The Diels–Alder Reaction of α,β-Unsaturated Trihalosilanes with Cyclopentadiene

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The Diels–Alder reaction of cyclopentadiene with some ethylenic and acetylenic α,β-unsaturated silanes was investigated to determine the synthetic potential of such compounds as dienophiles. Although trimethylsilyl species displayed low reactivity in these reactions, the corresponding trichloro and trifluorosilyl analogs were quite reactive. Trifluorosilyl compounds induced polymerization of cyclopentadiene, and in the case of ethynyltrifluorosilane this polymerization precluded the formation of cycloaddition product. The geometrical isomers of β-chlorovinyltrichlorosilane were characterized for the first time, and the lowest member of a new class of compounds, alkynyltrifluorosilanes, was prepared.

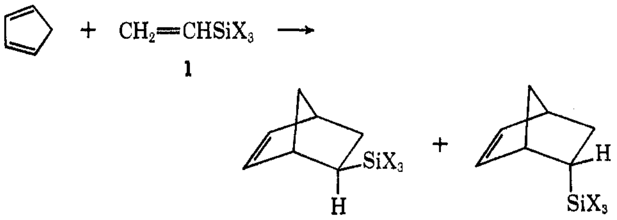
Organosilicon compounds possessing unsaturation adjacent to the heteroatom have not enjoyed widespread use as dienophilic participants in Diels–Alder reactions.[1] This neglect may be due to the reluctance of many such organosilicon compounds to readily undergo 1,4 cycloaddition with diene systems such as cyclopentadiene and 1,3-butadiene. Most reports in this area thus involve either dienes which are reactive by virtue of "inverse electron demand,"[2] or reaction conditions of high temperatures and long reaction times have been employed.[3]

In the latter cases, a trimethylsilyl group was usually present in the dienophile. Since Diels–Alder reactions of electron-rich dienes are favored by electron-withdrawing substituents in the dienophile,[4] the electrical effect of the trimethylsilyl group ($\sigma_p = -0.07$)[5] would dampen the dienophilicity of an unsaturated site. Conversely, a group such as trichlorosilyl ($\sigma_p = +0.24$)[6] should enhance the reactivity of an olefin or acetylene.

Although this latter point has been confirmed by the observation that vinyltrichlorosilane (**1a**) and cyclopentadiene react exothermically to give a near-quantitative yield of Diels–Alder adduct,[7] no extension of this principle to similarly substituted alkynes has been attempted. Moreover, it was of interest to investigate the behavior of α,β-unsaturated trifluorosilanes in order to assess the value of the trifluorosilyl group ($\sigma_p = +0.30$) as an activating moiety.

Results and Discussion

Vinylsilanes.—To establish a reference point against which to judge the dienophilic reactivity of some trihalovinylsilanes (**1a**, **1b**), the Diels–Alder reaction of trimethylvinylsilane (**1c**) and cyclopentadiene was carried out. The cycloaddition afforded only a 4% yield of adduct after 8 hr at 100°, but at 170° a 58% yield of product was obtained, identified as a 1:1 mixture of 5-*exo*-trimethylsilylbicyclo[2.2.1]hept-2-ene (**2c**) and the corresponding endo isomer **3c**. Since the reactivity of other highly α-branched dienophiles is very low,[8] this result suggests that additional parameters not measured by σ_p values may contribute to the behavior of **1c**.[9]



a, X = Cl
b, X = F
c, X = CH_3

a, X = Cl; R = H
b, X = F; R = H
c, X = CH_3; R = H
d, X = Cl; R = Ph
e, X = CH_3; R = Ph

The exo (**2a**) and endo (**3a**) adducts of cyclopentadiene and vinyltrichlorosilane (**1a**) were easily prepared and individually characterized for the first time. The ratio of 24:76 for the exo to endo distribution in the product (obtained in 93% yield) agrees well with the 20:80 ratio determined previously for this mixture by indirect methods.[7b] Inasmuch as the steric requirements of the trichlorosilyl and trimethylsilyl groups should be similar,[12] the predominant influence on the promoting effect of the former is probably its electron-withdrawing capability.

The reaction between vinyltrifluorosilane (**1b**) and cyclopentadiene occurred readily (a mildly exothermic

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[1] Recent reviews in this area include (a) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); (b) *ibid.*, **6**, 16 (1967); (c) S. Seltzer, *Advan. Alicyclic Chem.*, **2**, 1 (1968).

[2] (a) For a discussion, see ref 1b, pp 26–27. (b) Dienes used, this category have usually been hexahalocyclopentadienes.

[3] (a) D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organometal. Chem.*, **2**, 417 (1964); (b) M. E. Freeburger and L. Spialter, *J. Org. Chem.*, **35**, 652 (1970); (c) C. S. Kraihanzel and M. L. Losee, *ibid.*, **33**, 1983 (1968); (d) D. Seyferth, D. R. Blank, and A. B. Evnin, *J. Amer. Chem. Soc.*, **89**, 4793 (1967); (e) C. S. Kraihanzel and Losee, *ibid.*, **90**, 4701 (1968).

[4] See ref 1b, pp 24–26.

[5] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[6] J. Hradil and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **32**, 171 (1967).

[7] (a) G. H. Wagner, D. L. Bailey, A. N. Pines, D. L. Dunham, and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953); (b) H. G. Kuivila and C. R. Warner, *J. Org. Chem.*, **29**, 2845 (1964).

[8] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); also, see ref 1c, pp 26–29.

[9] A vinylsilane may well be less hindered than in its carbon analog because of the longer silicon–(vinyl) carbon bond, said to be 1.853 Å in vinylsilane,[10] for example, as compared with 1.448 Å in propene.[11]

[10] J. M. O'Reilly and L. Pierce, *J. Chem. Phys.*, **34**, 1176 (1961).

[11] D. R. Lide and D. E. Mann, *ibid.*, **27**, 868 (1957).

[12] Calculations based on reported bond lengths[13] and van der Waals radii[14] of the atoms involved give 4.2, 3.8, and 2.9 Å, respectively, for the effective radii of trimethylsilyl, trichlorosilyl, and trifluorosilyl groups.

[13] C. Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, Chapter 16.

[14] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

reaction ensued spontaneously at ambient temperatures) to afford a 77% yield of product. Although the enhanced reactivity of **1b** *vs.* its trimethyl analog **1c** (possibly due to a combination of electrical and steric[12] effects) is thus evident, the answer to a similar comparison with vinyltrichlorosilane awaits further information of a more quantitative nature. Again, the cycloaddition produced more endo isomer **3b** than exo isomer **2b**, obtained in a ratio of 69:31. During this preparation, **1b** apparently initiated the polymerization of cyclopentadiene.[15] This was not a serious complication in the present case, since the use of excess diene led to good yields of adducts, but less reactive alkenyltrifluorosilanes might not afford useful quantities of Diels–Alder products from cyclopentadiene.

Ethynylsilanes.—Kraihanzel and Losee[3c] have reported that ethynyltrimethylsilane (**4c**) and cyclopentadiene in benzene yielded only 10% **5c** after 50 hr at 180°, but 87% after similar treatment at 270°. In contrast to the behavior of **4c**, its trichloro analog **4a** undergoes reaction with cyclopentadiene within 2 hr at 70° to give 93% bicycloheptadiene **5a**.

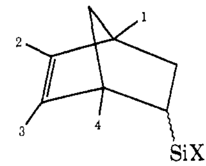
When ethynyltrifluorosilane (**4b**) was employed in this reaction, polymerization of the diene occurred to the exclusion of cycloaddition. Since alkynes are less potent dienophiles than corresponding alkenes,[19] it appears that the balance in rates between cycloaddition and polymerization which existed in the case of **1b** has with **4b** become much more favorable for polymer formation.

In order to estimate the difference in reactivity between trimethylsilyl- and trichlorosilyl-substituted dienophiles possessing increased steric requirements, the reactions of cyclopentadiene with acetylenes **4e** and **4d** were also investigated. Although phenylethynyltrimethylsilane (**4e**) afforded adduct **5e** in only 10% yield after 8 hr at 170°, the trichloro analog **4d** underwent cycloaddition at 100° to afford a 50% yield (96% based on recovered **4d**) of **5d** within 5.5 hr. Although excess cyclopentadiene was used in the reactions carried out at 100°, conversion of **4d** to adduct was only about half complete. A higher conversion of **4d** to **5d** was not realized by operating above the dissociation temperature of dicyclopentadiene (170–180°), since higher boiling materials were then formed at the expense of **5d**.

Spectral Assignment of Structure.—Kuivila and Warner have assigned exo and endo configurations to several 5-silyl-substituted bicyclo[2.2.1]hept-2-enes on the basis of chemical and pmr evidence.[7b] Although most compounds studied were obtained as mixtures of epimers, characteristic differences in the vinylic and bridgehead proton regions of their pmr spectra allowed for spectral identification of the two isomers in each case. Of special significance was the conclusion that the exo isomers exhibited two separate unsymmetrical doublet of doublets in the vinylic region, while in the spectra of the endo isomers the absorptions due to the two vinylic protons had merged to afford an apparent triplet. This method of epimer assignment was used here to identify **2a** and **3a** and has been extended to assign the stereochemistry of the corresponding trifluorosilyl isomers **2b** and **3b** (Table I).

TABLE I

PMR DATA FOR 5-TRIHALOSILYLBICYCLO[2.2.1]HEPT-2-ENES[a–c]



	2a	**2b**	**3a**	**3b**
H_1	3.09 (bs)	3.10 (bs)	3.02 (bs)	3.06 (bs)
H_2, H_3	6.01 (dd) or 6.29 (dd)	5.97 (dd) or 6.13 (dd)	6.02 (t)	6.12 (t)
H_4	3.09 (bs)	3.10 (bs)	3.22 (bs)	3.18 (bs)
Other	0.92–1.69 (c)	0.55–2.1 (c)	1.07–2.35 (cm)	0.93–2.23 (c)

[a] Data obtained on *ca.* 30% CCl_4 solutions with TMS as internal standard and reported as δ values. [b] In all cases, integrated peak areas were consistent with the assignments made. [c] Chemical shifts are measured to the estimated center of a singlet or multiplet.

One discordant observation intrudes upon the configurational assignments thus made however. In all other examples of exo–endo pairs of 5-substituted bicyclo[2.2.1]hept-2-enes for which pmr data has been found, the difference in chemical shifts between the two vinylic protons is larger for the endo than for the exo isomer.[20] As can be seen from Table I and the data reported by Kuivila and Warner,[7b] the assignments originally made lead to an inversion of this relationship for the corresponding silyl-substituted compounds. The explanation for this disparity is beyond the scope of the present investigation and will be the subject of a future report.

The pmr spectra of several 2-silyl-substituted bicyclo[2.2.1]hepta-2,5-dienes have been discussed previously.[3c] Pmr data for similar compounds prepared in this study are recorded in Table II; no unusual features were observed in these spectra.

Experimental Section

General.—Cyclopentadiene was prepared from its dimer just prior to use by a standard procedure.[21] Dicyclopentadiene was obtained from the redimerization of freshly cracked cyclopentadiene upon overnight standing. The following stainless steel 0.25-in. columns were used for vpc analyses: A, 10-ft FFAP; B, 12-ft QF-1; C, 16-ft QF-1 ($^3/_8$ in.); D, 5-ft SE-30. For halosilane analysis, columns were preconditioned by the injection of *ca.* 10 μl of ethyltrichlorosilane. Compositions obtained from vpc data are based on relative peak areas. All infrared data was obtained on neat films employing a Beckman IR-8 spectrophotometer, except the ir spectrum of **4b** which was recorded by a Beckman IR-12 spectrophotometer. Pmr spectra were obtained on *ca.* 30%

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(15) The cationic polymerization of cyclopentadiene can be initiated by a variety of protonic[16] or nonprotonic[17] acids. However, the observed effect of **1b** in this regard appears to be the first report of a halosilane acting in this capacity.[18] Evidence of such extensive polymerization was absent from any of the cycloaddition reactions involving organotrichlorosilanes.

(16) (a) H. Staudinger and H. A. Bruson, *Justus Liebigs Ann. Chem.*, **447**, 97 (1926); (b) J. Upadhyay, P. Gaston, A. A. Levy, and A. Wasserman, *ibid.*, 3252 (1965), and references therein.

(17) (a) H. Staudinger and H. A. Bruson, *ibid.*, **447**, 110 (1926); (b) P. V. French and A. Wasserman, *J. Chem. Soc.*, 1044 (1963).

(18) The possibility that traces of hydrogen fluoride were inducing the polymerization cannot be rigorously excluded.

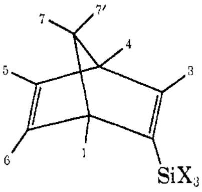
(19) Reference 1b, p 25.

(20) (a) J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965); (b) W. L. Dilling, R. D. Kroening, and J. C. Little, *ibid.*, **92**, 928 (1970); (c) J. Paasivirta, *Soumen Kemistilehti, B*, **38**, 130 (1965); (d) R. V. Moen and H. S. Makowski, *Anal. Chem.*, **39**, 1860 (1967); (e) R. J. Ouellette and G. E. Booth, *J. Org. Chem.*, **30**, 423 (1965); (f) L. A. Paquette, *ibid.*, **29**, 2851 (1964).

(21) R. B. Moffett in "Organic Syntheses," Collect. Vol. IV, N. Rabjohn, Ed., Wiley, New York, N. Y., 1963, p 238.

TABLE II

PMR DATA FOR BICYCLO[2.2.1]HEPTA-2,5-DIENES[a]



	5a	**5d**	**5e**[b]
H_1, H_4	3.82 (bs) or 3.92 (bs)	3.87 (bs) or 4.13 (bs)	3.92 (bs) or 4.05 (bs)
H_3	7.64 (dd)		
H_5, H_6	6.65 (ddd) or 6.82 (ddd)	6.86 (t)	7.01 (m)
H_7, $H_{7'}$	2.03 (t)	2.00 (dt) or 2.22 (dt)	2.21 (cm)
$SiCH_3$			0.25 (s)
3-Ph		7.26 (s)	7.39 (s)

[a] Footnotes to Table I apply. [b] CH_2Cl_2 as internal standard.

CCl_4 solutions with tetramethylsilane as internal standard using a Varian A-60A spectrometer. The pmr spectra of halosilanes could be conveniently recorded (and the samples then stored indefinitely) by sealing the solution in a melting point capillary tube. The sample and some CCl_4 were then put into an nmr tube and the spectrum obtained as usual.[22] Unless stated otherwise, distillations were carried out by the use of short-path apparatus.

5-*exo*- and 5-*endo*-Trimethylsilylbicyclo[2.2.1]hept-2-ene (2c and 3c).—A mixture of 4.0 g (0.04 mol) of vinyltrimethylsilane (**1c**) and 2.9 g (0.044 mol) of cyclopentadiene was sealed in a glass ampoule and held at 170° for 8 hr. Distillation gave 3.8 g (58%) of a 1:1 mixture[23] of **2c** and **3c**, bp 75–79° (21 mm). These isomers were inseparable on a variety of vpc columns and were collected together from column A (90°).

Anal. Calcd for $C_{10}H_{18}Si$: C, 72.22; H, 10.91. Found: C, 72.19; H, 10.98.

In another run as above, but at 100°, vpc showed that only a 4% yield of an exo–endo mixture of adducts was obtained.

5-*exo*- and 5-*endo*-Trichlorosilylbicyclo[2.2.1]hept-2-ene (2a and 3a).—A mixture of 8.1 g (0.05 mol) of **1a** and 4.0 g (0.06 mol) of cyclopentadiene became mildly exothermic upon gentle heating. After 1 hr, followed by 10 min at 100°, distillation gave 10.6 g (93%) of adduct, bp 77–81° (8 mm) [lit.[7a] bp 116–117° (49 mm)]. This distillate consisted of 24% exo isomer **2a** and 76% endo isomer **3a** (order of elution from column B, 165°). Preparative vpc (column C, 140°) afforded pure **2a**: ir 3.25 (w), 7.47 (m), 11.23 (s), 12.30 (m), 13.55 (s), 14.33 μ (s).

Anal. Calcd for $C_7H_9Cl_3Si$: C, 36.94; H, 3.99. Found: C, 36.79; H, 4.00.

The endo isomer **3a** was similarly obtained: ir 3.25 (w), 7.47 (m); 11.23 (s), 12.10 (m), 13.81 (s), 14.07 μ (m).

Anal. Calcd for $C_7H_9Cl_3Si$: C, 36.94; H, 3.99. Found: C, 37.10; H, 3.91.

5-*exo*- and 5-*endo*-Trifluorosilylbicyclo[2.2.1]hept-2-ene (2b and 3b).—An ampoule containing 6.2 g (0.094 mol) of cyclopentadiene at −78° was charged with 4.0 g (0.036 mol) of **1b**[24] (distilled into the ampoule from anhydrous KF or calcium hydride). After sealing, the ampoule was warmed to 25°, initiating a mildly exothermic reaction of 10-min duration. After 13 hr, the ampoule was opened, allowing a low boiler to distil off (unreacted **1b**?). The residue consisted of a rubbery white gel and a mobile, water-white liquid. Distillation of the latter gave 4.9 g (77%) of adduct, bp 115–121° (740 mm). Vpc showed it to contain 31% exo isomer **2b** and 69% endo isomer **3b** (order of elution from column B, 115°).

Preparative vpc[25] (column C, 130°) afforded pure **2b**: ir 3.24 (w), 7.47 (m), 10.5–10.7 (vs), 11.16 (s), 11.74 (s), 12.51 (m), 13.70 (s), 14.46 μ (m).

Anal. Calcd for $C_7H_9F_3Si$: C, 47.18; H, 5.09. Found: C, 46.98; H, 4.93.

The endo isomer **3b** was similarly obtained: ir 3.24 (w), 7.47 (m), 10.5–10.7 (vs), 11.14 (s), 11.84 (vs), 12.39 (m), 13.82 μ (s).

Anal. Calcd for $C_7H_9F_3Si$: C, 47.18; H, 5.09. Found: C, 47.53; H, 4.83.

Freshly distilled or vpc-collected samples of **2b** or **3b** were initially colorless but soon became dark when stored.[26] However, redistillation of this mobile liquid led to excellent recovery of colorless material. A mixture of **2b** and **3b** which was sealed in a capillary tube soon darkened but afforded identical nmr spectra over a period of 3 months.

Reaction of 1,2-Dichloroethylene with Trichlorosilane. Ethynyltrichlorosilane and *cis* and *trans*-β-Chlorovinyltrichlorosilane.—Because of the brevity of experimental detail in the published procedure,[27] a description of technique and results is given here.

A 30-mm-diameter Vycor tube filled to a height of 30 cm with 5-mm Kimax glass beads was mounted vertically and heated by an electric furnace. The mixed reactants were added under a slow flow of nitrogen; pyrolysate was collected in a −78° trap. A mixture of 97 g (1.0 mol) of *trans*-1,2-dichloroethylene and 68 g (0.50 mol) of trichlorosilane was passed dropwide through the hot zone at 630° over 2 hr to give 119.3 g of dark pyrolysate. Fractionation of this material (760 mm) on a 24-in. annular Teflon spinning-band column[28] gave the following fractions: bp 48.5–74° (39.3 g, mixed dichloroethylenes); bp 74–76° (lit.[27] bp 73°) [34.3 g (43%), ethynyltrichlorosilane (purity in excess of 99%); ir 3.01 (s), 4.84 (s), 7.20 (m), 14.2 μ (s, br); pmr δ 2.88 (s)]; bp 131.5–132° [21.5 g, *trans*-β-chlorovinyltrichlorosilane (98% pure)]; bp 132–136° (5.8 g, 1:3 ratio of *trans*- to *cis*-β-chlorovinyltrichlorosilane). Pure samples of the geometric isomers were obtained by preparative vpc (column D, 75°). The trans isomer eluted first and had ir 3.24 (vw), 3.28 (vw), 6.16 (m), 6.44 (s), 8.49 (s), 10.60 (s),[29] 12.54 (s), 12.99 μ (m), and pmr δ 6.30 (d, 1, J = 15.5 cps, C=CHSi), 7.07 (d, 1, J = 15.5 cps, ClCH=C).[30]

Anal. Calcd for $C_2H_2Cl_4Si$: C, 12.26; H, 1.03. Found: C, 12.34; H, 1.00.

The cis isomer had ir 3.23 (vw), 3.28 (vw), 6.07 (w), 6.40 (s), 7.61 (m), 12.25 (s), 14.4–14.9 μ (s, br), and pmr δ 6.12 (d, 1, J = 9.5 cps, C=CHSi), 7.07 (d, 1, J = 9.5 cps, ClCH=C).[30]

Anal. Calcd for $C_2H_2Cl_4Si$: C, 12.26; H, 1.03. Found: C, 11.94; H, 1.08.

When the pyrolysis was carried out as above, but at 540°, 95.4 g of starting material was recovered, and only about 1 g of ethynyltrichlorosilane was obtained. The major product of the reaction was 40.5 g of a 4:1 mixture of *trans*- and *cis*-β-chlorovinyltrichlorosilane. This material could be pyrolyzed in turn (at 640°) to afford 9.9 g (39%) of ethynyltrichlorosilane.

2-Trichlorosilylbicyclo[2.2.1]hepta-2,5-diene (5a).—A mixture of 1.6 g (0.01 mol) of **4a** and 0.8 g (0.012 mol) of cyclopentadiene was heated at 70° for 2 hr under nitrogen. Distillation gave 2.1 g (93%) of **5a**, bp 60–64° (4 mm), which vpc (column B, 170°) showed was at least 95% pure: ir 3.23 (w), 6.36 (w), 6.48 (m), 7.71 (s), 9.74 (s), 14.29 μ (vs).

Anal. Calcd for $C_7H_7Cl_3Si$: C, 37.27; H, 3.13. Found: C, 37.43; H, 2.80.

2-Trimethylsilylbicyclo[2.2.1]hepta-2,5-diene (5c).—A solution of 2.1 g (0.0094 mol) of **5a** in 20 ml of dry ethyl ether was slowly treated with 0.038 mol of ethereal methylmagnesium bromide. After a 3.5-hr reflux, the reaction mixture was worked up to give 1.1 g (73%) of **5c**: bp 73–74° (30 mm) [lit.[3c] bp 58.5–59.5° (18 mm)]; vpc (column A, 150°) showed a purity of 96%. A vpc-collected sample had $n^{27}D$ 1.4645; ir 3.23 (w), 3.26 (w),

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(22) The author wishes to thank Mr. E. M. Dexheimer for bringing this technique to his attention.

(23) The isomer content was determined *via* the nmr technique detailed in ref 7b.

(24) Prepared from **1a** by the method of L. Spialter, R. S. Towers, and M. M. Kent, *Tetrahedron Lett.*, **11** (1960); see R. Mueller, H. Witte, and C. Dathe, *Z. Chem.*, **3**, 391 (1963).

(25) The temperature of the thermal conductivity detector was 200°. Material obtained at 300° contained cyclopentadiene, as evidenced by nmr, presumably formed *via* a partial retrodiene reaction.

(26) This dark material may be similar to the polymer described by J. Upadhyay, P. Gaston, A. A. Levy, and A. Wasserman, *J. Chem. Soc.*, 3252 (1965).

(27) E. A. Chernyshev and G. F. Pavelko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12**, 2205 (1966).

(28) Nester Faust Mfg. Co., Newark, Del.

(29) Strong absorption in this region is indicative of a *trans*-substituted ethylene: see R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, pp 101–102.

(30) The observed J values suggest the *cis–trans* assignments made: see L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, London, 1969, pp 301–302.

6.35 (vw), 6.48 (w), 7.69 (m), 8.01 (s), 10.03 (m), 12.0 (vs), 13.34 (s), 14.42 μ (s). Confirmation of structure was provided by spectra comparison with published data.[3c]

Ethynyltrifluorosilane (4b).—A flask was fitted with a train of apparatus consisting of a water condenser, glass tubing to a −78° trap, and a drying tube. The flask was charged with 6.8 g (0.038 mol) of powdered SbF$_3$, 30 ml of dry heptane, and 5.0 g (0.031 mol) of **4a**. No observable reaction occurred upon stirring for 1 hr at 25°, but reaction was rapid at 65–70°. After all volatile material had condensed, the product was purified by trap to trap distillation at 25 and −78°. This afforded 2.2 g (64%) of ethynyltrifluorosilane (**4b**): ir (gas, 20 mm, 10-cm cell) 3.01 (m), 4.80 (m), 7.12 (w), 8.52 (w, br), 9.20 (w, br), 10.0 (s), 11.2 (s), 13.7 μ (s); pmr (neat plus TMS) δ 2.46 (s); mass spectrum (70 eV) m/e (rel intensity) 110 (75), 91 (65), 90 (11) 85 (100), 47 (12); vapor pressure 84 mm at −63.5° (chloroform slush).

An attempt to prepare **4b** by the use of aqueous HF[24] produced a rush of gas, noncondensable at −78°, and afforded no detectable amount of product.

2-Trifluorosilylbicyclo[2.2.1]hepta-2,5-diene (5b) (Attempted).—An ampoule containing 3.0 g (0.046 mol) of cyclopentadiene was cooled in liquid nitrogen, and 1.5 g (0.014 mol) of **4b** was allowed to distill in. The sealed ampoule was then agitated 3 hr at 25°. After recovery of 1.0 g of **4b**, a residue of stringy, water-white polymer was extracted with pentane, and this solution was examined by vpc (column D, 100°). The only solutes present were dicyclopentadiene and a trace (estimated at no more than 0.03 g) of unknown material.

Reaction of Phenylethynyltrimethylsilane (4e) with Cyclopentadiene.—A mixture of **4e** and cyclopentadiene (threefold molar excess) was heated in an ampoule 8 hr at 170°. Vpc (column D, 190°) then indicated that only 17% of the reaction mixture consisted of material boiling higher than starting acetylene. This material was represented by two closely spaced peaks in the chromatogram, the first of which to elute (10%) was identified as **5e** by retention time comparison with an authentic sample.

3-Phenyl-2-trichlorosilylbicyclo[2.2.1]hepta-2,5-diene (5d).—A flask fitted with a condenser and nitrogen inlet was charged with 4.2 g (0.018 mol) of phenylethynyltrichlorosilane (**4d**)[31] and 1.2 g (0.018 mol) of cyclopentadiene and then held at 100°. Two more identical increments of diene were added at 2-hr intervals, followed by a 1.5-hr heating period. Distillation then gave two fractions: bp 66–73° (0.25 mm), 2.0 g, and bp 98–100° (0.25 mm), 2.7 g. The former cut was recovered **4d**, and the latter adduct **5d** (96% yield based on recovered acetylene). Vpc (column D, 230°) indicated a purity in excess of 95% for the adduct: ir 3.23 (w), 6.30 (m), 6.43 (m), 6.71 (m), 7.69 (m), 9.78 (m), 13.11 (s), 13.84 μ (s). A peak of variable intensity at 4.58 μ always appeared in vpc-collected samples of **5d**. Re-vpc of such samples showed the presence of *ca.* 4% **4d**. This impurity probably arose *via* a retrodiene reaction induced by the high temperature (300°) of the thermal conductivity detector.

Anal. Calcd for C$_{13}$H$_{11}$Cl$_3$Si: C, 51.76; H, 3.68. Found: C, 51.57; H, 3.75.

In another run, a mixture of 2.4 g (0.010 mol) of **4d** and 0.72 g (0.0055 mol) of dicyclopentadiene was heated under nitrogen at 170° for 1.5 hr. Vpc then showed dicyclopentadiene (**4d**) and adduct **5d** in a ratio of 1.0:2.7:3.0. An additional 0.5 hr at 170° did not alter this distribution; the mixture was distilled to give 0.9 g of recovered **4d** and 1.0 g (53% based on recovered **4d**) of adduct. Increasing the amount of dicyclopentadiene relative to **4d** in an attempt to maximize conversion led to the formation of higher boiling products. When a mixture of 3.0 g (0.013 mol) of **4d** and 1.3 g (0.0099 mol) of dicyclopentadiene was treated as above for 1 hr, vpc showed only 2% of starting acetylene, and distillation gave 1.8 g (47%) of adduct **5d** and 2.0 g of a viscous yelow liquid, bp 160–170° (0.4 mm).

3-Phenyl-2-trimethylsilylbicyclo[2.2.1]hepta-2,5-diene (5e).—A solution of 2.2 g (0.0073 mol) of **5d** in 20 ml of dry benzene was treated with 0.030 mol of ethereal methylmagnesium bromide. More benzene was then introduced (20 ml), and 30 ml of distillate was removed over a 1-hr period. After an additional 1.5 hr at reflux, the reaction mixture was worked up. Distillation gave 1.4 g (80%) of **5e**: bp 78–84° (0.5 mm); $n^{27}\mathrm{D}$ 1.5435; ir 3.23 (w), 6.29 (w), 6.43 (w), 6.70 (w), 8.01 (s), 11.57 (s), 12.04 (vs), 13.26 (s), 14.00 (s), 14.39 (s), 15.32 μ (s).

Anal. Calcd for C$_{16}$H$_{20}$Si: C, 79.74; H, 8.39. Found: C, 79.84; H, 8.54.

Registry No.—**2a**, 27610-02-2; **2b**, 27544-80-5; **2c**, 27544-81-6; **3a**, 27544-82-7; **3b**, 27544-83-8; **3c**, 27544-84-9; **4b**, 27544-85-0; **5a**, 27544-86-1; **5d**, 27544-87-2; **5e**, 27544-88-3; *cis*-β-chlorovinyltrichlorosilane, 27544-89-4; *trans*-β-chlorovinyltrichlorosilane, 27544-90-7; cyclopentadiene, 542-92-7.

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(31) A. D. Petrov and L. L. Shchukovskaya, *Zh. Obshch. Khim.*, **25**, 1128 (1955); *Chem. Abstr.*, **50**, 3275 (1956).