# Ethynylsilanes. III. Syntheses of Some 2-Organosilicon Bicyclo[2.2.1]heptadienes and Bicyclo[2.2.1]hept-2-enes

CHARLES S. KRAIHANZEL AND MICHAEL L. LOSEE

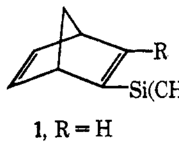
*Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015*

*Received December 6, 1967*

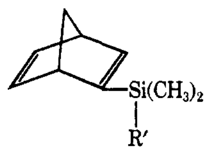
The syntheses of several new 2-organosilicon bicyclo[2.2.1]heptadiene derivatives by the Diels–Alder addition of alkynylsilanes to cyclopentadiene are reported. Reactions were carried out in sealed bombs and temperatures in the range of 180–260° were necessary to obtain the expected cycloaddition products with the acetylenes $(CH_3)_3SiC{\equiv}CR$ (where R = H, $COOC_2H_5$, $COCH_3$), $(CH_3)_2(C_6H_5)SiC{\equiv}CH$, and $(CH_3)_2Si(C{\equiv}CH)_2$. Atmospheric catalytic hydrogenation of the unsubstituted double bond in the bicyclo addition products from the first three alkynylsilanes yielded the corresponding organosilicon bicyclo[2.2.1]hept-2-enes. Proton magnetic resonance spectral data are reported and several unusual features of the spectra are discussed in the paper.

Although considerable interest in the syntheses of metalloid acetylenes has been evoked in recent years, relatively little use of these compounds as synthetic intermediates has been demonstrated. The ability of certain metalloid acetylenes to act as dienophiles in Diels–Alder reactions has been recognized only recently. Seyferth and his coworkers have shown that alkynyltin and alkynylsilicon compounds will undergo cycloaddition reactions with tetraphenylcyclopentadienone[1] and $\alpha$-pyrone[2,3] to yield benzene derivatives. Some metalloid acetylenes react with hexachlorocyclopentadiene to yield hexachlorobicyclo[2.2.1]heptadiene derivatives.[4] The syntheses of several new 2-organosilylbicyclo[2.2.1]heptadiene and -[2.2.1]hept-2-ene derivatives are reported in this paper.

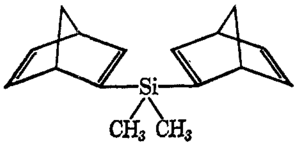
**Bicyclo[2.2.1]heptadienes.**—Whereas the synthesis of a bicyclo[2.2.1]heptadiene derivative from cyclopentadiene and a reactive dienophile such as dimethyl acetylenedicarboxylate usually proceeds readily even at room temperature, considerably higher reaction temperatures are required with acetylenes bearing electron-donating substituents. Inasmuch as the trimethylsilyl group also has a strong positive inductive effect, an effect which is opposed in part by dative $\pi$ bonding between the $\pi$-bonding levels of the triple bond and the vacant 3d levels of silicon,[5] alkynylsilanes would be expected to require fairly vigorous reaction conditions in order to undergo cycloaddition to cyclopentadiene. This was found to be the case in the syntheses of compounds **1**–**4** and **6**.



**1**, R = H
**2**, R = $COOC_2H_5$
**3**, R = $COCH_3$



**4**, R′ = $C_6H_5$
**5**, R′ = C≡CH

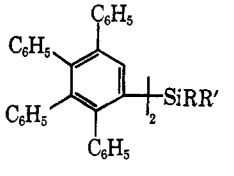


**6**

In general, high temperatures of 250–270° for periods of up to 3 days were necessary to obtain reasonable yields of compounds **1**, **4**, and **6**. The two more reactive acetylenes $(CH_3)_3SiC{\equiv}CCOR$, where R is $OC_2H_5$ or $OCH_3$, gave good yields of **2** and **3**, respectively, after only 12-24 hr at 180–190°.

The reaction of $CH_3(CH_2)_3C{\equiv}CCOOC_2H_5$ with cyclopentadiene was not found to differ appreciably from the syntheses of **2** and **3**.

Attempts to obtain **5** by reaction of $(CH_3)_2Si(C{\equiv}CH)_2$ with cyclopentadiene in a 1:1 mole ratio were unsuccessful. However, as has been reported in the Experimental Section, infrared spectral evidence does indicate that one of the products obtained in this reaction did contain the SiC≡CH group. Two adjunct reactions demonstrated the ease with which both triple bonds of a diethynylsilane react. Tetraphenylcyclopentadienone reacted readily with both methylphenyldiethynylsilane and diphenyldiethynylsilane to yield the highly substituted benzene derivatives **7** and **8**.



**7**, R = $CH_3$; R′ = $C_6H_5$
**8**, R = R′ = $C_6H_5$

Several attempts were made to prepare 2,3-bis(trimethylsilyl)bicyclo[2.2.1]heptadiene from cyclopentadiene and bis(trimethylsilyl)acetylene at temperatures up to 270° over several days. In each instance the starting silicon compound was recovered nearly quantitatively.

The isolation of these organosilicon norbornadienes is possible because they and the alkynylsilanes are both thermally stable. The utility of this synthetic method with other metalloid acetylenes remains to be shown, but the range of applicability is not expected to be great because organosilicon acetylenes appear to be among the most robust of the compounds in this class.

The 2-organosilylbicyclo[2.2.1]heptadiene derivatives were identified mainly from their pmr spectra. These observations are listed in Table I and the spectra of **1**, **3** and **4** are shown in Figure 1. The numbering system employed here is the usual one, although for purposes of reference the organosilicon group is situated at position 2.

Several aspects of these spectra deserve attention. First, no coupling is detectable between the vinyl and

---

[1] D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organometal. Chem.*, **2**, 417 (1964).

[2] A. B. Evnin and D. Seyferth, *J. Amer. Chem. Soc.*, **89**, 952 (1967).

[3] D. Seyferth, D. R. Blank, and A. B. Evnin, *ibid.*, **89**, 4793 (1967).

[4] D. Seyferth and A. B. Evnin, *ibid.*, **89**, 1468 (1967).

[5] R. West and C. S. Kraihanzel, *Inorg. Chem.*, **1**, 967 (1962).

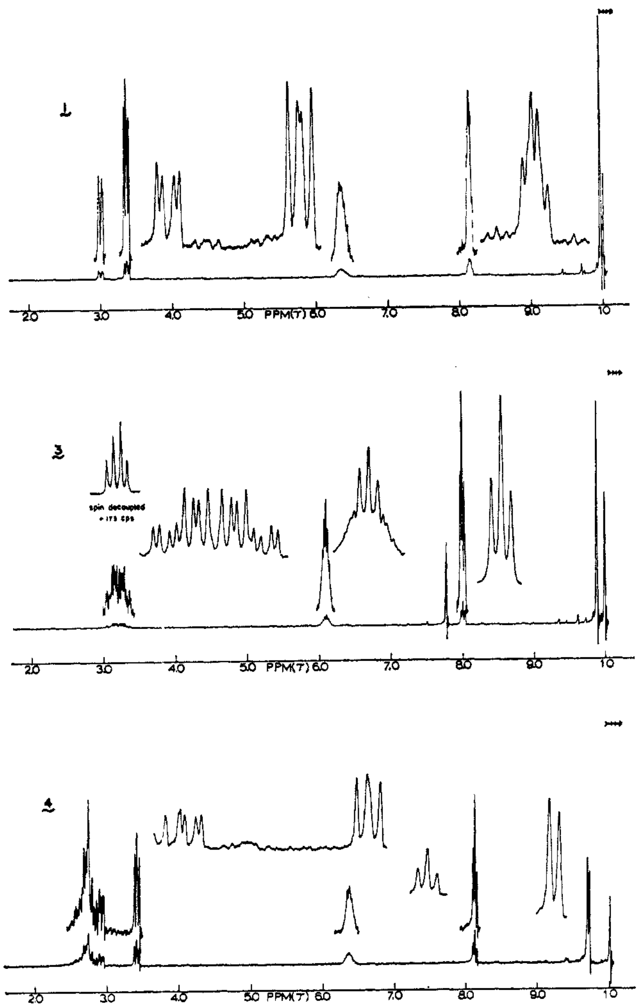


Figure 1.—Proton magnetic resonance spectra of compounds **1**, **3**, and **4** in $CCl_4$ (30%). Expanded scale inserts are five times normal sweep width. Spin-decoupled spectrum was obtained at normal sweep width.

TABLE I

BICYCLO[2.2.1]HEPTADIENE COMPOUNDS. PROTON MAGNETIC RESONANCE DATA[a,b]

| | **1** | **2** | **3** | **4** | **6** |
|---|---|---|---|---|---|
| $H_3$ | 3.02 (1) | ... | ... | 2.92 (1) | 3.00 (1) |
| $H_5$, $H_6$ | 3.40 (2) | 3.27 (2) | 3.23 (2) | 3.40 (2) | 3.42 (2) |
| $H_1$, $H_4$ | 6.35 (2) | 6.05 (2) | 6.08 (2) | 6.36 (2) | 6.38 (2) |
| $H_7$ | 8.13 (2) | 8.08 (2) | 8.03 (2) | 8.12 (2) | 8.17 (2) |
| $CH_3$–Si | 9.59 (9) | 9.82 (9) | 9.87 (9) | 9.70 (6)[e] | 9.92 (6)[e] |
| Other | ... | $C_2H_5$ | $CH_3CO$ | $C_6H_5$ | ... |
| | | 5.82 (quart., 2) | 7.81 (3) | ~7.17 (5) | |
| | | 8.07 (trip., 3) | | | |
| $J_{3,4}$ | 3.0 | ... | ... | 2.8 | 2.4[f] |
| $J_{3,1}$ | 0.9 | ... | ... | 1.0 | 1.4[f] |
| $J_{5,6}$ | c | 5.2 | 5.3 | c | c |
| $J_{5,4} = J_{6,1}$ | 2.2 | 2.8 ± 0.2 | 2.6 ± 0.2 | 2.1 | 2.0 |
| $J_{5,1} = J_{6,4}$ | 1.7 | 1.1 ± 0.2 | 1.3 ± 0.3 | 1.9 | 1.9 |
| $J_{7,1} = J_{7,4}$ | 1.6 | 1.6 | 1.5 | 1.5 | 1.5 |
| $J_{7a,7c}$ | 6.0 | d | d | d | d |

[a] Measurements on 30% $CCl_4$ solutions; TMS as internal standard. Multiplicity of lines is apparent from spectra in Figure 1; $\tau$ in parts per million (area). [b] $J$ values are approximately ±0.1 cps except as indicated. [c] Chemical shifts of H-5 and H-6 are equal. [d] Chemical shifts of H-$7_a$ and H-$7_c$ are equal. [e] 1:1 doublet for **4** and 1:2:1 triplet for **6**; see text. [f] Estimated from poorly resolved quartet.

bridge protons in any of the norbornadiene derivatives, although such coupling has been noted in 7-substituted norbornadiene systems.[6] Second, a most striking feature in the spectra of both **2** and **3** is a symmetrical 16-line signal for H-5 and H-6. A spin-decoupled spectrum of **3** was obtained and the collapse of the $\tau$ 3.23 signal to an AB quartet was complete upon irradiation at the relative position of the bridgehead proton signals at $\tau$ 6.05. This is shown as an insert in Figure 1 from which $J_{5,6} = 5.3 \pm 0.1$ cps is readily obtained. The central pair of lines in each of the inner four line groups was not resolved when the pure liquid was examined; only upon dilution with carbon tetrachloride were these lines resolved as shown in Figure 1. A first-order calculation of the pattern expected for the AB protons of an ABXY system with $J_{XY} = 0$ requires that four pairs of lines in each of the A and B parts of the signal be separated by $J_{AB}$. This requirement is very nearly fulfilled for **2**, but less so for **3**. Most probably these apparent but reproducible deviations are primarily a result of solvent effects. The highly symmetrical nature of the signal arises from an equivalence of the pairs of coupling constants $J_{1,6} = J_{5,4}$ and of $J_{1,5} = J_{6,4}$.

The third feature in these spectra worth mentioning is the multiplet nature of the signals for the silicon methyl protons for **4** and **6**.

For **4**, this signal appears as a doublet at $\tau$ 9.70 with a separation of 1.5 cps. The Si–$CH_3$ resonance in **6** appears as a 1:2:1 triplet at $\tau$ 9.92 with a separation of 1.2 cps. We feel that this anomalous splitting arises as a result of intrinsic diastereoisomerism.[7,8] Compound **4** is a mixture of *d* and *l* isomers. In each of these isomers the two methyl groups bonded to silicon are affected by different electromagnetic fields and as such should exhibit different chemical shifts as was noted for isopropyl mandelate.[8]

Unfortunately, the isomeric distribution between the *meso* and optical isomers of **6** is not known. However, if no separation was achieved in the purification steps the composition would still be 50% *meso* and 25% each for the *dd* and *ll* isomers. The two optically active isomers should be pmr equivalent. Whether the two methyl groups in the *meso* or in each of the optical isomers will be differentiated by intrinsic diastereoisomerism is not known at this time; however, differentiation should occur theoretically in one of these types of isomer and not in the other. In either event, if the two types of isomers are present in equal amounts the methyl resonances for the mixture should then consist of a doublet and of a singlet whose chemical shift is the average of the chemical shifts of the lines of the doublet. This is in agreement with the observed spectrum. Further investigations on materials of known isomer distribution are planned to clarify this point.

The infrared spectra of the new compounds reported here do not reveal anything unusual. The wave numbers of the stretching modes for the unsaturated bonds are listed in Table II.

**Bicyclo[2.2.1]heptenes.**—Each of the compounds **1**, **2**, and **3** was hydrogenated over a 5% palladium-on-carbon catalyst to the corresponding bicyclo[2.2.1]-hept-2-ene derivative **9**, **10**, and **11**. The identification of these compounds is based on both pmr (Table III) and infrared data (Table II). Compound **9** has been synthesized by an alternate route[9] and the pmr spec-

---

(6) P. Laszlo and P. von Ragué Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964).

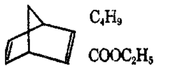
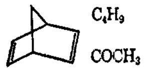
(7) M. Raban, *Tetrahedron Lett.*, 3105 (1966).

(8) M. Raban and K. Mislow, *ibid.*, 3961 (1966).

(9) H. G. Kuivila and C. R. Warner, *J. Org. Chem.*, **29**, 2845 (1964).

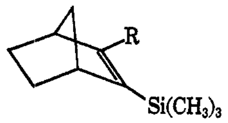
TABLE II

INFRARED BANDS OF BICYCLO COMPOUNDS[a]

| Compound | $\nu_{C=O}$ | $\nu_{C=C}$ |
|---|---|---|
| **1** | . . . | 1575 w, 1541 m |
| **2** | 1710 s | 1582 w, 1550 m |
| **3** | 1675 s | 1574 w, 1538 m |
| **4** | . . . | 1570 w, 1532 m |
| **6** | . . . | 1571 w, 1539 m |
|  | 1708 s | 1625 m, 1555 w |
|  | 1718 s | 1625 m, 1555 w |
| **9** | . . . | 1563 m |
| **10** | 1705 s | 1570 m |
| **11** | 1678 s | 1570 m |

[a] Approximately 10% in $CCl_4$.

trum obtained here agrees with that reported earlier.[9] Products **10** and **11** are assigned their respective structures on the basis of an absence of pmr signals in the vinyl proton region and the general similarity of their spectra to that of compound **9**. In addition, an infrared band is noted near 1570 cm$^{-1}$ for each of these compounds in agreement with previous observations on norbornene derivatives.[9]



**9**, R = H
**10**, R = $COOC_2H_5$
**11**, R = $COCH_3$

TABLE III

BICYCLO[2.2.1]HEPT-2-ENE COMPOUNDS. PROTON MAGNETIC RESONANCE DATA

| | **9** | **10** | **11** |
|---|---|---|---|
| $H_3$ | 3.73 (2)[a] | . . . | . . . |
| $H_1$, $H_4$ | 7.05, 7.13 (2)[b] | 6.75, 6.83 (2)[b] | 6.80 (2) |
| $H_5$, $H_6$, $H_7$ | 8.3–9.2[c] | 8.1–9.2[c] | 8.1–9.2[c] |
| $CH_3$–Si | 9.95 (9)[d] | 9.83 (9)[d] | 9.88 (9)[d] |
| Other | . . . | $C_2H_5O$<br>8.79 (3)<br>9.83 (4) | $CH_3CO$<br>7.82 (3)[d] |

[a] Doublet, $J_{3,4}$ = 2.8 cps; $\tau$ in parts per million (area). [b] Overlapping unresolved multiplets. [c] Complex. [d] Sharp singlet.

## Experimental Section

**General Comments.**—Infrared spectra were recorded as 5–10% solutions in carbon tetrachloride on a Perkin-Elmer Model 21 spectrophotometer. Proton magnetic resonance spectra (pmr) of 25–30% solutions in carbon tetrachloride were recorded on a Varian A-60 spectrophotometer. Tetramethylsilane was employed as an internal standard.

The hydrogenations were carried out with a standard atmospheric pressure apparatus. Electrolytic grade hydrogen, purchased from the Matheson Co., was used. The catalyst, 5% palladium on carbon, was obtained from Matheson Coleman and Bell, East Rutherford, N. J.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Professor V. B. Fish, Lehigh University.

**General Synthetic Procedure for Bicyclo[2.2.1]heptadiene Compounds.**—Cyclopentadiene, obtained by thermal cracking of dicyclopentadiene, was collected at liquid nitrogen temperature and was used immediately to minimize dimerization. Appropriate amounts of cyclopentadiene and the alkynylsilane, the syntheses of which have been reported elsewhere,[10] were placed in a stainless steel bomb of 150- or 300-ml capacity (Matheson Co., East Rutherford, N. J.) together with dry benzene as a diluent. The bomb was sealed and heated in an oven. At the end of the reaction period, the bomb was emptied and flushed with clean solvent. After evaporation of the solvent at aspirator vacuum, the residue was fractionally distilled under aspirator or high vacuum.

**2-Trimethylsilylbicyclo[2.2.1]heptadiene, 1.**—A mixture of 13 g (0.20 mol) of cyclopentadiene, 20 g (0.20 mol) of trimethylethynylsilane, and 100 ml of dry benzene was heated for 50 hr at 270°. The yield of **1** was 29 g (87%): bp 58.5–59.5° (18 mm).

*Anal.* Calcd for $C_{10}H_{16}Si$: C, 73.17; H, 9.76. Found: C, 72.99; H, 10.04.

The same amounts of materials at 180° for 50 hr yielded only 3.3 g (10%) of the product.

**2-Trimethylsilyl-3-ethylcarboxylatobicyclo[2.2.1]heptadiene, 2.**—A mixture of cyclopentadiene (3.2 g, 0.048 mol), ethyl 3-trimethylsilylpropynoate (8.2 g, 0.048 mol), and 30 ml of dry benzene was heated for 24 hr at 190°. Vacuum distillation yielded 7.4 g (66%) of **2** as a clear liquid: bp 133.5–135° (21 mm).

*Anal.* Calcd for $C_{13}H_{20}O_2Si$: C, 66.10; H, 8.48. Found: C, 66.28; H, 8.33.

**2-Trimethylsilyl-3-acetylbicyclo[2.2.1]heptadiene, 3.**—Cyclopentadiene (6.6 g, 0.10 mol), 1-trimethylsilylbutyn-3-one (17 g, 0.10 mol), and 60 ml of dry benzene were heated together for 12 hr at 180°. Distillation under vacuum gave 18 g (89%) of **3**: bp 116–117.5° (16 mm).

*Anal.* Calcd for $C_{12}H_{18}OSi$: C, 69.85; H, 8.74. Found: C, 69.58; H, 8.54.

**2-(Phenyldimethylsilyl)bicyclo[2.2.1]heptadiene, 4.**—The reaction between 3.3 g (0.050 mol) of cyclopentadiene and 8.0 g (0.050 mol) of phenyldimethylethynylsilane in 60 ml of benzene was carried out at 250° for 72 hr. The yield of **4** as a clear colorless liquid was 6.1 g (54%): bp 92–94° (0.38 mm).

*Anal.* Calcd for $C_{15}H_{18}Si$: C, 79.65; H, 7.99. Found: C, 79.36; H, 8.11.

**Attempted Preparation of 2-[Dimethyl(ethynyl)silyl]bicyclo[2.2.1]heptadiene, 5.**—A mixture of 3.3 g (0.050 mol) of cyclopentadiene and 5.4 g (0.050 mol) of dimethyldiethynylsilane in 60 ml of benzene was heated at 270° for 72 hr. A mixture of products amounting to 5.1 g was obtained as a clear liquid: bp 71–77° (0.025 mm). Glpc analysis of this liquid with an SF-96 silicon oil on Chromosorb P column indicated that at least two materials were present in a 60:40 ratio. The material which comprised 40% of the mixture appeared to be **6** from a comparison of its retention time with that of a pure sample.

An attempt to obtain a purer sample of the larger component of the product mixture was made by glpc on a preparative size (5 ft × $^3/_8$ in.) glpc column of SF-96 on Chromosorb P. The separation was difficult and yielded a material of about 80% apparent purity. An infrared spectrum of this sample in carbon tetrachloride revealed two bands at 3295 and 2056 cm$^{-1}$, characteristic of the SiC≡CH group, several bands characteristic of the bicyclo[2.2.1]heptadienyl moiety, and a band at 1250 cm$^{-1}$, characteristic of the $SiCH_3$ group were observed. A pmr spectrum of this mixture (30% in carbon tetrachloride) contained a sharp singlet at $\tau$ 7.60, also indicative of an acetylenic proton. Although the spectral evidence clearly indicates the presence of the SiC≡CH group in this mixture, no positive identification as **5** can be made.

**Dimethylsilylbis(2-bicyclo[2.2.1]heptadiene) or Dimethylbis-(2-bicyclo[2.2.1]heptadienyl)silane, 6.**—Cyclopentadiene (6.6 g, 0.10 mol), dimethyldiethynylsilane (5.4 g, 0.050 mol), and 35 ml of dry benzene were heated together for 48 hr at 250°. The reaction yielded 5.8 g (48%) of **6**: bp 64–66° (0.020 mm).

*Anal.* Calcd for $C_{16}H_{20}Si$: C, 80.00; H, 8.33. Found: C, 79.64; H, 8.55.

**Phenylmethylbis-[(2,3,4,5-tetraphenyl)phenyl]silane.**—A mixture of 1.7 g (0.010 mol) of phenylmethyldiethynylsilane and 7.5 g (0.020 mol) of 2,3,4,5-tetraphenylcyclopentadienone (Aldrich Chemical Co.) in 50 ml of xylene was heated at reflux with stirring for 104 hr. The xylene was removed by distillation. The purple solid which remained was taken up in 30 ml of diethyl ether. The solution was then stirred briefly with 1.0 g of char-

---

(10) C. S. Kraihanzel and M. L. Losee, *J. Organometal. Chem.*, **10**, 427 (1967).

coal and filtered. Addition of 10 ml of ethanol followed by 10 ml of methylene chloride to the filtrate caused white crystals to form. Recrystallization of this solid from a 1:1:1 mixture of diethyl ether, ethanol, and methylene chloride (total volume, 30 ml) gave 7.0 g (79%) of the desired product: mp 285–286.5°.

*Anal.* Calcd for $C_{67}H_{50}Si$: C, 91.10; H, 5.70. Found: C, 90.80; H, 5.77.

An infrared spectrum as a 15% solution in carbon tetrachloride showed bands characteristic of the phenyl groups and of the $SiCH_3$ group (1250 $cm^{-1}$). No band was observed which would be indicative of a carbonyl group.

**Diphenylbis-[(2,3,4,5-tetraphenyl)phenyl]silane.**—A mixture of 1.2 g (0.050 mol) of diphenyldiethynylsilane, 3.7 g (0.010 mol) of 2,3,4,5-tetraphenylcyclopentadienone, and 50 ml of xylene was allowed to reflux for 72 hr. The product, obtained by exactly the same method as was employed in the previous experiment, amounted to 2.8 g (59%): mp 283–284°.

*Anal.* Calcd for $C_{72}H_{52}Si$: C, 91.50; H, 5.50. Found: C, 91.34; H, 5.60.

An infrared spectrum of this product in a 15% solution in carbon tetrachloride displayed no carbonyl stretching band.

**Ethyl 3-Trimethylsilylpropynoate.**—To a solution of 0.15 mol of ethylmagnesium bromide in 125 ml of dry THF, prepared from 16 g (0.15 mol) of ethyl bromide and 3.7 g (0.15 mol) of magnesium, was added 14 g (0.14 mol) of trimethylethynylsilane. After frothing caused by the evolution of ethane had subsided, the solution was transferred to a 250-ml pressure-equalizing dropping funnel from which it was added slowly to a solution of 22 g (0.20 mol) of ethyl chloroformate in 250 ml of THF at 0°. This mixture was allowed to stir at 0° for 3 hr. The solution, from which magnesium halides had begun to precipitate, was poured into 300 ml of distilled water. The organic layer was separated and retained. The aqueous layer was extracted several times with 50-ml portions of diethyl ether. The organic layers were combined, dried ($MgSO_4$), and filtered. After evaporation of the solvents under aspirator vacuum, the liquid residue was distilled giving 13 g (53%) of a colorless liquid: bp 83–85° (16 mm) [lit.[11] bp 92–96° (28 mm)].

*Anal.* Calcd for $C_8H_{14}SiO_2$: C, 56.50; H, 8.25. Found: C, 56.53; H, 8.49.

**1-Trimethylsilylbutyn-3-one.**—A solution of 0.30 mol of ethylmagnesium bromide in 200 ml of THF was prepared in the usual manner. To this was added 29 g (0.30 mol) of trimethylethynylsilane. The solution was transferred to a 250-ml pressure equalizing dropping funnel and added to 24 g (0.35 mol) of acetyl chloride in 250 ml of THF at 0°. After the mixture had been allowed to stir at 0° for 3 hr, the solution was poured into 500 ml of distilled water. The product was obtained by a method similar to that employed in the previous experiment. Vacuum distillation of the crude product gave 25 g (60%) of a clear colorless liquid: bp 72–74° (16 mm) [lit.[12] bp 156°].

*Anal.* Calcd for $C_7H_{12}SiO$: C, 60.00; H, 8.67. Found: C, 60.18; H, 8.75.

**2-Trimethylsilylbicyclo[2.2.1]hept-2-ene, 9.**—A mixture of 2-trimethylsilylbicyclo[2.2.1]heptadiene (0.020 mol, 2.5 g) and 100 mg of 5% Pd/C catalyst in 50 ml of ethyl acetate absorbed 350 ml of hydrogen when it was maintained under a slight positive pressure of the gas. The solution was filtered and the filtrate was concentrated by evaporation at aspirator pressure. The residue was distilled to give 2.4 g (94%) of a clear liquid: bp 53–54° (13 mm) [lit.[9] bp 30° (0.60 mm)].

*Anal.* Calcd for $C_{10}H_{18}Si$: C, 72.21; H, 10.91. Found: C, 72.40; H, 10.97.

**2-Trimethylsilyl-3-ethylcarboxylatobicyclo[2.2.1]hept-2-ene, 10.**—2-Trimethylsilyl-3-ethylcarboxylatobicyclo[2.2.1]heptadiene (0.010 mol, 2.4 g) in 75 ml of ethyl acetate was hydrogenated (250 ml of hydrogen) in the presence of 100 mg of 5% Pd/C. The crude product yielded 1.7 g (70%) of clear liquid, bp 123–125° (16 mm), which was at least 99% pure by glpc analysis.

*Anal.* Calcd for $C_{13}H_{22}SiO_2$: C, 65.49; H, 9.30. Found: C, 65.37; H, 9.50.

**2-Trimethylsilyl-3-acetylbicyclo[2.2.1]hept-2-ene, 11.**—2-Trimethylsilyl-3-acetylbicyclo[2.2.1]heptadiene (0.010 mol, 2.1 g), 100 mg of 5% Pd/C, and 50 ml of ethyl acetate were treated with hydrogen (260 ml) as above. Distillation of the crude product after filtration and removal of solvent by evaporation at aspirator pressure gave 1.9 g (92%) of a clear liquid, bp 115–116° (16 mm).

**Ethyl 2-Hexynoate.**—A solution of ethylmagnesium bromide (0.32 mol) was prepared in 225 ml of THF and 25 g (0.20 mol) of 1-hexyne in 30 ml of THF was added. After ethane evolution had stopped, the resultant solution was added to 36 g (0.33 mol) of ethyl chloroformate in 300 ml of THF at 0°. Stirring was continued at 0° for 4 hr. The solution was then poured into 500 ml of distilled water and extracted with ether. Distillation of the liquid residue after evaporation of the ether at aspirator vacuum gave 34 g (74%) of a clear liquid: bp 101.5–103.5° (15 mm) [lit.[13] bp 74–75° (3 mm)].

**2-*n*-Butyl-3-(ethylcarboxylato)bicyclo[2.2.1]heptadiene.**—A mixture of 8.5 g (0.13 mol) of cyclopentadiene and 19.7 g (0.13 mol) of ethyl 2-hexynoate in 200 ml of dry benzene was heated at 195° for 24 hr. After removal of the benzene by evaporation at aspirator vacuum, the crude product was vacuum distilled to give 18 g (64%) of the desired product: bp 67–69° (0.14 mm).

*Anal.* Calcd for $C_{14}H_{20}O_2$: C, 82.31; H, 9.44. Found: C, 82.11; H, 9.48.

**Registry No.**—**1,** 16205-92-8; **2,** 16205-82-6; **3,** 16205-83-7; **4,** 16223-70-4; ethyl 3-trimethylsilylpropynoate, 16205-84-8; **6,** 16205-93-9; **7,** 16205-85-9; **8,** 16205-86-0; **9,** 16205-87-1; **10,** 16205-94-0; **11,** 16205-88-2; 1-trimethylsilylbutyn-3-one, 5930-98-3; ethyl 2-hexynoate, 16205-90-6; 2-*n*-butyl-3-(ethylcarboxylato)bicyclo-[2.2.1]heptadiene, 16205-91-7.

**Acknowledgment.**—The National Science Foundation is to be acknowledged for funds to support this work (GP-6245) and for the purchase of the nuclear magnetic resonance spectrometer.

---

[11] G. E. Bennett and W. E. Lee, U. S. Patent 2,887,371 (1960); *Chem. Abstr.*, **53**, 19883*h* (1961).

[12] L. Birkofer, A. Ritter, and H. Uhlenbrauk, *Ber.*, **96**, 3280 (1963).

[13] S. Ishikawa and E. Yamamoto, *Rept. Sci. Research Inst.*, **28**, 50 (1952); *Chem. Abstr.*, **47**, 3231*e* (1953).