REACTIONS OF THE AZOBENZENE–DILITHIUM ADDUCT WITH SOME SUBSTITUTED CHLORO COMPOUNDS OF SILICON, GERMANIUM, TIN AND LEAD

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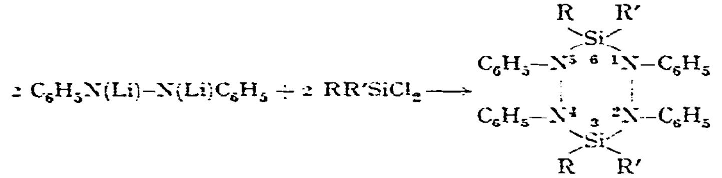
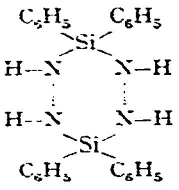
In an earlier paper[1] we reported some of the preliminary studies concerning the reaction of the azobenzene–dilithium adduct with substituted chlorosilanes. For example, it was observed that the azobenzene–dilithium adduct reacts with dichlorodiphenylsilane to give octaphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (I), a new type of heterocyclic compound containing silicon and nitrogen atoms. Similarly, dichloromethylphenylsilane gave 1,2,3,4,5,6-hexaphenyl-3,6-dimethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (II).

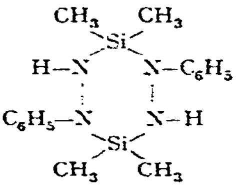


(I), R = R' = C_6H_5 (II), R = C_6H_5, R' = CH_3 (III), R = R' = CH_3 (IV), R = R' = C_2H_5
(V), R = R' = $CH_2C_6H_5$ (VI), R = C_6H_5, R' = $—CH{=}CH_2$ (VII), R, R' = $—CH_2CH_2CH_2CH_2CH_2—$

The syntheses of related cyclic compounds have been reported by Wannagat and Niederprum[2] who prepared 3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VIII) by the reaction of dichlorodiphenylsilane with hydrazine. They also prepared 3,3,6,6-tetramethyl-1,4-diphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (IX) using phenylhydrazine and dichlorodimethylsilane.



(VIII)



(IX)

The object of the present investigation was to extend the study of the reactions of the azobenzene–dilithium adduct with chlorosilane with a view to preparing different

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substituted tetraazadisilacyclohexanes. Also, attention was directed towards preparing heterocyclic compounds, containing Ge–N, Sn–N and Pb–N bonds, analogous to the tetraazadisilacyclohexanes.

The reaction of dichlorodimethylsilane with the azobenzene–dilithium adduct gave an 86.6% yield of 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (III), m.p. 226–227°. This compound, though reasonably stable in air, was easily hydrolyzed to hydrazobenzene on treatment with boiling water or acids. In a separate run employing a slightly different procedure for work-up which involved the treatment of the reaction mixture with water resulted in the isolation of a 64.9% yield of hydrazobenzene. No cyclic product, (III), could be obtained from this run. Similar reactions of dichlorodiethylsilane and dibenzyldichlorosilane gave 1,2,4,5-tetraphenyl-3,3,6,6-tetraethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (IV), m.p. 200–201°, and 1,2,4,5-tetraphenyl-3,3,6,6-tetrabenzyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (V), m.p. 153–155°, in 67.6% and 30.7% yields, respectively. The comparatively low yield of (V) could be attributed to the hindrance exerted by bulky benzyl groups attached to the silicon atom. It was observed that in a reaction using dichlorodi-*o*-tolylsilane and the azobenzene–dilithium adduct no cyclic tetraazadisilacyclohexane corresponding to product (V) could be isolated. The greater steric requirements of *o*-tolyl groups would considerably increase the difficulty in forming this compound.

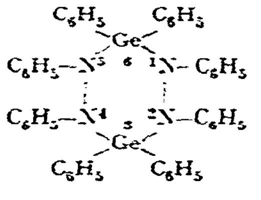
From the reaction of dichlorophenylvinylsilane and the azobenzene–dilithium adduct, a 57.2% yield of 1,2,3,4,5,6-hexaphenyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VI) was obtained. This product melted over the range 215–220° and could probably be a mixture of the two possible isomers. On using cyclopentamethylenedichlorosilane, a 70% yield of 1,2,4,5-tetraphenyl-3,6-dicyclopentamethylene-1,2,4,5-tetraaza-3,6-disilacyclohexane (VII), m.p. 331–332° (decomp.), was obtained.

The trisubstituted chlorosilanes reacted with the azobenzene-dilithium adduct in an expected manner to give substituted silylhydrazines.

$$C_6H_5N(Li)-N(Li)C_6H_5 + 2\ RR'R''SiCl \longrightarrow C_6H_5-\underset{(RR'R'')Si}{N}-\overset{Si(RR'R'')}{N}-C_6H_5$$

(X), $R = R' = R'' = CH_3$ (XI), $R = R' = R'' = C_2H_5$ (XII), $R = R' = CH_3$, $R'' = C_6H_5$
(XIII), $R = CH_3$, $R' = R'' = C_6H_5$

N,N'-Diphenyl-N,N'-bis(trimethylsilyl)hydrazine (X), N,N'-diphenyl-N,N'-bis(triethylsilyl)hydrazine (XI), N,N'-diphenyl-N,N'-bis(dimethylphenylsilyl)hydrazine (XII) and N,N'-diphenyl-N,N'-bis(diphenylmethylsilyl)hydrazine (XIII) were obtained in yields of 89.8%, 72.7%, 67.2% and 78.0%, respectively, from the reaction of the corresponding chlorosilanes with the azobenzene–dilithium adduct.



(XIV)

The reaction of dichlorodiphenylgermane with the azobenzene–dilithium adduct was quite similar to that of dichlorodiphenylsilane. The product obtained was octaphenyl-1,2,4,5-tetraaza-3,6-digermacyclohexane (XIV), a new heterocyclic compound. This substance melted at 306–307° (decomp.).

Unlike the reactions of silicon and germanium halides, diphenyltin dichloride reacted with the azobenzene–dilithium adduct to give a 90.9% yield of diphenyltin (polymer) and a 93.4% yield of azobenzene. No cyclic product containing tin and nitrogen, analogous to the tetraazadisilacyclohexanes, could be isolated. The formation of diphenyltin and azobenzene in nearly quantitative yields would suggest the possibility of an initial halogen–metal exchange reaction followed by the elimination of lithium chloride. From the reaction of the azobenzene–dilithium adduct and diphenyllead dichloride, the products isolated were metallic lead and azobenzene. However, none of the desired cyclic product was obtained.

EXPERIMENTAL

All melting points are uncorrected. In general, reactions were carried out under an atmosphere of dry, oxygen-free[3] nitrogen. Tetrahydrofuran boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium followed by distillation from lithium aluminum hydride. Dibenzyldichlorosilane[4], dichlorodi-o-tolylsilane[5], diphenyltin dichloride[6] and diphenyllead dichloride[7] were prepared by standards procedures. Silicon[8] and germanium[9] analyses were carried out using previously reported procedures. Solutions of the azobenzene–dilithium adduct in tetrahydrofuran were prepared as in a reported procedure[1,10].

The azobenzene–dilithium adduct and dichlorodimethylsilane

A solution of 0.1 mole of the azobenzene–dilithium adduct in 150 ml of tetrahydrofuran was added during 1 h to a stirred solution of 12.9 g (0.1 mole) of dichlorodimethylsilane in 25 ml of tetrahydrofuran. The reaction mixture became warm and the flask was cooled in a water bath (approx. 15°). The solution was colored light orange-yellow when the addition was completed. The solvent was removed by distillation and the residue extracted with 200 ml of hot, sodium-dried benzene. The benzene-insoluble portion was 8.0 g of lithium chloride, identified by qualitative tests. Subsequent to removal of the solvent from the benzene solution and treatment of the residue with petroleum ether (b.p. 60–70°) there was obtained 20.8 g (86.6%) of 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (III), m.p. 224–226°. After one crystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) the product melted at 226–227°. (Found: C, 69.66, 69.46; H, 6.33, 6.51; N, 11.64, 11.68; Si, 11.32. $C_{28}H_{32}N_4Si$ calcd.: C, 69.97; H, 6.71; N, 11.65; Si, 11.69%.)

From the petroleum ether-soluble portion an orange-red solid was obtained after removal of the solvent. This residue was chromatographed on alumina and elution with petroleum ether (b.p. 60–70°) gave 1.8 g (9.9%) of azobenzene, m.p. 67–68° (mixed m.p.).

In a second run using the same quantities of reactants and solvent, a slightly different procedure was adapted for the work-up of the mixture. After the addition of the azobenzene–dilithium adduct was completed (1 h), the reaction mixture was hydrolyzed with water and worked up to give a 64.9% yield of hydrazobenzene, m.p. 125–127° (mixed m.p.). A small quantity (7.1%) of azobenzene, m.p. 67–68° was also isolated. No 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane could be obtained from this run.

The azobenzene-dilithium adduct and dichlorodiethylsilane

To a stirred solution of 15.5 g (0.1 mole) of dichlorodiethylsilane in 50 ml of tetrahydrofuran was added during a 1-h period, 0.1 mole (130 ml) of a tetrahydrofuran solution of the azobenzene–dilithium adduct. The reaction was exothermic and the temperature was controlled by cooling the flask in a water bath (approx. 15°). After the addition was completed the solvent from the mixture was removed by distillation and the residue was then extracted with 300 ml of sodium-dried benzene. Removal of the solvent from the benzene solution gave a light orange-yellow solid which on treatment with dry petroleum ether (b.p. 60–70°) gave 18.0 g (67.6%) of 1,2,4,5-tetraphenyl-3,3,6,6-tetraethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (IV), m.p. 199–200°. The compound melted at 200–201°, after crystallization from a mixture of benzene and petroleum ether (b.p. 60–70°). (Found: C, 71.78, 71.98; H, 7.31, 7.16; N, 10.72, 10.62. $C_{32}H_{40}N_4Si_2$ calcd.: C, 71.65; H, 7.46; N, 10.44%.)

The azobenzene–dilithium adduct and dibenzyldichlorosilane

The azobenzene–dilithium adduct (0.075 mole, 125 ml) was added to 21.1 g (0.075 mole) of dibenzyldichlorosilane[4] (in 25 ml of tetrahydrofuran) during 1 h. Subsequent to stirring the reaction mixture at room temperature for 12 h and removal of the solvent, there was obtained a yellow-orange residue which was extracted with hot benzene. The benzene-insoluble portion was 6.1 g of lithium chloride. The benzene solution was worked up as in the previous experiment to give 18.1 g (30.7%) of 1,2,4,5-tetraphenyl-3,3,6,6-tetrabenzyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (V), m.p. 150–154°. Two crystallizations from petroleum ether (b.p. 60–70°) raised the m.p. to 153–155°. (Found: C, 79.46; 79.50; H, 6.05, 6.10; N, 7.06, 7.10. $C_{52}H_{48}N_4Si_2$ calcd.: C, 70.52; H, 6.16; N, 7.13%.)

From the reaction mixture 0.6 g (6.6%) of azobenzene, m.p. 66–68° (mixed m.p.), was also isolated.

The azobenzene–dilithium adduct and dichlorophenylvinylsilane

To 10.2 g (0.05 mole) of dichlorophenylvinylsilane dissolved in 25 ml of tetrahydrofuran was added during 1 h 0.05 mole (100 ml) of the azobenzene–dilithium adduct. The solvent was removed by distillation and the residue was extracted with hot, sodium-dried benzene. Subsequent to removal of the solvent from the benzene solution there was obtained a light orange-yellow, viscous liquid, which solidified on treatment with 50 ml of cold methanol. The light yellow solid was crystallized several times from a mixture of benzene and petroleum ether (b.p. 60–70°) to give 9.0 g (57.2%) of 1,2,3,4,5,6-hexaphenyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VI), melting over the range 215–220°. Repeated crystallizations from different solvents did not improve the melting point of this sample. (Found: C, 76.84, 76.89; H, 5.59, 5.47; N, 9.04, 9.03; Si, 8.68, 8.79. $C_{40}H_{36}N_4Si_2$ calcd.: C, 76.38; H, 5.77; N, 8.90; Si, 8.93%.)

The methanol solution was evaporated and the orange-red residue obtained was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.8 g (8.8%) of azobenzene, m.p. 67–68° (mixed m.p.).

The azobenzene–dilithium adduct and cyclopentamethylenedichlorosilane

The azobenzene–dilithium adduct (0.1 mole, 130 ml) was gradually added to 18.2 g (0.1 mole) of cyclopentamethylenedichlorosilane dissolved in 50 ml of tetrahydrofuran. After the addition was completed (1 h), the mixture was stirred for 18 h at room temperature and then refluxed for 1 h. The solvent was removed by distillation and the residue hydrolyzed by water. The water-insoluble portion was a light yellow solid which after repeated treatments with benzene gave 18.0 g (70.0 %) of 1,2,4,5-tetraphenyl-3,6-dicyclopentamethylene-1,2,4,5-tetraaza-3,6-disilacyclohexane (VII), m.p. 325–326° (decomp.). This substance was found to be poorly soluble in common organic solvents like acetone, ethyl acetate, benzene, toluene and xylene. Several washings with hot tetrahydrofuran raised the melting point to 331–332° (decomp.). (Found: C, 72.74, 72.88; H, 7.11, 7.04; N, 10.06, 9.98; Si, 10.14, 9.98. $C_{44}H_{40}N_4Si_2$ calcd.: C, 72.88; H, 7.01; N, 9.99; Si, 10.00 %.)

The azobenzene–dilithium adduct and dichlorodi-o-tolylsilane

A solution of 28.1 g (0.1 mole) of dichlorodi-*o*-tolylsilane[5] in 50 ml of ether was added to 0.1 mole of the azobenzene–dilithium adduct (in 125 ml of tetrahydrofuran) over a 3-h period. The mixture was refluxed for 7 h and subsequent work-up in the usual manner gave 10.0 g (54.7 %) of azobenzene, m.p. 66–67° (mixed m.p.). None of the expected cyclic compound was obtained. A small quantity (2.7 g) of an unidentified product, m.p. 263–264°, was isolated from this run.

The azobenzene–dilithium adduct and chlorotrimethylsilane

A solution of 0.1 mole of the azobenzene–dilithium adduct in 150 ml of tetrahydrofuran was added dropwise to a stirred solution of 21.8 g (0.2 mole) of chlorotrimethylsilane in 30 ml of tetrahydrofuran. The addition was carried out during 30 min and the mixture was colored light orange-yellow at the end of this period. The solvent was removed by distillation after stirring the mixture for 12 h at room temperature. The residue was extracted with 200 ml of hot benzene. The benzene-insoluble portion was a white solid (8.2 g) which was identified as lithium chloride by qualitative tests. The benzene solution was distilled to remove all the solvent, and the residue was treated with 50 ml of cold methanol to give 29.5 g (89.8 %) of crude N,N′-diphenyl-N,N′-bis(trimethylsilyl)hydrazine (X), m.p. 105–110°. Two crystallizations from petroleum ether (b.p. 60–70°) gave 25.5 g (77.6 %) of the product melting at 111.5–112.5°. (Found: C, 65.65, 65.61; H, 8.24, 8.39; N, 8.63, 8.80. $C_{18}H_{28}N_2Si_2$ calcd.: C, 65.8; H, 8.59; N, 8.52 %.)

The methanol solution was evaporated to give an orange-red residue which was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 0.2 g (1.1 %) of azobenzene, m.p. and mixed m.p. 67–68°.

The azobenzene–dilithium adduct and chlorotriethylsilane

To a solution of 22.6 g (0.15 mole) of chlorotriethylsilane in 30 ml of tetrahydrofuran, 0.75 mole of the azobenzene–dilithium adduct (130 ml) was added during 30 min. After the addition was completed, the mixture was stirred for 12 h at room temperature. The solvent was then removed by distillation; the residue was extracted with 200 ml of hot benzene and worked up as in the previous experiment to give 22.5 g (72.7 %) of N,N′-diphenyl-N,N′-bis(triethylsilyl)hydrazine (XI), which melted at 83–84° after crystallization from a mixture of petroleum ether (b.p. 60–70°) and methanol. (Found: C, 69.79; H, 9.37; N, 6.83. $C_{24}H_{40}N_2Si_2$ calcd.: C, 69.89; H, 9.70; N, 6.79 %.)

Also 0.8 g (5.9 %) of azobenzene, m.p. and mixed m.p. 67–68°, was isolated from this run.

The azobenzene–dilithium adduct and chlorodimethylphenylsilane

The azobenzene–dilithium adduct (0.05 mole, 130 ml) was added to a stirred solution of 17.1 g (0.1 mole) of chlorodimethylphenylsilane in 30 ml of tetrahydrofuran during 30 min. The mixture was stirred at room temperature for 12 h and afterwards the solvent was removed by distillation. Work-up of the residue by the usual procedure gave 17.8 g (78.7 %) of crude N,N'-diphenyl-N,N'-bis(dimethylphenylsilyl)hydrazine (XII), m.p. 110–115°. Crystallization from a mixture of petroleum ether (b.p. 60–70°) and methanol gave 15.2 g (67.2 %) of the pure product, m.p. 118–119°. (Found: C, 74.65, 74.65; H, 6.73, 6.92; N, 6.4, 6.23. $C_{28}H_{32}N_2Si_2$ calcd.: C, 74.29; H, 7.13; N, 6.19 %.)

A small quantity of azobenzene (0.5 g, 5.5 %), m.p. 67–68° (mixed m.p.) was also obtained from this reaction.

The azobenzene–dilithium adduct and chlorodiphenylmethylsilane

To a solution of 23.3 g (0.1 mole) of chlorodiphenylmethylsilane in 30 ml of tetrahydrofuran was added 0.05 mole of the azobenzene–dilithium adduct (100 ml) during a 1-h period. After stirring the mixture for 12 h at room temperature, the solvent was removed and the residue was worked up as in the previous experiments to give 26.2 g (90.8 %) of crude N,N'-diphenyl-N,N'-bis(diphenylmethylsilyl)hydrazine (XIII), which melted at 150–155° (shrinks at 120°). Several crystallizations from benzene gave 22.5 g (78.0 %) of a product melting at 161–163°. Repeated crystallizations from different solvents failed to improve the melting point of this sample. (Found: C, 79.0, 79.18; H, 6.40, 6.27; N, 4.5, 4.48. $C_{38}H_{36}N_2Si_2$ calcd.: C, 79.14; H, 6.29; N, 4.86 %.)

The azobenzene–dilithium adduct and dichlorodiphenylgermane

A solution of 0.05 mole (100 ml) of the azobenzene-dilithium adduct was gradually added to 14.9 g (0.05 mole) of dichlorodiphenylgermane. After the addition was completed (1 h), the mixture was stirred at room temperature for 12 h. The solvent was removed and extraction of the residue with hot benzene left 5.2 g of lithium chloride. Subsequent to removal of the solvent from the benzene extract and treatment with cold methanol, there was obtained 9.5 g (23.2 %) of octaphenyl-1,2,4,5-tetraaza-3,6-digermacyclohexane (XIV), which melted at 306–307° (decomp.) after crystallization from hot benzene. (Found: C, 70.13, 70.28; H, 5.10, 4.95; N, 6.96, 7.08; Ge, 17.64. $C_{48}H_{40}N_4Ge_2$ calcd.: C, 70.47; H, 4.93; N, 6.85; Ge, 17.75 %.)

Work-up of the methanol-soluble portion by the usual procedure gave 3.5 g (38.1 %) of hydrazobenzene, m.p. 127–129° (mixed m.p.), and 1.8 g (19.8 %) of azobenzene, m.p. 66–68° (mixed m.p.).

The azobenzene–dilithium adduct and diphenyltin dichloride

The azobenzene–dilithium adduct (0.1 mole, 130 ml) was added slowly to a stirred solution of 34.3 g (0.1 mole) of diphenyltin dichloride in 50 ml of diethyl ether.

The reaction was exothermic and the temperature was maintained at 0° by cooling the flask in an ice-salt bath. After the addition was completed (1 h) the mixture was stirred at room temperature for 1 h and the solvent removed by distillation. Subsequent to the usual work-up and treatment of the residue with petroleum ether (b.p. 60–70°), there was obtained 24.8 g (90.9%) of a light yellow solid, identified as diphenyltin polymer, m.p. 270–272°. Several crystallizations from benzene raised the m.p. to 271–273°. (Found: C, 53.19, H, 3.96. $C_{12}H_{10}Sn$ calcd.: C, 52.80; H, 3.67%.)

This substance lost its light yellow color on prolonged exposure to air, probably due to oxidation to diphenyltin oxide.

The petroleum ether-soluble portion was evaporated to give an orange-red solid which after crystallization from the same solvent gave 17.0 g (93.4%) of azobenzene, m.p. 70–71° (mixed m.p.).

The azobenzene–dilithium adduct and diphenyllead dichloride

To a suspension of 6.5 g (0.015 mole) of diphenyllead dichloride[7] in 25 ml of tetrahydrofuran, 45 ml (0.015 mole) of the azobenzene–dilithium adduct was added during 30 min. The reaction was exothermic and the mixture turned black due to the precipitation of a black solid. After stirring for 1 h at room temperature, the solvent was removed and the residue treated with hot benzene. The benzene-insoluble portion was washed several times with water to give 1.2 g of a black solid, identified as metallic lead. A few lead particles in the form of shot were also visible in the black residue.

Removal of the solvent from the benzene solution gave a light orange-red solid which after treatment with petroleum ether (b.p. 60–70°) gave 1.4 g (21.5%) of unchanged diphenyllead dichloride, m.p. 270° (decomp.).

The petroleum ether-soluble portion was chromatographed on alumina to give 2.5 g (91.6%) of azobenzene, m.p. 67–68° (mixed m.p.).

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SUMMARY

Treatment of the azobenzene–dilithium adduct with dichlorodimethylsilane gave 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane. Similar reactions of dichlorodiethylsilane, dichloridibenzylsilane, dichlorophenylvinylsilane, and cyclopentamethylenedichlorosilane gave the corresponding cyclic compounds. Substituted silylhydrazines were obtained from the reaction of the azobenzene–dilithium adduct with chlorotrimethylsilane, chlorotriethylsilane, chlorodimethylphenylsilane and chlorodiphenylmethylsilane. Reaction of dichlorodiphenylgermane with the azobenzene–dilithium adduct gave octaphenyl-1,2,4,5-tetraaza-3,6-digermacyclohexane. Diphenyltin and azobenzene were obtained from the reaction of diphenyltin dichloride with the azobenzene–dilithium adduct; whereas, metallic lead and azobenzene were isolated from the corresponding reaction employing diphenyllead dichloride.

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