Table IV. Bond Angles (deg) with Estimated Standard Deviations

Cl(1)-Rh(1)-Cl(1)*	82.35 (3)	C(4)-C(3)-C(8)	118.0 (4)
Cl(1)-Rh(1)-Cl(2)	94.15 (3)	C(3)-C(4)-C(5)	120.4 (4)
Cl(1)-Rh(1)-P(1)	176.65 (3)	C(4)-C(5)-C(6)	120.4 (5)
Cl(1)-Rh(1)-P(2)	93.74 (3)	C(5)-C(6)-C(7)	120.4 (5)
Cl(1)-Rh(1)-C(27)	80.70 (7)	C(6)-C(7)-C(8)	119.9 (5)
Cl(1)*-Rh(1)-Cl(2)	93.07 (3)	C(3)-C(8)-C(7)	121.0 (4)
Cl(1)*-Rh(1)-P(1)	99.23 (3)	P(1)-C(9)-C(10)	121.4 (3)
Cl(1)*-Rh(1)-P(2)	175.99 (3)	P(1)-C(9)-C(14)	120.3 (3)
Cl(1)*-Rh(1)-C(27)	80.29 (7)	C(10)-C(9)-C(14)	118.2 (3)
Cl(2)-Rh(1)-P(1)	88.72 (3)	C(9)-C(10)-C(11)	120.2 (4)
Cl(2)-Rh(1)-P(2)	86.30 (3)	C(10)-C(11)-C(12)	121.1 (4)
Cl(2)-Rh(1)-C(27)	172.0 (1)	C(11)-C(12)-C(13)	119.6 (4)
P(1)-Rh(1)-P(2)	84.72 (3)	C(12)-C(13)-C(14)	120.1 (4)
P(1)-Rh(1)-C(27)	96.62 (8)	C(9)-C(14)-C(13)	120.8 (4)
P(2)-Rh(1)-C(27)	100.02 (7)	P(2)-C(15)-C(16)	119.4 (3)]
Rh(1)-Cl(1)-Rh(1)*	76.20 (2)	P(2)-C(15)-C(20)	121.8 (3)
Rh(1)-P(1)-C(1)	108.8 (1)	C(16)-C(15)-C(20)	118.7 (3)
Rh(1)-P(1)-C(3)	117.3 (1)	C(15)-C(16)-C(17)	120.4 (4)
Rh(1)-P(1)-C(9)	116.2 (1)	C(16)-C(17)-C(18)	120.2 (4)
C(1)-P(1)-C(3)	105.4 (2)	C(17)-C(18)-C(19)	119.8 (4)
C(1)-P(1)-C(9)	106.2 (2)	C(18)-C(19)-C(20)	120.6 (4)
C(3)-P(1)-C(9)	101.8 (2)	C(15)-C(20)-C(19)	120.2 (4)
Rh(1)-P(2)-C(2)	105.5 (1)	P(2)-C(21)-C(22)	120.0 (3)
Rh(1)-P(2)-C(15)	116.2 (1)	P(2)-C(21)-C(26)	121.5 (3)
Rh(1)-P(2)-C(21)	120.9 (1)	C(22)-C(21)-C(26)	118.0 (4)
C(2)-P(2)-C(15)	107.2 (2)	C(21)-C(22)-C(23)	121.9 (4)
C(2)-P(2)-C(21)	102.2 (2)	C(22)-C(23)-C(24)	118.8 (5)
C(15)-P(2)-C(21)	103.4 (2)	C(23)-C(24)-C(25)	120.4 (5)
P(1)-C(1)-C(2)	109.4 (2)	C(24)-C(25)-C(26)	120.7 (5)
P(2)-C(2)-C(1)	106.4 (2)	C(21)-C(26)-C(25)	120.2 (5)
P(1)-C(3)-C(4)	123.6 (3)	Rh(1)-C(27)-Rh(1)*	95.2 (2)
P(1)-C(3)-C(8)	118.3 (3)		

when CH_2Cl_2 is used as a solvent for catalytic reactions involving rhodium and chelating-phosphine systems.

Experimental Section

All synthetic reactions were performed under nitrogen in standard Schlenk-type glassware. CH_2Cl_2 was dried over CaH_2 under nitrogen and vacuum degassed immediately prior to use. The NMR spectra were recorded in CD_2Cl_2 on a Bruker AMX-500 or a Bruker AC-200 spectrometer. The ^1H NMR spectra were referenced to the residual solvent proton at 5.32 ppm, and the $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 set at 0.00 ppm. $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ (1) was prepared according to the literature procedure;[8] the $^{31}P\{^1H\}$ NMR spectrum of 1 in C_6D_6 showed a doublet at 73.5 ppm ($^1J_{Rh}$ = 199 Hz) with a doublet due to a minor component (5–7%) at 77.5 ppm ($^1J_{Rh}$ = 200 Hz).

$[(dppe)RhCl]_2(\mu\text{-}Cl)(\mu\text{-}CH_2)$. $[(dppe)Rh]_2(\mu\text{-}Cl)_2$ (219 mg, 0.204 mmol) was dissolved in CH_2Cl_2 (5 mL), and the solution was allowed to stand for 24 h. The solvent volume was slowly reduced over a period of 24 h to ≈1.5 mL, during which time large yellow-orange crystals separated. After the mixture was cooled to −15 °C for 1 h, the crystals were filtered off and washed with cold CH_2Cl_2 (0.5 mL). Drying in vacuo (18 h) caused the crystals to rapidly become opaque due to loss of solvated CH_2Cl_2. Yield: 120 mg (51%). Anal. Calcd for $C_{53}H_{50}Cl_4P_4Rh_2$: C, 54.95; H, 4.35. Found: C, 54.68; H, 4.39. ^1H NMR (ppm, CD_2Cl_2, 500 MHz): $P(C_6H_5)_2$, 7.98 (m, 8 H), 7.49 (m, 4 H), 7.43 (m, 8 H), 7.17 (m, 12 H), 7.03 (m, 8 H); μ-CH_2, 4.09 (br, 2 H); PCH_2CH_2P, 2.92 (m, 4 H), 2.23 (m, 4 H). $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2, 81 MHz): 66.7 (d, $^1J_{Rh}$ = 153 Hz). FAB Mass Spectrum: *m/e* 1159, $(M + 1)^+$.

X-ray-quality crystals were grown by diffusion of a near-saturated solution of the complex in CH_2Cl_2 into diethyl ether; crystals were sealed in glass capillaries under N_2.

X-ray Crystallographic Analysis of $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$. Crystallographic data appear in Table I. The final unit-cell parameters were obtained by least-squares methods on the setting angles for 25 reflections with 2θ = 76.5–91.4°. The intensities of three standard reflections, measured every 150 reflections throughout the data collection, showed only small random variations. The data were processed and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for three reflections).[15]

The structure was solved by conventional heavy-atom methods, the coordinates of the Rh atom being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference Fourier synthesis. The molecule has crystallographically imposed C_2 symmetry, the 2-fold axis passing through the bridging methylene carbon atom. All non-hydrogen atoms were refined with anisotropic thermal parameters. The crystallographically unique hydrogen atom of the μ-CH_2 group was refined with an isotropic thermal parameter, and the remaining hydrogen atoms were fixed in calculated positions (C–H = 0.98 Å, $B_H = 1.2B$(bonded atom)). Neutral-atom scattering factors and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 16. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables II–IV, respectively. Hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, least-squares planes, and measured and calculated structure factor amplitudes are included as supplementary material.

Acknowledgment. This research was supported by the NSERC of Canada Strategic Grants Programme and by Ciba-Geigy. We also thank Johnson-Matthey for the generous loan of rhodium salts.

Registry No. 1, 53204-14-1; CH_2Cl_2, 75-09-2; $[(dppe)RhCl]_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)$, 136060-75-8.

Supplementary Material Available: Tables of hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes (13 pages); a table of measured and calculated structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

(15) TEXSAN/TEXRAY structure analysis package, which includes versions of the following: MITHRIL, integrated direct methods, by C. J. Gilmore; DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy: ORTEP II, illustrations, by C. K. Johnson.

(16) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Photodimerization of 1-Phenyl-2-(trimethylsilyl)ethyne

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Received December 14, 1990

Summary: **Room-temperature photolysis at 254 nm of 1-phenyl-2-(trimethylsilyl)ethyne (1) produces two cyclooctatetraenes, 2 and 3, for which structures 2a and 3a are suggested from ^1H NMR spectra.**

Several years ago, while studying some photochemical reactions involving 1-phenyl-2-(trimethylsilyl)ethyne (1), we noticed the formation of yellow products when 1 was irradiated. Mass spectrometry showed that the products were dimers of 1, but their structure was unknown until recently. We now present evidence that the photolysis of 1 leads, via intermolecular dimerization, to cyclo-

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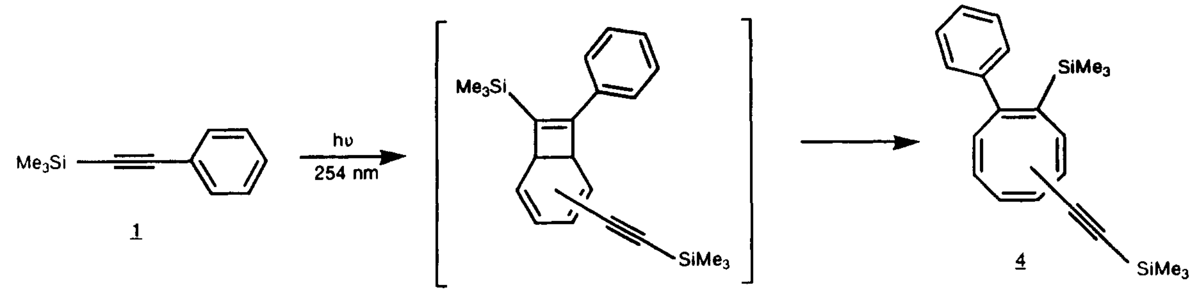
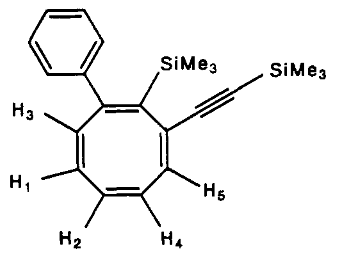
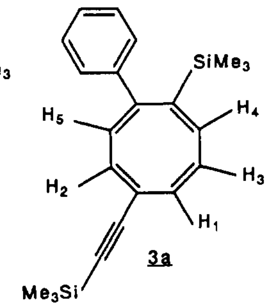
Scheme I



octatetraene derivatives **2** and **3**. From detailed consideration of the ^1H NMR spectra of **2** and **3**, the most likely structures for these isomers are **2a** and **3a**.



2a



3a

The formation of cyclooctatetraene derivatives by photochemical cycloaddition of acetylenes and benzene was first investigated over 30 years ago[1,2] and has been reviewed extensively by Bryce-Smith.[3] In addition to intermolecular cycloadditions, intramolecular annulations can also lead to bicyclic cyclooctatetraene derivatives.[4] Recently, Pirrung has extended this intramolecular arene–alkyne photocyloaddition to trimethylsilyl–substituted acetylenes.[5]

Experimental Section

General Data. 1-Phenyl-2-(trimethylsilyl)ethyne (1) was prepared by literature methods.[6] Pentane was deolefinated by washing twice each with H_2SO_4, 50% H_2SO_4 and 50% HNO_3 mixture, H_2O, KOH (aqueous), and H_2O, 200 mL per 600 mL of pentane. The pentane was dried over $MgSO_4$ and then distilled over CaH_2 under nitrogen. All reactions were conducted under a nitrogen atmosphere by using standard Schlenk techniques. The photolysis products were separated by using a Japan Analytical Industry recycling preparative HPLC apparatus with Jaigel-1H columns, using toluene as the eluent. Infrared spectra were obtained on a Mattson Polaris FTIR spectrometer. Routine ^1H NMR (200-MHz) spectra were collected on a Bruker WP 200 spectrometer, while the high-resolution proton NMR spectra (500 MHz) were recorded on a Bruker AM 500 spectrometer. The vinyl region of each dimer was simulated by using Bruker PANIC85 software. The ^{13}C NMR (67.5-MHz) spectra were collected on a Bruker WP 270 spectrometer. High-resolution mass spectra were recorded on Kratos MS-80 mass spectrometer. Gas chromatographic analysis were performed on a Hewlett-Packard (HP) 5890A gas chromatograph with HP series 530μ fused silica column and HP 3390A integrating recorder.

Synthesis of the Cyclooctatetraenes (2 and 3). Method A. A quartz tube containing 1 (0.13 g, 7.6 × 10^{-4} mol) and deolefinated pentane (5 mL) was degassed and left under vacuum. This solution was photolyzed at 254 nm at room temperature for 24 h to yield a yellow solution. The solvent and starting material (85%) were removed in vacuo to yield 20 mg (15%) of the yellow cyclooctatetraene dimer mixture.

Method B. For the production of a greater quantity of 2 and 3, the quartz photolysis tube was charged with neat 1 (3.0 g, 0.017 mol), degassed, and photolyzed at 254 nm at room temperature for 24 h, yielding a yellow liquid. Distillation of the remaining starting material left 0.15 g (5%) of the yellow-brown cyclooctatetraene dimer mixture (this method is lower yielding but produces more product). GC analysis indicated the same product ratio for both methods: 2:3:other dimers = 65:30:5. The cyclooctatetraene mixture was separated by recycling preparative HPLC, yielding pure 2 and 3 as yellow oils.

1-Phenyl-2-(trimethylsilyl)-3-[2-(trimethylsilyl)-ethynyl]cyclooctatetraene (2). ^1H NMR (d_6-acetone): δ 7.54–7.49 (m, 2 H, phenyl), 7.36–7.29 (m, 3 H, phenyl), 6.3–5.6 (m, 5 H, vinyl), 0.09 (s, 9 H, Me_3Si), –0.16 (s, 9 H, Me_3Si). ^1H NMR (500 MHz): δ 6.26 (m, 1 H, H_5), 6.26 (m, 1 H, H_4), 6.04 (d, 1 H, H_3), 5.99 (dddd, 1 H, H_2), 5.85 (dddd, 1 H, H_1). ^{13}C NMR (d_6-acetone, quaternary carbons): δ 151.99, 140.4, 128.3, 127.8, 105.7, 96.0. ^{13}C NMR (d_6-acetone, tertiary carbons): δ 139.3, 133.9, 133.1, 132.1, 131.4, 130.7, 128.7, 128.3. ^{13}C NMR (d_6-acetone, Me_3Si carbons): δ –0.10, –0.52. IR ($CHCl_3$, cm^{-1}): 3039, 2956, 2899, 2132. HRMS Calcd. for $C_{22}H_{28}Si_2$: 348.1729. Found: 348.1747.

1-Phenyl-4-[2-(trimethylsilyl)ethynyl]-8-(trimethylsilyl)cyclooctatetraene (3). ^1H NMR (d_6-acetone): δ 7.31 (s, 5 H, phenyl), 6.45–5.55 (m, 5 H, vinyl), 0.17 (s, 9 H, Me_3Si), –0.12 (s, 9 H, Me_3Si). ^1H NMR (500 MHz): δ 6.40 (d, 1 H, H_5), 6.39 (ddd, 1 H, H_4), 6.20 (ddd, 1 H, H_3), 6.07 (ddd, 1 H, H_2), 5.78 (dtd, 1 H, H_1). ^{13}C NMR (d_6-acetone, quaternary carbons: δ 151.2, 149.1, 141.8, 125.5, 106.4, 92.4. ^{13}C NMR (d_6-acetone, tertiary carbons): δ 140.2, 139.9, 134.4, 131.8, 129.1, 128.5, 128.2, 125.3. ^{13}C NMR (d_6-acetone, Me_3Si carbons): δ 0.05, –0.44. IR ($CHCl_3$, cm^{-1}): 3034, 2961, 2901, 2140. HRMS calcd for $C_{22}H_{28}Si_2$: 348.1729. Found: 348.1721.

Results and Discussion

Photolysis of 1. Synthesis of Substituted Cyclooctatetraenes 2 and 3. The photolysis of 1 either neat or in pentane solution with 254-nm light produces a yellow mixture or solution (Scheme I). Upon workup, the yellow-brown oil is found by GC and GCMS analysis to be a mixture of dimeric isomers. Proton NMR spectra of 2 and 3 indicated the presence of aromatic, vinyl, and trimethylsilyl protons in ratios of 5:5:18. The ^{13}C NMR spectra provided evidence for six different quaternary carbons, eight different tertiary carbons, and two trimethylsilyl carbons for each isomer. IR spectroscopy confirmed the presence of an asymmetric acetylene stretch. From these data and the assumption that the products are formed by the cycloaddition mechanism represented in Scheme I, generalized structure **4** was assigned to the dimeric isomers.

After a variety of unsuccessful attempts to separate the isomers by using traditional methods, the two major isomers were separated by using recycling preparative HPLC. The vinyl regions of the purified isomers were then analyzed by 500-MHz high-resolution proton NMR (Figures 1 and 2). Fortunately, the vinyl region was highly resolved and the majority of the patterns could be subjected to a

(1) Atkinson, J. G.; Ayer, D. E.; Buchi, G.; Robb, E. W. *J. Amer. Chem. Soc.* **1963**, *85*, 2257.
(2) Bryce-Smith, D.; Lodge, J. E. *J. Chem. Soc.* **1963**, 695.
(3) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309. Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1977**, *33*, 2459.
(4) Lippke, W.; Feree, W.; Morrison, H. *J. Am. Chem. Soc.* **1974**, *96*, 2134.
(5) Pirrung, M. C. *J. Org. Chem.* **1987**, *52*, 1637.
(6) Eisch, J. J. *Organometallic Syntheses*; Academic Press: New York, 1981; Vol. 2, p 159. Compound 1 can now be purchased directly from either Aldrich Chemical Company or Petrarch Systems.

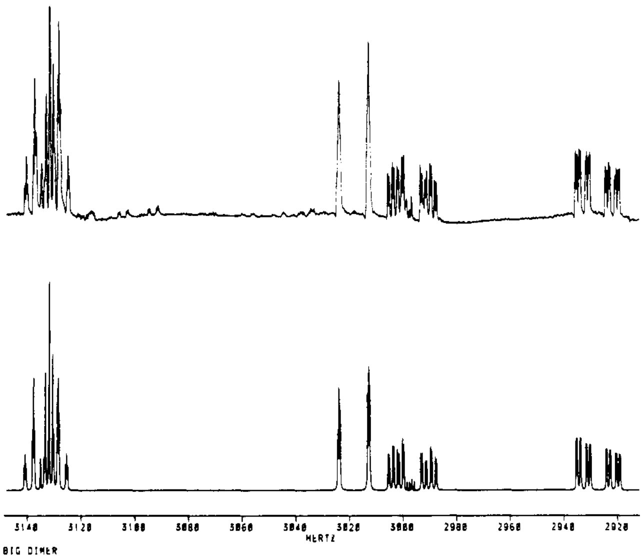


Figure 1. Experimental (top) and calculated (bottom) high-resolution ^{1}H NMR of the vinyl region for **2**.

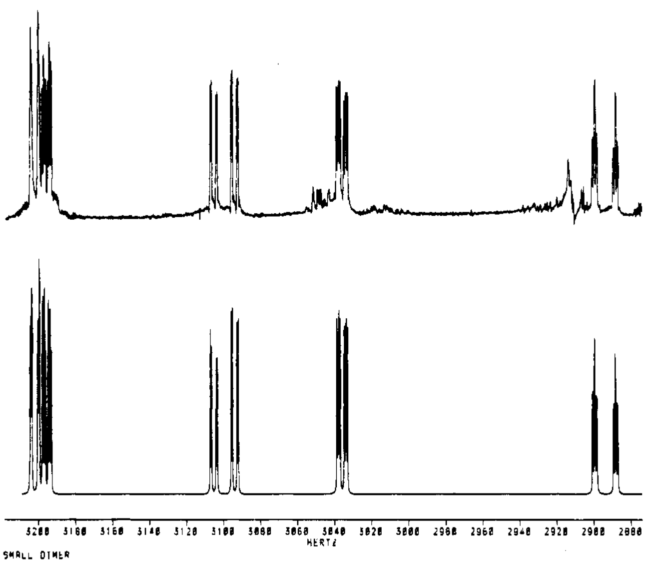
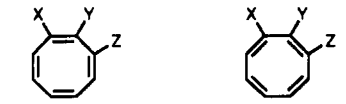
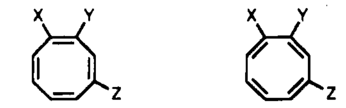
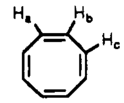


Figure 2. Experimental (top) and calculated (bottom) high-resolution ^{1}H NMR of the vinyl region for **3**.

Table I

addition	possible cyclooctatetraenes	
[1,2]	 **5a**	**5b**
[1,3]	 **6a**	**6b**
[1,4]	 **7a**	**7b**



H_{ab} = 12 Hz X, Y = Ph, $SiMe_3$
H_{bc} = 3 Hz Z = —$SiMe_3$

addition		coupling const 12 Hz	3 Hz	isolated protons
[1,2]	**5a**	2	2	0
	5b	2	2	0
[1,3]	**6a**	2	1	1
	6b	1	2	1
[1,4]	**7a**	2	1	0
	7b	1	2	0

Table II. Experimental and Calculated ^{1}H NMR Data for 2

	exptl	calcd
ω1	5.85 ppm	5.854 ppm
ω2	5.99 ppm	5.992 ppm
ω3	6.04 ppm	6.035 ppm
ω4	6.2 ppm	6.264 ppm
ω5	6.2 ppm	6.262 ppm
J(1,2)	3.66 Hz	3.65 Hz
J(1,3)	11.05 Hz	11.08 Hz
J(1,4)	0.48 Hz	0.35 Hz
J(1,5)	1.24 Hz	1.46 Hz
J(2,3)	0.55 Hz	0.51 Hz
J(2,4)	12.30 Hz	11.55 Hz
J(2,5)	1.76 Hz	-1.03 Hz
J(3,4)		0.39 Hz
J(3,5)		-0.06 Hz
J(4,5)	3.15 Hz	3.15 Hz

Table III. Experimental and Calculated ^{1}H NMR Data for 3

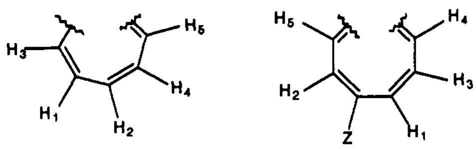
	exptl	calcd
ω1	5.78 ppm	5.788 ppm
ω2	6.07 ppm	6.071 ppm
ω3	6.20 ppm	6.198 ppm
ω4	6.39 ppm	6.390 ppm
ω5	6.40 ppm	6.403 ppm
J(1,2)	1.21 Hz	1.19 Hz
J(1,3)	11.24 Hz	11.25 Hz
J(1,4)	1.05 Hz	1.04 Hz
J(1,5)	0.41 Hz	0.31 Hz
J(2,3)	0.57 Hz	0.66 Hz
J(2,4)		-0.03 Hz
J(2,5)	4.03 Hz	4.04 Hz
J(3,4)	3.12 Hz	3.16 Hz
J(3,5)		-0.01 Hz
J(4,5)	0.76 Hz	0.71 Hz

first-order analysis. The vinyl region spectra were then simulated, generating patterns nearly identical with the actual ones. These simulations were used to confirm the values for coupling constants and chemical shifts.

Structural Assignment of 2 and 3. Table I lists the possible structures and also their predicted structural and NMR environments for **2** and **3**. The coupling constants for the adjacent vinyl protons differ greatly depending on whether the carbon atoms are joined by a single or double bond. Cyclooctatetraenes normally exhibit two sets of coupling constants, at 11–12 Hz and around 3 Hz.[7] By using bond angle approximations for cyclooctatetraene and the Karplus correlation, the 11–12-Hz couplings can be assigned to $^3J_{HH}$ across a double bond and the 3-Hz couplings to $^3J_{HH}$ across a single bond.[8]

Table II lists both the experimental and calculated ^{1}H NMR data for **2**, the major isomer. Compound **2** contains two 12- and 3-Hz coupling constants and no isolated protons (lacking $^3J_{HH}$ couplings). From Table I, **2** must be a 1,2-addition product with structure **5a** or **5b**. The minor isomer **3** contains one 12- and two 3-Hz coupling

(7) Lyttle, M. H.; Streitwieser, A.; Miller, M. J. *J. Org. Chem.* **1989**, *54*, 2331.
(8) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley and Sons: New York, 1981; p 210.



2 3

Figure 3. Proton sequences for 2 and 3 determined from $^3J_{HH}$ coupling constants.

constants and one $^3J_{HH}$ value for every proton; these data are consistent with [1,4] addition (Table III) to give structure **7b**.

For **2**, distinguishing between structures **5a** and **5b** and assignement of the final structure was done by using standard NMR correlation logic. From Table II, one can see that protons 1 and 3 and protons 2 and 4 are vicinally coupled through a double bond, whereas protons 1 and 2 and protons 4 and 5 display vicinal coupling through a single bond. These couplings yield the sequence shown in Figure 3. Final assignment of structure **2** between the four remaining possibilities depends on determining a relationship between proton H_3 or H_5 and one of the substituents on the cyclooctatetraene ring. In the proton NMR spectrum of **2**, the signal of H_3 is broadened while all the other protons give sharp lines. This broadening may be due to residual coupling between H_3 and the aromatic protons, implying that the aromatic ring and H_3 are on adjacent carbons.[9] Hence, the probable structure for **2** is **2a**.

For **3**, correlating the coupling as above, one can see that pairs of protons H_1 and H_3 are vicinally coupled through a double bond, while protons H_2 and H_5 and also protons H_3 and H_4 display vicinal coupling through a single bond. For **3**, proton H_5 is broadened compared to H_4, and from this we infer residual coupling between H_5 and the aromatic ring. The most likely structure for **3** is therefore **3a**.[10]

The photolytic reaction described here is apparently the first example of an intermolecular arene–alkyne dimerization. The predominance of [1,2] addition in our reactions is not without precedent. Cycloaddition of cyanobenzene and internal symmetrical acetylenes takes place to form [1,2]-addition products,[1] and products from [1,2] addition to the aromatic moiety are also found in intramolecular arene–alkyne photocycloadditions.[5]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research Air Force Systems Command, USAF, under Contract No. AFOSR-89-0004 and by the National Science Foundation Grant No. CHE-8318820-02. R.S.A. thanks E. I. du Pont de Nemours & Company for a summer fellowship.

Registry No. 1, 2170-06-1; 2, 135865-57-5; 3, 135865-58-6.

Supplementary Material Available: Figures showing expansions of the individual regions of Figures 1 and 2 (3 pages). Ordering information is given on any current masthead page.

(9) NOE differentiation was attempted, but in this highly coupled system, no clear enhancement was seen.

(10) Other less likely substitution patterns (1,3,5 and 1,3,6) and 2 and 3 can be excluded from the coupling constants given in Tables II and III.

Mechanism of Pyrolysis of 2,2-Diethylhexamethyltrisilane

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Received February 8, 1991

Summary: The main silicon-containing product besides trimethylsilane in the pyrolysis of the title compound is vinyltrimethylsilane, whereas cyclic carbosilanes are formed in the pyrolysis of permethylated oligosilanes. A mechanistic explanation, of relevance to the breakdown of polysilanes, is suggested.

We are undertaking studies of the thermal[1] and photochemical[2] breakdown of oligosilanes as simple models for polysilanes; the latter are of topical interest in view of their potential as photoresists[3] and as precursors to new polymers. We now report on the gas-phase pyrolysis of 2,2-diethylhexamethyltrisilane; the course of this pyrolysis proved to be different from that of octamethyltrisilane, where the major silicon-containing products other than Me_3SiH were cyclic carbosilanes, formed in part by a novel elimination of Me_3SiH.[1]

Experimental Section

2,2-Diethylhexamethyltrisilane, $(Me_3Si)_2SiEt_2$ (I), was a gift from Dr. R. G. Taylor of Dow Corning Ltd., who synthesized it by standard methods. Its purity was checked at Leicester by GC/mass spectrometry (HP5995C) and by ^1H NMR spectroscopy (AM300).

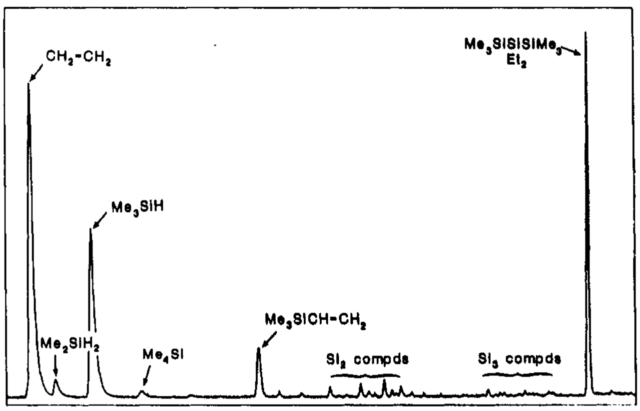

Figure 1.

Pyrolysis of compound I was carried out by our stirred-flow (SFR) technique[4] in a carrier gas of dried deoxygenated helium or nitrogen, with analysis by GC/mass spectrometry or packed-

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(2) Davidson, I. M. T.; Michl, J.; Simpson, T. *Organometallics* **1991**, *10*, 842.
(3) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.
(4) Baldwin, A. C.; Davidson, I. M. T.; Howard, A. V. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 972. Davidson, I. M. T.; Eaton, G.; Hughes, K. J. *J. Organomet. Chem.* **1988**, *347*, 17.

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