Traces of blue solid, probably octabromofulvalene, were observed in some of the above reactions. When solutions of **6** in hexane were chromatographed on acid-washed alumina, a blue band was observed to form. Elution gave green solutions containing small amounts of **8**, mp 170° dec, identical with the material described below.

Reductive Coupling of Hexabromocyclopentadiene by Metals. The 1:1 Complex of 2 and 6 (7). In a typical reaction, 10.8 g (0.020 mol) of **2** was dissolved in 200 ml of solvent (benzene, ether, or petroleum ether (bp 30–60°)). An equivalent amount of metallic copper, zinc, magnesium, or zinc–copper couple was added, and the mixtures were refluxed for periods ranging from 6 to 18 hr. After this period, the organic solutions were separated from the inorganic material by filtration, evaporated to a volume of 15 to 20 ml, and chromatographed on columns packed with silicic acid or silica gel. The solvent sequence hexane–carbon tetrachloride–ether was used for all separations. The results are summarized in Table III. In several reactions, after recovered starting material was eluted, fractions were obtained which gave orange crystals of the 1:1 complex **7**. This material had mp 108–109° and was not separated into its components by fractional crystallization. The infrared spectrum showed all of the bands found for **2** and **6**.

Anal. Calcd for $C_{15}Br_{16}$: C, 12.35; Br, 87.6. Found: C, 12.50; Br, 86.5.

The same 1:1 crystalline complex, mp 110–111°, was obtained by crystallizing solutions of equivalent amounts of **2** and **6** from hexane.

Octabromofulvalene (8). In 25 ml of 1,2-dimethoxyethane was dissolved 10.8 g (0.020 mol) of **2**. Water (2 ml) was added, and the mixture was cooled to −80° with stirring, then 5.75 g (0.040 mol) of copper(I) bromide was introduced. The mixture was allowed to warm slowly. Near 0° the water melted and the mixture turned dark green. The CuBr dissolved in 3–5 min at 0°, and a purple precipitate formed. The mixture was immediately filtered, and the purple solid was purified by chromatography on silicic acid in a 1:1 hexane–chloroform solution, yield 0.50 g (6.6%) of **8** as dark blue crystals, mp 170° dec.

Anal. Calcd for $C_{10}Br_8$: C, 15.8; H, 0.00; Cl, 0.00; Br, 84.2. Found: C, 15.95; H, 0.00; Cl, 0.00; Br, 82.9.

The infrared spectrum of **8** is given in Table II and Figure 1. The electronic spectrum is shown in Figure 2; ν_{max}, cm^{-1} (log ϵ): 45,240 (4.32); 24,150 (4.67); and 15,690 (2.37).

Acknowledgments. The authors thank the National Science Foundation and the U. S. Public Health Service for financial support.

Ethynylsilanes. IV. The Effect of Temperature on the Diels–Alder Addition of Acetylenic Dienophiles to 1-Trimethylsilylcyclopentadiene

Charles S. Kraihanzel and M. L. Losee

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Abstract: Dimethyl acetylenedicarboxylate was treated with 1-trimethylsilylcyclopentadiene to yield a mixture of 7-trimethylsilyl- and 5-trimethylsilyl-2,3-bis(methylcarboxylato)bicyclo[2.2.1]heptadienes. Thermal isomerization of the 7-trimethylsilyl derivative to the 5-trimethylsilyl isomer was shown not to occur. Reactions between $(CH_3)_3SiC{\equiv}CR$, where R is H, $COCH_3$, or $CO_2C_2H_5$, and 1-trimethylsilylcyclopentadiene were carried out at 180–260°, and only vinyl-substituted derivatives were obtained. It is suggested that 1-trimethylsilylcyclopentadiene undergoes temperature-dependent tautomerism, which may be viewed as a 1,3-proton shift, to form 3-trimethylsilylcyclopentadiene. The reactions between the various dienophiles and this tautomeric form of the diene would be expected to yield the products observed at the high temperature.

We have shown that 2-organosilylnorbornadienes may be obtained from the cycloaddition of alkynylsilanes to cyclopentadiene.[1] In a continuance of our studies on organometallic acetylenes and bicyclo systems we wished to synthesize some 7-organosilyl- and 2,7-bis(organosilyl)bicyclo[2.2.1]heptadienes. 1-Trimethylsilylcyclopentadiene seemed to be an ideal diene for these reactions. However, when the Diels–Alder reactions between 1-trimethylsilylcyclopentadiene and several acetylenes and alkynylsilanes were carried out, the products were found to be 2-organosilylbicyclo[2.2.1]heptadienes and mixtures of 2,5- and 2,6-bis(organosilyl)bicyclo[2.2.1]heptadienes. The results of these reactions and a possible mechanism whereby these unexpected products arise are discussed in this paper.

Experimental Section

General. The preparations of the alkynylsilanes employed in the following experiments have been reported elsewhere.[1] The high-temperature Diels–Alder reactions were carried out in a 150-ml stainless steel bomb purchased from the Matheson Company, East Rutherford, N. J.

Infrared spectra were recorded as 5–10% solutions in carbon tetrachloride on a Perkin-Elmer Model 21 spectrophotometer. Proton magnetic resonance spectra (nmr) were recorded on 30% solutions in carbon tetrachloride on a Varian A-60 spectrophotometer. Tetramethylsilane was used as an internal standard.

An Aerograph Model 221 gas chromatograph was employed for both analytical and preparative purposes (glpc). A stainless steel column (5 ft; 1/4 in. in diameter) packed with 20% SF-96 silicone oil on Chromosorb P was employed. Separations were effected on an aluminum column (5 ft; 3/8 in. in diameter) filled with the same material. The carrier gas was helium. Approximate instrument temperatures for analyses and separation were as follows: column, 225°; injector, 280°; detector, 300°. The maximum sample size used in the preparative work was 0.5 ml. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

1-Trimethylsilylcyclopentadiene. Freshly distilled cyclopentadiene (33 g; 0.50 mol) was added dropwise during 0.5 hr to a stirred mixture of 12 g (0.50 mol) of sodium sand in 150 ml of THF. The reaction mixture was allowed to stir for 3 hr at room temperature. After this time, 54 g (0.50 mol) of trimethylchlorosilane was added dropwise over 1 hr and stirring was continued for 3 hr. The reaction mixture was poured into 150 ml of cold, distilled water and the

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[1] C. S. Kraihanzel and M. L. Losee, *J. Org. Chem.*, **33**, 1983 (1968).

organosilicon product was extracted into ether. The ethereal extract was concentrated by evaporation under aspirator vacuum, and the residue was vacuum distilled to give 50 g (73%) of 1-trimethylsilylcyclopentadiene, bp 41–43° (16 mm) [lit.[2] bp 32° (12 mm)].

Reaction of 1-Trimethylsilylcyclopentadiene with Trimethylethynylsilane. 1-Trimethylsilylcyclopentadiene (6.9 g, 50 mmol), trimethylethynylsilane (4.9 g, 50 mmol), and 60 ml of benzene were heated at 260° for 52 hr. The resultant pale yellow solution was evaporated under aspirator vacuum to remove benzene. Glpc analysis of the crude product showed the presence of two species in a 3:1 ratio. Vacuum distillation gave 8.7 g (82%) of the mixture of products, bp 105–106° (16 mm).

A separation of the components of the distilled mixture was effected by glpc. The major component comprised 74% of the mixture and had the shorter retention time. *Anal.* Calcd for $C_{13}H_{24}Si_2$: C, 66.10; H, 10.17. Found: C, 66.29; H, 10.38. This fraction was a clear, colorless liquid which, after standing in the refrigerator, solidified to a white solid, mp 25.5–26.0°. This component was identified as 2,5-bis(trimethylsilyl)bicyclo[2.2.1]heptadiene (**1a**) from its nmr spectrum.

The second component, comprising 26% of the total yield of the mixture, was obtained as a colorless liquid which did not crystallize. It was identified as 2,6-bis(trimethylsilyl)bicyclo[2.2.1]heptadiene (**2b**). *Anal.* Calcd for $C_{13}H_{24}Si_2$: C, 66.10; H, 10.17. Found: C, 66.40; H, 10.43.

Reaction of 1-Trimethylsilylcyclopentadiene with Ethyl 3-Trimethylsilylprop-2-ynoate. A mixture of 6.8 g (40 mmol) of ethyl 3-trimethylsilylprop-2-ynoate, 5.5 g (50 mmol) of 1-trimethylsilylcyclopentadiene, and 60 ml of benzene was heated at 180° for 20 hr. A gas chromatogram of the residue left after removal of benzene under aspirator vacuum showed the presence of two species in the ratio of about 5:1. Distillation of this liquid gave 8.2 g (67%) of a mixture of products, bp 78–80° (0.08 mm).

The distilled mixture was separated by preparative glpc. The major product which was a clear, colorless liquid had the shorter retention time and comprised 84% of the mixture. *Anal.* Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.34; H, 9.09. Found: C, 62.20; H, 9.11. This was identified as 2,5-bis(trimethylsilyl)-3-ethylcarboxylatobicyclo[2.2.1]heptadiene (**2a**).

The minor product, 16% of the mixture, was also obtained as a clear colorless liquid. *Anal.* Calcd for $C_{16}H_{28}O_2Si_2$: C, 62.34; H, 9.09. Found: C, 62.48; H, 9.18. The substance was shown to be 2,6-bis(trimethylsilyl)-3-ethylcarboxylatobicyclo[2.2.1]heptadiene (**2b**).

Reaction of 1-Trimethylsilylcyclopentadiene with 1-Trimethylsilylbut-2-yn-3-one. A mixture of 7.0 g (50 mmol) of 4-trimethylsilylbut-3-yn-2-one, 6.9 g (50 mmol) of 1-trimethylsilylcyclopentadiene, and 60 ml of dry benzene was heated at 190° for 20 hr in the sealed bomb. The reaction mixture was concentrated under aspirator vacuum, and the presence of two species in the residue in an approximate ratio of 3:1 was indicated by glpc. Vacuum distillation of this residue gave 10 g (73%) of a mixture, bp 75–76° (0.06 mm).

Separation of the mixture was effected by glpc. The major product, which comprised 75% of the total yield, was a clear, colorless liquid and had the shorter retention time. *Anal.* Calcd for $C_{15}H_{27}OSi_2$: C, 64.75; H, 9.35. Found: C, 65.06; H, 9.38. This first isomer was identified as 2,5-bis(trimethylsilyl)-3-acetylbicyclo[2.2.1]heptadiene (**3a**).

The minor product comprised 25% of the mixture and also was a colorless liquid. *Anal.* Calcd for $C_{15}H_{27}OSi_2$: C, 64.75; H, 9.35. Found: C, 64.82; H, 9.28. This substance was shown to be 2,6-bis(trimethylsilyl)-3-acetylbicyclo[2.2.1]heptadiene (**3b**).

Reactions of 1-Trimethylsilylcyclopentadiene with Dimethyl Acetylenedicarboxylate. **1.** To 6.9 g (50 mmol) of 1-trimethylsilylcyclopentadiene was added with stirring 7.1 g (50 mmol) of dimethyl acetylenedicarboxylate as one amount at room temperature. After approximately 5 min, the reaction mixture became hot. Stirring was continued for 20 min. The mixture was analyzed by glpc, and the formation of two products in a 1:2 ratio was evident. Distillation of this material gave 10 g (71%) of a mixture, bp 101–103° (0.020 mm).

Separation of these two components as clear, colorless liquids was effected by glpc. The component with the shorter retention time comprised 35% of the mixture. *Anal.* Calcd for $C_{14}H_{20}O_4Si$: C, 60.00; H, 7.14. Found: C, 60.07; H, 7.25. The second component amounted to 65% of the mixture. *Anal.* Calcd for $C_{14}H_{20}O_4Si$: C, 60.00; H, 7.14. Found: C, 59.77; H, 7.22.

The first component was identified as 2,3-bis(methylcarboxylato)-5-trimethylsilylbicyclo[2.2.1]heptadiene (**4a**). The second component was found to be 2,3-bis(methylcarboxylato)-7-trimethylsilylbicyclo[2.2.1]heptadiene (**4c**).

2. To a refluxing solution of 6.9 g (50 mmol) of 1-trimethylsilylcyclopentadiene in 25 ml of xylene was added dropwise 7.1 g (50 mmol) of dimethyl acetylenedicarboxylate. After heating at reflux (140°) for 30 min the solution was cooled to room temperature. The reaction mixture was analyzed by glpc and found to have a 2:1 product distribution of **4a** to **4c**. The components of the mixture were identified by comparison of retention times with those of known samples.

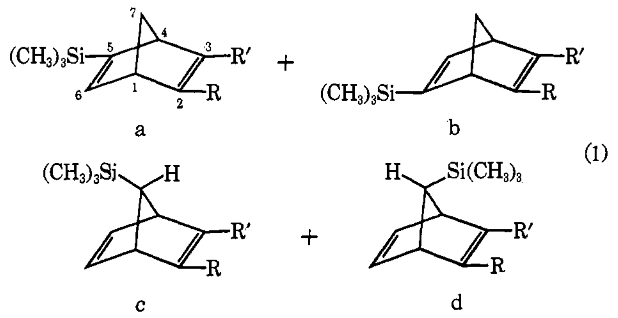
3. To 1.0 g (7.3 mmol) of 1-trimethylsilylcyclopentadiene in 15 ml of benzene was added dropwise 1.0 g (7.3 mmol) of dimethyl acetylenedicarboxylate while the solution was stirred at 16°. After the reaction had run for 10 hr, the mixture was analyzed by glpc. A 1:4 product distribution of **4a** to **4c** was found.

4. To a solution of 1.0 g (7.3 mmol) of 1-trimethylsilylcyclopentadiene in 15 ml of toluene at 0° was added with stirring 1.0 g (7.3 mmol) of dimethyl acetylenedicarboxylate. After a reaction time of 10 hr at 0° a 1:9 product distribution of **4a** and **4c** was observed.

Results and Discussion

An acetylenic dienophile RC≡CR′ would be expected to add to 1-trimethylsilylcyclopentadiene to yield the *syn*- and *anti*-7-trimethylsilylbicyclo[2.2.1]heptadienes, structures c and d in reaction 1.

$$C_5H_5Si(CH_3)_3 + R-C\equiv C-R' \longrightarrow$$



(1)

However, under the conditions (180–260° in a sealed bomb) necessary to effect addition of the alkynylsilanes $(CH_3)_3SiC\equiv CR'$, where R′ is H, $COCH_3$, or $COOC_2H_5$, to 1-trimethylsilylcyclopentadiene no detectable amount of any 7-trimethylsilylbicyclo[2.2.1]heptadiene derivative was found. Instead, the isolated products were found to be mixtures of the isomers represented by structures a and b in reaction 1. The isomers were identified mainly from their nmr spectra as discussed in the next section. The isomer distribution of the products in each reaction is shown in Table I. The

Table I. Product Distribution (Relative Percentages) from Diels–Alder Reactions between $R-C\equiv C-R'$ and $(CH_3)_3SiC_5H_5$

Compd	R	R′	Temp, °C	a	b	c
1	$(CH_3)_3Si$	H	260	74	26	..
2	$(CH_3)_3Si$	$COOC_2H_5$	180	84	16	..
3	$(CH_3)_3Si$	$COCH_3$	190	75	25	..
4	CH_3O_2C	CO_2CH_3	0	10[a]	..	90
			16	20	..	80
			Room temp[b]	35	..	65
			140[c]	65	..	35

[a] **4a** and **4b** have the same structure. [b] Reaction started at room temperature and temperature allowed to rise naturally from the heat of reaction. [c] Addition of the dienophile to 1-trimethylsilylcyclopentadiene in refluxing xylene.

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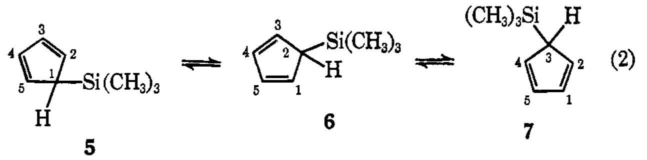
[2] H. P. Fritz and C. G. Kreiter, *J. Organometal. Chem.* (Amsterdam), 4, 313 (1965).

isomer listed as **a** in each of these cases was found to predominate over **b** and was the first eluted from the glpc column.

Dimethyl acetylenedicarboxylate is an extremely reactive dienophile and as is shown in Table I reacts with 1-trimethylsilylcyclopentadiene even at 0° in a dilute toluene solution. Notably different from the reactions with the alkynylsilanes as outlined above, dimethyl acetylenedicarboxylate was found to yield varying amounts of the norbornadiene derivative **4c** depending upon the temperature of the reaction. At low temperature a high proportion of **4c** was obtained in the product mixture, while at higher temperatures a much higher proportion of **4a**, which is equivalent to **4b** with this dienophile, was obtained. The percentage of **4a** in the product mixture obtained at 140° is about 65% and may be compared to effectively exclusive formation of the vinylsilane structures with the alkynylsilanes. The possibility that **4a** and **4c** might be thermally interconvertible was eliminated as an isolated sample of **4c** was found to undergo no isomerization after heating at 140° for 24 hr as shown by nmr. Furthermore, the fact that some **4a** was formed even at 0° would also suggest that the **4a** must not arise from a simple isomerization of **4c**.

Unfortunately, without pure samples of the unknown compounds **1c**, **2c**, or **3c**, no test can be made that would ensure that these are not precursors to the isomers with general structures a and b.

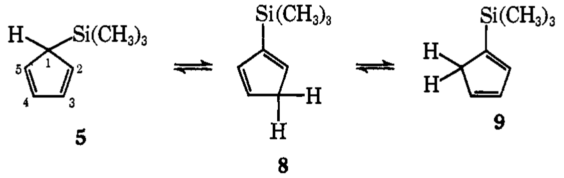
As has been explained above, the formation of only a single 7-trimethylsilylnorbornadiene derivative in the several reactions of 1-trimethylsilylcyclopentadiene with acetylenic dienophiles is unexpected from a classical understanding of the Diels–Alder reaction mechanism. However, we feel that these apparent anomalies are not the result of any deviation from the normally proposed 1,4-addition mechanism. Instead, we suggest that the culprit in this reaction is the 1-trimethylsilylcyclopentadiene. For some time now, the nmr spectrum of 1-trimethylcyclopentadiene has been known to be temperature dependent.[2] Distinguishable nmr signals for the olefinic and tertiary ring protons are seen at or below room temperature, verifying the presence of the σ-C_5H_5 group. At higher temperatures, these two resonance signals merge initially into a single broad signal of intermediate frequency and finally become a sharp singlet. This effect has been explained in terms of a temperature-dependent migration of the silicon atom about the C_5H_5 ring in a series of 1,2 and/or 1,3 shifts at such a rate that apparent proton equivalence results. This process is illustrated by the proposed interconversion of **5**, **6**, and **7** as shown in reaction 2.



(2)

An important feature of this previously proposed temperature-dependent process is the structural indistinguishability of **5**, **6**, and **7**. As such, the reaction of the diene $(CH_3)_3Si(C_5H_5)$ with a dienophile $RC\equiv CR'$ ought to yield only the *syn*- and *anti*-7-trimethylsilyl-2,3-R,R′-norbornadiene products, and the nature of the products should be temperature independent, in disagreement with the present observations.

An alternate temperature-dependent rearrangement process for $(CH_3)_3Si(C_5H_5)$ may explain (1) the formation of **4a**, (2) the increasing relative yield of **4a** over **4c** with increasing temperature, and (3) the nmr equivalence of the ring protons in **4** at elevated temperatures. This rearrangement process, as is illustrated by the interconversion of **5**, **8**, and **9** as shown in reaction 3, corresponds to a series of 1,3 and/or 1,2 tautomeric hydrogen shifts. Whereas structure **5** should yield **4c** directly with the dienophile $CH_3O_2CC\equiv CCO_2CH_3$, species **8** represents the only reasonable diene structure that would react with this dienophile to yield **4a**. Structure **9**, even if present, probably would not combine readily with dienophiles owing to the positioning of the large $(CH_3)_3Si$ group at one of the normal Diels–Alder addition sites. In any event, no product that might arise from **9** has been observed. If the assumption is made that the rapid interconversion of **5**, **8**, and **9** by successive 1,3 (and/or 1,2) hydrogen shifts at high temperature can account for the nmr equivalence of the ring protons, then the proportion of **8** over **5** would also increase with temperature.



(3)

The percentage of **4a** over **4c** would also be expected to increase with increasing temperature providing that the rates of reaction of the dienophile with **5** and **8** are comparable. The other Diels–Alder reactions between $(CH_3)_3Si(C_5H_5)$ and $(CH_3)_3SiC\equiv CH$, $(CH_3)_3SiC\equiv COCH_3$, and $(CH_3)_3SiC\equiv CCOOCH_3$ had to be carried out at temperatures near 200° in order to obtain reaction at all. Under these conditions **8** would be expected to be much favored in the equilibrium between **5** and **8**. If so, then very little, if any, of a 7-trimethylsilylnorbornadiene derivative would be obtained in agreement with the actual experimental facts. Furthermore, the formation of the various isomer pairs, such as **1a**, **1b**, is also readily explained if **8** is considered to be the form of the diene present at the high temperatures employed. There are two ways that an unsymmetrical dienophile $RC\equiv CR'$ may add at the 2 and 5 positions of **8**. With the trimethylsilyl group at position 3, it would be expected that the steric interaction with R or R′ would favor the addition of the smaller of the two groups at position 2. The experimental results in Table I are in complete agreement with this prediction as structure **a**, in which the two bulky trimethylsilyl groups are in the 2,5 positions, is found to predominate over **b** for the products obtained from the reactions with the unsymmetrical acetylenes.

There is a real difference between the mechanisms proposed for the thermal dependence of the nmr spectra of $(CH_3)_3SiC_5H_5$ (reaction 3), and of $(\sigma\text{-}C_5H_5)Cu\text{-}P(C_2H_5)_3$,[3] $(\sigma\text{-}C_5H_5)Fe(CO)_2(\pi\text{-}C_5H_5)$,[4] and $(\sigma\text{-}C_5H_5)$-

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(3) G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).

(4) M. J. Bennett, Jr., F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966).

Table II. Nuclear Magnetic Resonance Data[a,b]

	τ or J (area)							
	1a	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
H_1	6.27 (2)	6.13 (1)	6.03 (1)[d]	5.95 (2)[d]	6.02 (1)[g]	5.90 (1)	~6.0 (2)[h]	6.08 (2)
H_4		6.38 (1)	5.88 (1)[d]		5.93 (1)	6.05 (1)		
H_5		3.03 (2)	...	2.88 (1)	...	2.82 (1)	...	No H_3 $H_5 = H_6$ = 3.14 (2)
H_3	3.08 (2)		...	...	...	...	...	
H_6		...	3.10 (1)	...	2.98 (1)	...	2.87 (1)	
H_7	8.25 (2)	8.23 (2)	8.17 (2)[e]	8.13 (2)[e]	8.07 (2)	8.07 (2)	7.95 (2)[i]	7.70 (1)
$(CH_3)_3Si$	9.97 (18)	9.93 (18)	9.93 (9)	9.92 (9)	9.92 (9)	9.92 (9)	9.90 (3)	10.07 (3)
			9.85 (9)	9.83 (9)	9.88 (9)	9.87 (9)		
Other[j]			C_2H_5	C_2H_5	CH_3	CH_3	CH_3	CH_3
			q, 5.82 (2)	q, 5.80 (2)	s, 7.73 (3)	s, 7.73 (3)	s, 6.30 (6)	s, 6.30 (6)
			t, 8.70 (3)	t, 8.68 (3)	...	...	...	...
$J_{1,3}$	1.4	0.9	...	...	...	0.8	...	1.0
$J_{1,5}$	...	0.9	...	1.0	3.0	...	3.0	2.0
$J_{1,6}$	2.3	...	3.0	...	...	...	...	...
$J_{3,4}$	2.3	3.0	...	...	...	3.1	...	2.0
$J_{4,5}$	...	3.0	...	2.9	0.9	...	0.7	1.0
$J_{4,6}$	1.4	...	0.8	...	1.5	1.5	1.4	1.2
$J_{1,7} = J_{4,7}$	1.5	1.5	1.5	1.5	*f*	*c*	6.8	...
$J_{7a,7s}$	*c*	*c*	~6.5[e]	~5–6[e]				

[a] Measurements on 30% CCl_4 solutions; TMS as internal standard at τ 10. τ values in parts per million; J values in cycles per second. [b] J values are all reproducible to ±0.2 cps. [c] Chemical shifts of **7a** and **7c** are identical. [d] Partially obscured by C_2H_5 resonance signals; integration checks well. [e] Chemical shift is center of an AB quartet of triplets with very weak outer triplets. [f] Indeterminable; outer triplets not detectable. [g] Overlapping signals. [h] Signals for H_7 and H_4 are unseparated. [i] Quartet of triplets; see Figure 1. [j] s, singlet; q, quartet; t, triplet.

$Cr(NO)_2(\pi\text{-}C_5H_5)$[5] (reaction 2). Possibly, the well-known ability of transition metals in low valence states to participate in π-bond formation, a property which the nontransition elements do not possess, could account for this difference.

Identification of Products

Nmr Spectra. The first indication that the products isolated in the above reactions were not 7-trimethylsilylnorbornadiene derivatives came from their nmr spectra. These data have been tabulated in Table II; the numbering system is shown on **a** in reaction 1.

1a and 1b. The nmr spectra of 2,5- and of 2,6-bis(trimethylsilyl)bicyclo[2.2.1]heptadiene (**1a** and **1b**) are shown in Figure 1. The pertinent facts to be noted in each of these two spectra are: (i) an indication of only two vinyl protons instead of three as would be expected in **1c** or **1d**; (ii) a sharp symmetrical triplet near τ 8 corresponding to two bridge protons: (iii) a sharp singlet of relative intensity 18 at τ 9.95 indicating that the two trimethylsilyl groups are equivalent; and (iv) the relative intensity of the signals for the bridgehead protons is two. Thus, the only possible conclusion is that the trimethylsilyl groups are to be found exclusively in the vinyl positions in each compound. Other than minor differences in chemical shifts and some coupling constants, a difference in the bridgehead proton resonances for **1a** and **1b** represents the only tangible distinguishing feature. For **1a** a single, partially resolved signal is noted at τ 6.13 corresponding to both H-1 and H-4; the general appearance is that expected of two close-lying triplets arising from splitting of the equivalent bridgehead protons by a pair of equivalent H-7 protons and by the adjacent vinylic proton. Further splitting by the allylic protons does occur, as is noted from the vinyl proton signal, but the effect is not readily apparent on the bridgehead proton resonance. For **1b** two separate bridgehead proton resonances are seen, with the higher field signal being better resolved than the lower field signal for H-1. Theoretically, the H-1 and H-4 signals should each consist of nine lines as a triplet of triplets. However, although $J_{1,7}$ and $J_{4,7}$ are identical, $J_{1,3} = J_{1,5}$ should be smaller than $J_{4,3} = J_{4,5}$ with the result that accidental overlap of lines should be greater for H-1 than for H-4. Some accidental overlap is apparent in the H-4 signal as only six, possibly seven, lines were readily observed. The various coupling constants for **1a** and **1b** are tabulated in Table I and are internally consistent.

2a, 2b, and 3a, 3b. Other than the obvious differences to be expected between the resonance signals arising from a methyl or ethyl group, the nmr spectra of **2a** and **3a** are very similar as seen from the data in Table I. Also, **2b** and **3b** are very similar. None of these compounds is a 7-trimethylsilylnorbornadiene derivative as is readily apparent from the ratio between the relative intensities of the various signals, vinyl: bridgehead:bridge, is 1:2:2. Two sharp and separate signals are seen for the two different trimethylsilyl groups in each compound. Although AB splitting is expected for the H-7 protons in each instance, only for **2a** is J_{AB} of reasonable magnitude, while in **2b** and **3b** the effect is very small and in **2a** essentially nonobservable.

Although there may be some question as to whether the assignments for **2a** and **2b** (and therefore **3a** and **3b** as well) should be reversed, there are two factors which point to the assignments proposed here. First, the **a** isomers were each eluted from the glpc column before their corresponding **b** isomer. Owing to the nature of this separation method, this would indicate that the **a** isomer must be the more symmetrical isomer and have the lower dipole moment. We note that **1a** was eluted prior to **1b** and that **1a** in fact does have unequivocally the more symmetrical structure. Thus, the two trimethylsilyl groups in **2a** and **3a** are most

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[5] F. A. Cotton, A. Musco, and G. Yagupsky, *J. Am. Chem. Soc.* **89**, 6136 (1967).

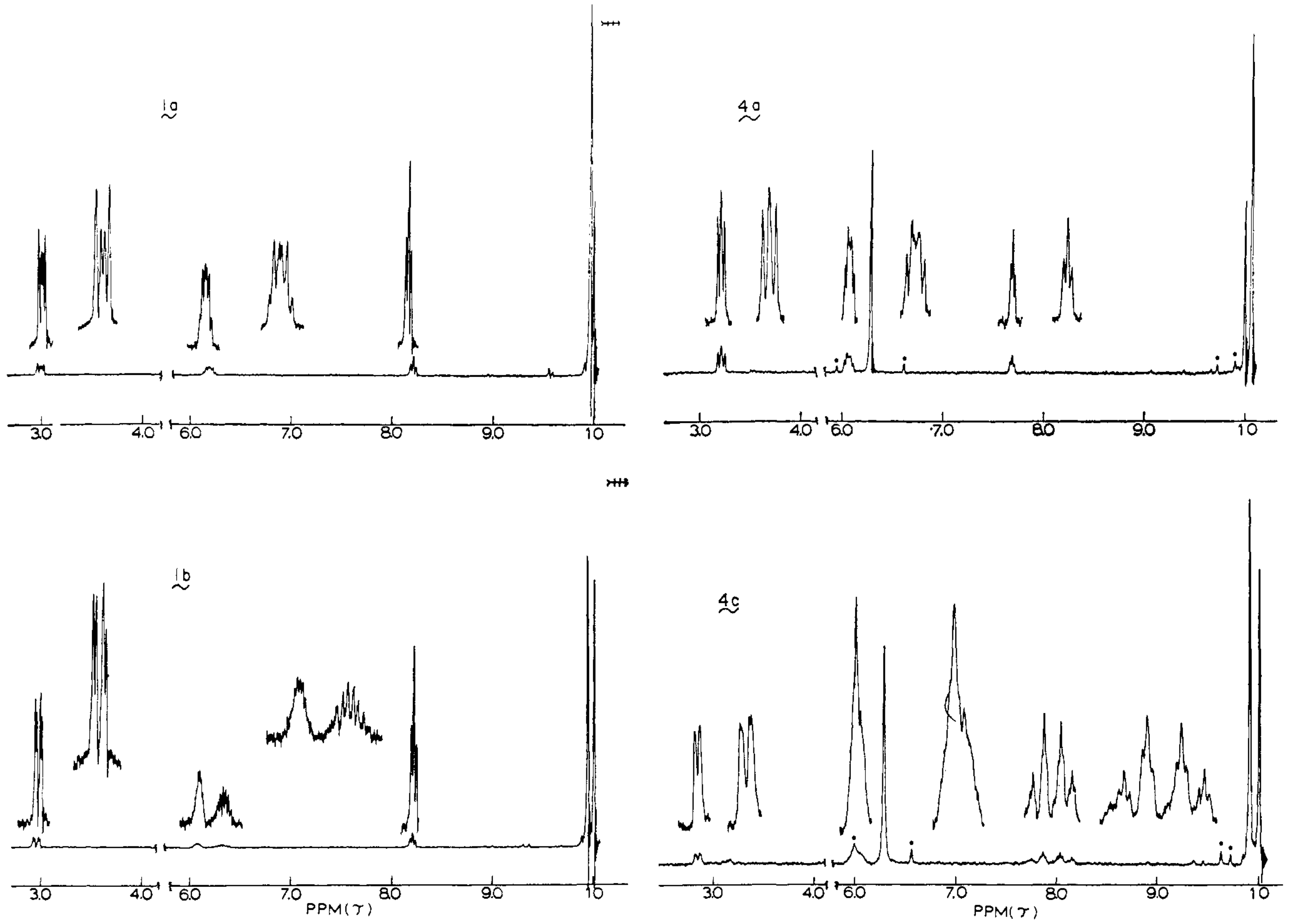

Figure 1. Nmr spectra of compounds **1a**, **1b**, **4a**, and **4c** in CCl_4 with TMS as the internal standard at τ 10. Strong spinning side bands are indicated by °. Sweep width for the expanded scale inserts is twice that of the normal scale.

likely in the 2 and 5 positions. A second observation which indicates that these assignments are correct involves the relative chemical shifts of the single vinylic proton in each type of isomer. In general, a 6-vinyl proton opposed to a 2-trimethylsilyl group is less deshielded than when it is opposed to a 2-ester moiety.[1] The present assignments for **2a** and **2b** agree with this trend as the signal for the single vinyl proton in **2a** appears at τ 3.10, whereas in **2b** the single vinyl proton, is more deshielded and the signal is at τ 2.88. A similar difference is noted between **3a** and **3b**.

4a and 4c. The nmr spectra of these compounds are shown in Figure 1. In contrast to the three previously discussed pairs of isomers, **4a** and **4c** have decidely different structures. Compound **4a** resembles the first six compounds in that the trimethylsilyl group is bonded at a vinyl position. A strong AB pattern is noted for the two bridge protons and is centered at τ 7.9. Only a simple doublet corresponding to a single vinyl proton is noted at τ 2.87. Separation of the signals for H-1 and H-4 is not apparent.

Compound **4c** is unique among the bicyclo[2.2.1]-heptadienes prepared here. It is the only compound with the trimethylsilyl group attached in the 7 or bridge position. Although no proof is available as to whether this group is *syn* or *anti* to the ester groups, the *anti* structure would appear to be favored structurally. As can be noted from Table II and Figure 1, the vinyl proton signal is similar to that seen earlier and results from $J_{1,6} \approx J_{1,5}$. The bridgehead proton signal is highly symmetrical, as would be expected with H-1 and H-4 equivalent, and is obviously a result of partial overlap of two triplets arising from coupling with the effectively equivalent H-5 and H-6 and by the single bridge proton.

One further difference between **4c** and the other compounds may be noted. Only in **4c** is the trimethylsilyl resonance observed at higher field than TMS. Possibly such an observation may have some qualitative use in judging the position of attachment of silicon in related systems.

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