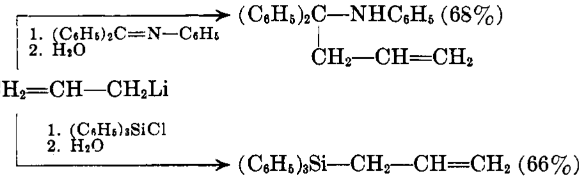
proximately 5% higher. This suggests that the yields based upon the titration data are to be viewed as minimum values.

The methods employed for the formation of chemical derivatives of allyllithium illustrate the high reactivity of this organometallic reagent in two types of reactions. The first involved the facile addition of allyllithium to the azomethine linkage of benzophenone anil[11] (equation 2), while the second was the substitutional allylation of chlorotriphenylsilane[12] (equation 3).

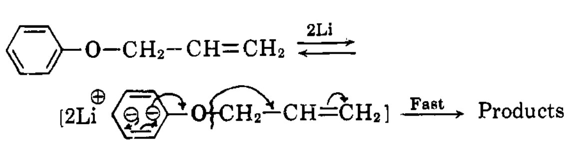


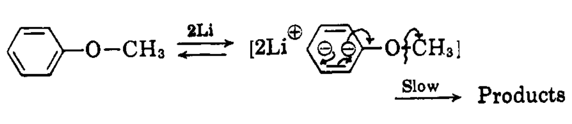
$$CH_2{=}CH{-}CH_2Li \xrightarrow[2.\ H_2O]{1.\ (C_6H_5)_2C{=}N{-}C_6H_5} (C_6H_5)_2C(CH_2{-}CH{=}CH_2){-}NHC_6H_5\ (68\%) \quad (2)$$

$$CH_2{=}CH{-}CH_2Li \xrightarrow[2.\ H_2O]{1.\ (C_6H_5)_3SiCl} (C_6H_5)_3Si{-}CH_2{-}CH{=}CH_2\ (66\%) \quad (3)$$

If it is assumed that the preceding reactions (equations 2 and 3) occur quantitatively, the yield of allyllithium (equation 1) must be at least about 70%. The cleavage of allyl phenyl ether by lithium metal, therefore, constitutes a convenient method for the preparation of allyllithium from readily accessible and stable starting materials. Moreover, its preparation in tetrahydrofuran furnishes directly an excellent solvent medium for subsequent chemical reactions.[13] It should be noted that the by-product, phenol, can be separated easily from the hydrolyzed reaction products simply by extraction of the lithium phenoxide with water.

The striking ease with which allyl phenyl ether undergoes lithium metal cleavage contrasts sharply with the inertness of anisole toward lithium metal alone in refluxing tetrahydrofuran.[1c,8] Rather it is with other allylic ether types, such as alkyl cumyl ethers[14] and alkyl benzyl ethers,[15] that a similar facility toward metal cleavage must be sought. In a previous study[1c] the ease with which related unsaturated substrates were cleaved by lithium metal was correlated with the tendency of such substrates to form transitory lithium adducts. In this view the marked facility with which allyl phenyl ether is cleaved, compared with methyl phenyl ether, can be related to the resonance stabilization of *both* the incipient anionic fragments in the transition state of the cleavage reaction (equation 4).


(4)


(5)

Amplification of these principles for the preparation of other useful organometallic compounds is being actively investigated.

Experimental[16]

Cleavage of Allyl Phenyl Ether.—To a 500-ml., three-necked, round-bottomed flask, equipped with a sealed paddle stirrer, a Friedrichs condenser surmounted by a nitrogen inlet tube and a pressure-equalized addition funnel, were added 50 ml. of anhydrous tetrahydrofuran and 4.2 g. (0.60 g.-atom) of freshly cut lithium pieces (2 × 12 mm.). The system was cooled to −15 ± 5° (external temperature) by an ice–salt bath while a solution of 6.7 g. (0.050 mole) of allyl phenyl ether[17] in 25 ml. of anhydrous ethyl ether was added dropwise to the rapidly stirred lithium suspension. (If a pale green or blue color signaling the start of the cleavage was not noticed after a portion of the allyl phenyl ether was added, a pinch of biphenyl was introduced.[1c]) At the close of the 45-min. addition period the cooling bath was removed and the reaction mixture was stirred for an additional 15 min. The dark red solution was decanted through glass wool from the lithium metal and aliquots were analyzed by the usual double titration technique.[10] Yields obtained in this manner ranged from 62 to 66%.

The titrated yields of allyllithium ranged from 40 to 50% in runs in which 0.10 mole of the allyl phenyl ether in 25 ml. of ethyl ether were added to 0.22 g.-atom of lithium pieces in 50 ml. of tetrahydrofuran over a 60-min. period at 0°.

Derivatives of Allyllithium. (a) With Benzophenone Anil.—A solution of 12.85 g. (0.050 mole) of benzophenone anil in 50 ml. of dry benzene was added to the allyllithium solution obtained from the treatment of 0.050 mole of allyl phenyl ether with 0.60 g.-atom of lithium, according to the first procedure described in the preceding section. The system was allowed to stir for 12 hr. and then was treated with water. The organic components were extracted with ether and the ether layer then dried with anhydrous calcium sulfate. The organic solvents were evaporated and the residue was taken up in a minimum of petroleum ether (b.p. 30–60°). This solution was chromatographed on an alumina column and the 1-allyl-1,1-diphenylmethylaniline was eluted from the column selectively by additional portions of petroleum ether. The total yield of 1-allyl-1,1-diphenylmethylaniline thereby obtained was 10.2 g. (68%), m.p. 75–77° (lit.[11] m.p. 78.5–80°). Recrystallization of this product from 95% ethanol raised the melting point to 77.5–79.5°. Admixture with an authentic sample caused no melting point depression.

(b) With Chlorotriphenylsilane.—A solution of 13.28 g. (0.045 mole) of chlorotriphenylsilane in 50 ml. of anhydrous ethyl ether was added to a solution of allyllithium which was prepared in the aforementioned manner and was estimated to contain 0.031 mole by the double titration method.[10] The resulting solution was stirred at the reflux temperature for 12 hr. and thereupon hydrolyzed. The separated ether layer was dried with anhydrous calcium sulfate and then evaporated. The residual colorless solid was recrystallized from 95% ethanol to yield 9.90 g. (66%) of allyltriphenylsilane, m.p. 88–89° (lit.[12] m.p. 91°).

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(11) *Cf.* H. Gilman and J. J. Eisch, *J. Am. Chem. Soc.*, **79**, 2150 (1957), for the reaction of benzophenone anil with allyl and alkyl Grignard reagents.

(12) R. H. Meen and H. Gilman, *J. Org. Chem.*, **22**, 684 (1957).

(13) For the enhanced rates of organolithium reactions in tetrahydrofuran, *cf.* H. Gilman and B. J. Gaj, *ibid.*, **22**, 447, 1165 (1957), and H. Gilman and S. Gray, *ibid.*, **23**, 1476 (1958).

(14) K. Ziegler, F. Crössman, K. Kleiner, and O. Schäfer, *Ann.*, **473**, 1 (1929); K. Ziegler and H. Dislich, *Chem. Ber.*, **90**, 1107 (1957).

(15) *Cf.* H. Gilman and G. L. Schwebke, *J. Org. Chem.*, **27**, 4259 (1962), for the preparation of benzyllithium from such ether cleavages.

(16) All organometallic reactions were conducted under an atmosphere of dry, oxygen-free nitrogen. The tetrahydrofuran was purified by successive treatments with sodium hydroxide pellets, sodium slices, and lithium aluminum hydride. The tetrahydrofuran was distilled from the lithium aluminum hydride directly into the reaction vessel. All glassware was dried at 120° for at least 4 hr. All melting points are uncorrected.

(17) L. Claisen, *Ann.*, **418**, 78 (1919).

Cleavage of Silicon–Silicon Bonds on an Alumina Column

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In a recent publication from these laboratories,[1] it was proposed that dilute hydrochloric acid promoted the hydrolytic cleavage of the silicon–silicon bonds in 1,4-dihydroxyoctaphenyltetrasilane (II) which were

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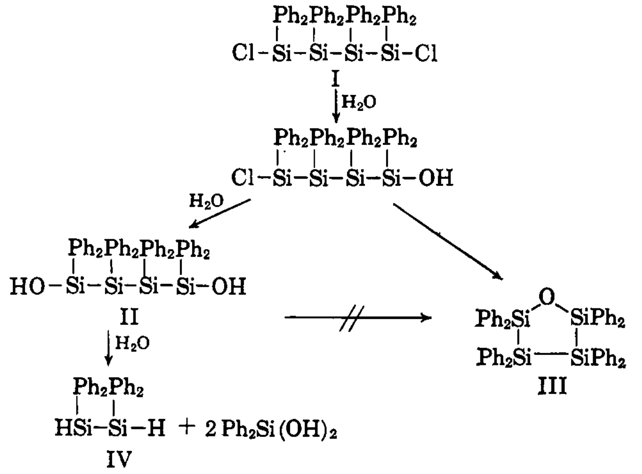
(1) A. W. P. Jarvie and H. Gilman, *Chem. Ind.* (London), 1271 (1960).

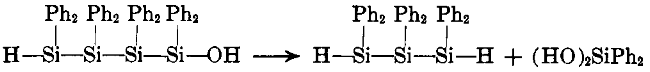
adjacent to the hydroxy groups. Isolation of *sym*-tetraphenyldisilane (IV) by chromatography on alumina of the crude hydrolysate obtained from 1,4-dichlorooctaphenyltetrasilane (I)[2] was taken as indication of the validity of this proposal. In this previous investigation, the 1,4-dihydroxy compound was not isolated in pure form; large amounts of its condensation product, octaphenyloxacyclopentasilane (III), were isolated.



Subsequent work in this area has shown that basic alumina is an effective reagent in causing scission of silicon–silicon bonds adjacent to hydroxy groups. Therefore, in the present work and probably in the previous investigation, it appears that silicon–silicon bond cleavage occurs during chromatography.

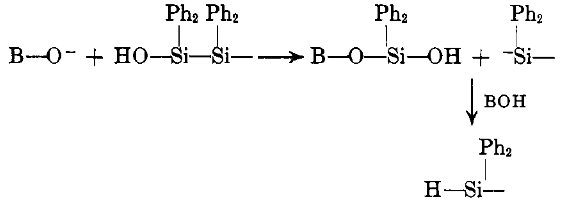
When 1,4-dichlorooctaphenyltetrasilane was hydrolyzed in tetrahydrofuran by dilute hydrochloric acid, 1,4-dihydroxyoctaphenyltetrasilane (II) was the main product isolated. The high yield of this compound may be due to the rapid hydrolysis of both Si-Cl groups to Si-OH. Similarly, the product obtained from the reaction between Kipping's Compound B[2] and phosphorus pentachloride[3] was hydrolyzed in a mixture of tetrahydrofuran and dilute hydrochloric acid to give the corresponding dihydroxy compound.[4]

When 1,4-dihydroxyoctaphenyltetrasilane was chromatographed on an alumina column, there was obtained a 46% yield of *sym*-tetraphenyldisilane (IV) and a 4% yield of octaphenylcyclotetrasiloxane[5] $(Ph_2SiO)_4$ which may have been formed by the action of base on diphenylsilanediol. 1,5-Dihydroxydecaphenylpentasilane afforded a 62% yield of 1,1,2,2,3,3-hexaphenyltrisilane (VI). This latter reaction supports the view that the dihydroxy derivative of Kipping's compound B is 1,5-dihydroxydecaphenylpentasilane and not (as previously designated) 1,6-dihydroxydodecaphenylhexasilane.[4] Similarly, 1,5-dichlorodecaphenylpentasilane gave 1,1,-2,2,3,3-hexaphenyltrisilane (VI) in 50% yield and 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol (V)[6] gave the same product in 51% yield. Instead of the previous silanol, its chloro derivative (1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane) also could be used directly and gave a 52% yield of 1,1,2,2,3,3-hexaphenyltrisilane. 1,1,2,2,3,3-Hexaphenyltrisilan-1-ol was not isolated from the alumina column treatment of 1,4-dihydroxyoctaphenyltetrasilane. However, 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol (V) was obtained from 1,5-dihydroxydecaphenylpentasilane.



$$\underset{\mathrm{V}}{\mathrm{H{-}\overset{Ph_2}{Si}{-}\overset{Ph_2}{Si}{-}\overset{Ph_2}{Si}{-}\overset{Ph_2}{Si}{-}OH}} \longrightarrow \underset{\mathrm{VI}}{\mathrm{H{-}\overset{Ph_2}{Si}{-}\overset{Ph_2}{Si}{-}\overset{Ph_2}{Si}{-}H}} + \mathrm{(HO)_2SiPh_2}$$

In order to ascertain whether the silicon–silicon bond cleavage is enhanced by the presence of acids, 1,4-dihydroxyoctaphenyltetrasilane was treated with 6 *N* hydrochloric acid for two hours. No change in the infrared spectrum was observed and it seems that, under these conditions, no cleavage of silicon–silicon bonds or cyclization to octaphenyloxacyclopentasilane occurred. The alumina[7] used in these experiments was basic and this basicity is considered to be responsible for the observed reaction. Whether the base effecting the cleavage is alumina itself or some other adsorbed inorganic base is not known. In any case, the diphenylsilanediol postulated as forming in the previous reaction scheme is probably bound chemically to the alumina through oxygen bonds. This would account for the absence of the product in the eluates. The course of the reaction might be as depicted. The same scheme might apply equally well to the chloropolysilanes, with possible conversion of the silicon–chlorine linkage to silicon–oxygen. Silicon–silicon bond cleavage can conceivably occur at other points in the reactants and products, which could account for the only moderate yields of silicon–hydrogen compounds.



$$\mathrm{B{-}O^- + HO{-}\overset{Ph_2}{Si}{-}\overset{Ph_2}{Si}{-} \longrightarrow B{-}O{-}\overset{Ph_2}{Si}{-}OH + {}^-\overset{Ph_2}{Si}{-}}$$
$$\downarrow \mathrm{BOH}$$
$$\mathrm{H{-}\overset{Ph_2}{Si}{-}}$$

From these results, it may be expected that when polysilanes have strongly electron-withdrawing groups on the terminal silicon atoms they may be cleaved fairly specifically on alumina.

Experimental

Preparation of 1,4-Dihydroxyoctaphenyltetrasilane.—To 5 g. (0.0062 mole) of 1,4-dichlorooctaphenyltetrasilane in 100 ml. of tetrahydrofuran was added 150 ml. of dilute hydrochloric acid. The mixture was stirred for 15 min. The hydrolyzate was then extracted with ether and 0.35 g. (7%) of solid, m.p. 183–185° (mixture melting point with starting material undepressed), was isolated as an insoluble solid. The ether extracts, after drying over anhydrous sodium sulfate, were evaporated. All residues were fractionally crystallized from benzene–petroleum ether (b.p. 50–60°) to give 2.65 g. (70%) of a solid, m.p. 208–210°. Recrystallization from benzene–petroleum ether raised the m.p. to 212–213°. This solid, which showed no Si–H or Si–O–Si bands in the infrared spectrum, but had a band due to Si–OH, is 1,4-dihydroxyoctaphenyltetrasilane.

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

[3] D. R. Chapman, unpublished studies.

[4] A. W. P. Jarvie, H. J. S. Winkler, and H. Gilman, *J. Org. Chem.*, **27** 614 (1962).

[5] C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, pp. 228–264.

[6] G. L. Schwebke, unpublished studies.

[7] The activated alumina for chromatography was obtained from the Chicago Apparatus Co., Chicago 22, Ill.

Anal. Calcd. for $C_{48}H_{42}O_2Si_4$: Si, 14.71. Found: Si, 14.50, 14.51.

Similarly, hydrolysis of 1,5-dichlorodecaphenylpentasilane (19.2 g.) in tetrahydrofuran (150 ml.) using 80 ml. of 0.1 *N* hydrochloric acid gave 1,5-dihydroxydecaphenylpentasilane, 17.05 g. (92.2%); m.p. after recrystallization from cyclohexane and benzene, 172–174°; m.m.p. with an authentic specimen, 171–174°. Additional identification of the product was obtained from the superimposability of the infrared spectra.

1,4-Dihydroxyoctaphenyltetrasilane on an Alumina Column.—1,4-Dihydroxyoctaphenyltetrasilane (1.45 g.) was placed on an alumina column. Elution with successive portions of petroleum ether (b.p. 50–60°), carbon tetrachloride, benzene, and ethyl acetate gave 0.32 g. (46%) of *sym*-tetraphenyldisilane, m.p. 76–78°, and 0.02 g. (4%) of octaphenylcyclotetrasiloxane, m.p. 184–185°, identified by mixture melting point and infrared spectra.

Treatment of 1,4-Dihydroxyoctaphenyltetrasilane with Hydrochloric Acid.—1,4-Dihydroxyoctaphenyltetrasilane (3.0 g.) in 10 ml. of ether was treated with 10 ml. of 6 *N* hydrochloric acid solution for 2 hr. The ether layer was separated and evaporated to yield a solid, m.p. 198–200°, which had an infrared spectrum identical with that of the starting material and contained no bands due to Si–H and Si–O–Si.

1,5-Dihydroxydecaphenylpentasilane on an Alumina Column.—1,5-Dihydroxydecaphenylpentasilane (23.7 g.) was dissolved in benzene and placed on an alumina column 16 in. high and 2 in. in diameter. Fractions were eluted with benzene and, subsequent to recrystallization from acetone and methanol, gave 1,1,2,2,3,3-hexaphenyltrisilane, 8.54 g. (62.1%), m.p. 95–97°; m.m.p. with an authentic specimen, 95–97°.

In a second run, 1,5-dihydroxydecaphenylpentasilane (5.7 g.) was placed on an alumina column and eluted with benzene, to give 0.4 g. of a solid, m.p. 97–98°. This had the same infrared spectrum as the 1,1,2,2,3,3-hexaphenyltrisilane isolated from the chromatography of 1,1,2,2,3,3,4,4-octaphenyltetrasilane-1-ol. There was no depression of the melting point of a mixture of the two products. Ethyl acetate elutions afforded 1.9 g. of a mixture of 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol, m.p. 180–181° (identified by mixture melting point and infrared spectrum); and also some of the starting material (infrared).

1,5-Dichlorodecaphenylpentasilane on an Alumina Column.—1,5-Dichlorodecaphenyl pentasilane (29.5 g.) was dissolved in benzene and placed on an alumina column 18 in. high and 2 in. in diameter. Elution of all the fractions with benzene and recrystallization from methanol and acetone gave 8.25 g. (50.0%) of 1,1,2,2,3,3-hexaphenyltrisilane, m.p. 95–97° (mixture melting point with authentic specimen undepressed). The other products were glues which could not be crystallized. The 1,1,2,2,3,3-hexaphenyltrisilane was identified additionally from the superimposability of its infrared spectrum with that of an authentic specimen.

1,1,2,2,3,3,4,4-Octaphenyltetrasilan-1-ol on an Alumina Column.—A solution of 2.7 g. of 1,1,2,2,3,3,4,4-octaphenyltetrasilan-1-ol in 25 ml. of carbon tetrachloride was placed on an alumina column. Carbon tetrachloride and benzene elutions afforded 0.99 g. (51%) of a solid, m.p. 96–98°, which was 1,1,2,2,3,3-hexaphenyltrisilane.

Anal. Calcd. for $C_{36}H_{32}Si_3$: Si, 15.3. Found: Si, 15.40, 15.45.

The infrared spectrum is similar to those of *sym*-tetraphenyl disilane and 1,1,2,2,3,3,4,4-octaphenyltetrasilane, but possesses an Si-H band of intermediate intensity. This trisilane was separated from the starting material, which was also partially eluted, by its solubility in hot petroleum ether (b.p. 50–60°). In the preparatory method for the trisilane, better results were obtained with a long alumina column.

Similarly, 50 g. of 1-chloro-1,1,2,2,3,3,4,4-octaphenyltetrasilane afforded 18.5 g. (52%) of 1,1,2,2,3,3-hexaphenyltrisilane. This latter reaction appeared to take a longer time than that starting with the corresponding silanol.

Acknowledgment.—This research was supported by the U. S. Air Force under contract AF 33(616)-6463 and monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright Patterson Air Force Base, Ohio.

The Structures of Substituted *o*-Quinone Methide Trimers

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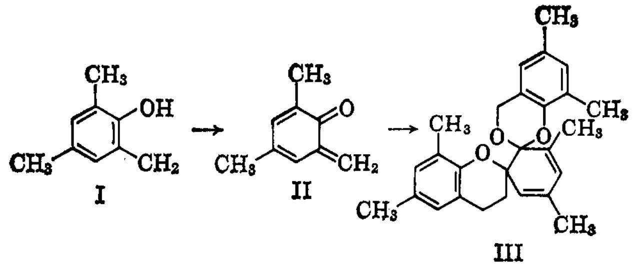
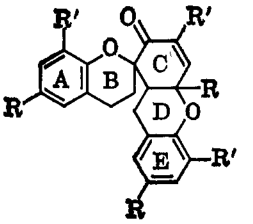
The facility with which substituted *o*-quinone methides dimerize and trimerize was recognized as early as 1907.[1] While a great deal of literature bearing on the structures of trimers has been written, most of it is concerned specifically with the trimer of 3,5-dimethylquinone-(2)-methide (II).[2] No less than three structures have been proposed for this substance. The most recent of these, the "benzodioxan" structure (III), was suggested[3] in 1941 and given additional support more recently.[4,5]



Recent studies on the structure of the trimer of *o*-quinone methide itself led to the assignment shown in IV[2] and prompted a re-examination of the properties of earlier reported substituted trimers. The trimer of 3,5-dimethylquinone-(2)-methide and of 3-chloromethyl-5-methylquinone-(2)-methide were studied as representative cases. Evidence is now presented establishing that these two are related and have a ring system identical with that of the parent (IV). They are, therefore, formulated as V and VI, respectively.



IV, R = R' = H
V, R = R' = CH_3
VI, R = CH_3, R' = CH_2Cl

Although V does not form carbonyl derivatives, the presence of an α,β-unsaturated ketone functionality was suggested by infrared data (ν_{max} 5.91 μ) and confirmed by quantitative microhydrogenation. It absorbed 0.97 mole equivalent of hydrogen to afford a dihydroketone (VII), m.p. 180–181°, ν_{max} 5.81 μ. Further reduction with lithium aluminum hydride

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(1) K. Fries and K. Kann, *Ann.*, **353**, 339 (1907).

(2) S. B. Cavitt, H. Sarrafizadeh R., and P. D. Gardner, *J. Org. Chem.*, **27**, 1211 (1962), and references cited therein.

(3) G. Schiemann and K. Hultzsch, *Naturwissenschaften*, **35**, 124 (1948).

(4) G. Schiemann, *Rev. fac. sci. univ. Istanbul*, **17A**, 290 (1952); *Chem. Abstr.*, **48**, 3293 (1954).

(5) H. Civelekoglu, *Rev. fac. sci. univ. Istanbul.*, **18A**, 14 (1953); *Chem. Abstr.*, **48**, 5139 (1954).