5.43 (apparent d, 1, $J_{3,4}$ = 2 Hz, H_4), 6.22 (dd, 1, $J_{1,2}$ = 9.5 Hz, $J_{2,3}$ = 5 Hz, H_2), 6.70 (d, 1, $J_{1,2}$ = 9.5 Hz, H_1), 7.36-8.33 (m, 6, aromatic), 8.55–8.88 (m, 2, $H_{10,11}$).

***trans*-3,4-Dihydroxy-*anti*- and -*syn*-3,4-epoxy-1,2,3,4-tetrahydrochrysene (4 and 3b).** A solution of **2a** (37 mg, 0.014 mmol) and *m*-chloroperbenzoic acid (250 mg) in dry THF (15 mL) was stirred at ambient temperature for 30 min under N_2. The resulting solution was partitioned between ethyl acetate and cold 10% NaOH solution (2 × 80 mL), and the organic layer was washed with water (100 mL), dried ($MgSO_4$), and evaporated to dryness (ambient temperature) to afford a mixture of the anti and syn isomeric diol epoxides (18 mg, 46%) in the ratio of 5:3. NMR of the anti isomer (acetone-d_6–D_2O) δ 3.90(m, 1, H_2), 4.06 (m, 1, H_1), 4.22 (m, 1, H_3), 5.18 (m, 1, H_4), $J_{3,4}$ = 8 Hz, $J_{2,3}$ = 1–2 Hz, $J_{1,2} \simeq$ 4 Hz; NMR of the syn isomer δ 4.22 (m, 1, H_2), 4.35 (m, 1, H_1), 4.67 (m, 1, H_3), 5.37 (m, 1, H_4) (coupling constants were too difficult to estimate accurately on the small amount of this component present).

Acknowledgment. This investigation was supported by Grants CA 11968 and CA 14599 and a research contract (CP 033385) from the National Cancer Institute, DHEW.

Registry No. **1a**, 64920-31-6; **1b**, 69303-41-9; **2a**, 64920-32-7; **2b**, 66267-16-1; **3a**, 64938-66-5; **3b**, 64920-33-8; **4**, 70951-83-6; **5**, 2091-92-1; **6**, 2091-90-9; **7**, 2091-91-0; **8**, 69104-29-6; **9**, 69104-30-9; **10**, 69275-38-3; **11**, 18930-98-8; **12**, 71435-43-3; **13**, 66267-12-7; chrysene, 218-01-9; 1,2,3,4-tetrahydrochrysene, 2091-90-9; 4-bromo-*trans*-1,2-bis(benzoyloxy)-1,2,3,4-tetrahydrochrysene, 71435-44-4; 1,2,3,4,7,8,9,10-octahydrochrysene, 2091-87-4.

New Synthetic Approach to 4-Alkylidenecyclohexenes. Reduction–Protodesilylation of Benzylsilanes

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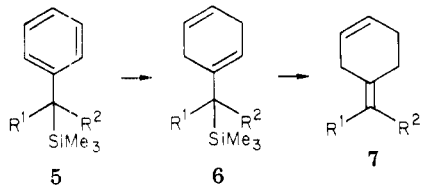
Synthetic methodology is described which allows conversion of benzylsilanes into 4-alkylidenecyclohexenes or 4-alkylidenecyclohexanones in good yields. Structurally specific syntheses are readily achieved for various derivatives which are not efficiently accessible by conventional methods. These include the natural product, terpinolene, as well as 2-methyl-4-methylenecyclohexan-1-one and 3-carbomethoxy-5-methylenecyclohex-1-ene.

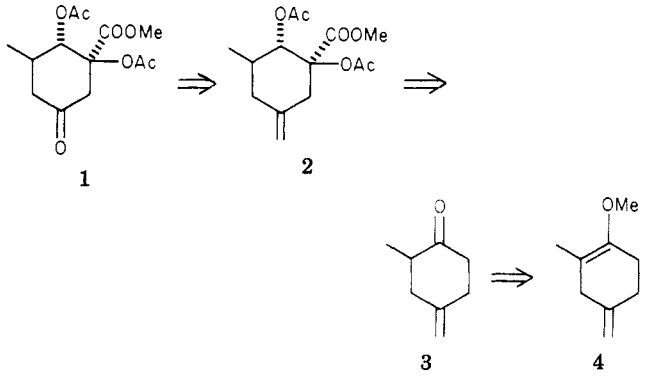
Alkylidenecyclohexyl structures are ubiquitous in natural products. Alkylidenecyclohexanones are important rudimentary synthons for elaboration of natural products.[1] In connection with our studies on leucogenenol,[2] we envisioned synthetic applications of 4-methylenecyclohexanones which exploit the C=C unit as a latent carbonyl.[4] This is illustrated in a projected synthesis of ketone **1**, the structure proposed for a keto triester obtained from a hydrolytic fragment of leucogenenol.[5] Thus, the retrosynthetic analysis shown in Scheme I uses an olefin **2** as the penultimate target. Our interest in developing an efficient synthesis of the key intermediate **3**, and recognition that this ketone could be obtained from the enol ether **4**, provided the impetus to demonstrate a synthetic equivalency of 4-alkylidene-1-cyclohexenes **7** and benzylsilanes **5**. Thus, (3,6-dihydrobenzyl)silanes **6**,



5 **6** **7**

obtained from benzylsilanes **5** by Birch reduction,[6] should

Scheme I



1 **2** **3** **4**

afford **7** by protodesilylation.[7] Electrophilic substitution of the allylic silicon in **6** by a proton was expected to occur regiospecifically with transposition of an endocyclic C=C bond into the desired exocyclic position.[7,8] The present study demonstrates the feasibility and explores the scope of this new synthetic method.

Results

Synthesis of Benzylsilanes. A representative selection of primary, secondary, and tertiary benzylsilanes was prepared by replacement of a benzylic halogen or hydrogen with a trimethylsilyl group by several methods. Thus benzylsilanes **5a–e** (Table I) were prepared by in situ

(1) For some examples including nootkatone, isonootkatone, and perfume compositions see: Marshall, J. A.; Ruden, R. A. *J. Org. Chem.* **1971**, *36*, 594. Marshall, J. A.; Warne, T. M. *Ibid.* **1971**, *36*, 178; Swiss Patent 554934, 1975; *Chem. Abstr.* **1975**, *82*, 98214.

(2) Leucogenenol is a natural product which functions as a hormone in regulating the rate of maturation and transformation of blood cells[3a] and which facilitates antibody production.[3b]

(3) (a) Rice, F. A. H. *J. Infect. Dis.* **1968**, *118*, 76. Rice, F. A. H.; Darden, J. H. *Ibid.* **1968**, *118*, 289. (b) Rice, F. A. H.; Lepick, J.; Darden, J. H. *Radiat. Res.* **1968**, *36*, 144. Rice, F. A. H.; Lepick, J.; Hepner, P. *Ibid.* **1970**, *42*, 164.

(4) For reviews see: Lednicer, D. *Adv. Org. Chem.* **1972**, *8*, 179. Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Seebach, D.; Enders, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 15.

(5) Rice, F. A. H. *J. Chem. Soc. C* **1971**, 2599. Rice, F. A. H. *Carbohydr. Res.*, **1972**, *21*, 65.

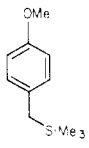
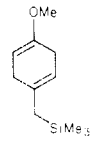
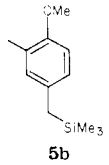
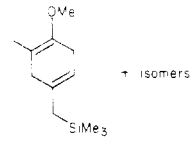
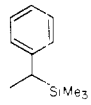
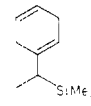
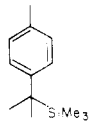
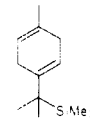
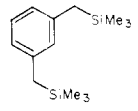
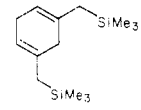
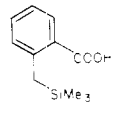
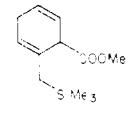
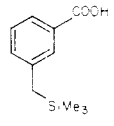
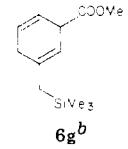
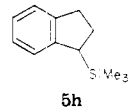
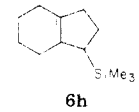
(6) Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 470.

(7) Fleming, I. *Chem. Ind. (London)* **1975**, *7*, 449.

(8) (a) Somi, A. H.; Sakurai, H. *Tetrahedron Lett.*, **1976**, 1295. (b) Carter, M. J.; Fleming, I., *J. Chem. Soc., Chem. Commun.* **1976**, 679. (c) Calas, R.; Dunogues, J.; Pillot, J.-P.; Biran, C.; Pisciotti, F.; Arreguy, B. *J. Organomet. Chem.* **1975**, *85*, 149. (d) Deleris, G.; Dunogues, J.; Calas, R. *Ibid.* **1975**, *93*, 43. (e) Au-Yeung, B.-W.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1977**, *79*. (f) Frainnet, E. *Bull. Soc. Chim. Fr.* **1959**, 1441. (g) Wilson, S. R.; Phillips, L. R.; Natalie, K. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3340.

0022-3263/79/1944-3784$01.00/0

Table I. Synthesis of (3,6-Dihydrobenzyl)silanes

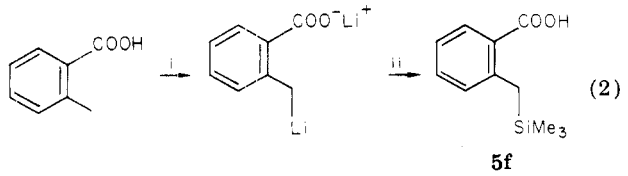
		6		
benzylsilane	dihydrosilane	bp, °C (pressure, mm)	yield, %	^{1}H NMR,[a] δ
 5a	 6a	50-53 (0.05)	84	5.26-5.04 (br s, 1 H), 4.70-4.38 (br s, 1 H), 3.48 (s, 3 H), 2.66 (s, 4 H), 1.41 (s, 2 H), 0.0 (s, 9 H)
 5b	 + isomers 6b	120-125 (12)	88	5.25-5.03 (m, 1 H), 3.46 (s, 3 H), 2.85-2.48 (m, 4 H), 1.58 (s, 3 H), 1.42 (s 2 H), 0.0 (s, 9 H)
 5c	 6c	102-105 (15)	67	5.7 (br s, 2 H), 5.28 (br s, 1 H), 3.0-2.32 (m, 4 H), 1.75-0.85 (m, 4 H), 0.0 (s, 9 H)
 5d	 6d	110-112 (15)	100	5.48-5.28 (br m, 2 H), 2.65 (br s, 4 H), 1.70 (br s, 3 H), 1.10 (s, 6 H), 0.0 (s, 9 H)
 5e	 6e	55-59 (0.05)	83	5.2-4.85 (br m, 2 H), 2.75-2.08 (m, 4 H), 1.41 (s, 4 H), 0.0 (s, 18 H)
 5f	 6f[b]	68-70 (0.07)	93	6.01-5.73 (br m, 2 H), 5.68-5.40 (br m, 1 H), 3.73-3.35 (br m, 1 H), 3.70 (s, 3 H), 2.90-2.59 (br m, 2 H), 1.61-1.41 (m, 2 H), 0.0 (s, 9 H)
 5g	 6g[b]	68-70 (0.1)	95	5.98-5.81 (br m, 2 H), 5.36 (br s, 1 H), 4.1-3.58 (m, 1 H), 3.60 (s, 3 H), 2.62 (d, 2 H, J = 9 Hz), 1.50 (s, 2 H), 0.00 (s, 9 H)
 5h	 6h	103-105 (15)	70	5.71 (s, 2 H), 2.60 (s, 4 H), 2.41-1.55 (m, 5 H), 0.0 (s, 9 H)

[a] In CCl_4 except 6b, 6f, and 6g which were in $CDCl_3$. [b] Esterified with diazomethane after reduction.

Grignard coupling of the corresponding benzylmagnesium halides with excess chlorotrimethylsilane in THF[9] (eq 1).

$$ArCXR^1R^2 + ClSiMe_3 \xrightarrow[THF]{Mg} ArC(SiMe_3)R^1R^2 \quad (1)$$

Lithiation of *o*-toluic acid with lithium diisopropylamide (LDA) in the presence of HMPA and silylation of the resulting dianion afford **5f** (eq 2). The indenylsilane **5i**

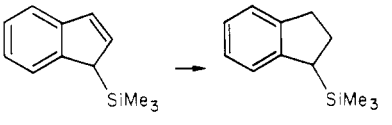


(2)

5f

(i) $LiN(i\text{-}Pr)_2$, (ii) $ClSiMe_3$

was prepared via metalation of indene with *n*-butyllithium and subsequent action with chlorotrimethylsilane.[10] The stability of the benzylic C–Si bond toward catalytic hydrogenation permits synthesis of **5h** in excellent yield by selective reduction of **5i**. The benzylic C–Si bond is also



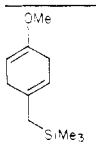
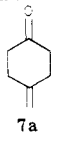
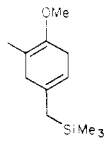
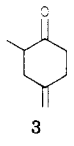
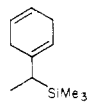
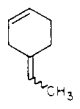
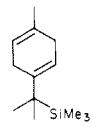
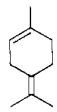
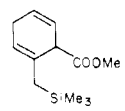
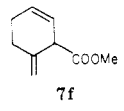
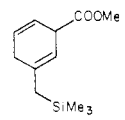
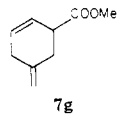
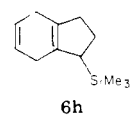
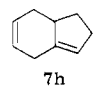
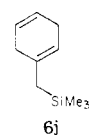
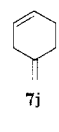
5i **5h**

stable toward aryllithium reagents, allowing functional elaboration on a pre-formed benzylsilane. Thus, *o*- and *m*-[(trimethylsilyl)methyl]benzoic acids **5f** and **5g** are available from the corresponding (chlorobenzyl)tri-

(9) A modification of the usual two-step approach; see for example ref 6.

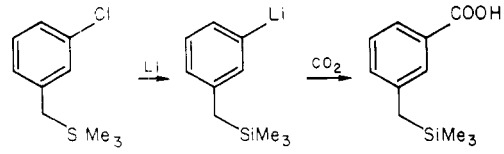
(10) Sommer, L. H.; Marans, N. S. *J. Am. Chem. Soc.* **1951**, *73*, 5135.

Table II. Protodesilylation of (3,6-Dihydrobenzyl)silanes

silane	alkylidene-cyclohexene	bp, °C (pressure, nm)	yield, %	^{1}H NMR, δ
 6a	 7a	70-80 (15)	80	[a] 4.90 (s, 2 H), 2.75-2.18 (br m, 8 H)
 6b	 3	67-68 (12)	60	[b] 4.88 (s, 2 H), 2.83-2.0 (br m, 7 H), 1.06 (d, 3 H, J = 5.7 Hz)
 6c	 7c	145-148	95	[a] 5.57 (br s, 2 H), 5.40-4.90 (m, 1 H), 2.54 (br s, 2 H), 2.38-1.85 (br m, 4 H), 1.51 (d, 3 H, J = 7 Hz)
 6d	 7d	85-87 (10)	80	[a] 5.50-5.34 (br m, 1 H), 2.95-1.88 (br m, 6 H), 1.78 (s, 9 H)
 6f	 7f	82-85 (10)	75	[b] 6.15-5.54 (m, 2 H), 5.03-4.86 (br s, 2 H), 3.87-3.58 (m, 1 H), 3.69 (s, 3 H), 2.67-1.95 (m, 4 H)
 6g	 7g	78-85 (10)	84	[b] 5.89 (s, 2 H), 4.90 (s, 2 H), 3.76 (s, 3 H), 3.20-3.42 (m, 1 H), 3.06-2.40 (m, 4 H)
 6h	 7h	62-68 (15)	98[c]	[b] 5.75-5.57 (br m, 2 H), 5.50-5.25 (m, 1 H), 2.96-2.70 (m, 2 H), 2.71-1.10 (br m, 7 H)
 6j	 7j	98-104	71[d]	[b] 5.73-5.57 (m, 2 H), 4.71 (br s, 2 H), 2.85-2.65 (m, 2 H), 2.45-2.00 (m, 4 H)

[a] In CCl_4. [b] In $CDCl_3$. [c] Including other isomers (see text). [d] >90% isomerically pure by GC.

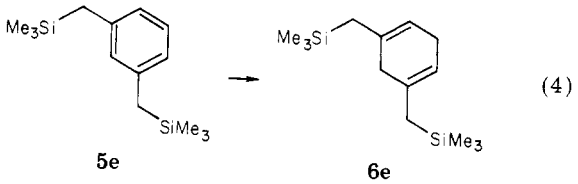
methylsilanes by reaction of the derived aryllithium with carbon dioxide (eq 3).[11]



(3)

5g

Reduction of Benzylsilanes. Reduction of benzyltrimethylsilane with lithium/liquid ammonia/ethanol was first reported 4 years ago.[6] We found that this reduction is generally useful for the preparation of variously substituted (3,6-dihydrobenzyl)silanes (Table I, entries **6a–d,f,g**). The reduction yields are good to excellent, ranging from 67–100%. However, the published reduction procedure fails in two cases, **5e** and **5h**. Excellent yields of **6e** were obtained from **5e** by using a large excess of lithium metal and employing *tert*-butyl alcohol instead of ethanol as the proton source (eq 4). Similarly, indanylsilane **5h**



(4)

5e 6e

was reduced smoothly to its dihydro derivative **6h** utilizing *tert*-butyl alcohol as the proton source in place of ethanol, preventing nucleophilic alkoxide cleavage of the benzylic C–Si bond.

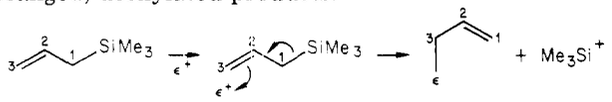
Protodesilylation of (3,6-Dihydrobenzyl)silanes. Mild conditions were required for protodesilylation of the (3,6-dihydrobenzyl)silanes in order to avoid acid-catalyzed rearrangement of the exocyclic π bond into the six-membered ring. We found that allylic silanes **6c,d,g** were desilylated in good yields (70–95%) by reaction with aqueous HCl in THF–methanol at 20 °C (Table II). In each case proton addition and loss of trimethylsilyl cation

(11) Eaborn, C.; Parker, S. H. *J. Chem. Soc.* **1951**, *73*, 5135.

occurred regiospecifically with allylic shift of an endocyclic carbon–carbon π bond (see Table II). Protodesilylation of **6a** and **6b** was performed without methanol as cosolvent and afforded the desired methylenecyclohexanones **7a** and **3** directly via concomitant enol ether hydrolysis. The functionalized silane **6f** did not undergo desilylation under the usual conditions. However, a good yield (75%) of methylenecyclohexenecarboxylic ester **7f** was realized by using a heterogeneous reaction medium of 48% HI in benzene. Protodesilylation of indanylsilane **6h** did not give monoisomeric product but rather gave a 12:7:1 mixture of isomeric bicyclo[4.3.0]nonadienes with the desired isomer **7h** as the major product. Two minor isomers were not isolated. Similarly, protodesilylation of (3,6-dihydrobenzyl)silane (**6j**) gave 4-methylenecyclohexene (**7j**) contaminated with double bond isomers (<10%) presumably generated by competing acid-catalyzed bond migrations.

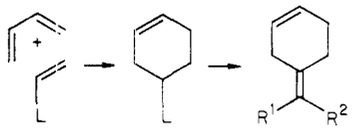
Discussion

Our new synthetic approach to 4-alkylidenecyclohexenes and 4-alkylidenecyclohexanones depends on protodesilylation of an allylsilane[7] with transposition of an endocyclic C=C bond into an exocyclic position. Silicon, an excellent electrofugal leaving group,[7] has been displaced with a variety of electrophiles,[8] all giving allylically rearranged, desilylated products.



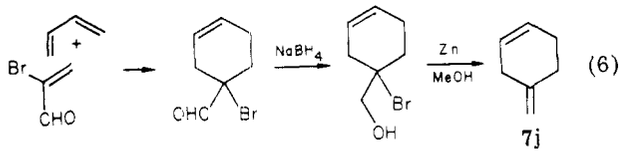
The requisite endocyclic allylsilanes are readily available by Birch reduction of benzylsilanes.

The Diels–Alder reaction is often pivotal in previous methodology for construction of 4-alkylidene-1-cyclohexenes. Since alkyl-substituted allenes are unreactive dienophiles,[12] 4-alkylidene-1-cyclohexenes are generally prepared indirectly from Diels–Alder adducts which incorporate an alkylidene moiety in latent form (eq 5). For



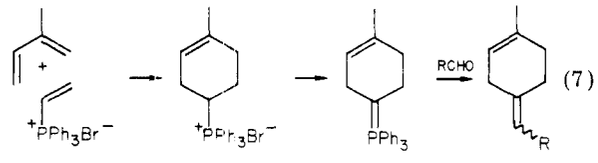
(5)

example, Diels–Alder adducts of α-bromoacrolein afforded 4-methylene-1-cyclohexenes upon sequential reduction with sodium borohydride and zinc dust in methanol (eq 6).[13] Alternatively, Diels–Alder adducts of vinyltri-



(6)

phenylphosphonium bromide afford 4-alkylidene-1-cyclohexenes upon reaction of the corresponding ylides with aldehydes (eq 7).[14] One limitation of the ylide

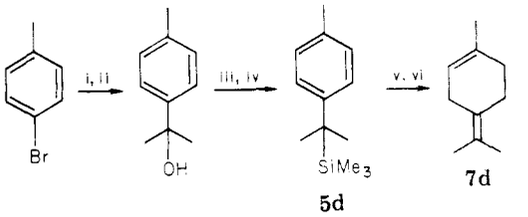


(7)

8

approach is the failure of the Wittig reaction to allow formation of tetrasubstituted olefins. Thus, an attempt at synthesis of the natural product terpinolene[15] (**7d**) by condensation of acetone with ylide 8 led to recovery of starting material.[14]

The benzylsilane approach provides a facile total synthesis of terpinolene (**7d**)[15] using *p*-bromotoluene as starting material. Two reactions are performed in tandem at each of the three stages of the synthesis without distillation of the intermediates (eq 8). Terpinolene is



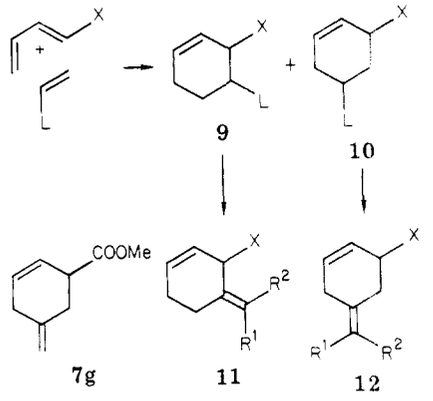
(8)

5d

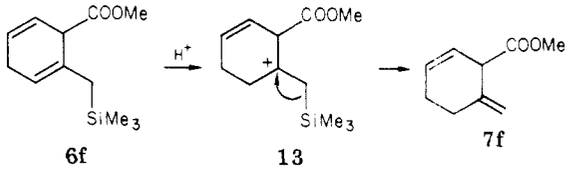
(i) Mg/Et_2O, (ii) Me_2CO, (iii) HCl, (iv) $Mg/Me_3SiCl/THF$, (v) $Li/EtOH/NH_3$, (vi) $HCl/H_2O/THF/MeOH$

obtained uncontaminated with double bond isomers.

Because of the structural specificity of the Diels–Alder reaction, which favors 3,4-disubstituted cyclohexenes **9** over 3,5-disubstituted cyclohexenes **10**, starting with 1-substituted 1,3-butadienes,[16] an approach via this route is not well suited for the preparation of alkylidenecyclohexenes of general structure **12**. However, the benzylsilane strategy



is applicable to structural isomer **12** as demonstrated by the synthesis of ester **7g**. Alternatively, the synthesis of ester **7f** demonstrates the applicability of our strategy to

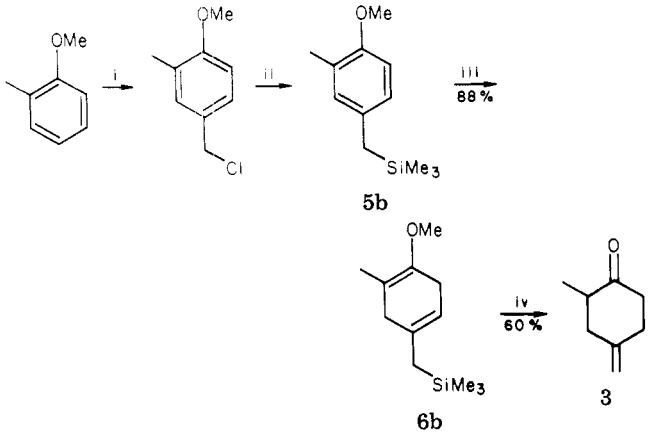


the preparation of structural isomer type **11**. It is noteworthy that **6f** is not protodesilylated under the standard conditions, requiring instead a two-phase HI–benzene, H_2O mixture.[17] This refractoriness may reflect the destabilization of an electron-deficient intermediate (e.g., **13**) by the neighboring electron-withdrawing carbomethoxyl substituent.

We required a synthesis of 2-methyl-4-methylenecyclohexanone (**3**) which was not readily available by previous methodology. The best previous synthesis of

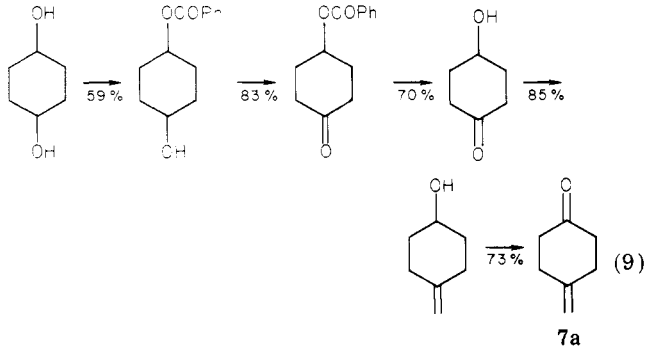
(12) Pledger, H. *J. Org. Chem.* **1960**, *25*, 278; *Chem. Abstr.* **1961**, *55*, 7321; **1966**, *64*, 3380.
(13) Snider, B B. *J. Org. Chem.* **1973**, *38*, 3961 and references cited therein.
(14) Bonjouklian, R.; Ruden, R. A. *J. Org. Chem.* **1977**, *42*, 4095.
(15) Thomas, A. F. "The Total Synthesis of Natural Products"; J. A. Simon, Ed.; Wiley: New York, 1973; pp 100–2.
(16) Onishchenko, A. S. "Diene Synthesis"; Israel Program for Scientific Translations: Jerusalem, 1964. Carruthers, W. "Some Modern Methods of Organic Synthesis", 2nd ed.; Cambridge University Press: Cambridge, 1978; p 161 ff.
(17) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825.

Scheme II



(i) CH_2O/HCl, (ii) $Mg/ClSiMe_3$, (iii) $Li/NH_3/EtOH$, (iv) $HCl/H_2O/THF$

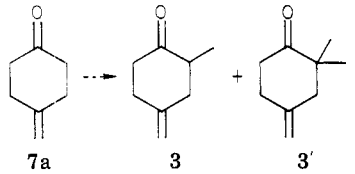
4-methylenecyclohexanone (**7a**) provides a 21% overall yield after five steps (eq 9) from 1,4-cyclohexanediol.[18]



(9)

7a

Utilizing the benzylsilane strategy, ketone **7a** is now readily available from (*p*-methoxybenzyl)silane (**5a**) in 67% overall yield by the two-step reduction–protodesilylation procedure. Moreover, this new synthetic approach enjoys advantages which facilitate extension to the methyl-substituted derivative **3**. Conversion of **7a** into **3** is complicated by the prospect of polyalkylation (e.g., **3** → **3′**). Fortunately, the aegis of aromaticity prevents at-



7a 3 3′

tachment of more than one substitutent per carbon atom of the six-membered ring. Moreover, the predictable and often high regiospecificity of aromatic substitution reactions provides excellent control for elaboration of benzylsilanes. The requisite benzylsilane **5b** for synthesis of **3** (Scheme II) is readily available from *o*-cresyl methyl ether by chloromethylation[19] and subsequent in situ Grignard coupling with chlorotrimethylsilane in 66% overall yield.

Experimental Section

General Methods. Proton magnetic resonance spectra were recorded with a Varian A60A. Mass spectra were recorded with a Du Pont Model 21-094 GC/MS instrument with an interfaced computer. Microanalyses were performed by Chemalytics Inc., Tempe, AZ.

Materials. Tetrahydrofuran (THF) used for all Grignard reactions and Birch reductions was freshly distilled from potassium benzophenone ketyl. Diethyl ether used in the Birch reductions was freshly distilled from lithium aluminum hydride. α,α,4-Trimethylbenzyl chloride[20] and 4-methoxy-3-methylbenzyl chlorides[19,21] were prepared by reported procedures. All other benzyl halides used in the Grignard reaction were commercially available and were used without further purification.

General in Situ Grignard Method for Preparation of Benzylsilanes. A flame-dried, 2-L, three-neck, round-bottom flask, equipped with a mechanical stirrer, reflux condenser, N_2 inlet, and 1-L addition funnel, was charged with dry magnesium turnings (24 g, 1 mol), dry tetrahydrofuran (100 mL), and chlorotrimethylsilane (127 mL, 108.65 g, 1.0 mol). The appropriate benzyl halide (0.9 mol) in dry tetrahydrofuran (900 mL) was added slowly, at a rate to maintain gentle reflux. After addition was complete, the mixture was heated under reflux 2 h, cooled, and poured into 1 L of cold water. Pentane (700 mL) was added and the pentane layer washed three times with cold water (500 mL) and once with saturated NaCl solution (500 mL), dried ($MgSO_4$), and then rotary evaporated to yield the crude benzylsilane.

[(4-Methoxyphenyl)methyl]trimethylsilane[21] **(5a)**, bp 73–78 °C (0.1 mm), was prepared in 92% yield from 4-methoxybenzyl chloride. ^1H NMR (CCl_4) δ 7.0–6.58 (m, 4 H), 3.76 (s, 3 H), 2.0 (s, 2 H), 0.0 (s, 9 H).

[(4-Methoxy-3-methylphenyl)methyl]trimethylsilane (5b), bp 125 °C (12 mm), was prepared in 91% yield from the corresponding benzylic chloride.[19] ^1H NMR (CCl_4) δ 6.68–6.87 (m, 3 H), 3.82 (s, 3 H), 2.19 (s, 3 H), 1.94 (s, 2 H), 0.00 (s, 9 H).

Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 68.92; H, 9.42.

(1-Phenylethyl)trimethylsilane[22] **(5c)**, bp 98–100 °C (15 mm), was prepared in 76% yield from α-phenethyl bromide. ^1H NMR (CCl_4) δ 7.45–6.87 (m, 5 H), 2.13 (q, 1 H, J = 7.5 Hz), 1.4 (d, 3 H, J = 7.5 Hz), 0.0 (s, 9 H).

[2-(4-Methylphenyl)-2-propyl]trimethylsilane (5d), bp 120–125 °C (15 mm), was prepared in 60% yield from 2-(4-methylphenyl)-2-propanol via the benzylic chloride.[20] ^1H NMR (CCl_4) δ 7.15 (s, 4 H), 2.38 (s, 3 H), 1.43 (s, 6 H), 0.0 (s, 9 H).

Anal. Calcd for $C_{14}H_{22}Si$: C, 75.65; H, 10.74. Found: C, 74.93; H, 10.60.

1,3-Bis(trimethylsilylmethyl)benzene (5e), bp 60–70 °C (0.05 mm), was prepared in 26% yield from *m*-xylyene dibromide. ^1H NMR (CCl_4) δ 7.2–6.5 (m, 4 H), 2.0 (s, 4 H), 0.0 (s, 18 H).

Anal. Calcd for $C_{14}H_{26}Si$: C, 67.12; H, 10.46. Found: C, 67.04; H, 10.66.

***o*-[(Trimethylsilyl)methyl]benzoic acid (5f).** Dry diisopropylamine (7.6 g, 10.5 mL, 75 mmol) was added to dry THF (75 mL) in a flame-dried, 500 mL, three-neck flask, equipped with a magnetic stirrer, dropping funnel, and rubber septum cap, and kept under N_2. The solution was cooled to −78 °C (dry ice–acetone), and *n*-butyllithium in hexane (44.5 mL, 1.65 N, 73.5 mmol) was added via syringe. The solution was allowed to warm to 0 °C, stirred at 0 °C 0.5 h, and then cooled to −78 °C. Dry hexamethylphosphoramide (HMPA) (13.4 g, 13.0 mL, 75 mmol) was added to the flask and the mixture stirred at −78 °C for 0.5 h. *o*-Toluic acid (10.0 g, 73.4 mmol) in dry THF (25 mL) was added slowly at −78 °C over 15 min. After addition was complete, the solution was stirred 10 min at −78 °C, allowed to warm to 0 °C, stirred at 0 °C for 10 min, and cooled to −78 °C. HMPA (26.4 g, 26.0 mL, 150 mmol) was added followed by addition of a previously prepared lithium diisopropylamide (LDA) solution [from 183 mL of THF, diisopropylamine (15.2 g, 21 mL, 150 mmol), and *n*-butyllithium (89 mL of a 1.65 N hexane solution, 147 mmol); prepared and maintained −78 °C] over 10 min via syringe. Intense erubescence of the reaction accompanied the addition of the LDA. Chlorotrimethylsilane (31.9 g, 37.3 mL, 295

(18) Rickborn, R.; Wuesthoff, M. T. *J. Am. Chem. Soc.* **1970**, *92*, 6894. For alternative syntheses see also: Ooba, S.; Ohta, M.; Kato, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1782. Sonoda, A.; Moritani, I.; Miki, M.; Tsuji, T.; Nishida, S. *Ibid.* **1972**, *45*, 1777.

(19) Mndzhoyan, A. L.; Aroyan, A. A. *Izv. Akad. Nauk Arm. SSR, Fiz.-Mat. Estestr.-Tekh. Nauk* **1955**, *8*, 29; *Chem. Abstr.* **1955**, *50*, 11982h.

(20) Brown, H. C.; Brady, J. D.; Grayson, M.; Bonner, W. H. *J. Am. Chem. Soc.* **1957**, *79*, 1897.

(21) Cuttress, N. C.; Grindly, T. B.; Kattitzky, A. R.; Eaborn, C.; Walton, D. R. M.; Topsom, R. D. *J. Organomet. Chem.* **1974**, *65*, 17.

(22) Ryan, J. W.; Speier, J. L. *J. Org. Chem.* **1959**, *24*, 2052. Eaborn, C.; Najam, A. A.; Walton, D. R. M. *J. Organomet. Chem.* **1972**, *46*, 255.

mmol) in dry THF (45 mL) was added dropwise from the dropping funnel and the cold solution allowed to stir at room temperature for 3 h. The solution was poured into ice-cold aqueous HCl (50 mL of concentrated HCl and 300 mL of H_2O) and extracted with ether (400 mL). The ether layer was washed with 5% HCl (4 × 200 mL), water (200 mL), and saturated sodium chloride (200 mL), and dried ($MgSO_4$). Rotary evaporation of the ether gave a viscous yellow oil which yielded 13.5 g (88%) of *o*-(trimethylsilyl)benzoic acid (**5f**) upon recrystallization (ethanol–water, 60:40). The product gave identical spectral characteristics with those of the compound prepared by the method of Eaborn and Parker.[11] ^1H NMR ($CDCl_3$) δ 8.45–8.06 (m, 1 H), 7.54–7.12 (m, 3 H), 2.80 (s, 2 H), 0.00 (s, 9 H).

***m*-[(Trimethylsilyl)methyl]benzoic acid (5g)** was prepared by the method of Eaborn and Parker.[11] ^1H NMR ($CDCl_3$) δ 8.16–7.83 (m, 2 H), 7.53–7.34 (m, 2 H), 2.20 (s, 2 H), 0.00 (s, 9 H).

1-(Trimethylsilyl)indan (5h) was prepared in 75% yield from catalytic hydrogenation (5% Pd/C, EtOH, 3 atm of H_2) of 1-(trimethylsilyl)indene[10] in a Parr pressure bomb apparatus. ^1H NMR (CCl_4) δ 7.12 (s, 4 H), 3.1–1.83 (m, 5 H), 0.0 (s, 9 H). ^1H NMR (CCl_4) of 1-(trimethylsilyl)indene δ 7.68–7.17 (m, 4 H), 7.08–6.55 (m, 2 H), 3.6–3.4 (m, 1 H), 0.0 (s, 9 H).

[(4-Methoxy-1,4-cyclohexadien-1-yl)methyl]trimethylsilane (6a). To a flame-dried, 2-L, three-neck flask, equipped with a magnetic stirrer, gas inlet, and dry ice–acetone cold-finger condenser and kept under nitrogen, was added [(4-methoxyphenyl)methyl]trimethylsilane (**5a**; 20.0 g, 21.5 mL, 0.1 mol) in dry THF (100 mL) and dry absolute ethanol (23.6 g, 30.0 mL, 0.51 mol). Ammonia (1000 mL) was condensed in the flask. Lithium wire (3 g, 0.43 mol) cut into about 12 pieces was added over the course of 1 h, and the mixture was stirred for 1 h. Ammonium chloride (27 g, 0.5 mol) was added in small portions, care being taken to avoid foaming of the liquid NH_3. The dry ice condenser was removed and the liquid NH_3 allowed to evaporate from the flask. Ether (500 mL) was added to the flask, followed by water (1 L). The layers were separated, and the ether layer was washed two times with water (500 mL) and with saturated sodium chloride solution (500 mL), dried ($MgSO_4$), and rotary evaporated to yield **6a** after distillation (16.0 g, 84%), bp 50–53 °C (0.05 mm). For the NMR spectrum, see Table I.

Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 66.99, H, 10.02.

[(4-Methoxy-5-methyl-1,4-cyclohexadien-1-yl)methyl]trimethylsilane (6b). [(4-Methoxy-3-methylphenyl)methyl]trimethylsilane (**5b**; 18.2 g, 0.087 mol) was reduced with lithium wire (7.5 g, 1.07 mol) in liquid ammonia (600 mL), dry diethyl ether (100 mL), and absolute ethanol (71 g, 90 mL, 1.54 mol). The reaction was worked up as for **6a**, yielding a product [bp 120–125 °C (12 mm), 6.1 g, 88%] which by ^1H NMR appeared to be a mixture of [(4-methoxy-5-methyl-1,4-cyclohexadien-1-yl)-methyl]trimethylsilane (**6b**; ~70%) and dihydrobenzene isomers (~30%). ^1H NMR ($CDCl_3$) δ 5.16 (m, 1 H), 3.46 (s, 3 H), 2.85–2.48 (m, 4 H), 1.58 (s, 3 H), 1.42 (s, 2 H), 0.00 (s, 9 H).

[(1,4-Cyclohexadien-1-yl)ethyl]trimethylsilane (6c), bp 102–105 °C (15 mm), was prepared in 67% yield from **5c** following the reduction procedure above. For the NMR spectrum see Table I.

Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 72.24; H, 11.02.

[2-(4-Methyl-1,4-cyclohexadienyl)-2-propyl]trimethylsilane (6d) was prepared by Birch reduction of the corresponding aromatic silane **5d** (0.01 mol) in dry THF (50 mL) and liquid NH_3 (125 mL) using 0.5 mol of Li wire and dry ethanol (0.25 mol, 1.18 g, 1.5 mL), the ethanol being added after complete addition of the Li metal. Workup with excess ammonium chloride afforded a quantitative yield of **6d**, bp 110–112 °C (15 mm). For the NMR spectrum, see Table I.

Anal. Calcd for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.82; H, 11.47.

1,5-Bis[(trimethylsilyl)methyl]-1,4-cyclohexadiene (6e) was prepared by Birch reduction of **3e** (9.0 g, 0.036 mol) in THF (180 mL) and liquid NH_3 (900 mL). Lithium wire (25.2 g, 3.6 mol) was added to give a deep bronze solution. After the bronze solution was stirred for 1 h, dry ethanol (8.3 g, 10.6 mL, 0.18 mol) was added dropwise and the reaction stirred another 2 h. Quenching with NH_4Cl (21.4 g, 4 mol) was performed slowly to avoid vigorous foaming, and subsequent dropwise addition of H_2O (500 mL) afforded a white paste which was poured into water (1.5 L) and extracted with pentane (800 mL). The pentane layer was washed with saturated NaCl, dried ($MgSO_4$), rotary evaporated, and distilled to afford the product **6e**: 7.52 g (83%), bp 55–59 °C (0.05 mm). For the NMR spectrum, see Table I.

Anal. Calcd for $C_{14}H_{28}Si$: C, 66.58; H, 11.18. Found: C, 66.41; H, 10.91.

[(6-Carbomethoxy-1,4-cyclohexadien-1-yl)methyl]trimethylsilane (6f) was prepared from the known aromatic acid **5f**[11] by Birch reduction of the acid (3.5 g, 0.0255 mol) in dry diethyl ether (100 mL), dry *tert*-butyl alcohol (9.4 g, 12.08 mL, 0.127 mol), and liquid NH_3 (530 mL) with Li wire (0.71 g, 0.10 mol). Subsequent workup and addition of excess ethereal diazomethane afforded an 87% yield of distilled [(6-carbomethoxy-1,4-cyclohexadien-1-yl)methyl]trimethylsilane **6f**, bp 68–70 °C (0.07 mm). For the NMR spectrum, see Table I.

Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 63.91; H, 8.79.

[(3-Carbomethoxy-1,4-cyclohexadien-1-yl)methyl]trimethylsilane (6g) was prepared by Birch reduction of the known[11] acid **5g** (3.75 g, 0.018 mol) in dry ether (75 mL), dry *tert*-butyl alcohol (6.7 g, 8.55 mL, 0.09 mol), and liquid ammonia (375 mL) with Li wire (5.02 g, 0.72 mol). Subsequent workup and addition of excess etheral diazomethane afforded the methyl ester **6g** in 95% yield; bp 68–70 °C (0.1 mm). For the NMR spectrum, see Table I.

Anal. Calcd for $C_{12}H_{20}O_2Si$: C, 64.24; H, 8.98. Found: C, 64.03; H, 8.62.

4,7-Dihydro-1-(trimethylsilyl)indan (6h) was prepared by reduction of 1-(trimethylsilyl)indan (**5h**; 0.052 mol) in THF (130 mL), dry *tert*-butyl alcohol (20.0 g, 25.4 mL, 0.27 mol), and liquid NH_3 (670 mL) with Li wire (2.66 g, 0.38 mol). Quenching 1 h after complete addition of the Li metal with 50 g of NH_4Cl, extraction with pentane, and distillation afforded 7.0 g (70%) of the product **6h**, bp 103–105 °C (15 mm). For the NMR spectrum, see Table I.

Anal. Calcd for $C_{12}H_{20}Si$: C, 74.92; H, 10.48. Found: C, 74.61; H, 10.51.

Protodesilylation of (Dihydrobenzyl)silanes. General Procedure. The (dihydrobenzyl)silane (1.0 g) was dissolved in THF (15 mL), treated with concentrated HCl (1 mL), H_2O (1 mL), and methanol (1 mL), and allowed to stand for 20 h. Subsequent workup included extraction with pentane (30 mL) and washing of the pentane layer with water (2 × 25 mL), saturated $NaHCO_3$ solution (25 mL), and saturated NaCl solution (25 mL). Rotary evaporation of the pentane afforded the crude, rearranged olefins. Boiling points, yields, and NMR spectra are reported in Table II. Compounds **7c** and **7d** were prepared exactly by this procedure.

4-Methylenecyclohexanone (7a) was prepared in 80% yield from **6a**, as above, except that methanol was omitted and the amount of HCl doubled.

4-Methylene-2-methylcyclohexanone (3) was prepared by hydrolysis of [(4-methoxy-5-methyl-1,4-cyclohexadien-1-yl)-methyl]trimethylsilane (**6b**, 18 g) in THF (400 mL), concentrated HCl (36 mL), and H_2O (18 mL) at room temperature for 30 h. Workup with water, extraction into ether, and careful distillation through a glass helices packed column gave the ketone **3** (60%).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.42; H, 9.73.

3-Carbomethoxy-4-methylenecyclohex-1-ene (7f) was prepared by dissolving [(6-carbomethoxy-1,4-cyclohexadien-1-yl)methyl]trimethylsilane (**6f**; 2.24 g, 10.6 mmol) in benzene (20 mL) with subsequent addition of constant-boiling, 48% hydriodic acid (0.8 mL). The solution was stirred for 24 h, and then washed with H_2O (2 × 20 mL), saturated $NaHCO_3$ (20 mL), and saturated NaCl (20 mL), dried ($MgSO_4$), and rotary evaporated to give 3-carbomethoxy-4-methylenecyclohex-1-ene (**5f**). An analytical sample was prepared by gas chromatography (15 ft × $^1/_4$ in., DC 710, 60/80 Chromosorb W, 160 °C). Mass spectrum, *m/e* (rel intensity) 152 (13, M^+), 94 (14), 93 (100), 92 (45), 91 (52), 77 (39), 65 (11).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.81; H, 7.86.

3-Carbomethoxy-5-methylenecyclohex-1-ene (7g) was prepared by hydrolysis of [(3-carbomethoxy-1,4-cyclohexa-

dien-1-yl)methyl]trimethylsilane (**6g**; 3.0 g) in THF (60 mL) with H_2O (4.2 mL), methanol (4.2 mL), and concentrated HCl (4.2 mL). After 24 h the product was worked up with ether by the general procedure. Mass spectrum, *m/e* (rel intensity) 152 (15, M^+), 94 (17), 93 (100), 92 (51), 91 (60), 77 (30), 65 (12), 39 (11).

Anal. Calcd for $C_9H_{12}O$: C, 71.03; H, 7.95. Found: C, 71.21; H, 8.18.

Bicyclo[4.3.0]nona-3,6-diene (7h) was prepared by protodesilylation of 4,7-dihydro-1-(trimethylsilyl)indan (**6h**). Distillation of the crude product gave a 12:7:1 mixture of isomers which could be readily separated by gas chromatography (6 ft × $^1/_4$ in., 10% DC 710, 60/80 Chromosorb W, 110 °C) to give bicyclo[4.2.0]nona-3,6-diene (**7h**) as the major product.

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.72; H, 9.93.

4-Methylenecyclohex-1-ene (7j)[23] was prepared by protodesilylation of (1,4-cyclohexadien-1-yl-methyl)trimethylsilane (**6j**).[6] Distillation gave 4-methylenecyclohexene which was greater than 90% pure by gas chromatography (6 ft × $^1/_4$ in., 10% DC 710, 60/80 Chromosorb W, 95 °C).

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Registry No. 3, 71435-90-0; **5a**, 17988-20-4; **5b**, 71435-91-1; **5c**, 17961-78-3; **5d**, 71435-92-2; **5e**, 18412-15-2; **5f**, 71435-93-3; **5g**, 17998-93-5; **5h**, 18036-88-9; **5i**, 18053-75-3; **6a**, 71435-94-4; **6b**, 71435-95-5; **6c**, 71435-96-6; **6d**, 71435-97-7; **6e**, 71435-98-8; **6f**, 71435-99-9; **6g**, 71436-00-5; **6h**, 71436-01-6; **6j**, 55861-00-2; **7a**, 29648-66-6; **7c**, 16631-66-6; **7d**, 586-62-9; **7f**, 71436-02-7; **7g**, 71436-03-8; **7h**, 71436-04-9; **7j**, 13407-18-6; chlorotrimethylsilane, 75-77-4; 4-methoxybenzyl chloride, 824-94-2; 4-methoxy-3-methylbenzyl chloride, 60736-71-2; α-phenethyl bromide, 585-71-7; 2-(4-methylphenyl)-2-propanol, 1197-01-9; α,α,4-trimethylbenzyl chloride, 7243-79-0; *m*-xylene dibromide, 626-15-3; *o*-toluic acid, 118-90-1; lithium diisopropylamide, 4111-54-0; [(4-methoxy-3-methyldihydrophenyl)-methyl]trimethylsilane, 71486-15-2.

1,1,2,2-Tetrabromonaphtho[*b*]cyclobutene: A New Source of Naphtho[*b*]cyclobutene-1,2-dione and Substituted Naphtho[*b*]cyclobutadienes

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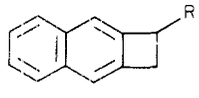
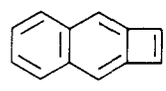
Reaction of naphtho[*b*]cyclobutene (**1**) with excess *N*-bromosuccinimide gives 1,1,2,2-tetrabromonaphtho[*b*]cyclobutene (**4**), which is hydrolyzed by silver nitrate in aqueous acetonitrile to naphtho[*b*]cyclobutene-1,2-dione (**5**). Several reactions of dione **5** are described, including its peracetic acid oxidation, its lithium aluminum hydride reduction, and its reaction with methylmagnesium bromide to give the dimethyl diols **10**. Diols **10** and tetrabromide **4** may be used as precursors of the unstable 1,2-dimethylnaphtho[*b*]cyclobutadiene (**12**) and 1,2-dibromonaphtho[*b*]cyclobutadiene (**15**), respectively.

Some time ago we described the synthesis of 1-bromonaphtho[*b*]cyclobutene (**2**) from naphtho[*b*]cyclobutene (**1**), as well as the generation of naphtho[*b*]-cyclobutadiene (**3**) from monobromide **2**.[1]



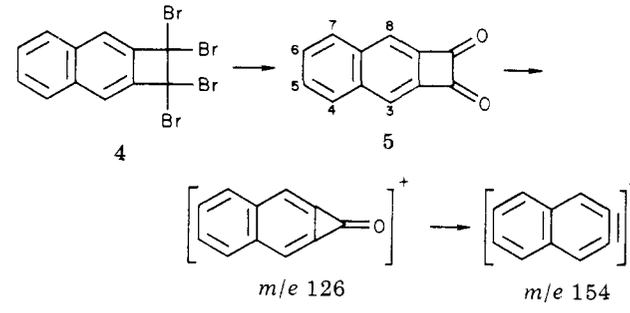
1, R = H
2, R = Br



3

In this paper, we report the conversion of naphtho[*b*]cyclobutene (**1**) to 1,1,2,2-tetrabromonaphtho[*b*]-cyclobutene (**4**) and describe some reactions of the latter, including a simple synthesis of naphtho[*b*]cyclobutene-1,2-dione (**5**). A synthesis of dione **5** by an unrelated pyrolytic route was reported in 1973 in preliminary form;[2] however, other than its electrochemical behavior,[3] no chemical or physical properties of **5** have yet been described.

Scheme I



4 5

m/e 126 *m/e* 154

Results and Discussion

Partial free-radical bromination of naphtho[*b*]cyclobutene (**1**) leads to a very difficultly separable mixture of **1** and its mono- and dibromo derivatives.[1] In contrast, reaction of **1** with excess *N*-bromosuccinimide for several days affords a fair yield (38%) of the readily purified 1,1,2,2-tetrabromonaphtho[*b*]cyclobutene (**4**), mp 186–187 °C. Hydrolysis of tetrabromide **4** with silver trifluoroacetate in aqueous acetonitrile gave (46%) yellow needles of naphtho[*b*]cyclobutene-1,2-dione (**5**), mp 256.5–258 °C.

The mass spectrum of **5**, while also showing a fairly strong molecular ion (40%), shows two base peaks cor-

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