$$\text{C}_{12}\text{H}_{25}\overset{+}{\underset{\underset{\text{Me}_2}{|}}{\text{P}}}\text{—NH}_2\text{Cl}^- + \text{Me}_2\text{S}\overset{\overset{\displaystyle O}{\diagup}}{\diagdown}_{\displaystyle\text{NH}} \quad —\!/\!\!/\!\!\to \text{IIa} + \text{NH}_3$$

the two reagents even when they were heated without a solvent for 17 hr at 125°.

Experimental Section[9]

N-Lithiodimethyl Sulfone Imine.—Dimethyl sulfone imine (mp 56–58°) was prepared as described by Bentley, McDermott, and Whitehead.[10] To a solution of 514 mg (5.52 mmoles) of the sulfone imine in 5 ml of benzene under argon at room temperature was added 4.08 ml (5.52 mmoles) of 1.35 N n-BuLi. The resulting, milky white liquid was then stirred for 2 hr and evaporated to dryness in vacuo (0.5 mm). The infrared spectrum of the resulting, white solid was similar to that of the free sulfone imine except that it lacked the NH absorption and the strong band at 8.3 μ in the spectrum of the latter substance. The solid completely dissolved in 10 ml of water to give a very basic solution. Upon adjusting the solution pH to 7 and evaporating the water, a solid was obtained which was sublimed at 60° (0.1 mm) to give 323 mg (63%) of a light yellow solid. Resublimation yielded white crystals identified as Me₂S(O)(NH) by the identity of its infrared spectrum to that of an authentic sample, and by its melting point and mixture melting point.

N-Lithiohexadecylmethyl Sulfone Imine.—Hexadecylmethyl sulfone imine (mp 70–72°) was prepared using a procedure analogous to that described for its dimethyl analog.[10] Its infrared and nmr spectra were completely consistent with the structure and were essentially identical with those of an authentic sample of dodecylmethyl sulfone imine.[11] A solution of 152 mg (0.5 mmole) of the sulfone imine in 10 ml of benzene under argon at room temperature was treated with 1 equiv of n-BuLi, and the resulting, clear solution was stirred for 2 hr. Evaporation of the solvent at 0.5 mm gave a white solid which, as was the case for the dimethyl analog, lacked the NH absorption and the band at ca. 8.3 μ in the infrared spectrum of the free sulfone imine. Addition of water gave a basic solution which was adjusted to pH 7 and evaporated to dryness. The resulting solid was extracted twice with chloroform, and the extracts were combined, dried (MgSO₄), and evaporated to yield 48 mg (32%) of a solid which, after it was sublimed, was identified as the starting sulfone imine by infrared analysis, melting point, and mixture melting point.

N-(Dimethyldodecylphosphoranylidene) Dimethyl Sulfone Iminium Chloride (IIa).—A solution of 17.8 mmoles of N-lithiodimethyl sulfone imine in 50 ml of benzene was prepared as described above. This was added via a syringe to a stirred dispersion of 17.8 mmoles of dimethyldodecylphosphine dichloride[7] in 400 ml of benzene under argon, and the resulting mixture was stirred over night at room temperature. Evaporation of the solvent in vacuo gave an oily solid which was partially dissolved by 100 ml of dichloromethane. Centrifugation caused the insoluble lithium chloride by-product to separate, and the remaining, clear, yellow liquid was again evaporated to dryness to yield a gum which slowly crystallized. One recrystallization from 1:1 benzene–hexane gave 4.02 g (63%) of a white solid identified as IIa. (Infrared analysis of the mother liquor clearly showed it to contain more of the same solid.) Several more recrystallizations gave the analytical sample, mp 120–122°. *Anal.* Calcd for C₁₆H₃₇ClNOPS: C, 53.68; H, 10.42; Cl, 9.91; N, 3.91; S, 8.96. Found: C, 53.64; H, 10.40; Cl, 9.78; N,

3.63; S, 9.05. The infrared spectrum showed bands at 8.08, 8.54, 9.28, 9.59, 10.27, 10.60, 10.82, and 11.44 μ.

A 307-mg portion of IIa was dissolved and stirred for 5 hr at room temperature in 10 ml of 0.6 N NaOH. Evaporation of the solvent in vacuo followed by sublimation of the resulting solid gave 163 mg (77%) of white crystals identified as dimethyldodecylphosphine oxide by infrared analysis, melting point, and mixture melting point (undepressed). The residue in the bottom of the sublimer was dissolved in water, and after the solution pH was adjusted to 2 with HCl, the solvent was again evaporated, and the residue was sublimed. A white solid (64 mg, 58%) collected which was identified as Me₂S⁺(O)(NH₂)Cl⁻ by infrared and melting point comparisons to the compound formed by treating Me₂S(O)(NH) with 1 equiv of HCl gas in benzene. Also, a mixture melting point of the two materials was undepressed.

N-(Dimethyloctadecylphosphoranylidene) Dimethyl Sulfone Iminium Chloride (IIb).—To a stirred suspension of 2.53 mmoles of dimethyloctadecylphosphine dichloride[7] in 150 ml of benzene under argon was added 2.53 mmoles of N-lithiohexadecylmethyl sulfone imine in 100 ml of benzene. (The latter solution was prepared as described above.) After the mixture had been stirred for 40 hr at room temperature, the solvent was removed in vacuo and 40 ml of dichloromethane was added to the resulting residue. A white solid (IIb) separated which weighed 490 mg (30%) after washing with acetone to remove the LiCl by-product, followed by drying. Several recrystallizations from methanol-acetonitrile gave the analytical sample, mp 143–145°. *Anal.* Calcd for C₃₇H₇₉ClNOPS: C, 68.10; H, 12.21; Cl, 5.43; N, 2.15; S, 4.92. Found: C, 67.80; H, 12.26; Cl, 5.22; N, 2.19; S, 4.98. The infrared spectrum was fairly similar to that of IIa and showed absorptions at 8.08, 8.52, 10.31, 10.67, 11.38, 12.50, and 13.93 μ.

A 146-mg (0.22 mmole) portion of IIb was stirred overnight with 0.6 N NaOH in 90% aqueous methanol. Evaporation of the solvent in vacuo yielded a solid which was sublimed to give 37 mg (54%) of a white solid. This was shown to be C₁₈H₃₇P(Me₂)(=O) by the identity of its infrared spectrum to that of an authentic sample, and by its melting point, and mixture melting point. The residue in the sublimer bottom was dissolved in water, the solution pH was adjusted to 7, and the solvent was evaporated. Sublimation of the residue gave 25 mg (37%) of C₁₆H₃₃S(Me)(O)(NH), as shown by infrared analysis and melting point.

The Reduction of Thiol Esters by Lithium Aluminum Hydride–Aluminum Chloride

DONALD E. BUBLITZ

The Dow Chemical Company, Western Division Research Laboratories, Walnut Creek, California 94598

Reductions of thiol esters to sulfides by means of modified lithium aluminum hydride (either by boron trifluoride etherate or aluminum chloride) have recently been reported.[1,2] This report describes the effect of various metal halides as modifiers, and the influence of their molar ratios upon this reaction.

The yields of sulfides are presented in Table I. The data, which reveal that increasing the steric bulk surrounding the thiol ester grouping results in decreased

(9) Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer Model 137 Infracord. The proton nmr spectra were obtained using a Varian spectrometer Model HA-100; the spectrum of IIa was measured in deuteriochloroform while that of IIb was measured in CD₃OD–CDCl₃. In all cases, TMS was used as an internal standard. Phosphorus nmr spectra were recorded on a Varian HR-60 spectrometer using benzene (IIa) or methanol (IIb) as solvents. Microanalyses were carried out by Spang Microanalytical Laboratories. n-Butyllithium was purchased from Foote Mineral Co. and was titrated immediately before use. All solvents were distilled and dried over molecular sieves. Solids were handled under argon in glove bags purchased from Instruments for Industry and Research, Cheltenham, Pa. Melting points are uncorrected.

(10) H. R. Bentley, E. E. McDermott, and J. K. Whitehead, *Proc. Roy. Soc.* (London), **B138**, 265 (1951).

(11) J. S. Berry, U. S. Patent 3,255,116 (1966); *Chem. Abstr.*, **65**, 5684 (1966).

(1) E. L. Eliel and R. A. Daignault, *J. Org. Chem.*, **29**, 1630 (1964).

(2) D. E. Bublitz, *J. Organometal. Chem.*, **6**, 436 (1966).

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$_3$COS(CH$_2$)$_5$CH$_3$	40	1.4:1.2
CH$_3$COS(C$_6$H$_{11}$)	80[a]	2.0:15[b]
CH$_3$COS(C$_6$H$_5$)	7.6	1.3:1.1
(CH$_3$)$_2$CHCOSC$_6$H$_{11}$	73[a]	2.0:15[b]
(CH$_3$)$_3$CCOSC$_6$H$_{11}$	60 (37)[a]	1.5:3.7
C$_6$H$_{11}$COSCH$_2$CH$_3$	49	1.4:1.2
CH$_2$=CH(CH$_2$)$_8$COSCH$_2$CH=CH$_2$	89	1.6:3.7
CH$_2$=CH(CH$_2$)$_8$COS(C$_6$H$_{11}$)	79	1.4:3.6
C$_6$H$_5$COSCH$_3$	79	1.4:1.2
C$_6$H$_5$COSC$_6$H$_5$	...	1.4:1.2
C$_6$H$_5$COS(C$_6$H$_{11}$)	93	1.4:1.2

[a] Data are from ref 1. [b] Mole ratio indicated is LiAlH$_4$/BF$_3$·Et$_2$O.

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.

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

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.

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

JOHN L. KICE AND J. DOUGLAS CAMPBELL[1b]

Department of Chemistry, Oregon State University, Corvallis, Oregon

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

(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.