cal wave length of nitrobenzene in the pure liquid state is evidently due to dipole–dipole forces since, in cyclohexane and benzene solutions, where dipole–dipole forces are unimportant, its values are close to those of bromobenzene.

The critical wave lengths of the solutions in benzene are generally higher than would be expected from the viscosity of the liquid. Benzene is a better solvent than aliphatic hydrocarbons. It has been found[16] to have an abnormal effect upon the dipole moment of ethylene chloride, raising it above the values observed in other non-polar solvents. Although the benzene molecule has no dipole moment as a whole, it has six symmetrically located C–H dipoles, which, on the basis of comparative boiling points, Van Arkel[17] has proposed to have moments of the same magnitude as the highly polar C–F bonds. Such a moment value (about 1.4×10^{-18}) is far larger than that ordinarily attributed to the C–H bond, 0.3 to 0.5×10^{-18}, in both aromatic and aliphatic compounds.[18] However, from the intensities of vibration bands, Cole and Thompson[19] have obtained a mean value of about 0.57×10^{-18} with the hydrogen atom positive with respect to the carbon. If the relatively small size of the hydrogen atom permits these dipoles to come close to neighboring molecules, they may well give sufficiently strong dipole–dipole forces to account for the abnormality of benzene.

The values of the distribution constant α in Table IV resemble those previously found[4] for pure liquids in that they tend to increase with increasing viscosity. The temperature dependence of α for the solutions of low viscosity is within the large experimental error in the parameter. The nearly spherical molecule of *t*-butyl chloride shows a distribution constant indistinguishable from zero in the pure liquid state and in solution among the nearly spherical molecules of carbon tetrachloride. The large and somewhat unsymmetrical molecules of α-chloronaphthalene and α-bromonaphthalene[8] in heptane solution similarly show little or no distribution, and only a small distribution in the pure state.[4] All of the solutes show a considerable distribution in the viscous paraffin oil, the distribution being greater, the larger the molecules. More data are needed before definite conclusions may be drawn, but the few available results suggest that when the solvent molecules are sufficiently large in comparison to those of the solute, their distribution may not average out sufficiently during the orientation process to give uniform environment to the solute molecules. Variation of molecular shape and segment orientation should give distribution in the tetradecyl bromide solutions, irrespective of the solvent molecules.

PRINCETON, NEW JERSEY

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[16] A. E. Stearn and C. P. Smyth, THIS JOURNAL, **56**, 1667 (1934).

[17] A. E. Van Arkel, *Trans. Faraday Soc.*, **42B**, 81 (1946); see also J. H. van Santen, *ibid.*, **42A**, 165 (1946).

[18] W. L. G. Gent, *Quart. Rev.*, **2**, 383 (1948); C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

[19] A. R. H. Cole and H. W. Thompson, *Trans. Faraday Soc.*, **46**, 103 (1950).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The Formation of Arylsilylpotassium Compounds

BY ROBERT A. BENKESER, HERBERT LANDESMAN AND DONALD J. FOSTER

Organosilylpotassium compounds have been prepared by the reaction of substances containing the ≯Si–H or ≯Si–OR linkages with a 1:5 Na/K alloy. Thus triphenylmethoxysilane, triphenylsilane and tri-*p*-xenylsilane all react with this alloy and the resultant organometallics can be coupled with bromobenzene, triethylchlorosilane, methyl iodide and *p*-bromobiphenyl. Diphenylsilane and phenylsilane also react with Na/K alloy and the product can be coupled with bromobenzene to yield tetraphenylsilane. Triethylsilane does not seem to react with the alloy under the conditions of the experiment.

In a previous publication from this Laboratory[1] triphenylsilylpotassium was prepared in ethyl ether by the cleavage of phenylisopropyltriphenylsilane with liquid Na/K alloy (1:5 by weight).[2] We are now reporting the preparation of arylsilylpotassium compounds by the reaction of Na/K alloy with compounds containing the ≯SiH or ≯Si-OR linkages. The following reactions were carried out.

$$(C_6H_5)_3SiOCH_3 \xrightarrow[(2)\ (C_2H_5)_3SiCl]{(1)\ Na/K} (C_6H_5)_3SiSi(C_2H_5)_3 \tag{a}$$

$$(C_6H_5)_3SiH \xrightarrow[(2)\ C_6H_5Br]{(1)\ Na/K} (C_6H_5)_4Si \tag{b}$$

$$(C_6H_5)_3SiH \xrightarrow[(2)\ CH_3I]{(1)\ Na/K} (C_6H_5)_3SiSi(C_6H_5)_3 + (C_6H_5)_3SiCH_3 \tag{c}$$

$$(p\text{-}C_6H_5C_6H_4)_3SiH \xrightarrow[(2)\ p\text{-}C_6H_5C_6H_4Br]{(1)\ Na/K} (p\text{-}C_6H_5C_6H_4)_4Si \tag{d}$$

$$(C_6H_5)_2SiH_2 \xrightarrow[(2)\ C_6H_5Br]{(1)\ Na/K} (C_6H_5)_4Si \tag{e}$$

$$(C_6H_5)SiH_3 \xrightarrow[(2)\ C_6H_5Br]{(1)\ Na/K} (C_6H_5)_4Si \tag{f}$$

$$(C_2H_5)_3SiH \xrightarrow{Na/K} \text{N.R.} \tag{g}$$

It is to be noted that in reaction (c) two products were obtained. In fact the hexaphenyldisilane was formed in larger yield than the expected coupling product. This is in contrast to the previous report[3] that triphenylsilylsodium reacts with methyl

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[1] R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

[2] In a private communication to us Dr. Henry Gilman reported that potassium alone will undergo similar reactions. Thus far we have not been successful with sodium alone but have continued with the use of the Na/K alloy because of the convenience involved in pipetting it into the reaction flask.

[3] C. A. Kraus and H. Eatough, THIS JOURNAL, **55**, 5008 (1933).

iodide in liquid ammonia to form apparently only triphenylmethylsilane.

In reactions (e) and (f) it appears at first sight that a di- or even a tripotassium compound is formed as an intermediate. This is by no means certain, however, and, in fact, seems rather unlikely. It remains for a mechanism study to establish the actual path of these reactions.

It is of interest that triethylsilane failed to react with the alloy (reaction g above). Apparently when no aromatic nuclei are attached to the central silicon atom the formation of the organometallic derivative is seriously curtailed. This is somewhat in keeping with the previous observation that phenylisopropyltrimethylsilane did not undergo cleavage with Na/K alloy.[1] A possible explanation might be that resonance in the silicon fragment is a contributing factor in these reactions.

Experimental

Triphenylmethoxysilane.—A saturated solution of 34.0 g. (0.115 mole) of triphenylchlorosilane in anhydrous ethyl ether was added slowly to 6.5 g. (0.12 mole) of sodium methoxide in 200 ml. of anhydrous methanol under a nitrogen atmosphere. After the addition was complete, the solvents were removed and that portion boiling between 164–165°(0.5 mm.) was collected. The distillate solidified on standing and after recrystallization from absolute ethanol gave 24 g. (71%) of crystals melting at 54.5–55° (uncor.).

Anal. Calcd. for $C_{19}H_{18}OSi$: Si, 9.65. Found: Si, 9.4.

Triphenylmethoxysilane with Alloy.—(a) Fourteen and five-tenths grams (0.05 mole) of triphenylmethoxysilane in 250 ml. of anhydrous ethyl ether and 10 ml. of liquid (1:5 by weight) Na/K alloy were stirred together for 6 hours at room temperature under a nitrogen atmosphere. A dark color was observed almost immediately and a heavy precipitate formed. Then 15.1 g. (0.10 mole) of triethylchlorosilane was added which discharged the color. The ether solution was filtered under nitrogen pressure and after removal of the solvent there was obtained 7.6 g. (41%) of 1,1,1-triphenyl-2,2,2-triethyldisilane melting at 96.5–97°[4] (uncor.). This showed no depression in melting point when mixed with an authentic sample.

(b) In a similar experiment 15.7 g. (0.1 mole) of bromobenzene dissolved in 25 ml. of anhydrous ether was added to the solution containing the organometallic. The excess alloy was destroyed by the careful addition of dilute hydrochloric acid under a nitrogen atmosphere. At this point the solid suspended in the ether layer was filtered off and combined with the material obtained upon evaporation of the ether. After recrystallization of this material from xylene there was obtained 13.2 g. (79%) of tetraphenylsilane melting at 229–230°.

Triphenylsilane with Alloy.—To 7.8 g. (0.03 mole) of triphenylsilane in 250 cc. of anhydrous ether under nitrogen was added 8 cc. of alloy. The mixture became red and then black and a precipitate was noted. The mixture was stirred two days at room temperature and then 9.36 g. (0.06 mole) of bromobenzene was added. The color diminished immediately. Alcohol was added under nitrogen to remove excess alloy and the mixture was then filtered. The ether insoluble material was washed with water and ether and then dried. There was obtained 6 g. (67%) of tetraphenylsilane, melting point and mixed melting point 229–230°.

Triphenylmethylsilane.—To 13 g. (0.05 mole) of triphenylsilane in 400 ml. of anhydrous ethyl ether was added 10 ml. of sodium-potassium alloy. After 16 hours of vigorous stirring at room temperature under a nitrogen atmosphere there was added 14.2 g. (0.1 mole) of methyl iodide in 25 ml. of ether which completely decolorized the reaction mixture. After the excess alloy was destroyed with 6 *N* hydrochloric acid, the colorless precipitate was filtered and after crystallization from xylene amounted to 5.8 g. of hexaphenyldisilane melting at 352–354°. An additional 0.9 g. was recovered from the ether layer making the total yield 6.7 g. (52%). The residue from the ether layer was distilled (fraction up to 200°(0.5 mm.) was collected) and the semi-solid distillate was fractionally crystallized from 95% ethanol. There was recovered 1.2 g. (9%) triphenylsilane and 4.5 g. (33%) of colorless crystals melting at 68.5–69° (uncor.). This gave no depression with an authentic sample of triphenylmethylsilane made from methyllithium and triphenylchlorosilane.

Tri-*p*-xenylsilane.—*p*-Xenylmagnesium bromide was prepared from 19.6 g. (0.8 g. atom) of magnesium, 98 g. (0.42 mole) of *p*-bromobiphenyl, 53.2 g. (0.49 mole) of ethyl bromide and 400 ml. of anhydrous ethyl ether according to the method of Goldschmidt and Modderman.[5] To the Grignard reagent was added 33.3 g. (0.246 mole) of trichlorosilane in 50 ml. of ether over a two-hour period. After refluxing for 15 hours the solution was hydrolyzed by the addition of dilute sulfuric acid. The crude product suspended in the ether layer was filtered off and amounted to 19 g. (16%). After repeated crystallizations from xylene it melted at 210.5–211° (uncor.) and gave no depression when mixed with tri-*p*-xenylsilane prepared by the lithium aluminum hydride reduction of tri-*p*-xenylbromosilane.

Anal. Calcd. for $C_{36}H_{28}Si$: Si, 5.74. Found: Si, 5.79.

This compound can also be prepared by the reaction of three equivalents of *p*-xenyllithium and trichlorosilane.

Tri-*p*-xenylsilane with Alloy.—Four and nine-tenths grams (0.01 mole) of tri-*p*-xenylsilane and 8 ml. of sodium-potassium alloy were stirred for 10 hours at room temperature in 200 ml. of anhydrous ether under a nitrogen atmosphere. A green-black color developed immediately. The addition of 9.3 g. (0.04 mole) of *p*-bromobiphenyl in 25 ml. of anhydrous ether caused some evolution of heat but the color of the solution was not completely removed. The excess alloy was destroyed by the careful addition of 6 *N* hydrochloric acid. The crude precipitate in the ether layer when dried weighed 3.3 g. (55%). After two crystallizations from xylene, 3.1 g. (48%) of material melting at 280–281° was obtained which gave no depression of melting point when mixed with an authentic sample of tetra-*p*-xenylsilane[6] prepared by the reaction of trichlorosilane with four equivalents of *p*-xenyllithium.

Anal. Calcd. for $C_{48}H_{36}Si$: Si, 4.38. Found: Si, 4.2.

Diphenylsilane.—To 9.75 g. (0.257 mole) of lithium aluminum hydride in 250 cc. of anhydrous ether was added 127 g. (0.5 mole) of diphenyldichlorosilane. The solution was heated at reflux for one hour and then hydrolyzed with dilute hydrochloric acid. The ether layer was separated and evaporated. The residue was distilled to give 62 g. of the silane (75.6%), b.p. 75–76° at 0.5 mm., n^{20}_{D} 1.5795, d^{20}_{4} 0.9969; $MR_{\text{calcd.}}$ 61.3, MR_{found} 61.5.

Anal. Calcd. for $C_{12}H_{12}Si$: Si, 15.2. Found: Si, 15.4.

Diphenylsilane with Alloy.—A mixture of 10 g. (0.0543 mole) of the silane and 10 cc. of alloy was stirred in 250 cc. of anhydrous ether under nitrogen for 8 hours at room temperature. A yellow color was developed immediately on mixing and the solution turned red then deep black. To the black solution was added 17.0 g. (0.108 mole) of bromobenzene. The mixture was decolorized and refluxed vigorously. The ether solution was filtered immediately through a filter stick and hydrolyzed. The ether layer was separated and evaporated to give a solid (6.3 g.) melting at 223–227°. This was crystallized from xylene. The material, m.p. 228–229°, did not depress the melting point of authentic tetraphenylsilane. The flask residue was hydrolyzed and filtered. The solid obtained and that from evaporation of the ether layer gave 2.0 g. of tetraphenylsilane. Recrystallized from xylene, it did not depress the melting point of an authentic sample; total yield 8.3 g. (45.5%).

Phenylsilane.—To a solution of 14.6 g. (0.375 mole) of lithium aluminum hydride in 500 cc. of anhydrous ether was added 106 g. (0.5 mole) of trichlorophenylsilane under P_2O_5 drying tubes. The mixture was stirred 3 hours and then allowed to stand overnight. It was then poured onto cracked ice and the ether layer was separated. The ether solution was then dried over Drierite and the solvent evap-

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(4) In our previous publication,[1] the melting point of both this compound and 1,1,1-triphenyl-2,2,2-trimethyldisilane were reported 4° low because of a faulty thermometer. The correct melting point of the aforementioned methyl compound is accordingly 107–108° (uncor.), instead of 103–104° as reported.

(5) St. Goldschmidt and P. Modderman, *Rec. trav. chim.*, **69**, 1109 (1950).

(6) C. A. Kraus and W. K. Nelson, THIS JOURNAL, **56**, 195 (1934).

orated. The residue gave 37 g. (69%) of the silane boiling at 120° (760 mm.).[7]

Phenylsilane with Alloy.—A mixture of 10 g. (0.092 mole) of the silane and 8 cc. of alloy in 250 cc. of anhydrous ether was stirred under nitrogen for 12 hours at room temperature. The solution became red after 4 hours and deep black after an additional 2 hours of stirring. To the mixture was added 43 g. (0.27 mole) of bromobenzene. The solution refluxed vigorously and was decolorized. The ether solution was filtered through a filter stick and evaporated to give a white solid, m.p. 170–228°. Recrystallized from xylene, it melted at 200–228°. The material was shaken with anhydrous ether and filtered. The solid obtained melted at 227–228° and did not depress the melting point of authentic tetraphenylsilane. The yield was 2.1 g. (7%).

Triethylsilane with Alloy.—To 10 cc. of 1:5 sodium-potassium alloy in 250 cc. of anhydrous ether under nitrogen was added 8.5 g. of triethylsilane. The mixture was stirred 30 hours at room temperature without visible reaction. To this mixture was added 30 g. of triphenylchlorosilane in 200 cc. of ether. There was slight reaction as evidenced by slow reflux. The mixture was stirred 2 hours then filtered from the alloy through a filter stick. The residue in the flask was stirred with 100-cc. portions of ether and filtered twice. The combined filtrates were evaporated. Distillation of the residue gave 7.5 g. (88% recovery) of triethylsilane, b.p. 107°. The residue was slightly impure triphenylchlorosilane, 16 g., m.p. 85–92°. The flask residue from filtration was treated with *i*-amyl alcohol to destroy the alloy and ethanol was added. The mixture was then filtered to give 7.3 g. of hexaphenyldisilane, m.p. 340–352°.

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LAFAYETTE, INDIANA RECEIVED AUGUST 9, 1951

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[7] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Trifluoropropyne. II. The Triple Bond and the Acetylenic Hydrogen

BY ALBERT L. HENNE AND MAXWELL NAGER[1]

Addition of hydrogen bromide to $CF_3C{\equiv}CH$ yields $CF_3CH{=}CHBr$, illustrating the direction of addition in an electrophilic reaction. Addition of ethanol with base catalysis yields $CF_3CH{=}CHOC_2H_5$. In the presence of mercuric salts, addition of water yields a mixture of CF_3COCH_3 and CF_3CH_2CHO. Polymerization occurs with cuprous salts. Ethane is displaced from C_2H_5MgBr by $CF_3C{\equiv}CH$, and the resulting $CF_3C{\equiv}CMgBr$ condenses normally with acetone to yield $CF_3C{\equiv}CC(CH_3)_2OH$. The acidity of the acetylenic hydrogen (${\equiv}C{-}H$) is discussed.

The influence of a trifluoromethyl group on an adjacent double bond has been reported in directed additions to $CF_3CH{=}CH_2$ by electrophilic,[2] nucleophilic[3] and free radical mechanisms.[4] The influence on a triple bond has been investigated only in nucleophilic additions to $CF_3C{\equiv}CCF_3$,[5,6] and found to occur easily and in stepwise manner. To learn how the CF_3-group affects the direction of addition of the triple bond and the acidity of an acetylenic hydrogen, trifluoropropyne, $CF_3C{\equiv}CH$, was synthesized[7] and is here examined.

Three asymmetrical reagents have been added to the triple bond of $CF_3C{\equiv}CH$, namely hydrogen bromide, ethanol and water. Addition of hydrogen bromide occurred easily and without need of any catalyst, to give only one product, $CF_3CH{=}CHBr$. The direction of addition is thus the same as in $CF_3CH{=}CH_2$ and is attributed to the polarization of the triple bond induced by the CF_3- group; the ease of addition was, however, much greater and since addition stopped with the first molecule of hydrogen bromide, the difference in the deactivations of the double and triple bond is clearly contrasted. A further example is the stepwise hydrogenation of $CF_3C{\equiv}CC(CH_3)_2OH$ shown in the experimental section.

Addition of alcohol in the presence of a base was very exothermic and, under the conditions used, stopped with the formation of the vinyl ether, $CF_3CH{=}CHOC_2H_5$; the direction of addition therefore was again that expected from the electronegativity of the CF_3- group, and the ease of stopping the addition after the first step paralleled the results reported for $CF_3C{\equiv}CCF_3$. By limited hydrogenation, the vinyl ether, $CF_3CH{=}CHOC_2H_5$ underwent splitting rather than addition and CF_3CH_2CHO was isolated, which proved its structure. This split is in accord with the previous observations of Baker and co-workers,[8] that vinyl ethers activated by an electronegative group (*i.e.*, carbonyl, quaternary ammonium) undergo hydrogenolysis easily.

Addition of water could not be brought about without the use of mercuric salts as catalyst, but in their presence a mixture of CF_3CH_2CHO and CF_3COCH_3 was obtained, in which the ketone predominated. We believe this orientation to be due to the formation of an intermediate mercurated complex in which the directing effect of the CF_3-group is overshadowed. Listing the hydration of α,β-acetylenic acids and esters, Johnson[9] states that all give β-keto derivatives, but his list does not include mercuric salt catalyzed hydrations. Hennion[10] states that all terminal alkynes yield 2-ketones, but found both possible ketones in the mercuric salt hydration of 2-heptyne and concluded that "the direction of electromeric polarization in alkyl and dialkyl acetylenes is not seriously affected by hyperconjugation or other factors ascribable to simple alkyl groups." Evidence for the exist-

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[1] Shell Oil Co., Houston, Texas.

[2] A. L. Henne and S. Kaye, THIS JOURNAL, **72**, 3369 (1950).

[3] A. L. Henne, M. A. Shook and R. L. Pelley, *ibid.*, **72**, 4756 (1950).

[4] A. L. Henne and M. Nager, *ibid.*, **73**, 5527 (1951).

[5] A. L. Henne, J. V. Schmitz and W. G. Finnigan, *ibid.*, **72**, 4195 (1950).

[6] D. W. Chaney, U. S. Patent 2,522,566 (1950); *C. A.*, **45**, 2015 (1951).

[7] A. L. Henne and M. Nager, THIS JOURNAL, **73**, 1042 (1951).

[8] R. H. Baker, *et al.*, *ibid.*, **66**, 343 (1944); **68**, 2009 (1946); **70**, 1490 (1948).

[9] A. W. Johnson, "The Chemistry of the Acetylene Compounds, Vol. II, The Acetylenic Acids," Arnold and Co., London, 1950.

[10] G. F. Hennion and C. J. Pillar, THIS JOURNAL, **72**, 5317 (1950).