Steric Hindrance to Benzocyclobutene Openings. First Synthesis of a 1,2,3-Tris(trimethylsilylated) Arene by Cobalt-Catalyzed Alkyne Cyclizations and Application of Fully Coupled Two-Dimensional Chemical Shift Correlations to a Structural Problem

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Received September 18, 1984

Abstract: $CpCo(CO)_2$ catalyzes the cocyclization of a 3-alkenylated 1-(trimethylsilyl)-1,5-hexadiyne with bis(trimethylsilyl)ethyne to give a 1,2,3-tris(trimethylsilylated) benzocyclobutene **4**. The steric and possibly electronic effect of the silyl group next to the four-membered ring prevents ring opening to the *o*-xylylene. The corresponding bis(trimethylsilyl)benzocyclobutene **5**, lacking the extra substituent, undergoes *o*-xylylene formation and intramolecular ring closure to the benzhydrindane nucleus. Structural analyses of **4** and **5** were provided by a new high-field NMR technique—fully coupled (FUCOUP) two-dimensional chemical shift correlation.

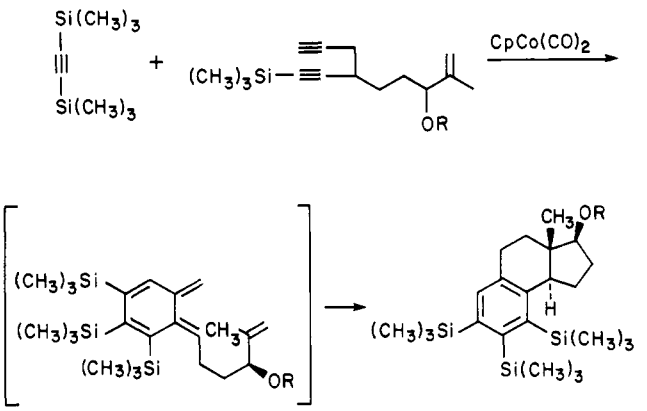
Substituted benzocyclobutenes have been employed via the intermediacy of their *o*-xylylene isomers as versatile synthetic building blocks in the construction of complex molecules.[1] In connection with our efforts to develop methodology based on cobalt-catalyzed alkyne cocyclizations to give benzocyclobutenes in tandem with intramoelcular Diels–Alder cycloadditions to resultant *o*-xylylene intermediates,[1c,2] we were interested in the stereo- and regioselective one-step construction of the benzhydrindane nucleus[3] according to Scheme I. The scheme's attractive features include the formation of five carbon–carbon bonds in one operation, the possibility of regiocontrolled electrophilic aromatic substitution chemistry[4] on the 1,2,3-tris(trimethylsilyl)arene portion of the product, and an opportunity to explore further the mechanistically complex[5] potential diastereoselectivity of the intramolecular Diels–Alder reaction with allylic ether functions of the type depicted.

In this paper we report the execution of Scheme I which has led to the first synthesis of a 1,2,3-tris(trimethylsilylated) benzocyclobutene and the discovery of an unprecedented strong steric hindrance to its four-membered ring opening. In order to separate electronic from steric contributions to this effect, a complete carbon and proton NMR assignment was required and was achieved by the application of a novel 2D NMR technique.

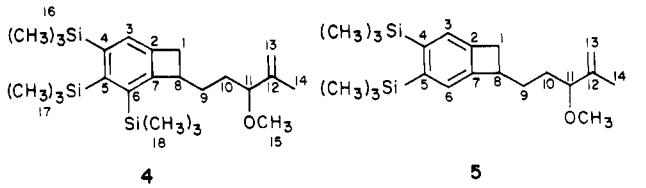
Results and Discussion

Synthesis of Starting Enediyne. As a target starting material, we chose the enediyne **2**, prepared as shown in Scheme II. 2-Methylpropenal was subjected to aldol condensation with isopropyl ethanoate, followed by methylation, lithium aluminum hydride reduction, tosylation, and bromide displacement to furnish **1**, the five-step sequence proceeding in 38% overall yield. This compound was then used to alkylate 3,6-dilithio-1-(trimethylsilyl)-1,5-hexadiyne, prepared from the silyldiyne[6,7] by a new[8] regioselective propargylic metalation.[9] Evidently the charge at C-6 and/or the acceptor capability of the silicon[4] prevented deprotonation at C-4. Protodesilylation of the resulting enediyne **2** gave **3** (94%), each isolated as an approximately 3:2 mixture of diastereomers. With our desired starting material in hand, the stage was set to attempt cyclizations of the type outlined in Scheme I.

Scheme I



Cobalt-Catalyzed Cyclization of 2 and 3. When compound **2** was exposed to bis(trimethylsilyl)ethyne (btmse) at reflux with simultaneous irradiation in the presence of a catalytic amount of (η^5-cyclopentadienyl)cobalt dicarbonyl [$CpCo(CO)_2$], benzocyclobutene **4** (mixture of diastereomers) was the only cocyclization product observed (24%) even after prolonged heating of the reaction mixture. The structure of **4** was in accord with



4 5

(1) (a) Oppolzer, W. *Synthesis* **1978**, 793. (b) Oppolzer, W. *Heterocycles* **1980**, *14*, 1615. (c) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, *9*, 41. (d) Kametani, T.; Nemoto, H. *Tetrahedron* **1981**, *37*, 3. (e) Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183.

(2) Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(3) (a) Kametani, T.; Matsumoto, H.; Honda, T.; Fukumoto, K. *Tetrahedron Lett.* **1980**, *21*, 4847. (b) Kametani, T.; Matsumoto, H.; Honda, T. *Tetrahedron* **1981**, *37*, 2555. (c) Shishido, K.; Shimada, S.; Fukumoto, K.; Kametani, T. *Chem. Pharm. Bull.* **1984**, *32*, 922.

(4) Colvin, E. "Silicon in Organic Synthesis"; Butterworths: London, 1981.

(5) See, for example: Roush, W. R.; Peseckis, S. M. *J. Am. Chem. Soc.* **1981**, *103*, 6696. Franck, R. W.; John, T. V.; Olejniczak, K. *Ibid.* **1982**, *104*, 1106. Funk, R. L.; Zeller, W. E. *J. Org. Chem.* **1982**, *47*, 180. Caramella, P.; Rondan, N. G.; Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 2438.

(6) Now available in 53% yield by the procedure outlined in ref 7.

(7) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058.

(8) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, *102*, 5245, 5253.

(9) Klein, J. In "The Chemistry of the Carbon–Carbon Triple Bond"; Patai, S., Ed.; Wiley: New York, 1978; p 343.

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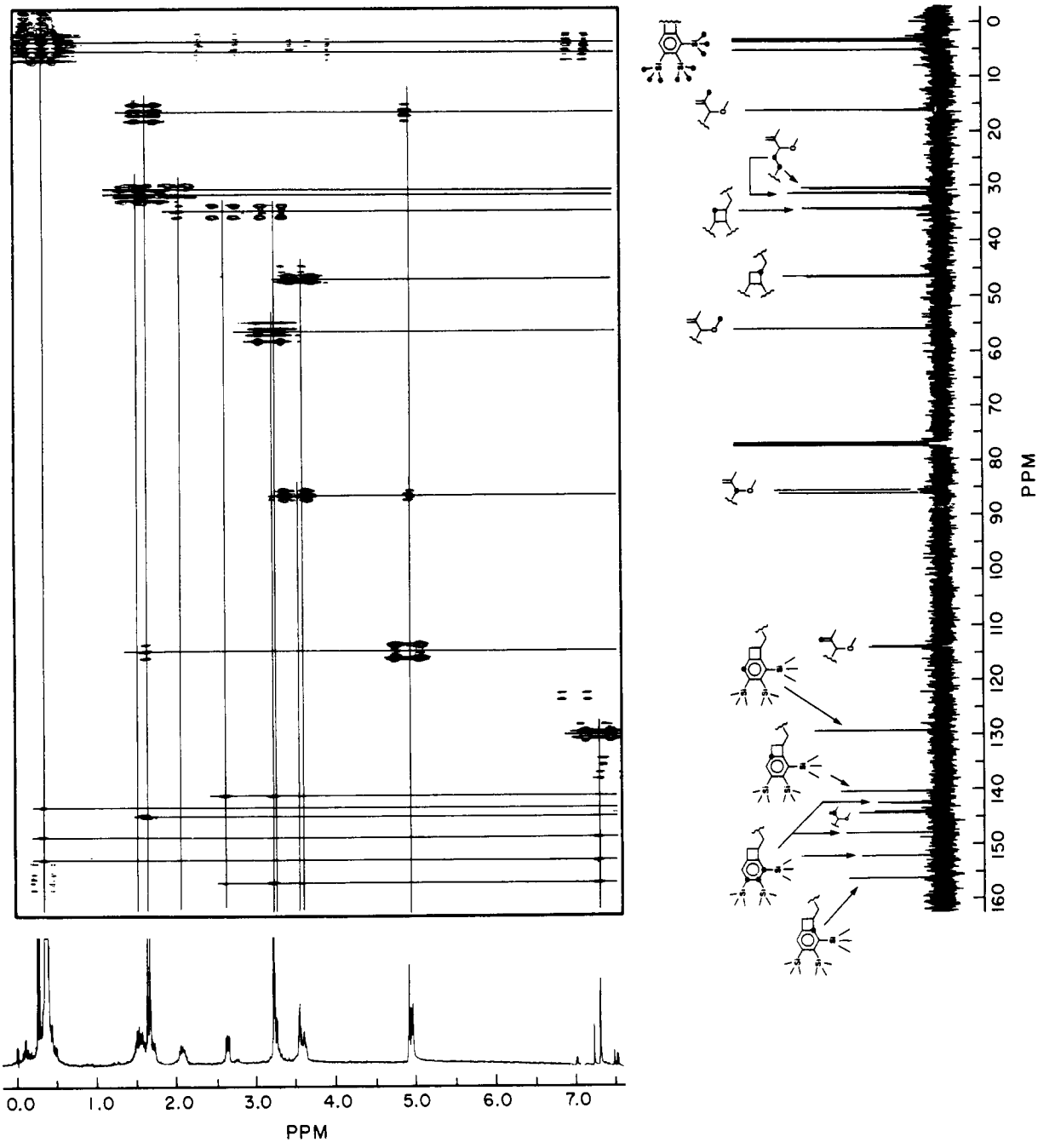
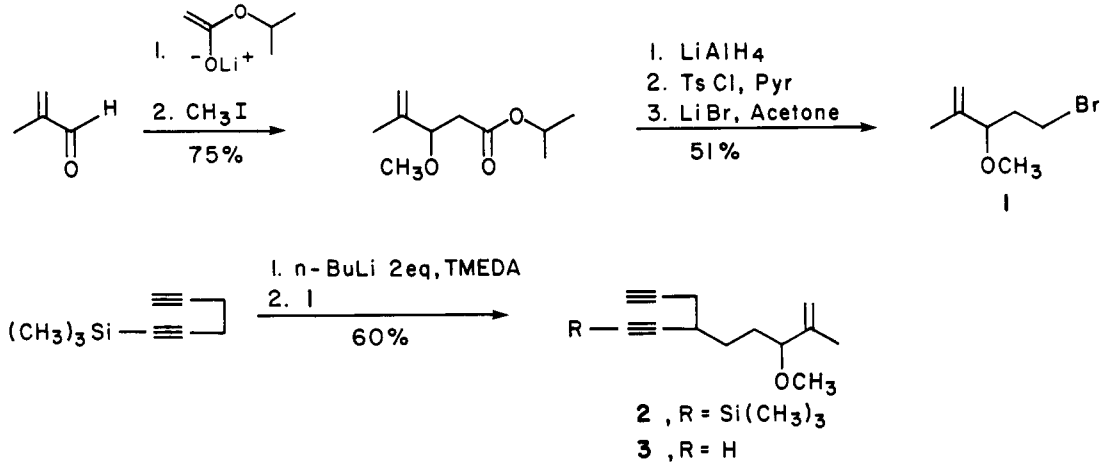


Figure 1. Seven-level contour plot of FUCOUP-generated $^{1}H-^{13}C$ chemical shift correlation map of **4**.

Scheme II



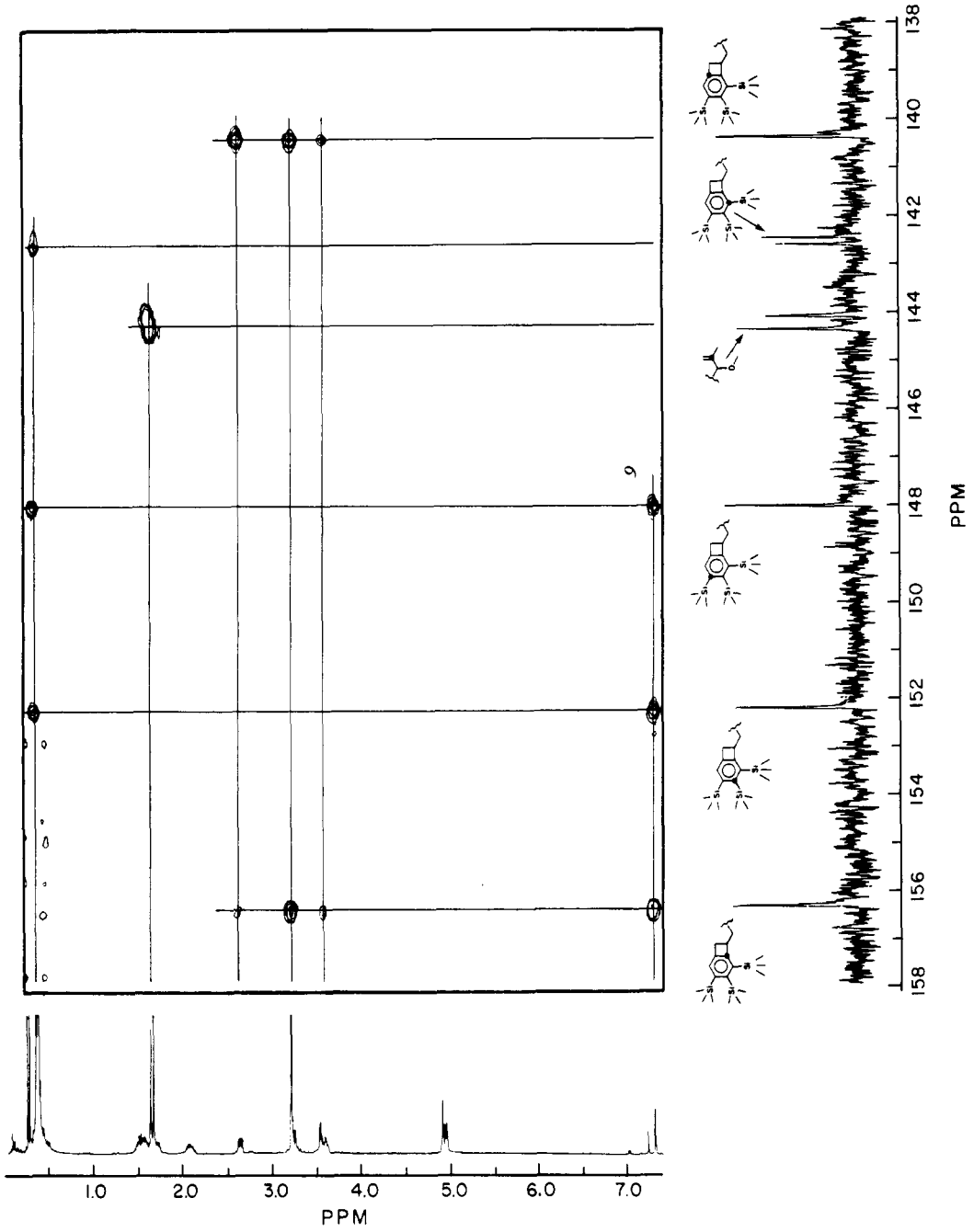


Figure 2. Five-level contour plot of expanded ^{13}C region of **4**.

its analytical and spectral data (see also Figures 1 and 2), except for the completely unambiguous assignment of the 1,2,3-tris-(trimethylsilyl)benzene pattern. Because trimethylsilyl (TMS) groups are known to undergo acid-catalyzed migrations, primarily to escape the steric encumbrance of a bulky neighbor,[4,7] the simple spectral analysis could not distinguish the substituent arrangement shown in **4** from one in which the three silyl moieties were not completely adjacent. A strong indication that the formulation as **4** was correct came from its spontaneous quantitative monoprotodesilylation on standing in dichloromethane at 4 °C to give not **5** but a new bis(trimethylsilyl) derivative formulated as the 4,6-silyl analogue of **4**, in which the (presumably) most strained TMS group had been removed. Its ^1H NMR spectrum revealed the absence of ortho aromatic hydrogens and the presence of two broad singlets at δ 7.47 and 7.22, consistent with a meta substitution pattern. Although these data are also compatible with a structure with TMS groups at C-3 and C-5 (derived from the hypothetical rearrangement product of **4** with TMS substituents at C-3, C-5, and C-6), its formation would have necessitated the unlikely regioselective protodesilylation at the much less reactive (by a factor of about 500)[7] position α to the strained ring. Regardless of the ultimate structural assignment (eventually proven to be ~4, vide infra), it is remarkable that the cyclization reaction tolerates the degree of strain that must be present in **4** and the intermediates[2] en route to it.

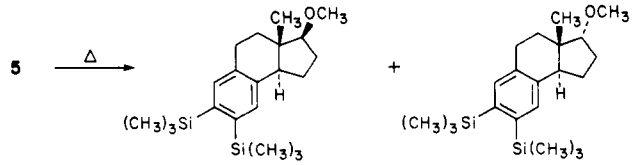
Surprisingly, **4** was recovered completely unchanged after 22 h in boiling decane (bp 175 °C). When heated to 220 °C (dodecane) it decomposed into a number of uncharacterizable alkenes (see Experimental Section), not a trace of the desired benzhydrindane being detectable.

That this inability to undergo intramolecular ring closure must have been due to the presence of the TMS group at C-6 (for the numbering scheme, see **4**) was indicated by the finding that **5**, obtained by cobalt-catalyzed cocyclization of **3** with btmse in 88% yield (as a mixture of diastereomers), when heated to 175 °C (decane) smoothly and efficiently (83%) was converted to **6** and **7** in a stereoconvergent but not completely diastereospecific manner (Scheme III). While the crude reaction mixture contained **6** and **7** in a 1:1 ratio, the isolated yields, after chromatographic separation, were 39% for **6** and 44% for **7**. In both cases the presence

Table I. Carbon and Proton Chemical Shift Assignments (ppm) in **4** and **5**

compound **4**			compound **5**		
carbon no.	δ ^{13}C	δ ^{1}H	carbon no.	δ ^{13}C	δ ^{1}H
1	34.22, 34.06	2.64, 3.25	1	36.59, 36.54	2.80, 3.37
2	140.38		2	143.70	
3	129.32, 129.26	7.32	3, 6	128.32, 129.50	7.45
4	148.00		4	144.08, 144.05	
5	152.19		5	144.69	
6	142.60, 142.41				
7	156.31		7	149.54, 149.44	
8	46.50, 46.30		8	44.10, 43.98	3.53
9	30.49, 30.31	2.08, 1.48–1.76	9	30.46, 30.22	1.60, 1.95
10	31.35, 31.23		10	32.20, 32.02	
11	85.96, 85.38		11	85.83, 85.61	3.58
12	144.35, 144.08		12	144.28, 144.16	
13	114.08, 113.89	4.96, 4.92	13	113.91, 113.87	4.98, 4.94
14	16.19	1.68, 1.65	14	16.25, 16.20	1.69
15	55.96	3.23, 3.22	15	55.98, 55.95	3.26
16, 17, 18	5.15, 3.50	0.385, 0.379	16, 17	2.39, 2.04	0.391
	3.49, 3.12	0.377, 0.358			

Scheme III



6 (39%) **7** (44%)

of the trans B,C ring junction was established by the characteristic chemical shifts of the angular methyl group.[3,10] The assignments of stereochemistry at the methoxy carbon was tentative,[3,10,11] again relying on the (less distinct) chemical shift trends of the neighboring methyl substituent. In contrast to the results of Kametani in a related system,[3c] no cis B,C-fused product was detected, even in the crude material.

Why does **4** not undergo ring opening? There are two explanations, one of steric, the other of electronic origin. The former would predict the conrotatory outward movement[2] of the alkyl substituent on the four-membered ring to be prohibited by the steric bulk of the TMS group on C-6. The normally energetically more costly inward rotation in turn would produce intermediates likely to be prone to 1,5-hydrogen shifts,[2b] giving rise to sensitive styrene derivatives, which can be envisaged to decompose by a variety of pathways.

The second rationale for the lack of reactivity in **4** would attribute it to some deactivating electronic influence of the silyl substituent at C-6. Kametani has argued[12] that such an electronic substituent effect may indeed exist and can be qualitatively estimated by ^{13}C NMR spectroscopy. For example, it has been found that depending on the nature and the location of the substituents, various substituted benzocyclobutenes require differing amounts of energy to undergo ring opening. Thus, whereas 1-hydroxybenzocyclobutene is readily converted into the corresponding *o*-xylylene at 110 °C,[13] the parent benzocyclobutene and the derivatives methoxylated β to the strained ring have been reported to be stable at temperatures higher than 200 °C.[14] It was suggested[12] that the ring opening might be facilitated by substituents which stabilize the developing sp^2 character of the saturated carbon atoms involved in the ring opening to the *o*-xylylene (and/or destabilize their sp^3 character). Such an influence was thought to be measurable by the changes in the chemical shift differences, Δ, involving the rehybridizing carbons as expressed by the equation (numbering as in **4** and **5**)

$$\Delta = (\delta_2 + \delta_7) - (\delta_1 + \delta_8)$$

It was qualitatively found[12] that benzocyclobutenes which undergo ring opening at temperatures higher than 200 °C have relatively high Δ values (benzocyclobutene, Δ = 232), whereas those transforming at "moderate temperatures" (150–170 °C) have lower Δ values ($\Delta \sim 200$). The unusually reactive 1-hydroxybenzocyclobutene also has an unusually low Δ value of 174.5. However arguable the importance of the absolute size of Δ may be, it appeared that within a set of closely related structures, it might provide a reasonable insight into the potential operation of such electronic effects.

In order to obtain the required chemical shifts of the carbon atoms making up the four-membered rings, the ^{13}C NMR spectra of **4** and **5** had to be completely assigned and, of course, the structure of **4** ascertained. This could not be done with conventional high-resolution, high-field, and 2D NMR methods. However, it provided the opportunity to apply a novel, fully coupled (FUCOUP) chemical shift correlation NMR technique.[15]

Fully Coupled Chemical Shift Correlation and Determination of Δ for 4 and 5. The FUCOUP sequence represents the original two-dimensional ^{1}H–^{13}C chemical shift correlation method developed[16] but has, until very recently, not been used in chemical structure determinations.[15] This lack of application has presumably been due to the low sensitivity and poor digitizer resolution of the original method. By incorporation of a suitable quadrupole-phase cycle to the sequence[17] and because of the increased sensitivity of the high field magnets available today, the difficulties of the experiment are no longer insurmountable. Although the more recent standard heteronuclear chemical shift correlation methods[18] are more sensitive, they provide correlations only for ^{1}H–^{13}C pairs which have coupling constants within a preselected range. The latter is chosen generally to reveal directly bound nuclei. In the FUCOUP experiment, there is no dependence on the heteronuclear coupling constants. Therefore, in addition to

(10) Jackman, L. M.; Sternhell, S. "Application of NMR Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: New York, 1969; p 243.
(11) Clinet, J.-C.; Duñach, E.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1983**, *105*, 6710.
(12) Kametani, T.; Kajiwara, M.; Takahashi, T.; Fukumoto, K. *Tetrahedron* **1975**, *31*, 949.
(13) Arnold, B. J.; Sammes, P. G. *J. Chem. Soc., Chem. Commun.* **1972**, 30.
(14) Jensen, F. R.; Coleman, W. E.; Berlin, A. J. *Tetrahedron Lett.* **1962**, 15.
(15) (a) Holden, I., personal communication. (b) Waterhouse, A. L.; Holden, I.; Casida, J. E. "Abstracts of Papers" 188th National Metting of the American Chemical Society, Aug 26–31, 1984; American Chemical Society: Washington, DC, 1984; ORG 69; *J. Chem. Soc., Perkin Trans. 2*, in press.
(16) (a) Maudsley, A. A.; Ernst, R. R. *Chem. Phys. Lett.* **1977**, *50*, 368. (b) Bodenhausen, G.; Freeman, R. *J. Am. Chem. Soc.* **1978**, *100*, 320.
(17) Bleich, H.; Gould, S.; Pitner, P.; Wilde, J. *J. Magn. Reson.* **1984**, *56*, 515.
(18) (a) Thomas, D. M.; Bendall, M. R.; Pegg, D. T.; Doddrell, D. M.; Field, J. *J. Magn. Reson.* **1981**, *42*, 298. (b) For reviews on applications and theory of 2D NMR spectroscopy, see: Bax, A. "Two-Dimensional Nuclear Magnetic Resonance in Liquids"; Reidel: Dordrecht, 1982. Benn, R.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 350.

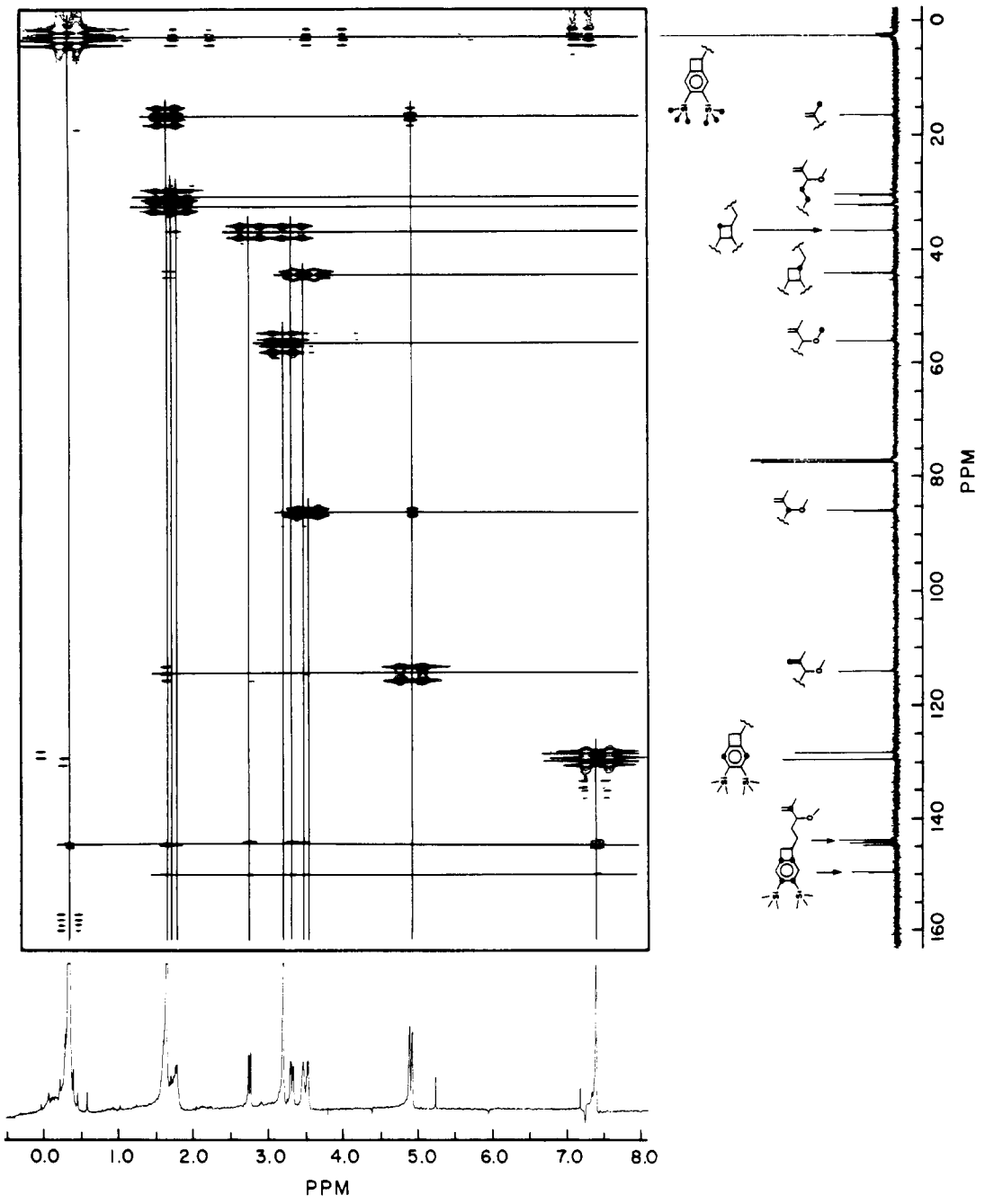


Figure 3. Seven-level contour plot of FUCOUP-generated $^1H-^{13}C$ chemical shift correlation map of **5**.

the large one-bond couplings, the smaller two- and three-bond $^1H-^{13}C$ couplings are observable in a single experiment. In our cases, all correlations due to couplings above the resolution limit (approximately 1.0 Hz) were detectable.

Contour plots of the fully coupled $^1H-^{13}C$ FUCOUP measurements for **4** and **5** are depicted in Figures 1–4. In these plots, the ^1H spectrum is located on the vertical and the ^{13}C absorptions on the horizontal axis. A relatively large signal is seen at the intersection of perpendicular lines emanating from the ^1H and ^{13}C signals arising from directly bound $^1H-^{13}C$ pairs. The less intense contours correspond to $^1H-^{13}C$ pairs coupled via two or three bonds.[19] Although signals for two diastereomers are present in each spectrum, it is apparent that the chemical shifts for the related carbons (from now on referred to as "diastereomeric") are either isochronous or so close in chemical shift that they give only one contour pattern in the two-dimensional map. By systematic analysis of the chemical shift correlations in Figures 1–4 the ^{13}C and ^1H chemical shift assignments in Table I were deduced. Only the more interesting or important assignments will be discussed.

In order to calculate Δ, the ^{13}C chemical shifts of the cyclobutenyl carbons were needed. First, for **4**, the benzylic carbons were readily assigned by comparison with literature values and correlation with the characteristic benzylic proton signals.[7,8,10,12,20] The diastereotopic benzylic methylene protons absorb at 2.64 and 3.25 ppm in Figure 1, peaks which correlate with the diastereomeric ^{13}C signals at 34.1 and 34.2 ppm, and hence must be due to C-1. The absorptions at 46.5 and 46.3 ppm can be assigned to C-8 based on the strong coupling with the remaining benzylic ^1H signal at 3.55 ppm. Interestingly, benzylic carbons C-1 at 34.1 and 34.2 ppm show a weak long-range interaction with the diastereotopic methylene ^1H signal at 2.08 ppm. A reasonable ex-

(19) Comprehensive reviews of the extent of $^1H-^{13}C$ coupling can be found in: (a) Hansen, P. E. *Progr. NMR Spectrosc.* **1981**, *14*, 175. (b) Marshall, J. L. "Carbon–Carbon and Carbon–Proton NMR Couplings: Applications to Organic Stereochemistry and Conformational Analysis"; Verlag Chemie: Deerfield Beach, FL, 1983.

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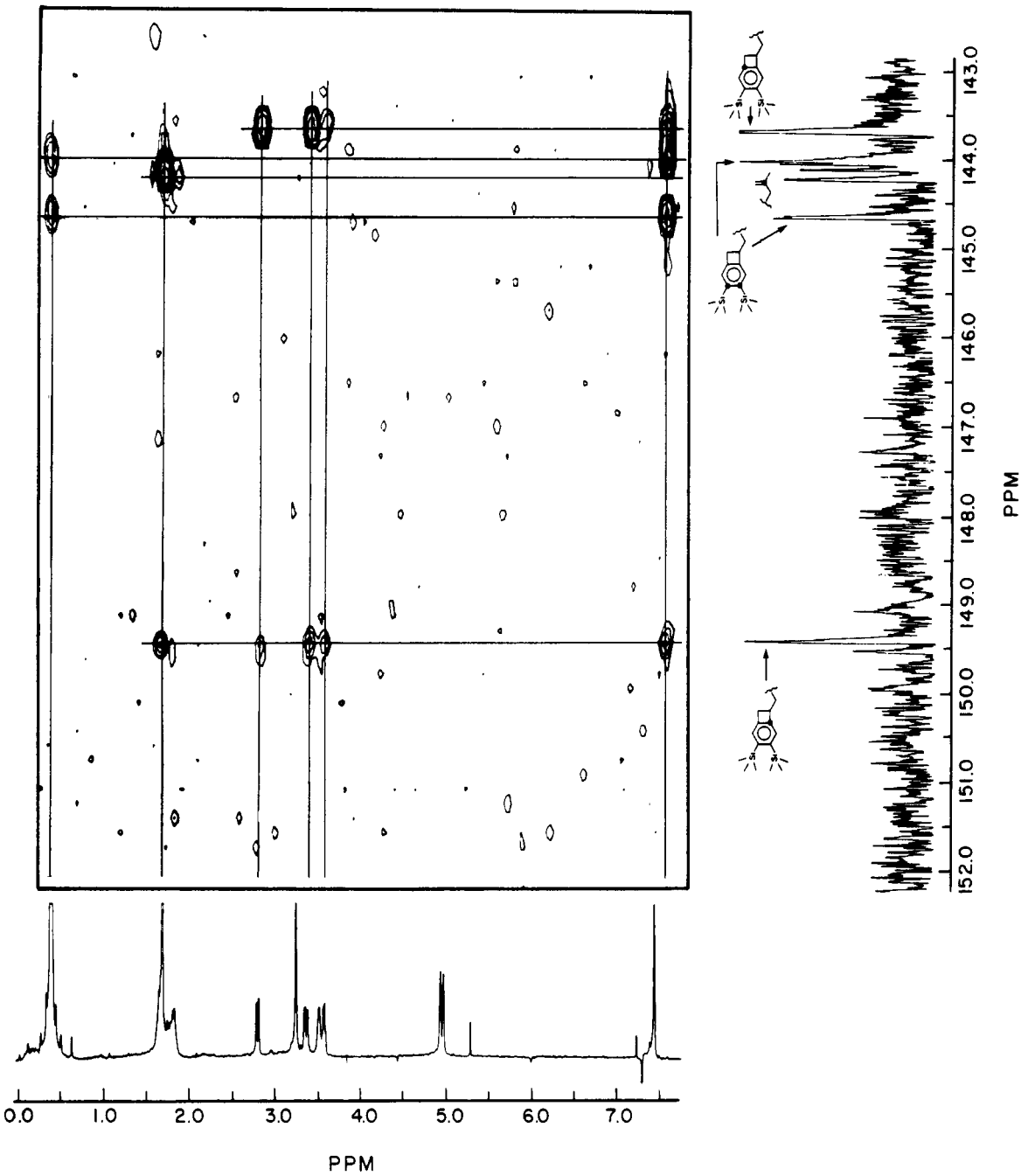

Figure 4. Five-level contour plot of expanded ^{13}C region of **5**.

planation for this observation is the occurrence of a three-bond coupling between C-1 and a proton on C-9. This allows the assignments of the closely situated secondary ^{13}C signals to C-9 and C-10. In the aromatic region, the aromatic carbon bearing a hydrogen is readily identified by its strong correlated signal to this hydrogen.

An expansion of the spectral region for the remaining aromatic carbons of **4** is shown in Figure 2. Since all signals are associated with quaternary nuclei, the contours in the two-dimensional map must arise from long-range coupling. Of interest are the assignments of the cyclobutene carbons and proof that the three TMS groups are indeed adjacent. The elegance of the FUCOUP sequence is demonstrated by the ease with which the TMS-substituted positions are assigned. The three-bond coupling of the methyl hydrogens through silicon to the aromatic nucleus is clearly visible, allowing the ^{13}C signals at 152.2 and 148.0 and the diastereomeric pair at 142.4 and 142.6 to be so identified. The diastereomeric ^{13}C absorptions at 144.0 and 144.3 ppm show coupling to the allylic methyl proton singlets at 1.68 and 1.65 ppm, establishing these resonances as arising from the quaternary vinyl carbon, C-12. The two remaining ^{13}C signals at 156.3 and 140.3 ppm must be due to the cyclobutenyl carbons C-2 and C-7 needed for the estimation of Δ. The nucleus C-7, being located β to both the TMS substituents and the alkyl chain,[7,8,20] was assigned to the lower field signal. Both of these absorptions show two- and three-bond couplings to the benzylic protons. The aromatic hydrogen is coupled only to the two lower field TMS-substituted carbons. This is consistent with having the three TMS groups adjacent as in **4**, giving rise to observable two- and three-bond couplings, the small four-bond coupling being unobservable as expected.[21] Had silyl group migration occurred, there would have been only two- and three-bond couplings between the aromatic proton and the TMS substituted carbons, all of which should have been observable. The diastereomeric ^{13}C signals at 142.4 and 142.6 ppm can thus be attributed to C-6. Carbon-5, having two β-TMS groups, was assigned to the lower field ^{13}C signal at 152.2 ppm and C-4 to the peak at 148.0 ppm. Typically, exchanging a proton with a TMS substituent induces a chemical shift increase of about

(21) Seel, H.; Aydin, R.; Günther, H. *Z. Naturforsch., B* **1978**, *33B*, 353.

10 ppm for the α carbon and 6–8 ppm for the β carbon.[7,8,20,22] This assignment is also corroborated by the chemical shift for C-5 in **5**. The deviations from the estimated values at C-4 and C-6 in **4** may be a reflection of strain effects.[22]

Figures 3 and 4 show plots of the correlation maps for **5**. As with **4**, the benzylic and protonated aromatic carbons were readily assigned. Again the signals for the two TMS-substituted carbons are readily recognized. Unfortunately, the exact assignments of the C-3, C-6 and C-4, C-5 pairs were not possible. The ^{13}C signals at 143.6 and 149.4 ppm can be attributed to the cyclobutene carbons, C-2 and C-7. The lower field resonance shows long-range coupling to the methylene ^1H signals at 1.70 and 1.85 ppm. This is explained by assigning the ^{13}C signal to C-7 which would exhibit three-bond coupling to the methylene protons on C-9. The complete carbon and proton chemical shift assignments for **4** and **5** are shown in Table I.

From these data and taking the average chemical shift values of those diastereomeric carbons giving rise to two distinct peaks, the following Δ values are calculated for **4** and **5**:

$$\Delta(\mathbf{4}) = 296.7 - 80.5 = 216.2$$

$$\Delta(\mathbf{5}) = 293.2 - 80.6 = 212.6$$

The results indicate the possible operation of a small retarding electronic effect for the ring opening of **4** compared to **5**. However, the differences in Δ are too small to account for the drastic reactivity change in going from **5** to **4**. We believe that the major contribution to the inertness of **4** arises from the steric impediment between the TMS group at C-6 and the alkyl chain as the benzocyclobutene attempts to ring open.

Conclusion

We have demonstrated the potential utility of cobalt-catalyzed enediyne cocyclizations to give benzhydrindanes bearing A-ring trimethylsilyl groups located β to the B ring. Stereoselectivity in the intramolecular Diels–Alder addition to the intermediate *o*-xylylene is observed with respect to the B/C ring junction but not with respect to a methoxy group adjacent to the angular methyl group. We have shown that the cyclization can be used to generate a new 1,2,3-tris(trimethylsilylated) arene pattern[23] and that the TMS group adjacent to a benzocyclobutene four-membered ring sterically (and perhaps also electronically) blocks thermal ring opening to the intermediate *o*-xylylene. This effect is potentially exploitable in future synthetic planning, since it allows the isolation of an intact benzocyclobutene, subjectable to further synthetic manipulation (e.g., by selective electrophilic substitution of TMS groups) before further cyclization. We also hope that this successful application of the fully coupled ^1H–^{13}C correlation technique will stimulate other workers to apply it to their structural problems.

Experimental Section

General Data. Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without further purification. THF was dried over boiling sodium benzophenone. Decane was distilled from calcium hydride and stored over molecular sieves (4 Å). All reactions involving air- or moisture-sensitive organometallic reagents were carried out under dry nitrogen. Btmse was degassed by boiling for 30 min under a nitrogen stream. Vacuum-line operations were carried out with a multiple-line apparatus.

Ordinary ^1H and ^{13}C NMR spectra were recorded on UCB 200-MHz, UCB 250-MHz, and BVX 300-MHz instruments consisting of Cryomagnet System magnets, Nicolet 293A or 293A′ pulse programmers, and Nicolet Model 1180 or 118E data collection systems. Data are reported as follows: chemical shifts in part per million (ppm) downfield of internal tetramethylsilane or residual solvent peaks (multiplicity, coupling constants in hertz, number of protons). For ^1H NMR spectra, the peak due to residual $CHCl_3$ is listed at 7.24 ppm, and for ^{13}C NMR spectra, the central peak of the deuteriochloroform triplet is assigned a chemical shift of 77.0 ppm downfield from tetramethylsilane.

Infrared spectra were obtained on one of the Perkin-Elmer Models 681 or 1420 and were referenced to polystyrene (1601 cm^{-1}). Only characteristic and strong signals are reported. Mass spectra [reported as *m/e* (rel intensity) at 70 eV unless mentioned otherwise] and elemental analyses were provided by the Mass Spectral Service and Microanalytical Laboratory, respectively, at the University of California—Berkeley. Melting points were determined in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected.

Isopropyl 3-Hydroxy-4-methyl-4-pentenoate. To a solution of LDA (200.0 mmol in 150 mL of THF) under N_2 at −78 °C was introduced isopropyl acetate (20.43 g, 200.0 mmol) dropwise by syringe. The mixture was stirred at this temperature for 1 h. To it was added dropwise methacrolein (15.42 g, 220.0 mmol). The solution was allowed to stir at −78 °C for 2 h. The cold bath was removed, and after stirring for another hour, the solution turned from a deep aqua-green color to light yellow. The flask was cooled to 0 °C, and excess saturated NH_4Cl solution was added to quench the reaction. After aqueous workup, fractional distillation provided the desired alcohol (25.84 g, 75%): colorless liquid, bp 104–105 °C (15 mmHg); IR (neat) 3660–3120 (OH), 1730 (C=O), 1650 cm^{-1} (C=C); MS, *m/e* (rel intensity) 172 (M^+, 2.4), 130 (45.6), 112 (37.5), 71 (82.5); ^1H NMR (300 MHz, $CDCl_3$) δ 4.93 (sep, J = 6.4 Hz, 1 H), 4.91 (s, 1 H), 4.75 (s, 1 H), 4.35 (br t, J = 5.5 Hz, 1 H), 3.28 (br s, 1 H), 2.42 (m, 2 H), 1.64 (s, 3 H), 1.13 (d, J = 6.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 171.8, 145.5, 111.2, 71.4, 68.0, 40.2, 21.6, 17.9.

3-Methoxy-4-methyl-4-penten-1-ol. To a cooled solution of isopropyl 3-hydroxy-4-methyl-4-pentenoate (1.72 g, 10.0 mmol) and methyl iodide (1.24 mL, 20.0 mmol) in Me_2SO (5 mL) was added powdered NaOH (0.60 g, 15.0 mmol). The mixture was allowed to stir at 0 °C for 4 h, monitored by TLC (30% ether–hexane). Additional methyl iodide (10.0 mmol) was added, followed by NaOH (5.0 mmol), and the mixture stirred for an additional hour at 0 °C. Aqueous workup gave a yellow oil of product (1.836 g, 9.96 mmol). This material was judged pure by ^1H NMR [(90 MHz, $CDCl_3$) δ 4.80 (s, J = 6 Hz, 1 H), 4.73 (m, 2 H), 3.80 (dd, J = 9, 6 Hz, 1 H), 2.38 (s, 3 H), 2.24 (m, 2 H), 1.42 (d, J = 1 Hz, 3 H), 0.98 (d, J = 6 Hz, 6 H)] and was used in the following reaction without further purification.

The crude ether from above in THF (5 mL) was cannulated into a solution of lithium aluminum hydride (0.40 g, 95%, 10.0 mmol) in THF (10 mL) at 0 °C. The reaction mixture was allowed to stir at 0 °C for 4 h. After aqueous workup, the crude concentrated material was purified by silica flash chromatography by using ether to give the desired alcohol (0.97 g, 74.5%): pungent, colorless oil, bp 173–174 °C (760 mmHg); IR (neat) 3600–3100 (OH), 1650 (C=C), 900 cm^{-1} (COC); ^1H NMR (200 MHz, $CDCl_3$) δ 4.92 (br s, 2 H), 3.73 (m, 1 H), 3.21 (s, 3 H), 2.58 (br s, 1 H), 2.00–1.79 (m, 1 H), 1.74–1.60 (m, 1 H), 1.64 (br s, 3 H). Anal. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84. Found: C, 64.85; H, 10.67.

5-Bromo-3-methoxy-2-methyl-1-pentene (1). 3-Methoxy-4-methyl-4-penten-1-ol (4.0 g, 30.7 mmol) was cannulated into a solution of *p*-toluenesulfonyl chloride (8.78 g, 46.1 mmol) in dry pyridine (20 mL) at −10 °C. The mixture was allowed to stir for 20 h at −15 °C, poured onto ice (30 g), cold ether (100 mL) added, and the material washed with three portions (25 mL) of a cold 25% aqueous H_2SO_4 solution. Standard aqueous workup gave a light yellow oil (8.36 g, 95.7%): IR (neat) 1595, 1355, 1190, 1170 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.77 (d, J = 8 Hz, 2 H), 7.32 (d, J = 8 Hz, 2 H), 4.89 (br s, 1 H), 4.85 (br s, 1 H), 3.97–4.18 (m, 2 H), 3.57 (dd, J = 8, 5 Hz, 1 H), 3.08 (s, 3 H), 2.43 (s, 3 H), 1.81 (m, 2 H), 1.59 (br s, 3 H). The product was used in the next step without further purification.

To a solution of the tosylate (8.36 g, 29.4 mmol) in dry acetone (100 mL) at 0 °C was added dry lithium bromide (4.92 g, 56.6 mmol). The mixture was heated to reflux under N_2 for 4.5 h and monitored by TLC (silica, 20% ether–hexane). The mixture was allowed to cool to room temperature and let stand for 12 h. Aqueous workup, followed by flash chromatography (silica, ether–hexane, 1:10), gave the desired product (4.03 g, 71.3%): colorless oil; IR (neat) 1650 (C=C), 1100, 903 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 4.96 (s, 1 H), 4.95 (s, 1 H), 3.71 (dd, J = 8.2, 5.0 Hz, 1 H), 3.53–3.34 (m, 2 H), 3.21 (s, 3 H), 2.04–1.85 (m, 1 H), 1.99–1.85 (m, 1 H), 1.63 (t, J = 1 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.2, 113.9, 82.9, 56.0, 36.7, 29.9, 16.3. Anal. Calcd for $C_7H_{13}BrO$: C, 43.54; H, 6.79; Br, 41.38. Found: C, 43.61; H, 6.90; Br, 41.47.

7-Methoxy-8-methyl-4-((trimethylsilyl)ethynyl)-8-nonen-1-yne (2). 1-(Trimethylsilyl)-1,5-hexadiyne (0.648 g, 4.31 mmol) in THF (20 mL) and TMEDA (1.33 mL, 8.80 mmol) was cooled to −11 °C (ice–acetone), and *n*-butyllithium (6.52 mL of a 1.35 M solution in hexane, 8.80 mmol) was added dropwise. After the addition was complete, the reaction mixture was allowed to stir at ~−5 °C for one additional hour, cooled

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to −78 °C, and the bromide **1** (0.820 g, 4.31 mmol) in THF (5 mL) added by cannula. The solution was allowed to warm to room temperature and stirred for 12 h. After a cold (0 °C) aqueous quench, the workup proceeded by using ether–1 N HCl. After flash chromatography (silica, 15% ether–hexane) pure product **2** was obtained (0.678 g, 59.9%): IR (neat) 3305 (≡CH), 3069 (=CH), 2167 (C≡C), 2119 (C≡C), 1650 (C=C), 1250 (SiC), 1110, 1090 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 4.86 (br s, 1 H), 4.83 (br s, 1 H), 3.44 (br t, J = 4.5 Hz, 1 H), 3.12 (s, 3 H), 2.50 (m, 1 H), 2.31 (m, 2 H), 1.94 (t, J = 2 Hz, 1 H), 1.26–1.73 (m, 4 H), 1.59 (br s, 3 H), 0.06 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 144.1, 143.9, 113.9, 113.5, 108.2, 108.1, 85.4, 85.0, 81.4, 69.9, 55.8, 31.9, 31.5, 30.7, 30.4, 29.8, 29.3, 24.7, 24.5, 16.3, 16.0, 0.01. Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.99. Found: C, 73.31; H, 9.98.

7-Methoxy-8-methyl-4-ethynyl-8-nonen-1-yne (3). Compound **2** (0.20 g, 0.76 mmol) in methanol (10 mL) was treated with anhydrous K_2CO_3 (0.42 g, 3.05 mmol) and the mixture stirred for 14 h under N_2. The methanol was removed by rotary evaporation and the residue worked up with water–ether. Silica flash chromatographic purification yielded **3** (0.136 g, 94%): colorless oil; IR (neat) 3301 (≡CH), 3072 (=CH), 2122 (C≡C), 1649 (C=C), 1111, 1092 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 4.92 (br q, J = 1.6 Hz, 1 H), 4.89 (br s, 1 H), 3.49 (dt, J = 5.2, 2.8 Hz, 1 H), 3.18 (s, 3 H), 2.50–2.58 (m, 1 H), 2.31–2.46 (m, 2 H), 2.11 (d, J = 2.3 Hz, 1 H), 2.03 (t, J = 2.5 Hz, 1 H), 1.37–1.85 (m, 4 H), 1.63 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 144.2, 144.1, 114.0, 113.7, 85.7, 85.5, 85.2, 81.4, 70.2, 70.1, 56.0, 30.9, 30.7, 30.1, 29.8, 24.7, 24.5, 16.4, 16.2. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 81.91; H, 9.70.

1-[1,2-Dihydro-4,5,6-tris(trimethylsilyl)benzocyclobuten-1-yl]-3-methoxy-4-methyl-4-pentene (4). A solution of the diyne **2** (023 g, 0.88 mmol) and $CpCo(CO)_2$ (18 μL, 0.14 mmol) in degassed btmse (5 mL) was added dropwise by using a syringe pump over 4 h to a boiling degassed solution of btmse (5 mL) and $CpCo(CO)_2$ (4 μL, 0.03 mmol). Light from a projector lamp (GE-ENH 250 W) was directed at the reaction mixture during the addition. After the mixture was boiled and irradiated, for an additional 2 h, the solvent was removed by vacuum transfer. The crude residue was purified by flash chromatography (silica, first with 20% ether–hexane, then with 20% CH_2Cl_2–hexane) to give **4** (90 mg, 23.7%): colorless oil; MS, m/e (rel intensity) 432 (M^+, 9.7), 313 (8.9), 241 (8.7), 183 (5.4), 149 (27.7), 73 (100); IR (neat) 3071 (C=CH), 2949, 2920, 2855, 2819, 1876, 1807, 1649 (C=C), 1264, 1251 (SiC), 1099 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32, 7.31 (s, 1 H), 4.96 (m, 1 H), 4.92 (br s, 1 H), 3.61 (m, 1 H), 3.55 (dt, J = 6.7, 2.1 Hz, 1 H), 3.25 (dd, J = 13, 5.7 Hz, 1 H), 3.23, 3.22 (s, 3 H), 2.64 (dt, J = 14.0, 3.2 Hz, 1 H), 2.08 (m, 1 H), 1.48–1.76 (m, 3 H), 1.68, 1.65 (s, 3 H), 0.385 (s, 9 H), 0.378 (s, 9 H), 0.358 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 156.3, 152.2, 148.0, 144.4, 144.1, 142.6, 140.4, 129.3, 114.1, 113.9, 86.0, 85.4, 56.0, 46.5, 46.3, 34.2, 34.1, 31.4, 31.2, 30.5, 30.3, 16.2, 5.15, 3.50, 3.49, 3.12. HRMS calcd for $C_{24}H_{44}OSi_3$ 432.2700, found 432.2699.

1-[1,2-Dihydro-4,6-bis(trimethylsilyl)benzocyclobuten-1-yl]-3-methoxy-4-methyl-4-pentene. Compound **4** underwent quantitative spontaneous protodesilylation upon standing in CH_2Cl_2 at ~4 °C for 4 weeks to give the 4,6-bissilylated benzocyclobutene: light yellow oil; MS, m/e (rel intensity) 360 (M^+, 6.5), 345 (4.0), 313 (5.3), 287 (3.6), 272 (4.3), 260 (8.0), 245 (15.9), 241 (14.8), 199 (4.3), 187 (11.2), 89 (15.9), 85 (43.1), 73 (100); IR (neat) 2962, 2933, 2907, 2865, 2830, 1653, 1588, 1255 (SiC), 1105 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (br s, half-width 3 Hz, 1 H), 7.22 (br s, half-width 3 Hz, 1 H), 4.94 (m, 1 H), 4.90 (br s, 1 H), 3.54 (m, 1 H), 3.49 (m, 1 H), 3.30 (dd, J = 13.9, 5.1 Hz, 1 H), 3.22, 3.21 (s, ratio 1:1, 3 H), 2.75 (ddt, J = 14.0, 4.6, 2.4 Hz, 1 H), 2.10–1.91 (m, 1 H), 1.78–1.49 (m, 3 H), 1.66, 1.64 (s, 3 H), 0.27 (s, 9 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 156.1, 144.4, 144.1, 142.3, 138.2, 136.8, 133.6, 133.5, 128.0, 114.1, 113.8, 85.9, 85.5, 56.0, 44.7, 44.5, 35.5, 35.3, 31.6, 31.4, 30.5, 16.2, 16.1, −0.73, −0.87. HRMS calcd for $C_{21}H_{36}OSi_2$ 360.2304, found 360.2314.

1-[1,2-Dihydro-4,5-bis(trimethylsilyl)benzocyclobuten-1-yl]-3-methoxy-4-methyl-4-pentene (5). A solution of **3** (0.15, 0.788 mmol) and $CpCo(CO)_2$ (20 μL, 0.16 mmol) in degassed btmse (5 mL) was added dropwise by using a syringe pump over 6 h to a boiling solution of degassed btmse (5 mL) and $CpCo(CO)_2$ (5 μL, 0.04 mmol). Light from a projector lamp was directed at the reaction mixture during the addition. After the mixture was boiled and irradiated for an additional 30 min, the solvent was removed by vacuum transfer. The crude residue was filtered through a short silica gel packed pipet (CH_2Cl_2). The organic material was concentrated and purified by flash chromatography (silica, 60% CH_2Cl_2–hexane) to give **5** (0.251 g, 88.3%): light yellow oil; IR (neat) 3071 (=CH), 1649 (C=C), 1250 (SiC), 1090 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ7.46, 7.45 (s, ratio 2:3, 1 H), 4.98 (br q, J = 1.5 Hz, 1 H), 4.94 (br s, 1 H), 3.58 (dt, J = 6.3, 4.2 Hz, 1 H), 3.53 (m, 1 H), 3.37 (m, 1 H), 3.26, 3.25 (s, ratio 2:3, 3 H), 2.80 (dd, J = 4.2, 2.5 Hz, 1 H), 1.60–1.95 (m, 4 H), 1.70, 1.69 (t, J = 0.8 Hz, 3 H), 0.391 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 149.5, 149.4, 144.7, 144.3, 144.2, 144.1, 143.7, 129.5, 128.3, 113.9, 85.8, 85.6, 56.0, 44.1, 44.0, 36.6, 36.5, 32.0, 32.0, 30.5, 30.2, 16.3, 16.2, 2.39, 2.04. Anal. Calcd for $C_{21}H_{36}OSi_2$: C, 69.93; H, 10.06. Found: C, 69.75; H, 9.96.

Thermolysis of Benzocyclobutene 5. 2,3,3a,4,5,9b-Hexahydro-3α-methoxy-3aα-methyl-7,8-bis(trimethylsilyl)-9bβ-(1*H*)benz[*e*]indene (6) and 2,3,3a,4,5,9b-Hexahydro-3β-methoxy-3aα-methyl-7,8-bis(trimethylsilyl)-9bβ-(1*H*)benz[*e*]indene (7). The benzocyclobutene **5** (100 mg, 0.28 mmol) was dissolved in decane (5 mL) and heated at reflux under N_2 for 10 h. The solvent was removed by vacuum transfer, and the residue (1:1 ratio of **6** and **7** by ^1H NMR) was purified by flash chromatography (silica, 40% CH_2Cl_2–hexane) to give first **6** (39 mg, 39%): colorless crystals, mp 95–97 °C; IR ($CDCl_3$) 2932, 2860, 1252, (SiC), 1127, 1108 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (s, 1 H), 7.28 (s, 1 H), 3.46 (t, J = 7.5 Hz, 1 H), 3.40 (s, 3 H), 2.90 (m, 2 H), 2.64 (dd, J = 11, 7.5 Hz, 1 H), 2.46 (m, 1 H), 2.10 (m, 2 H), 1.71 (m, 3 H), 0.68 (s, 3 H), 0.33 (s, 9 H), 0.32 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.4, 138.6, 135.6, 135.3, 132.8, 89.7, 58.0, 46.4, 43.0, 35.0, 28.3, 26.7, 22.6, 11.2, 2.03. Anal. Calcd for $C_{21}H_{36}OSi_2$: C, 69.93; H, 10.06. Found: C, 70.24; H, 9.99.

The second fraction contained **7** (44 mg, 44%): colorless oil; IR (neat) 2909, 2884, 2825, 1540, 1460, 1430, 1380, 1365, 1251 (SiC), 1109 cm^{-1} (COC); ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1 H), 7.34 (s, 1 H), 3.36 (d, J = 5.7 Hz, 1 H), 3.30 (s, 3 H), 3.00 (dd, J = 7.6, 4.5 Hz, 1 H), 2.92 (m, 2 H), 2.23 (ddd, J = 10.5, 5.2, 2.2 Hz, 1 H), 2.12 (m, 2 H), 1.83 (ddd, J = 15.5, 9.5, 8.1 Hz, 1 H), 1.69 (ddd, J = 9.5, 6.0, 3.3 Hz, 1 H), 1.57 (ddd, J = 12.0, 8.2, 1.2 Hz, 1 H), 0.58 (s, 3 H), 0.33 (s, 9 H), 0.32 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.1, 141.9, 139.8, 135.8, 133.8, 131.3, 88.7, 57.1, 47.4, 45.2, 45.2, 29.5, 29.4, 26.9, 24.1, 17.0, 2.04. Anal. Calcd for $C_{21}H_{36}OSi_2$: C, 69.93; H, 10.06. Found: C, 69.87; H, 9.89.

Thermolysis of Benzocyclobutene 4. Compound **4** was recovered unchanged from boiling decane (bp 175 °C). When **4** (10 mg, 0.220 mmol) was dissolved in dodecane (1 mL, bp 220 °C) and heated at reflux for 43 h, all the starting material disappeared (TLC) and two UV active spots were detected. These fractions were isolated by flash chromatography (silica, 5% ether–hexane). Each consisted of more than one compound (many trimethylsilyl signals in the NMR spectrum). Crude product: IR (neat) 3071, 2923, 2854, 2819, 2169, 1648 (C=C), 1447, 1410, 1374, 1263, 1250 (SiC), 1098 cm^{-1} (COC); MS, m/e (rel intensity) 433 (0.01), 345 (0.02), 329 (0.23), 313 (0.72), 241 (0.52), 187 (2.4), 85 (61.3), 73 (100).

FUCOUP Experiments

General. The data were acquired and processed with the aid of a Bruker AM-500 spectrometer equipped with an Aspect 3000 computer and an Oxford superconducting magnet operating on a proton frequency of 500.13 MHz. A 5-mm broad band dual probe was employed. A microprogram implementing the following pulse sequence was used: relaxation delay; 90° ^1H pulse from the decoupler; incremental delay; 90° ^1H pulse from the decoupler with a simultaneous 90° ^{13}C pulse from the transmitter; acquisition of the ^{13}C free induction decays (FIDs); store accumulated FIDs; increment file extension and incremental delay. The 90° ^{13}C pulse from the transmitter lasted 12 μs. The 90° ^1H pulse from the decoupler lasted 16 μs. Phase cycling was performed according to the literature.[17]

FUCOUP of 4. The transmitter frequency (125.76 MHz) was set at 80.0 ppm in the center of the ^{13}C region. The total sweep width was 165.7 ppm. The decoupler frequency (500.13 MHz) was set at 3.70 ppm in the center of the ^1H region. The total sweep width for the ^1H dimension was set to half that of the normal ^1H spectrum, 3.90 ppm. A 0.23 M solution of **4** in $CDCl_3$ was used. Two hundred 2K transients were acquired for each of the 128 incremental spectra. The relaxation delay was 1.4 s. The total time for data acquisition was 12 h.

The free induction decay data were processed in the carbon dimension by a Gaussian window function apodization (line broadening of −3.00 applied to 0.4 of the FID) and Fourier transformation. The proton dimension was then processed by π/3-shifted sine bell window apodization, Fourier transformation, and power spectra multiplication to yield the final processed matrix. After appropriate scaling for plotting, seven level contour plots of the entire matrix and several submatrices were obtained on a Watanabe digital plotter. Total processing time was under 5 min. Plotting time was about 1 h.

FUCOUP of 5. The transmitter frequency (125.76 MHz) was set at 81.0 ppm in the center of the ^{13}C region. The total sweep width was 167 ppm. The decoupler frequency (500.13 MHz) was set at 3.78 ppm in the center of the ^1H region. The total sweep width for the ^1H dimension was set to half of that of the normal ^1H spectrum, 4.3 ppm. A 0.37 M solution of **5** in $CDCl_3$ was used. A total of 96 transients was acquired for each of the 128 incremental spectra. The relaxation delay was 1.5 s. The total time for data acquisition was 6 h. The FID data in the

carbon dimension were processed by a $\pi/6$-shifted sine bell window apodization and Fourier transformation. The proton dimension was then processed by $\pi/3$-shifted sine bell window apodization, Fourier transformation, and power spectra multiplication to yield the final matrix. After scaling for plotting, seven level contour plots of the entire matrix and several submatrices were printed on a Watanabe digital plotter. The total processing time was under 5 min. The plotting time was about 1 h.

Acknowledgment. We are grateful to Dr. I. Holden for introducing us to FUCOUP. This work was supported by NIH GM-22479. R.L.H. was and N.H.N. is a recipient of a Univesity of California Regents' Fellowship (1982–1984 and 1984–1985, respectively).

Registry No. 1, 94621-19-9; **2**, 94621-20-2; **3**, 94621-21-3; **4**, 94621-22-4; **5**, 94621-23-5; **6**, 94621-24-6; **7**, 94621-25-7; btmse, 14630-40-1; *i*-PrOAc, 108-21-4; CH_2=$C(CH_3)CH(OH)CH_2C(O)OPr$-*i*, 94621-15-5; CH_2=$C(CH_3)CH(OMe)(CH_2)_2OH$, 94621-16-6; CH_2=$C(CH_3)CH(OMe)CH_2C(O)OPr$-*i*, 94621-17-7; CH_2=$C(CH_3)CH(OMe)(CH_2)_2OTs$, 94621-18-8; $CpCo(CO)_2$, 12078-25-0; HC≡$C(CH_2)_2$C≡$CSiMe_3$, 1578-34-3; methacrolein, 78-85-3; 1-[1,2-dihydro-4,6-bis(trimethylsilyl)benzocyclobuten-1-yl]-3-methoxy-4-methyl-4-pentene, 94621-26-8.

Base-Induced Proton Tautomerism in the Primary Photocyclization Product of Stilbenes

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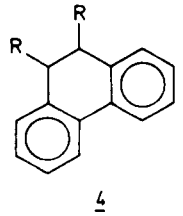
Received April 2, 1984

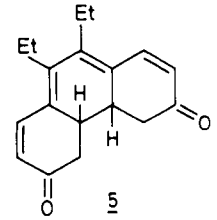
Abstract: The mechanism of the photoformation of 1,4-dihydrophenanthrenes (1,4-DHP) and 9,10-dihydrophenanthrenes from 1,2-diarylethylenes in amine solution is clarified by demonstrating that the amine reacts as a base with the initially formed 4a,4b-dihydrophenanthrene. The predominant formation of 1,4-DHP from stilbene is ascribed to an easy proton transfer from C(4b) to C(4) in 4a,4b-DHP via a deprotonation/protonation step, in which the amine operates as the transferring agent. The product formation in basic *methanolic* solutions proceeds with another mechanism or with less selectivity. When propyl thiolate, having a weak hydrogen-bonding capability, is used as the base, the *solvent*-mediated protonation in the deprotonation/protonation step occurs exclusively at C(9) and leads eventually to 9,10-DHP. When the stronger base sodium methoxide is used, solvent-mediated protonation proceeds rather unselectively at C(2), C(4), and C(9) and causes the ultimate formation of a mixture of 1,2-, 1,4-, and 9,10-DHP. Deuteration experiments indicate that 1,2- and 3,4-DHP are intermediates in the formation of 1,4-DHP (Scheme VII). The former compounds isomerize *photochemically* in the presence of a base. Larger diarylethylenes give only compounds analogous to 9,10-DHP.

In the last decades the photodehydrocyclization of stilbene (**1**) and stilbene-like compounds to phenanthrenes (**3**) has become a well-known photochemical reaction (Scheme I). The 4a,4b-dihydrophenanthrenes (4a,4b-DHP's, **2**) have been accepted as the initially formed photoproducts;[1] their dehydrogenation occurs mostly under oxidative conditions in the presence of O_2, I_2, TCNE, and other oxidants.[1,2] Besides the oxidative reaction, the 4a,4b-DHP's undergo, thermally as well as photochemically, a ring-opening reaction to the parent stilbene.[1a]

Another class of reactions which is exhibited by a number of 4a,4b-DHP's concerns the rearrangement to more stable isomers. Thus, 9,10-DHP's (**4**) have been isolated upon irradiation of several stilbenes with enolizable substituents at the olefinic double bond.[1b,3] Their formation was ascribed to prototropic shifts,[3a,b]



4



5

sometimes in combination with hydrogen radical abstraction recombination steps[3c,d] or thermal as well as photochemical hydrogen shifts[3e,f] in the primary formed 4a,4b-DHP's. According to Doyle and co-workers,[4] 4,4'-dihydroxy-α,α'-diethylstilbene undergoes upon irradiation in a protic medium, even in the presence of oxygen, quantitative conversion into a diketo compound **5**, derived by tautomerism from the corresponding 4a,4b-dihydrophenanthrenediol.

Isomerizations of unsubstituted 4a,4b-DHP's, derived from stilbene or other diarylethylenes, seem to be very rare. Very recently some of us[5] reported on *trans*-6a,16d-dihydrohexahelicene (**8**) formed under argon (Ar) by a [1,5]-suprafacial hydrogen shift from the primary formed photocyclization product (**7**) of 2-styrylbenzo[*c*]phenanthrene (**6**) (Scheme II). Curiously the

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