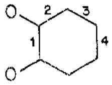
Table III. Structural Parameters for *cis*-Dioxomolybdenum(VI) Complexes with *o*-Quinone Ligands

	$MoO_2Cl_2(O_2C_{14}H_8)$	$Mo_2O_5(O_2C_{14}H_8)_2$[10]	$Mo_2O_5(O_2C_6H_4)_2^{2-}$[11]	$MoO_2(O_2C_6H_4)_2^{2-}$[12]
Mo–O_Q, Å	2.305 (3)	2.041 (5),[a] 2.242 (5),[b] 2.495 (5)[b]	1.98,[a] 2.16,[b] 2.37[b]	2.05 (2),[c] 2.15 (2)[d]
Mo–$O_{(oxo)}$, Å	1.671 (3)	1.686 (5)	1.70	1.77 (2)
C–O, Å	1.234 (4)	1.31 (1)	1.36	1.39 (3)
$(C–C)_1$, Å[e]	1.530 (5)	1.43 (1)	1.39	1.41 (3)
$(C–C)_2$, Å	1.431 (5)	1.43 (1)	1.42	1.36 (3)
$(C–C)_3$, Å	1.405 (5)	1.41 (1)	1.40	1.42 (3)
$(C–C)_4$, Å	1.487 (6)	1.47 (1)	1.41	1.36 (3)
O_Q–Mo–O_Q, deg	68.5 (1)	73.8 (2)	*f*	75 (1)
$O_{(oxo)}$–Mo–$O_{(oxo)}$, deg	104.8 (2)	105.0 (2)	*f*	101 (1)

[a] Terminal quinone oxygen. [b] Bridging quinone oxygens. [c] Position trans to catecholate oxygen. [d] Position trans to an oxo ligand. [e] Ring carbon–carbon bonds are numbered sequentially:



[f] Bond angles not reported.

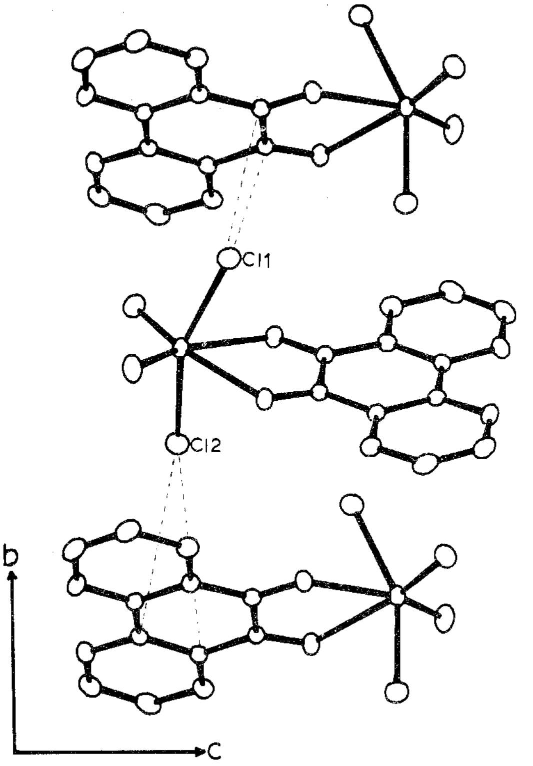
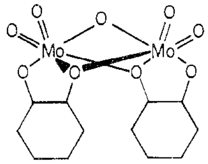


Figure 2. View of the shortest intermolecular contacts between molecules stacked along the 2_1 screw axis.

$Mo_2O_5(O_2C_6H_4)_2^{2-}$ and $Mo_2O_5(O_2C_{14}H_8)_2$ differing by two electrons have related structures (I) with semiquinone ligands



I

paired in the diamagnetic $Mo_2O_5(O_2C_{14}H_8)_2$ molecule. Molybdenum–oxygen lengths of 2.15 (2) Å for $MoO_2(O_2C_6H_4)_2^{2-}$ and 2.16 Å for the shorter of the two bridging lengths in $Mo_2O_5(O_2C_6H_4)_2^{2-}$ reflect stronger donor activity for the catecholates relative to the corresponding Mo–O length of 2.24 Å for $Mo_2O_5(O_2C_{14}H_8)_2$ and the long values of 2.305 (3) Å in the present structure. These structural features are in accord with the anticipated trend that, in the absence of π-acceptor bonding, oxygen donor activity decreases as ketonic character of the C–O bond increases.

Registry No. $MoO_2Cl_2(O_2C_{14}H_8)$, 63915-44-6.

Supplementary Material Available: Tables containing positional and thermal parameters for hydrogen atoms of the structure and a listing of structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) R. H. Thompson, "Naturally Occurring Quinones", 2nd ed, Academic Press, New York, N.Y., 1971; (b) R. A. Morton, "Biochemistry of Quinones", Academic Press, New York, N.Y., 1965; (c) A. Berger, "Medicinal Chemistry", 3rd ed, Wiley, New York, N.Y., 1970.
(2) M. Schnitzer and S. V. Khan, "Humic Substances in the Environment", Marcel Dekker, New York, N.Y., 1972.
(3) O. B. Maksimov and L. I. Glebko, *Geoderma*, **11**, 17 (1974).
(4) R. C. Pierce and M. Katz, *Environ. Sci. Technol.*, **10**, 45 (1976).
(5) S. S. Isied, G. Kuo, and K. N. Raymond, *J. Am. Chem. Soc.*, **98**, 1763 (1976), and references therein.
(6) A. E. Martell and M. M. Taqui Kahn, *Inorg. Biochem.*, **2**, 654 (1973).
(7) (a) C. G. Pierpont and H. H. Downs, *J. Am. Chem. Soc.*, **98**, 4834 (1976), and references therein; (b) Y. S. Sohn and A. L. Balch, *ibid.*, **94**, 1144 (1972).
(8) (a) R. F. Japp and A. E. Turner, *J. Chem. Soc.*, **57**, 4 (1890); (b) K. H. Meyer, *Ber. Dtsch. Chem. Ges.*, **41**, 2568 (1908); (c) J. Knox and H. R. Innes, *J. Chem. Soc., Trans.*, **105**, 1451 (1914).
(9) P. J. Crowley and H. M. Haendler, *Inorg. Chem.*, **1**, 904 (1962).
(10) C. G. Pierpont and R. M. Buchanan, *J. Am. Chem. Soc.*, **97**, 6450 (1975).
(11) L. O. Atovmyan, V. V. Tkachev, and T. G. Shishova, *Dokl. Akad. Nauk SSSR*, **205**, 609 (1972).
(12) V. V. Tkachev and L. O. Atovmyan, *Coord. Chem. (USSR)*, **1**, 845 (1975).
(13) This complex was prepared previously[9] by addition of 9,10-phenanthrenequinone to $MoCl_5$ in glacial acetic acid.
(14) C. G. Pierpont, *Inorg. Chem.*, **16**, 636 (1977).
(15) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
(16) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(17) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(18) L. R. Florian and E. R. Corey, *Inorg. Chem.*, **7**, 722 (1968).
(19) J. Bernstein, M. D. Cohen, and L. Leisenowitz, "The Chemistry of the Quinoid Compounds", Vol. I, S. Patai, Ed., Wiley, New York, N.Y., 1974, p 37.

Contribution from the Department of Chemistry,
University of Texas at Austin, Austin, Texas 78712

Chemistry of Polylithiated Species. Reactions of Polylithiated Silanes and Germanes

John A. Morrison and Richard J. Lagow*

Received February 16, 1977 AIC70122P

The interaction of a number of halogenated alkanes with a gaseous stream of lithium atoms has been shown to result in the formation of several poly- and perlithioalkanes including CLi_4, C_2Li_6, and C_3Li_8.[12] Under similar conditions, the reaction of a series of alkenes with lithium has also resulted in a variety of products such as $Li_3CC(Li)=(CLi)CLi_3$, the perlithioalkenes.[3] These results along with the earlier preparation of C_3Li_4[4] indicate the existence of a variety of perlithiated organic species, conceptually similar to the well-known hydrocarbons, but in which the carbon–hydrogen bonds have been replaced by carbon–lithium bonds. The structures of these polylithium compounds are yet unknown, but their polymeric "electron deficient" nature may lead to structures which rival the boron hydrides in complexity. Indeed Schleyer and Pople have very intriguing predictions for structures in the gas phase.[5]

The lower group 4A elements, silicon and germanium, are also known to form compounds with lithium,[6] e.g., $SiLi_4$ and $GeLi_4$, but the reaction chemistry of these compounds has received little study. In particular, no effort appears to have been made to utilize these reagents to prepare tetrasubstituted organic species. A survey of the reactions of the products formed by the interaction of $SiCl_4$ and $GeCl_4$ with gaseous lithium has been conducted for several reasons: to ascertain whether this reaction results in the formation of the perlithiated group 4A compounds; to initiate a study of the parameters involved in the solvation and derivatization of these species; and finally to determine if tetrasubstituted organometallic compounds can be prepared directly from the reaction of the perlithiometalloid with alkylating agents.

Experimental Section

Reactions between the tetrahalides of silicon or germanium with lithium were carried out in a manner similar to that reported for the alkyl halides.[3] Lithium, 10–25 g (Alfa Inorganics), was placed in the Knudsen cell of a stainless steel reactor which was then evacuated to 10^{-4} Torr. A resistively heated oven was placed around the cell and heated to 700–800 °C volatilizing the lithium. Simultaneously the gaseous chloride, ca. 1.5 g, was admitted through a port in the reactor. The products formed were condensed at −196 °C. After the reaction was terminated, the reactor was opened under argon and the solid material was removed.

Hydrolysis of the lithium-containing material was effected by reaction at −10 °C with a phosphoric acid solution (1:1 H_2O:85% H_3PO_4) in a vacuum line. The products were separated by fractionation and identified by their spectra and vapor pressures. Yields are based on the amount of chloride originally admitted to the reactor. The effects of a variety of solvents were surveyed; these were stored over $LiAlH_4$ and vacuum distilled into the flask containing the lithiated materials or redistilled immediately prior to use (hexamethylphosphoramide, HMPA).

Alkylation was accomplished by placing about 5 g of the lithium-containing solids in a flask followed by evacuation of the vessel and addition of 20 mL of the solvent and then excess alkylating agent. Typically, the reaction was held at −15 °C for 1 h and then slowly warmed to room temperature. The organometallic products prepared were separated by fractionation and identified by their mass, infrared, or NMR spectra. In each case the desired products were accompanied by large amounts of alkane formed by the Wurtz coupling reaction. Several attempts to gain structural and solubility information via ^{7}Li NMR were made on the lithiated silanes and germanes either prepared as indicated above or prepared from the direct reaction of the elements.[6] These experiments using the solvents diethyl ether or THF resulted in little useful information presumably due to the low solubility of the reagents. At −80 °C, in the absence of LiCl, only an extremely small singlet was observed (δ 0.1 ppm vs. external aqueous LiCl).

Results and Discussion

Hydrolysis Reactions. In the absence of solvent, silicon-containing samples which had been prepared using a great excess of lithium (100:1) liberated silane in 12% yield with a negligible amount of disilane. Samples in which the molar ratio of Li:$SiCl_4$ was lower gave smaller total yields of silanes but the ratio of silane to dislane varied, occasionally reaching 1:3. This indicates that in the presence of a great excess of lithium the formation of tetralithiosilane is favored, whereas if the relative concentration of lithium is lower, the formation of the catenated species, $(SiLi_2)_x$, becomes competitive. Hydrolysis of the products from the reaction of $GeCl_4$ gave similar results; in the case of very large excesses of lithium the yield of GeH_4 was 11% with no Ge_2H_6 formed. If the relative lithium concentration was less, the amount of GeH_4 decreased and small (3%) amounts of digermane were observed. The effects of several solvents upon the yield of hydride were investigated by allowing excess solvent to react at 20 °C with the Li/Si containing products for a variable period of time and then hydrolyzing in the usual manner. Butyl ether, monoglyme ($CH_3OCH_2CH_2OCH_3$), tetrahydrofuran, and hexamethylphosphoramide resulted in no change in the yields observed if the contact time between the solvent and the lithiated species was very short. If the reaction vessel was maintained at 20 °C before hydrolysis, the reactivity of the solid declined to zero. The time required for this decline varied but was approximately 24 h for the most reactive solvent HMPA. Concurrent with the loss of reactivity, a reddish brown lithium-containing solid which was unreactive toward hydrolysis separated from solution. Similar results were obtained for the germanium-containing species.

Alkylation Reactions. Reaction of excess methyl chloride for 12–24 h with the lithiated silanes in the presence of monoglyme resulted in the formation of tetramethylsilane in 5–10% yield. If hexamethylphosphoramide was used the yield of tetramethylsilane was much less, presumably because this solvent reacts with the starting materials as indicated above. The reactions of the germanium-containing analogues were considerably more complex and reminisicent of the reactions of polylithiated organic species.[7] The reaction of the methyl halides in the indicated solvents did not result in the formation of tetramethylgermane. The use of stronger alkylating conditions, either more basic solvents such as THF with the complexing agent tetramethylenediamine (TMEDA) or stronger alkylating agents such as the dialkyl sulfates, however, did result in the formation of polyalkylgermanes although proton abstraction from the solvent was a competitive reaction. For example, the reaction of $GeLi_4$ with dimethyl sulfate in butyl ether for 48 h resulted in a 20% yield of dimethylgermane. In THF, reaction of the germanium species with ethyl bromide in the presence of 1 equiv yielded the more fully substituted derivative $HGeEt_3$ in similar yields along with smaller amounts of tetraethylgermane.

Conclusion

In conclusion the reaction of $SiCl_4$ and $GeCl_4$ with gaseous lithium appears to result in $SiLi_4$ and $GeLi_4$, respectively, provided that the lithium is in sufficient excess. Upon hydrolysis the hydrides are liberated, the yield of silane, for example, being equal to or greater than that reported by Stock in his study of the hydrolysis of the silicides of a variety of electropositive elements.[8] As indicated by ^{7}Li NMR the lithiated species appear to be only marginally soluble in ethereal solvents. Reaction of the perlithiated silane with alkyl halides results in the tetraalkyl species, albeit in moderate yields. Alkylation reactions of perlithiogermanes require the use of stronger reagents, the dialkyl sulfates, resembling in this respect the polylithiated alkynes.[7] Further experiments, designed to maximize the yields and increase the number of substituted alkyl groups, will require the use of strongly coordinating trialkyl nitrogeneous bases such as diazobicyclo-[2.2.2]octane.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for partial support of this work.

Registry No. $GeCl_4$, 10038-98-9; $SiCl_4$, 10026-04-7; Li, 7439-93-2; $SiLi_4$, 63784-76-9; $GeLi_4$, 63937-05-3; GeH_4, 7782-65-2; SiH_4, 7803-62-5; $SiMe_4$, 75-76-3; GeH_2Me_2, 1449-64-5; $HGeEt_3$, 1188-14-3.

References and Notes

(1) C. Chung and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 1078 (1972).
(2) L. G. Sneddon and R. J. Lagow, *J. Chem. Soc., Chem. Commun.*, 302 (1975).
(3) J. A. Morrison, C. Chung, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 5015 (1975).
(4) R. West and P. C. Jones, *J. Am. Chem. Soc.*, **91**, 6155 (1969).
(5) J. B. Collins, J. D. Dill, E. D. Jammis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, **98**, 18 (1976); Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and W. L. Jorgensen, *Tetrahedron Lett.*, **43**, 3923–3926 (1976).
(6) W. Kelmm and M. Stuck, *Z. Anorg. Allg. Chem.*, **278**, 117 (1955); Q. Johnson, G. S. Smith, and D. Wood, *Acta Crystallogr.*, **18**, 131 (1965).
(7) R. West. *Adv. Chem. Ser.*, **No. 130**, 211 (1974).
(8) A. Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N.Y., 1933.

Contribution from the Department of Chemistry,
University of Texas at Austin, Austin, Texas 78712

Direct Fluorination of Carbon Disulfide. A Practical Synthesis for Difluoromethylenebis(sulfur trifluoride)

Lawrence A. Shimp and Richard J. Lagow*

Received April 7, 1977 AIC70252Y

The compound difluoromethylenebis(sulfur trifluoride) has been previously reported only as a very minor by-product in the electrochemical fluorination of carbon disulfide to CF_3SF_5[1] by Clifford, Haszeldine, El-Shamy, and Emeleus. The quantity produced was sufficient only to allow a boiling point and molecular weight determination to be carried out. Other fluorinations of CS_2 using AgF_2[2] or CoF_3[3] or direct fluorination in a diffusion-controlled fluorine flame[4] have yielded SF_5CF_3, $(SF_5)_2CF_2$, $SF_5CF_2SF_3$, and SF_3CF_3, but $(SF_3)_2CF_2$ was never detected in any of these cases.

Our technique of direct fluorination, using low temperatures and helium dilution, has been shown to be capable of very mild fluorination.[5,6] For this reason, reaction conditions providing a high yield of $(SF_3)_2CF_2$ were sought:

$$CS_2 \xrightarrow[-120\ ^\circ C]{F_2/He} SF_3CF_2SF_3$$

Experimental Section

^{19}F NMR spectra were taken on a Varian A56-60 spectrometer at 56.4 MHz and a Varian HA-100 spectrometer at 94.1 MHz equipped with a variable-temperature probe. $CFCl_3$ was used as an external standard for room-temperature spectra. At low temperatures $CFCl_3$ was used as an internal standard and solvent. Infrared spectra were taken on a Beckman IR20A spectrometer using a Pyrex gas cell equipped with KBr windows. Mass spectra were run on a Bell and Howell Model 21-491 instrument. The molecular weight determinations were carried out in a stainless steel and Kel-F vacuum line equipped with a Wallace and Tiernan metal gauge. The four-zone cold reactor fluorination system used has been described previously.[6]

In a typical reaction, 2 g of reagent grade CS_2 was injected into the reactor in which the second zone was held at −120 °C by means of a liquid nitrogen temperature controller system. The helium flow was set to 30 cm^3/min and the fluorine flow was set to 1.5 cm^3/min. These conditions were held for 3 days, after which the fluorine flow was terminated and the reactor warmed to room temperature. The products collected in the glass trap were transferred to a vacuum line and separated using a −78 °C trap. The materials which passed the trap were found to consist mainly of CF_4 and SF_4 with a trace of SF_6.[7] The material not passing the trap was pure $(SF_3)_2CF_2$. The yield based on the CS_2 injected was 60%, 3.6 g of $(SF_3)_2CF_2$.

$(SF_3)_2CF_2$. Calculated molecular weight, 228; found, 229. IR (cm^{-1}) 1255 (s), 1196 (s), 923 (m), 850 (s), 765 (w), 700 (vs), 578 (m), 527 (m). Mass spectral $(P - F)^+$ peak at *m/e* 209. ^{19}F NMR, room temperature (neat): broad peak at −6.6 ppm (assigned to SF_3 groups), sharp peak at 88.2 ppm (assigned to CF_2). Integral ratios were 3:1. At −80 °C (in $CFCl_3$) the SF_3 resonance had merged into the baseline and some splitting began to appear in the methylene resonance. The sample froze before the low-temperature exchange limit was reached. Similar temperature-dependent NMR behavior has been found for other SF_3 compounds.[2]

$(SF_5)_2CF_2$. The IR spectrum was in agreement with that reported by Clifford, El-Shamy, Emeleus, and Haszeldine.[1] The mass spectrum showed a parent peak at *m/e* 304. The ^{19}F NMR had three sets of peaks in the CF_2, axial S–F, and equatorial S–F regions. The spectrum was second order.

A second series of reactions was studied. The conditions were the same as the previous set for the first 3 days. Then the temperature was raised to −80 °C and the reaction allowed to continue for 3 more days. The product collection and separation were carried out in the same manner as the previous sample. The material passing the −78 °C trap was found to be mainly CF_4 and SF_4 with some SF_6 and possibly CF_3SF_3 and CF_3SF_5. The material not passing the −78 °C trap was found to be a mixture of $(SF_3)_2CF_2$ and $(SF_5)_2CF_2$ in the mole ratio of 23:27 (from integration of the CF_2 peaks in the ^{19}F NMR). Under these conditions the overall yield of $(SF_3)_2CF_2$ and $(SF_5)_2CF_2$ was found to be about 25% (0.7 g of $(SF_3)_2CF_2$ and 1.1 g of $(SF_5)_2CF_2$).

Results and Discussion

The major product of the −120 °C reaction was $(SF_3)_2CF_2$. The only other products, SF_4, CF_4, and SF_6, were much more volatile, and by collecting the reaction products with a −78 °C trap, essentially pure $(SF_3)_2CF_2$ can be obtained. This feature makes this a particularly convenient synthesis.

Despite the mild fluorination conditions, about 30% of the CS_2 starting material fragmented. No significant amounts of $\cdot SF_5$ compounds were found under these conditions. This would lead one to assume that higher temperature fluorination would lead to more fragmentation, rather than to the production of $\cdot SF_5$ compounds. Yet fluorination of CS_2 by Tyczkowski and Bigelow[4] in a controlled fluorine flame gave only about 35% CF_4, SF_4, and SF_6, and led to the formation of several $\cdot SF_5$ compounds.

The second series of reactions was carried out in an attempt to explain this discrepancy. These reactions were run for 3 days under conditions identical with the first set in order to produce $(SF_3)_2CF_2$ in the reactor. (The yield for this step was assumed to be about 50%. Running the reaction for less than 3 days leaves unreacted CS_2 in the reactor.) The temperature was then raised to −80 °C and the fluorination of the $\cdot SF_3$ compound was continued for 3 more days. The results showed that about 25% of the $(SF_3)_2CF_2$ was converted to $(SF_5)_2CF_2$, about 50% was converted to CF_4 and SF_4 (and possibly CF_3SF_3 and CF_3SF_5), and the rest was unchanged.

A possible explanation is that the fluorination first proceeds smoothly to $(SF_3)_2CF_2$; then further fluorination leads to $SF_3CF_2SF_4\cdot$ as an unstable intermediate. From there the intermediate can react further with fluorine to yield an $\cdot SF_5$ compound or decomposition products.

It is possible that at low temperatures the reactivity or reaction rate of the fluorine is reduced to the extent that SF_4 may be eliminated before the fluorination can be completed. It is also possible that as the temperature is raised, the fluorine becomes more reactive and forms $\cdot SF_5$ products more readily before the loss of SF_4 can occur.

Trifluorosulfur compounds in general are useful as reagents for the conversion of carbonyl and carboxyl groups to difluoroethylene and trifluoromethyl groups.[2] Difluoromethylenebis(sulfur trifluoride) would be expected to behave in a similar manner and should be investigated to discover the advantages it could offer for these reactions.

Acknowledgment. Fluorine chemistry at the University of Texas is supported by the Air Force Office of Scientific Research (AFOSR-76-3031A).

Registry No. $(SF_3)_2CF_2$, 374-49-2; $(SF_5)_2CF_2$, 1512-21-6; CS_2, 75-15-0; F_2, 7782-41-4.