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POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS
XVIII*. REDUCTIVE TRIMETHYLSILYLATION OF *p*-DIBROMO-, *p*-DICHLORO- AND *p*-BIS(TRIMETHYLSILYL)BENZENES

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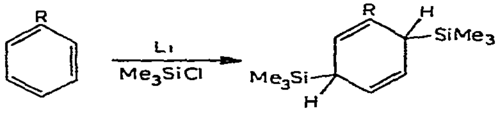
SUMMARY

The reductive trimethylsilylation of 1,4-bis(trimethylsilyl)benzene to 1,3,4,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene(III) and of *p*-dibromo- and *p*-dichlorobenzenes to (III) and in addition to 1,4,5,6-tetrakis(trimethylsilyl)-1,3-cyclohexadiene-(IV) and 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene(VI) is described. The proposed mechanism involves anion radical intermediates. An attempted preparation of (VI) by metalation of the methine hydrogens of 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene(I) and derivatization with chlorotrimethylsilane was unsuccessful; only partial dehydrogenation of (I) to 1,4-bis(trimethylsilyl)benzene occurred.

INTRODUCTION

The chemical reduction of aromatic systems with alkali metals in liquid ammonia[1,2] and with lithium in low molecular weight amines[3] is a useful and common procedure. An accepted mechanism[1] involves electron transfer from the alkali metal to the aromatic nucleus to form anions or dianions which subsequently abstract protons from a protic solvent (ethanol, etc.) to give the observed reduction products.

The related reduction of certain aromatic systems by lithium and chlorotrimethylsilane in aprotic basic ether solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME) has been observed more recently. Weyenberg and Toporcer[4] have found that benzene undergoes reductive trimethylsilylation on treatment with lithium and chlorotrimethylsilane in THF to give 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene [(I), R = H]. Similar reduction was found to occur with toluene[4], anisole[4] and with naphthalene[5]. The mechanism proposed for such reductions involves the intermediacy of anion radical species. The formation of anion radicals by electron transfer from lithium to certain monocyclic and fused polycyclic aromatic molecules



(R = H, Me, OMe)

(I)

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[*] For Part XVII see ref. 18.

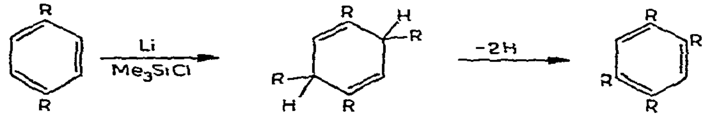
is now well substantiated by physical (ESR) and chemical methods of detection[6]. Anion radicals so formed would be expected to behave as typical nucleophilic reagents towards chlorotrimethylsilane and, in fact, the latter is known to be an excellent anion radical trapping agent[5]. In the *in situ* reductions already referred to, only a small equilibrium concentration of anion radicals may be present at any time, but their reaction with the halosilane ensures that the reduction goes to completion.

As a possible route to some poly(trimethylsilylated)polychlorobenzenes, the *in situ* interaction of hexachlorobenzene with excess of lithium (20 equiv.) and chlorotrimethylsilane (15 equiv.) in THF has already been studied in this laboratory. It was found that under these reaction conditions, several polyhalobenzenes and derivatives [hexachlorobenzene, (pentachlorophenyl)trimethylsilane and 1,4-bis(trimethylsilyl)-tetrachlorobenzene[7], chloropentafluorobenzene, bromopentafluorobenzene, (pentafluorophenyl)trimethylsilane and 1,4-bis(trimethylsilyl)tetrafluorobenzene[8]] underwent an unusual ring cleavage to afford tetrakis(trimethylsilyl)allene, $(Me_3Si)_2C{=}C{=}C(SiMe_3)_2$ (II), as the only major product. Some additional polyhalo-compounds have since been shown to give the allene (II) in varying yields under similar conditions[9]: hexabromobenzene, pentachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,3,5-tris(trimethylsilyl)trichlorobenzene, 1,4-dichlorotetrabromobenzene and 1,4-dibromotetrachlorobenzene. The allene(II) was not found to be a product from the reactions of hexafluorobenzene[7] and 1,3,5-trichlorobenzene[9] under similar conditions. Furthermore, the formation of the allene(II) from various polyhalogen substrates has so far been effected only by lithium and chlorotrimethylsilane in basic ether solvents, *e.g.*, THF and DME. A possible precursor of (II) in these reactions may be of the benzyne[10], anion radical[6] or carbenoid[11] type.

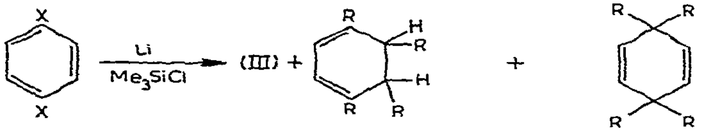
As an extension of our studies on the interaction of various halobenzenes and derivatives with a liberal excess of lithium and chlorotrimethylsilane in THF, we have examined the reactions of *p*-dibromo-, dichloro- and bis(trimethylsilyl)benzenes under these conditions. The allene(II) was not formed in any of these reactions as might have been expected by extrapolation from the results with 1,3,5-trichlorobenzene under analogous conditions. A facile reaction did, however, occur to produce trimethylsilyl-substituted cyclohexadienes as the major products in addition to hexamethyldisilane which is an expected product under such conditions, in view of the ready formation of hexamethyldisilane from chlorotrimethylsilane with lithium in THF[12].

Treatment of 1,4-bis(trimethylsilyl)benzene with lithium (10 equiv.) and chlorotrimethylsilane (10 equiv.) in THF at 20° afforded a product which was a tetrasilyl-substituted cyclohexadiene according to spectral and mol.wt. data. Two structural isomers were possible: either 1,3,4,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene (III) or 1,4,5,6-tetrakis(trimethylsilyl)-1,3-cyclohexadiene (IV). The isomer (III) was shown to be the one involved by aromatization[13] of the product with chloranil in benzene to give 1,2,4,5-tetrakis(trimethylsilyl)benzene (V). Compound (V) was obtained independently by an *in situ* Grignard method from 1,2,4,5-tetrabromobenzene and chlorotrimethylsilane in THF. The tetrakis compound (V) had also been obtained previously in low yield, in addition to the allene(II), from the reaction of 1,2,4,5-tetrachlorobenzene with excess lithium and chlorotrimethylsilane[9].

p-Dibromo- and dichlorobenzenes, under similar conditions, gave the cyclohexadiene(III) as the major product. Two additional tetrasilyl-substituted cyclohexadienes were also obtained in low yield from both these latter reactions. One was assigned the isomeric structure(IV) on the basis of analytical, physical and mol.wt. data and from its failure to undergo dehydrogenation with chloranil; the expected 1,2,3,4-tetrakis(trimethylsilyl)benzene would be strongly hindered sterically. The second product was assigned the symmetrical structure(VI): 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene, from a consideration of its IR, NMR and mol.wt. data.



III V



(X = Cl, Br; R = SiMe$_3$) (IV) (VI)

An attempt to obtain (VI) independently by metalation of the two methine hydrogens of 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene[4] and derivatization with chlorotrimethylsilane was unsuccessful; metalation did not occur with n-butyllithium nor with the more powerful metalating agent n-BuLi·TMEDA[14] (tetramethylethylenediamine). Partial dehydrogenation occurred in the latter case to give some 1,4-bis(trimethylsilyl)benzene in addition to recovered starting material.

The orientation of reduction of the main product(III), above, is similar to that obtained in the reduction of *p*-xylene with lithium in ammonia[2]. These products may arise by direct addition of lithium to the aromatic nucleus and subsequent reaction with chlorotrimethylsilane or through the intermediacy of anion radicals. The latter mechanism is more probable due to the substantial evidence now available for the formation of such radicals in these systems and the rarity of direct addition of alkali metals to monocyclic aromatic nuclei. That anion radicals are involved in these reductions may also be inferred from the rather varied and intense colors which the reaction mixtures, hereinafter described, usually displayed.

EXPERIMENTAL

All reactions involving lithium and organometallic reagents were performed under an atmosphere of dry, oxygen-free nitrogen. THF was freed from peroxides and moisture by drying over sodium and distillation from sodium benzophenone ketyl. The lithium wire used contained 1 % sodium. Dihalobenzenes were obtained commercially in reagent grade. 1,4-Bis(trimethylsilyl)benzene had previously been obtained by K. Shiina[15] by a conventional *in situ* Grignard method from *p*-dichlorobenzene and chlorotrimethylsilane. IR and NMR spectra were obtained using Perkin–Elmer Model 21 and Varian HR-60 spectrometers, respectively. Molecular weights were obtained mass spectrometrically. Vapor phase chromatographic (VPC) analyses were made with an F and M Model 500 Gas Chromatograph using a column packed with silicone gum rubber SE30 on Chromosorb W (1 : 20). Melting points are uncorrected. The identities of certain compounds were confirmed by comparison of physical properties with the known values.

Reaction of 1,4-*bis(trimethylsilyl)benzene with excess of lithium and chlorotrimethylsilane*

Lithium (7 g, 1 g-atom) was added in portions over a period of 2 h to a solution of 1,4-bis(trimethylsilyl)benzene (22.2 g, 0.1 mole) and chlorotrimethylsilane (108.5 g, 1 mole) in THF (130 ml) at 20°. The mixture was stirred vigorously with a nichrome-wire stirrer. After 24 h, VPC of a hydrolysed aliquot showed that none of the starting 1,4-bis(trimethylsilyl)benzene remained. At this stage, a general work-up procedure was employed: (1) filter the mixture to remove unreacted lithium; (2) hydrolyse the filtrate in cold dilute hydrochloric acid; (3) extract the hydrolysate with ether; (4) dry the ether extracts over magnesium sulfate and remove volatile solvents. The residual oil thus obtained was distilled using a semimicro Nester–Faust spinning band column to afford: (1) hexamethyldisilane (5.1 g), b.p., 112–113°, n_D^{25} 1.4215; (2) b.p. 90–92°, 0.15 mm (20.0 g), n_D^{20} 1.4983. The ^{1}H NMR spectrum of this product showed Si–Me (doublet, center 9.90 τ), olefinic (doublet, center 4.09 τ) and methine (doublet, center 7.33 τ) protons in the integrated ratio 18 : 1 : 1, respectively. There was no absorption due to aromatic protons. Found: mol.wt. 368. This evidence suggested as possible structures either of the isomers: 1,3,4,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene(III) or 1,4,5,6-tetrakis(trimethylsilyl)-1,3-cyclohexadiene(IV). (Calcd. proton ratio Si–Me : olefinic : methine = 18 : 1 : 1. Calcd. mol.wt.: 368.) The IR spectrum of this product did not show Si–Ph absorption and was in accord with a cyclohexadienoid structure (Found C, 58.31; H, 10.57; Si, 30.30. $C_{18}H_{40}Si_4$ calcd.: C, 58.70; H, 10.87; Si, 30.44 %.) The isomer(III) was confirmed by aromatization.

Aromatization of (III) to 1,2,4,5-*tetrakis(trimethylsilyl)benzene (V)*

The cyclohexadiene(III) (2.5 g, 0.0068 mole) was dissolved in dry benzene (30 ml) and chloranil (2.09 g, 0.0085 mole) was added. The mixture was heated under reflux for 6 h under nitrogen. Work-up was as follows: (1) Add a large volume of petroleum ether (b.p. 60–70°) to the cooled reaction mixture and filter; (2) concentrate the filtrate to *ca.* 30 ml; (3) chromatograph the residue over neutral alumina using petroleum ether (b.p. 60–70°) as eluting agent; (4) concentrate the eluates. This procedure gave 1,2,4,5-tetrakis(trimethylsilyl)benzene (1.4 g, 56.2 %), m.p. (from ethanol) 170–171°, identical in all respects with an authentic sample prepared as described below.

In situ Grignard preparation of 1,2,4,5-*tetrakis(trimethylsilyl)benzene*

Magnesium turnings (30 g, 1.2 g-atoms) were activated[16] by stirring vigorously with a nichrome wire stirrer under nitrogen for 12 h. Chlorotrimethylsilane (86.80 g, 0.8 mole) and THF (50 ml) were added to the black, finely-powdered magnesium. A solution of 1,2,4,5-tetrabromobenzene (39.4 g, 0.1 mole) in THF (130 ml) was added dropwise to the reaction mixture; an exothermic reaction soon set in. After completion of the addition, the reaction mixture was heated at reflux for 12 h and worked-up as follows: (1) add THF to the semi-solid reaction mixture to solubilize; (2) filter to remove unreacted magnesium and precipitated salts; (3) wash the precipitate with THF; (4) hydrolyse the combined filtrates in cold dilute hydrochloric acid; (5) extract the hydrolysate with ether; (6) dry the ether extracts over magnesium sulfate and remove volatile solvents. The residue thus obtained gave on distillation a mixture of THF degradation products: 4-(trimethylsilyl)butanol and 1-(trimethylsiloxy)-4-(trimethylsilyl)butane, b.p. 79–81°/15 mm (12.5 g). The residue from the distillation was crystallized from ethanol to give 1,2,4,5-tetrakis(trimethylsilyl)benzene (4 g, 11 %), m.p. 170–171°). (Found: C, 59.20; H, 10.06. $C_{18}H_{38}Si_4$ calcd.: C, 59.02; H, 10.39 %.) The ^{1}H NMR spectrum of this compound showed Si–Me (singlet, 9.67 τ) and aromatic (singlet, 2.18 τ) protons in the integrated ratio 18.3 : 1. (Calcd. ratio 18 : 1).

Reaction of p-dibromobenzene with excess lithium and chlorotrimethylsilane

Lithium (14 g, 2 g-atoms) was added in portions to a solution of *p*-dibromobenzene (47.2 g, 0.2 mole) and chlorotrimethylsilane (217 g, 2 moles) in THF (150 ml) over a 4 h period. After stirring for 24 h, VPC indicated the absence of unreacted *p*-dibromobenzene. The reaction mixture was worked up as before to give on distillation: (1) hexamethyldisilane, (18.1 g), b.p. 113°, n_D^{20} 1.4215; (2) b.p. 33–44°/0.06 mm (9.3 g,); (3) b.p. 45–100°/0.06 mm (6.1 g); (4) b.p. 100–130°/0.06 mm (54.6 g). Fractions (3) and (4) deposited a solid. This was isolated and crystallized from ethanol to afford colorless needles, m.p. 98–99° (2.2 g). The ^{1}H NMR spectrum of this product showed Si–Me, (doublet, center 9.94 τ), olefinic (doublet, center 4.12 τ) and methine (doublet, center 7.58 τ) protons in the integrated ratio 18 : 1 : 1, respectively. The mass spectrum gave a molecular weight of 368. The IR spectrum also agreed with a cyclohexadienoid structure. The compound resisted aromatization by chloranil in benzene. This evidence suggested this product to be the isomeric tetrasilylated cyclohexadiene (IV), 1,4,5,6-tetrakis(trimethylsilyl)-1,3-cyclohexadiene. (Found: C, 59.28; H, 10.97; Si, 30.25. $C_{18}H_{40}Si_4$ calcd.: C, 58.70; H, 10.87; Si, 30.44 %.)

The oil remaining after removal of the above product showed several components by VPC. It was redistilled using a spinning band column to give an oil, pure by VPC, b.p. 90–95°/0.2 mm, n_D^{20} 1.4985 (29.5 g). This product was identical to that obtained from 1,4-bis(trimethylsilyl)benzene, *viz.* 1,3,4,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene(III). This was confirmed by aromatization of the liquid product (8.5 g) with chloranil (7.1 g) in benzene (60 ml) to give 1,2,4,5-tetrakis(trimethylsilyl)-benzene(V) (4.4 g, 50.7 %), m.p. and mixed m.p. 169–171°.

The residue remaining after distillation of the cyclohexadiene (III) deposited some crystals. These were isolated and crystallized from ethanol to give 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene (VI) (0.9 g), m.p. 112–113°. The ^{1}H NMR spectrum of this product showed only Si-Me (singlet, 9.92 τ) and olefinic (singlet, 4.90 τ) protons in the integrated ratio 9 : 1, respectively (calcd. 9 : 1). (Found: C, 58.90; H, 10.85; Si, 30.4; mol.wt., 368. $C_{18}H_{40}Si_4$(VI) calcd.: C, 58.70; H, 10.87; Si, 30.44 %; mol.wt., 368.)

Reaction of p-dichlorobenzene with excess lithium and chlorotrimethylsilane

Lithium (14 g, 2 g-atoms) was added to a solution of *p*-dichlorobenzene (29.4 g, 0.2 mole) and chlorotrimethylsilane (217 g, 2 moles) in THF (150 ml) at 20° over a period of 4 h. The reaction mixture was stirred vigorously for 30 h after which time VPC indicated the absence of unreacted *p*-dichlorobenzene. The reaction mixture was worked up as above and the product distilled through a Widmer column unit to afford: (1) hexamethyldisilane (7.3 g), b.p. 113°, n_D^{20} 1.4210; (2) b.p. 58–100°/0.04 mm; (3) b.p. 100–130°/0.04 mm; (4) b.p. 130–135°/0.04 mm. Fractions (2) and (3) deposited a solid. This was isolated and crystallized from ethanol to afford 1,4,5,6-tetrakis-(trimethylsilyl)-1,3-cyclohexadiene (IV) (2.5 g), m.p. 99–100°, mixed m.p. with a similar product from *p*-dibromobenzene: 98–100°.

After removal of (IV), an oil remained (32.5 g). VPC showed this oil to consist of one major and three minor components. It was fractionated using a spinning band column to yield a pure material, b.p. 91–94°/0.2 mm (13.5 g), n_D^{20} 1.4886. The product was identical with respect to physical properties to 1,3,4,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene (III) obtained previously. The distillation residue deposited needle crystals on standing. These were isolated and crystallized from ethanol to give 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene (VI) (0.6 g), m.p. 111–112°, mixed m.p. with a similar product obtained previously: 111–112°.

Preparation of 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (I).

The procedure employed was essentially that described by Weyenberg[4]. Lithium (21 g, 3 g-atoms) was added in portions to benzene (58.5 g, 0.75 mole) and chlorotrimethylsilane (244.1 g, 2.25 moles) in THF (200 ml) over a 6 h period. The reaction mixture was vigorously stirred with a nichrome wire stirrer for 72 h. The customary work-up gave an oil which was distilled through a Widmer column unit to give 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene, b.p. 90–94°/4.3 mm, m.p. 50° (106.9 g, 63.6%). After the distillation, a residual oil remained (16.2 g). The cyclohexadiene(I), on further treatment with excess lithium and chlorotrimethylsilane in THF failed to undergo further reduction; (I) was recovered unchanged.

Attempted metalation of the methine hydrogens of (I) with n-BuLi·TMEDA

TMEDA (redistilled under N_2 and stored over molecular sieves) (0.05 mole) was dissolved in hexane (30 ml). This solution was slowly added with stirring to n-butyllithium (0.05 mole) in hexane cooled below 10°. The resultant n-BuLi·TMEDA complex was added dropwise to a solution of 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene (5.6 g, 0.025 mole) in n-hexane (100 ml) at −78°. The resulting mixture was stirred at −78° for 5 h. Color Test II[17] remained positive. The solution was allowed to reach 20° to give a colored mixture; Color Test II still was positive. Chlorotrimethylsilane (0.1 mole) was added to the reaction mixture. The normal work-up gave a mixture of recovered (I) and its dehydrogenation product, 1,4-bis(trimethylsilyl)benzene (1.5 g), m.p. and mixed m.p. 92–93°. A similar result was obtained when (I) was treated with n-BuLi at 20° in ether; no metalation was effected in either case.

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