethanolysis gives $t = 2.17$, with 16 degrees of freedom. $P < 5\%$.

t-Test for the hypothesis that the isotope effect for VIb is the same in acetolysis and ethanolysis gives $t = 2.61$, with 23 degrees of freedom, $P < 2.5\%$.

In the same way it was found that the isotope effect per atom deuterium in acetolysis was not significantly different with Vb than with VIb.

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The Cleavage of Sulfides and Sulfones by Alkali Metals in Liquid Amines. II. The Cleavage of Sulfides by Lithium in Methylamine[1,2]

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The direction of cleavage has been determined for a series of unsymmetrical dialkyl sulfides and alkyl-aryl sulfides. The results obtained are explained on the basis of a gradation of mechanism.

Earlier, it was reported[1] that sulfides and sulfones were cleaved in good yields to the hydrocarbon and mercaptan or sulfinic acid by sodium in liquid ammonia or lithium in methylamine. Another recent report[3] has shown that sulfides can also be cleaved by the use of calcium hexammine.

In the latter report, the authors state that their results can be explained on the basis of a reaction scheme involving either a one- or a two-electron transfer. In the case of ether cleavage with sodium in ammonia[4] the results are best explained on the basis of a two-electron transfer,[5] whereas in the case of the cleavage of tetraalkylammonium halides by sodium in ammonia,[6] the authors suggest a gradation of mechanism involving both a one- and a two-electron transfer. They propose that *t*-butyl, isopropyl and *sec*-butyl groups cleave as radicals, while ethyl and higher primary alkyl groups cleave as carbanions.

In this work, a series of unsymmetrical dialkyl and alkylaryl sulfides were prepared and treated with lithium in methylamine to determine the direction of preferred cleavage. Cleavage of alkyl-aryl sulfides produced exclusively the aromatic thiol and aliphatic hydrocarbon regardless of the amount of branching in the alkyl chain. In the dialkyl series, the preference for cleavage is *t*-alkyl > *sec*-alkyl ≈ *n*-alkyl. The compounds prepared and the results of their cleavages are presented in Table I of the Experimental part.

The preferred direction of cleavage of groups from sulfides by lithium in methylamine does not correspond in a simple way to the order expected for either radical cleavage (one-electron transfer) or carbanion cleavage (two-electron transfer). The stability of carbanions is given as CH_3 > Et *n*- Bu > *i*-Pr, *sec*-Bu > *t*-Bu,[7] while the stability of alkyl free radicals is the reverse of that given for carbanions, with methyl being the least stable and *t*-butyl the most stable.[8] Reductive cleavage also involves the formation of thiolates as well as hydrocarbons, so differences in stability of thiolates could affect the preferred direction of cleavage: the more basic the thiolate, the less readily it might be expected to be formed by reductive cleavage. This factor cannot account for the large preference of *t*-alkyl cleavage over *n*-alkyl cleavage since all of the thiolates formed in the alkyl series have about the same basicity.[9] However, the fact that aromatic thiols are about 10^4 times more acidic than aliphatic thiols[9] may be an important factor in the cleavage of alkyl-aryl sulfides

Steric factors would not be expected to play an important role in determining the direction of cleavage since models show no steric compression in the starting sulfides.

In the dialkyl series, it is postulated that the *t*-butyl group cleaves as a free radical under these conditions and that some other factor than stability of radicals or carbanions is involved in the cleavage of the less highly branched alkyl groups. The cleavage procedure used would seem to favor the formation of radicals as intermediates since the metal is added to a solution of the sulfide and is, therefore, never in excess. These results correspond closely to those observed by Grovenstein.[6]

In the alkyl-aryl series, it is postulated that the alkyl groups may cleave as free radicals although, as mentioned above, the basicity of the thiols may be an important factor in determining the direction of cleavage. This reaction path is suggested by the

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[1] Paper I, W. E. Truce, D. P. Tate and D. N. Burdge, *J. Am. Chem. Soc.*, **82**, 2872 (1960).

[2] Taken from the Ph.D. Thesis of J. J. B.

[3] J. Van Schooten, J. Knotnerus, H. Boer and Ph. M. Duinker, *Rec. trav. chim.*, **77**, 935 (1958).

[4] P. A. Sartoretto and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 603 (1937); A. L. Kranzenfelder, J. J. Verbance and F. J. Sowa, *ibid.*, **59**, 1488 (1937); F. C. Weber and F. J. Sowa, *ibid.*, **60**, 94 (1938).

[5] A. J. Birch, *Quart. Revs.*, **4**, 69 (1950).

[6] E. Grovenstein and R. W. Stevenson, *J. Am. Chem. Soc.*, **81**, 4850 (1959).

[7] H. Pines and co-workers, *ibid.*, **78**, 4316, 5946, 5950 (1956).

[8] 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).

[9] E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y., 1958, pp. 74, 131.

SULFIDES PREPARED IN A MANNER SIMILAR TO THAT DESCRIBED

Sulfide	Yield, %	B.p. °C.	Mm.	$n^{25}D$	Analyses, % Calcd. C	Calcd. H	Calcd. S	Found C	Found H	Found S
sec-Butyl *t*-butyl	60	50–51	17	1.4442	65.75	12.33	...	65.87	12.13	...
n-Octyl *sec*-butyl	82	78–80	0.3	1.4453	71.29	12.87	15.84	71.16	12.63	15.95
n-Octyl *t*-butyl	80	79–82	0.6	1.4530	71.29	12.87	15.84	71.09	12.94	15.51
p-Tolyl *n*-octyl	75	122–123	0.7	1.5200	76.27	10.17	13.56	76.24	10.20	13.74

greater stability of alkyl radicals[10] and is supported by the observation that cleavage of *p*-tolyl *n*-butyl sulfide in a minimum amount of solvent gave octane in 15% yield. On the other hand, cleavage of *n*-butyl *t*-butyl sulfide and phenyl *t*-butyl sulfide under similar conditions gave no coupling products and cleavage of *p*-tolyl *n*-octyl sulfide gave no coupling or disproportionation products.

It was hoped that cleavage of allyl *t*-butyl sulfide would provide additional information concerning the factors influencing the cleavage of sulfides. When this compound was cleaved, a mixture of 67% *n*-propyl mercaptan and 33% *t*-butyl mercaptan was obtained. It is not apparent whether the *n*-propyl mercaptan arose from an initial reduction of allyl *t*-butyl sulfide to *n*-propyl *t*-butyl sulfide followed by cleavage, or by cleavage of the sulfide to allyl mercaptan followed by reduction. That there was competition between cleavage and reduction was shown by treating a 1:1 mixture of di-*n*-decyl sulfide and 1-octene with lithium in methylamine. From the ratio of *n*-decane to *n*-octane formed, it was possible to estimate that cleavage occurred six times faster than reduction.

Experimental[11]

Preparation of *n*-Octyl *n*-Butyl Sulfide.—To a solution of sodium ethoxide, prepared by dissolving 11.49 g. (0.5 g.-atom) of sodium in 300 ml. of absolute ethanol, was added 73.15 g. (0.5 mole) of *n*-octyl mercaptan. To this mixture was added dropwise 68.5 g. (0.5 mole) of *n*-butyl bromide over a period of 2 hours and the mixture was refluxed for 1 hour. The mixture was allowed to cool, the sodium bromide was filtered off, and the solvent was removed by distillation. The residue was distilled under reduced pressure to give 77.3 g. (76%) of *n*-octyl *n*-butyl sulfide, b.p. 110–112° (2 mm.), $n^{23}D$ 1.4572; sulfone, m.p. 52–53°.

Anal. Calcd. for $C_{12}H_{26}O_2S$: C, 61.54; H, 11.11. Found: C, 61.33; H, 10.97.

Preparation of *p*-Tolyl *n*-Butyl Sulfide.—The sulfide was prepared in 65% yield by the procedure of Gilman[12]; b.p. 80–82° (1 mm.), $n^{25}D$ 1.5383 (lit.[12] b.p. 135–138° (15 mm.)).

Preparation of Phenyl *sec*-Butyl Sulfide.—The sulfide was prepared in 45% yield by the method of Taylor[13]; b.p. 83–84° (6 mm.), $n^{25}D$ 1.5396 (lit.[12] b.p. 104–105° (25 mm.)).

Preparation of *n*-Butyl *sec*-Butyl Sulfide.—The thiuronium salt of *n*-butyl bromide was prepared by refluxing a mixture of 68.5 g. (0.5 mole) of the bromide and 38 g. (0.5 mole) of thiourea in 200 ml. of water for 2 hours. To this was added 40 g. (1.0 mole) of sodium hydroxide in 200 ml. of water and the mixture was refluxed for 1 hour and then 68.5 g. (0.5 mole) of *sec*-butyl bromide was added and the mixture was refluxed for an additional hour. The water-insoluble layer was separated, dried over anhyrous sodium sulfate, and distilled under reduced pressure to give 25 g. (35%) of *n*-butyl *sec*-butyl sulfide, b.p. 81–84° (35 mm.), $n^{25}D$ 1.4494 (lit.[14] b.p. 175.5–177.5°).

Procedure for the Cleavage of Sulfides.—The procedure used was described in detail in Paper I of this series.[1] The results of the cleavages are presented in Table I.

TABLE I

CLEAVAGE OF SULFIDES WITH LITHIUM IN METHYLAMINE

Compound	Thiol(s) (mole %)[a]	Yield,[b] %
p-$C_7H_7SC_4H_9$-*n*	*p*-C_7H_7SH (100)	70
$C_6H_5SC_4H_9$-*sec*	C_6H_5SH (100)	..
$C_6H_5SC_4H_9$-*t*	C_6H_5SH (100)	90
p-$C_7H_7SC_8H_{17}$-*n*	*p*-C_7H_7SH (100)	81
n-$C_4H_9SC_4H_9$-*sec*	*n*-C_4H_9SH (50), (47) *sec*-C_4H_9SH (50), (53)	82
n-$C_4H_9SC_4H_9$-*t*	*n*-C_4H_9SH (97.5), (100) *t*-C_4H_9SH (2.5), (0)	91
sec-$C_4H_9SC_4H_9$-*t*	*sec*-C_4H_9SH (99.5) *t*-C_4H_9SH (0.5)	88
n-$C_8H_{17}SC_4H_9$-*n*	*n*-$C_8H_{17}SH$ (70) *n*-C_4H_9SH (30)	89
n-$C_8H_{17}SC_4H_9$-*sec*	*n*-$C_8H_{17}SH$ (75) *sec*-C_4H_9SH (25)	..
n-$C_8H_{17}SC_4H_9$-*t*	*n*-$C_8H_{17}SH$ (100) *t*-C_4H_9SH (0)	98
$CH_2{=}CHCH_2SC_4H_9$-*t*	*n*-C_3H_7SH (67) *t*-C_4H_9SH (33)	65

[a] Determined by vapor phase chromatography. [b] Based on isolated material.

Reaction of 1-Octene and di-*n*-Decyl Sulfide with Lithium in Methylamine.—A mixture of 8.62 g. (0.0276 mole) of di-*n*-decyl sulfide and 3.1 g. (0.0276 mole) of 1-octene was treated under the general cleaving conditions with 0.373 g. (0.0552 g.-atom) of lithium in about 250 ml. of methylamine. The base-insoluble fraction contained unreacted sulfide, decane, octane and unreacted 1-octene. The ratio of decane to octane was determined by vapor phase chromatography and was found to be 6:1. The material balance was 85%.

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(10) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 433.

(11) All melting points and boiling points are uncorrected. Microanalyses were performed by C. S. Yeh, I. Groten and V. Keblys.

(12) H. Gilman and N. Beaber, *J. Am. Chem. Soc.*, **47**, 1449 (1925).

(13) W. H. Taylor, *ibid.*, **58**, 2649 (1936).

(14) M. Vecera, J. Gaspari, D. Snohl and M. Jurecek, *Chem. Listy*, **50**, 770 (1956).