TABLE I

THIOL ESTERS CONVERTED TO SULFIDES BY LITHIUM ALUMINUM HYDRIDE–ALUMINUM CHLORIDE

Thiol ester	Yield of sulfide, %	Mole ratio of $LiAlH_4/AlCl_3$ (per mole of ester)
$CH_3COS(CH_2)_5CH_3$	40	1.4:1.2
$CH_3COS(C_6H_{11})$	80[a]	2.0:15[b]
$CH_3COS(C_6H_5)$	7.6	1.3:1.1
$(CH_3)_2CHCOSC_6H_{11}$	73[a]	2.0:15[b]
$(CH_3)_3CCOSC_6H_{11}$	60 (37)[a]	1.5:3.7
$C_6H_{11}COSCH_2CH_3$	49	1.4:1.2
$CH_2{=}CH(CH_2)_8COSCH_2CH{=}CH_2$	89	1.6:3.7
$CH_2{=}CH(CH_2)_8COS(C_6H_{11})$	79	1.4:3.6
$C_6H_5COSCH_3$	79	1.4:1.2
$C_6H_5COSC_6H_5$	...	1.4:1.2
$C_6H_5COS(C_6H_{11})$	93	1.4:1.2

[a] Data are from ref 1. [b] Mole ratio indicated is $LiAlH_4/BF_3 \cdot Et_2O$.

amounts of sulfide, are in complete agreement with the earlier findings of Eliel and Daignault.[1] However, a more important effect, an electronic effect, is that of an aryl group bonded directly to sulfur. Thus, while cyclohexyl thiolbenzoate provides cyclohexyl benzyl sulfide in 93% yield, no benzyl phenyl sulfide is observed when phenyl thiolbenzoate is utilized. Similarly, cyclohexyl thiolacetate provides the corresponding sulfide in 80% yield,[1] while phenyl thiolacetate gives only 8% of ethyl phenyl sulfide. In both cases, when phenyl thiol esters are employed, the usual thiol ester reduction products (*i.e.*, an alcohol and a thiol[3]) are obtained.

The yield of sulfide obtained from cyclohexyl thiolbenzoate is related to the molar ratios of thiol ester, lithium aluminum hydride, and aluminum chloride employed. The best yields of sulfide were obtained using molar ratios 1.0:1.4:3.6 (82%) and 1.0:1.2:1.2 (93%) of thiol ester/lithium aluminum hydride/aluminum chloride. Other things being equal, increasing the molar ratio of lithium aluminum hydride results in a corresponding decrease in the amount of sulfide and an increase in the amount of alcohol and thiol obtained. Separately, increasing amounts of aluminum chloride result in the recovery of increasing amounts of unchanged thiol ester. Substitution of aluminum chloride for boron trifluoride etherate, in the exact conditions used by Eliel and Daignault,[3] produced an 87% yield of benzyl cyclohexylsulfide from the corresponding thiol ester. When 2 molar equiv of aluminum hydride, prepared from lithium aluminum hydride–aluminum chloride (3:1), are used as the reducing reagent, benzyl cyclohexyl sulfide is obtained in 45% yield.

A variety of modifiers were substituted for aluminum chloride and in all instances studied some sulfide was obtained. The results obtained in the reduction of cyclohexyl thiolbenzoate using these various modifiers are summarized in Table II. The data show that the best results are obtained when boron trifluoride etherate, aluminum chloride, gallium(III) chloride, or indium(III) chloride are used. Tin(IV), titanium(III), titanium(IV), and iron(III) halides produce lesser amounts of benzyl cyclohexyl sulfide.

TABLE II

EFFECT OF ADDED HALIDES UPON THE REDUCTION OF CYCLOHEXYL THIOLBENZOATE BY LITHIUM ALUMINUM HYDRIDE

Added halide	Mole ratio of thiol ester/LiAlH/MCl_n	Sulfide, %
Iron(III)	1.0:1.4:0.65	20
Gallium(III)	1.0:2.7:2.0	80
Indium(III)	1.0:2.7:2.4	80
Titanium(III)	1.0:1.4:2.4	*Ca.* 9–18
Titanium(IV)	1.0:1.4:0.61	*Ca.* 5–10
Tin(IV)	1.0:1.8:3.6	0
	1.0:1.4:3.7	0
	1.0:1.4:0.67	46
	1.0:1.4:0.47	*Ca.* 50
	1.0:1.4:0.89	*Ca.* 35
Aluminum(III)	1.0:1.4:1.2	93

Experimental Section

The starting thiol esters were prepared by standard procedures. Satisfactory elemental analyses were obtained for all new compounds. Gas–liquid partition chromatographic analyses were performed on an Aerograph Autoprep Model A-700 equippped with $^3/_8$ in. × 20 ft aluminum column packed with 20% SE 30 on 60–80 Chromosorb P.

Allyl Undecenyl Sulfide.—To a stirred solution of 3.0 g (0.08 mole) of lithium aluminum hydride in 100 ml of dry ether there was added slowly a solution of 25 g (0.19 mole) of aluminum chloride in 300 ml of dry ether. After stirring the resulting solution at reflux for 30 min a solution containing 12.0 g (0.052 mole) of allyl thiolundecenylate in 100 ml of dry ether was added dropwise over a period of 20 min. The reaction mixture was maintained at reflux with stirring for 1 hr, then cooled and hydrolyzed by careful addition of water. The organic phase was separated and dried and the solvent was removed *in vacuo*. The residual oil (10.2 g, 89%) was analyzed by glpc and found to contain small amounts (*ca.* 3%) of allyl mercaptan and undecenyl alcohol in addition to allyl undecenyl sulfide.

Similar reduction of cyclohexyl thiolundecenylate gave cyclohexyl undecenyl sulfide in addition to traces of undecenyl alcohol and cyclohexyl mercaptan.

Registry No.—$CH_3COS(CH_2)_5CH_3$, 2307-12-2; $CH_3COS(C_6H_{11})$, 10039-63-1; $CH_3COS(C_6H_5)$, 934-87-2; $(CH_3)_2CHCOSC_6H_{11}$, 10035-84-4; $(CH_3)_3CCOSC_6H_{11}$, 10035-85-5; $C_6H_{11}COSCH_2CH_3$, 10035-86-6; $CH_2{=}CH(CH_2)_8COSCH_2CH{=}CH_2$, 10035-87-7; $CH_2{=}CH(CH_2)_8COS(C_6H_{11})$, 10035-88-8; $C_6H_5COSCH_3$, 5925-68-8; $C_6H_5COSC_6H_5$, 884-09-3; $C_6H_5COS(C_6H_{11})$, 10035-90-2; aluminium chloride, 7446-70-0.

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[3] M. S. Newman, M. W. Renoll, and I. Auerbach, *J. Am. Chem. Soc.*, **70**, 1023 (1948).

The Effect of Ring Size on the Rate of Pyrolysis of Cycloalkyl Phenyl Sulfoxides[1a]

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On being heated in aprotic solvents alkyl sulfoxides undergo pyrolysis fairly readily and yield an olefin (eq 1).[2-4] Cram and Kingsbury[2] have shown that

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[1] (a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-106-65. (b) Participant in the National Science Foundation Research Participation for College Teachers Program, Oregon State University, 1965 and 1966.

[2] C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

[3] C. Walling and L. Bollyky, *J. Org. Chem.*, **29**, 2699 (1964).

[4] The sulfenic acid formed along with the olefin in eq 1 is not stable and decomposes to give as yet uninvestigated products.

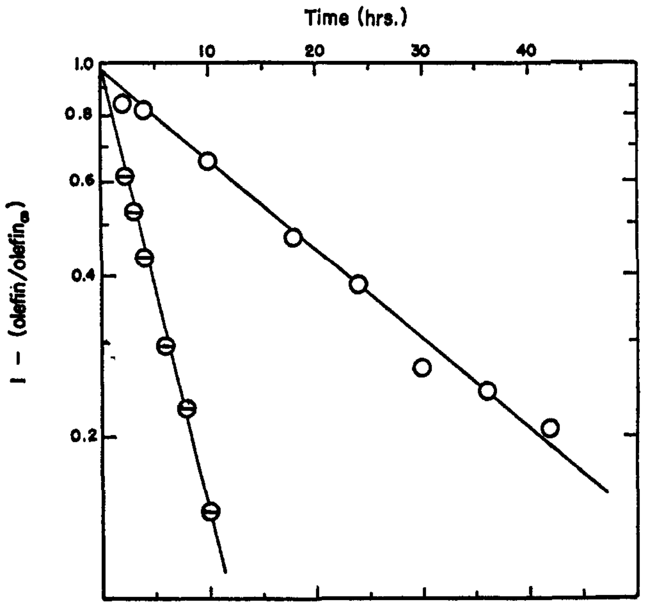
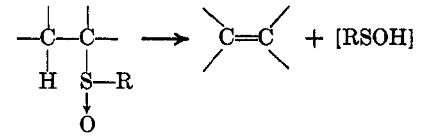
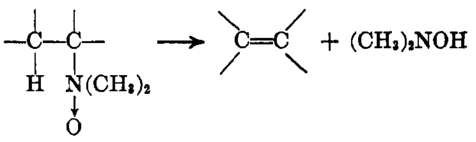


Figure 1.—Pyrolysis of cycloalkyl phenyl sulfoxides in diglyme; representative kinetic runs: O, cyclopentyl phenyl sulfoxide, 90°; ⊖, cycloheptyl phenyl sulfoxide, 90°.



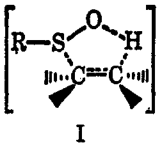
$$-\underset{\text{H}}{\overset{|}{\text{C}}}-\underset{\text{S}(\to\text{O})-\text{R}}{\overset{|}{\text{C}}}- \longrightarrow \text{C}=\text{C} + [\text{RSOH}] \qquad (1)$$

sulfoxide pyrolysis is very closely related mechanistically to the pyrolysis of amine oxides[5] (eq 2) and that



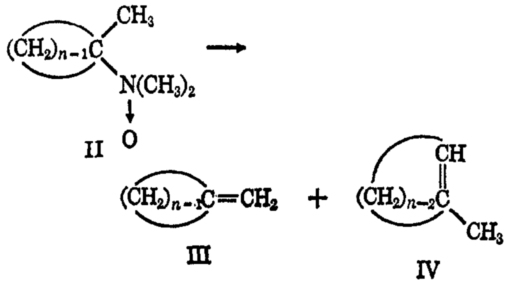
$$-\underset{\text{H}}{\overset{|}{\text{C}}}-\underset{\text{N}(\text{CH}_3)_2(\to\text{O})}{\overset{|}{\text{C}}}- \longrightarrow \text{C}=\text{C} + (\text{CH}_3)_2\text{NOH} \qquad (2)$$

under normal conditions the reaction is a quite stereospecific *cis* elimination, the geometry of the transition state being best represented as is shown in I.



I

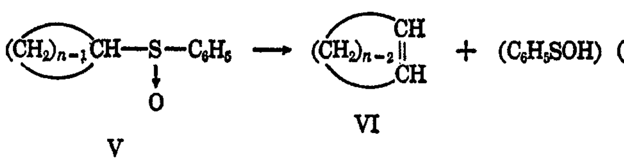
In examining the elimination (eq 3) of a series of N,N-dimethyl-1-methylcycloalkylamine oxides (II), Cope and co-workers[5b] found that there was a large variation with ring size in the ratio of endocyclic (IV) to exocyclic (III) elimination product. Thus, for the compound with $n = 5$, the ratio of IV to III was 39:1, for $n = 7$ it was 5.6:1, but for $n = 6$ it was several orders of magnitude smaller (0.029:1). The almost exclusive formation of the exocyclic olefin in the last case presumably results principally from the fact that in order to achieve a planar, five-membered transition state for endocyclic elimination in the 1-methylcyclohexyl system the stable staggered conformation of the six-membered ring must be altered. However, since one does not know how ring size influences the rate of exocyclic elimination, one cannot actually say



(3)

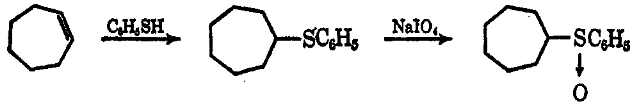
just how much of the variation in the IV/III ratio is the result of variations in the ease of endocyclic elimination. For this reason it would be desirable to have a direct measurement of the rate of endocyclic elimination as a function of ring size for a reaction of this type. In the present Note we report such results for the pyrolysis of a series of cycloalkyl phenyl sulfoxides.

We have investigated the rate of pyrolytic elimination (eq 4) of cycloalkyl phenyl sulfoxides (V) in diglyme solution. The sulfoxides studied were those



(4)

with n = 5–7. They were all prepared by the same general route, which is illustrated below for the cycloheptyl compound.



The rates of elimination of the sulfoxides were determined by following the production of olefin, using the procedures described by Walling and Bollyky.[3] The final yield of olefin in every case was better than 85%. All of the runs exhibited satisfactory first-order kinetics, typical runs being shown in Figure 1. Duplicate runs indicated that individual rate constants were reproducible to ±10%. The various rate data are summarized in Table I.

TABLE I

RATES OF PYROLYSIS OF CYCLOALKYL PHENYL SULFOXIDES[a]

Sulfoxide	Temp, °C	$k_1 \times 10^4$, sec^{-1}
Cyclopentyl phenyl	90.0	0.11
	99.4	0.27
	109.2	0.79
	129.6	(6.0)[b]
Cyclohexyl phenyl	129.6	0.24
Cycloheptyl phenyl	79.8	0.14
	90.0	0.50
	99.4	1.4
	129.6	(28)[b]

[a] All runs in diglyme; initial sulfoxide concentration, 0.15–0.20 *M*. [b] Calculated from data at lower temperatures.

The relative rates of decomposition of the three cycloalkyl sulfoxides at 129.6° are as follows: cyclo-

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[5] (a) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949); (b) A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957); (c) A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *ibid.*, **79**, 4720 (1957).

pentyl, 25; cyclohexyl, 1.0; cycloheptyl, 120. We see that while there is indeed a pronounced minimum in rate with the C_6 sulfoxide the over-all spread in relative reactivities is considerably less than the spread in endocyclic to exocyclic elimination ratios observed with 1-methylcycloalkylamine oxides. Furthermore, although the C_5 amine oxide showed the largest IV/III ratio,[5b] the C_5 sulfoxide actually undergoes elimination about five times as slow as the C_7 compound. It would therefore appear that in the pyrolysis of the 1-methylcycloalkylamine oxides there are probably significant variations in *both* exocyclic and endocyclic elimination rates with ring size. For this reason we believe that the data in Table I for the sulfoxide pyrolysis represent a more accurate indicator of the general effect of ring size on elimination rate for Ei reactions of this type than do the IV/III ratios for the pyrolysis of the amine oxides II. The observed variations in the rate of pyrolysis are, of course, directly indicative of the variation with ring size in the free energy required to convert the cycloalkyl group from its preferred conformation in the starting sulfoxide to the conformation it must assume for transition state I.

Experimental Section

Cycloheptyl Phenyl Sulfoxide.—Technical grade cycloheptene (Aldrich Chemical Co.) was fractionally distilled using a spinning-band column, and the fraction boiling at 113–114° was collected. A 20-ml (0.172 mole) portion of this olefin was combined with 18 ml (0.177 mole) of thiophenol and 0.3 g of azobisisobutyronitrile, and the resulting solution was heated at 70–80° under nitrogen for 15 hr. At the end of that time 0.2 g of fresh azobisisobutyronitrile was introduced and heating was continued for an additional 16 hr. The final reaction mixture was fractionally distilled under reduced pressure, and, after recovery of considerable unreacted olefin and thiol, cycloheptyl phenyl sulfide (19.9 g, 56%) was collected, bp 179–181° (17 mm).

The sulfide (19.9 g) was dissolved in 350 ml of methanol, and a solution of 22 g of sodium metaperiodate in 100 ml of water was added to it at 0°. The resulting mixture was stirred at 0° for 10 hr. It was then filtered, and the filtrate was extracted several times with chloroform. The combined extracts were dried over anhydrous magnesium sulfate, and the chloroform was removed under reduced pressure to leave a red-brown oil. This was dissolved in hot petroleum ether (bp 30–60°) and cooled. The cycloheptyl phenyl sulfoxide which crystallized out was recrystallized several more times to give 6.2 g (28%) of pure sulfoxide, mp 44–45°.

Anal. Calcd for $C_{13}H_{18}OS$: C, 70.02; H, 8.03. Found: C, 70.09; H, 7.95.

Cyclohexyl Phenyl Sulfoxide.—Cyclohexyl phenyl sulfide[6] was synthesized in 65% yield from cyclohexane and thiophenol by a procedure analogous to that used for cycloheptyl phenyl sulfide, bp 160–165° (17 mm). The sulfide was then converted to the sulfoxide with sodium metaperiodate, using the general procedure outlined by Johnson and McCants.[7] The crude sulfoxide, obtained in 76% yield, was purified by several recrystallizations from petroleum ether, mp 62–64° (lit.[8] 61–64°).

Cyclopentyl Phenyl Sulfoxide.—Reaction of cyclopentene with thiophenol afforded cyclopentyl phenyl sulfide,[9] bp 149–150° (20 mm), in 77% yield. The sulfide was oxidized to the sulfoxide using the same procedure as for the cyclohexyl compound. A number of attempts to induce the sulfoxide to crystallize failed. Accordingly, it was purified by distillation in a molecular still. Infrared examination of the distillate suggested that the sulfoxide still contained some hydroxylic impurities. It was therefore treated with Linde 4A Molecular Sieves and redistilled in the molecular still. To further ensure the removal of hydroxylic impurities the distillate from this second distillation was treated with calcium hydride and distilled once more. The purified sulfoxide was obtained in about 30% yield based on the sulfide.

Anal. Calcd for $C_{11}H_{14}OS$: C, 67.98; H, 7.27. Found: C, 67.35; H, 7.25.

Procedure for Kinetic Runs.—Diglyme was purified by distilling it first from sodium metal at reduced pressure and then from lithium aluminum hydride at atmospheric pressure. The general procedure for the runs was patterned closely after that described by Walling and Bollyky.[3] The only changes made were the following: (1) *n*-hexane, rather than tetralin, was used as the internal standard in the solutions of the sulfoxide in diglyme; (2) after the contents of an ampoule had been poured into water, *n*-pentane, rather than *n*-hexane, was used as the extracting solvent; (3) a nitrile silicone column (XF-1150, Wilkens Instrument and Research) was used for glpc separation of the olefin and the internal standard.

At least six points plus an infinity time point were taken for each run. The final yield of olefin was from 85 to 100% of theory in every case. Unlike the situation noted by Walling and Bollyky[3] we did not observe any tendency for the experimental first-order rate constants to decrease with increasing conversion.

Registry No.—Cyclopentyl phenyl sulfoxide, 10181-73-4; cyclohexyl phenyl sulfoxide, 3324-82-1; cycloheptyl phenyl sulfoxide, 10181-75-6; cycloheptyl phenyl sulfide, 10181-76-7; cyclohexyl phenyl sulfide, 7570-92-5.

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[6] R. W. Saville, *J. Chem. Soc.*, 2880 (1958).

[7] C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 1109 (1965).

[8] B. Weibull, *Arkiv. Kemi*, **3**, 171 (1951).

[9] I. N. Tits-Skvortsova, S. Ya. Levina, A. I. Leonova, and T. A. Danilova, *Zh. Obshch. Khim.*, **22**, 135 (1952).

Low-Temperature Fluorination of Aliphatic Isocyanates and Carbamyl Halides

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The fluorination of many simple organic substrates has been studied in great detail by many workers.[1] Conditions chosen were such that little discrimination was shown by the fluorine in its site of attack. An interesting exception was Bockemuller[2] who was able to add fluorine cleanly to tetrachloroethylene at −80°. A similar, low-temperature approach has been shown to be selective and successful with a wide variety of olefins[3-5] as well as Schiff bases.[6] In view of the ease of addition of fluorine to the carbon–nitrogen double bond of Schiff bases, it was expected that a similar process with aliphatic isocyanates would also be successful.

Halogenation of aryl isocyanates has been examined briefly by Gumpert,[7] but no direct adducts were formed. However, the products found could be rationalized with the intermediacy of N-bromocarbamyl bromides. Aliphatic isocyanates were not con-

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[1] For a comprehensive review, see (a) M. Hudicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1963; (b) A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," American Chemical Society Monograph No. 155, Reinhold Publishing Corp., New York, N. Y., 1962; (c) A. M. Lovelace, D. A. Rausch, "Aliphatic Fluorine Compounds," W. Postelnek, American Chemical Society Monograph No. 138, Reinhold Publishing Corp., New York, N. Y., 1958.

[2] W. Bockemuller, *Ann.*, **506**, 20 (1933).

[3] R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966)

[4] R. F. Merritt, *J. Org. Chem.*, **31**, 3871 (1966).

[5] R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).

[6] R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **32**, 416 (1967).

[7] F. Gumpert, *J. Prakt. Chem.*, **32**, 278 (1885).