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REACTION OF (TRIPHENYLSILYL)LITHIUM WITH SOME DI- AND TRIHALOBENZENES

O. W. STEUDEL*, A. C. RANADE** AND H. GILMAN
Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

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SUMMARY

Reactions of (triphenylsilyl)lithium with some di- and trihalobenzenes include coupling and halogen–metal exchange transformations. Of particular significance is the reaction with 1,2,4-tribromobenzene which gives, additionally, some 1,3,5-tribromobenzene. The extent of this isomerization is apparently determined by the base involved.

INTRODUCTION

In reactions of silylalkali-metal compounds with organic halides, three different modes of interaction have been observed: direct coupling; halogen–metal exchange; and dehydrohalogenation. In the reaction***[2,3] of (triphenylsilyl)potassium and (diphenylsilyl)potassium with monohalobenzenes, tetraphenylsilane was the major product, but hexaphenyldisilane and biphenyl were also isolated. Excellent and extensive studies by Brook and Wolfe[4] have demonstrated that halogen–metal exchange can account for the products isolated. Recently the reaction of (triphenylsilyl)lithium with hexachlorobenzene was reported[5] to give (pentachlorophenyl)lithium and hexaphenyldisilane. However, the reaction of (triphenylsilyl)lithium with an excess of hexafluorobenzene at low temperatures gives hexaphenyldisilane and 1,4-bis(triphenylsilyl)tetrafluorobenzene instead of the expected (pentafluorophenyl)triphenylsilane.

RESULTS

We report here interesting results in the reactions of (triphenylsilyl)lithium with some di- and trihalobenzenes. The addition of (triphenylsilyl)lithium to 1,2,4-tribromobenzene in a 3/1 molar ratio gave hexaphenyldisilane in high yield (71%), very small amounts of tetraphenylsilane (0.1%), 1,4-bis(triphenylsilyl)benzene (0.1%), and brown resins. Evidence for the presence of triphenylsilyl groups in these resins is

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* Metallgesellschaft, A.G. Frankfurt (Main), Germany.

** Present address: Department of Chemistry, North Texas State University, Denton, Texas, 76203.

*** For a comprehensive survey of (organosilyl)metallic compounds see ref. 1.

afforded by the IR spectra which show intense bands attributable to silicon–phenyl bonds, and by the total weight of the resins, which is 80% higher than that calculated for a polymer containing (C_6H_3) units only. The formation of tetraphenylsilane can be explained, in part, by the cleavage of a silicon–phenyl bond by an organolithium compound to form phenyllithium. The phenyllithium would react with bromotriphenylsilane, which was formed by halogen–metal interconversion, to give tetraphenylsilane. The observed 1,4-bis(triphenylsilyl)benzene might have arisen from a contamination of the tribromobenzene with 1,4-dibromobenzene. We could not, however, detect 1,4-dibromobenzene to the extent of 0.1% in our 1,2,4-tribromobenzene. It is interesting to note that no 1,4-bis(triphenylsilyl)benzene could be isolated from the reaction of (triphenylsilyl)lithium with 1,4-dibromobenzene in a 2/1 ratio. The products were hexaphenyldisilane (72.5%), tetraphenylsilane (4.4%) and brown resinous solids.

Reaction of 1,3,5-trichlorobenzene with (triphenylsilyl)lithium in a 1/3 molar ratio, gave hexaphenyldisilane (70.5%) and tetraphenylsilane (2.2%). No bis(triphenylsilyl)benzene could be detected. The yield of resins was 70% higher than the yield calculated for a polymer containing (C_6H_3) units only.

When 1,3,5-tribromobenzene was used, the products were hexaphenyldisilane (65%), tetraphenylsilane (1.1%), and resins as the sole additional organic product.

When 1,2,4-tribromobenzene was treated with (triphenylsilyl)lithium in a 1/1 molar ratio, hexaphenyldisilane was obtained in 65.5% yield, tetraphenylsilane in 0.8% yield, and brown resins. In addition to these products, 0.7 g of 1,3,5-tribromobenzene corresponding to 2.9% of the 1,2,4-tribromobenzene used as the starting material was also isolated. This experiment was checked.

$$1,2,4\text{-}C_6H_3Br_3 + Ph_3SiLi \longrightarrow 1,3,5\text{-}C_6H_3Br_3 + Ph_3SiSiPh_3 + Ph_4Si \qquad (1)$$

The 1,2,4-tribromobenzene used, (from Aldrich, m.p. 41–43°) was pure, as shown by NMR, GLC and thin layer chromatography. It is interesting to note that, in the reaction of 1,2,4-tribromobenzene with sodamide in liquid ammonia, Wotiz and Huba[6] obtained 1,3,5-tribromobenzene in 33% yield, far more than could be attributed to impurities in the starting material. Later, Moyer and Bunnett[7] observed that the isomerization also occurs, in higher yields, when potassium anilide is used. They also noted that under their conditions 1-bromo-2,4-dichlorobenzene isomerized to 1-bromo-3,5-dichlorobenzene; but neither 1,2,4-trichlorobenzene nor 1,2,4-triiodobenzene isomerized. They suggested that the steps involved were nucleophilic displacements by phenyl anions on halogen atoms, perhaps related to the halogen–lithium exchange reaction[8].

EXPERIMENTAL

Reaction of (triphenylsilyl)lithium with 1,2,4-tribromobenzene (1/3 ratio)

A solution of (triphenylsilyl)lithium in tetrahydrofuran was prepared from 20 g (0.039 mole) of hexaphenyldisilane, 4 g of lithium wire and 150 ml of THF. The solution was filtered through glass wool and added to a stirred solution of 7.93 g (0.025 mole) of 1,2,4-tribromobenzene in 50 ml of THF over a period of 1 h. There was a slightly exothermic reaction and a solid formed. Color Test[9] I, after 3 h of stirring, was negative. Water (200 ml) was added and the reaction products were filtered. The solid was thoroughly washed successively with water, ethanol, THF, benzene, and ether. This solid was shown to be hexaphenyldisilane by m.p. (365–368°), mixed m.p. with an authentic specimen, and IR spectrum (yield 12.7 g, 63.5%).

The washings were combined with the liquid reaction products, whereupon more solid precipitated. After separation of this material (hexaphenyldisilane, 1.5 g, 7.5%), the aqueous layer was washed twice with ether. The ether was added to the organic layer, the combined liquids were dried, and the solvents were cautiously evaporated. The residue was taken up in carbon tetrachloride and chromatographed on alumina. By elution, first with petroleum ether (b.p. 60–70°) and then cyclohexane, there was obtained 0.03 g of tetraphenylsilane, m.p. 233–235°, (mixed m.p. and comparison of infrared spectra). Elution with a mixture of cyclohexane (0.8 l) and carbon tetrachloride (0.2 l) yielded a solid, which on crystallization from ethyl acetate afforded 1,4-bis(triphenylsilyl)benzene, m.p. 353–354°, identified by mixed m.p. and comparison of IR spectra. Further elution gave additional hexaphenyldisilane (0.07 g). The overall yield of the latter compound was 14.3 g, containing 71.5% of the original Ph_3Si groups.

Elution with 0.5 l of 1/1 mixture of cyclohexane and carbon tetrachloride yielded 1.73 g of a brown, resinous solid. No further material was eluted by the mixture of these solvents and by carbon tetrachloride alone, but benzene and eventually ether eluted 1.66 g of a similar resinous material. These solids were soluble in benzene, ethyl acetate, carbon tetrachloride and carbon disulfide but did not crystallize. Their IR spectra showed the presence of silicon–phenyl bonds.

Reaction of (triphenylsilyl)lithium with 1,2,4-tribromobenzene (1/1 *ratio*)

A solution of (triphenylsilyl)lithium (prepared from 0.039 mole of hexaphenyldisilane) was added to a solution of 24.3 g, (0.077 mole) of 1,2,4-tribromobenzene in 50 ml of THF over a 1 h period. Color Test I was negative when the addition was complete. Water was added, and the reaction mixture was worked up as described. There were obtained 13.1 g (65.5%) of hexaphenyldisilane, 0.2 g (0.8%) of tetraphenylsilane, brown, resinous solids, and 0.7 g of 1,3,5-tribromobenzene (2.9%, based on 1,2,4-tribromobenzene), m.p. 121–122°, mixed m.p. 121–123°. The IR spectrum of the last mentioned product was superimposable on that of an authentic sample. (1,3,5-Tribromobenzene was also obtained in a check experiment as the first fraction in the chromatography on alumina.) Using Baker–Flex Silica Gel IB–F TLC sheets and petroleum ether (b.p. 60–70°) as the solvent, R_f values for 1,3,5-tribromobenzene and 1,2,4-tribromobenzene were 0.78 and 0.66, respectively, and the starting material did not show any 1,3,5-tribromobenzene. By NMR spectroscopy we were able to detect 0.2% of 1,3,5-tribromobenzene (purposely added) in 1,2,4-tribromobenzene. The NMR spectrum of the starting material did not show the presence of 1,3,5-tribromobenzene.

Reaction of (triphenylsilyl)lithium with 1,3,5-trichlorobenzene (3/1 *ratio*)

A solution of (triphenylsilyl)lithium in THF prepared from 20 g (0.039 mole) of hexaphenyldisilane, 4 g of lithium wire and 150 ml of THF, was added to a stirred solution of 4.66 g (0.025 mole) of 1,3,5-trichlorobenzene in 50 ml of THF over a period of 1 h. After that time Color Test I was negative. Following the customary work-up, hexaphenyldisilane was obtained in a yield of 14.1 g [70.5%, based on (triphenylsilyl)-

lithium]. Chromatography on alumina gave 0.58 g ([illegible].2%) of tetraphenylsilane, a minor amount of hexaphenyldisilane and 3.32 g of brown resinous solids.

Reaction of (triphenylsilyl)lithium with 1,3,5-*tribromobenzene* (3/1 *ratio*)

When a solution of (triphenylsilyl)lithium in THF (prepared from 0.039 mole of hexaphenyldisilane) was added to a solution of 1,3,5-tribromobenzene (7.6 g, 0.024 mole) in THF in the same manner described above, a 65% yield of hexaphenyldisilane, 1.1% yield of tetraphenylsilane, and brown resinous solids were obtained.

Reaction of (triphenylsilyl)lithium with 1,4-*dibromobenzene* (2/1 *ratio*)

A solution of (triphenylsilyl)lithium (prepared from 0.039 mole of hexaphenyldisilane) in THF was added to a solution of 1,4-dibromobenzene (9.11 g, 0.039 mole) in 50 ml of THF over 2 h. Maximum temperature was 40°. Color Test I was positive after 3 h, but it was negative after 4 h. Hexaphenyldisilane (14.5 g, 72.6%), tetraphenylsilane (1.14 g, 4.4%), and brown resinous solids were obtained.

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