

CHEMISTRY OF DIANIONS

II. SYNTHESIS OF TETRAAZADISILACYCLOHEXANES EMPLOYING THE REACTION OF DIANIONS WITH DIORGANODICHLOROSILANES

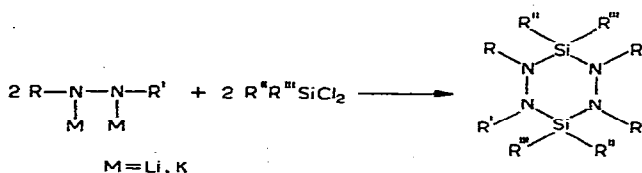
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In recent years, the chemistry of silicon–nitrogen compounds has received considerable attention and various silicon–nitrogen heterocyclics of different ring systems have been synthesised**. One of the ways of establishing a bond between silicon and nitrogen is by the nucleophilic displacement of nitranions on silicon***. It has been reported earlier that the addition of alkali metals to azo compounds gives rise to dianions which are good nucleophiles^{6,7}. These dianions react with triorganochlorosilanes to give bis(triorganosilyl)hydrazines, whereas their reaction with diorganodichlorosilanes leads to the formation of tetraazadisilacyclohexanes^{8,9}. Tetraazadisilacyclohexanes form an interesting class of fairly stable silicon–nitrogen compounds****. Wannagat and coworkers have reported the preparation of this type of compounds by employing the reaction of hydrazines with diorganodichlorosilanes¹⁰.

In an earlier paper¹¹, we have described the preparation of several dianions derived from azo compounds and some of their reactions with triorganochlorosilanes. The object of the present investigation was to study the reaction of these dianions with different diorganodichlorosilanes, with a view to preparing new silicon–nitrogen heterocyclics. In this connection, we have examined the reaction of the dimetal adducts of azobenzene, 3,3'-dimethylazobenzene, 3,3'-dimethoxyazobenzene, 4-methylazobenzene, 4-methoxyazobenzene, 4,4'-dimethylazobenzene, 4,4'-dimethoxyazobenzene, 4,4'-diisopropylazobenzene, 4,4'-di-tert-butylazobenzene, 4,4'-diphenylazobenzene, dibenzopyridazine and diethyl azodicarboxylate with several diorganodichlorosilanes.



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** For a recent review on silicon–nitrogen heterocycles, see ref. 1.

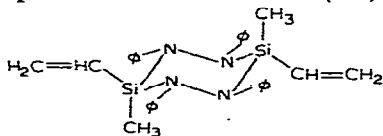
*** For some of the displacement reactions on silicon employing nitranions, see refs. 2–5.

**** Our preliminary studies on the DTA and TGA of these compounds indicate that they are thermally stable up to about 300°.

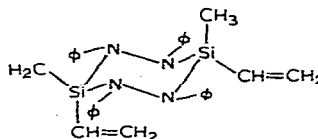
- (I): $R = R' = C_6H_5$, $R'' = R''' = CH_3$
 (II): $R = R' = C_6H_5$, $R'' = CH_3$, $R''' = CH_2=CH$
 (III): $R = R' = m\text{-}CH_3C_6H_4$, $R'' = R''' = CH_3$
 (IV): $R = R' = m\text{-}CH_3C_6H_4$, $R'' = CH_3$, $R''' = CH_2=CH$
 (V): $R = R' = m\text{-}CH_3C_6H_4$, $R'' = R''' = C_6H_5$
 (VI): $R = R' = m\text{-}CH_3OC_6H_4$, $R'' = R''' = CH_3$
 (VII): $R = R' = m\text{-}CH_3OC_6H_4$, $R'' = R''' = C_6H_5$
 (VIII): $R = C_6H_5$, $R' = p\text{-}CH_3C_6H_4$, $R'' = R''' = C_6H_5$
 (IX): $R = C_6H_5$, $R' = p\text{-}CH_3OC_6H_4$, $R'' = R''' = C_6H_5$
 (X): $R = R' = p\text{-}CH_3C_6H_4$, $R'' = R''' = CH_3$
 (XI): $R = R' = p\text{-}CH_3C_6H_4$, $R'' = R''' = C_6H_5$
 (XII): $R = R' = p\text{-}CH_3OC_6H_4$, $R'' = R''' = C_6H_5$
 (XIII): $R = R' = p\text{-}(CH_3)_2CHC_6H_4$, $R'' = R''' = C_6H_5$
 (XIV): $R = R' = p\text{-}(CH_3)_3CC_6H_4$, $R'' = R''' = C_6H_5$
 (XV): $R = R' = p\text{-}C_6H_5C_6H_4$, $R'' = R''' = C_6H_5$

From the reaction of azobenzene–dilithium adduct and dichloromethylvinylsilane, a 70% yield of 1,2,4,5-tetraphenyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (II), was obtained.

An unsymmetrically substituted tetraazadisilacyclohexane like (II) can exist in two possible stereoisomers, (IIa) and (IIb). Structure (IIa) represents a rapidly



(IIa)



(IIb)

interconverting chair conformer and hence we would expect a single peak due to Si-CH₃ protons in the NMR spectrum of this isomer. In this connection, we have examined the NMR spectrum of a symmetrically substituted tetraazadisilacyclohexane, namely, 1,2,4,5-tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (I)⁹. The spectrum of this compound showed only a single sharp signal at τ 9.13 ppm (12H), showing thereby that all the Si-CH₃ protons are chemically equivalent. A similar observation has been made in the case of symmetrically substituted triazatrisilacyclohexanes, which show only one Si-CH₃ peak¹². Structure (IIb), on the other hand, should show two distinct types of Si-CH₃ protons, as they are in different environments.

The NMR spectrum of (II) showed two sharp singlets at τ 9.31 and 9.25 ppm respectively. These peaks were of equal intensities and corresponded to a total of six Si-CH₃ protons (Fig. 1). In addition, a multiplet centred around τ 3.7 ppm (6H) due to vinylic protons and another multiplet centred around τ 3.1 ppm due to aromatic protons, were observed. On the basis of the NMR spectral data, structure (IIb) is assigned for 1,2,4,5-tetraphenyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane.

The reactions of the dilithium adducts obtained from 4-methylazobenzene

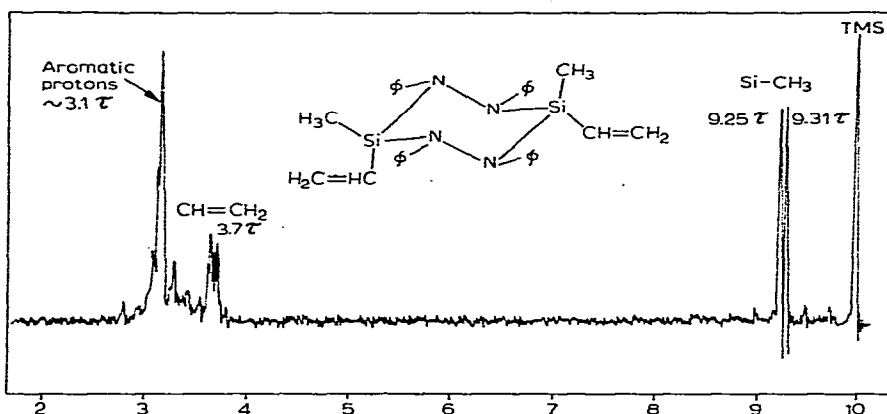
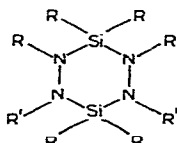


Fig. 1. The NMR spectrum of 1,2,4,5-tetraphenyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane, (Iib), in CS₂.

and 4-methoxyazobenzene with dichlorodiphenylsilane gave 61 % and 52 % of cyclic products, 1,3,3,4,6,6-hexaphenyl-2,5-di-*p*-tolyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VIII) and 1,3,3,4,6,6-hexaphenyl-2,5-di-*p*-anisyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (IX). The alternative structures possible for these compounds are (VIIIa) and (IXa), arising due to a different mode of combination between the dilithium adducts and dichlorodiphenylsilane. We have assigned the symmetrical structures, (VIII) and (IX) for these cyclic products on the basis of their infrared spectra which show only a single absorption band around 890 cm⁻¹, characteristic of Si-N-N vibrations³.



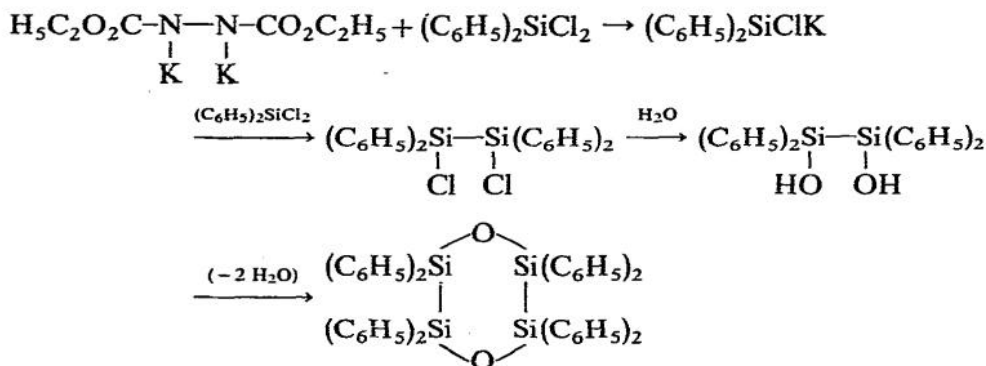
(VIIIa) : R = C₆H₅, R' = *p*-CH₃C₆H₄

(IXa) : R = C₆H₅, R' = *p*-CH₃OC₆H₄

We have tried the reaction of the dilithium adducts of 4,4'-dimethylazobenzene with dichlorodimethylsilane and dichlorodiphenylsilane and of the dilithium adducts of 4,4'-dimethoxyazobenzene, 4,4'-diisopropylazobenzene, 4,4'-di-*tert*-butylazobenzene and 4,4'-diphenylazobenzene with dichlorodiphenylsilane. In all these cases, the expected tetraazadisilacyclohexanes were obtained.

From the reaction of the dipotassium adduct of diethyl azodicarboxylate and dichlorodiphenylsilane, none of the expected cyclic product containing silicon and nitrogen could be isolated, but a 74 % yield of 2,2,3,3,5,5,6,6-octaphenyl-1,4-dioxane-2,3,5,6-tetrasilacyclohexane and 83 % of diethyl azodicarboxylate were isolated. The formation of this cyclic siloxane can be explained in terms of an initial halogen-metal exchange reaction between dichlorodiphenylsilane and the dipotassium adduct to give chlorodiphenylsilylpotassium. This intermediate could then initiate a displacement reaction on dichlorodiphenylsilane to give 1,2-dichlorotetraphenyldisilane which under the conditions of work-up could be converted to 1,2-dihydroxytetraphenyldisilane. This disilane can subsequently give rise to the dioxatetrasilacyclohexane by the loss of water. The fact that N,N'-dicarbethoxyhydrazine, the expected

product of hydrolysis of the dipotassium adduct of diethyl azodicarboxylate could not be isolated from this reaction indirectly supports the postulated halogen-metal exchange reaction.



The reaction of the dilithium adduct of dibenzopyridazine with dichlorodiphenylsilane has also been attempted but none of the expected cyclic product could be isolated under the conditions of work-up. This could probably be due to the greater steric requirements of the expected products.

The ultraviolet spectra of several tetraazadisilacyclohexanes (I)-(XIV) have been examined and the data are presented in Table 1. All these compounds showed

TABLE 1

ULTRAVIOLET SPECTRA OF TETRAAZADISILACYCLOHEXANES

Compound	λ_{max} (log ϵ)	Compound	λ_{max} (log ϵ)	Compound	λ_{max} (log ϵ)
(I)	256(4.62), 285(3.87)	(VI)	256(4.68), 288(3.90)	(XI)	256(4.70), 285sh(3.89)
(II)	254(4.63), 290sh(4.2)	(VII)	256(4.65), 288(3.99)	(XII)	255(4.69), 305(3.63)
(III)	258(4.73), 288(3.87)	(VIII)	258(4.62)	(XIII)	257(4.93)
(IV)	256(4.77), 288sh(4.08)	(IX)	258(4.79), 285sh(3.4)	(XIV)	257(4.78), 315(3.30)
(V)	252(4.69), 308sh(3.30)	(X)	258(4.72), 293(3.89)	(XV)	288(4.90)

sh = shoulder

a strong absorption band between 250–260 $m\mu$, characteristic of benzenoid absorptions. In addition, most of the compounds showed a second absorption band between 290–315 $m\mu$. A similar band was observed in all the silylhydrazines that we had examined earlier¹¹. Such an absorption band is also present in hydrazobenzene¹³. In compounds (VIII), (XIII) and (XV), however, we were not able to detect any absorption within the range 290–315 $m\mu$. It might be mentioned in this connection that hydrazobiphenyl shows only a single absorption band at 284 $m\mu$ (log ϵ , 4.6).

EXPERIMENTAL

All melting points are uncorrected. Reactions employing dianions were carried out under an atmosphere of dry, oxygen-free nitrogen¹⁴. Tetrahydrofuran, boiling at 65–66°, was freed from peroxides and moisture before use by refluxing over sodium and was directly distilled into the reaction vessel. Silicon analyses were carried out

as per a reported procedure¹⁵. Ultraviolet spectra were determined in tetrahydrofuran using a Cary-14 Spectrometer and molecular weights were determined in a Vapour Pressure Osmometer (Mechrolab, Inc.), using benzene as solvent. NMR traces were determined in a Varian A-60 NMR Spectrometer.

3,3'-Dimethylazobenzene¹⁶, 3,3'-dimethoxyazobenzene¹⁶, 4-methylazobenzene¹⁷, 4-methoxyazobenzene¹⁷, 4,4'-dimethylazobenzene¹⁸, 4,4'-dimethoxyazobenzene¹⁹, 4,4'-diisopropylazobenzene¹¹, 4,4'-di-tert-butylazobenzene¹¹, 4,4'-diphenylazobenzene¹¹, dibenzopyridazine²⁰, and diethyl azodicarboxylate²¹, were prepared by previously reported procedures.

The dianions were prepared by shaking the requisite amount of the azo compounds with excess of alkali metal in tetrahydrofuran inside a modified Schlenk tube²².

1,2,4,5-Tetraphenyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (I)

This compound was prepared in 75% yield as per a reported procedure⁹. The NMR spectrum of (I) (in THF) showed a sharp singlet at τ 9.13 ppm (12H) and a multiplet centred at τ 3.07 ppm due to aromatic protons.

1,2,4,5-Tetraphenyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (II)

A solution of 0.01 mole of N,N'-dilithiohydrazobenzene, prepared from 1.8 g (0.01 mole) of azobenzene and 0.28 g of lithium (0.04 g-atom) in 15 ml of tetrahydrofuran, was added to 1.41 g (0.01 mole) of dichloromethylvinylsilane, dissolved in 10 ml of tetrahydrofuran. The reaction was exothermic and the mixture had to be cooled in an ice bath during the addition of the dianion. Tetrahydrofuran was removed under vacuum and the residue was extracted with hot benzene. The benzene extract was evaporated and the residue on treatment with petroleum ether (b.p. 40–60°) gave 1.7 g (70%) of (II), m.p. 224–228°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 40–60°) gave a pure product, m.p. 228–230°. (Found: C, 71.6; H, 6.18; N, 11.27; Si, 10.54; mol. wt., 511. $C_{30}H_{32}N_4Si_2$ calcd.: C, 71.42; H, 6.34; N, 11.12; Si, 11.12%; mol. wt., 504.) The NMR spectrum of (II) (in CS_2) showed two sharp singlets at τ 9.25 and 9.31 ppm respectively. The vinyl protons were observed around τ 3.7 and the aromatic protons around 3.1 ppm.

1,2,4,5-Tetra-m-tolyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (III)

A solution of 0.01 mole of N,N'-dilithio-3,3'-dimethylhydrazobenzene in 15 ml of tetrahydrofuran was prepared by the treatment of 2.1 g (0.01 mole) of 3,3'-dimethylazobenzene with 0.28 g (0.04 g-atom) of lithium. The dianion solution was added to 1.29 g (0.01 mole) of dichlorodimethylsilane in 10 ml of tetrahydrofuran over a period of 30 min. Work-up of the mixture as in the previous case gave 2.1 g (72%) of (III), m.p. 162–164°. Recrystallization from benzene/petroleum ether (b.p. 60–80°) mixture gave a product melting at 165–166°. (Found: C, 71.40; H, 7.50; N, 10.29; Si, 10.73; mol. wt., 543. $C_{32}H_{40}N_4Si_2$ calcd.: C, 71.64; H, 7.46; N, 10.45; Si, 10.45%; mol. wt., 536.)

1,2,4,5-Tetra-m-tolyl-3,6-dimethyl-3,6-divinyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (IV)

A solution of 0.01 mole of N,N'-dilithio-3,3'-dimethylhydrazobenzene in 10

ml of tetrahydrofuran was treated with 1.41 g (0.01 mole) of dichloromethylvinylsilane, dissolved in 15 ml of tetrahydrofuran. Work-up of the reaction mixture in the usual manner gave 2.2 g (75%) of (IV), m.p. 162–168°. Repeated recrystallization from a mixture of benzene and petroleum ether (b.p. 40–60°) gave a pure sample of (IV), m.p. 166–169°. Further crystallizations from different solvents did not improve the melting point. (Found: C, 72.18; H, 7.59; N, 10.34; Si, 9.93; mol. wt., 554. $C_{34}H_{42}N_4Si_2$ calcd.: C, 72.86; H, 7.14; N, 10.00; Si, 10.00; mol. wt., 560.)

1,2,4,5-Tetra-m-tolyl-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (V)

Treatment of a solution of 0.01 mole of N,N'-dilithio-3,3'-dimethylhydrazobenzene with 2.53 g (0.01 mole) of dichlorodiphenylsilane in 25 ml of tetrahydrofuran and work-up in the usual manner gave 2.6 g (66%) of (V), m.p. 258–59°. (Found: C, 79.43; H, 6.08; mol. wt., 770. $C_{52}H_{48}N_4Si_2$ calcd.: C, 79.61; H, 6.12; mol. wt., 784.)

1,2,4,5-Tetra-m-anisyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VI)

A solution of 0.01 mole of N,N'-dilithio-3,3'-dimethoxyhydrazobenzene was prepared by treatment of 2.4 g (0.01 mole) of 3,3'-dimethoxyazobenzene and 2.28 g (0.04 g-atom) of lithium in 10 ml of tetrahydrofuran. The dilithium adduct was added slowly to a solution of 1.29 g (0.01 mole) of dichlorodimethylsilane in 15 ml of tetrahydrofuran. Removal of the solvent under vacuum and work-up as in the previous cases gave 2.5 g (82%) of (VI), m.p. 190–205°. Repeated recrystallization from a mixture of benzene and petroleum ether (b.p. 40–60°) gave a pure sample of (VI), melting at 211–212°. (Found: C, 63.86; H, 6.90; N, 9.58; Si, 9.28; mol. wt., 595. $C_{32}H_{40}N_4O_4Si_2$ calcd.: C, 64.0; H, 6.66; N, 9.34; Si, 9.34%; mol. wt., 600.)

1,2,4,5-Tetra-m-anisyl-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VII)

Treatment of 0.01 mole of N,N'-dilithio-3,3'-dimethoxyhydrazobenzene with dichlorodiphenylsilane (2.53 g, 0.01 mole) in 25 ml of tetrahydrofuran and work-up of the mixture by the usual procedure gave 2.2 g (52%) of the impure (VII), melting over the range of 200–220°. Several crystallizations from benzene gave a product melting at 230–231°. (Found: C, 74.05; H, 5.9; mol. wt., 818. $C_{52}H_{48}N_4O_4Si_2$ calcd.: C, 73.63; H, 5.66%; mol. wt., 848.)

1,3,3,4,6,6-Hexaphenyl-2,5-di-p-tolyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (VIII)

To a solution of 2.53 g (0.01 mole) of dichlorodiphenylsilane in 5 ml of tetrahydrofuran was added a tetrahydrofuran solution of N,N'-dilithio-4-methylhydrazobenzene (0.01 mole in 15 ml). Removal of solvent and work-up of the mixture gave 2.3 g (61%) of (VIII), melting over the range of 318–322°. Two crystallizations from benzene raised the m.p. to 326–328°. (Found: C, 79.27; H, 5.91; mol. wt., 760, 769. $C_{50}H_{44}N_4Si_2$ calcd.: C, 79.36; H, 5.82%; mol. wt., 756.) The infrared spectrum of (VIII) (KBr pellet) showed a single absorption band around 890 cm^{-1} .

1,3,3,4,6,6-Hexaphenyl-2,5-di-p-anisyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (IX)

Treatment of 0.01 mole of N,N'-dilithio-4-methoxyhydrazobenzene with dichlorodiphenylsilane (2.53 g, 0.01 mole) in tetrahydrofuran (15 ml) gave 2.1 g (52%) of (IX), m.p. 282–287°. (Found: C, 76.02; H, 6.0; mol. wt., 813. $C_{50}H_{44}N_4O_2Si_2$ calcd.: C, 76.14; H, 5.88%; mol. wt., 788.) Infrared spectrum of (IX) (KBr pellet) showed a single absorption peak around 890 cm^{-1} .

1,2,4,5-Tetra-p-tolyl-3,3,6,6-tetramethyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (X)

A solution of N,N'-dilithio-4,4'-dimethylhydrazobenzene (0.01 mole) was prepared by the treatment of 2.1 g (0.01 mole) of 4,4'-dimethylazobenzene and 0.28 g (0.04 g-atom) of lithium in 15 ml of tetrahydrofuran. The dilithium adduct was added slowly to a solution of 1.29 g (0.01 mole) of dichlorodimethylsilane in 10 ml of tetrahydrofuran. Removal of solvent gave a residue which was worked up as in previous cases to give 1.9 g (70%) of (X), melting over the range 226–230°. A pure sample of (X), m.p. 228–230° was obtained by repeated recrystallization from a mixture of benzene and petroleum ether (b.p. 40–60°). (Found: C, 71.8; H, 7.53; N, 10.40; Si, 10.81; mol. wt., 542. $C_{32}H_{40}N_4Si_2$ calcd.: C, 71.64; H, 7.46; N, 10.45; Si, 10.45%; mol. wt., 536.)

1,2,4,5-Tetra-p-tolyl-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (XI)

A solution of 0.01 mole of N,N'-dilithio-4,4'-dimethylhydrazobenzene in 15 ml of tetrahydrofuran was treated with 2.53 g (0.01 mole) of dichlorodiphenylsilane dissolved in 10 ml of tetrahydrofuran. The reaction mixture was worked up as usual to give 2.2 g (56%) of (XI), m.p. 332–335°. After two crystallizations from benzene, the product melted at 340–341°. (Found: C, 79.9; H, 6.3; mol. wt., 762, 768. $C_{32}H_{48}N_4Si_2$ calcd.: C, 79.61; H, 6.13%; mol. wt., 784.)

1,2,4,5-Tetra-p-anisyl-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (XII)

To a stirred solution of 2.53 g (0.01 mole) of dichlorodiphenylsilane in 10 ml of tetrahydrofuran was added 0.01 mole of N,N'-dilithio-4,4'-dimethoxyhydrazobenzene (prepared from 2.4 g of 4,4'-dimethoxyazobenzene and 0.28 g of lithium in 15 ml of tetrahydrofuran). Work-up of the mixture gave 2.2 g (50%) of (XII), m.p. 275–290°. Repeated crystallization from benzene raised the melting point to 289–290°. (Found: C, 74.08; H, 5.78; mol. wt., 832. $C_{52}H_{48}N_4O_4Si_2$ calcd.: C, 73.63; H, 5.66%; mol. wt., 848.)

1,2,4,5-Tetrakis(4-isopropylphenyl)-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (XIII)

A solution of N,N'-dilithio-4,4'-diisopropylhydrazobenzene was prepared by shaking 2.7 g (0.01 mole) of 4,4'-diisopropylazobenzene with 0.28 g (0.04 g-atom) of lithium in 15 ml of tetrahydrofuran. This dilithium adduct was added to a tetrahydrofuran solution (10 ml) of dichlorodiphenylsilane (2.53 g, 0.01 mole). Work-up of the mixture gave 2.2 g (49%) of (XIII), which melted at 299–300° after recrystallization from benzene. (Found: C, 80.26; H, 6.94; mol. wt., 912. $C_{60}H_{64}N_4Si_2$ calcd.: C, 80.36; H, 7.14%; mol. wt., 896.)

1,2,4,5-Tetrakis(4-tert-butylphenyl)-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (XIV)

To a solution of 1.8 g (0.007 mole) of dichlorodiphenylsilane in 5 ml of tetrahydrofuran was added 0.007 mole of N,N'-dilithio-4,4'-di-tert-butylhydrazobenzene, prepared from 2.1 g (0.007 mole) of 4,4'-di-tert-butylazobenzene and 0.2 g (0.03 g-atom) of lithium in 10 ml of tetrahydrofuran. Work-up of the reaction mixture as in the previous cases gave 2.1 g (61%) of (XIV), melting over the range 325–337°. Recrys-

tallization from benzene gave a pure sample of (XIV), m.p. 343–344°. (Found: C, 80.60; H, 7.30; mol. wt., 984. $C_{64}H_{72}N_4Si_2$ calcd.: C, 80.67; H, 7.45; mol. wt., 952.)

1,2,4,5-Tetrakis(4-biphenyl)-3,3,6,6-tetraphenyl-1,2,4,5-tetraaza-3,6-disilacyclohexane (XV)

Treatment of a solution of 0.01 mole of N,N'-dilithio-4,4'-diphenylhydrazobenzene in 15 ml of tetrahydrofuran with 2.53 g (0.01 mole) dichlorodiphenylsilane in 10 ml of tetrahydrofuran and work-up as usual gave 2.5 g (50%) of (XV), m.p. 241–243°. Recrystallization from benzene raised the melting point to 247–248°. (Found: C, 82.40; H, 5.66; mol. wt., 955. $C_{72}H_{56}N_4Si_2$ calcd.: C, 83.73; H, 5.43%; mol. wt., 1032.)

Diethyl azodicarboxylate-dipotassium adduct and dichlorodiphenylsilane

A solution of 0.01 mole of diethyl azodicarboxylate-dipotassium adduct [prepared from 1.74 g (0.01 mole) of diethyl azodicarboxylate and 0.78 g (0.02 g-atom) of potassium in 25 ml of tetrahydrofuran] was added dropwise, to a tetrahydrofuran solution of 2.53 g (0.01 mole) of dichlorodiphenylsilane. The reaction was exothermic and was over within few minutes of the addition. Removal of the solvent under vacuum gave a viscous solid which was extracted with hot benzene. The benzene extract was distilled under vacuum to give a viscous solid, which on treatment with methanol gave 1.2 g (74%) of 2,2,3,3,5,5,6,6-octaphenyl-1,4-dioxo-2,3,5,6-tetrasilacyclohexane, m.p. 186–187° (lit.²³ m.p. 186°), after recrystallization from cyclohexane. (Found: C, 76.1; H, 5.52; mol. wt., 713. $C_{48}H_{40}O_2Si_4$ calcd.: C, 75.8; H, 5.26%; mol. wt., 760.) The infrared spectrum (KBr pellet) showed all absorption bands characteristic of this compound²³.

Dibenzopyridazine-dilithium adduct and dichlorodiphenylsilane

A solution of 0.01 mole of the dilithium adduct of dibenzopyridazine was prepared by the treatment of 1.80 g (0.01 mole) of dibenzopyridazine with 0.28 g (0.04 g-atom) of lithium in 10 ml of tetrahydrofuran. The dilithium adduct was added to a tetrahydrofuran solution of dichlorodiphenylsilane (2.53 g, 0.01 mole) in 10 ml. The red colour of the dilithium adduct changed to green, which persisted even on stirring the reaction mixture for 6 h. Removal of solvent and lithium chloride gave a product which when chromatographed on alumina employing benzene gave 1.2 g (67%) of dibenzopyridazine, m.p. 153° (mixed m.p.).

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SUMMARY

Treatment of the dilithium adducts of azobenzene, 3,3'-dimethylazobenzene, 3,3'-dimethoxyazobenzene, 4-methylazobenzene, 4-methoxyazobenzene, 4,4'-dimethylazobenzene, 4,4'-dimethoxyazobenzene, 4,4'-diisopropylazobenzene, 4,4'-di-tert-butylazobenzene, and 4,4'-diphenylazobenzene with dichlorodimethylsilane, dichloromethylvinylsilane and dichlorodiphenylsilane gave tetraazadisilacyclohexanes.

Reaction of dichlorodiphenylsilane with the dipotassium adduct of diethyl azodicarboxylate did not give any silicon-nitrogen containing heterocycle, but a dioxatetrasilacyclohexane was isolated from this run. Dibenzopyridazine was obtained from the reaction of dichlorodiphenylsilane with dibenzopyridazine-dilithium adduct.

REFERENCES

- 1 W. FINK, *Angew. Chem. Intern. Ed. Engl.*, 5 (1966) 760.
- 2 U. WANNAGAT AND H. NIEDERPRÜM, *Z. Anorg. Allgem. Chem.*, 310 (1961) 32.
- 3 U. WANNAGAT, C. KRUGER AND H. NIEDERPRÜM, *Z. Anorg. Allgem. Chem.*, 321 (1963) 199.
- 4 W. FINK, *Chem. Ber.*, 96 (1963) 1071.
- 5 U. WANNAGAT AND O. BRANDSTATTER, *Monatsh. Chem.*, 97 (1966) 1352.
- 6 J. W. B. REESOR AND G. F. WRIGHT, *J. Org. Chem.*, 22 (1957) 375.
- 7 D. WITTENBERG, M. V. GEORGE, T. C. WU, D. H. MILES AND H. GILMAN, *J. Am. Chem. Soc.*, 80 (1958) 4532.
- 8 M. V. GEORGE, D. WITTENBERG AND H. GILMAN, *J. Am. Chem. Soc.*, 81 (1959) 361.
- 9 M. V. GEORGE, P. B. TALUKDAR AND H. GILMAN, *J. Organometal. Chem.*, 5 (1966) 397.
- 10 U. WANNAGAT AND H. NIEDERPRÜM, *Z. Anorg. Allgem. Chem.*, 311 (1961) 270.
- 11 S. S. DUA AND M. V. GEORGE, *J. Organometal. Chem.*, 9 (1967) 413.
- 12 L. W. BREED AND R. L. ELLIOTT, *Inorg. Chem.*, 3 (1964) 1622.
- 13 R. C. CARLIN, R. G. NELB AND R. C. ODIOSO, *J. Am. Chem. Soc.*, 73 (1951) 1002.
- 14 L. J. BRADY, *Ind. Eng. Chem. (Anal. Ed.)*, 20 (1948) 1034.
- 15 H. GILMAN, H. MELVIN, JR. AND G. E. DUNN, *J. Am. Chem. Soc.*, 72 (1953) 5766.
- 16 G. M. BADGER, R. J. DREWER AND G. E. LEWIS, *Australian J. Chem.*, 16 (1963) 1047.
- 17 J. BURN AND H. A. SCARBOROUGH, *J. Chem. Soc.*, (1928) 2928.
- 18 A. H. COOK, *J. Chem. Soc.*, (1938) 877.
- 19 O. H. WHEELER AND D. GONSALEZ, *Tetrahedron*, 20 (1964) 189.
- 20 G. M. BADGER, R. S. PEARCE AND R. POTTIT, *J. Chem. Soc.*, (1951) 3199.
- 21 C. W. HUFFMAN, *Can. J. Chem.*, 41 (1963) 1018.
- 22 J. W. B. REESOR, J. G. SMITH AND G. F. WRIGHT, *J. Org. Chem.*, 19 (1954) 940.
- 23 H. J. S. WINKLER AND H. GILMAN, *J. Org. Chem.*, 26 (1961) 1265.

J. Organometal. Chem., 10 (1967) 219-227