was prepared by the method of Scarbourgh.[22] Its purity by mass spectroscopy was 86% d_3 and 14% d_2. The corresponding hexadeuterated diphenylmercurial was prepared by the reaction of the Grignard reagent made from the bromide with anhydrous mercuric chloride. Reaction of the deuterated diphenylmercury with a slight excess of trimethylvinylsilane in methanol solvent in the presence of a catalytic amount of anhydrous palladium chloride and a stoichiometric amount of cupric chloride to affect the reoxidation of the palladium overnight at room temperature led to a 10% yield of the desired compound. This procedure is basically that of Heck, applied to trimethylvinylsilane.[23,24] Surprisingly only the trans olefin was obtained. The compound was purified for mass spectral study by gc on a 3 m × 0.25 in. SE-30 column at 160°. The deuterated β-(trimthylsilyl)styrene obtained had the following isotopic purity: 86% d_3 and 14% d_2 by mass spectroscopy.

Registry No.—1-(Trimethylsilyl)-3-phenylpropane, 775-24-6; 1,1-dideuterio-1-(trimethylsilyl)-3-phenylpropane, 28901-25-9; 1-deuterio-1-phenyl-3-(trimethylsilyl)propane, 28901-26-0; 1-phenyl-4-(trimethylsilyl)-butane, 777-82-2; 1-(trimethylsilyl)-2-phenylethane, 772-64-5; β-(trimethylsilyl)styrene, 18001-47-3; 1-phenyl-2-deuterio-2-(trimethylsilyl)ethylene, 28901-30-6; 1-phenyl-1-deuterio-2-(trimethylsilyl)ethylene, 28901-31-7; 1-pentadeuteriophenyl-2-(trimethylsilyl)-ethylene, 28901-32-8; 1-(2′,4′,6′-trideuteriophenyl)-2-(trimethylsilyl)ethylene, 28901-33-9; 2-(trimethylsilyl)-phenylacetylene, 2170-06-1; 1-bromo-1-phenyl-3-(trimethylsilyl)propane, 28841-13-6.

Acknowledgments.—We wish to acknowledge a National Science Foundation grant for purchase of the Hitachi RMU-6 mass spectrometer. This research was partially supported by the Caltech President's Fund and NASA Contract NAS 7-100.

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[22] J. M. Scarbourgh, U. S. Atomic Energy Commission, NAA-SR-2144 (1957); *Chem. Abstr.*, **52**, 9042*d* (1958).

[23] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5538 (1968).

[24] R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, *Chem. Commun.*, 1293 (1970).

The Reaction of 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene with Diphenylacetylene, 2,3-Dimethyl-1,3-butadiene, and Benzyne[1]

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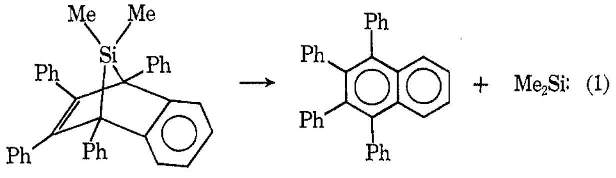
Received October 28, 1970

Diphenylacetylene reacts with 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (4) to give an isolable 1:1 adduct. Upon pyrolysis in a sealed tube, the adduct not only undergoes dimethylsilylene elimination as has been reported for 7-silanorbornadienes but also disassociates to reactants. When heated under high vacuum or when placed in solution, the adduct again disassociates to reactants. The title silacyclopentadiene reacts with 2,3-dimethyl-1,3-butadiene to give 1,8-diphenyl-3,4,9,9-tetramethyl-9-silabicyclo[4.3.0]nona-3,7-diene (6). In this reaction silacyclopentadiene **4** reacts as the dienophile and butadiene as the diene.

Recently, considerable work has been reported on the generation and reaction of several analogs of carbenes.[2-6] As a follow-up of some of this work, an investigation of the reaction of organosilylenes, $R_2Si:$, with a number of compounds was undertaken. This is not only an effort to help characterize these reactive intermediates but is also an effort to prepare compounds which have eluded preparation by other means.

There appears in the literature three distinctly different ways of generating organosilylenes.[2] The first reported was the reaction of an active metal with a dihalodiorganosilane. The other two methods involve the pyrolysis of either a peralkylated polysilane[2] or methoxypolysilanes[5] or the pyrolysis of a 7-silanorbornadiene.[3] The last method has been adopted for this study because it appears to give the silylene intermediate employing the least drastic conditions and also has the least reactive by-products being formed. This last consideration is very important as the coreactants under consideration in the above mentioned investigation are quite reactive with a number of compounds.

Rather than use 2:3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (**1**)[3] or 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene (**2**)[3] as the precursor to dimethylsilylene (eq 1 and 2), the decision



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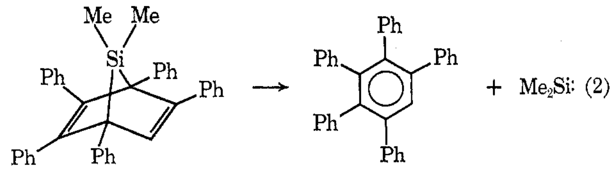

2

was made to prepare yet another one of these compounds to aid in determining the generality of this method of generation of silylenes as well as to try to obtain a 7-silanorbornadiene which is less stable toward dimethylsilylene elimination than **1** and **2**. The 7-silanorbornadienes are prepared by the Diels-Alder reaction of a silacyclopentadiene with an acetylene. For this investigation it was decided to try to prepare 7,7-dimethyl-1,2,3,4-tetraphenyl-7-silanorbornadiene (**3**) by the reaction (eq 3) of 1,1-dimethyl-2,5-diphenyl-1-

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[1] Presented in part at the 2nd Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 4, 1970.

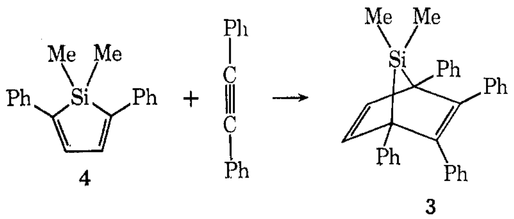
[2] O. M. Nefedov and M. N. Manakov, *Angew. Chem. Int. Ed. Engl.*, **5**, 1021 (1966).

[3] H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Amer. Chem. Soc.*, **86**, 1596 (1964).

[4] M. E. Vol'pin, *J. Organometal. Chem.*, **8**, 87 (1967).

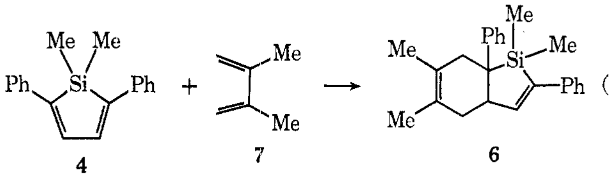
[5] W. H. Atwell and D. R. Weyenberg, *J. Amer. Chem. Soc.*, **90**, 3438 (1968).

[6] P. L. Timms, *Endeavour*, **27**, 133 (1968).



(3)

silacyclopentadiene (4)[7] with diphenylacetylene (tolan). When silacyclopentadiene **4** was reacted with tolan, a good yield of a 1:1 adduct was obtained as a yellow solid. However, this adduct (**5**) not only eliminates dimethylsilylene as well as any 7-silanorbornadiene reported but also undergoes a disassociation reaction. The acetylenic product from the disassociation is reactive with the coreactants of interest to us, thus eliminating **5** from consideration as a precursor for organosilylenes in this study. Besides the preparation and reactions of the 1:1 adduct, the reaction of silacyclopentadiene **4** with other unsaturated compounds was investigated and the results of these reactions are discussed. In particular, 1,8-diphenyl-3,4,9,9-tetramethyl-9-silabicyclo[4.3.0]nona-3,7-diene (**6**) is formed by the reaction of **4** as a dienophile with 2,3-dimethyl-1,3-butadiene (**7**) as the diene (eq 4).



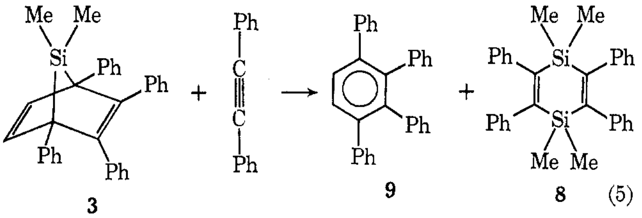
(4)

Results and Discussion

That the reaction of 1,1-dimethyl-2,5-diphenylsilacyclopentadiene with tolan gives a product with a 1:1 stoichiometry has been shown in many ways. All the physical data given for this product are exactly reproducible when determined on samples prepared under different conditions. Using the procedure given in the Experimental Section, preparations were carried out where the molar ratio of silacyclopentadiene to tolan was varied from about 1.5 to 0.5. The same product was received when this reaction was carried out in diglyme solution at 168° or in THF at 68° or when purification was accomplished by recrystallization from petroleum ether (bp 60–90°) hexane or by repeated recrystallization from either of these solvents. The elemental analyses are also in complete agreement with a 1:1 molar ratio of reactants in the product. The real question to be answered, then, concerns the exact nature of the product. That is, is the product a 1:1 solid state complex of some sort or is it a compound having the structure of 7-silanorbornadiene **3**?

The infrared spectrum and melting point of the above 1:1 adduct were determined on solid samples and both are consistent with those expected for a compound or a stable adduct. However, all the rest of the physical data, which were determined on samples of the material in solution or in the gas phase, do not necessarily support this conclusion. In particular, the observed molecular weight is almost exactly half that expected for a stable 1:1 adduct. This is good evidence that there are twice as many species in solution as expected; yet, when the solvent is removed, adduct **5** is recovered unchanged. This and, indeed, all the rest of the physical data taken on solutions are identical with those expected for a 1:1 molar mixture of silacyclopentadiene **4** and tolan, indicating that **5** is a 1:1 solid state complex which dissociates in solution.

A look at some of the chemical reactions of this 1:1 adduct does shed some additional light on its nature. The copyrolysis of it with tolan gives the products expected for 7-silanorbornadiene **3** (eq 5) by analogy to

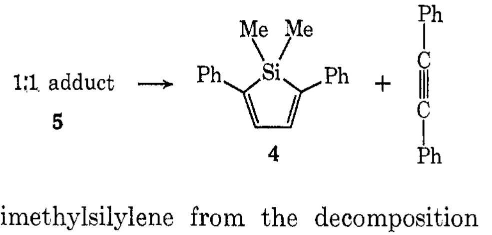


(5)

similar reactions for other 7-silanorbornadienes (eq 1 and 2). In fact, the yield of 1,1,4,4-tetramethyl-2,3,5,6 tetraphenyl-1,4-disilacyclohexa-2,5-diene (**8**) is as good as that reported for the copyrolysis of other 7,7-dimethyl-7-silanorbornadienes with tolan.[3] The formation of **8** does indicate that adduct **5** is either 7-silanorbornadiene **3** or that, under pyrolytic conditions, it goes to **3** at least as an unstable intermediate. This conclusion is further substantiated by the formation of 1,2,3,4-tetraphenylbenzene (**9**) in a good yield, since substituted naphthalenes and benzenes have been shown to be by-products when 7-silanorbornadienes are pyrolyzed to give dimethylsilylene[3] (eq 1 and 2).

The exact nature of adduct **5** at high temperatures is given by mass spectrometry and the pyrolytic reactions other than the one discussed above. In fact, the mass spectrum and high vacuum pyrolytic decomposition reactions of **5** show that it also undergoes disassociation in the gas phase.

The pyrolysis of the 1:1 adduct by itself in a sealed tube gives mainly disilacyclohexadiene **8** and tetraphenylbenzene. The formation of **8** indicates that some of the 1:1 adduct disassociates to give silacyclopentadiene **4** and tolan (eq 6). The tolan then reacts



(6)

with dimethylsilylene from the decomposition of 7-silanorbornadiene **3** to give disilacyclohexadiene **8** (eq 7 and 8). The tetraphenylbenzene is formed as a by-product of the elimination of dimethylsilylene from 7-silanorbornadiene **3** (eq 7). The copyrolysis of the 1:1 adduct with butadiene **7** to give silacyclopentadiene **4**, disilacyclohexadiene **8**, tetraphenylbenzene **9**, silabicyclononadiene **6**, and 1,1,3,4-tetramethyl-1-silacyclopent-3-ene (**10**) further indicates that adduct **5** disassociates and also forms 7-silanorbornadiene **3** in a sealed tube at 300°. The main products which are

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[7] W. H. Atwell, D. R. Weyenberg, and H. Gilman, *J. Org. Chem.*, **32**, 885 (1967).

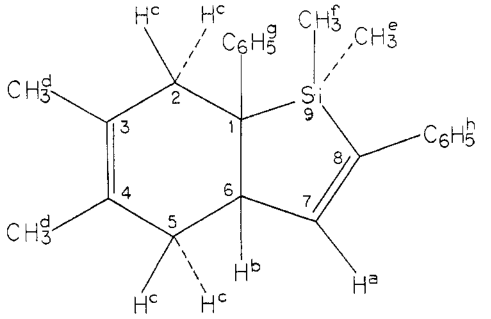
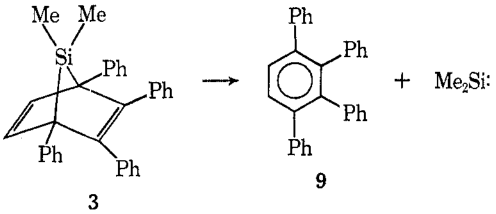
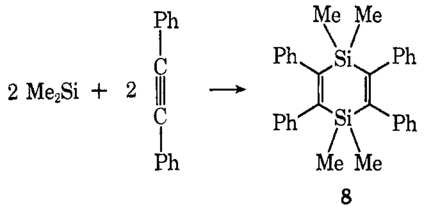


Figure 1.—1,8-Diphenyl-3,4,9,9-tetramethyl-9-silabicyclo[4.3.0]-nona-3,7-diene (6).

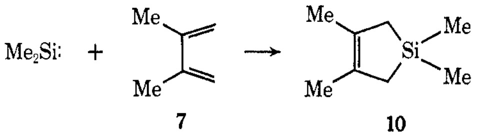


(7)



(8)

formed in this pyrolysis can be explained by the simultaneous occurrence of reactions given by eq 6–9 and 4.



(9)

The reaction of 2,3-dimethyl-1,3-butadiene with dimethylsilylene[5] (eq 9) has been reported and the reaction of 1,1-dimethyl-2,5-diphenylsilacyclopentadiene with 2,3-dimethyl-1,3-butadiene (eq 4) will be discussed below.

Although the structure of the 1:1 adduct of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with tolan in the solid state cannot be determined from the data collected during this investigation, it certainly appears to be a very interesting material. If it is 7-silanorbornadiene 3, it is very unstable with respect to a retro-Diels–Alder reaction. If it is not a 7-silanorbornadiene, but some other type of adduct, to the best of our knowledge it is the only reported example of a stable adduct between an alkyne and a silane. Speculation about the possible bonding in this adduct will be resisted since an X-ray structural determination will be necessary to prove the structure and such an investigation is underway.[8] However, data obtained during this investigation does show that adduct 5 dissociates to a 1:1 molar mixture of silacyclopentadiene 4 and tolan in solution and in the gas phase at low pressure. In a sealed tube at high temperature where both gas and liquid phase are present, the 1:1 adduct exists as a complex mixture of silacyclopentadiene 4, tolan, and 7-silanorbornadiene 3.

The reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with 2,3-dimethyl-1,3-butadiene to give silabicyclononadiene 6 is rather surprising because, to give this product, silacyclopentadiene 4 is reacting as a dienophile and butadiene 7 as diene. In fact, this reaction proceeds very well at 200° to give a 62% yield of 6. The assignment of the 9-silabicyclo[4.3.0]nonadiene structure to 6 was made mainly from ^1H nmr and mass spectral data.

The mass spectrum of silabicyclononadiene 6 has large peaks at m/e 91, 105, 121, 135, and 145. Most of these peaks are found to be major ones in the spectra of organosilicon compounds which have two phenyl groups α and α' to a dimethylsilicon functional group.[9] An assignment of the ^1H nmr is given below using the lettering system in Figure 1.

The phenyl protons H^g and H^h, having a total relative intensity of 10, give rise to the multiplet at τ 2.80. This multiplet appears to be made up of two separate resonances separated by about 2 cps. The multiplet observed at τ 3.29 and having a relative intensity of 1 H is assigned to the olefinic proton H^a. This olefinic proton falls τ 0.6 upfield from those in 4 which fall under the aromatic resonances. The resonance assigned to H^a is, however, about where one would expect to find it for an olefinic proton on a small-ring olefinic compound.[10] The multiplet at τ 6.51 has a relative intensity of 1 H and is assigned to the remaining methine proton H^b. The very broad, 60-cps, ill-defined multiplet centered about τ 7.85 has been assigned to the four methylene protons H^c. The resonances due to these protons would be expected to be ill-defined since two of them are unequally shielded by the phenyl ring at the 1 position and the other two are unequally coupled to proton H^b. The singlet at τ 8.39 having a relative intensity of 6 H is exactly where expected for olefinic methyl protons[10] and this singlet is assigned to H^d. The remaining two singlets at τ 9.61 and 10.07 have relative intensities of 3 H each and are assigned to H^e and H^f, respectively. The H^f protons would be expected to fall at a higher field than H^e since the former are on the same side of the five-membered ring as the phenyl group at the 1 position and a model shows that these protons lie in the shielding zone of the phenyl group.[11] The 9-silabicyclononadiene structure given for 6 is indeed consistent with the data available.

The product of the reaction of silacyclopentadiene 4 as the diene with 2,3-dimethyl-1,3-butadiene as the dienophile would have structure 11. It is easy to see that this structure does not fit the observed ^1H spectrum since the ten types of protons in structure 11 should give a ^1H spectrum with distinct resonances having relative intensities of 10:2:2:2:3:3:3:3 as you go from low field to high field. The observed spectrum has relative intensities of 10:1:1:4:6:3:3. The product from the

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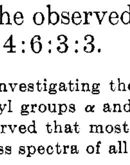
[8] T. J. Barton, personal communication.

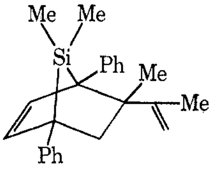
[9] During the course of investigating the properties of several organosilicon compounds with phenyl groups α and α' to a dimethylsilicon group (see structure a), it was observed that most or all of the above peaks were major contributors to the mass spectra of all these compounds.



a

[10] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 138.

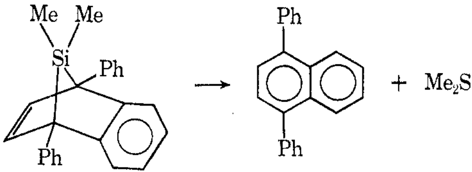
[11] The model was constructed from CPK space filling models and the stereochemistry assumed was that expected for maximum overlap of unsaturation in the transition state for the Diels–Alder reaction.



11

Diels–Alder reaction of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene with 2,3-dimethyl-1,3-butadiene is thus concluded to be the silabicyclononadiene **6**.

The attempted synthesis of 2:3-benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (**12**) appears to shed some light on the decomposition of other 7-silanorbornadienes. In an attempt to prepare 7-silanorbornadiene **12** by the procedure used to prepare **1**,[3] the products isolated and identified were diphenylnaphthalene **13** and a siloxepinone.[12] The substituted naphthalene **13** is the expected product for the elimination of dimethylsilylene from 7-silanorbornadiene **12** according to eq 10. It appears, then, that **12** is not stable and eliminates dimethylsilylene under preparative conditions were a maximum temperature of 68° was encountered. This is somewhat surprising since 7-silanorbornadienes **1** and **2** must be heated to between 200 and 300° to effect dimethylsilylene elimination. One explanation for this is that the four adjacent phenyl groups in **1** and the five adjacent ones in **2** give these compounds large activation energies for elimination of dimethylsilylene. This would be expected if the activated complex for elimination has a planar structure similar to the structure of the products, since a planar activated complex would force the four or five adjacent phenyl groups very close together. However, 7-silanorbornadiene **12** has isolated phenyl groups and can attain a planar structure more easily, giving a lower activation energy and a more facile elimination of dimethylsilylene.



(10)

12 13

From the data given here it is apparent that the Diels–Alder behavior of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (**4**) is quite varied. It readily undergoes a reaction with tolan to give a 1:1 adduct which can go to 7-silanorbornadiene **3** or dissociate to give silacyclopentadiene **4** and tolan back again. With benzyne as dienophile, 7-silanorbornadiene **12** is formed but is so unstable that it readily eliminates dimethylsilylene to give the substituted naphthalene **13**. The reaction of **4** with butadiene **7** indicates that **4** can also react as a dienophile. Further studies of Diels–Alder reactions of silacyclopentadienes and the nature of the products formed in these reactions are now underway.

Experimental Section

Instrumentation.—Infrared spectra were recorded using a Perkin-Elmer Model 237b Infracord and were standardized against polyethylene. The peaks are reported in reciprocal centimenters with S = strong, M = medium, and W = weak absorbances. Melting points were obtained on a Thomas-Hoover melting point apparatus and are reported uncorrected. The ultraviolet spectra were determined using a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Jeolco C-60H spectrometer using dichloromethane as the primary reference. The chemical shifts reported are relative to tetramethylsilane and have been corrected for solvent effects to the primary reference signal.

The mass spectra were obtained using a Hitachi RMU-6H mass spectrometer. Only the parent peak, base peak, and other important peaks are reported here. A detailed examination of the mass spectra of these organosilicon compounds will be published elsewhere. Elemental analysis of the compounds was done by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

Materials.—Dichlorodimethylsilane (Matheson), diphenylacetylene (Aldrich), styrene (Matheson), 2,3-dimethyl-1,3-butadiene (Aldrich), petroleum ether (bp 60–90°) (Matheson), and hexane (Matheson) were used without further purification. All other solvents were dried over lithium aluminum hydride, barium oxide, or phosphorus pentoxide and distilled before use.

Preparation of 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentane (14).—This compound was prepared by a previously reported procedure.[10] Vacuum distillation of the reaction mixture at 0.25 Torr gave a 65% yield of silacyclopentane **14** and a dark brown sticky, oily residue. After purification of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane by a triple vacuum distillation, the following physical data were determined: bp 120–130° (0.25 Torr) [lit.[13] 137–150° (0.3–0.4 Torr)]; $n^{25}\text{D}$ 1.5759 (lit.[13] 1.5740); ^{1}H nmr (60 MHz, CCl_4) three singlets at τ 10.37, 9.90, and 9.47 (total 6 H), 7.50 (m, 6 H), 2.70 (m, 10 H); mass spectrum (80 eV) *m/e* (rel intensity) 266 (75) P, 117 (100); uv max (cyclohexane) 230 nm (ϵ 25,000), 254 (940), 269 (1000), 277 (720); ir 3106 (W), 3086 (W), 3040 (M), 2941 (M), 2865 (M), 1942 (W), 1866 (W), 1799 (W), 1733 (W), 1600 (S), 1580 (W), 1493 (S), 1449 (M), 1406 (W), 1348 (W), 1300 (W), 1248 (S), 1208 (M), 1152 (W), 1109 (W), 1092 (M), 1073 (M), 1031 (M), 1000 (W), 971 (W), 945 (W), 901 (M), 849 (S), 826 (S), 794 (S), 776 (S), 758 (S), 746 (S), 698 (VS).

Preparation of 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene (4).—Silacyclopentadiene **4** was prepared by bromination of silacyclopentane **14** with *n*-bromosuccinimide followed by dehydrobromination using sodium acetate as described previously.[7] After addition of the dehydrobromination reaction product mixture to twice its own volume of a 50:50 ethanol–water mixture, an 82% yield of silacyclopentadiene **4** was isolated by filtration. Purification of this silacyclopentadiene **4** by recrystallization from acetone yielded a material which gave the following physical data: mp 133–134° (lit.[7] 130–133°); ^{1}H nmr (60 MHz, CCl_4) τ 9.44 (s, 6 H), 2.68 (m, 12 H); mass spectrum (80 eV) *m/e* (rel intensity) 262 (100) P; uv max (cyclohexane) 229 nm (ϵ 13,200), 375 (20,000) [lit.[6] 230 (13,000), 370 (20,000)]; ir (KBr pellet) 3058 (W), 3040 (W), 2976 (W), 2907 (W), 1949 (W), 1873 (W), 1739 (W), 1590 (S), 1572 (M), 1488 (S), 1441 (S), 1410 (W), 1321 (M), 1299 (W), 1276 (W), 1259 (W), 1244 (S), 1155 (W), 1100 (W), 1073 (M), 1028 (M), 979 (W), 929 (S), 868 (S), 847 (W), 831 (S), 791 (S), 773 (VS), 749 (S), 691 (S), 638 (M).

Anal. Calcd for $C_{18}H_{18}Si$: C, 82.5; H, 6.88; Si, 10.7. Found: C, 82.6; H, 6.85; Si, 10.5.

Preparation of the 1:1 Adduct of 1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene with Tolan (5).—In a typical preparation of adduct **5**, 0.78 g (3.0 mmol) of silacyclopentadiene **4** and 0.79 g (4.4 mmol) of tolan were dissolved in 60–90° boiling petroleum ether and, upon cooling, 0.78 g (1.8 mmol) of crystalline adduct **5** was isolated by filtration and was purified by recrystallization from the same solvent. Material prepared and purified by this procedure gave the following physical data: mp 101–102°; ^{1}H nmr (60 MHz, CCl_4) τ 9.31 (s, 3 H), 2.69 (m, 11 H); mass

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[12] T. J. Barton, A. J. Nelson, J. Clardy, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14, 1970, or *Chem. Eng. News*, **48**, 36 (1970). This recent preliminary report indicates that **12** can be formed at low temperatures, but that it decomposes, according to eq 10, below room temperature, thus substantiating the conclusions drawn here. However, when the preparation of **12** was carried out by Dr. Barton using a method different from ours, it underwent further reaction with the benzyne intermediate to give a siloxepinone. After Barton's report appeared, we were also able to identify this siloxepinone as a product of our reaction.

[13] D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Org. Chem.*, **30**, 4096 (1965).

spectrum (80 eV) *m/e* (rel intensity) 262 (100), no parent peak was observed; uv max (cyclohexane) 265 nm (ϵ 22,200), 273 (22,800), 281 (30,000), 289 (20,500), 298 (26,600), 375 (19,000); ir (KBr pellet) 3067 (W), 3040 (W), 2976 (W), 1961 (W), 1890 (W), 1602 (W), 1590 (W), 1570 (M), 1497 (M), 1490 (S), 1445 (S), 1406 (W), 1319 (M), 1274 (W), 1250 (S), 1182 (W), 1179 (W), 1161 (W), 1100 (W), 1073 (M), 1022 (M), 997 (W), 988 (W), 927 (M), 917 (W), 908 (W), 868 (S), 850 (W), 833 (S), 792 (M), 776 (VS), 756 (VS), 746 (S), 692 (S), 686 (S), 633 (M).

Anal. Calcd for $C_{32}H_{28}Si$: C, 87.3; H, 6.37; Si, 6.37. Found: C, 87.2; H, 6.43; Si, 6.49; mol wt (benzene solution, 42°, by vapor pressure osmometry), 229.

Pyrolysis of Adduct 5 in the Presence of Tolan.—A 0.97-g (2.3 mmol) sample of **5** and 1.11 g (6.2 mmol) of tolan were sealed, under vacuum, in a pyrex tube and then pyrolyzed at 300° for 16 hr. The tube was opened and the pyrolysis residue dissolved in hot benzene. Then petroleum ether (bp 60–90°) was added to the benzene solution, at reflux, until precipitation occurred. A white polymeric material, 0.24 g, was collected by filtration after the solution had been cooled to 0°. The solvent was removed from the filtrate and the residue thus received was fractionally recrystallized from petroleum ether to give 0.27 g (51%) of disilacyclohexadiene **8** and 0.75 g (87%) of tetraphenylbenzene **9**.

When 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disila-2,5-cyclohexadiene (**8**) was purified by sublimation at 140° under high vacuum (10^{-6} Torr), it gave the following physical data: mp 315 ± 5° (lit.[3] 323–326°); ^{1}H nmr (60 MHz, CS_2) τ 3.15 (m, 20 H), 9.92 (s, 12 H); mass spectrum (80 eV) *m/e* (rel intensity) 472 (36) P, 73 (100); uv (cyclohexane) no distinct max, just an increasing absorption from 300 to 220 nm; ir (KBr pellet) 3086 (W), 3030 (W), 2976 (W), 1946 (W), 1872 (W), 1801 (W), 1597 (W), 1575 (W), 1481 (M), 1439 (M), 1414 (W), 1326 (W), 1250 (S), 1242 (S), 1185 (W), 1156 (W), 1070 (M), 1029 (W), 996 (M), 911 (W), 883 (S), 834 (S), 797 (M), 769 (S), 752 (S), 721 (M), 696 (VS), 662 (S).

Anal. Calcd for $C_{32}H_{32}Si_2$: C, 81.3; H, 6.78; Si, 11.9. Found: C, 81.4; H, 6.78; Si, 11.7.

Pyrolysis of Adduct 5 in a Sealed Tube.—A 0.50-g sample of **5** was sealed, under vacuum, in a 50-ml pyrex tube and pyrolyzed at 300° for 24 hr. The tube was cooled and opened, and the solid product mixture was fractionally recrystallized from petroleum ether (bp 90–120°). The first fraction of crystals, which were insoluble in hot 90–120° petroleum ether, was identified, by comparison of its properties with those of an authentic sample, as 1,4-disilacyclohexadiene **8**. This fraction amounted to an estimated 10% yield. Then several fractions of tetraphenylbenzene **9** were recovered and identified as such by melting point,[14] mass spectral, infrared, nuclear magnetic resonance, and elemental analysis. After recovery of as much **9** as possible, the petroleum ether filtrate was red brown and appeared to be similar to the dimethylsilicon polymer solutions described previously.[3]

Pyrolysis of Adduct 5 under High Vacuum. Method A.—A piece of pyrex tubing 60 cm long and 25 mm in diameter was sealed on one end and affixed with a joint at the other. The sealed end of the tube was charged with 0.85 g of **5** and the tube placed in a 30-cm horizontal tube furnace, such that the sealed end with sample was outside the oven. The tube was connected to the high vacuum system, evacuated to 10^{-6} Torr and the oven heated to 200°. After the temperature had reached equilibrium, the furnace was slowly moved toward the sample until, after 48 hr, the sample was just inside the open end of the furnace where the temperature was 50–70°. At this time, the pyrolysis was stopped and three bands of crystals were observed in the tube. The first band, 0.47 g, was where starting sample had been placed and was identified as an approximately 1:1 mixture of silacyclopentadiene **4** and adduct **5** by comparison of its ir with that of a known 1:1 mixture. The second band, 0.17 g, was just outside the exit end of the furnace and was identified as 1:1 adduct **5**. The third band, 0.17 g, was about 20 cm from the exit end of the furnace and was identified as tolan.

Method B.—A sublimator was charged with about 1 g of adduct **5** and heated to 50° under high vacuum. After 24 hr under these conditions, the sublimator was opened, the sublimate was shown to be tolan, and the residue was identified as pure silacyclopentadiene **4**.

Pyrolysis of Adduct 5 in the Presence of 2,3-Dimethyl-1,3-butadiene 7.—A 100-ml pyrex bomb fitted with a break tip seal was charged with 0.72 g (1.63 mmol) of **5** and 0.37 g (4.5 mmol) of **7**. The tube was evacuated, sealed, and then placed in an oven at 300° for 16 hr. Upon cooling, the tube was connected to the high vacuum system and opened, and all volatile products were removed, leaving behind only the nonvolatile products. The volatile products were separated by trap-to-trap fractionation and were identified by mass spectrometry and gas chromatography as silacyclopentene **10** (0.05 g),[5] unreacted butadiene **7** (0.20 g), and a dimer of butadiene **7** (trace).

Hot *n*-hexane was added to the nonvolatile material from the vacuum fraction. This gave a reddish-brown solution and a white precipitate. The precipitate was identified by ir, nmr, and mass spectrometry as tetraphenylbenzene **9** (0.21 g) and 1,4-disilacyclohexadiene **8** (0.09 g). The reddish-brown solution was subjected to gas chromatographic analysis using an SE-30 silicon gum rubber column maintained at 210°. Using these conditions and by changing the flow rate of carrier gas, it was possible to to observe at least 15 peaks; however, the peaks due to four compounds made up more than 75% of the integrated total of all the peaks. These four compounds were identified by ir, mass spectrometry, and vpc retention times as silabicyclononadiene **6** (50%), silacyclopentadiene **4** (10%), an unknown material having a parent *m/e* of 264 (7%), and a second unknown compound having a parent *m/e* of 258 (8%). Because of the extreme complexity of this reaction and difficulty in separating and identifying products, absolute percentage yields for the major products were not determined.

Reaction of Silacyclopentadiene 4 with Butadiene 7. Preparation of Silabicyclononadiene 6 in Good Yield.—A pyrex pyrolysis tube was charged with 1.01 g (3.9 mmol) of silacyclopentadiene **4** and 4.5 mmol of butadiene **7**. The tube was sealed under high vacuum and placed in a furnace at 200° for 48 hr. Upon cooling, the tube was opened; unreacted butadiene was removed under high vacuum and the solid residue was taken up in hot *n*-hexane. After cooling the *n*-hexane solution, 0.83 g (62%) of pure white silabicyclononadiene **6** was collected by filtration. When **6** was purified by a second recrystallization from *n*-hexane, it gave the following physical data: mp 115–116°; ^{1}H nmr (60 MHz, CCl_4) τ 10.07 (s, 3 H), 9.61 (s, 3 H), 8.38 (s, 6 H), 7.85 (m, 4 H), 6.51 (m, 1 H), 3.29 (m, 1 H), 2.80 (m, 10 H); mass spectrum (80 eV) *m/e* (rel intensity) 344 (25) P, 262 (100); uv max (cyclohexane) 256 nm (ϵ 14,000); ir (KBr pellet) 3067 (W), 3030 (W), 3012 (W), 2994 (M), 2976 (W), 2941 (M), 2890 (M), 2874 (M), 2841 (M), 1949 (W), 1876 (W), 1799 (W), 1595 (S), 1572 (M), 1497 (M), 1493 (S), 1447 (S), 1431 (M), 1406 (W), 1372 (W), 1339 (W), 1302 (W), 1287 (W), 1250 (S), 1209 (W), 1192 (W), 1181 (W), 1149 (W), 1124 (W), 1112 (W), 1101 (W), 1063 (W), 1042 (W), 1031 (W), 1007 (W), 998 (W), 974 (W), 935 (M), 923 (W), 910 (W), 888 (M), 876 (S), 857 (M), 835 (S), 828 (S), 790 (S), 780 (S), 771 (S), 754 (S), 742 (S), 696 (VS), 662 (W), 637 (M).

Anal. Calcd for $C_{24}H_{28}Si$: C, 83.9; H, 8.15; Si, 8.19. Found: C, 84.4; H, 8.18; Si, 8.19.

The above reaction did not go when carried out in dyglyme solvent at 100, 150, 200, or 250°. When it was attempted without solvent at 300°, the result was such a complex mixture that attempts to isolate and identify all products failed. However, no products were isolated and identified which indicated dimethylsilylene elimination. In particular, none of silacyclopentene **10** could be isolated.

An Attempted Preparation of 2:3-Benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (12).—The procedure used was the same as the one reported in the literature[3] for the preparation of 2:3-benzo-7-silanorbornadiene **1** except that silacyclopentadiene **4** was used instead of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene. Anthranilic acid (4.0 g) and 6.0 g of isoamyl nitrite were dissolved in 60 ml of dry THF. These solutions were then added simultaneously over a period of 2.5 hr to 2.9 g of silacyclopentadiene **4** dissolved in gently refluxing dry THF. After addition of anthranilic acid and isoamylnitrite was completed, the solution was refluxed for an additional 2 hr. The solvent was removed from the reaction mixture and the residue was then subjected to column chromatography using neutral alumina as packing and petroleum ether (bp 60–90°) to develop the column. The products isolated and identified from this separation were substituted naphthalene **13** and a siloxepinone.[12] Other fractions were obtained from the column fractionation; however, they appeared to be polymeric as mass spectra could

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[14] M. Tsutsui and H. Zeiss, *J. Amer. Chem. Soc.*, **81**, 6090 (1959).

not be obtained for these materials even when they were heated 200° in the inlet system of the mass spectrometer.

Registry No.—**4**, 7688-03-1; **5**, 28861-05-4; **6**, 28861-04-3; **8**, 751-37-1; **14**, 2762-95-0; diphenylacetylene, 501-65-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; benzyne, 462-80-6.

Acknowledgment.—We thank P. Maruca and L. Roseman for assistance in the laboratory and Drs. J. Grunwell and R. Schaeffer for valuable discussions. We also gratefully acknowledge The Research Corporation for partial financial support of this research.

Steric Deshielding in Nonrigid Systems. II.[1] The Preparation and Nuclear Magnetic Resonance Spectra of the Hexachlorocyclopentadiene Adducts of 1,3-Alkadienes

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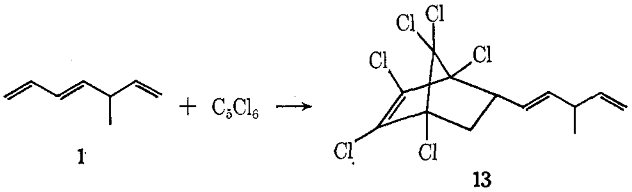
Received September 11, 1970

Hexachlorocyclopentadiene is remarkably regiospecific in its reaction with olefins, reacting more readily with terminal than with internal olefins and more readily with conjugated than with isolated olefins. A steric deshielding mechanism is invoked to account for the difference in the nmr spectra of the adducts of *cis*- and *trans*-1,3-alkadienes. The mechanism is extended to include the deshielding of allylic protons by *cis*-alkyl substituents in rigid and nonrigid systems.

Hexachlorocyclopentadiene (C_5Cl_6) is a well-known and very reactive diene in Diels–Alder chemistry. Its reactions have been well studied and have led to the synthesis of many interesting and useful hexachlorobicyclo[2.2.1]heptenes.[3] It reacts readily under mild conditions even with "unactivated" olefins but differs from the typical Diels–Alder diene in that it has been shown to have an "inverse electron demand;" that is, it reacts preferentially with electron-rich dienes and not at all with tetracyanoethylene.[4] This characteristic may be associated with the concept of "spiroconjugation" as described by Simmons and Fukunaga.[5]

We have studied the reaction of C_5Cl_6 with various 1,3-alkadienes and have found that the reaction is remarkably regiospecific. Hexachlorocyclopentadiene reacts more readily with a conjugated than with an isolated olefin and more readily with a terminal than with an internal olefin giving good yields of single products. Moreover, we have found that a diene capable of assuming a cisoid geometry is more reactive than one for which this conformation is disfavored.[6] In addition, the nmr spectra of the products have proven interesting and very useful in determining the geometry of the double bond adjacent to the bicyclic moiety.

Regiospecificity.—Reaction of 5-methyl-1-*trans*-3,6-heptatriene (**1**) with C_5Cl_6 for 6 hr at 90° gives a single product (**13**) in 84% yield. The ultraviolet spectrum of **13** shows no absorption characteristic of a conjugated diene [for **1**, λ_{max} 227 nm (log ϵ 4.40)].[7] Thus, the reaction occurs at one of the conjugated double bonds. The appearance of five olefinic protons in the nmr spectrum shows that it is the terminal, conjugated double bond that reacts. Examination of the spectra of the products derived from 1,3,7-octatriene (**2**) and 1,3,6-octatriene (**3**) showed that here, also, reaction occurs exclusively at the terminal, conjugated double bond. The generality of this regiospecificity was shown by examination of a series of 1,3-alkadienes (see Table I). With only one exception, the reaction occurs exclusively at the terminal position. In the case of *cis*-1,3-pentadiene, about 7% of the alternate product is apparent from the presence of a doublet (J = 7.0 Hz) at τ 9.04 in the nmr spectrum.



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Specificity in the reaction of C_5Cl_6 with monoolefins was also demonstrated by treating *trans*-1,4,9-decatriene with an excess of the halocarbon. The only product isolated (~60% yield of recrystallized material) exhibits a 1.8-proton multiplet at τ 4.5–4.8 and analyzes correctly for the 2:1 product. Therefore, reaction occurs specifically to give the terminal diadduct. A brief study of *cis*-1,5,9-decatriene indicated that here, also, reaction occurs exclusively at the terminal sites.

Considering the "inverse electron demand" of C_5Cl_6, one would expect conjugation to decrease reactivity and, furthermore, one would expect alkyl substitution to increase reactivity. In both instances, the reverse has been found to be true. Although electronic effects are undoubtedly important in this reaction, they are handily outweighted by steric factors.[8] In the case of conjugation, the decrease in electron density caused

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(2) Address correspondence to author at Glidden-Durkee.

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