

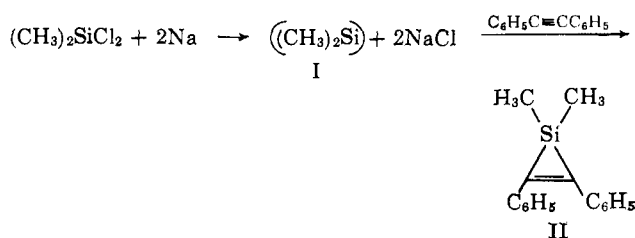
Reaction of Diphenyldichlorosilane with Lithium¹

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Contribution from the Chemical Department,
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The reaction of diphenyldichlorosilane with lithium in tetrahydrofuran was investigated with the intent of determining the significance of diphenylsilylene as an intermediate in this system. No products which could be regarded as arising from the capture of diphenylsilylene by cyclohexene when the olefin was used as a possible trapping reagent were isolated. Incidental to this study, however, it was found that 2-cyclohexen-1-yl hydroperoxide and 2-cyclohexen-1-ol reacted with some intermediate of the diphenyldichlorosilane-lithium reaction to give 2-cyclohexen-1-yl diphenylsilane. Evidence for the mechanism of formation of this compound is presented.

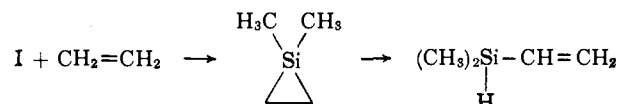
During the past three years several significant developments in the chemistry of bivalent organosilicon compounds have been reported.²⁻⁸ In 1961 Vol'pin and co-workers reported² the possible generation of dimethylsilylene (I) from the reaction of dimethyldichlorosilane with sodium in boiling xylene. The claim for the intermediacy of I was based on the isolation of the "silirene"⁹ (II) when the reaction was carried out in the



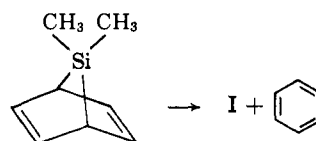
presence of diphenylacetylene. Thus, as proposed by Vol'pin, it appeared that I exhibited "carbenoid" character by reacting with a center of unsaturation to form two covalent bonds. More recent publications describe other means of generating and capturing I.

- (1) Communicated in part: H. Gilman, *Angew. Chem.*, **74**, 950 (1962).
- (2) M. E. Vol'pin, Yu. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1355 (1961).
- (3) M. E. Vol'pin, Yu. D. Koreshkov, V. G. Dulova, and D. N. Kursanov, *Tetrahedron*, **18**, 107 (1962).
- (4) L. A. Leites, V. G. Dulova, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 731 (1963).
- (5) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).
- (6) H. Gilman, S. G. Cottis, and W. H. Atwell, *ibid.*, **86**, 1596 (1964).
- (7) O. M. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, **3**, 226 (1964).
- (8) O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, 395 (1964); *Chem. Abstr.*, **60**, 9304 (1964).
- (9) A reinvestigation of this reaction has revealed that compound II is actually 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene: R. A. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963). However, this finding does not necessarily alter the possibility of dimethylsilylene as a reaction intermediate; see ref. 5, footnote 6.

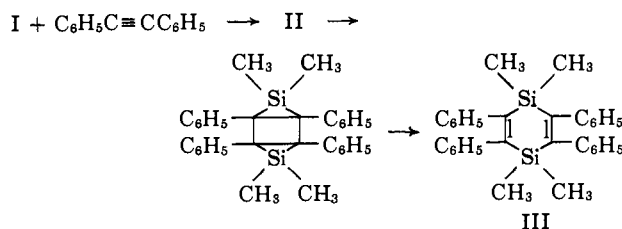
Thus, Skell and Goldstein⁶ formed I from the reaction of dimethyldichlorosilane with sodium-potassium vapors at temperatures between 260 and 280°. In the presence of ethylene dimethylvinylsilane was formed. Nefedov and co-workers^{7,8} have similarly proposed the transient existence of I to rationalize the products obtained from



the reaction of dimethyldichlorosilane with lithium in the presence of various olefins. It has been suggested that I is a product from the pyrolysis of substituted 7-silanolbornadienes.⁶ When the pyrolysis is conducted



in the presence of diphenylacetylene 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene (III) is formed.



These publications prompt us to report some results we have obtained from an investigation that was initiated for the purpose of determining the significance of diphenylsilylene,¹⁰ $(\text{C}_6\text{H}_5)_2\text{Si}$, as an intermediate in the reaction of diphenyldichlorosilane (IV) with lithium, sodium, and magnesium in tetrahydrofuran. Studies¹¹ in these laboratories have demonstrated that IV reacts with these metals to give octaphenylcyclotetrasilane as the initial isolable product. Although the predominant process occurring in this system can be postulated as a series of "Wurtz-type" coupling reactions to give the cyclic silane, it seemed conceivable that a competing reaction might involve the α -elimination¹⁰ of

(10) In view of recent findings on related carbene systems, it is questionable whether the diphenylsilylene moiety would actually exist free of lithium chloride; see, for example, H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); W. T. Miller, *ibid.*, **86**, 2089 (1964).

(11) For a review of this complex reaction see H. Gilman and G. L. Schwabke, *Advan. Organometal. Chem.*, **1**, 89 (1964).

reactivity to V) afforded allyltriphenylsilane (1.5–5.8%) and 2-cyclohexen-1-yltriphenylsilane¹⁷ (trace); (3) allyloxytriphenylsilane is cleaved by lithium in tetrahydrofuran to give allyllithium in yields of 2¹⁷–13.3%. The last two experiments are of additional interest since they clearly show that alkoxysilanes not only undergo attack by nucleophiles¹⁸ and alkali metals at the silicon atom but also, to a small extent, at the carbon atom of the C–O–Si linkage. This observation has also been made recently in a study of reactions of alkoxysilanes with sodium at high temperatures.¹⁹ In that study it was also postulated that sodium methoxide is capable of cleaving methoxysilanes through attack at the methyl group, leading to the formation of dimethyl ether.¹⁹

It has been shown that the C–O bond of alkoxysilanes is more reactive when derived from benzylic alcohols. The observation was made in reactions of alkoxysilanes with phosphorus oxychloride.²⁰ The same reactivity relationship appears to be valid for reactions of alkoxysilanes with triphenylsilyllithium and with lithium.¹⁷ Herein lies the most probable reason for the different behavior of cycloalkyl and cycloalkenyl hydroperoxides in the IV–lithium reaction, since the latter hydroperoxides would give rise to alkoxysilanes having a more reactive, allylic C–O bond.

Experimental²¹

Reaction of Diphenyldichlorosilane with Lithium in the Presence of Some Trapping Reagents. (A) *Nonpurified Cyclohexene.* A solution of 63.25 g. (0.25 mole) of diphenylchlorosilane, 120 ml. of tetrahydrofuran (THF), and 100 ml. of cyclohexene was added dropwise to an excess (7 g., 1.0 g.-atom) of lithium wire cut into fine pieces. A reaction occurred immediately as evidenced by the evolution of heat and the formation of a precipitate. Subsequent to the addition of *ca.* 25 ml. of the solution there was added 30 ml. of cyclohexene to the reaction flask. Following the addition and 1 hr. of stirring, the reaction mixture had a brown coloration and gave a positive Color Test I,²² characteristic of organometallic compounds. Stirring was continued for an additional 4 hr. and the reaction mixture was then hydrolyzed with dilute hydrochloric acid.

The organic layer was separated, dried over sodium sulfate, concentrated, and chromatographed on alumina. Petroleum ether (b.p. 60–70°) as eluent gave an oil that was distilled under reduced pressure to give the following fractions: (1) 7.4 g., b.p. 140–145° (0.5 mm), *n*²⁰_D 1.5860; (2) 1.1 g., b.p. 145–155° (0.5 mm.), *n*²⁰_D 1.5890. The infrared spectra of these fractions were superimposable on the spectrum of 2-cyclohexen-1-yl-diphenylsilane. The yield of crude product was 12.8%.

Continued elution of the column with carbon tetrachloride and benzene produced polymeric oils that resisted purification and identification.

Treatment of 2.64 g. (0.01 mole) of fraction 1 with an excess of phenyllithium gave 1.75 g. of product,

(18) Reference 16, Chapter 2.

(19) J. W. Ryan, *J. Am. Chem. Soc.*, **84**, 4730 (1962).

(20) J. Fertig, W. Gerrard, and H. Herbst, *J. Chem. Soc.*, 1488 (1957).

(21) All reactions involving organometallics were carried out under an atmosphere of dry, oxygen-free nitrogen using oven-dried glassware.

(22) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

m.p. 138–142° (cloudy). Subsequent to unsuccessful attempts to purify this material by crystallizations from several solvents, it was dissolved in petroleum ether (b.p. 60–70°) and chromatographed on alumina. Careful fractionation afforded 1.1 g. (32.3%) of 2-cyclohexen-1-yltriphenylsilane, m.p. 131–133°, after a crystallization from ethanol. An infrared spectrum of the silane was superimposable on the spectrum of an authentic sample. Also, a mixture melting point determination was not depressed.

In a repeat run, a solution of 63.25 g. (0.25 mole) of dichlorodiphenylsilane, 125 ml. of THF, and 110 ml. of cyclohexene was added to an excess of lithium wire at room temperature. The rate of addition was maintained in such a manner that extensive cleavage of the intermediates did not occur. Seven hours after the complete addition cleavage started as evidenced by the evolution of heat and the formation of a yellow color. Stirring was continued for an additional 12 hr. The reaction mixture was then hydrolyzed with dilute sulfuric acid and worked up as described in the previous experiment. The yield of 2-cyclohexen-1-yl-diphenylsilane was 4.8% (3.2 g.), *n*²⁰_D 1.5910.

(B) *Purified Cyclohexene.* A solution of 96.0 g. (0.38 mole) of dichlorodiphenylsilane and 275 ml. of THF was added simultaneously with 125 ml. of cyclohexene to 5.7 g. (0.8 g.-atom) of lithium wire at room temperature. Following the complete addition (1 hr. required) cleavage of the intermediates (which consumed all of the lithium) was allowed to occur.

Subsequent to acid hydrolysis the reaction mixture was filtered to remove 23.9 g. (34.6%) of octaphenylcyclotetrasilane.²³ The silane was boiled in acetone and filtered hot, m.p. 316–320° (23.2 g.).

The organic layer was separated from the filtrate, concentrated, dried, and chromatographed on alumina to give 15.25 g. of crude decaphenylcyclopentasilane.²⁴ A crystallization from a benzene–petroleum ether (b.p. 60–70°) mixture gave 12.40 g. (18%) of product, m.p. 452–456°. A mixture melting point determination with an authentic sample was not depressed. Attempts to purify and identify other products of the reaction were unsuccessful.

(C) *Cyclohexene Containing 2-Cyclohexen-1-yl Hydroperoxide.* A solution of 25.3 g. (0.1 mole) of dichlorodiphenylsilane and 100 ml. of THF was added to an excess of lithium (1.8 g., 0.26 g.-atom) simultaneously with 50 ml. of cyclohexene containing 2 g. (0.018 mole) of 2-cyclohexen-1-yl hydroperoxide over a period of 1 hr. The reaction mixture was hydrolyzed with dilute sulfuric acid immediately after the complete addition.

The organic layer was separated from the aqueous layer, dried, concentrated, and treated with petroleum ether (b.p. 60–70°). Filtration afforded 2.2 g. of material melting over the range 169–172°. A crystallization from benzene narrowed the melting point to 171–173°. An infrared spectrum of the compound revealed the absence of aliphatic hydrogen. There were strong absorption bands (in μ) at 3.10, 8.9, and 8.99, indicative of a silanol containing diphenylsilylene units.

(23) H. Gilman, D. J. Peterson, A. W. Jarvie, and H. J. S. Winkler, *ibid.*, **82**, 2076 (1960).

(24) H. Gilman and G. L. Schwebke, *ibid.*, **86**, 2693 (1964).

A mixture melting point determination with diphenylsilanediol was not depressed.

The mother liquor was chromatographed on alumina. Petroleum ether (b.p. 60–70°) eluted 0.5 g. of a solid, melting over the range 180–186°. An infrared spectrum of this material had bands (in μ) at 3.28, 8.9, 8.99, and 9.50, indicative of a cyclic siloxane. No attempts were made to identify the compound. The petroleum ether fractions were combined, concentrated, and distilled under reduced pressure to give the following fractions: (1) 0.23 g., b.p. 110° (0.06 mm.), n_D^{20} 1.5907; (2) 0.75 g., b.p. 110–112° (0.06 mm.), n_D^{20} 1.5925. Infrared spectra of the two fractions were superimposable on the spectrum of an authentic sample of 2-cyclohexen-1-yl diphenylsilane.

Continued elution of the column with carbon tetrachloride and benzene produced polymeric oils that did not have infrared absorptions characteristic of aliphatic hydrogen.

(D) *Cyclopentene Containing 2-Cyclohexen-1-yl Hydroperoxide*. A solution of 25.3 g. (0.1 mole) of diphenyldichlorosilane, 80 ml. of THF, 40 ml. of cyclopentene, and 3.0 g. (0.027 mole) of 2-cyclohexen-1-yl hydroperoxide was added dropwise to 2.1 g. (0.3 g.-atom) of lithium wire. Subsequent to the addition, the reaction mixture was stirred for 0.3 hr., hydrolyzed with dilute acid, and worked up as described in the preceding experiment to give the following fractions: (1) 0.37 g., b.p. 90–107° (0.05 mm.), n_D^{20} 1.5854; (2) 0.57 g., b.p. 107–111° (0.05 mm.), n_D^{20} 1.5893; (3) 0.85 g., b.p. 111° (0.05 mm.), n_D^{20} 1.5903; (4) 0.42 g., b.p. 111–117° (0.05 mm.), n_D^{20} 1.5960. Fraction 1 is impure 2-cyclohexen-1-yl diphenylsilane. Fractions 2 and 3 are relatively pure product (17.4%). Fraction 4 appears to be a mixture of triphenylsilane and 2-cyclohexen-1-yl diphenylsilane, based on the refractive index and an infrared spectrum. No attempts were made to isolate any other product of the reaction.

(E) *Nonpurified Cyclohexene (Trimethyl Phosphate Derivatization)*. A solution of 25.3 g. (0.1 mole) of diphenyldichlorosilane, 75 ml. of THF, and 40 ml. of cyclohexene was added to an excess of lithium (2.1 g., 0.3 g.-atom) at a rate sufficient to maintain a rapid, exothermic reaction. Subsequent to the complete addition, stirring was continued for 0.5 hr. The reaction mixture was then treated with an excess of trimethyl phosphate (11.25 g., 0.08 mole) resulting in a negative Color Test I.²²

Work-up as described in experiment C afforded the following fractions: (1) 0.15 g., b.p. 95–110° (0.02 mm.), n_D^{20} 1.591; (2) 1.75 g., b.p. 110° (0.02 mm.), n_D^{20} 1.5974. Fraction 1 is pure 2-cyclohexen-1-yl diphenylsilane. Fraction 2 appears to be a mixture of 2-cyclohexen-1-yl diphenylsilane and triphenylsilane.

Continued elution of the column with carbon tetrachloride and benzene produced polymeric material that resisted work-up. Infrared spectra of two representative samples lacked absorption bands in the 3.38–3.50 μ region characteristic of the cyclohexenyl group.

(F) *Cyclopentene Containing 2-Cyclopenten-1-yl Hydroperoxide*. This reaction was conducted in the same manner as the preceding experiment: 50.6 g. (0.2 mole) of diphenyldichlorosilane, 120 ml. of THF, 0.043 mole of 2-cyclopenten-1-yl hydroperoxide, 85 ml. of cyclopentene, and 3.5 g. (0.5 g.-atom) of lithium were used.

The following distillation fractions were obtained: (1) 0.55 g., b.p. 100° (0.07 mm.), n_D^{20} 1.5824; (2) 1.15 g., b.p. 101° (0.07 mm.), n_D^{20} 1.5847; (3) 1.08 g., b.p. 101 (0.07 mm.), n_D^{20} 1.5846. Fraction 1 is impure 2-cyclopenten-1-yl diphenylsilane. Fractions 2 and 3 are pure product: an infrared spectrum of the compound was superimposable on that of an authentic sample. The total yield of product was 25.8%.

Treatment of 1.5 g. (0.006 mole) of 2-cyclopenten-1-yl diphenylsilane with a slight excess of phenyllithium gave 0.7 g. (36.7%) of 2-cyclopenten-1-yl triphenylsilane, m.p. 90–92°. A mixture melting point determination with an authentic sample was not depressed. Also, the infrared spectra were superimposable.

(G) *Cyclopentene Containing Cyclohexyl Hydroperoxide*. The cyclohexyl hydroperoxide was prepared according to the procedure described by Walling and Buckler,¹³ n_D^{25} 1.4644; lit.¹⁵ value n_D^{25} 1.4645.

A solution of 25.3 g. (0.1 mole) of diphenyldichlorosilane and 70 ml. of THF contained in an addition funnel was added simultaneously with 3.05 g. (0.026 mole) of cyclohexyl hydroperoxide in 30 ml. of cyclopentene in a second addition to 2.1 g. (0.3 g.-atom) of lithium over a period of 0.75 hr. Subsequent to the addition and 0.1 hr. of cleavage, the reaction mixture was hydrolyzed with dilute sulfuric acid and worked up in the usual manner. The oil obtained was chromatographed on alumina and the petroleum ether (b.p. 60–70°) eluates were combined, concentrated, and distilled under reduced pressure to give a trace of material, b.p. 110° (0.05 mm.), n_D^{20} 1.5721. An infrared spectrum of the material differed from the spectrum of cyclohexyldiphenylsilane. The infrared spectrum of the product had a strong absorption band at 9.30 μ characteristic of an Si–O–C linkage. The distillation residue was a polymer. Continued elution of the column with carbon tetrachloride and benzene also gave polymers.

(H) *Cyclohexene Containing Cyclopentyl Hydroperoxide*. This reaction was conducted in the same manner as the preceding experiment: 50.6 g. (0.2 mole) of diphenyldichlorosilane, 110 ml. of THF, 50 ml. of cyclohexene, 3.5 g. (0.5 g.-atom) of lithium, and 4.35 g. of 83% cyclopentyl hydroperoxide²⁵ were used.

There was obtained the following distillation fractions: (1) 0.3 g., b.p. 114° (0.08 mm.), n_D^{24} 1.5574; (2) 0.2 g., b.p. 114–121° (0.08 mm.), n_D^{24} 1.5565. The infrared spectra of these fractions differed from the spectrum of cyclopentyl diphenylsilane in the 9.55 μ region, indicative of an Si–O–C linkage in the former. Attempts to isolate crystalline compounds from the remainder of the reaction mixture were without success.

Preparation of 2-Cyclohexen-1-yl diphenylsilane. In Ether. A solution of 30 g. (0.186 mole) of 3-bromocyclohexene dissolved in 200 ml. of diethyl ether contained in an addition funnel was added simultaneously with 43.8 g. (0.20 mole) of diphenylchlorosilane dissolved in 50 ml. of the same solvent in a second addition funnel to an excess of magnesium (12 g., 0.5 g.-

(25) The cyclopentyl hydroperoxide was prepared by oxidation of cyclopentylmagnesium chloride.¹⁶ The peroxide content of the distilled product, b.p. 25° (0.2 mm.), was determined by iodometric analysis: J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 278.

atom). During the addition, the ether refluxed gently and a precipitate formed. Subsequent to the complete addition, the reaction mixture was allowed to warm to room temperature and was then hydrolyzed with dilute acid.

The organic layer was separated, dried, concentrated, and distilled under reduced pressure to give the following fractions: (1) 7.30 g., b.p. 130° (0.15 mm.), n^{20}_D 1.5904; (2) 7.65 g., b.p. 130–132° (0.15 mm.), n^{20}_D 1.5908; (3) 3.95 g., b.p. 132° (0.15 mm.), n^{20}_D 1.5888. The total yield of 2-cyclohexen-1-yl-diphenylsilane was 38.1%.

Anal. Calcd. for $C_{18}H_{20}Si$: C, 81.81; H, 7.57; Si, 10.62. Found: C, 81.85, 81.48; H, 7.91, 7.80; Si, 10.43, 10.57.

An n.m.r. spectrum of the compound supports the structure assignment: aromatic protons (10) 2.6, olefinic protons (2) 4.35, silane proton (1) 5.25 (doublet), and cycloaliphatic protons (7) 7.26–8.67.

In THF. The substitution of THF for ether in the preceding reaction resulted in a 58% yield of 2-cyclohexen-1-yl-diphenylsilane, b.p. 124–125° (0.15 mm.), n^{20}_D 1.5905.

Preparation of 2-Cyclohexen-1-yltriphenylsilane. To 6.85 g. (0.026 mole) of 2-cyclohexen-1-yl-diphenylsilane dissolved in diethyl ether was added a slight excess of phenyllithium at room temperature. Following the usual work-up, the solid obtained was crystallized twice from 1-propanol to give 6.74 g. (82.7%) of 2-cyclohexen-1-yltriphenylsilane, m.p. 130–132°. Infrared and nuclear magnetic resonance spectra are in accord with the assigned structure.

Anal. Calcd. for $C_{24}H_{24}Si$: C, 84.66; H, 7.10; Si, 8.24. Found: C, 84.49, 84.56; H, 7.03, 7.22; Si, 8.23, 8.29.

Preparation of 2-Cyclopenten-1-yl-diphenylsilane. A solution of 4.0 g. (0.027 mole) of freshly prepared 3-bromocyclopentene, 6.5 g. (0.03 mole) of diphenylchlorosilane, and 40 ml. of ether was added dropwise to 2.4 g. (0.1 g.-atom) of magnesium turnings. Following the complete addition, the reaction mixture was stirred at room temperature for 0.5 hr. and hydrolyzed with dilute acid. Subsequent to work-up, the oil obtained was distilled under reduced pressure to give 2.2 g. (32.6%) of 2-cyclopenten-1-yl-diphenylsilane, b.p. 111° (0.05 mm.), n^{20}_D 1.5880.

Anal. Calcd. for $C_{17}H_{18}Si$: Si, 11.2. Found: Si, 10.85, 10.90.

An n.m.r. spectrum of the compound supports the structure assignment: (in τ) aromatic protons (10) 2.6, olefinic protons (2) 4.33, silane proton (1) 5.25 (doublet), and cycloaliphatic protons (5.5) complex centered at 7.8.

Preparation of 2-Cyclopenten-1-yltriphenylsilane. Treatment of 1.45 g. (0.0034 mole) of 2-cyclopenten-1-yl-diphenylsilane with a slight excess of phenyllithium gave 1.1 g. (58.6%) of 2-cyclopenten-1-yltriphenylsilane, m.p. 91–93°, after a crystallization from ethanol.

Anal. Calcd. for $C_{23}H_{22}Si$: C, 84.66; H, 6.75. Found: C, 84.30, 84.58; H, 6.68, 6.74.

Reaction of Diphenyldichlorosilane, Lithium, and 2-Cyclohexen-1-ol. A solution of 2.8 g. (0.028 mole) of 2-cyclohexen-1-ol, n^{20}_D 1.4890, and 30 ml. of tetrahydrofuran in an addition funnel was added simultaneously

with 25.3 g. (0.1 mole) of diphenyldichlorosilane and 70 ml. of THF in a second addition funnel to an excess of lithium (2.8 g., 0.4 g.-atom) at a rate sufficient to maintain a very slight yellow color. Following the complete addition (0.5 hr. required), the reaction mixture was hydrolyzed with dilute acid and the organic layer was separated, concentrated, and chromatographed on alumina. The petroleum ether (b.p. 60–70°) eluates were combined and distilled under reduced pressure to give 0.65 g. of 2-cyclohexen-1-yl-diphenylsilane, b.p. 150–151° (0.15 mm.), n^{20}_D 1.5906, and 0.1 g. of impure product, b.p. 151–153° (0.15 mm.), n^{20}_D 1.5920. The infrared spectra of these fractions were superimposable on the spectrum of an authentic sample. The total yield of the silane was 10%. Continued work-up of the reaction residue afforded no crystalline products.

Reaction of Allyl Alcohol, Diphenyldichlorosilane, and Lithium. A solution of 25.3 g. (0.1 mole) of diphenyldichlorosilane and 70 ml. of tetrahydrofuran (THF) contained in an addition funnel was added simultaneously with 2.90 g. (0.05 mole) of allyl alcohol dissolved in 30 ml. of THF in a second addition funnel to 2.1 g. (0.3 g.-atom) of lithium at a rate sufficient to maintain a slight yellow color in the reaction mixture.

Subsequent to the complete addition, the reaction mixture was stirred until an intense yellow color developed. The mixture was then hydrolyzed with dilute acid and worked up as described in the preceding reaction to give 0.6 g. (5.4%) of allyldiphenylsilane, b.p. 76–78° (0.06 mm.), n^{20}_D 1.5745; lit.²⁶ n^{20}_D 1.5745. An infrared spectrum of the compound was superimposable on that of an authentic sample. No attempt was made to work up the remainder of the reaction mixture.

A repeat of the above reaction employing 38 g. (0.15 mole) of diphenyldichlorosilane in 80 ml. of THF, 5.8 g. (0.1 mole) of allyl alcohol in 40 ml. of THF, and 2.8 g. (0.4 g.-atom) of lithium gave 2.1 g. (9.4%) of allyldiphenylsilane, b.p. 83–87° (0.15 mm.), n^{20}_D 1.5750.

Reaction of Allyloxytriphenylsilane with Triphenylsilyllithium. A solution of 0.03 mole of triphenylsilyllithium and 30 ml. of tetrahydrofuran was added to 6 g. (0.02 mole) of allyloxytriphenylsilane dissolved in 30 ml. of THF. Subsequent to 4 hr. of stirring, the reaction mixture was hydrolyzed with dilute acid and filtered to remove 6.3 g. (60.8%) of hexaphenyldisilane, m.p. 355–358°. The organic layer was concentrated and treated with petroleum ether (b.p. 60–70°). On standing, 1.45 g. of triphenylsilanol melting over the range 150–155° crystallized and was removed by filtration. A recrystallization from a benzene-petroleum ether (b.p. 60–70°) mixture gave 1.32 g. of product, m.m.p. 150–152°.

The remaining oil was dissolved in ethanol and, on standing, 0.1 g. (1.7%) of allyltriphenylsilane²⁶ crystallized, m.m.p. 86–88°.

Reaction of Allyloxytriphenylsilane with Lithium in Tetrahydrofuran. A solution of 3.2 g. (0.01 mole) of allyloxytriphenylsilane in 40 ml. of tetrahydrofuran was slowly added to an excess of lithium. An immediate reaction occurred as evidenced by the evolution of heat

(26) H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959).

and the formation of a yellow color. Subsequent to 1 hr. of stirring, the black solution was added to 3 g. (0.01 mole) of chlorotriphenylsilane dissolved in 30 ml. of THF.

The reaction mixture was then hydrolyzed with dilute acid and filtered. The filtrate was concentrated and treated with petroleum ether (b.p. 60–70°). On standing 2.2 g. of crude triphenylsilanol crystallized and was removed by filtration. The mother liquor was then chromatographed on alumina. Petroleum

ether (b.p. 60–70°) eluted 0.5 g. of crude allyltriphenylsilane.²⁶ A recrystallization from the same solvent gave 0.4 g. (13.3%) of product, m.m.p. 84–86°.

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Nitrous Acid Deamination of *cis*- and *trans*-2-Hydroxycyclooctylamines^{1,2}

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Deaminations of cis- and trans-2-hydroxycyclooctylamines in aqueous acetic acid have been found to be completely different from the related reactions of cyclooctene oxides and glycols. The amino alcohols react to form cyclooctanone and cycloheptanecarboxaldehyde as major products. Transannular processes, which dominate reactions of cyclooctene oxides and glycols, account for less than 4% of the products from the amino alcohols. Alternate descriptions of reaction mechanisms are discussed, but the available data do not dictate an unequivocal choice.

The report³ that the oxide, glycol, halohydrin, and amino alcohol derivatives of tetramethylethylene all give equivalent proportions of glycol (substitution) and ketone (rearrangement) products has led to the claim that "the accepted mechanism for pinacolic transformation involves the prior formation of a carbonium ion intermediate."⁴ When the leaving group is attached to a tertiary carbon, this path appears to be well established. However studies of pinacolic transformations with compounds in which the leaving group is attached to a secondary carbon are far less extensive, and descriptions of reaction mechanism are considerably less certain. A recent paper from this research group described a study of some medium ring cycloalkene glycols, and the suggestion was made that, at least in some cases, acid-catalyzed rearrangements of these glycols may not involve carbonium ion mechanisms.⁵ The present paper is a continuation of our investigation of rearrangements of 2-substituted

cycloalkanols⁶ and describes nitrous acid deaminations of *cis*- and *trans*-2-hydroxycyclooctylamines. The data to be described lead us to the conclusion that either these deaminations do not involve carbonium ions or carbonium ions from different, but related, sources behave totally differently from each other.

Nitrous acid deaminations of primary amines have been extensively investigated.⁶ In some systems rearrangements quite similar to those characteristic of solvolyses occur during deamination,^{6,6i} while in others substantial differences in stereochemistry^{6e} and/or proportions of the same products^{6f,k,7a} have been reported. Both solvolytic and deamination reactions have often been described as carbonium ion processes, with differences in composition of product mixtures from different (related) reactants usually being ascribed to energetic differences in the ions formed by the two kinds of reaction.^{6f,j,l,o} The cation left by exothermic loss of nitrogen from a diazonium ion has been described as a "hot" carbonium ion which may react differently from a "normal" solvolytic carbonium ion. On occasion, direct displacement on the diazonium cation has been preferred over "hot"

(6) Some selected recent references particularly pertinent to the present discussion are: (a) V. Prelog, H. J. Urech, A. A. Bothner-By, and J. Würsch, *Helv. Chim. Acta*, **38**, 1095 (1955); (b) A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957); (c) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.*, **79**, 6160 (1957) [footnote 9 of this paper provides a succinct summary, with references, of some data pertaining to carbonium ions in deaminations]; (d) C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, **81**, 466 (1959); (e) J. A. Berson and B. A. Ben-Efraim, *ibid.*, **81**, 4094 (1959); (f) M. S. Silver, *ibid.*, **83**, 3482, 3487 (1961); (g) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); (h) J. Meinwald, P. G. Gassman, and J. J. Hurst, *ibid.*, **84**, 3722 (1962); (i) P. Warrick, Jr., and W. H. Saunders, Jr., *ibid.*, **84**, 4095 (1962); (j) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963); (k) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963); (l) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963); (m) W. Hüchel and L. Heyder, *Ber.*, **96**, 220 (1963); (n) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **86**, 1749 (1964); (o) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **86**, 1994 (1964); (p) T. Cohen and E. Jankowski, *ibid.*, **86**, 4217 (1964).

(7) (a) D. Y. Curtin and M. C. Crew, *ibid.*, **76**, 3719 (1954); (b) D. J. Cram and J. E. McCarthy, *ibid.*, **79**, 2866 (1957); (c) see, for example, D. Y. Curtin and M. C. Crew, *ibid.*, **77**, 354 (1955), and A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 866 (1957).

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(2) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(3) Y. Pocker, *Chem. Ind.* (London), 332 (1959).

(4) Y. Pocker in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., Division of John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 1.

(5) J. G. Traynham and P. M. Greene, *J. Am. Chem. Soc.*, **86**, 2657 (1964).