action. Sodium hydroxide pellets were added to raise the *p*H past 10 in order to convert all phenol present to the sodium salt. Extraction with ether followed, to recover the iodobenzene, and the residual solution was divided into two portions. To one portion aqueous sodium iodide was added to recover unreacted diphenyliodonium ion as the insoluble diphenyliodonium iodide. To the other portion bromine water was added to precipitate the phenol formed as the tribromo derivative. The crude solids were recrystallized and identified by melting point. The crude iodobenzene was redistilled and identified by boiling point and refractive index.

The results of the analyses are listed in Table VII. The amounts of phenol and diphenyliodonium ion indicated are corrected for aliquot size. The small amount of diphenyliodonium ion unaccounted for was lost partly through the finite solubility of diphenyliodonium iodide and partly in handling.

TABLE VII

PRODUCT ANALYSES FOR THE AQUEOUS DECOMPOSITION OF DIPHENYLIODONIUM SALTS[a]

			Starting material			Products		
Anion	$CuSO_4$	Hours	Initial	Recov.	Reacted	C_6H_5I	H_3O^+	C_6H_5-OH
$C_6H_5SO_3^-$	None	1392	40.1	26.7	13.4	12.7	12.3	9.1
$C_7H_7SO_3^-$	0.048	120	43.0	1.6	41.4	41.0	40.4	28.0

[a] All amounts in millimoles.

Reactions in Organic Solvents. Kinetic Runs in Dioxane–Water.—To a weighed amount of diphenyliodonium nitrate there were added measured volumes of water, dioxane, aqueous sodium nitrate and, sometimes, allyl alcohol. After the flask had been in the constant-temperature bath for 15 minutes, the salt was dissolved by swirling, and a known volume of aqueous sodium hydroxide was added from a transfer pipet. The total volume of liquids added was 120 ml.

After the solutions had been mixed, an aliquot was withdrawn, the time being taken as zero time. This sample, usually 10 ml., and subsequent samples were added to 10 ml. of water and sufficient nitric acid, added from a buret, to neutralize 80–90% of the base. The titration was completed with nitric acid to a brom cresol green-methyl red end-point.

Benzene from Diphenyliodonium Chloride and Potassium Hydroxide in Water–Ether Solutions.—A mixture of 330 g. of diglyme (freshly distilled from sodium), 500 ml. of distilled water, 113 g. of 85% potassium hydroxide in 68 ml. of water and 50 g. of diphenyliodonium chloride was boiled for two hours. Distillation gave a forerun, approximately 1 ml., of b.p. 71°. This halogen-free material gave with mixed acids *m*-dinitrobenzene, m.p. 89.5°, undepressed by admixture with an authentic sample.

TABLE VIII

ACID PRODUCTION BY DIPHENYLIODONIUM TOSYLATE IN ORGANIC HYDROXYLIC SOLVENTS, REPORTED AS APPROXIMATE FIRST-ORDER CONSTANTS

T, °C.	Mmoles/ liter *a*	Solvents	Hr.$^{-1}$ 10^4k
~25	100	Methanol	0.3
		4:1 Methanol–water	0.2
		4:1 Acetone–water	0.5
		DEG[a]	1
		9:1 DEG–water[a]	2
	20	DEG[a]	4
51	100	Methanol	0–0.8
		Diethylene glycol	25
		9:1 DEG[a]–water	26
92	50	Diethylene glycol	470
		DEG[a] + hydroquinone[b]	0–50
		Ethylene glycol	0–20
		Propylene glycol	650
		Methyl Cellosolve (peroxide)[c]	7600
		Methyl Cellosolve (no peroxide)	0–300
		Methyl Cellosolve + hydroquinone[b]	0–20
98[d]	100	Diethylene glycol	1000
	50	Diethylene glycol	2000
	20	Diethylene glycol	5000

[a] Diethylene glycol. [b] 0.01 molar hydroquinone. [c] Solvent gave a positive test for peroxides. [d] Obtained by interpolation from data of Irving Kuntz, ref. 6.

Diphenyliodonium Tosylate in Organic Hydroxylic Solvents.—Diphenyliodonium tosylate in various organic hydroxylic solvents produced acids, by solvolysis or oxidation–reduction or both. Some exploratory runs were made under the following conditions: room temperature, 20–30° (68 days); 51° (40 hours); 92° (2.5 hours). Acid production was treated as a first-order process, giving the rough values for *k* shown in Table VIII.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Reactions of Azobenzene- and Stilbene-Dilithium Adducts with Some Chlorosilanes

BY M. V. GEORGE, DIETMAR WITTENBERG AND HENRY GILMAN

RECEIVED JULY 25, 1958

Dichlorodiphenylsilane and dichloromethylphenylsilane on treatment with azobenzene–dilithium adduct gave octaphenyl-1,2,4,5-tetraza-3,6-disilacyclohexane and 1,2,3,4,5,6-hexaphenyl-3,6-dimethyl-1,2,4,5-tetraza-3,6-disilacyclohexane, respectively. The stilbene–dilithium adduct in tetrahydrofuran reacts with chlorotriphenylsilane to give hexaphenyldisilane and stilbene. Reactions of the stilbene–dilithium adduct with dichlorodiphenylsilane, dichlorodimethylsilane and dichloromethylsilane were attempted.

A systematic, elegant study of the addition of the alkali metals lithium, sodium and potassium to azobenzene was made by Reesor and Wright,[1] who observed that nearly quantitative yields of the dimetal adducts could be obtained by shaking excess of the alkali metal with azobenzene in ethylene glycol dimethyl ether. This addition reaction was, however, reported to be slow in a solvent like diethyl ether giving an unidentified product,[2] but tetrahydrofuran has been found to be effective as a medium for this reaction.[3] The same dilithium adduct of azobenzene was prepared by Wittig[4] from hydrazobenzene and methyllithium.

Reesor and Wright[1] have studied a number of reactions of azobenzene–dimetal adducts. Normal

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[1] J. W. B. Reesor and G. F Wright, *J. Org. Chem.*, **22**, 375 (1957).

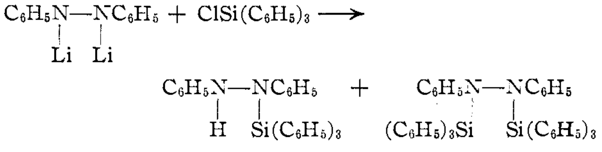
[2] W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

[3] D. Wittenberg, M. V. George, T. C. Wu, D. H. Miles and H. Gilman, THIS JOURNAL, **80**, 4532 (1958).

[4] G. Wittig, *Angew. Chem.*, **53**, 241 (1940).

alkyl halides and methyl sulfate were reported to give N,N′-disubstituted hydrazobenzenes whereas secondary and tertiary halides and triisopropyl phosphate gave N-monosubstituted hydrazobenzenes.

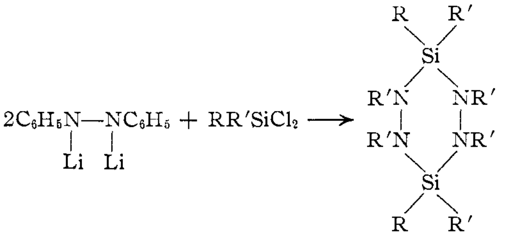
In an earlier investigation[3] it was observed that the azobenzene–dilithium adduct reacts with chlorotriphenylsilane to give a mixture of N,N′-diphenyl-N-(triphenylsilyl)-hydrazine and N,N′-diphenyl-N,N′-bis-(triphenylsilyl)-hydrazine.



$$\underset{\text{Li}}{C_6H_5N}-\underset{\text{Li}}{NC_6H_5} + ClSi(C_6H_5)_3 \longrightarrow \underset{\text{H}}{C_6H_5N}-\underset{Si(C_6H_5)_3}{NC_6H_5} + \underset{(C_6H_5)_3Si}{C_6H_5N}-\underset{Si(C_6H_5)_3}{NC_6H_5}$$

It seemed of interest to study further this type of reaction as a means of preparing cyclic compounds containing the Si–N linkage.

The reaction of dichlorodiphenylsilane with the azobenzene–dilithium adduct gave a 50.5% yield of octaphenyl-1,2,4,5-tetraza-3,6-disilacyclohexane (I). The identity of this compound was established by a quantitative analysis, and a molecular weight determination by a reported procedure using perylene.[5]



I, $R = R' = C_6H_5$
II, $R = CH_3$; $R' = C_6H_5$

The compound I melts to a clear liquid at 329–330°, but decomposes when heated above its melting point to a brown liquid. It is not readily attacked by air or moisture and in this respect is unlike many silazanes which are rather sensitive to hydrolytic agents.[6]

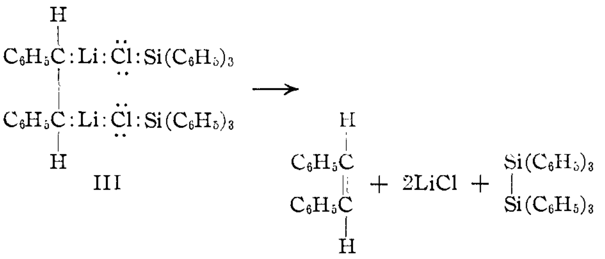
Dichloromethylphenylsilane similarly reacts with the azobenzene–dilithium adduct to give the corresponding 1,2,3,4,5,6-hexaphenyl-3,6-dimethyl-1,-2,4,5-tetraza-3,6-disilacyclohexane (II) in a 54.6% yield. Compound II slowly decomposed on repeated attempts to crystallize it from different solvents.

The successful preparation of compounds containing the tetrazadisilacyclohexane ring suggested related reactions of dichlorosilanes with the stilbene–dilithium adduct, with a view to preparing compounds containing the disilacyclohexane ring. As a model experiment, the reaction of chlorotriphenylsilane with the stilbene–dilithium adduct was investigated. However, none of the expected 1,2-diphenyl-1,2-bis-(triphenylsilyl)-ethane, a compound previously obtained from the reaction of triphenylsilyllithium with *trans*-stilbene,[7] was isolated. Instead, hexaphenyldisilane was formed in a 58.1% yield, together with an 88.9% yield of *trans*-stilbene.

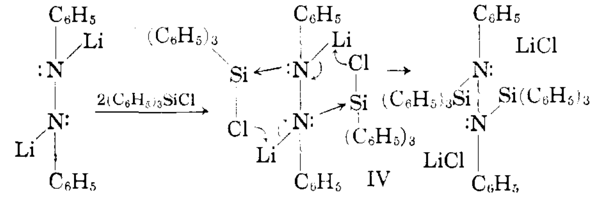
Similarly, no octaphenyl-1,4-disilacyclohexane was found when dichlorodiphenylsilane was allowed to react with the stilbene–dilithium adduct. A 69% yield of *trans*-stilbene was isolated together with a large amount of a silicon-containing polymer. In addition, a 33% yield of a compound was obtained, m.p. 313-317°, which is probably identical with octaphenylcyclotetrasilane. This substance was obtained by Kipping and Sands[8] together with a variety of other products from the reaction of dichlorodiphenylsilane with sodium. These workers reported that the compound melts above 300°.

Dichlorodimethylsilane and dichloromethylsilane also were treated with the stilbene–dilithium adduct. Silicon-containing polymers resulted from these reactions together with varying amounts of *trans*-stilbene.

Reactions similar to the above-mentioned ones in which the dimetal-adducts of azobenzene and of stilbene show differences in behavior are known. Reesor and Wright[1] have found that a substance like benzyl chloride gives N,N′-dibenzyl-N,N′-diphenylhydrazine as the sole product when treated with the azobenzene–dipotassium adduct, whereas the stilbene–disodium adduct gives exclusively bibenzyl and stilbene.[1] These workers have explained this difference in behavior of the two adducts on the basis of a homopolar *versus* a heteropolar scission of the unstable reaction intermediates. The difference in the behavior of the reaction of chlorotriphenylsilane also could be explained on the basis of the same postulate. The homopolar scission of the stilbene–dilithium adduct is shown by structure III.



Structure IV, on the other hand, represents the heteropolar scission of the transient intermediate in the case of the reaction of azobenzene–dilithium adduct with chlorotriphenylsilane.



However, the formation of the monoaddition product, namely, N,N′-diphenyl-N-(triphenylsilyl)-hydrazine, may be explained on the basis of steric considerations which are accentuated by the greater covalence of the N–Li bond.

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(5) G. Wittig and G. Lehmann, *Ber.*, **90**, 875 (1957).

(6) S. D. Brewer and C. P. Haber, THIS JOURNAL, **70**, 3888 (1948).

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(8) F. S. Kipping and J. E. Sands, *J. Chem. Soc.*, **119**, 830 (1921).

Experimental

All melting points are uncorrected. In general, all reactions were carried out under dry, oxygen-free[9] nitrogen. In every instance when tetrahydrofuran was employed, it was the grade boiling at 65–66°, freed from peroxides and moisture by refluxing over sodium followed by distillation from lithium aluminum hydride. The chlorosilanes employed were of the purified grade purchased from Dow Corning Corp. Silicon analyses were carried out by a reported procedure.[10]

Preparation of the Azobenzene–Dilithium Adduct.—Tetrahydrofuran (125 ml.) was added slowly to a mixture of 18.2 g. (0.1 mole) of azobenzene and 2.8 g. (0.4 g. atom) of lithium wire, cut into small pieces, with constant stirring over a period of 30 minutes. The reaction mixture was deep green in color and stirring was continued for 24 hours. The green color of the solution gradually changed to orange-yellow. The solution was decanted from excess metal before use.

Azobenzene–Dilithium Adduct and Dichlorodiphenylsilane.—A solution of 0.075 mole of azobenzene–dilithium adduct in 115 ml. of tetrahydrofuran was added dropwise to a stirred solution of 0.075 mole (19.0 g.) of dichlorodiphenylsilane in 25 ml. of tetrahydrofuran. The addition was carried out during one hour and afterward the mixture was hydrolyzed by adding water (100 ml.), extracted with ether (200 ml.) and the insoluble residue was separated by filtration. The insoluble residue (13.8 g., 50.5%) of octaphenyl-1,2,4,5-tetraza-3,6-disilacyclohexane melted at 329–330°, after crystallization from benzene.

Anal. Calcd. for $C_{48}H_{40}N_4Si_2$: C, 79.11; H, 5.53; N, 7.69; Si, 7.72; mol. wt., 728.5. Found: C, 79.37; H, 5.77; N, 7.91; Si, 7.74; mol. wt., 720.5[5].

The ether extract was dried over anhydrous sodium sulfate and the orange-yellow solid obtained after removal of the solvent was chromatographed on alumina. Elution with petroleum ether (b.p. 60–70°) gave 2.3 g. (16.5%) of azobenzene, m.p. and mixed m.p. 67–68°.

Azobenzene–Dilithium Adduct and Dichloromethylphenylsilane.—Azobenzene–dilithium adduct (0.1 mole, 120 ml.) was added during one hour to a solution of 19.1 g. (0.1 mole) of dichloromethylphenylsilane in 25 ml. of tetrahydrofuran. The mixture was hydrolyzed with water and extracted with ether. Removal of the solvent from the ether solution gave a solid which was treated with petroleum ether (b.p. 60–70°). The soluble portion was purified by chromatographing on alumina. Elution with petroleum ether gave 2.1 g. (11.5%) of azobenzene, m.p. and mixed m.p. 67–68°.

The petroleum ether-insoluble portion was crystallized from a mixture of benzene and cyclohexane (1:1) to give 16.5 g. (54.6%) of 1,2,3,4,5,6-hexaphenyl-3,6-dimethyl-1,2,-4,5-tetraza-3,6-disilacyclohexane. It melted at 240–243° even after repeated crystallizations. The melting point range may indicate that the substance is an isomeric mixture.

Anal. Calcd. for $C_{38}H_{36}N_4Si_2$: C, 75.41; H, 6.00; N, 9.26; Si, 9.29; mol. wt., 604.8. Found: C, 75.41; H, 6.04; N, 9.50; Si, 9.07, mol. wt., 614.5.

Preparation of the Stilbene–Dilithium Adduct.—A mixture of 18 g. (0.1 mole) of *trans*-stilbene and 3.5 g. (0.5 g. atom) of lithium with 140 ml. of freshly distilled tetrahydrofuran was stirred in a three-necked reaction flask for 24 hours. The solution was black in color, and acid titration of an aliquot after hydrolysis indicated a 95.5% yield of the dilithium adduct. It was decanted from excess metal and used for the subsequent reactions.

Stilbene–Dilithium Adduct and Chlorotriphenylsilane.—The stilbene–dilithium adduct (0.025 mole) was added to a solution of 14.7 g. (0.05 mole) of chlorotriphenylsilane in 25 ml. of tetrahydrofuran during 30 min. The black color of the lithium adduct was discharged immediately and the mixture did not give a positive Color Test I[11] after the addition was complete. The mixture was hydrolyzed, extracted with ether and the insoluble residue was filtered to give 7.5 g. (58.1%) of hexaphenyldisilane, m.p. and mixed m.p. 365–366°.

The ether layer on evaporation gave a solid which was chromatographed on alumina and eluted with petroleum ether (b.p. 60–70°) to give 4.0 g. (88.9%) of stilbene, m.p. and mixed m.p. 124–125°.

Stilbene–Dilithium Adduct and Dichlorodiphenylsilane.—A solution of 0.095 mole of stilbene–dilithium adduct was added dropwise during one hour to 24 g. (0.095 mole) of dichlorodiphenylsilane. Color Test I[11] was negative after the addition was complete. Subsequent to hydrolysis with water, ether was added and the mixture filtered to give 5.9 g. of a residue, m.p. 295–317°. Recrystallization from benzene raised the melting point to 313–317°.

Anal. Calcd. for $(C_{12}H_{10}Si)_n$: Si, 15.38. Found: Si, 15.05, 15.20.

The solvent from the ether layer was removed by evaporation and the residue chromatographed on alumina. Using petroleum ether (b.p. 60–70°) as the eluent, 12.3 g. (69%) of stilbene, m.p. 124–125°, was isolated which was identified by a mixed melting point determination with an authentic sample (mixed m.p. 124–125°). Elution of the column with solvents such as carbon tetrachloride and benzene gave some viscous oils from which no pure product could be isolated.

Stilbene–Dilithium Adduct and Dichlorodimethylsilane.—Treatment of 0.075 mole of stilbene–dilithium adduct with 9.7 g. (0.075 mole) of dichlorodimethylsilane resulted in the isolation of 18.5% of stilbene and some unidentified polymeric substances which could not be purified either by crystallization or chromatography.

Stilbene–Dilithium Adduct and Dichloromethylsilane.—Unidentified polymeric substances containing silicon and 5.8 g. (32.2%) of stilbene, m.p. and mixed m.p. 125–126°, were obtained on treatment of dichloromethylsilane (0.1 mole, 11.5 g.) with 0.1 mole of stilbene–dilithium adduct.

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