of methylene chloride. The addition required 15 min. The reaction mixture was stirred for 15 min and evaporated *in vacuo* and the residue was washed with ether. The crude product was dissolved in a chloroform–ethyl acetate mixture (9:1) and filtered through silicic acid (20 g). The solvent was evaporated and the residue was suspended in ethyl acetate, warmed, and filtered. The insoluble portion was dissolved in a minimum amount of methylene chloride, diluted with ethyl acetate and concentrated. The precipitated powder was dried to yield 0.473 g (38.9%) of white powder: mp 188–191°, $[\alpha]^{24}\text{D}$ −86.6° (*c* 0.93, DMF). A mixture melting point with the sample obtained in A was 188–190°.

The Pyrolysis of Unsymmetrical Dialkyl Sulfoxides. Rates of Alkene Formation and Composition of the Gaseous Products

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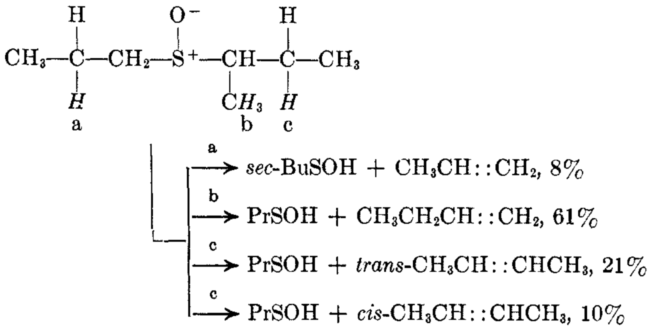
The relative yields of alkenes produced in the thermal decomposition of some unsymmetrical dialkyl sulfoxides were determined. The olefinic products produced are those predicted on the basis of the currently accepted mechanism involving the loss of a sulfenate moiety and any one of the available β hydrogens. Secondary alkyl groups are cleaved to form alkenes more readily than primary alkyl groups when both are embodied in the same molecule. Cleavage of a *sec*-butyl group results in the formation of 1-butene and a mixture of the 2-butenes. Sulfoxides having both a primary and a secondary alkyl group decompose at a substantially greater rate than sulfoxides in which both alkyl groups are primary.

The thermal instability of certain dialkyl sulfoxides was noted as early as 1875.[1] More recently, several studies[2-6] have dealt with the general features of the sulfoxide pyrolysis reaction including the nature of the products formed. The sulfoxides in these studies were either symmetrical[3,4,6] or had only one alkyl group which could be cleaved to form alkenes.[2,3,5] In one study[7] unsymmetrical sulfoxides were considered, but the composition of the olefinic products was not reported.

The present work was undertaken to gain insight on the relative yields of alkenes produced in the pyrolysis of unsymmetrical dialkyl sulfoxides of such structure that both alkyl groups could afford alkenes. Five sulfoxides of the type RSOR′ were prepared of such structure that the alkenes produced would identify the alkyl groups from which they were formed by pyrolytic cleavage.

The sulfoxides were prepared by hydrogen peroxide oxidation of appropriate dialkyl sulfoxides of high purity. The sulfoxides studied were all either racemic mixtures or mixtures of diastereoisomers depending on whether the asymmetry was inherent in the unsymmetrical sulfoxide or whether additional asymmetry was present in a *sec*-butyl group. The neat sulfoxides were pyrolyzed in a controlled-temperature reactor and the quantity of gas was measured by water displacement. The composition of the gas was determined by gas–liquid partition chromatography. Satisfactory first-order rates were observed, although there was some acceleration of the rate after 2 half-lives.

CHART I



A. ***n*-Propyl *sec*-Butyl Sulfoxide.**—A thorough discussion of the pyrolysis of *n*-propyl *sec*-butyl sulfoxide will serve to illustrate the methodology of the study. Chart I shows what products might be expected on the basis of the Ei mechanisms proposed by Kingsbury and Cram.[2] Since one alkyl group is primary (*n*-propyl) and the other is secondary (*sec*-butyl), the ratio of propene to the isomeric butenes indicates the relative ease of cleavage of a primary carbon–sulfur bond compared to a secondary carbon–sulfur bond. Since the *sec*-butyl group embodies two types of β hydrogens, b and c, the ratio of 1-butene to the isomeric 2-butenes reveals whether or not electrical effects operating on the acidity of the β hydrogens are significant as have been shown to be the case in the base-catalyzed cleavage of tetraalkylammonium ions[8,9] and trialkylsulfonium ions.[10,11] Our results, given in Table I, show that, in the pyrolysis of dialkyl sulfoxides, an inductive effect is not of extreme importance within the *sec*-butyl group since the yield of 1-butene is only twice the yield of the 2-butenes. Statistically, on the basis of the numbers of b and c hydrogens, the yield ratio of 1-butene to the 2-butenes would be 3:2. It is concluded, therefore, that the attack of a strongly basic oxygen atom on an acidic β hydrogen is not of overriding importance in the rate-determining step. In this respect the reaction most closely resembles the pyrolysis of amine oxides.[12] A comparison with some

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TABLE I

PYROLYSIS OF UNSYMMETRICAL DIALKYL SULFOXIDES. RATES OF GAS FORMATION AND COMPOSITION OF GASEOUS PRODUCTS

	Sulfoxide, RR'SO				
	Et/*n*-Bu	Et/*sec*-Bu	*n*-Pr/*n*-Bu	*n*-Pr/*sec*-Bu	IsoPr/*n*-Bu
Temp, °C	180.0	180.0	180.0	180.0	180.0
Yield of gas[a]	76	71	84	86	92
k_1, sec^{-1} × 10^4	2.31 ± 0.06	16.6 ± 0.1	2.4 ± 0.1	20.6 ± 0.4	13.0 ± 0.2
Gas compn[b]					
Ethane + ethene	62.5	15.2	0	0	0
Propane	0	0	0.4	0.1	0.3
Propene	0	0	47.3	8.1	88.5
n-Butane	0.5	0.1	0.4	0.06	0.2
1-Butene	36.8	59.6	51.9	60.7	11.0
t-2-Butene	0.1	17.2	trace	20.9	0
2-Cyclobutene	0.1	7.9	trace	10.1	0
Temp, °C	190.0	169.4	190.0	170.0	170.0
Yield of gas[a]	80	73	84	81	91
k_1, sec^{-1} × 10^4	5.0 ± 0.2	7.4 ± 0.1	5.2 ± 0.2	9.8 ± 0.6	5.7 ± 0.2
Gas compn[b]					
Ethane + ethene	61.0	17.2	0	0	0
Propane	0	0	0.3	0.1	0.2
Propene	0	0	47.1	7.9	88.9
n-Butane	0.2	0.1	0.2	0.1	0.1
1-Butene	38.5	59.1	52.3	61.8	10.8
t-2-Butene	0.2	16.0	trace	20.3	trace
2-Cyclobutene	0.1	7.6	trace	9.8	trace
Temp, °C	200.0	160.0	200.0	160.0	160.0
Yield of gas[a]	86	64	90	82	90
k_1, sec^{-1} × 10^4	10.6 ± 0.8	4.4 ± 0.2	10.7 ± 0.4	4.6 ± 0.1	2.5 ± 0.1
Gas compn[b]					
Ethane + ethene	60.0	16.6	0	0	0
Propane	0	0	0.3	0.1	0.2
Propene	0	0	45.5	8.4	87.7
n-Butane	0.3	0.1	0.2	0.06	0.1
1-Butene	39.6	58.3	54.0	60.8	12.0
t-2-Butene	0.06	16.4	trace	20.8	0
2-Cyclobutene	0.03	8.6	trace	9.8	0
Activation energy, kcal/mole	31.2 ± 1.1	26 ± 5	32.0 ± 1.1	29.3 ± 1.1	32.2 ± 1.1
Entropy of activation, eu	−9.2 ± 2.4	−17 ± 11	−7.4 ± 2.4	−5.1 ± 2.4	−3.6 ± 2.4

[a] Mole per cent basis sulfoxide. [b] Mole per cent basis gas produced.

other pyrolytic eliminations involving *sec*-butyl compounds is given in Table II. On statistical grounds, the yield of propene should be about 28.6% but only 8% of propene was found. Thus the yield structure cannot necessarily be predicted on a statistical basis when the degree of alkyl substitution on the carbon atoms attached to the sulfur is different in the two alkyl branches.

TABLE II

BUTENE YIELDS FROM PYROLYSIS OF *sec*-BUTYL COMPOUNDS

	Relative yields			
Compound	1-Butene	*trans*-2-Butene	*cis*-2-Butene	Ref
Sulfoxide				
Ethyl *sec*-butyl, 180°	70.4	20.3	9.3	
n-Propyl *sec*-butyl, 180°	66.2	22.8	11.0	
Amine oxide				
Dimethyl *sec*-butyl	67	21	12	*a*
Acetate				
sec-Butyl	57	28	15	*b*
Xanthate				
S-Methyl *sec*-butyl	41	40	19	*c*
Amide				
sec-Butyl acetamide	46	34	20	*c*

[a] Reference 12. [b] Reference 13. [c] C. H. DePuy, C. A. Bishop, and C. N. Goeders, *J. Am. Chem. Soc.*, **83**, 2151 (1961).

B. *n*-Butyl Isopropyl Sulfoxide.—Pyrolysis of *n*-butyl isopropyl sulfoxide should produce 1-butene and propene. This was the case (Table I) and, again, the yield of propene (88%) derived from the secondary alkyl group exceeds the amount (75%) to be expected on the basis of the relative numbers of β hydrogens in the two alkyl groups. The absence of *cis*- and *trans*-2-butenes shows that no significant isomerization of 1-butene occurs under the reaction conditions.

C. *n*-Propyl *n*-Butyl Sulfoxide.—The thermal decomposition of *n*-propyl *n*-butyl sulfoxide produces nearly equal quantities of propene and 1-butene. This suggests that when the carbon atoms bonded to sulfur are similarly substituted, the yield structure may be predicted with fair accuracy on the statistical basis of the numbers of β hydrogens.

D. Ethyl *n*-Butyl Sulfoxide.—Decomposition of ethyl *n*-butyl sulfoxide produces ethene and 1-butene in nearly the amount predicted on the basis of the β hydrogens present in the two alkyl groups. Again it is seen that the acidity of the β hydrogens is not particularly significant in governing the course of the reaction.

E. Ethyl *sec*-Butyl Sulfoxide.—Pyrolysis of ethyl *sec*-butyl sulfoxide leads to relative yields of 1-butene to the 2-butenes in the ratio of 7:3, greater than the statistical ratio of 3:2 predicted from the statistical ratio of β hydrogens in the *sec*-butyl group. Ethene is found in significantly smaller yield than the 37.5 mole % to be predicted from the relative numbers of β hydrogens found in the two alkyl groups. Again, this shows the tendency of a secondary alkyl group to be cleaved at a significantly greater rate than a primary alkyl group.

The approximate 2:1 ratio of *trans*- to *cis*-2-butene obtained in the pyrolysis of *sec*-butyl acetate has been explained in terms of the steric interaction of eclipsed methyl groups in the transition state leading to *cis*-2-butene.[13] The sulfoxide pyrolysis has been shown[2] to have less rigorous steric requirements than ester pyrolysis and the observed 2:1 mole ratio of *trans*- to *cis*-2-butene in *sec*-butyl sulfoxide pyrolysis also happens to be the equilibrium ratio of *trans*- to *cis*-2-butene at temperatures employed in this study. Although we are unable categorically to differentiate between the suppression of *cis*-2-butene formation by a sterically strained transition state and the production of an equilibrium mixture of 2-butenes in a thermodynamically controlled decay of caged radical pairs,[2] the rather considerable negative entropy of activation bespeaks an intramolecular *cis* elimination.

A possible interpretation of the fact that the ratio of 1-butene to the 2-butenes is somewhat greater than would be predicted from the numbers of β hydrogens may lie in the observation that the eclipsed conformations of S/S (sulfoxide configuration/*sec*-butyl configuration) and R/R ethyl or *n*-propyl *sec*-butyl sulfoxides leading to *trans*-2-butene and the eclipsed conformations of all configurations of *sec*-butyl sulfoxides leading to *cis*-2-butene involve some crowding of the alkyl groups if a *cis* elimination is involved. The eclipsed conformations of all configurations which could lead to 1-butene by an intramolecular *cis* elimination are relatively uncrowded.

The rates of decomposition of the sulfoxides reported in this study were determined at three different temperatures. The plots of log k_1 *vs.* $1/T$ were linear except for ethyl *sec*-butyl sulfoxide in which the plot was slightly concave upward. The results of the rate studies are shown in Table I. The entropies of activation are negative in keeping with previous observations.[2] In all cases the rates of decomposition of the sulfoxides containing a primary and a secondary alkyl group were faster by factors of 4.8 to 8.8 than the sulfoxides containing two primary alkyl groups.

Some interesting observations may be made on examining the rate constants for the formation of various alkenes which are shown in Table III. For example, after dividing the rate constants by the number of β hydrogens in the primary alkyl group, it is seen that the presence of a secondary alkyl group in the sulfoxide enhances not only the rate of formation of the alkene derived from the secondary alkyl group, but also the rate of formation of the alkene from the primary alkyl group. This effect decreases monotonically as the size of the primary alkyl group increases. Also, it may be noted that both 1-butene and the 2-butenes form faster from *n*-propyl *sec*-butyl sulfoxide than from ethyl *sec*-butyl sulfoxide. 1-Butene is produced more rapidly from *n*-propyl *n*-butyl sulfoxide than from ethyl *n*-butyl sulfoxide.

TABLE III

RATE CONSTANTS FOR OLEFIN FORMATION AT 180°

	$k_1 \times 10^4$ sec^{-1}				
Sulfoxide	Ethene	Propene	1-Butene	*trans*-2-Butene	*cis*-2-Butene
Ethyl *n*-butyl	1.4		0.85		
Ethyl *sec*-butyl	2.5		9.9	2.8	1.3
n-Propyl *sec*-butyl		1.7	12.5	4.3	2.1
n-Propyl *n*-butyl		1.1	1.2		
Isopropyl *n*-butyl		11.5	1.4		
n-Butyl *n*-butyl[a]			4.1		

	Rate constant divided by no. of β hydrogens			
Sulfoxide	Ethene	Propene	1-Butene	*trans*-2-Butene + *cis*-2-butene
Ethyl *n*-butyl	0.48		0.42	
Ethyl *sec*-butyl	0.83		3.3	2.1
n-Propyl *sec*-butyl		0.84	4.1	3.2
n-Propyl *n*-butyl		0.57	0.62	
Isopropyl *n*-butyl		1.9	0.72	
n-Butyl *n*-butyl			1.0	

[a] Reference 6; compound decomposed in cetane solution.

Experimental Section

Decomposition of Sulfoxides. General Procedure.—Reactors were made from 24 cm × $^3/_8$ in. o.d. pieces of copper tubing bent into the shape of a U. One end of the reactor was fitted with a silicone rubber injection gasket through which samples of the sulfoxides could be injected with a hypodermic syringe. To the other end of the reactor was affixed a 6 × 0.5 in. brass nipple packed with 15 g of anhydrous calcium sulfate. The drying agent is required because water has been shown to be a product in sulfoxide pyrolyses.[6] The gas produced passed through the drying train and then into a 500-ml boiling flask containing distilled water and a magnetic stirring bar. The water displaced from the boiling flask was conveyed to a graduate cylinder so that the quantity of water displaced by the gas could be measured. The pressure of gas inside the system was adjusted to atmospheric pressure by moving the graduate up or down until the water levels in the gas reservoir and the graduate were the same. An electric timer was used. Reactor bath temperatures were determined by use of a copper–constantan thermocouple and a potentiometer.

A run was conducted in the following manner. The reactor and drying train were assembled, flushed with nitrogen, and tested for leaks by immersion in water while under pressure. The reactor was then dried off and almost fully immersed in the thermostated oil bath. A hypodermic syringe was loaded with the sulfoxide and weighed. The sulfoxide (0.5–1 g) was then injected into the reactor, the timer was started, the water level in the graduate was recorded, and the empty syringe was weighed. The amount of water displaced was recorded periodically with the pressure being adjusted to atmospheric pressure before each reading. At the conclusion of the run (6 half-lives or more), the gum rubber tubing connecting the drying with the gas reservoir was pinched off and the graduate was raised 1 in. to keep the gas under positive pressure. A 2-ml portion of 3 *N* sodium hydroxide was injected into the gas reservoir to absorb the carbon dioxide present in the distilled water. The water in the reservoir was stirred vigorously for at least 5 min by means of a magnetic stirrer in order to mix the gases thoroughly. The gas mixture was analyzed by gas chromatography using a 50 ft × 0.25 in. column packed with a 20% by weight mixture of [20% by weight of bis(2-ethylhexyl) sebacate and 80% by weight of bis(2-methoxyethyl) adipate] on Chromosorb W DMCS.[14] The Wilkens Aerograph gas chromatograph was equipped with a thermal conductivity detector and sensitivity factors for the various components were determined by analyzing a known mix-

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(13) D. H. Froensdorf, C. H. Collins, G. S. Hammond, and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

(14) D. M. Golden, K. W. Egger, and S. W. Benson, *ibid.*, **86**, 5416 (1964).

TABLE IV

PROPERTIES OF DIALKYL SULFIDES AND SULFOXIDES

Sulfide	Bp, °C (mm) Lit.	Bp, °C (mm) Found	$n^{25}D$ Lit.	$n^{25}D$ Found	Yield, % mole	Purity[a]	Ref
Ethyl *n*-butyl	144–142 (?)	71.5 (97)	1.4491[b]	1.4472	55	99.2	*c, d*
Ethyl *sec*-butyl	133.6 (?)	63–64 (66)	1.4477[b]	1.4461	45	99.8	*d*
n-Propyl *n*-butyl	153–154 (?)	77.0 (38)		1.4480	47	99.9	*e*
n-Propyl *sec*-butyl	153–155 (?)	71.2 (41)		1.4472	82	99.9	*f*
Isopropyl *n*-butyl	154–156 (?) 78.5–79 (61)	70 (38)	1.4479	1.4440	49	99.9	*f, g*

Sulfoxide	Bp, °C (mm)	$n^{25}D$	Yield, % mole	Anal,[h] % C Calcd	C Found	H Calcd	H Found	S Calcd	S Found	Ref
Ethyl *n*-butyl	65 (0.6)	1.4662	68							*i*
Ethyl *sec*-butyl	45–48 (0.035–0.05)	1.4687	71	53.68	53.88	10.51	10.49	23.89	23.85	*i*
n-Propyl *n*-butyl	66–67 (0.025)	1.4647	78							*i*
n-Propyl *sec*-butyl	46–47 (0.02)	1.4679	81	56.70	56.69	10.88	10.73	21.62	21.68	
Isopropyl *n*-butyl	46.5–47.6 (0.02)	1.4652	75	56.70	56.59	10.88	10.84	21.62	21.70	*i*

[a] By gas–liquid partition chromatography. [b] At 20°. [c] T. C. Whitner, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **43**, 639 (1921). [d] D. T. McAllan, T. V. Cullum, R. A. Dean, and F. A. Fidler, *ibid.*, **73**, 3627 (1951). [e] J. von Braun and P. Engelbertz, *Ber.*, **56**, 1573 (1923). [f] M. Vecera, J. Gasparic, D. Snobl, and M. Jurecek, *Chem. Listy.*, **50**, 770 (1956). [g] F. Drahowzal and D. Klammann, *Monatsch.*, **82**, 594 (1951). [h] Performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. [i] No physical properties of the compounds were given: V. Horak and J. Pecka, *J. Chromatog.*, **14**, 97 (1964).

ture of hydrocarbons obtained from the Phillips Petroleum Co. Two analyses were performed on the gas from each run, and the reported compositions are average values.

The rate constants were obtained from a plot of log ($V_\infty - V_t$) *vs.* time, where V_∞ is the total volume of gas produced in the run and V_t is the volume at time t. A good straight line could be drawn through the points obtained for the first 50–60% of reaction. There was usually a slight deviation toward a more rapid reaction by the second half-life and this became more pronounced as the run progressed. Two or more runs were made on each compound at each temperature. It was determined that the copper surface of the reactor was not significantly affecting the reaction by performing one run in which the surface area of copper was doubled by adding copper shot to the reactor.

Preparation of Sulfides.—The sulfides were prepared by adding the appropriate mercaptan to an equimolar solution of sodium ethoxide in absolute ethanol, then adding an equimolar quantity of the appropriate alkyl bromide. The reaction mixtures were allowed to stand for at least 16 hr at room temperature and diluted with water and the sulfides were extracted with 60–75° boiling petroleum ether which had been shaken with concentrated sulfuric acid, washed with sodium hydroxide, and distilled. The extracts were dried over calcium chloride and distilled in an 18-cm column packed with glass helices. The pertinent data are given in Table III.

Preparation of the Sulfoxides.—The sulfoxides were prepared by oxidation of the appropriate sulfides using an equimolar quantity of 30% hydrogen peroxide in *t*-butyl alcohol.[8] The reaction mixtures were concentrated by evaporating the solvent in a stream of air and distilling the resulting oil at reduced pressure. The distillates were stored over Linde 13 X Molecular Sieves. In all cases the distillates were water white liquids with a pleasant but almost imperceptible odor quite unlike the sulfides from which they were derived. The pertinent data are given in Table IV.

Acknowledgments.—We are indebted to Professor A. R. Emery for a computer program which aided in the processing of compositional data and to the Division of Literature, Science, and the Arts for funds to pay for the chemicals and the microanalyses.

Alkynyllithium Compounds from the Reaction of 1-Alkenes with Lithium

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Several 1-alkenes have been found to react with lithium dispersion under relatively mild conditions (20–120°) to give the corresponding 1-alkynyllithium compounds and lithium hydride as the major products. The yields of the alkynyllithium compounds varied markedly with variations in chain length of the 1-alkene, with the highest yield (65%) of organolithium compound obtained from the reactions of 1-hexene with lithium. Attempts to extend this novel reaction to include olefins other than 1-alkenes were unsuccessful.

The literature contains many reports describing reactions of alkali metals with olefins. For example, olefins containing double bonds in conjugation with centers of unsaturation, such as arylethylenes and 1,3-butadienes, readily form alkali metal addition compounds in ether solvents.[2] Under somewhat more vigorous conditions, nonactivated olefins are known to undergo metalations, dimerizations, and polymerizations with alkali metals.[3]

$$R_2C{=}CH_2 + M \longrightarrow [R_2CCH_2]^-M^+$$
$$R = \text{unsaturated group}$$

This paper describes the finding that some 1-alkenes react with lithium dispersion, under mild conditions, to give primarily the corresponding alkynyllithium compounds (up to 65%) and lithium hydride, according to the following equation.

$$RCH{=}CH_2 + 4Li \longrightarrow RC{\equiv}CLi + 3LiH$$
$$R = n\text{-}C_2H_5\text{-}n\text{-}C_{10}H_{21}$$

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(1) To whom inquiries concerning this paper should be sent.

(2) G. E. Coates, "Organo-Metallic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1960, pp 27–42.

(3) See, for example, W. V. Bush, G. Holzman, and A. W. Shaw, *J. Org. Chem.*, **30**, 3290 (1965).