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# THE PREPARATION AND SOME REACTIONS OF TRIPHENYLSILYLSODIUM AND METHYLDIPHENYLSILYLSODIUM*

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## INTRODUCTION

The preparation of silylmetallic species by the cleavage of polysilanes with alkali metals in ethereal solvents, generally THF, is well established and has been reviewed[2,3]. 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-dimethoxyethane[4] or in liquid ammonia[5]. However, in the ethereal solvent this compound is difficult to prepare and unstable, whereas preparations in liquid ammonia are complicated by the presence of the highly reactive solvent.

It was reported by Coates and co-workers[6] that solutions of triphenylstannylsodium could be prepared by the action of sodium naphthalenide on hexaphenyldistannane, tetraphenylstannane, on bromotriphenylstannane. In an extension of this work it was shown[7] that triphenylsilylsodium could be prepared in THF by the action of sodium naphthalenide or 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 series of investigations, Eisch *et al.*[8] have shown that solutions of the lithium–biphenyl complexes in THF are effective in promoting certain reactions which proceed only slowly with the bulk metal. In these investigations it was shown that catalytic quantities of biphenyl in the presence of the bulk metal were frequently effective.

We have found[1] that triphenylsilylsodium, or methyldiphenylsilylsodium, can be easily prepared in THF from the corresponding disilanes using metallic sodium in the presence of small quantities of naphthalene or biphenyl, or from the corresponding chlorosilanes and sodium in the presence of naphthalene. All attempts to prepare dimethylphenylsilylsodium by the cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane under similar conditions failed.

Some of the properties of the above silylsodium compounds have been examined, and have been found to be somewhat different from those of the analogous silyllithium compounds.

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* A preliminary note was published on this subject[1].

## RESULTS AND DISCUSSION

The reaction between hexaphenyl-, or 1,2-dimethyltetraphenyldisilane ($x$ moles) and excess sodium in the presence of biphenyl or naphthalene (0.1–0.2 $x$ moles) in THF gave solutions of triphenylsilyl- and methyldiphenylsilylsodium during 5–12 hours. The presence of the silylmetallic species in these solutions was demonstrated by: (*a*) hydrolysis to the known silanes and (*b*) reaction with a suitable chlorosilane to give the known disilanes (see Table 1). The yields of derived products obtained from these reactions were comparable to those obtained from the known silyllithium compounds[2].

TABLE 1

PRODUCTS OBTAINED FROM REACTIONS OF TRIPHENYLSILYLSODIUM AND METHYLDIPHENYLSILYLSODIUM

| *Silylsodium[a] compound* | *Reactant[b]* | *Products* (%) | *Products from corresponding silyllithium compound* (%) |
|---|---|---|---|
| $Ph_3SiNa$ | $H_3O^+$ | $Ph_3SiH$, 83 (67)[c] | $Ph_3SiH$, 81[d] |
| $MePh_2SiNa$ | $H_3O^+$ | $MePh_2SiH$, 71 (66.7)[c] | $MePh_2SiH$, 79[d] |
| $Ph_3SiNa$ | $Me_3SiCl$ | $Me_3SiSiPh_3$, 78.5[e] (70)[c] | $Me_3SiSiPh_3$, 79[9] |
| $MePh_2SiNa$ | $Ph_3SiCl$ | $MePh_2SiSiPh_3$, 67[e] | $MePh_2SiSiPh_3$, 52[10] |
| $Ph_3SiNa$ | PhCl | $Ph_6Si_2$, 19 | $Ph_6Si_2$, 66.3[2] |
| | | $Ph_4Si$, 45 | $Ph_4Si$, 17.7 |
| $MePh_2SiNa$ | PhCl | $MeSiPh_3$, 61 | $MeSiPh_3$, 16.8 |
| | | $MePh_2SiSiPh_2Me$, 16.7 | $MePh_2SiSiPh_2Me$, 57 |
| $Ph_3SiNa$ | n-BuBr | $Ph_3SiBu$-n, 22[e] | $Ph_3SiBu$-n, 10[11] |
| | | $Ph_6Si_2$, 43 | $Ph_6Si_2$, 60 |
| $Ph_3SiNa$ | $HSiCl_3$[f] | $Ph_6Si_2$, 13.3[e] | $Ph_6Si_2$, 20.6[12] |
| | | $(Ph_3Si)_3SiH$, 17 | $Ph_3SiH$, 29.5, |
| | | | $(Ph_3Si)_3SiH$, 4.4 |

[a] The silylsodium compounds were prepared from the respective disilanes and sodium in the presence of biphenyl, unless otherwise stated. [b] The ratio of halogen compound to silylsodium compound was 1:1, unless otherwise stated. [c] The silylsodium compounds were prepared from the respective chlorosilanes and sodium in the presence of naphthalene. [d] The silyllithium compounds[2] were hydrolyzed and worked up in the same manner as the silylsodium compounds. [e] The reaction of the silylsodium compound with the halide was carried out and the products were isolated in a similar manner to that previously reported for the analogous silyllithium compound. [f] A 3:1 molar ratio of $Ph_3SiNa$ to $HSiCl_3$ was used.

It was not possible to determine the concentration of the silylsodium compounds directly by the established double titration technique[13] for, on completion of the preparation, excess sodium naphthalenide or biphenylide was always present. In an attempt to overcome this difficulty, the solutions were decanted from the excess sodium and treated with a further amount of the respective disilane. It was observed that the greenish-brown solutions acquired the red-brown color characteristic of silylmetallic compounds[2], during 30 minutes to 1 hour. Working on the assumption that all of the anion radical had been consumed, the solutions were then analyzed by double titration with allyl bromide. In this way it was estimated that triphenylsilylsodium was obtained in *ca.* 80% yield from hexaphenyldisilane while methyldiphenylsilylsodium was obtained in *ca.* 75% yield from 1,2-dimethyltetraphenyldisilane.

The preparation of the silylsodium compounds was also attempted from the corresponding chlorosilanes. Here difficulty was experienced, for although the reaction between chlorotriphenylsilane or chlorodiphenylmethylsilane proceeded smoothly in the presence of naphthalene to give the required silylsodium compounds, similar reactions did not occur in the presence of biphenyl. In the latter cases the characteristic blue-green color of the sodium biphenylide initially formed on the surface of the sodium but was rapidly discharged and did not reform. Examination of the reaction mixtures by VPC at this stage showed that biphenyl was still present.

The reaction of sodium with naphthalene or biphenyl in THF gives rise to the naphthalenide or biphenylide anion radicals, by transfer of an electron from the metal into the lowest empty molecular orbital of the aromatic hydrocarbon (Ar)[14,15]:

$$\mathrm{Ar}+\mathrm{Na} \overset{\mathrm{THF}}{\rightleftharpoons} \overset{\cdot-}{\mathrm{Ar}}\mathrm{Na}^+$$

Such anion radicals are capable of transferring the extra electron to a suitable acceptor molecule of higher electron affinity during which process the hydrocarbon is regenerated[15]. It has been shown[7] that this type of electron transfer probably occurs between equimolar amounts of sodium naphthalenide and a triphenylhalosilane to give, initially, a triphenylsilyl radical*. Reactions of this type could possibly account for the formation of the silylsodium compounds obtained in this work.

$$\mathrm{R_3SiSiR_3}+\overset{\cdot-}{\mathrm{Ar}}\mathrm{Na}^+ \rightarrow \mathrm{R_3Si^{\bullet}}+\mathrm{R_3SiNa}+\mathrm{Ar} \qquad (1)$$

$$\mathrm{R_3SiCl}+\overset{\cdot-}{\mathrm{Ar}}\mathrm{Na}^+ \rightarrow \mathrm{R_3Si^{\bullet}}+\mathrm{NaCl}+\mathrm{Ar} \qquad (2)$$

$$\mathrm{R_3SiSiR_3}+2\,\overset{\cdot-}{\mathrm{Ar}}\mathrm{Na}^+ \rightarrow [\mathrm{R_3SiSiR_3}]^{2-}\ 2\,\mathrm{Na}^+ +2\,\mathrm{Ar} \rightarrow 2\,\mathrm{R_3SiNa}+2\,\mathrm{Ar} \qquad (3)$$

Reactions of type (1) or (2) should give an intermediate silyl radical, but this would be expected to be rapidly transformed to a silylsodium compound by reaction with either another anion radical, or metallic sodium:

$$\mathrm{R_3Si}+\overset{\cdot-}{\mathrm{Ar}}\mathrm{Na}^+ \rightarrow \mathrm{R_3SiNa}+\mathrm{Ar}$$

$$\mathrm{R_3Si^{\bullet}}+\mathrm{Na} \rightarrow \mathrm{R_3SiNa}$$

It is also possible that the disilane could react consecutively with two molecules of the anion radical (eqn. 3) to give an intermediate dianion, which could then decompose to yield two molecules of the silylsodium compound.

In the case of the chlorosilane reactions, the silylsodium compound initially formed would be expected to couple immediately with unreacted silyl halide to form a disilane, which, in turn, would be cleaved to the silylsodium compound. During the reaction of chlorotriphenylsilane with sodium in the presence of naphthalene this initial coupling was in fact observed and hexaphenyldisilane was identified as an intermediate product.

As only a small amount of aromatic hydrocarbon was required to convert a relatively large amount of the disilane, or chlorosilane, to the corresponding silylsodium compound, it must be assumed that the hydrocarbon liberated in reactions

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* It has been suggested[16] that reaction of chlorotrimethylsilane with sodium naphthalenide proceeds via nucleophilic attack of the naphthalenide anion radical on the silicon–halogen bond.

(1), (2) or (3) was immediately converted back to the anion radical, by reaction with excess sodium, to repeat the cycle.

A similar type of electron transfer mechanism to that described above was suggested by Eisch[8] to explain the high yields of, for instance, phenol obtained, subsequent to hydrolysis, by treatment of anisole with the 2 : 1 lithium–biphenyl adduct.

It was noted that the cleavage reaction proceeded more rapidly in the presence of biphenyl than with comparable molar amounts of naphthalene. For instance hexaphenyldisilane (0.05 mole) was cleaved by sodium in the presence of biphenyl (0.01 mole) during *ca.* 5 hours, whereas a similar reaction with naphthalene required *ca.* 12 hours. It has been shown[15] that the rate of electron transfer between an aromatic hydrocarbon anion radical and a suitable acceptor molecule is dependent on the difference in electron affinity between the parent hydrocarbon and the acceptor molecule. Naphthalene has a higher electron affinity than biphenyl, thus, assuming that similar factors govern the rate of electron transfer between sodium biphenylide, or naphthalenide, and hexaphenyl- or 1,2-dimethyltetraphenyldisilane, it is apparent why biphenyl promotes more rapid cleavage of the disilane than naphthalene.

Attempts to prepare dimethylphenylsilylsodium by the cleavage of 1,1,2,2-tetramethyl-1,2-diphenyldisilane with sodium in the presence of naphthalene or biphenyl gave no useful amount of the required compound. Initially the green, or blue-green, color of the anion radical was formed, but this was replaced during 6–8 hours by a red-brown color. Examination of hydrolyzed aliquots of the reaction mixtures at this stage showed that the hydrocarbons had been consumed and much unreacted disilane remained. A small amount of 4,4′-bis(dimethylphenylsilyl)biphenyl (2 %) was isolated from the biphenyl reaction. In order to attempt to establish the mode of consumption of the aromatic hydrocarbons, the reactions of 1,1,2,2-tetramethyl-1,2-diphenyldisilane ($x$ moles) with sodium in the presence of naphthalene or biphenyl ($x$ moles) were examined. Under these conditions all of the disilane was consumed in the biphenyl reaction and nearly all in the naphthalene reaction, during 24 hours. Some unreacted hydrocarbon remained in both reaction mixtures. After hydrolysis, VPC indicated that both reaction mixtures were complex, but it was possible to isolate some unreacted hydrocarbon from both reactions. In addition 19 % of 4,4′-bis(dimethylphenylsilyl)biphenyl was isolated from the biphenyl reaction and 3.5 % of 1-(dimethylphenylsilyl)naphthalene was isolated from the naphthalene reaction.

Unfortunately it was not possible to identify the remaining products in the above mixtures. However, in view of the fact that the disilane was mostly consumed in both reactions, it appears possible that cleavage to dimethylphenylsilylsodium may have occurred. The silylsodium compound may then have attacked the hydrocarbons to some extent resulting, eventually, in the formation of 4,4′-bis(dimethylphenylsilyl)biphenyl and 1-(dimethylphenylsilyl)naphthalene. This hypothesis is supported, to some extent, by the observation that reaction of dimethylphenylsilyllithium with biphenyl during 12 hours gave 7.1 % of 4,4′-bis(dimethylphenylsilyl)biphenyl. It is also possible that the silylsodium compound, if formed, may have been sufficiently reactive to attack the solvent (THF) to give a silyl-substituted butanol, a type of reaction which is known to occur under forcing conditions, with some silyllithium compounds[2].

*The reactions of triphenylsilyl- and methyldiphenylsilylsodium*

The stabilities of solutions of triphenylsilyl- and methyldiphenylsilylsodium were determined by periodically estimating the concentration of silylmetallic species by double-titration with allyl bromide[13]. The excess anion radical had previously been removed from these solutions by treatment with additional amounts of the respective disilanes. No change in the concentration of an 0.47 molar solution of triphenylsilylsodium could be detected during 50 hours. In the same time the concentration of an 0.45 molar solution of methyldiphenylsilylsodium dropped to 0.41 molar. These observations indicate that the stabilities of the silylsodium compounds in THF appear to approach those of the corresponding silyllithium compounds[17].

The greatest difference in reactivity between the silylsodium and silyllithium compounds so far observed is shown by their reactions with halogen compounds, in particular with chlorobenzene (see Table 1). The reaction of a silylmetallic compound with an organic halide can proceed by at least two routes[2] (*a*) nucleophilic attack of the silylmetallic on the halogen compound to give a tetrasubstituted silane and a metallic halide:

$$R_3SiM + R'X \rightarrow R_3SiR' + MX$$

(*b*) by an exchange reaction resulting in the formation of a silyl halide and a new organometallic compound:

$$R_3SiM + R'X \rightarrow R_3SiX + R'M$$

This reaction frequently leads to the formation of high yields of disilanes by coupling of the chlorosilane with unreacted silylmetallic compound:

$$R_3SiM + R_3SiX \rightarrow R_3SiSiR_3 + MX$$

The isolation of 45% of tetraphenylsilane from the reaction of triphenylsilylsodium with chlorobenzene, compared with 17.7% isolated from a similar reaction of triphenylsilyllithium[2], is typical of the increased yields of coupled products obtained from the reactions of the silylsodium compounds with halogen compounds. The increased yields of coupled products suggest that the silylsodium compounds are more powerful nucleophilic reagents than the corresponding silyllithium compounds.

The yield of tris(triphenylsilyl)silane (17%) obtained from triphenylsilylsodium and trichlorosilane is of significance, for it indicates that steric factors alone were not entirely responsible for the low yield of silane (4.4%)[12] obtained from triphenylsilyllithium and trichlorosilane.

## EXPERIMENTAL

Some of the reactions of triphenylsilylsodium described in this work have previously been carried out with triphenylsilyllithium. The reaction conditions and methods of work-up used in this work were identical to those previously reported so will not be described in detail. The experimental details can be found in references given in Table 1.

Unless otherwise stated all solid compounds were identified by mixed melting points and comparison of their infrared spectra with authentic materials. Liquids, or low melting solids, were identified by comparison of their boiling points, VPC retention times, and infrared spectra with authentic materials. The physical properties of these materials can be found in refs. 18 and 19. All reactions were carried out in oven-dried glassware, under an atmosphere of dry, oxygen-free nitrogen.

THF was purified by distillation from sodium benzophenone ketyl, after initial drying over sodium. The disilanes used were all prepared and purified by standard procedures[3]. Organosilicon halides were obtained from Dow Corning Corp. and were used without further purification. All other organic halides were dried over phosphorous pentoxide before use.

Infrared spectra were determined using a Perkin Elmer Model 21 Spectrophotometer. VPC analyses were carried out with an F and M Model 500 gas chromatograph, using an 18 × $\frac{1}{4}''$ column packed with silicon gum rubber, S.E. 30, on Chromosorb W (1 : 20).

*Triphenylsilylsodium and methyldiphenylsilylsodium by cleavage of the corresponding disilanes*

(1) *In the presence of biphenyl.* The respective disilanes (0.025 mole) and biphenyl (0.005 mole) were dissolved in THF (100 ml) in a nitrogen-flushed three-necked flask fitted with a paddle stirrer. Sodium (0.1 g-atom) was cut into the mixture through an emergent nitrogen stream. On stirring, the mixtures turned blue-green during 5–10 min. After 5 h stirring the solutions were decanted through a short tube plugged with glass wool into a nitrogen flushed addition funnel, before being added dropwise with stirring to 20% hydrochloric acid (100 ml). The ethereal layers were dried, concentrated and the residues distilled under reduced pressure to give triphenylsilane (10.8 g, 83%) and methyldiphenylsilane (7.95 g, 71%), respectively.

(2) *In the presence of naphthalene.* A similar reaction was carried out with hexaphenyldisilane using naphthalene (0.005 mole) instead of biphenyl. Twelve hours stirring was required to consume all the disilane. The mixture was hydrolyzed and worked up as described above to give triphenylsilane (10 g, 77%).

*Preparation of triphenylsilylsodium and methyldiphenylsilylsodium by the reaction of chlorotriphenylsilane and methyldiphenylchlorosilane with sodium*

(1) *In the presence of biphenyl (attempted).* The respective chlorosilanes (0.05 mole) and biphenyl (0.01 mole) were dissolved in THF (100 ml) and sodium (0.2 g-atom) was added in small pieces which immediately turned blue-green on the cut surfaces. On stirring the mixtures the blue-green color was rapidly discharged, the sodium acquiring a tarnished appearance. Examination of the reaction mixtures by VPC after 5 hours showed the presence of unreacted biphenyl.

(2) *In the presence of naphthalene.* Chlorotriphenylsilane (0.05 mole) and naphthalene (0.01 mole) were dissolved in THF (100 ml) and sodium (0.2 g-atom) was added. A faint green color was formed on the surface of the sodium which was not completely discharged on commencement of stirring. After 15 min a white solid began to separate out of solution, a portion of this was removed after 1 h and was shown to be almost pure hexaphenyldisilane. After 2 h stirring the solution turned deep green. The reaction was stirred for a total of 5 h before the solution was hydrolyzed and worked up as previously described to give triphenylsilane (8.7 g, 67%).

A similar reaction with methyldiphenylchlorosilane (0.05 mole) gave methyldiphenylsilane (6.6 g, 66%).

### *Determination of the stabilities of triphenylsilylsodium and methyldiphenylsilylsodium in THF*

The silylsodium compounds were prepared from 0.025 mole of the respective disilanes, 0.005 mole of biphenyl and 0.1 g-atom of sodium in THF. The dark blue-green solutions were decanted away from the excess sodium and treated with a further 0.005 mole of the respective disilanes. The blue-green colors faded during 30–60 min being replaced by red-brown colors. The solutions were stored under nitrogen and periodically analyzed by double titration[13] with allyl bromide. No change was observed in the concentration of triphenylsilylsodium, initially 0.047 molar, during 100 h. During the same time the concentration of methyldiphenylsilylsodium, initially 0.045 molar, dropped to 0.041 molar.

### *General procedure for the reaction of triphenylsilylsodium and methyldiphenylsilylsodium with halogen compounds*

The silylsodium compounds, prepared by the cleavage of the respective disilanes (generally 0.025 mole) with sodium in the presence of biphenyl, or by the reaction of the respective chlorosilane (0.05 mole) with sodium in the presence of naphthalene, were added to solutions of the halogen compounds (0.05 moles unless otherwise stated in Table 1) in THF (100 ml). The mixtures were stirred until Color Test I[20] was negative when they were hydrolyzed by addition to a mixture of ice and hydrochloric acid. Work-up details are given for those reactions not previously reported in detail with analogous silyllithium compounds.

*Triphenylsilylsodium and chlorobenzene.* The hydrolyzed mixture was filtered giving a solid m.p. 237–93° which, on extraction with hot benzene left hexaphenyldisilane (2.5 g, 19%). The ethereal layer was separated, dried, combined with the benzene extracts of hexaphenyldisilane and concentrated. Recrystallization of the residue from ethyl acetate gave tetraphenylsilane (7.5 g, 45%).

*Methyldiphenylsilylsodium and methyldiphenylsilyllithium with chlorobenzene.* The hydrolyzed mixture from the silylsodium reaction was separated, the ethereal layer dried, concentrated and the residue distilled under reduced pressure to give methyltriphenylsilane (8.35 g, 61%). Recrystallization of the stillpot residue from petroleum ether gave 1,2-dimethyltetraphenyldisilane (1.65 g, 16.7%).

A similar reaction with methyldiphenylsilyllithium gave methyltriphenylsilane (2.3 g, 16.8%) and 1,2-dimethyltetraphenyldisilane (5.7 g, 57%).

### *Attempted preparation of dimethylphenylsilylsodium by reaction of sodium with* 1,1,2,2-*tetramethyl*-1,2-*diphenyldisilane* (*I*)

(1) *In the presence of biphenyl.* (I) (0.05 mole) and biphenyl (0.01 mole) were dissolved in THF (100 ml). Sodium (0.2 g-atom) was added and stirring was commenced. After 15 mins the solution turned dark blue, a color which changed to light brown after 6 hours. A portion of the mixture was hydrolyzed and examined by VPC; only a small amount of dimethylphenylsilane and much unreacted (I) could be detected. The solution was decanted from excess sodium and hydrolyzed with dilute acid. Concentration of the dried ethereal layer and distillation under reduced pressure gave (I) (46%). Crystallization of the stillpot residue gave 4,4′-bis(dimethylphenylsilyl)-biphenyl[18] (2%).

(2) *In the presence of naphthalene.* A similar reaction was carried out in the

presence of naphthalene (0.01 mole). After 8 hours stirring only (I) (38.5%) was isolated after work-up as described above.

*Reaction of (I) (x moles) with (1) biphenyl (2x moles) or (2) naphthalene (x moles) and sodium in THF*

(1) (I) (0.025 mole) and biphenyl (0.05 mole) were dissolved in THF (75 ml). Sodium (0.1 g-atom) was added and the solution was stirred 24 h when examination by VPC showed no unreacted (I). The reaction mixture was hydrolyzed, concentrated and the residual oil sublimed (100°/5 mm) to give biphenyl (3.0 g, 39.5%). Crystallization of the residue from methanol gave 4,4'-bis(dimethylphenylsilyl)biphenyl (19%).

(2) A similar reaction was carried out between (I) (0.15 mole), naphthalene (0.15 mole) and sodium (0.4 g-atom) in THF (250 ml). After 24 h VPC indicated that most of (I) had been consumed. The reaction mixture was hydrolyzed, concentrated and the residual oil was sublimed (110°/7 mm) to give naphthalene (3.0 g, 15.7%). The sublimation residue was distilled through a 18 in × 6 mm Nester Faust spinning band column to give 1-(dimethylphenylsilyl)naphthalene (1.7 g, 3.5%). 1-(Dimethylphenylsilyl)naphthalene was prepared as a reference compound from 1-lithionaphthalene[21] (0.1 mole) and dimethylphenylchlorosilane (0.1 mole) in ether at $0 \pm 5°$ during 24 h. Hydrolysis and distillation gave 65% of the required product, b.p. 136–38.5°/1.5 mm, m.p. 53–4°. (Found: Si, 10.56, 10.62. $C_{18}H_{18}Si$ calcd.: Si, 10.67%.)

*Reaction of dimethylphenylsilyllithium with biphenyl*

Dimethylphenylsilyllithium[2] (0.1 mole) in THF (100 ml) was added to biphenyl (0.1 mole) in THF (50 ml). After 48 h stirring the mixture was hydrolyzed with dilute hydrochloric acid, concentrated, and the residue sublimed (100°/5 mm) to give biphenyl (39.5%). Repeated crystallization of the residue from methanol gave 4,4'-bis(dimethylphenylsilyl)biphenyl (7.1%).

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## SUMMARY

Triphenylsilylsodium and methyldiphenylsilylsodium have been prepared in THF in 70–80% yields by reaction between the corresponding disilanes and sodium in the presence of small amounts of naphthalene or biphenyl, or between the corresponding disilanes or chlorosilanes and sodium in the presence of naphthalene. No silylsodium compounds were formed by the reaction of the chlorosilanes with sodium in the presence of biphenyl.

Attempts to prepare dimethylphenylsilylsodium from 1,1,2,2-tetramethyl-1,2-diphenyldisilane and sodium in the presence of naphthalene or biphenyl failed. In these cases dimethylphenylsilyl-substituted derivatives of the hydrocarbons were isolated.

Triphenylsilylsodium and methyldiphenylsilylsodium are approximately as stable as the established silyllithium compounds. In reactions with halogen-containing compounds the silylsodium compounds gave higher yields of coupled products than the comparable silyllithium compounds.

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