available a wide range of organofunctional lead compounds and suggest the app tion of these compounds in some catalytic processes.

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- I A. J. BLOODWORTH AND A. G. DAVIES, J. Chem. Soc., (a) (1965) 5238, (b) (1965) 6245, (c) (16858, (d) (1966C) 299.
- 2 A. G. DAVIES AND P. R. PALAN, unpublished results.
- 3 A. G. DAVIES AND W. R. SYMES, J. Organometal. Chem., 5 (1966) 394.
- 4 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, Investigations in the Field of Organolead Chem
- International Lead Zinc Research Organization Inc., 1965, pp. 42, 98.
- 5 W. P. NEUMANN AND K. KÜHLEIN, Angew. Chem. Intern. Ed., 4 (1965) 784.

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Some improved preparations of silvlmetallic compounds

The preparation of silvlmetallic species by the cleavage of polysilanes with almetals in ethereal solvents, generally tetrahydrofuran, is well established and been reviewed^{1,7}. However, this work emphasized the fact that whereas lithipotassium, rubidium, and cesium derivatives are relatively easily obtained, the responding silvlsodium compounds are almost completely unknown.

Triphenylsilylsodium has been prepared by the cleavage of hexaphenyldisil in 1,2-dimethoxyethane² or in liquid ammonia³. However, in the ethereal solvent compound is difficult to prepare and unstable, whereas reactions in liquid ammo are complicated by the presence of the highly reactive solvent.

It was reported by Coates and co-workers⁴ that solutions of triphenylstanr sodium could be prepared by the action of sodium naphthaienide on hexapher distannane, tetraphenylstannane, or bromotriphenylstannane. In an extension of t work it was shown⁵ that triphenylsilylsodium can be prepared in tetrahydrofuran the action of sodium naphthalenide on triphenylsilane, hexaphenyldisilane, or chlc triphenylsilane. However, in all these reactions the stoichiometric quantity of sodi naphthalenide calculated to convert the tin or silicon compounds to the correspond sodium derivatives was employed.

In an excellent investigation, Eisch has shown⁶ that solutions of the lithiu biphenyl complexes in tetrahydrofuran are remarkably effective in promoting cert. cleavage reactions which proceed only slowly, or not at all, with the bulk metal. this investigation it was shown that catalytic quantities of biphenyl in the presen of the bulk metal were frequently effective.

We are currently undertaking a detailed investigation of the preparation silylmetallic compounds by the treatment of a variety of organosilicon compour with certain aromatic hydrocarbon adducts both preformed and prepared *in situ*.

Results so far obtained appear promising. Treatment of the cyclo- or polysila (x moles) with an excess of sodium in the presence of 0.05-0.3x mole of naphthalene

enyl in tetrahydrofuran gave good yields of triphenylsilylsodium, 1,4-disodioohenyltetrasilane and 1,5-disodiodecaphenylpentasilane, the latter two comids having not been previously reported. In a similar manner, 1,4-dilithiooctaiyltetrasilane and 1,5-dilithiodecaphenylpentasilane were obtained by cleavage of corresponding cyclosilanes with lithium in the presence of naphthalene or biiyl. Whereas the yield of the 1,5-dilithio compound was similar to that obtained he reaction of the cyclosilane with lithium alone⁷, the yield of the 1,4-dilithio pound was improved by 20–30 % (Ref. 7, 8).

All the silylmetallic compounds described above were characterized by treatt with acid or chlorotrimethylsilane to give 50–70 % yields of known compounds. late we have been unable to detect any products which suggest that the silylillic compounds react with the aromatic hydrocarbons.

While dodecamethylcyclohexasilane was slowly cleaved by sodium-potassium \cdot^9 it did not react with lithium¹⁰ alone^{*}. However, we have found that this comid reacted with the lithium/biphenyl system giving a mixture of dilithium pounds which yielded a mixture of α, ω -dihydropolysilanes on hydrolysis.

 $[(CH_3)_*Si]_s + Li \xrightarrow{C_{11}H_{10}} Li [(CH_3)_*Si]_nLi \xrightarrow{H_3O^+} H [(CH_3)_*Si]_nH$

above hydro-compounds have not been fully characterized as yet, but vapor se chromatography indicated the presence of compounds with values of n greater $n \sin x$.

The successful cleavage of the dodecamethyl compound suggested that the ium/biphenyl system might effectively cleave a hexaalkyldisilane to give a trisilyllithium compound. However, no reaction could be detected when hexa-hyldisilane was treated with lithium in the presence of biphenyl.

Preliminary investigations of the reactions of some of the silylsodium comnds indicate that they are by no means completely analogous to the corresponding lithium compounds. For instance, triphenylsilyllithium reacts with chlorobenzene lominantly via halogen-metal exchange¹ resulting in the formation of much hexanyldisilane, only a relatively low yield of the coupled product, tetraphenylsilane, ng formed. Triphenylsilylsodium, on the other hand, gives only a low yield of hexanyldisilane, the major product being tetraphenylsilane indicating that much less ogen-metal exchange occurred in this case.

The complete results of our systematic investigation will be published later. This research was supported by the United States Air Force under Contract 33(615)-2368 monitored by Materials Laboratory, Directorate of Laboratories, ight Air Development Center, Wright-Patterson A.F.B., Ohio.

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^{*} Electron spin resonance studies by Husk and West revealed that dodecamethylcyclohexane reacts with sodium-potassium alloy at low temperatures to form a radical-anion¹¹.

- I H. GILMAN AND H. J. S. WINKLER in H. ZEISS (ed.), Organometallic Chemistry, New Reinhold, 1960.
- 2 H. GILMAN AND A. G. BROOK, J. Am. Chem. Soc., 76 (1954) 278. 3 E. WIBERG, O. STECHER, H. J. ANDRASCHECK, L. KREUZBICHLER AND E. STAUDE, A Chem., Intern. Ed., 2 (1963) 507. 4 D. BLAKE, G. E. COATES, AND J. M. TATE, J. Chem. Soc., (1961) 613.
- 5 F. W. G. FEARON, Ph. D. Thesis, University of Wales, 1965.
- 6 J. J. EISCH, J. Org. Chem., 28 (1963) 707.
- 7 H. GILMAN AND G. L. SCHWEBKE, in F. G. A. STONE AND R. WEST (eds.), Advances in OI metallic Chemistry, Vol. I, Academic Press, New York, 1964.
- S H. GILMAN, R. HARRELL, K. Y. CHANG AND S. COTTIS, J. Organometal. Chem., 2 (1964 9 U. STOLBERG, Angew. Chem. Intern. Ed., 2 (1963) 150.
- H. GILMAN AND R. A. TOMASI, J. Org. Chem., 28 (1963) 1651.
 G. R. HUSK AND R. WEST, J. Am. Chem. Soc., 87 (1965) 3993.

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Thermolysis of methoxy-substituted polysilanes*

In a previous report¹ we have described the base-catalyzed sillicon-silicon silicon-methoxy redistribution with substituted polysilanes. In the case of dimethyltetramethoxydisilane (I), the base-catalyzed redistribution was extren rapid at 130°, and within five minutes 98% of the theoretical methyltrimethe silane was obtained based on the stoichiometry in equation (1).

Me Me $(MeO)_2Si-Si(OMe)_2 \longrightarrow MeSi(OMe)_3 + [(MeO)SiMe]_n$ Ι

During the course of this latter investigation we observed that I undergo thermal redistribution in the absence of added base. Thus, when I was heated at 1 for 40 h, the products were methyltrimethoxysilane, tris(methyldimethoxysil methylsilane (II) and a viscous nonvolatile polysilane residue (III)**.

Me $I \xrightarrow{d} MeSi(OMe)_2 + [(MeO)_2Si]_3SiMe + "higher polysilane residue"$ TT III

Compound II was isolated from the residue III by distillation; b.p. 110-111°, mm, vield 20-25 % (Anal. Found: C, 33.5, 33.8; H, S.53, S.60; Si, 30.8 %, mol. wt. by mass spectroscopy, calcd. for $C_{10}H_{20}Si_4O_6$: C, 33.5; H, S.40; Si, 31.3%; mol.

^{*} Redistribution studies with polysilanes. Part II. For Part I see ref. 1. Presented in at the Division of Organic Chemistry, 150th National Meeting of the American Chemical Soci Atlantic City, New Jersey, Sept. 13-17, 1965. Abstracts, p. 76S.

^{*} The reaction proceeds equally well in metal, Vycor* or acid-washed glass tubes.