

Synthesis of *peri*-Cyclobutarenes by Thermolysis of [Methoxy(trimethylsilyl)methyl]arenes

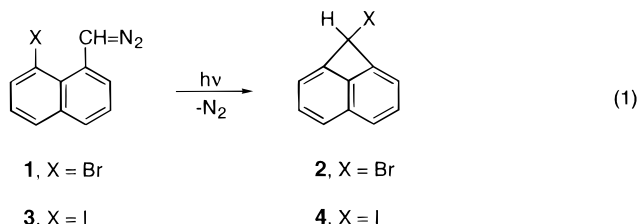
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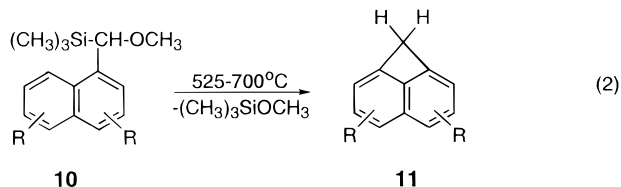
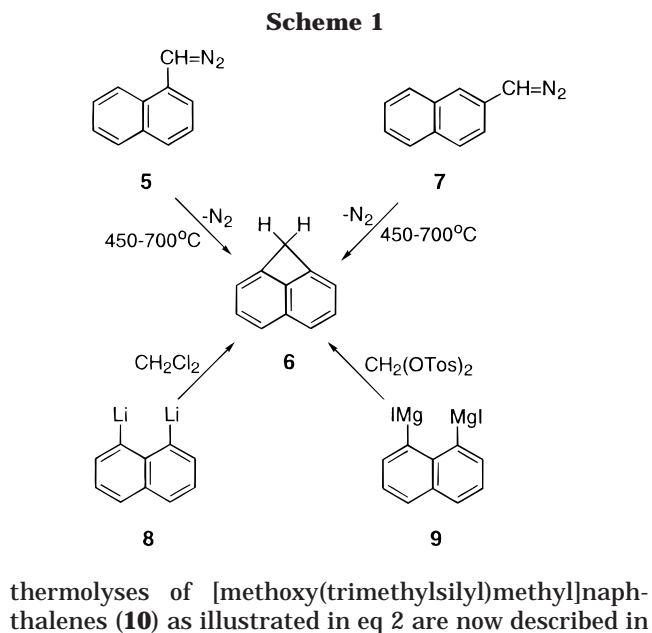
Received June 9, 1998

[Methoxy(trimethylsilyl)methyl]arenes are readily prepared by reactions of chlorotrimethylsilane with (α -methoxy)arenylmethyl lithium reagents as obtained from (methoxymethyl)arenes and *t*-BuLi. The [methoxy(trimethylsilyl)methyl]arenes eliminate methoxytrimethylsilane at 525–675 °C/0.05–0.10 mm to yield *peri*-cyclobutarenes as derived from arenylcarbenes. Of importance is the fact that the initial arenylcarbenes generated insert into adjacent *peri* C–H bonds and/or isomerize to other arenylcarbenes that insert into their *peri* C–H bonds to give *peri*-cyclobutarenes. Thus, flash-vacuum pyrolysis of 1-[methoxy(trimethylsilyl)methyl]naphthalene (**13**) at 575–675 °C/0.05–0.10 mm yields 1*H*-cyclobuta[*de*]naphthalene (**6**, up to 39%) in practical quantities. 2-[Methoxy(trimethylsilyl)methyl]naphthalene (**23**) also affords **6** as a major thermolysis product. At 510 °C/0.05–0.10 mm 4-methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (**29**) decomposes to 4-methoxy-1*H*-cyclobuta[*de*]naphthalene (**31**, 46%). Under similar conditions, 2-methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (**33**) converts to 1,2-dihydronaphtho[2,1-*b*]furan (**35**, 64%) and naphtho[2,1-*b*]furan (**36**, 31%), presumably by insertion of 2-methoxy-1-naphthylcarbene (**34**) into a C–H bond of its *o*-methoxy group and then dehydrogenation of the resultant dihydrofuran. Further, 1-[methoxy(trimethylsilyl)methyl]-6-methylnaphthalene (**39**) pyrolyzes (510 °C/0.10–0.20 mm) to 6-methyl-1-naphthylcarbene (**40**), which isomerizes in part to 7-methyl-1-naphthylcarbene (**49**); carbenes **40** and **49** then undergo *peri* C–H insertion to give 3-methyl-1*H*-cyclobuta[*de*]naphthalene (**41**) and 2-methyl-1*H*-cyclobuta[*de*]naphthalene (**42**) in an 8:1 ratio and a combined yield of 44%. The pyrolytic method is particularly valuable for preparing higher *peri* single carbon atom bridged arenes such as 4*H*-cyclobuta[*jk*]phenanthrene (**53**, 65%) and 3*H*-cyclobuta[*cd*]pyrene (**59**, 86%).

Naphthalenes have been bridged in *peri*-positions by single carbon atom moieties by (1) photolysis of 8-halo-1-naphthyldiazomethanes (**1**, X = Br, and **3**, X = I; eq 1),¹ (2) pyrolysis of 1(5)- and 2(7)-naphthyldiazomethanes



(Scheme 1), sodium 1- and 2-naphthaldehyde *p*-tosylhydrazonates, and 5-(1)- and 5-(2-naphthyl)tetrazoles, respectively at 450–700 °C/10⁻²–10⁻⁴ mm,² and (3) coupling of 1,8-dilithionaphthalene (**8**, Scheme 1) with dichloromethane and 1,8-bis(iodomagnesium)naphthalene (**9**, Scheme 1) with methylene bis(toluene-*p*-sulfonate).³ The above synthetic methods are often unsatisfactory, however, for preparative purposes. Practical syntheses of various *peri*-methanonaphthalenes (**11**) by vacuum



detail.^{4–6} The present method has also been extended to synthesis of various benzannelated derivatives of **11**.

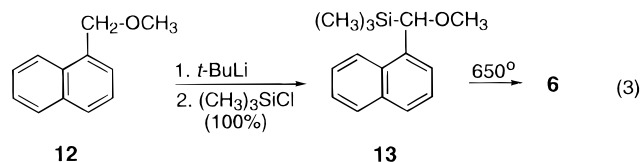
[†] Present address: Lilly Corporate Center, Eli Lilly and Company, Indianapolis, IN, 46285.

(1) (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (b) Bailey, R. J.; Card, P. J.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096.

(2) (a) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190. (b) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. *J. Tetrahedron* **1985**, *41*, 1601. (c) The *p*-tosylhydrazonates and the (naphthyl)tetrazoles decompose to **5** or **7** prior to formation of **6**.^{2a,b}

(3) Yang, L. S.; Engler, T. A.; Shechter, H. *J. Chem. Soc., Chem. Commun.* **1983**, 866.

1-[Methoxy(trimethylsilyl)methyl]naphthalene (**13**) is readily prepared (100%, eq 3) by deprotonation of 1-(methoxy-



oxymethyl)naphthalene (**12**) with *t*-BuLi in TMEDA/Et₂O at -78 °C and reaction of the subsequent lithio derivative with chlorotrimethylsilane.⁷ Vacuum pyrolysis of **13** upon volatilization through a packed quartz tube at 650 °C/0.05–0.10 mm occurs with loss of methoxytrimethylsilane to yield 1*H*-cyclobuta[*de*]naphthalene (**6**, eq 3) as a major product (39%)⁸ along with **12** (8%), naphthalene (**14**, 3%), 1-naphthaldehyde (9%), α -methyl-1-naphthalenemethanol (7%), 1-methylnaphthalene (5%), and intractables. Cyclobutanaphthalene **6** is obtainable, after chromatography of the pyrolysate, as the major component (60–70% by ¹H NMR) of a mixture containing **14**, 1-methylnaphthalene, and unidentified minor products. This mixture can be used conveniently for preparing derivatives of **6** as demonstrated by nitration with acetyl

(4) (a) A portion of these results were communicated: Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, 23, 2715. (b) For application of this chemistry, see: Jaworek, W.; Vögtle, F. *Chem. Ber.* **1991**, 124, 347.

(5) (a) Other methods for generating arenylcarbenes at elevated temperatures for preparing *peri*-cyclobutarenes are frequently impractical because of the instabilities of aryl diazomethanes and their facile conversions to azines, the low vapor pressures of sulfonylhydrazonate and sulfinate salts, the problems in introducing solids which are not free-flowing into pyrolysis equipment at low pressures, and the inefficiencies in decompositions of aryltetrazoles to their corresponding arenylcarbenes.^{2b,5b–d} (b) The principal thermal reactions of aryltetrazoles are conversions to nitriles and hydrogen azide.^{2b,5c,d} (c) Golden, A. H.; Jones, M., Jr. *J. Org. Chem.* **1996**, 61, 4460. (d) Kumar, A.; Narayanan, R.; Shechter, H. *J. Org. Chem.* **1996**, 61, 4462.

(6) (a) Photolysis of 2-diazoacene in argon at 8 K to 1,8-naphthyleneketene and irradiation of 8-hydroxy-1-naphthylglyoxylic acid lactone at -195 °C to give 1*H*-cyclobuta[*de*]naphthalen-1-one have been of significance to structural principles and mechanistic theory.^{6b} These transformations as yet, however, are not usable preparatively. (b) Chapman, O. *Chem. Eng. News* **1978**, Sept 18, p 78. (c) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1983**, 105, 7787.

(7) (a) α -Lithio(aryl)methyl alkyl ethers [ArCH(Li)OR] rearrange readily to lithio alkoxides [ArCH(R)OLi].^{7b–e} Such Wittig rearrangements are retarded at low temperatures by TMEDA. (b) Wittig, G.; Löhmann, L. *Liebigs Ann. Chem.* **1942**, 550. (c) Schafer, H.; Schöllkopf, U.; Walter, D. *Tetrahedron Lett.* **1968**, 2809. (d) Schöllkopf, U. *Angew. Chem., Int. Ed. Engl.* **1970**, 9, 763. (e) Hoffmann, R. W.; Rühl, T.; Harbach, J. *Liebigs Ann. Chem.* **1992**, 725. (f) That α -lithio(aryl)methyl ethers can be used synthetically in the presence of TMEDA at low temperatures without significant rearrangement was developed^{4a,7g} on knowledge that the migratory abilities of alkyl groups in isomerization of α -lithiobenzyl alkyl ethers in TMEDA/THF/Et₂O at -60 °C increase in the order methyl, ethyl, iso-propyl, and *tert*-butyl (*k*_{rel} 1:40:162:2080).^{7c} (g) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1983**, 24, 4645. (h) Yeh, M. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1652. The author found that benzyl methyl ether is deprotonated by *n*-BuLi/TMEDA in hexane at -10 °C and the α -lithiobenzyl methyl ether formed is alkylated by 1-bromobutane (80% yield) and adds to nonenolizable ketones. (i) Azzena, U.; Demartis, S.; Fiori, M. G.; Melloni, G.; Pisano, L. *Tetrahedron Lett.* **1995**, 36, 5641. The authors have communicated that α -lithio(aryl)methyl methyl ethers, as generated by metalation of arylmethyl methyl ethers with *n*-BuLi in THF at -40 °C in the absence of TMEDA, react with various electrophiles without serious complications from Wittig rearrangements.

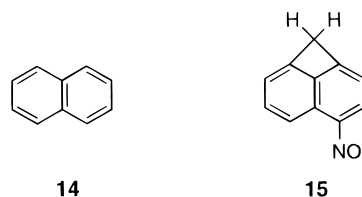
(8) Piptopyrolysis of sodium 1-naphthaldehyde *p*-tosylhydrazonate at 600 °C/10⁻³ to 10⁻¹ mm is reported to give **6**, **14**, and 1-methylnaphthalene in 39%, 15%, and 21% yields, respectively.^{2b} At 700 °C/10⁻³ to 10⁻¹ mm, 5-(1-naphthyl)tetrazole yields **6** (26%), 1-methylnaphthalene (6%), and naphthalene-1-carbonitrile (61%).^{2b} In the present investigation, piptopyrolysis of 5*H*-(1-naphthyl)tetrazole at 600 °C/0.05–0.1 mm in a quartz tube packed with quartz chips yields naphthalene-1-carbonitrile and hydrogen cyanide essentially totally.

Table 1. Effects of Temperature and Pressure on the Conversions to and the Yields of **6** on Pyrolysis of **13**

temp (°C)	pressure (mm)	6		13 % recovery ^c
		% conversion ^a	% yield ^b	
490–510	0.005	0	0	92
500–510	2.0	6–11	9–12	35
500–510	0.35–0.40	17	35	51
560	0.07–0.10	11	32	65
650	0.05–0.15	39	39	0
695–700	0.05–0.07	27	27	0
750	0.05–0.07	4	4	0
800	3.0	0	0	0

^a The percentage of **6** formed from **13** in a single pass. ^b The percentage of **6** formed from **13** that decomposed. ^c The percentage of initial **13** recovered.

nitrate to give pure 4-nitro-1*H*-cyclobuta[*de*]naphthalene (**15**).⁹ Purification of **6** (>90%) can be effected by fractional distillation, preparative GC, or preparation of its picrate followed by recrystallization and decomposition of the complex on silica gel.



Pyrolysis of **13** is conducted in simple equipment (see Experimental Section) at readily attainable temperatures and pressures. More than 10 g of **13** has been thermolyzed in a single experiment, and the decompositions can be conducted on a larger scale.¹⁰ Varying the pyrolysis temperature and pressure greatly affect the conversions and yields of **6** from **13**. As shown in Table 1, temperatures of at least 500 °C are required, and the best yields of **6** are obtained at lower pressures (<0.10 mm) and short contact times. Temperatures of 750–800 °C, even at low pressures, give poor yields of **6**, and production of intractables is extensive.

The mechanism of formation of **6** is presumed to involve α -elimination of methoxytrimethylsilane from **13** to form 1-naphthylcarbene (**16**),¹¹ which then inserts into the *peri*C–H bond of its naphthalene ring (Scheme 2).^{1,2,8} Although details of the ring closure are not known, a rational explanation is singlet reaction of **16** with its naphthalene π -system at C-8 to give **17**, followed by hydrogen migration from C-8 to the bridging carbon.¹² Alternatively, at temperatures of 500–750 °C, carbene **1** might react intramolecularly via its triplet and thus involve biradical **18**. Intramolecular hydrogen abstrac-

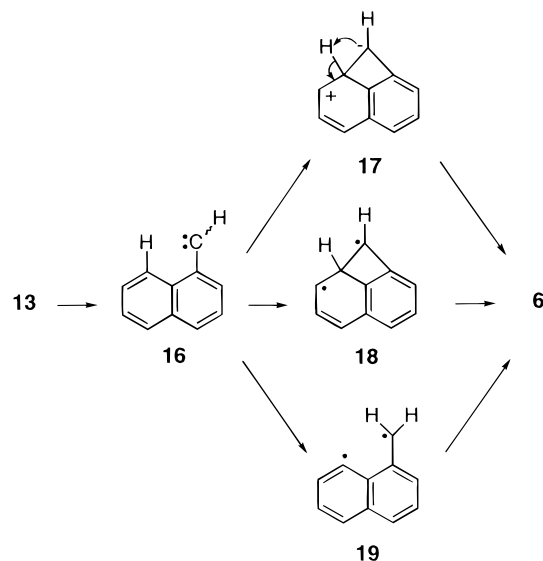
(9) Friedli, F. E.; Shechter, H. *J. Org. Chem.* **1985**, 50, 5710.

(10) A particular advantage of the present method is that **13** is a low-melting solid (mp 40.5–43.0 °C) and with slight heating can be conveniently admitted at low pressure into the pyrolysis equipment as a liquid or by simple distillation.

(11) Sekiguchi, A.; Ando, W. *Tetrahedron Lett.* **1979**, 4077. Sekiguchi, A.; Ando, W. *J. Org. Chem.* **1980**, 45, 5286. These authors report that substituted phenyl(trimethylsilyl)methanols eliminate trimethylsilylanol at ~500 °C to give products of the phenylcarbenes generated.

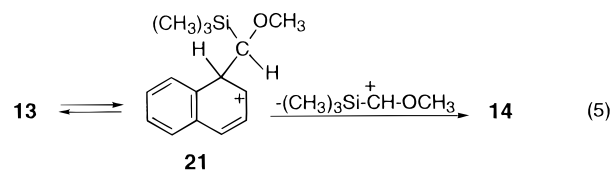
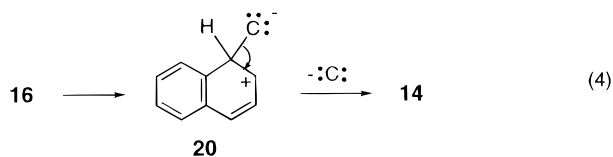
(12) For recent summaries and treatments of the theory of isomerization of arenylcarbenes, see: (a) Xie, Y.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., Jr. *J. Am. Chem. Soc.* **1997**, 119, 1370. (b) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, 118, 1535. (c) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, 51, 7022. (d) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaeffer, H. F. *J. Org. Chem.* **1996**, 61, 7030 and (e) references therein.

Scheme 2



tion–recombination via biradical **19**, although theoretically less likely, cannot be excluded at present.¹²

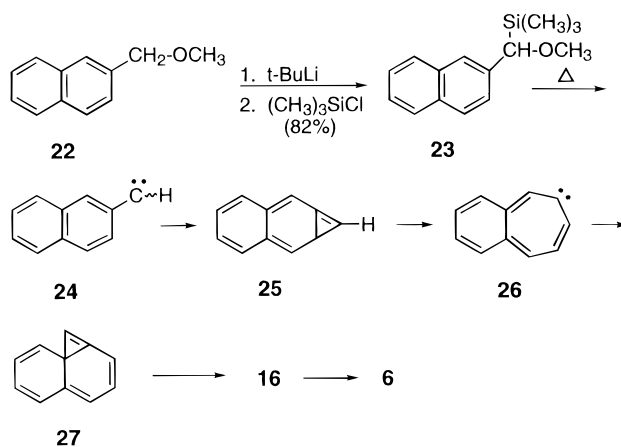
Of further interest is that **14** might be formed by rearrangement of **16** and loss of atomic carbon from **20** (eq 4) and/or *ipso* displacement of $(\text{CH}_3)_3\text{SiCHOCH}_3^+$ from **13** on acidic surfaces in the pyrolysis chamber (eq 5).^{5c,d,13} The thermal decompositions of **13** to **12**, 1-naph-



thaldehyde, α -methyl-1-naphthalenemethanol, and 1-methylnaphthalene are minor processes that are discussed in the Supplemental Information.

The thermal behavior of 2-[methoxy(trimethylsilyl)methyl]naphthalene (**23**), prepared (82%, Scheme 3) by reaction of 2-(methoxymethyl)naphthalene (**22**) with *t*-BuLi/TMEDA and then displacement of chlorotrimethylsilane, was then investigated. A purpose of this experiment was to obtain evidence that carbenes **24** and (then) **16** are generated. The result of pyrolysis of **23** to **6** are similar to that for **7**.^{2,12,14} The difference in the yields of **6** from **13** (39%) and from **23** (12%) is attributable to the

Scheme 3



Scheme 4

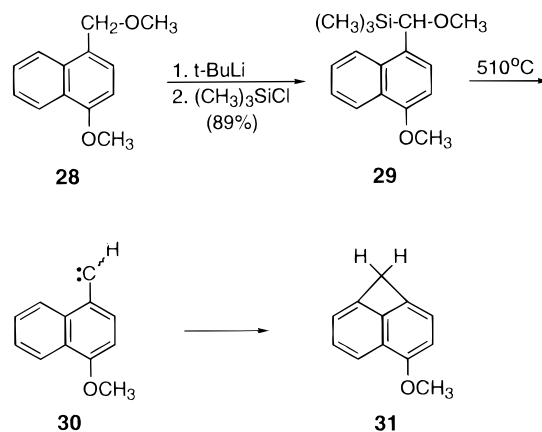


Table 2. Effects of Temperature and Pressure on the Conversions to and the Yields of **31** on Pyrolysis of **29**

temp (°C)	pressure (mm)	31		29
		% conversion ^a	% yield ^b	
445–455	0.2–0.3			87
510	0.05–0.10	29	46	35
520	0.05–0.10	27	35	21
535–545	0.1–0.4	6	7	10
560	0.2–0.3	tr	tr	0

^a The percentage of **31** formed from **29** in a single pass. ^b The percentage of **31** formed from **29** that decomposed. ^c The percentage of initial **29** recovered.

lengthy path for isomerization of **24** to **6**; the intermediates prior to **16** have many opportunities to be intercepted by various species in the reaction system.

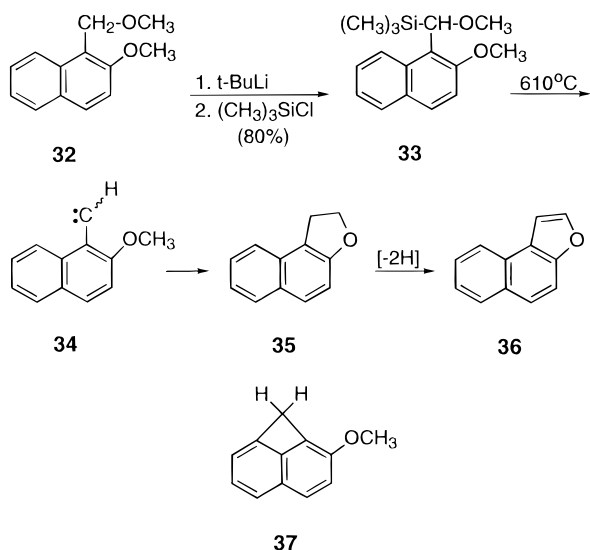
Decomposition of 4-methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (**29**), as prepared from 4-methoxy-1-methoxymethylnaphthalene (**28**, Scheme 4), then became of interest. Pyrolysis of **29** at 510 °C/0.05–0.1 mm yields 4-methoxy-1*H*-cyclobuta[*de*]naphthalene (**31**, 46%), a liquid of proper elemental analysis and spectral properties.

Formation of **31** from **29** presumably involves carbene **30** as a reaction intermediate. Methanonaphthalene **31** is the first 1*H*-cyclobuta[*de*]naphthalene in which the aromatic nucleus contains an oxygen substituent. Conversion of **29** to **31** is much more sensitive to the pyrolysis temperature (Table 2) than is conversion of **13** to **6**. Temperatures greater than 450 °C are required to eliminate methoxytrimethylsilane from **29**. Extensive decomposition of **31** occurs, however, above 520 °C.

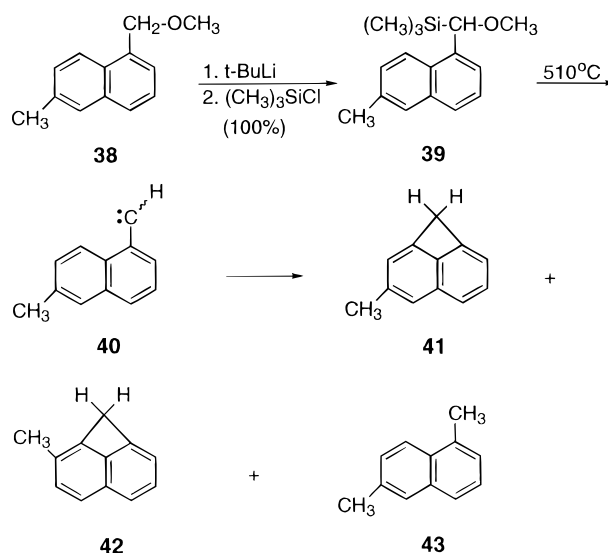
(13) In other studies from this laboratory, loss of carbon atoms from arylcarbene precursors become major processes at temperatures above 650 °C.

(14) Carbon–carbon rearrangements of arylcarbenes were initially reported by (a) Vander Stouw, G. G. Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1964; *Dissertation Abstracts*, Ann Arbor, Michigan, 1965. (b) Joines, R. C.; Turna, A. B.; Jones, W. *J. Am. Chem. Soc.* 1969, 91, 7754. (c) Crow, W. D.; Wentrup, C. *Chem. Commun.* 1969, 1387. (d) Schissel, P.; Kent, M. E.; McAdoo, D. J.; Hedeya, E. *J. Am. Chem. Soc.* 1970, 92, 2147. (e) Baron, W. J.; Jones, M., Jr.; Gaspar, P. P. *J. Am. Chem. Soc.* 1970, 92, 4739. (f) For excellent summaries and discussion of arylcarbene rearrangements, see: Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* 1985, 41, 1479 and ref 2b.

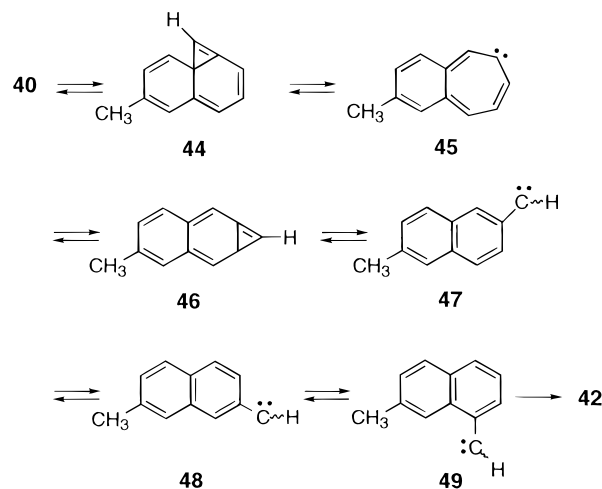
Scheme 5



Scheme 6



Scheme 7



To determine the preference of a 1-naphthylcarbene for reaction with an *ortho* substituent as compared to insertion into a *peri* $\text{C}_8\text{-H}$ center, synthesis and vacuum pyrolysis of 2-methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (**33**) were investigated as summarized in Scheme 5. Decomposition of **33** at $610^\circ\text{C}/0.05\text{--}0.10\text{ mm}$ gives 1,2-dihydronaphtho[2,1-*b*]furan (**35**, 64%) and naphtho[2,1-*b*]furan (**36**, 31%). The structures of **35** and **36** are assigned from their exact masses and by comparison of their ^1H NMR, IR, and MS results with literature values. Dihydrofuran **35** apparently results from insertion of 2-methoxy-1-naphthylcarbene (**34**) into a C–H bond of its *o*-methoxy group. Such cyclizations have been reported for arylcarbenes having *o*-dialkylamino, *o*-thioalkyl, *o*-methoxy, and certain *o*-alkyl substituents.¹⁵ Dehydrogenation of **35** yields **36**. There is no evidence for formation of 2-methoxy-1H-cyclobuta[*de*]naphthalene (**37**) in the pyrolysis of **33**.

The behavior of 6-methyl-1-naphthylmethylene (**40**), as generated from 1-[methoxy(trimethylsilyl)methyl]-6-methylnaphthalene (**39**), was then examined. Synthesis of silane **39** and the overall results of its pyrolysis are summarized in Scheme 6.

Of interest in the thermolysis of **39** at $510^\circ\text{C}/0.1\text{--}0.2\text{ mm}$ is the fact that 3-methyl-1H-cyclobuta[*de*]naphthalene (**41**) and 2-methyl-1H-cyclobuta[*de*]naphthalene (**42**) are formed in an 8:1 ratio in 44% overall yield along with 1,6-dimethylnaphthalene (**43**, 3%). The three hydrocarbon products **41**–**43** were partially separated by GC; the major *peri*-bridged naphthalene **41** and dimethylnaphthalene **43** were isolated pure. The minor *peri*-bridged naphthalene **42** could not be obtained free of **41** and **43**, and the assignments of **41** and **42** will be explained. The results of importance are (1) carbene ring closure of **40** at C-8 with hydrogen rearrangement to yield **41** is a major process, (2) **42** is apparently formed by multiple carbene–carbene rearrangements as partially illustrated in Scheme 7 to give 7-methyl-1-naphthylcarbene (**49**)^{12,14} which then cyclizes at its *peri* C–H position with hydrogen migration, and (3) with proper choice of initial

reactants, 2- and 3-substituted-1H-cyclobuta[*de*]naphthalenes are preparable from naphthylmethylene precursors.

Cyclobutanaphthalenes **41** and **42** are differentiated by their ^1H NMR as follows. A feature of the ^1H NMR of 1H-cyclobuta[*de*]naphthalenes is that aromatic protons which are *ortho* to *peri*-bridges absorb upfield (at 6.6–7.1 ppm) from that of their *meta* and *para* protons (at 7.2–8.1 ppm). In symmetrical 1-substituted-1H-cyclobuta[*de*]naphthalenes, the *ortho* hydrogens give resonances as doublets of doublets, whereas the *meta* and *para* protons exhibit multiplets. The 300 MHz aromatic ^1H NMR of **41** consists of a singlet at δ 6.97 (1H), a doublet at 7.04 (1H, $J = 6\text{ Hz}$), and a multiplet at 7.35–7.48 (3H), which corresponds to a structure having two protons *ortho* to the 1,8-methano bridge. H-2 gives a singlet (*meta* coupling to H-4 is small), and H-7 gives a doublet coupled to H-6. At 90 MHz the resonances of H-2 and H-7 overlap. Isomer **42** exhibits a ^1H NMR (spectrum) at 200 MHz as a doublet at δ 7.02 (1H, $J = 5\text{ Hz}$) and a multiplet at δ 7.2–7.8 (4H). This pattern is consistent with a structure having only one proton *ortho* to the *peri*-methylene bridge, H-7, in which there is splitting resulting from H-6. Coupling between H-5 and H-7 is too small to be observed. ^1H NMR signals for the

(15) (a) Garner, R. *Tetrahedron Lett.* **1968**, 221. (b) Garner, G. V.; Mobbs, D. B.; Suschitsky, H.; Millership, J. S. *J. Chem. Soc. C* **1971**, 3693. (c) Bailey, R. J. Ph.D. Dissertation, The Ohio State University, 1974, and ref 11.

Scheme 8

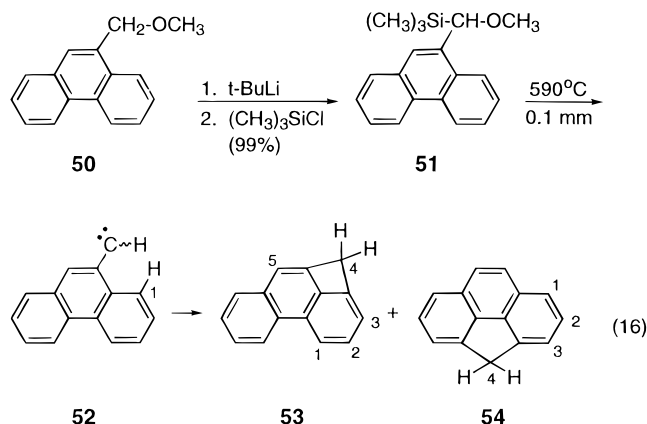


Table 3. Effects of Temperature and Pressure on the Conversions, Yields, and the Ratios of **53 and **54** on Pyrolysis of **51****

temp (°C)	pressure (mm)	53, 54		51 % recovery ^c	53/54 ratio
		% conversion ^a	% yield ^b		
500–520	0.05–0.10	7	31	80	> 100
590	0.3–0.5	21	56	63	10
590	0.10	38	72	48	9
600–650	0.2–0.4	35	57	39	6
650	0.10–0.15	56	77	27	4

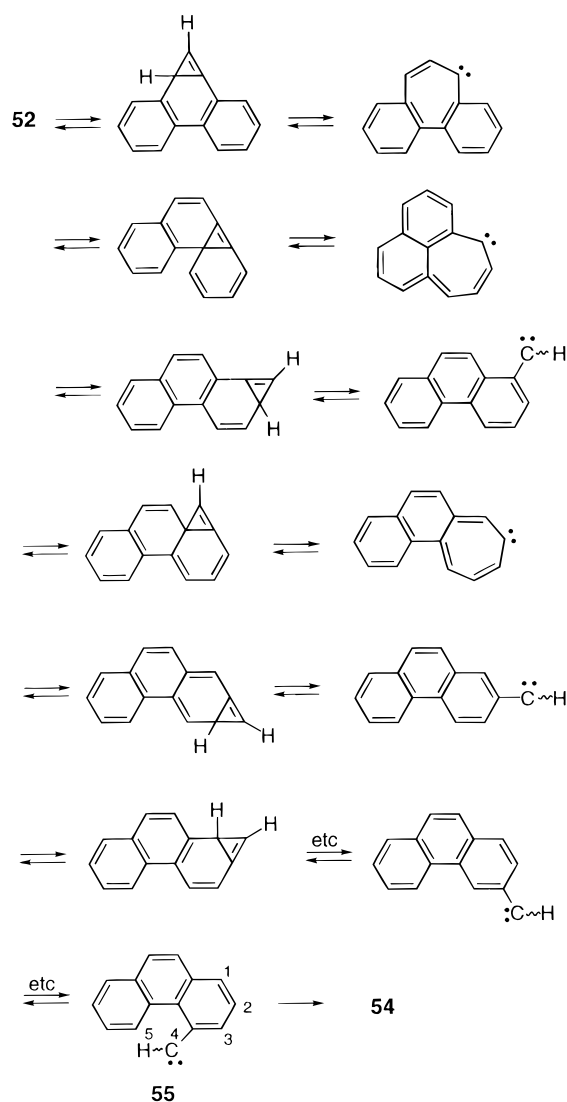
^a The percentage of **53** and **54** from **51** in a single pass. ^b The percentage of **53** and **54** formed from **51** that decomposed. ^c The percentage of initial **51** recovered.

bridging in **41** and **42** appear at δ 4.76 and 4.70, respectively.

Investigation was then initiated of the thermal behavior of benzannelated naphthylcarbenes as generated from methyl α -(trimethylsilyl)arylmethyl ether precursors. The first such carbene studied was 9-phenanthrylcarbene (**52**) upon synthesis and decomposition of 9-[methoxy(trimethylsilyl)methyl]naphthalene (**51**, Scheme 8).^{4,16} Pyrolysis of **51** at 590 °C/0.1 mm gives 4*H*-cyclobuta[*jk*]-phenanthrene (**53**) and 4*H*-cyclopenta[*def*]-phenanthrene (**54**) in a 9:1 ratio and a combined yield of 72%. The yield of **53** and the ratio of **53** to **54** vary greatly with the thermolysis conditions (Table 3). Indeed, no **54** is obtained when the pyrolysis is conducted at low conversion of **51** to products. In general, purification of **53** is much simpler when the decompositions are effected at lower temperatures. As expected, conversion of **52** to rearrangement product **54** increases with temperature.

The major product, **53**, is obtained pure by recrystallization and is assigned from its combustion analysis, exact mass, and spectral properties. The important spectral features of **53** are its ¹H NMR absorptions at δ 4.80 (s, 2H, CH₂), 7.25 (dd, 1H, H-3 on the phenanthrene nucleus, *J* = 2 and 6 Hz), 7.31 (s, 1H, H-5, this signal and that of H-3 partially overlap), and 7.5–8.5 (m, 7H, aromatic) and ¹³C NMR absorption at 46.6 (CH₂), as well as the proper number of aromatic C–H and quaternary C signals. Cyclobutaphenanthrene **53** is a sublimable, white crystalline material and forms a bright orange complex with 2,4,7-trinitrofluoren-9-one. Identification of **54** resulted from ¹H NMR and HPLC comparison of the

Scheme 9



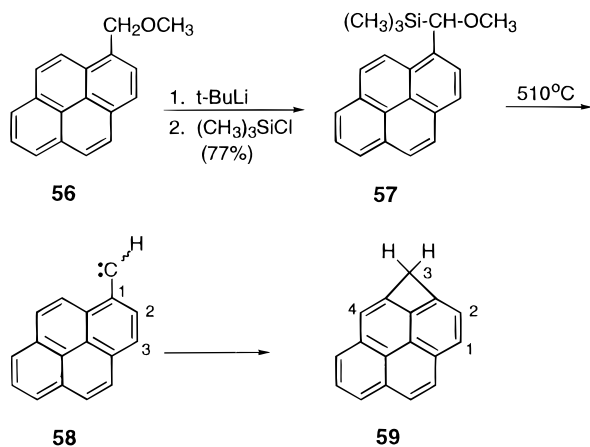
pyrolysis mixture of **53** and **54** with **54** that had been synthesized independently.

The mechanisms of rearrangement of **52** are similar to those of naphthylcarbenes. Thus, **53** is formed by cyclization of **52** at C-1 with hydrogen migration. Cyclopentaphenanthrene **54** results (Scheme 9) after at least 20 formal rearrangement steps in the isomerization of **52** to 4-phenanthrylcarbene (**55**), which then inserts into its C–H bond at C-5. Rearrangement of **52** to **55** and then **54** is also of interest in that carbenic migration through a fused ring juncture occurs.¹⁶

Synthesis of 1-[methoxy(trimethylsilyl)methyl]pyrene (**57**, 77%) from 1-methoxymethylpyrene (**56**), its thermolysis to 1-pyrenylmethylene (**58**), and the formation of 3*H*-cyclobuta[*cd*]pyrene (**59**, Scheme 10) were then studied. Indeed, volatilization of **57** through a quartz tube at 520–525 °C at 0.05–0.07 mm produces **59** in 86% yield. Identification of **59** is made from its exact mass and spectral properties including ¹H NMR absorptions at δ 5.19 (s, 2H, CH₂), 7.50 (s, 1H, H-4 on aromatic ring), 7.62 (d, 1H, H-2, *J* = 6 Hz), and 7.8–8.2 (m, 6H, aromatic) and a ¹³C NMR signal at δ 53.0 (CH₂). Pyrene **59** is a sublimable, white crystalline solid that reacts rapidly with air on standing at room temperature; however, **59** forms an air-stable bright maroon-purple

(16) Reference 2b reports that piropyrolysis of 5-(9-phenanthryl)-tetrazole at 700 °C/10⁻³ to ~5 × 10⁻¹ mm and sodium phenanthrene-9-carboxaldehyde *p*-tosylhydrazonate at 650 °C/10⁻³ to 10⁻¹ mm each yield **53** and **54** in ~7% and 1% yields; phenanthrene, 9-methylphenanthrene and 9-phenanthrenecarbonitrile are also formed.

Scheme 10

Table 4. Effects of Temperature and Pressure on the Conversions to and the Yields of **59** on Pyrolysis of **57**

temp (°C)	pressure (mm)	59		57 % recovery ^c
		% conversion ^a	% yield ^b	
510–530	0.02–0.05	29	47	39
520–525	0.05–0.07	32	86	62
520–540	0.05–0.10	31	47	34
660	0.05–0.20	<16 ^d	<16	26

^a The percentage of **59** formed from **57** in a single pass. ^b The percentage of **59** formed from **57** that decomposed. ^c The percentage of **57** recovered. ^d Part (~35%) of a complex mixture.

complex with 2,4,7-trinitrofluoren-9-one. The excellent yield in conversion of **57** to **59** presumably results from the flexibility of the many ring-atom arene system, and when there is carbene–carbene rearrangement, **58** is formed repeatedly. The yield of **59** is, however, sensitive to the pyrolysis temperature (Table 4).

In summary, various [methoxy(trimethylsilyl)methyl]arenes eliminate methoxytrimethylsilane preparatively at 525–675 °C/0.05–0.10 mm in flow equipment to give *peri*-cyclobutarenes as derived from precursor arenylcarbenes. Of further value is information with respect to the spectral and physical properties of various cyclobutarenes from the present and previous^{1,3,9} investigations from this laboratory. The ¹H and ¹³C NMR spectra of *peri*-methylene-bridged arenes are very distinct with respect to the positions of their *peri*-methano hydrogen and carbon resonances. The ¹H spectra show methylene signals at 4.39–5.15 ppm, depending upon the ring substituents. The ¹³C NMR display carbon signals at 44.3–53.0 ppm. Such resonances clearly indicate formation or retention of a *peri*-methanoarene structure in assigning the products from various experiments. Of further note is the fact that bridged arenes such as **6**, **31**, **41**, **53**, and **59** reveal intense molecular ion patterns and very little fragmentation.

Studies of (1) improved methods for generating arenylcarbenes, (2) further synthesis of mono- and poly-*peri*-methanoarenes, and (3) the varied chemistry of single-atom, *peri*-bridged arenes are in progress.

Experimental Section

General Methods. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, or Microanalysis, Inc., Wilmington, DE. Mass spectra were determined at 70 eV unless otherwise described. ¹H NMR were recorded at 90, 200, or 300 MHz. ¹³C NMR spectra were obtained at 20.1, 50.3, or 75.3 MHz.

Chemical shifts, unless otherwise specified, are reported in ppm (δ) relative to tetramethylsilane (TMS) with TMS, CH₂Cl₂, residual CHCl₃, or ClCH₂CH₂Cl as internal standards.

Procedure A; 1-[Methoxy(trimethylsilyl)methyl]naphthalene (13**).** *t*-BuLi in pentane (1.9 M, 17 mL, 32 mmol) was added to a mixture of 1-(methoxymethyl)naphthalene¹⁷ (**12**, 5.2 g, 30.0 mmol) and dry TMEDA (5.3 mL, 35 mmol) in dry Et₂O (100 mL) at –70 °C under argon. The purple-black solution was stirred 20 min at –70 °C, chlorotrimethylsilane (5.2 mL, 33 mmol) was added, and the dark green mixture was allowed to warm to room temperature. After addition of H₂O to the colorless solution, the organic layer was separated, washed with saturated aqueous NaHCO₃, dried (MgSO₄), and concentrated to a light yellow oil (7.6 g, 100%) which was pure by TLC and ¹H NMR. Vacuum distillation yielded a colorless oil, bp 123–125 °C/0.6 mm, which solidified in a freezer. Sublimation (40–60 °C at 0.05 mm) gave **13** as a white waxy solid: mp 40.5–43.0 °C; ¹H NMR (CDCl₃, CH₂Cl₂ as internal standard) –0.02 (s, 9H), 3.33 (s, 3H), 4.83 (s, 1H), 7.3–8.2 (m, 7H); exact mass calcd 244.1283, obsd 244.1289. Anal. Calcd for C₁₅H₂₀OSi: C, 73.71; H, 8.25. Found: C, 73.58, H, 8.13.

Pyrolysis of [Methoxy(trimethylsilyl)methyl]arenes. General Procedure. All pyrolyses, unless otherwise described, were performed by passing samples through a 3 cm × 35 cm vertical quartz tube packed with a 4–5 cm column of quartz chips placed approximately halfway down the tube. The pyrolysis tube was heated with a 100 V Hoskins electric furnace. A thermocouple was positioned between the furnace wall and the quartz tube approximately one-third of the way into the oven. Insulation material was packed around the tube at the top and bottom of the oven. A receiver, with a sidearm for vacuum connection, was attached to the bottom of the tube and cooled in a dry ice–acetone bath.

Samples were introduced into the hot zone by (1) distillation or sublimation by slowly heating a reservoir containing the sample with an oil bath, flame, or Nichrome wire wrapped around the reservoir, (2) dropping a neat sample into the tube using a Hershberg pressure-equalizing dropping funnel, or (3) dropping a solid sample into the tube utilizing a solid addition funnel. Generally, the distillation technique gave better and more reproducible results because stricter control over rate and amount of addition could be maintained. Also, there is less fluctuation in pressure during pyrolysis. Pressures were monitored with a manometer fitted into the vacuum system between the receiver and the vacuum pump.

Pyrolysis of 1-[Methoxy(trimethylsilyl)methyl]naphthalene (13**); 1*H*-Cyclobuta[de]naphthalene (**6**).** Distillation of **13** (3.0 g, 12 mmol) at 0.05–0.10 mm through a quartz tube heated to 650 °C afforded a dark brown pyrolysate that was chromatographed on silica gel while changing the eluent from hexane to benzene. The products obtained were (1) a mixture (1.02 g) of **6** (63% of the mixture, 39% yield), **14** (3% yield), and 1-methylnaphthalene (5% yield) in which the components were identified and the yields were determined by ¹H NMR with ClCH₂CH₂Cl added as an internal standard or by GC, (2) 1-(methoxymethyl)naphthalene **12** (0.11 g, 8%), (3) 1-naphthaldehyde (0.12 g, 9%), (4) α -methyl-1-naphthalenemethanol (0.14 g, 7%), and (5) unidentified products.

The yields of **6** varied greatly with the temperature and pressure at which the pyrolyses were conducted (Table 1). Cyclobutanaphthalene **6** was usually obtained by chromatography as the major component (60–70%) of a mixture with **14**, 1-methylnaphthalene, and other minor products. This mixture could be used directly for preparation of derivatives of **6**, as demonstrated by isolation of pure 4-nitro-1*H*-cyclobuta[de]naphthalene (**15**) from nitration of the mixture. Further purification (>90% purity) of **6** could be effected by fractional distillation or preparative GC (5% SE-30, 140 °C). Formation of the picric acid complex of **6**, followed by recrystallization and decomposition of the complex on silica gel (hexane eluent), afforded pure **6**.

Nitration of 1*H*-Cyclobuta[de]naphthalene (6**) Obtained by Pyrolysis of **13**; 4-Nitro-1*H*-cyclobuta[de]naphthalene (**15**).** Acetyl nitrate (6.2 mmol) was prepared by slowly

adding 70% nitric acid (0.4 mL, 6.2 mmol) to acetic anhydride (5 mL) at 0–5 °C. After 5 min, the mixture was added dropwise to **6** (1.02 g of pyrolysis product, 63% pure; 4.7 mmol) in acetic anhydride (20 mL) at 0–5 °C. The resulting solution was stirred for 1 h at 0–5 °C, allowed to warm to room temperature, stirred further for 1 h, and then poured into a mixture of Et₂O and 3.5 M aqueous KOH. After the mixture had been stirred for 2 h, the Et₂O layer was separated, dried (MgSO₄), and concentrated to a yellow solid, which was recrystallized from hexane to give **15** as yellow needles (0.29 g, 34%); mp 120–123 °C, lit.⁹ mp 124–125 °C. The product was homogeneous by TLC and spectrally identical to reported values. The mother liquor, upon chromatography on silica gel with 50% hexane/benzene, afforded additional **15** as a yellow solid (0.12 g, 14%).

2-[Methoxy(trimethylsilyl)methyl]naphthalene (23). Synthesis from 2-methoxymethylnaphthalene (**22**, 0.46 g) by Procedure A and column chromatography of the product on silica gel with 10% benzene/hexane as eluent yielded **23** (0.53 g, 82%) as a colorless liquid which crystallized at 0 to –10 °C: mp 33–35 °C; ¹H NMR (CDCl₃, CH₂Cl₂ as internal standard) 0.23 (s, 9H), 3.48 (s, 3H), 4.18 (s, 1H), 7.1–7.9 (m, 7H); exact mass calcd 244.1283, obsd 244.1276. Anal. Calcd for C₁₅H₂₀O₂Si: C, 73.71; H, 8.25. Found: C, 73.57; H, 8.04.

Pyrolysis of 2-[Methoxy(trimethylsilyl)methyl]naphthalene (23). Silane **23** (1.0 g, 4.1 mmol) was distilled at 0.2–0.3 mm through a quartz tube heated to 640–650 °C. Column chromatography of the black pyrolysate on silica gel with hexane as eluent afforded a complex mixture (0.25 g) in which **6** was shown to be a major component by ¹H NMR (28% of the mixture, 12% yield).

4-Methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (29). Crude **28** (3.5 g, 18 mmol) was converted by Procedure A and chromatography on silica gel with benzene/hexane (1:1) to **29** (4.2 g, 89%), a colorless oil which crystallized at ~5 °C: mp 55–60 °C; ¹H NMR (CDCl₃, CH₂Cl₂ as internal standard) 0.02 (s, 9H), 3.31 (s, 3H), 4.00 (s, 3H), 4.69 (s, 1H), 6.85 (d, *J* = 8 Hz, 1H), 7.3–7.5 (m, 3H), 8.0–8.2 (m, 1H), 8.3–8.5 (m, 1H); exact mass calcd 274.1389, obsd. 274.1398. An analytical sample was prepared by distillation at 86 °C/0.1 mm. Anal. Calcd for C₁₆H₂₂O₂Si: C, 70.02; H, 8.08. Found: C, 70.12; H, 8.28.

Pyrolysis of 4-Methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (29); 4-Methoxy-1H-cyclobuta[de]naphthalene (31). Volatilization of **29** (0.54 g, 2.0 mmol) at 0.05–0.10 mm through a quartz tube heated to 510 °C gave a dark red-black pyrolysate. Preparative thin-layer chromatography on silica gel with hexane as the eluent yielded (1) **31** (0.10 g, 29%) as a light yellow liquid and (2) initial **29**, a light yellow oil (0.19 g, 35%) identified by comparison with an authentic sample by TLC and ¹H NMR. Spectral data for **31**: ¹H NMR (CDCl₃, 90 MHz) 3.90 (s, 3H), 4.60 (s, 2H), 6.68 (d, 1H, *J* = 7 Hz), 6.84–7.48 (m, 3H), 7.62 (d, 1H, *J* = 9 Hz); ¹³C NMR (CDCl₃, 75.4 MHz) 46.0, 55.8, 108.9, 117.7, 118.1, 118.2 (2C), 129.5, 133.0, 140.7, 147.1, 153.4; UV (λ, ε, hexane) 324 nm (3 600), 315 (2 500), 310 (3 400), 304 (3 500), 296 (4 900), 292 (4 900), 285 (4 600), 242 (20 500), 234 (25 600), 216 (38 400); exact mass calcd 170.0732, obsd. 170.0737. An analytical sample was prepared by molecular distillation (45–50 °C/0.3 mm). Anal. Calcd for C₁₂H₁₀O: C, 84.68; H, 5.92. Found: C, 84.89; H, 6.24. The yield of **31** is 46% based on recovered **29**.

2-Methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (33). Procedure A was followed to convert **32** (0.28 g) to **33**, with the modification that in the deprotonation reaction the mixture was warmed to –30 °C prior to the addition of chlorotrimethylsilane. Workup and column chromatography on silica gel with 20% benzene/hexane as eluent yielded (1) **33** (0.21 g, 55%), a white solid, mp 75.5–77.5 °C (pentane) and (2) **32** (0.1 g, 36%), a colorless oil. Spectral data for **33**: ¹H NMR (CDCl₃, CH₂Cl₂ as internal standard) 0.02 (s, 9H), 3.24 (s, 3H), 3.88 (s, 3H), 5.18 (s, 1H), 7.2–7.5 (m, 3H), 7.65–7.85 (m, 2H), 8.65–8.75 (m, 1H); ¹³C NMR (CDCl₃, 75.43 MHz) –2.2, 56.3, 59.2, 74.1, 112.9, 122.1, 123.4, 125.4, 126.4, 128.0, 128.2, 129.6, 133.1, 154.3; exact mass calcd 274.1389, obsd.

274.1398. Anal. Calcd for C₁₆H₂₂O₂Si: C, 70.02; H, 8.08. Found: C, 69.68; H, 8.17. The yield of **33** is 80% based on recovered **47**.

Pyrolysis of 2-Methoxy-1-[methoxy(trimethylsilyl)methyl]naphthalene (33). Slow distillation of **33** (0.26 g, 0.95 mmol) at 0.05–0.10 mm through a quartz tube heated to 610 °C gave a pale yellow oil, which on preparative TLC on silica gel with hexane/benzene (5:1) yielded (1) naphtho[2,1-*b*]furan (**36**, 0.05 g, 31%) as a light yellow oil, (2) 1,2-dihydronaphtho[2,1-*b*]furan (**35**, 0.10 g, 64%) as a colorless liquid, and (3) initial **33** (0.01 g, 3%). Product **36** could be further purified by preparative VPC (10 ft × 1/4 in. 5% SE-30 on chromosorb P, isothermal at 160 °C) followed by sublimation at 35–40 °C and 0.02 mm to yield white crystals: mp 51–54 °C (lit.¹⁸ mp 61–62 °C); ¹H NMR¹⁸ (CDCl₃, 200 MHz) 7.27 (d, 1H, *J* = 2 Hz), 7.36–7.64 (m, 2H), 7.70 (d, 2H, *J* = 5 Hz), 7.76 (d, 1H, *J* = 2 Hz), 7.94 (d, 1H, *J* = 8 Hz), 8.14 (d, 1H, *J* = 8 Hz); MS *m/e* (relative intensity) 169 (15), 168 (100, M⁺), 140 (18), 139 (27); exact mass calcd 168.0575, obsd 168.0580. Spectral data for **35**: ¹H NMR¹⁹ (CDCl₃, 90 MHz, CH₂Cl₂ as internal standard) 3.46 (t, 2H, *J* = 9 Hz), 4.78 (t, 2H, *J* = 9 Hz), 7.1–7.9 (m, 6H); MS *m/e* (relative intensity) 171 (14), 170 (100, M⁺), 169 (58), 142 (13), 141 (30), 139 (13), 115 (21); exact mass calcd 170.0732, obsd 170.0737.

1-[Methoxy(trimethylsilyl)methyl]-6-methylnaphthalene (39). Reactions of 6-methyl-1-naphthalenemethanol with sodium hydride and then dimethyl sulfate followed by chromatography on silica gel using 1:5 benzene/hexane as eluent yielded 1-methoxymethyl-6-methylnaphthalene (**38**, 78%) as a colorless liquid: ¹H NMR (CDCl₃) 2.50 (s, 3H), 3.40 (s, 3H), 4.81 (s, 2H), 7.2–7.8 (m, 5H), 8.0 (d, 1H, *J* = 9 Hz). Procedure A was then followed to convert **38** (3.6 g) to **39** (4.9 g, 100%) as light yellow oil (100%): ¹H NMR (CDCl₃, CH₂Cl₂ as an internal standard) –0.08 (s, 9H), 2.41 (s, 3H), 3.19 (s, 3H), 4.67 (s, 1H), 7.1–7.6 (m, 5H), 7.9 (d, 1H, *J* = 9 Hz); exact mass calcd 258.1440, obsd. 258.1446. An analytical sample was prepared as a colorless liquid by molecular distillation at 66–68 °C/0.07 mm. Anal. Calcd for C₁₆H₂₂O₂Si: C, 74.36; H, 8.58. Found: C, 74.40; H, 8.48.

Pyrolysis of 1-[Methoxy(trimethylsilyl)methyl]-6-methylnaphthalene (39); 3-Methyl-1H-cyclobuta[de]naphthalene (41), and 2-Methyl-1H-cyclobuta[de]naphthalene (42). Volatilization of **39** (0.83 g, 3.22 mmol) at 0.1–0.2 mm through a quartz tube at 510 °C gave a dark red-black pyrolysate. Preparative TLC with hexane yielded (1) a mixture (0.16 g) of **41** (27%), **42** (3%), and 1,6-dimethylnaphthalene (**43**, 2%) in a ratio of 14.1:1.7:1 as determined by GC using **43** as an internal standard [partial separation of **41**, **42**, and **43** was achieved via GC (3% OV-17, 12 ft × 1/8 in., isothermal at 170 °C)] and (2) initial **39** (0.25 g, 28%). The properties of the products were (1) for **41**, a colorless liquid: ¹H NMR (CDCl₃, 300 MHz) 2.55 (s, 3H), 4.76 (s, 2H), 6.97 (s, 1H), 7.04 (d, 1H, *J* = 6 Hz), 7.35–7.48 (m, 3H); ¹³C NMR (CDCl₃, 75 MHz) 23.7, 47.1, 116.3, 119.1, 120.2, 120.6, 125.4, 130.6, 140.9, 141.0, 141.2, 144.9; UV (λ, ε, hexane) 322 nm (380), 312 (332), 305 (462), 274 (3 570), 228 (56 100); exact mass calcd 154.0782, obsd. 154.0787. Anal. Calcd for C₁₂H₁₀: C, 93.46; H, 6.54. Found: C, 93.29; H, 6.63; (2) for **42**, a colorless liquid: ¹H NMR (CDCl₃, 200 MHz) 2.38 (s, 3H), 4.70 (s, 2H), 7.02 (d, 1H, *J* = 5 Hz), 7.2–7.8 (m, 4H); and (3) for **43**, a colorless liquid: identified by comparison of its ¹H NMR and GC with an authentic sample (Aldrich). Yields of **41**, **42**, and **43** based on recovered starting material were 39%, 5%, and 3%, respectively. Cyclobuta[de]naphthalene **42** could not be cleanly separated from **43** and thus was not characterized further.

9-[Methoxy(trimethylsilyl)methyl]phenanthrene (51). 9-(Methoxymethyl)phenanthrene (**50**, 34.1 g, 0.15 mol) was converted as in Procedure A to a white solid (43.7 g, 99%) homogeneous by TLC. Recrystallization from hexane yielded

(18) (a) Emmott, P.; Livingstone, R. *J. Chem. Soc.* **1957**, 3144. (b) Narasimhan, N. S.; Mali, R. S. *Tetrahedron* **1975**, *31*, 1005. (c) Batterham, T. J.; Lamberton, J. A. *Aust. J. Chem.* **1964**, *17*, 1305. (d) Loader, C. E.; Timmons, C. J. *J. Chem. Soc. C* **1967**, 1677.

(19) Breuer, E.; Melumad, D. *Tetrahedron Lett.* **1969**, 1875.

white crystals of **51** (33.4 g, 76%): mp 106–108 °C; ¹H NMR (CDCl₃, CH₂Cl₂ as internal standard) 0.05 (s, 9H), 3.38 (s, 3H), 4.78 (s, 1H), 7.5–7.8 (m, 6H), 8.0–8.2 (m, 2H), 8.58–8.88 (m, 2H); exact mass calcd 294.1440, obsd. 294.1450. Anal. Calcd for C₁₉H₂₂OSi: C, 77.50; H, 7.53. Found: C, 77.62; H, 7.52.

4H-Cyclobuta[jk]phenanthrene (53) and 4H-Cyclopenta[def]phenanthrene (54). Solid phenanthrene **51** (0.54 g, 1.8 mmol) was dropped at 0.1 mm into a quartz tube heated to 590 °C. The black pyrolysate, on purification by preparative TLC on silica gel using hexane as eluent, yielded first a 9:1 mixture (by ¹H NMR) of **53** and **54** (0.13 g, 38%). Recrystallization from pentane afforded pure **53** as white flakes: mp 87.5–88.5 °C; ¹H NMR (CDCl₃, 90 MHz) 4.80 (s, 2H), 7.25 (dd, 1H, *J* = 6.2 Hz), 7.31 (s, 1H), 7.5–8.2 (m, 6H), 8.35–8.50 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) 46.6, 117.6, 119.3, 119.6, 124.0, 125.4, 126.2, 126.6, 129.6, 129.9, 130.2, 137.4, 139.1, 141.1, 145.0; UV (*λ*, *ε*, hexane) 345 nm (1,100), 338 (490), 330 (720), 323 (430), 314 (430), 294 (12 900), 282 (10 200), 275 (13 500), 264 (shoulder, 19 500), 249 (96 200), 244 (shoulder, 82 400), 228 (19 800), 223 (17 000), 205 (23 100); exact mass calcd 190.0782, obsd. 190.0788. An analytical sample (white crystals, mp 87.5–88.5 °C) was prepared by sublimation at 55–58 °C and 0.02 mm. Anal. Calcd for C₁₅H₁₀: C, 94.70; H, 5.30. Found: C, 94.35; H, 5.53. Further chromatography of this pyrolysate gave starting **51** (0.26 g, 48%) as a light yellow solid. The yield of **53/54** was 72% based on recovered starting material.

Identification of **54** as the minor component in the first fraction was based on comparison of the mixture's ¹H NMR spectrum and HPLC trace (Waters C-18 column; 1:1 methanol/water) with those of authentic **54**.²⁰ No change other than relative intensities of the peaks in the ¹H NMR spectrum or the HPLC trace was observed when authentic **54** was added to the mixture obtained from the pyrolysis.

Amounts of **51** up to 10 g were pyrolyzed. Purification of **53** was accomplished by column chromatography on silica gel, followed by recrystallization from pentane or methanol. Starting material **51** could easily be recycled, and thus no material was wasted.

4H-Cyclobuta[jk]phenanthrene:2,4,7-Trinitrofluoren-9-one Complex. Cyclobuta[jk]phenanthrene **53** (0.40 g, 2.1 mmol) in hot ethanol (10 mL) was added to a hot ethanolic solution (40 mL) of 2,4,7-trinitrofluoren-9-one (0.70 g, 2.2 mmol). Benzene (30 mL) was slowly added until the boiling solution became clear. Upon cooling of the reaction mixture, bright orange crystals separated that were recrystallized from benzene to give bright orange needles of the addition complex (0.58 g, 54%): mp 209.5–211 °C. Anal. Calcd for C₂₈H₁₅N₃O₇: C, 66.53; H, 2.99; N, 8.32. Found: C, 66.78; H, 3.09; N, 8.07. Decomposition of the complex on silica gel using 1:1 benzene/hexane as eluent regenerated initial **53**.

1-[Methoxy(trimethylsilyl)methyl]pyrene (57). Procedure A was used to convert **56** (2.7 g, 11 mmol) to crude **57**. Recrystallization from hexane afforded **57** as yellow crystals (2.7 g, 77%): mp 96.5–98.5 °C; ¹H NMR (CDCl₃, CHCl₃ as internal standard) 0.18 (s, 9H), 3.51 (s, 3H), 5.23 (s, 1H), 7.9–8.5 (m, 9H); exact mass calcd 318.1440, obsd. 318.1449. Anal. Calcd for C₂₁H₂₂OSi: C, 79.19; H, 6.97. Found: C, 79.42; H, 7.22.

Pyrolysis of 1-[Methoxy(trimethylsilyl)methyl]pyrene (57): 3H-Cyclobuta[cd]pyrene (59). Silane **57** (0.50 g, 1.6 mmol) was slowly distilled at 0.05–0.07 mm through a quartz tube at 520–525 °C. The pyrolysate, upon purification by preparative TLC using hexane as eluent, yielded **59** (0.11 g, 32%) as a light yellow solid. Recrystallization from pentane gave white crystals: mp 117–118 °C; ¹H NMR (CDCl₃, 90 MHz) 5.19 (s, 2H), 7.5 (s, 1H), 7.62 (d, 1H, *J* = 6 Hz), 7.8–8.2 (m, 6H); ¹³C NMR (CDCl₃, 20.1 MHz) 53.0, 116.8, 121.3, 123.3, 124.4, 124.8, 125.0, 125.8, 126.4 (2 C), 127.8, 128.4, 131.1, 135.6, 137.1, 139.8, 144.1; UV (*λ*, *ε*, hexane) 375 nm (299), 340 (36 300), 335 (24 800), 324 (26 100), 310 (12 700), 275 (41 000), 265 (24 200), 254 (15 200), 244 (58 400), 235 (shoulder, 36 000); exact mass calcd 214.0782, obsd. 214.0786. Anal. Calcd for C₁₇H₁₀: C, 95.30; H, 4.70. Found: C, 94.71; H, 4.95. A further product of chromatography is initial **57** (0.31 g, 62%), identical to an authentic sample by TLC and ¹H NMR. The yield of **59** based on recovered starting material is 86%.

Reanalysis of **59** after standing open to air for 1 day revealed that it contained 91.51% carbon and 5.09% hydrogen, thus indicating considerable oxidation. A more satisfactory analysis could not be obtained even after repeated chromatography, recrystallization, and sublimation (100 °C and 0.02 mm). All analytical samples were sealed in ampules under argon.

3H-Cyclobuta[cd]pyrene:2,4,7-Trinitrofluoren-9-one Complex. To a refluxing benzene solution (10 mL) of 2,4,7-trinitrofluoren-9-one (0.30 g, 0.95 mmol) was added **59** (0.19 g, 0.89 mmol) in benzene (2 mL). Upon cooling of the mixture, dark maroon crystals separated that recrystallized from benzene as glistening, bright maroon-purple needles (0.27 g, 57%). The 3H-cyclobuta[cd]pyrene:2,4,7-trinitrofluoren-9-one complex turned black when heated to 190 °C and charred to a black dust at 220 °C, with no visible sign of melting. Anal. Calcd for C₃₀H₁₅H₃O₇: C, 68.05; H, 2.86; N, 7.94. Found: C, 68.02; H, 3.10; N, 7.85.

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Supporting Information Available: Discussion of mechanisms of formation of minor products from pyrolysis of **13**, procedures for preparing 4-methoxy-1-naphthalenemethanol, 2-methoxy-1-naphthalenemethanol, 6-methyl-1-naphthalenemethanol, 1-pyrenemethanol and methoxymethylarenes **12**, **22**, **28**, **32**, and **56**, UV data, and copies of NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

(20) (a) Mendenwald, H. *Chem. Ber.* **1953**, *86*, 287. (b) Sadler Standard ¹H NMR Spectrum 2349M. Sadler Research Laboratories, Inc., Philadelphia, PA.