

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

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Received March 29th, 1966

J. Organometal. Chem., 5 (1966) 590-592

Some improved preparations of silylmetallic compounds

The preparation of silylmetallic species by the cleavage of polysilanes with alkali metals in ethereal solvents, generally tetrahydrofuran, is well established and has been reviewed^{1,2}. However, this work emphasized the fact that whereas lithium, potassium, rubidium, and cesium derivatives are relatively easily obtained, the corresponding silylsodium compounds are almost completely unknown.

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

It was reported by Coates and co-workers⁴ that solutions of triphenylstannane sodium could be prepared by the action of sodium naphthalenide on hexaphenyldistannane, tetraphenylstannane, or bromotriphenylstannane. In an extension of this work it was shown⁵ that triphenylsilylsodium can be prepared in tetrahydrofuran by the action of sodium naphthalenide on triphenylsilane, hexaphenyldisilane, or chlorotriphenylsilane. However, in all these reactions the stoichiometric quantity of sodium naphthalenide calculated to convert the tin or silicon compounds to the corresponding sodium derivatives was employed.

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

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

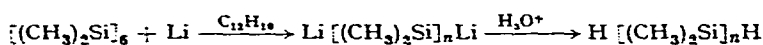
Results so far obtained appear promising. Treatment of the cyclo- or polysilane (x moles) with an excess of sodium in the presence of 0.05-0.31 mole of naphthalene

J. Organometal. Chem., 5 (1966) 592-594

enyl in tetrahydrofuran gave good yields of triphenylsilylsodium, 1,4-disodio-phenyltetrasilane and 1,5-disodiodecaphenylpentasilane, the latter two com-ids having not been previously reported. In a similar manner, 1,4-dilithioocta-yltetrasilane and 1,5-dilithiodecaphenylpentasilane were obtained by cleavage of corresponding cyclosilanes with lithium in the presence of naphthalene or bi-yl. 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 treat- 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 silyl- allic compounds react with the aromatic hydrocarbons.

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



above hydro-compounds have not been fully characterized as yet, but vapor se chromatography indicated the presence of compounds with values of n greater 1 six.

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

Preliminary investigations of the reactions of some of the silylsodium com- nds indicate that they are by no means completely analogous to the corresponding llithium compounds. For instance, triphenylsilyllithium reacts with chlorobenzene dominantly *via* halogen–metal exchange¹ resulting in the formation of much hexa- nyldisilane, only a relatively low yield of the coupled product, tetraphenylsilane, ng formed. Triphenylsilylsodium, on the other hand, gives only a low yield of hexa- nyldisilane, 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.

The authors are grateful to Dr. J. C. Young of the University College of Wales, erystwyth, for prior discussion and assistance.

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* Electron spin resonance studies by Husk and West revealed that dodecamethylcyclohexa- ne reacts with sodium–potassium alloy at low temperatures to form a radical-anion¹¹.

