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Preparative Methodology and Pyrolytic Behavior of Anthrylmonocarbenes: Synthesis and Chemistry of 1*H*-Cyclobuta[*de*]anthracene

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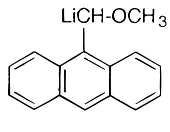
This study involves (1) the behavior of organolithium reagents (**1**−**6**), (2) development of efficient methods for preparing 9(**7**)- and 1(**8**)-[methoxy(trimethylsilyl)methyl]anthracenes and their analogues, (3) the intramolecular chemistry of the 9(**9**)- and 1(**10**)-anthrylcarbenes generated by pyrolyses of **7** and **8**, respectively, and (4) investigation of thermal behavior and bromination of the 1*H*-cyclobuta[*de*]anthracene (**11**) obtained from **9** or **10**. α-Methoxy-9-anthrylmethyllithium (**1**), prepared from 9-(methoxymethyl)anthracene (**14**) and *t*-BuLi in TMEDA/Et_2O/pentane, reacts at C-10 with D_2O, chlorotrimethylsilane, dimethyl sulfate, benzoyl chloride, acetaldehyde, benzaldehyde, and acetone to give, after neutralization, 9,10-dihydro-9-(methoxymethylene)-10-substituted-anthracenes **15** and **21a**−**f**. However, lithiation of 9-(thiomethoxymethyl)anthracene (**25**) with *t*-BuLi/TMEDA/Et_2O/pentane occurs by an apparent radical-anion displacement process to give 9-anthrylmethyllithium (**3**), which then reacts with chlorotrimethylsilane to yield 9-(trimethylsilylmethyl)anthracene (**28**). Similarly, **28** is formed from **25** and from 9-(trimethylsilyloxymethyl)-anthracene (**29**) with lithium and then chlorotrimethylsilane. The electrophiles D_2O, dimethyl sulfate, and benzaldehyde react with **3** at its methyl and its C-10 positions. [Methoxy(trimethylsilyl)-methyl]arenes **40**−**42** and **7** are obtained by reactions of their aryllithium and arylmagnesium bromide precursors with bromo(methoxy)methyltrimethylsilane (**39**). 1-(Methoxymethyl)anthracene (**45**) is converted conveniently by *t*-BuLi and chlorotrimethylsilane to **8**. Flash-vacuum pyrolyses of **7** and **8** yield **11** preparatively; **11** then thermolyzes to 2*H*-cyclopenta[*jk*]fluorene (**46**). Decomposition of 9-deuterio-10-[methoxy(trimethylsilyl)methyl]anthracene (**55**) at 650 °C/10^{-3} mm results in 10(**56**)- and 1(**57**)-deuteriocyclobutanthracenes, thus revealing that the 10-deuterio-9-anthrylcarbene inserts to give **56** and also isomerizes extensively before yielding **57**. Of note is that **56** isomerizes thermally by C_{10}−D movement to form 2-deuteriocyclopentafluorene **58**, **57** rearranges by C_{10}−H movement to yield deuteriocyclopentafluorene **59**, and **58** and **59** equilibrate 1,5-sigmatropically. Possible mechanisms for the isomerizations of **56** and **57** are outlined. Further, bromine adds rapidly to **11** to form 9,10-dibromo-9,10-dihydro-1*H*-cyclobuta[*de*]anthracene (**94**), which eliminates HBr on warming to yield 10-bromo-1*H*-cyclobuta[*de*]anthracene (**95**).



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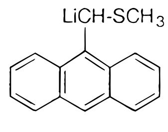

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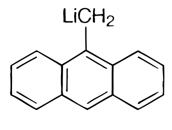

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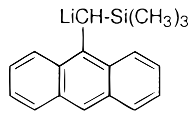

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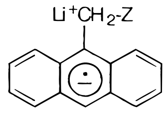

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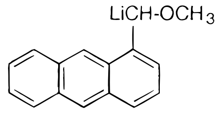

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Z = OCH_3, $C(CH_3)_3$, SCH_3 and $OSi(CH_3)_3$

The present investigation involves (1) the behavior of organolithium reagents **1**−**6** and development of methods for synthesis of 9(**7**)- and 1(**8**)-[methoxy(trimethylsilyl)-methyl]anthracenes (Scheme 1), (2) pyrolyses of **7** and **8** to their respective anthrylcarbenes **9** and **10** (Scheme 1), which insert into their *peri*-C−H bonds to give 1*H*-cyclobuta[*de*]anthracene (**11**) and isomeric products thereof, and (3) addition and aromatic substitution reactions of **11**. The initial results for preparation of cyclobutarene **11** from **8** have been communicated.[1] 9-Anthryltetrazole (**12**) has also been reported to thermolyze (11%) to **9** (Scheme 2) which converts to **11**.[2,3] The principal pyrolysis reaction of **12** (Scheme 2) however is conversion to 9-cyanoanthracene (**13**, 85%) and hydrogen azide.[2] As

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(1) The initial observation of conversion of **8** to **11** was communicated by Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2715.

(2) (a) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601. (b) Tetrazole **12** is presumed to be in equilibrium with its tautomer with the hydrogen on N-2. The structure represented as **12** is that in which the extended conjugation between the tetrazole and the 9-anthryl moieties is maximized.

(3) Present efforts in this laboratory to prepare **11** by vacuum pyrolysis of 9-anthryldiazomethane as generated in situ by decomposition of sodium 9-anthraldehyde *p*-tosylhydrazonate at 500−520 °C/0.33 mm have failed. The reaction products are 9-methylanthracene (20%), sodium *p*-tolylsulfinate, and intractables. Further, vacuum thermolysis of sodium 9-anthraldehyde *p*-tosylhydrazonate at 650 °C as above yields 9-methylanthracene (7%) and intractable products. Neither **11** nor **46** is obtained in the above experiments.

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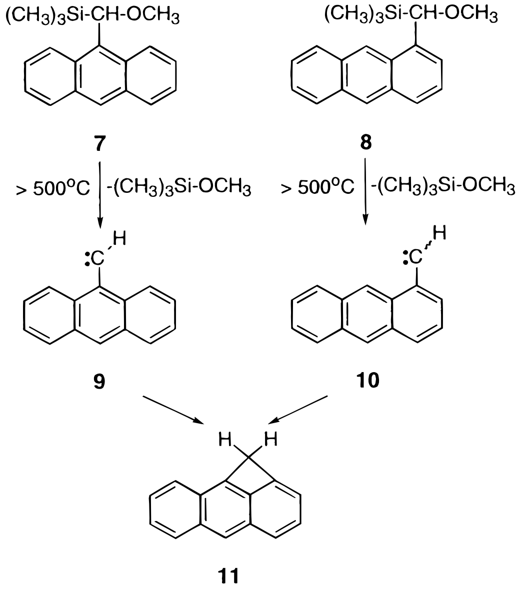
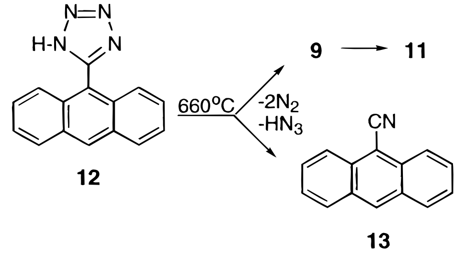
Scheme 1



Scheme 2

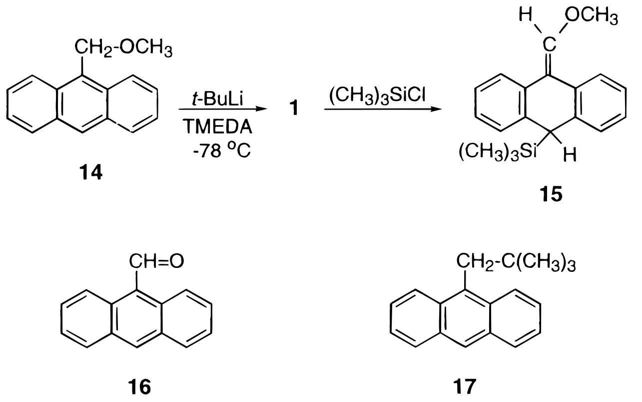


will be described, cyclobutarene **11** undergoes complicated rearrangement reactions that are major concerns of this research.

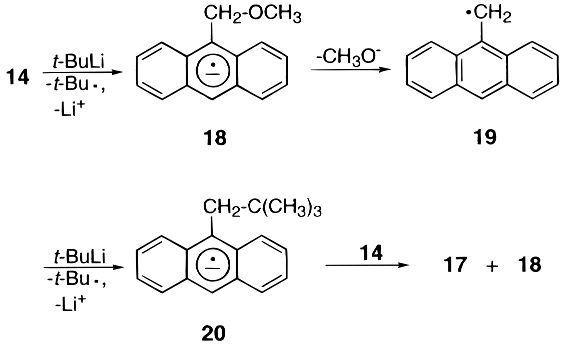
Results and Discussion

1. The Behavior of 1–6; Synthesis of 7 and 8. In the present program, synthesis of **7** was first attempted from 9-(methoxymethyl)anthracene (**14**) in Et_2O and tetramethylethylenediamine (TMEDA) by addition of *t*-BuLi in pentane and then chlorotrimethylsilane at −78 °C and warming the reactants to ∼25 °C. α-Methoxy-9-anthrylmethyllithium (**1**, Scheme 3), a green-black soluble material, is formed but reacts with chlorotrimethylsilane to give, after chromatography, (methoxymethylene)trimethylsilylanthracene **15** (>40%),[4] 9-anthraldehyde (**16**, 27%), and 9-neopentylanthracene (**17**, 16%). Silane **15** results from silylation of the ambident lithium reagent **1** at C-10 (Scheme 3). Anthraldehyde **16** arises from hydrolysis, desilylation, and air oxidation of **15** during workup and chromatography. Formation of **17** in competition with **15** can be rationalized by electron transfer from *t*-BuLi to **14** and the radical-anion process in Scheme 4. Less likely, coupling product **17** might result from combination of the *tert*-butyl radical and the 9-anthrylmethyl radical (**19**).

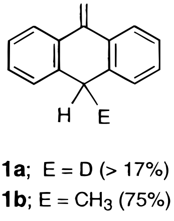
Scheme 3



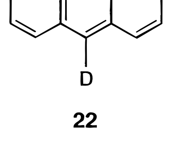
Scheme 4



The behavior of **1** was then investigated with various electrophiles. Reaction of D_2O with the mixture resulting from **14**/*t*-BuLi/TMEDA/Et_2O/pentane at −78 °C yields 10-deuterio-9,10-dihydro-9-(methoxymethylene)anthracene (**21a**, >17%), 9-anthraldehyde (**22**, 39%) containing 64% D at C-10, and **17**. Dimethyl sulfate and **14** as above give 10-methyl derivative **21b** (75%) along with **17** (20%). Benzoyl chloride, acetaldehyde, benzaldehyde, and acetone as described in detail in the Supporting Information react with **14** at −78 °C to yield **21c**–**f** (39–55%), respectively, along with **17** (23–36%). Thus, kinetically controlled reactions of **1** with electrophiles yield 9,10-dihydro-9-methoxymethylene-10-substituted-anthracenes (**15**, **21a**–**f**) regardless of the reactant.[4]



21a; E = D (> 17%)
21b; E = CH_3 (75%)
21c; E = COC_6H_5 (45%)
21d; E = $CHOHCH_3$ (53%)
21e; E = $CHOHC_6H_5$ (39%)
21f; E = $COH(CH_3)_2$ (55%)



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The fact that **1** does not react with electrophiles (E) to give anthracenes **23** implies that the transition states for attack at the methoxycarbanionic center at C-9 in **1** are sterically hindered by interactions of the electrophilic (E) and the methoxy (OCH_3) groups with the *peri*-hydrogens

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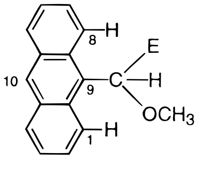
[4] (a) The behavior of **1** with electrophiles to give **15** and **21a**–**f** is similar to that reported for protonation and alkylation of (9-anthryl)-arylmethyl anions[4b] and suggested for reactions of 9-anthrylmethyl anions.[4c] (b) Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1983**, *105*, 4676. (c) Becker, H.-D.; Andersson, K.; Sandros, K. *J. Org. Chem.* **1980**, *45*, 4549 and references therein. For similar reactions of 9-(diphenyl)anthrylmethyl anions[4d] and 2-(3-methyl)naphthylmethyl anions,[4e] see (d) Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1*, **1979**, 2948, and (e) Mitchell, R. H.; Dingle, T. W.; Williams, R. V. *J. Org. Chem.* **1983**, *48*, 903.

at C-1 and C-8 and that the electron density at C-10 is substantial.[5] Indeed, X-ray and ^{1}H NMR studies of various 10-alkyl-9,10-dihydro-9-methyleneanthracenes (**24**; Y = H, E = alkyl) reveal that the central rings of the arene derivatives are in boat or butterfly conformations in which the C-10 alkyl groups prefer pseudoaxial positions to avoid confrontations with the *peri*-hydrogens.[6] Conversions of **1** to **15** and **21a**−**f** are thus facilitated as in **24** (Y = OCH_3) by entrance of the electrophiles (E) from pseudoaxial directions. That there are structural effects as presumed in **24** (Y = OCH_3) is revealed by the ^{1}H NMR spectrum of **15** in which there is downfield absorption (7.8−8.0 ppm) of its H-1 proton; thus, there is considerable deshielding by the oxygen atom in the nearby methoxy group.



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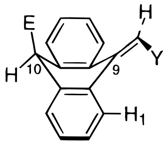

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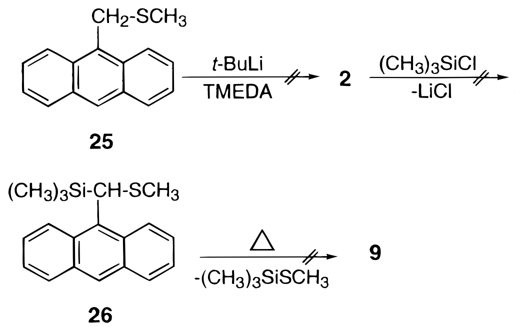
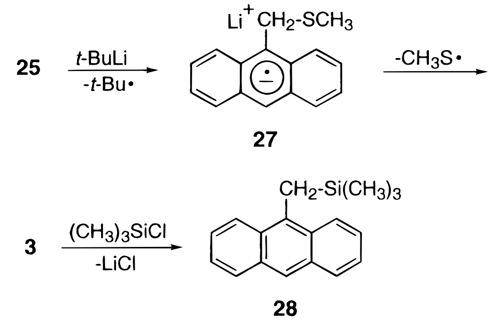
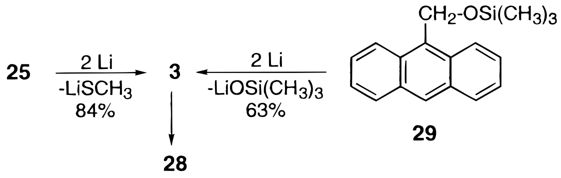
Scheme 5



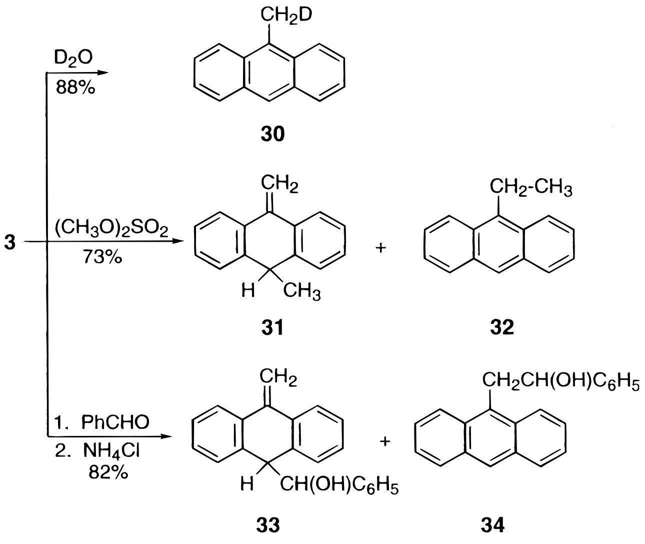
Scheme 6



Scheme 7



Scheme 8



Synthesis of 9-[thiomethoxy(trimethylsilyl)methyl]-anthracene (**26**) for possible conversion to anthrylcarbene **9** as in Scheme 5 was then investigated. The reactions of 9-(thiomethoxymethyl)anthracene (**25**) with *t*-BuLi (1.1 equiv)/TMEDA/Et$_2$O/pentane and then addition of chlorotrimethylsilane (1.1 equiv) at −78 °C are different however than those proposed in Scheme 5[7,8] in that 9-(trimethylsilylmethyl)anthracene (**28**, 91%) is produced, apparently from **3** as formed by the radical-anion mechanism in Scheme 6 and/or by a mechanism analogous to that in Scheme 4. That **28** is formed by a radical-anion displacement mechanism is supported by present findings (Scheme 7) that **25** and 9-(trimethylsilyloxymethyl)-anthracene (**29**) are converted by lithium (2 equiv)[9] to **3**, which undergoes displacement of chlorotrimethylsilane to give **28** in 84% and 63% yields, respectively.

Reactions of 9-anthrylmethyllithium (**3**), as prepared from **25** and *t*-BuLi, were then examined with other electrophiles. Treatment of **3** with D$_2$O yields 9-methylanthracene (**30**, Scheme 8, 88%), in which the methyl group is $\sim$90% monodeuterated; by ^{1}H NMR there is no deuterium at C-10. Dimethyl sulfate reacts with **3** (Scheme 8) however at its C-10 and its 9-anthrylmethyl positions, respectively, to give 9,10-dihydro-10-methyl-9-methyleneanthracene (**31**) and 9-ethylanthracene (**32**) in a 1:1 ratio. Further, reaction of benzaldehyde with **3** at −78 °C and then addition of aqueous NH$_4$Cl at $\sim$25 °C (Scheme 8) give 9,10-dihydro-10-methylene-α-phenyl-9-anthracenemethanol (**33**) and 2-(9-anthryl)-1-phenylethanol (**34**) in a 1:3 ratio in 82% overall yield. The sensitivities of 9-anthrylmethyllithium reagents to steric and electronic effects are thus impressively demonstrated in reactions of electrophiles with **1** to give C-10 derivatives **15** and **21a**−**f**, whereas depending on the electrophile, **3** reacts at its 9-anthrylmethyl and/or its C-10 positions (Scheme 8).

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(5) (a) Simple Huckël calculations indicate that the C-10 ring position in the α-methoxy-9-anthrylmethyl carbanion in **1** is the site of highest electron density (1.317 vs 1.149 at the exo-cis position).[5b] (b) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1984**, *24*, 4645.

(6) (a) Carruthers, W.; Hall, G. E. *J. Chem. Soc. B.* **1966**, 861. (b) Brinkman, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Stothers, J. B.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5912. (c) Zieger, H.; Gelbaum, L. T. *J. Org. Chem.* **1972**, *37*, 1012. (d) Harvey, R. G.; Cho, H. *J. Am. Chem. Soc.* **1974**, *96*, 2434. (e) Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140. (f) Fu, P. P.; Harvey, R. G.; Paschal, J. W.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1145. (g) Leung, P.-T.; Curtin, D. Y. *J. Am. Chem. Soc.* **1975**, *97*, 6790.

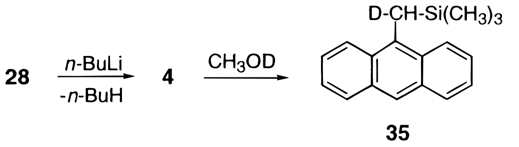
(7) Deprotonations of **25** with lithium diisopropylamide, lithium 2,2,6,6-tetramethylpiperidide, MeLi, or *n*-BuLi in TMEDA, Et$_2$O, or THF at various temperatures followed by reactions with chlorotrimethylsilane to give **26** were unsuccessful.

(8) Reaction of *n*-BuLi (1.2 equiv) at 0 °C with **25** (1 equiv) in Et$_2$O containing TMEDA (1.2 equiv) and addition of chlorotrimethylsilane (1.6 equiv) yield 9-*n*-pentylanthracene. No **26** is obtained.

(9) Biron, C.; Dunoques, J.; Calas, R.; Tskhovrebachvili, T. *Synthesis* **1981**, 220.

The behavior of (trimethylsilylmethyl)anthracene **28** with strong bases followed by electrophiles was then studied in efforts to prepare potential precursors to carbene **9**. α-Trimethylsilyl-9-(anthrylmethyl)lithium (**4**, Scheme 9) is produced upon addition of *n*-BuLi/pentane to Et_2O/TMEDA or THF/TMEDA solutions of **28** at 0 °C. Upon quenching **4** with CH_3OD, α-deuteriosilane **35** (~100%) is obtained, which is 70% monodeuterated at its anthrylmethyl position on the basis of ^1H NMR and MS analyses. Since no deuterium is at C-10 in the product, initial formation of 10-deuterio-9,10-dihydro-9-(trimethylsilylmethylene)anthracene followed by protiotropic rearrangement does not occur.[10]

Scheme 9



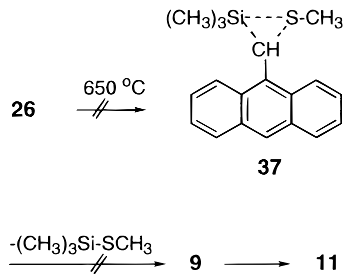
Silyl(anthrylmethyl)lithium **4** is of further interest because of its contrasting behavior with other electrophiles.[10a] As has been noted, **26** is not obtained as in Scheme 5. Reaction of **4** with dimethyl disulfide (**36**, eq 1) however does give 9-(thiomethoxymethyl)anthracene

$$4 + \underset{\mathbf{36}}{CH_3SSCH_3} \longrightarrow 26 + LISCH_3 \qquad (1)$$

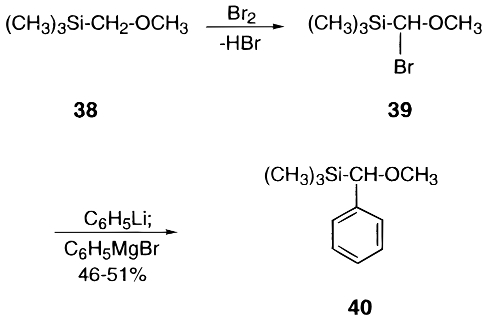
26 (97%) and lithium thiomethoxide. The silyl sulfide obtained is of proper mass and is assigned as **26** from its ^1H and ^{13}C NMR spectra and UV absorptions (see Experimental Section). A noteworthy feature in the ^{13}C NMR spectrum of **26** is the appearance of 14 aromatic signals due to restricted rotation of the anthryl−CH-$(SCH_3)Si(CH_3)_3$ single bond. Such restricted rotation has been observed in substituted 9-anthrylcarbinols.[11] The mechanism by which **36** converts **4** to **26** (eq 1) has not been established.[12a,b]

The thermal behavior of **26** was then investigated in efforts to generate **9** for production of cyclobutanthracene **11**. Piptopyrolyses of **26** at 650 °C/0.05−0.10 mm at various contact times result primarily however in formation of intractable products. There is no evidence for production of **11** in these experiments. Apparently the silicon−sulfur bonding in transition state **37** (Scheme 10) is insufficient for (thiomethoxy)trimethylsilane [$(CH_3)_3$-$Si-SCH_3$] to be effectively eliminated from **26** by thermolysis.

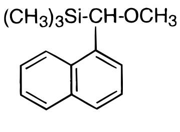
Scheme 10



Scheme 11



Because the above studies did not result in synthesis of **7**, investigation was then initiated toward methods for introduction of a methoxy(trimethylsilyl)methyl group [$CH_3O-CH-Si(CH_3)_3$] directly into the C-9 position in anthracene. Bromination of (methoxymethyl)trimethylsilane **38** in CCl_4 is known to give [bromo(methoxy)-methyl]trimethylsilane (**39**, Scheme 11) in 55% yield.[13,14] Phenyllithium and phenylmagnesium bromide are now found to react with **39** in THF to form [methoxy-(trimethylsilyl)methyl]benzene **40**[15] in 46% and 51% yields, respectively. Further, 1-naphthylmagnesium bromide and 5-acenaphthylmagnesium bromide are converted simply by **39** to 1-[methoxy(trimethylsilyl)methyl]-naphthalene (**41**, 61%)[16] and 5-[methoxy(trimethylsilyl)-methyl]acenaphthene (**42**, 71%), respectively. Of particu-



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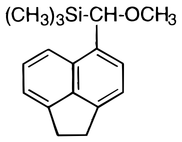

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[10] (a) Treatment of **4** with Cp_2ZrCl_2 also gives the product of reaction at C-9.[10b] (b) Leppert, M. F.; Raston, C. L.; Engelhardt, L. M.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 521. (c) Reaction of **4**, however, with chlorotrimethylsilane results in trimethylsilylation at C-10 to give 9,10-dihydro-10-[(trimethylsilylmethylene)-9-anthryl]-trimethylsilane in 55% yield.[5b]

[11] (a) de Riggi, I.; Virgili, A.; de Moragas, M.; Jaime, C. *J. Org. Chem.* **1995**, *60*, 27. (b) Jaime, C.; Virgili, A.; Claramunt, R. M.; López, C.; Elguero, J. *J. Org. Chem.* **1991**, *56*, 6521. (c) The ^{13}C NMR spectrum of **7** shows again a fourteen line pattern for the anthryl group.

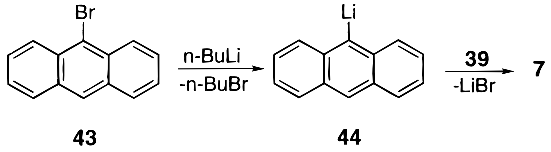
[12] (a) Among the attractive reaction mechanisms are (1) displacement of dimethyl disulfide by **4**, (2) electron transfer of **4** to dimethyl sulfide and then coupling of α-trimethylsilyl-9-anthrylmethyl and methanethio radicals, and (3) displacement of dimethyl disulfide at C-10 of **4** to give trimethyl[(10-methylthio)-9(10*H*)-anthrylidene]-methylsilane which is then conjugatively displaced at C-9 by methanethiolate ion. Displacements as in mechanism 3 have been observed previously for other 10-substituted-9-benzylidene-9,10-dihydroanthracenes.[10b,12b] (b) Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2637 and references therein.

[13] (a) Christiansen, M. L.; Benneche, T.; Undheim, K. *Acta Chem. Scand.* **1987**, *B41*, 536. (b) Similarly, chlorination of **38** gives chloro-(methoxy)trimethylsilylmethane.[13d] (c) Shimizo, S.; Ogata, M. *Tetrahedron* **1989**, *45*, 637. (d) Both halosilanes, **38** and chloro(methoxy)-trimethylsilylmethane, undergo nucleophilic displacements of halogen with enolates and with 1,2,4-triazole.[13a,c]

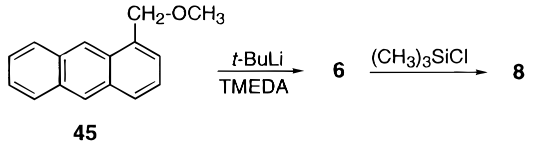
[14] We thank John E. Strode for bringing attention to ref 13a,c and for suggesting study of reactions of various aryl organometallic reagents with **39**.

[15] (a) Silyl derivative **40** was first prepared by (1) deprotonation of benzyloxytrimethylsilane [$(CH_3)_3SiOCH_2Ph$] with *t*-BuLi and (2) Wittig rearrangement of α-(trimethylsiloxy)benzyllithium [$(CH_3)_3$-SiOCH(Ph)Li] to lithium α-(phenyl)trimethylsilylmethoxide [$(CH_3)_3$-SiCH(Ph)OLi], followed by methylation with dimethyl sulfate.[15b] (b) Wright, A.; West, R. *J. Am. Chem. Soc.* **1974**, *96*, 3214. (c) Silane **40** has also been obtained[15d] by reaction of benzaldehyde with tris-(trimethylsilyl)aluminum and methylation with dimethyl phosphite [$HOP(OCH_3)_2$]. (d) Tsuge, O.; Kanemasa, S.; Nagahama, H.; Tanaka, J. *Chem. Lett.* **1984**, 1803.

Scheme 12



Scheme 13



lar importance is that **7** (59%)[11c] is now obtained satisfactorily from 9-bromoanthracene (**43**) and *n*-BuLi (1 equiv) and subsequent reaction of 9-anthryllithium (**44**) with **39** (Scheme 12). The new methodology for preparing methoxy(trimethylsilyl)methyl derivatives is simple and convenient.

In contrast to **7**, 1-[methoxy(trimethylsilyl)methyl]-anthracene (**8**) has been found to be preparable by traditional methodology.[16b] 1-(Methoxymethyl)anthracene (**45**, Scheme 13) is converted simply by *t*-BuLi/TMEDA/Et_2O/pentane to 1-lithio derivative **6** at approximately −110 °C; addition of chlorotrimethylsilane and warming to ∼ 25 °C then give **8** in 68% yield. The radical-anion reactions that plagued lithiation of **14** are avoided with **45** at approximately −110 °C. At temperatures of −78 °C however **45** is converted by *t*-BuLi/TMEDA/Et_2O/pentane and then chlorotrimethylsilane to **8** in only 23−33% yields.

2. Flash-Vacuum Pyrolyses of 7 and 8 to Cyclobutanthracene 11 and Products Thereof. Carbenic decompositions of methoxy(trimethylsilylmethyl)anthracenes **7** and **8** have now been studied in detail. Flash-vacuum pyrolysis of **7** at 550 °C/10^{-3} mm in quartz-packed equipment and column chromatography of the pyrolysate are now found (eq 2) to yield **11** (43%, Table 1)[17] along with 2*H*-cyclopenta[*jk*]fluorene (**46**, 35%).[18] The effects of reaction temperature and contact time on the yields of **11** and **46** are summarized in Table 1. As the temperature and contact time for decomposition of **7** increase, the ratios of **46** to **11** increase. Reducing the amount of the quartz chips in the pyrolysis tube by 66% has little effect on the ratio of **46** to **11** obtained.

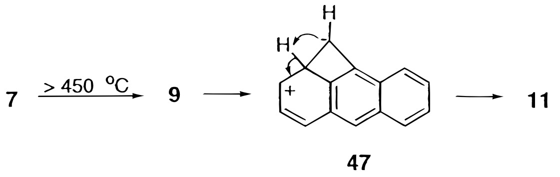
46 (2)

Table 1. Yields of 11 and 46 from 7 at Various Temperatures

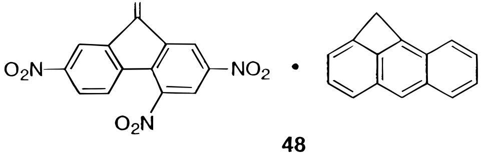
temp, °C	**11**, %	**46**, %	temp, °C	**11**, %	**46**, %
450	8		550^a	32	17
500	19	5	660	20	51
550	43	35	750		70

^{a} The contact time was ∼5% that of the other pyrolyses.

Scheme 14



Cyclobutanthracene **11** may be presumed to be formed from **7** (Scheme 14) upon generation of **9** and then *peri*-cyclization as in **47**.[19] It will be seen shortly however that the processes leading to the final insertion act to give **11** are far more complicated than summarized in Scheme 14. Also, upon isolation, **11** decomposes when warmed and turns brown-red rapidly when exposed to air. The structure of **11** is assigned from its exact mass and its ^1H and ^{13}C NMR spectra and by elemental analysis of its stable 1:1 solid complex (**48**) with 2,4,7-trinitrofluorenone. The chemistry of **11** will be described later.



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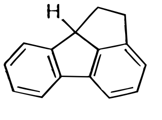
Cyclopentafluorene **46** is assigned (1) upon reduction with lithium aluminum hydride to 2,9*b*-dihydro-1*H*-cyclopenta[*jk*]fluorene (**49**) and agreement of its MS and ^1H NMR spectra with literature values[18] and (2) by direct comparison of its melting point, mixed melting point, and spectral properties (GC−IR−MS) with an authentic sample prepared by pyrolysis of spiro[indazol-3,1′-indene] (**50**) as synthesized by addition of 1-diazoindene to benzyne.[18] Probable mechanisms for formation of **46** will be discussed later.



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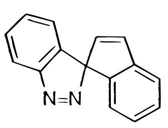

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Because **46** is formed along with **11** in decomposition of **7**, pyrolysis of tetrazole **12** was reinvestigated. As in the previous report[2] thermolysis of **12** gives **11** in low yield, nitrile **13** (85%, Scheme 2), and hydrogen azide. At 660 °C/10^{-3} mm however in the present experiments, decomposition of **12** also yields **46** (eq 3). Cyclobutanthracene **11** presumably forms from **9** as shown in Scheme 1 and detailed in **47**. Production of **46** during decomposition of **12** is similar to that from **7**.

$$\mathbf{12} \xrightarrow[-2N_2]{660\,^{\circ}C} \mathbf{11} + \mathbf{46} \qquad (3)$$

---

(16) (a) Obtained previously by reaction of chlorotrimethylsilane with α-methoxy-1-naphthylmethyllithium, as generated from 1-(methoxymethyl)naphthalene and *t*-BuLi in Et_2O containing TMEDA.[16b] (b) Engler, T. A.; Shechter, H. See the preceding paper in this issue.

(17) References 1 and 2 report previous preparations of **11**.

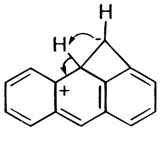
(18) Cyclopentafluorenes **46** and **49** have been prepared previously by Luger, P.; Tuchscherer, C.; Grosse, M.; Rewicki, D. *Chem. Ber.* **1976**, *109*, 2596.

(19) Such *peri*-cyclobutacyclizations have been reported by (a) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (b) Becker, J.; Wentrup, C. *J. Chem. Soc., Chem. Commun.* **1980**, 190. (c) References 1, 2, and 16b. (d) Bailey, R. J.; Card, P. J.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6096. (e) Jaworek, W.; Vögtle, F. *Chem. Ber.* **1991**, *124*, 347.

The thermal behavior of [methoxy(trimethylsilyl)-methyl]anthracene **8** has been compared to that of **7**. Flash-vacuum decomposition of **8** (eq 4) in a quartz-packed tube at 550 °C/10^{-3} mm results in elimination of methoxytrimethylsilane and formation of **11** (41%) and **46** (22%).

$$\mathbf{8} \xrightarrow[10^{-3}\ \mathrm{mm}]{550\text{-}660\,^{\circ}\mathrm{C}} \mathbf{11} + \mathbf{46} \qquad (4)$$

At 660 °C/10^{-3} mm, the yield of **46** is increased to 57% and that of **11** is reduced to 15%. The conversion of **8** to **11** presumably involves generation of anthrylcarbene **10** (Scheme 1) and then *peri*-cyclization as in **51**.[19] The present overall results of pyrolysis of **7** (eq 2), **12** (eq 3), and **8** (eq 4) are similar in that both **11** and **46** are found. Among the questions of interest then is if **46** is formed from **11**, directly from **9** and/or **10**, or otherwise.



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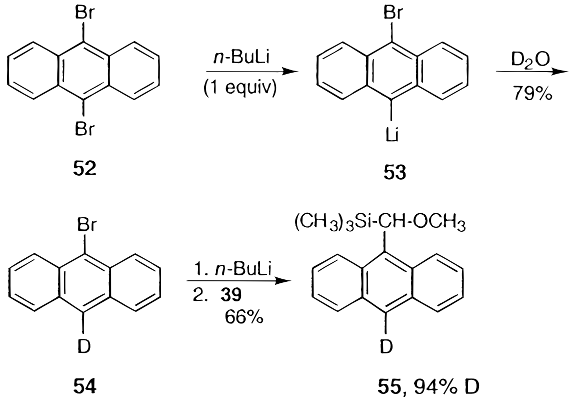
Pure cyclobutanthracene **11** was then pyrolyzed under conditions similar to those used previously for flash-vacuum decompositions of **7**, **8**, and **12**. At temperatures ranging from 525 to 725 °C, **46** (eq 5) is formed. At 550 °C/10^{-3} mm, **11** is 50% converted to **46**. Clearly **46** is produced by thermal isomerization of **11** (eq 5).

$$\mathbf{11} \xrightarrow[10^{-3}\ \mathrm{mm}]{525\text{-}575\,^{\circ}\mathrm{C}} \mathbf{46} \qquad (5)$$

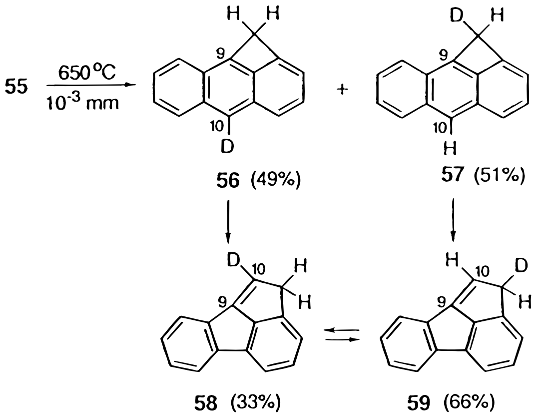
Because of the interesting rearrangement of **11** to **46**, investigation of the reaction mechanism was initiated by study of thermolysis of 9-deuterio-10-[methoxy(trimethylsilyl)methyl]anthracene (**55**, 94% monodeuterated at C-10) prepared from 9,10-dibromoanthracene (**52**)[20] as summarized in Scheme 15.

Pyrolysis of **55** at 650 °C/10^{-3} mm and separation of the products by MPLC yield first a fraction consisting of 10(**56**)- and 1(**57**)-deutero-1*H*-cyclobutanthracenes (Scheme 16) and a second composed of 1(**58**)- and 2(**59**)-deuteriocyclopenta[*jk*]fluorenes (Scheme 16). ^{1}H NMR spectral analysis reveals that the cyclobutanthracene product contains 0.38 deuterium at its *peri*-position (**56**) and 0.40 deuterium at its C-10 position. No deuterium is apparent at any other positions of the ring system. These results correspond to **56** and **57** being collected in essentially equal amounts with loss of 0.16 deuterium to the pyrolysis apparatus. The cyclopentafluorene product is **58** and **59** in a ratio of 1:2 with overall loss of 0.05 deuterium. Decomposition of **55** at 600 °C/$^{10-3}$ mm gives **56** and **57** in a 2:1 ratio (with loss of 0.07 deuterium), thus demonstrating that there is less carbene travel around the anthryl ring system when the pyrolysis temperature is lowered (see subsequent discussion). Isomers **58** and **59** are again produced in a ratio of 1:2. Production of **56**–**59** in the above experiments leads to questions of reaction mechanism that are now of concern.

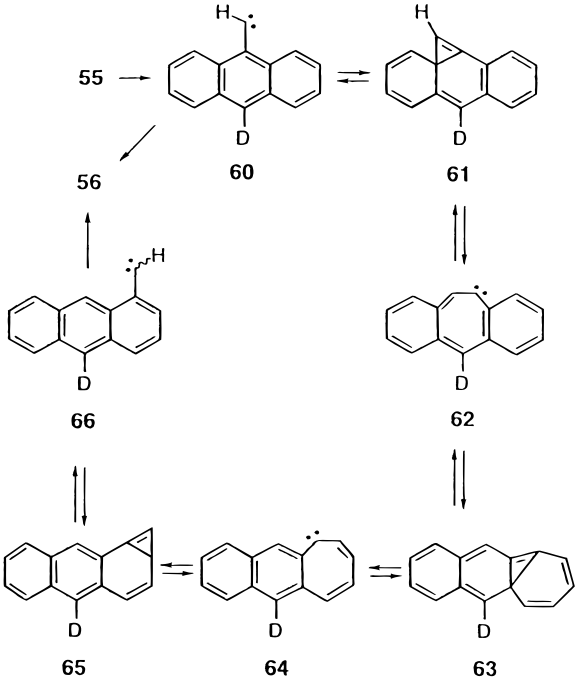
Scheme 15



Scheme 16



Scheme 17



In the decompositions of **55**, deuteriocyclobutanthracene **56** is apparently formed by (1) *peri*-insertion of 10-deuterio-9-anthrylcarbene (**60**, Scheme 17)[19] and/or by (2) multistep isomerization of **60** to 10-deuterio-1-anthrylcarbene (**66**)[21,22] followed by *peri*-insertion (Scheme 17).[19] Deuteriocyclobutanthracene **57** is also a significant product (Scheme 16) and presumably results (in part) from extended rearrangement of **60** to **67**,[21,22] which then

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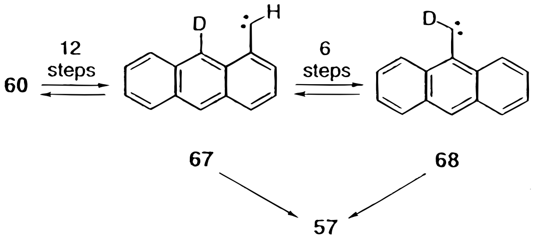
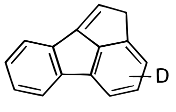
[20] (a) Heilbron, I. M.; Heaton, J. S. *Org. Synth. Coll. Vol 1*, **1941**, 207. (b) Bachmann, W. E.; Kloetzel, M. C. *J. Org. Chem.* **1938**, *3*, 55.

Scheme 18



inserts at C-9 (Scheme 18). A further possibility is multistep rearrangement of **67** to **68**[21,22] and then *peri*-insertion to yield **57** (Scheme 18). Whatever be the details of the mechanisms for conversion of **60** to **57**, it is impressive that the many step processes resulting in formation of **57** (Scheme 18) compete so well with direct *peri* C_1−H insertion of **60** to give **56** (Scheme 17).

Of interest also are the paths by which **56** and **57** are converted to **58** and **59**. It is significant that in rearrangements of **56** there are no products produced by dyotropic mechanisms[23] involving migration of deuterium from C-10 or any subsequent aromatic center to give cyclopentafluorenes (**69** or **70**) with deuterium at any of their benzenoid positions. Thus a dyotropic process as in Scheme 19 is not operative. There are many other thermal dyotropic mechanisms starting from **56** that have been considered which involve migration of deuterium from an aromatic ring to give deuteriocyclopentafluorenes, but none account for the conversions of **56** and **57** to **58** and **59**. Mechanisms of a completely different type must occur to produce **58** and **59** from **56** and **57**.



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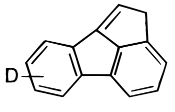

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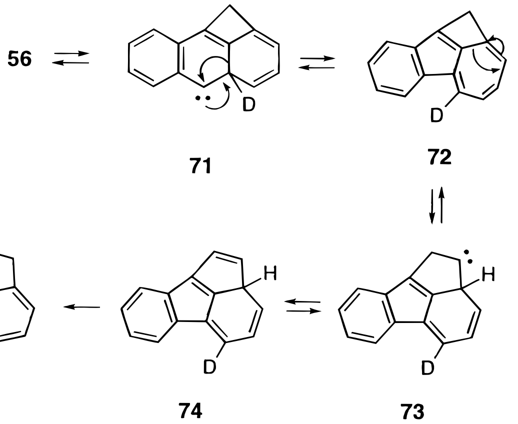
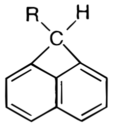
Important then is that decompositions of **56** and **57** yield **58** and **59** in a 1:2 ratio. This ratio is exactly that expected for equilibration of **58** and **59** by 1,5-sigmatropic rearrangements.[24] That **69** and **70** are not formed suggests that **56** isomerizes (Scheme 16) by movement of C_{10}−D to give **58**, which then undergoes deuterium−hydrogen rearrangment to yield **59**. A similar overall process (Scheme 16) involving movement of C_{10}−H in **57** to form **59** and then **58** by hydrogen−deuterium sigmatropic rearrangement would then be expected.

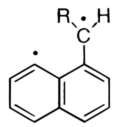
Scheme 19



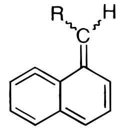
As has been noted, **11** begins to decompose on warming to 70−80 °C.[1] At higher temperatures, the simpler *peri*-bridged arene, 1*H*-cyclobuta[*de*]naphthalene (**76a**), ring-opens in hydrogen-donor environments to give 1-methylnaphthalene (**79**) presumably by reduction of **77a** or/and **78a**. Further, 1-methyl-1*H*-cyclobuta[*de*]naphthalene (**76b**) thermolyzes to 1-vinylnaphthalene (**80**) by hydrogen transfer from the methyl group in **77b** or/and **78b**.[25] As will be illustrated, analogues of **77a,b** and **78a,b** along with other intermediates may be involved in the deep-seated rearrangements (Scheme 16) of **56** and **57**.



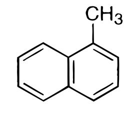
76a, R = H
76b, R = CH_3



77a, R = H
77b, R = CH_3



78a, R = H
78b, R = CH_3



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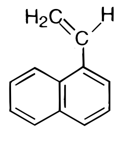

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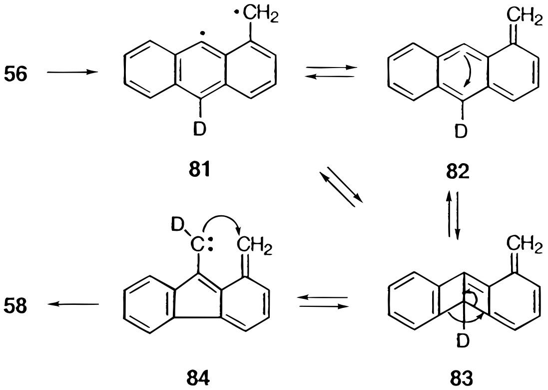
Scheme 20 illustrates a mechanism by which isomerization of **56** to **58** occurs initially by cleavage of the

Scheme 20



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(21) 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**, *25*, 6974. (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 summaries and detailed discussion of arylcarbene rearrangements, see Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479, refs 2 and 22, and references therein.

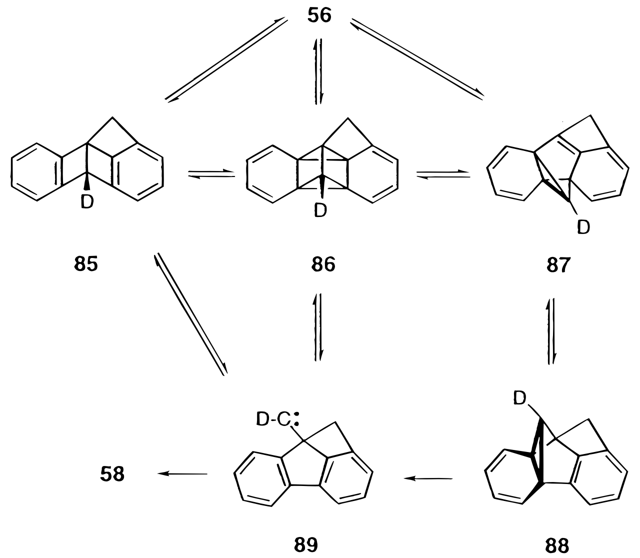
(22) For recent summaries and discussion of the mechanistic aspects of isomerization of arylcarbenes, see (a) Xie, Y.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 1370. (b) Matzinger, S.: Bally, T., Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1996. (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 references therein. (e) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855.

(23) (a) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52. (b) Scott, L. T.; Roelofs, N. H.; Tsang, T. H. *J. Am. Chem. Soc.* **1987**, *109*, 5456. (c) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692.

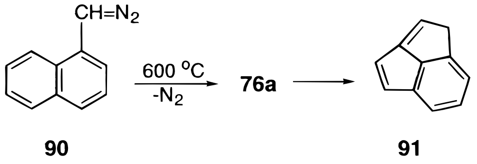
(24) For discussion of 1,5-sigmatropic rearrangements, see Woodward, R. B.; Hoffmann, R. *The Conservation of Symmetry*; Academic Press: New York, 1970; p 114.

(25) Card, P. J.; Friedli, F. E.; Shechter, H. *J. Am. Chem. Soc.* **1983**, *105*, 6104.

Scheme 21

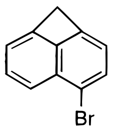


Scheme 22



cyclobuta bridge to give diradical **81**, followed by the indicated rearrangements. It is emphasized that rearrangement of **56** to **58** formalized as stepwise in Scheme 20 may be modified as in Scheme 21 to involve Dewar anthracene **85**, dibenzoprismane **86**, and anthravalene **87** routes[26] in which initial cleavage of the methanoanthracene bridge does not occur. In all of the proposals for isomerization of **56** in Schemes 20 and 21, C-10 transfers with its deuterium across the face of the ring system to become C-10 of **58** (as labeled in Scheme 16). The mechanisms of Schemes 20 and 21 also all account for isomerization of **57** to **58**. Of additional interest is that vacuum pyrolysis of (1-naphthyl)diazomethane (**90**, Scheme 22) to give cyclopenta[*cd*]indene (**91**)[2a] can be explained by formation of **76a**, which then isomerizes by sequences similar to those in Schemes 20 and 21.

3. Addition and Substitution Reactions of 11. Study has been initiated of chemical reactions of cyclobutane **11**. It has been previously established that **76a** undergoes electrophilic substitution at C-4 at 0 °C upon reaction with bromine as catalyzed by ferric bromide to give 4-bromo-1*H*-cyclobuta[*de*]naphthalene (**92**, 94%).[27] Irradiation (100-W light bulb) of **76a** and bromine in CCl_4 results however in addition to give 1aα,2β,3β,4α-tetrabromo-1a,2,3,4-tetrahydronaphthalene (**93**) as a single product.[27] Bromine has now been found to be much more reactive with **11** than with **76a**. Addition of bromine to **11** (Scheme 23) in CCl_4 at 20−25 °C occurs rapidly (<5 min) to yield 9,10-dibromo-9,10-dihydro-1*H*-cyclobuta[*de*]anthracene (**94**, 62%) of unknown stereochemistry. Elimination of hydrogen bromide from **94** occurs readily upon recrystallization from warm benzene to give 10-bromo-1*H*-cyclobuta[*de*]anthracene (**95**), a thermally sensitive product.



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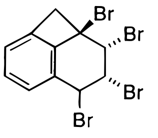

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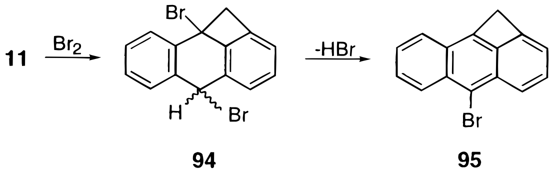
Scheme 23



Investigation is now to be made of the synthesis and thermal, photochemical, catalyzed, and cycloadditive behaviors of varied 10-substituted-1*H*-cyclobuta[*de*]anthracenes. Of particular importance will be determination of the details of the mechanism(s) of isomerization of **11** to **46**.

Experimental Section

General Methods. Methods by which melting points, spectra, and analyses were obtained are described in ref 16b. Unless otherwise specified, ^1H NMR spectra were recorded at 90 MHz. In most of the present experiments, reactions were conducted under argon and with solvents that were dried with either Na, LAH, CaH_2, or P_2O_5.

[9,10-Dihydro-10-(methoxymethylene)-9-trimethylsilyl]-anthracene (15). *t*-BuLi (2.2 M) in pentane (2.6 mL, 5.7 mmol) was added dropwise to a stirred yellow suspension of 9-(methoxymethyl)anthracene (**14**, 1.1 g, 5.0 mmol) in Et_2O (120 mL) containing TMEDA (0.80 mL, 5.3 mmol) at −78 °C. After stirring 30 min at −78 °C, the dark green-black solution of **1** was treated with chlorotrimethylsilane (0.69 mL, 5.7 mmol) and allowed to warm to room temperature. The solution became colorless and contained a white precipitate after 3 h. The mixture was washed with H_2O and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Flash chromatography of the yellow residue on silica gel using hexane as eluent gave (1) 9-neopentylanthracene (**17**, 0.20 g, 16%), mp 108−110 °C, lit.[28] mp 104−105 °C; ^1H NMR ($CDCl_3$) 0.96 (s, 9H), 3.64 (s, 2H); exact mass calcd 248.1565, obsd 248.1569 and (2) **15** (>0.59 g, >40%), mp 110−112 °C (hexane); IR (KBr, cm^{-1}) 1635 ($C{=}CHOCH_3$); ^1H NMR ($CDCl_3$, CH_2Cl_2 as internal standard) −0.55 (s, 9H), 3.55 (s, 1H), 3.83 (s, 3H), 6.55 (s, 1H), 7.0−7.5 (m, 7H), 7.8−8.0 (m, 1H); ^{13}C NMR ($CDCl_3$, 20 MHz) −2.3, 43.2, 60.7, 116.3, 122.8, 124.5, 125.2, 125.5, 126.0, 126.6, 126.9, 128.2, 131.5, 133.8, 137.4, 138.0, 144.9; UV (λ, ϵ, hexane) 311 (4 800), 272 (12 600), 242 (shoulder, 12 250), 223 (29 000), 208 nm (39 800); exact mass calcd 294.1440, obsd 294.1447. Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.49; H, 7.53. Found: C, 77.47; H, 7.18.

Hydrolysis and Oxidation of 15 to 9-Anthraldehyde (16). A hexane solution (4 mL) of **15** was stirred open to the air for 20 h over silica gel. After filtration, the silica gel was washed with benzene and Et_2O, and the filtrate was concentrated to a yellow solid. ^1H NMR analysis of the solid containing CH_2Cl_2 as an internal standard showed the mixture to be initial **15** (43%) and **16** (47% yield based on **15** that reacted).

9,10-Dihydro-9-(methoxymethylene)-10 *D*-anthracene (21a) and 10 *D*-9-Anthraldehyde (22). D_2O (2 mL) was added at −78 °C to **1** (1.4 mmol, prepared as for synthesis of **15**). Workup and column chromatography with 20% benzene/

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(26) For important examples, discussion, and references concerning such structures, see (a) Meador, M. A.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2336. (b) Gleiter, R.; Treptow, B.; Irngartinger, H.: Oeser, T. *J. Org. Chem.* **1994**, *59*, 2787 and (c) references therein.

(27) (a) Friedli, F. E.; Shechter, H. *Tetrahedron Lett.* **1985**, *26*, 1157. (b) Friedli, F. E.; Shechter, H. *J. Org. Chem.* **1985**, *50*, 5710.

(28) Bullpitt, M.; Kitching, W. *Synthesis* **1977**, 316.

hexane as eluent yielded (1) **17** (0.059 g, 18%), a white solid, mp 108−110 °C, identical with an authentic sample; (2) **21a** (0.05 g, 17%), a yellow oil; ^{1}H NMR ($CDCl_3$) 3.52 (s, 1H), 3.83 (s, 3H), 6.70 (s, 1H), 7.0−7.4 (m, 7H), 7.8−8.0 (m, 1H); mass spectrum *m*/*e* 223 (M^+); 95% D incorporation by ^{1}H HMR (satisfactory analysis for **21a** could not be obtained because of its instability); and (3) **22** (0.109 g, 39%), a yellow solid containing 64% deuterium at C-10 as shown by ^{1}H NMR and MS.

9,10-Dihydro-9-(methoxymethylene)-10-methylanthracene (21b). A solution of **1** prepared by addition of *t*-BuLi (2.0 M) in pentane (1.3 mL, 2.5 mmol) to a yellow suspension of **14** (0.50 g, 2.3 mmol) in Et_2O (60 mL) and TMEDA (0.4 mL, 3.7 mmol) was treated at −78 °C with dimethyl sulfate (0.35 mL, 3.7 mmol) under argon. The stirred mixture was warmed to room temperature, refluxed for 24 h, and worked up as for **15**. Flash chromatography of the products using 5% EtOAc/hexane as eluent gave (1) **17** (0.11 g, 20%), white crystals, as identified earlier and (2) **21b** (0.40 g, 75%), light yellow crystals, mp 123−126 °C; IR (KBr, cm^{-1}) 1640 ($C{=}CHOCH_3$), 1230 (C−O); ^{1}H NMR ($CDCl_3$, 200 MHz) 1.36 (d, *J* = 6.8 Hz, 3H), 3.86 (s, 3H), 4.02 (q, *J* = 6.8 Hz, 1H), 6.76 (s, 1H), 7.2−7.7 (m, 6H), 7.7−7.9 (m, 1H), 7.95−7.99 (m, 1H); ^{13}C NMR ($CDCl_3$, 20 MHz) 26.0, 42.0, 60.9, 113.8, 122.8, 125.7, 126.1, 126.2, 126.6, 126.7, 127.0, 128.1, 132.2, 134.7, 140.4, 141.1, 145.9; exact mass calcd 236.1201, obsd 236.1195. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.46; H, 6.59.

9-(Thiomethoxymethyl)anthracene (25). Sodium hydride (50% suspension in mineral oil, 1.9 g, 39 mmol) was washed twice with hexane under argon and suspended in dry THF (25 mL). Methanethiol (3.0 g, 60 mmol) was then added by distillation, and the resulting gray-white suspension was stirred for 15 min. A THF solution of 9-(chloromethyl)-anthracene (7.5 g, 33 mmol) was added dropwise (45 min). The mixture was stirred for 3 h, washed with H_2O and saturated $NaHCO_3$, and dried ($MgSO_4$). Removal of solvent left a yellow solid, which was recrystallized from methanol to give **25** (6.1 g, 77%): yellow needles, mp 112−114 °C, lit.[29] mp 110−112 °C.

Attempted Deprotonation and Silylation or Deuteration of 25. Reactions of LDA or LTMP (1 equiv) at −78 to 25 °C with **25** (1 equiv) in Et_2O containing TMEDA (1 equiv) and then addition of chlorotrimethylsilane (1 equiv) or CH_3OD did not yield **26** or α-deuterio-9-(thiomethoxymethyl)anthracene. Complex products were obtained.

9-(Trimethylsilylmethyl)anthracene (28). Method A: Reaction of 25 with *t*-BuLi and then Chlorotrimethylsilane. *t*-BuLi (2.0 M) in pentane (14 mL, 28 mmol) was added to **25** (6.1 g, 25 mmol) in Et_2O (150 mL) at −78 °C under argon. The dark blue-green solution that formed was then stirred for 40 min at −78 °C. Chlorotrimethylsilane (3.6 mL, 29 mmol) was added, and the mixture was stirred for 1 h at −78 °C. The clear yellow solution that resulted was washed with H_2O and saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. Chromatography of the solid on silica gel with hexane as eluent and recrystallization of the light yellow product (6.0 g, 91%) from hexane yielded colorless crystals of **28**: mp 66−68 °C, lit.[30] mp 59−60 °C; ^{1}H NMR ($CDCl_3$, CH_2Cl_2 as internal standard) 0.02 (s, 9H), 3.18 (s, 2H), 7.4−7.6 (m, 4H), 7.9−8.3 (m, 5H); ^{13}C NMR ($CDCl_3$, 20 MHz) −0.4, 18.9, 123.7, 124.5, 124.7, 125.5, 129.1 (2C), 131.8, 134.2; UV (λ, ϵ, hexane) 397 (8 500), 392 (shoulder, 5 300), 376 (9 000), 356 (5 300), 340 (2 600), 326 (shoulder, 1 200), 260 (177 000), 251 (81 000), 217 (14 400); exact mass calcd 264.1334, obsd 264.1344. Anal. Calcd for $C_{18}H_{20}Si$: C, 81.75; H, 7.62. Found: C, 82.02; H, 7.57.

Method B. Reaction of 25 with Lithium and Chlorotrimethylsilane. Lithium metal (12 mg, 1.7 mmol) was added to **25** (139 mg, 0.58 mmol) and chlorotrimethylsilane (0.30 mL, 2.38 mmol) in THF (4 mL). After the mixture had been stirred for 20 h, all of the lithium had dissolved. The solution was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel with hexane as eluent yielded **28** (89 mg, 58%). Elution with 10% ethyl acetate/hexane gave initial **25** (44 mg, 32%). The yield of **28** based on recovered **25** is 84%.

Method C. Synthesis and Reductive Silylation of 9-(Trimethylsiloxymethyl)anthracene (29). Chlorotrimethylsilane (1.0 mL, 7.9 mmol) was added to a solution of 9-anthracenemethanol (1.1 g, 5.0 mmol) in triethylamine (1.2 mL, 8.3 mmol) and Et_2O. The mixture was refluxed for 8 h, cooled to room temperature, filtered through Celite, and concentrated. Chromatography of the resulting solid on a short column of silica gel with benzene as the eluent yielded **29** (1.3 g, 94%): a yellow solid, mp 74−75 °C; ^{1}H NMR ($CDCl_3$) 0.16 (s, 9H), 5.58 (s, 2H), 7.3−7.6 (m, 4H), 7.9−8.1 (m, 2H), 8.3−8.5 (m, 3H); exact mass calcd 280.1283, obsd 280.1291.

Chlorotrimethylsilane (1.5 mL, 12 mmol) and lithium (0.10 g, 14 mmol) were then added to **29** (1.2 g, 4.2 mmol) in anhydrous THF (50 mL). The initial dark-green solution became brown-orange upon stirring overnight and was then poured into Et_2O, filtered, washed with H_2O, dried ($MgSO_4$), and concentrated. The yellow oil was chromatographed on silica gel (hexane as the eluent) to give **28** (0.88 g, 63%): a yellow solid, mp 64−67 °C, identical with the product prepared by Method A.

9-Deuteriomethylanthracene (30). D_2O (0.4 mL) was added to a dark, emerald-green solution of **3** prepared at −78 °C under argon by addition of 1.8 M *t*-BuLi in pentane (0.28 mL, 0.50 mmol) to **25** (92 mg, 0.39 mmol) in Et_2O (20 mL) containing TMEDA (0.11 mL, 0.73 mmol). The mixture was allowed to warm to room temperature, diluted with Et_2O, washed with saturated aqueous NH_4Cl and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel with hexane as eluent gave **30** (66 mg, 88%): mp 75−77 °C (hexane), with properties and mp (79−81 °C) essentially identical to that of an authentic sample. ^{1}H NMR (270 MHz) indicated 90% monodeuteration of the C-9 methyl group.

9,10-Dihydro-10-methyl-9-methylenanthracene (31) and 9-Ethylanthracene (32). A solution of **25** (101 mg, 0.42 mmol) in Et_2O (30 mL) and TMEDA (0.15 mL, 1.0 mmol) at −78 °C was treated with 1.9 M *t*-BuLi in pentane (0.32 mL, 0.61 mmol) at −78 °C. After 15 min, dimethyl sulfate (0.12 mL, 1.26 mmol) was added. The mixture, after warming to room temperature, was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Chromatography of the residue with hexane as eluent gave a 1:1 mixture (63 mg, 73%) of **31**,[31] ^{1}H NMR (270 MHz, $CDCl_3$) 1.37 (d, *J* = 7 Hz, 3H), 4.07 (q, *J* = 7 Hz, 1H), 5.68 (s, 2H), 7.2−7.4 (m, 6H), 7.7 (m, 2H) and **32**, ^{1}H NMR ($CDCl_3$) 1.45 (t, *J* = 7.5 Hz, 3H), 3.64 (q, *J* = 7.5 Hz, 2H), 7.4−7.6 (m, 4H), 7.95−8.05 (m, 2H), and 8.2−8.4 (m, 3H).

9,10-Dihydro-10-methylene-α-phenyl-9-anthracenemethanol (33) and 2-(9-Anthryl)-1-phenylethanol (34). A 2.0 M solution of *t*-BuLi in pentane (0.30 mL, 0.60 mmol) was added to **25** (107 mg, 0.45 mmol) and TMEDA (0.11 mL, 0.73 mmol) in Et_2O (20 mL) at −78 °C. After 15 min, benzaldehyde (0.095 mL, 0.93 mmol) was added to the dark emerald-green solution. Within 1−2 min, the mixture became colorless and was then allowed to warm to room temperature. The solution was washed with saturated aqueous NH_4Cl and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. Chromatography of the residue on silica gel with hexane gave **17** (11 mg, 10%). Further elution with 20% ethyl acetate/hexane yielded a 1:3 mixture (by ^{1}H NMR) of **33** and **34** (110 mg, 82%).

A sample of **33** from the mixture was collected by preparative HPLC (μ porasil; 7.5% EtOAc/hexanes): ^{1}H NMR ($CDCl_3$, 270 MHz) 2.05 (d, *J* = 3 Hz, 1H), 4.18 (d, *J* = 7 Hz, 1H), 4.63 (dd, *J* = 3 and 7 Hz, 1H), 5.57 (s, 1H), 5.59 (s, 1H), 6.7−6.9

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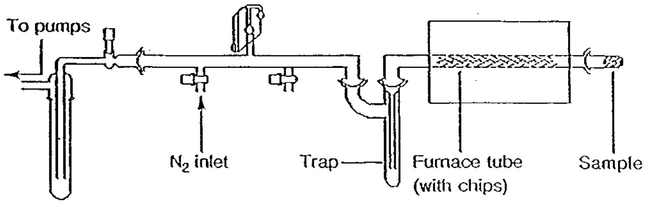

Figure 1. Flash-vacuum pyrolysis apparatus.

(dd, 3H), 7.0–7.4 (m, 8H), 7.6–7.7 (m, 2H). Fractional crystallization of the reaction product from ethyl acetate/hexane gave **34** as yellow crystals: mp 114–115.5 °C; IR ($CHCl_3$, cm^{-1}) 3590, 1210; ^{1}H NMR ($CDCl_3$, 270 MHz) 1.8 (d, 1H), 4.05 (d of AB pattern, $J = 15$, 9, and 4 Hz, 1H), 5.21 (ddd, $J = 9$ and 4 Hz, 1H), 7.3–7.6 (m, 9H), 8.05 (d, 2H), 8.35 (d, 2H), 8.4 (s, 1H); ^{13}C NMR ($CDCl_3$, 70 MHz) 37.9, 75.6, 124.6, 124.9, 125.6, 125.8, 126.7, 127.6, 128.5, 129.2, 130.3, 130.6, 131.6, 144.3; exact mass calcd 298.1358, obsd 298.1365.

α-D-9-(Trimethylsilylmethyl)anthracene (35). *n*-BuLi (1.6 M) in hexane (0.65 mL, 1.0 mmol) was added to **28** (0.23 g, 0.87 mmol) and TMEDA (0.30 mL, 2.0 mmol) in THF (60 mL) at 0 °C under argon. After the dark emerald-green solution had been stirred for 30 min at 0 °C, CH_3OD was added, and the colorless reaction mixture was washed with H_2O and saturated aqueous $NaHCO_3$ and dried ($MgSO_4$). Removal of solvent gave **35** in 100% yield containing 70% deuterium at its benzylic position as shown by ^{1}H NMR and MS analyses.

9-[Thiomethoxy(trimethylsilyl)methyl]anthracene (26). TMEDA (0.32 mL, 2.1 mmol) and then **28** (0.5 g, 1.9 mmol) were dissolved in THF (50 mL) under argon. Addition of *n*-BuLi (1.6 M) in hexane (1.3 mL, 2.1 mmol) gave a dark green solution. After 30 min, dimethyl disulfide (0.21 mL, 2.3 mmol) was added. The clear yellow mixture was stirred for 1 h, poured into Et_2O, washed with H_2O and saturated $NaHCO_3$, and dried ($MgSO_4$). Removal of solvent left a yellow oil, which on chromatography on silica gel using hexane as eluent yielded (1) initial **28** (0.20 g, 40%), identical with an authentic sample, and (2) **26** (0.34 g, 58%), mp 100–102 °C (hexane): ^{1}H NMR ($CDCl_3$, CH_2Cl_2 as internal standard) 0.10 (s, 9H), 1.84 (s, 3H), 4.80 (s, 1H), 7.3–8.9 (m, 9H); ^{13}C NMR ($CDCl_3$, 20 MHz) −0.4, 17.3, 33.6, 123.5, 123.8, 124.5, 125.1, 125.8, 126.3, 127.4, 129.1, 129.7, 129.8, 131.0, 131.5, 132.1, 134.1; UV (λ, ϵ, hexane) 396 (10 200), 390 (sh, 6 200), 375 (10 200), 356 (6 200), 340 (2 700), 325 (1 200), 259 (140 000), 252 (sh, 69 500), 276 (13 300); exact mass calcd 310.1211, obsd 310.1220. Anal. Calcd for $C_{19}H_{22}SSi$: C, 73.49; H, 7.14; S, 10.32. Found: C, 73.58; H, 7.06; S, 10.04. The yield of **26** based on the **28** that reacted was 97%.

Pyrolysis of 15. Volatilization of **15** (0.37 g, 1.26 mmol) at 0.05–0.10 mm through a quartz tube (Figure 1) heated to 600–650 °C gave a black pyrolysate that was collected at −78 °C. Preparative TLC of the condensate on silica gel with 10:1 hexane/benzene yielded **14**, **16**, anthracene, and **38**. The products were identified by ^{1}H NMR and comparison with authentic samples. Pyrolysis of **15** as above does not yield **11**.

Pyrolysis of 26. Silane **26** (0.52 g, 1.67 mmol) was dropped at 0.05–0.10 mm as a neat solid into a vertical quartz tube packed with quartz chips and heated to 650 °C. Chromatography of the pyrolysate on silica gel (hexane as eluent) afforded a complex mixture of products as revealed by TLC and ^{1}H NMR. No evidence was found for **11** in the reaction products.

[Methoxy(trimethylsilyl)methyl]benzene (40). Method D. Reaction of Phenylmagnesium Bromide and [Bromo(methoxy)methyl]trimethylsilane (39). A suspension of magnesium (0.13 g, 5.35 mmol) in bromobenzene (0.53 mL, 5.08 mmol)/THF (20 mL) was refluxed for 1 h. After the mixture had cooled, **39**[13,14] (1.0 g, 5.08 mmol) was added. The resulting solution was stirred for 1 h and diluted with Et_2O. The mixture was washed with H_2O and brine, dried ($MgSO_4$), and concentrated. Column chromatography of the concentrate on silica gel with petroleum ether as the eluent yielded **40** (0.56 g, 57%): ^{1}H NMR ($CDCl_3$) −0.01 (s, 9H), 3.31 (s, 3H), 3.95 (s, 1H), 7.1–7.4 (m, 5H). The properties of **40** correspond to those previously reported.[15]

Method E. Reaction of Phenyllithium and 39. Phenyllithium (1.6 M in pentane, 3.1 mL, 4.96 mmol) was syringed slowly into a solution of **39** (1.0 g, 5.08 mmol) in dry THF (10 mL). A slightly exothermic reaction ensued, and the cloudy yellow mixture was stirred for 10 min. After addition of Et_2O, the mixture was washed with H_2O and brine, dried ($MgSO_4$), concentrated, and chromatographed as in Method D to give **40** (0.44 g, 46%).[15] The spectra of the product match those for **40** prepared by Method D.

1-[Methoxy(trimethylsilyl)methyl]naphthalene (41). 1-Bromonaphthalene (0.65 mL, 4.68 mmol) was added to magnesium (0.12 g, 5.0 mmol) in THF (20 mL). The mixture was refluxed for 15 min and then cooled, and **39** (0.98 g, 4.98 mmol) was added. The solution was stirred for 1 h, Et_2O was added, and the mixture was washed with H_2O and brine, dried ($MgSO_4$), and concentrated. Column chromatography of the residue on silica with petroleum ether as eluent yielded **41** (0.70 g, 61%): ^{1}H NMR ($CDCl_3$) 0.04 (s, 9H), 3.37 (s, 3H), 4.86 (s, 1H), 7.3–8.1 (m, 7H). The properties of **41** match those previously reported.[1,16b]

5-[Methoxy(trimethylsilyl)methyl]acenaphthene (42). A mixture of magnesium (0.46 g, 20 mmol), 5-bromoacenaphthene (3.1 g, 13.3 mmol), and Et_2O (25 mL) was refluxed for 20 min. During this period, 1,2-dibromoethane (0.5 mL, 5.8 mmol) in Et_2O (10 mL) was added dropwise. The mixture was refluxed for 10 min and cooled, and then **39** (2.88 g, 14.62 mmol) was added. The resulting mixture was stirred for 3 h, during which a solid precipitated. Following addition of Et_2O, the solution was worked up as for **41**. Column chromatography on silica with petroleum ether and petroleum ether/toluene as eluents gave 5-bromoacenaphthene (1.44 g) and then **42** (1.36 g, 38% conversion, 71% yield): light yellow solid, mp 99–101 °C; ^{1}H NMR ($CDCl_3$) 0.03 (s, 9H), 3.32 (s, 3H), 3.41 (br s, 4H), 4.71 (s, 1H), 7.2–7.5 (m, 4H), 7.75 (d, 1H); ^{13}C NMR ($CDCl_3$) −3.2, 29.9, 30.6, 59.2, 77.6, 118.9, 119.1, 119.9, 125.0, 127.0, 129.8, 132.9, 139.5, 143.8, 146.4; exact mass calcd 270.1440, obsd 270.1435. Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.52; H, 8.21. Found: C, 75.29; H, 8.17.

9-[Methoxy(trimethylsilyl)methyl]anthracene (7). *n*-BuLi (8.6 mL, 1.4 M in pentane, 12 mmol) was slowly added to a solution of 9-bromoanthracene (2.57 g, 10 mmol) in Et_2O (100 mL) at 0 °C. A yellow precipitate formed. After the mixture stirred at room temperature for 30 min, **39** (2.6 g, 13 mmol) was added in one portion. The solution was then stirred for 3 h, washed with H_2O and brine, dried ($MgSO_4$), and absorbed on silica gel. Column chromatography on silica gel using petroleum ether/toluene (4:1) as eluent yielded crude **7**. Recrystallization from hexane gave pure **7** (1.74 g, 59%): white crystals, mp 92–94 °C; ^{1}H NMR ($CDCl_3$) 0.04 (s, 9H), 3.28 (s, 3H), 5.71 (s, 1H), 7.4–7.55 (m, 4H), 7.95–8.1 (m, 2H), 8.2–8.3 (m, 1H), 8.36 (s, 1H), 9.0–9.1 (m, 1H); ^{13}C NMR ($CDCl_3$) −1.7, 59.3, 77.2, 123.6, 124.4, 124.5, 125.1, 125.3, 126.6, 127.7, 128.8, 129.6, 129.9, 130.0, 131.4, 131.8, 132.7; exact mass calcd 294.1440, obsd 294.1443. Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.60; H, 7.50.

1-[Methoxy(trimethylsilyl)methyl]anthracene (8). *t*-BuLi (1.75 M) in pentane (9.0 mL, 16 mmol) was added slowly to **45** (3.4 g, 15 mmol) and TMEDA (2.4 mL, 16 mmol) in Et_2O (200 mL) at −110 °C. Some of the **45** crystallized on the walls of the reactor vessel but redissolved upon addition of the *t*-BuLi solution. The resulting purple-blue mixture was stirred for 15 min at −110 to −105 °C, and then chlorotrimethylsilane (2.1 mL, 17 mmol) was added. After warming to room temperature, the cloudy yellow solution was washed with H_2O and saturated aqueous $NaHCO_3$ and then dried ($MgSO_4$). Concentration of the solution left a yellow syrup, which on chromatography on silica gel with 20% benzene/hexane as eluent afforded **8** (3.0 g, 68%): a yellow syrup which slowly solidified, mp 59–61 °C (methanol); ^{1}H NMR ($CDCl_3$, CH_2Cl_2 as internal standard) 0.04 (s, 9H), 3.40 (s, 3H), 4.95 (s, 1H), 7.4–7.6 (m, 4H), 7.9–8.2 (m, 3H), 8.5 (s, 1H), 8.7 (s, 1H); exact mass calcd 294.1440; obsd 294.1447. An analytical sample was prepared by distillation at 105−107 °C/0.07 mm. Anal. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53. Found: C, 77.49; H, 7.50.

Methodology for Flash-Vacuum Pyrolyses of 7, 8, 11, 12, and 55. The material to be thermolyzed is placed in the sample tube of the pyrolysis apparatus (Figure 1). The entire system is placed under vacuum using initially a mechanical pump and then a mercury diffusion pump to lower the pressure. System pressure is measured by a McLeod vacuum gauge downline from the furnace tube. The vacuum is not monitored during pyrolysis.

An electric furnace (40 cm) is used to heat the quartz furnace tube (45 cm × 2.4 cm i.d.) filled with quartz chips (35 cm length). The temperature of the furnace is measured with a digital thermometer, external to the quartz tube, in the center of the furnace. Once the furnace tube has reached the proper temperature and pressure, a heater is placed around the sample tube. The heater is then warmed (75−110 °C), and the sample slowly sublimes and/or distills into the furnace tube. After pyrolysis is complete, the furnace and trap area are isolated from the vacuum pumps. The vacuum is broken with nitrogen, and the trap is removed. The pyrolysate is dissolved in degassed benzene and purified.

Pyrolysis of 7; Preparation of 11 and 46. Decomposition of **7** (0.2 g, 0.68 mmol) was effected at 550 °C/10^{-3} mm as previously described. The pyrolysate was dissolved in degassed benzene (5 mL), and silica gel was added. After concentration, the sample was separated by MPLC using degassed hexanes as eluents. Two fractions were collected: (1) **11** (0.056 g, 43%), white crystals; mp 62−69 °C (dec), lit.[1,2] mp 60−70 °C; ^{1}H NMR ($CDCl_3$) 5.05 (s, 2H), 7.10 (d, $J = 5$ Hz, 1H), 7.4−7.6 (m, 3H), 7.73 (d, 1H), 7.96 (dm, 1H), 8.12 (dm, 1H), 8.18 (s, 1H); ^{13}C NMR ($CDCl_3$) 46.3, 114.8, 120.9, 121.1, 123.8, 124.4, 125.3, 126.9, 128.2, 131.1, 131.4, 136.7, 137.3, 141.5, 144.6; UV (λ, ϵ, hexane) 384 (5 200), 378 (3 700), 364 (5 300), 360 (5 000), 348 (4 500), 343 (shoulder, 3 900), 333 (3 000), 256 (204 000), 250 (shoulder, 126 000), 222 (15 400); exact mass calcd 190.0782, obsd 190.0790 and (2) a yellow solid, which upon trituration with methanol yielded white **46** (0.045 g, 35%); mp 72−74 °C, lit.[18] mp 74−75 °C; ^{1}H NMR ($CDCl_3$) 4.08 (d, $J = 1.8$ Hz, 2H), 6.78 (t, $J = 1.8$ Hz, 1H), 7.3−7.55 (m, 4H), 7.59 (dd, $J = 1.6$ and 6.2 Hz, 1H), 7.83 (m,1H), 7.87 (m, 1H); ^{13}C NMR ($CDCl_3$) 46.0, 118.2, 122.1, 122.4, 124.7, 126.2, 126.5, 127.2, 128.2, 130.2, 134.8, 135.2, 142.6, 147.2, 154.9.

1*H*-Cyclobuta[de]anthracene: 2,4,7-Trinitrofluoren-9-one Complex (48). Freshly chromatographed (silica gel/hexane) **11** (0.12 g, 0.60 mmol) in hot ethanol (5 mL) was added to a boiling ethanol (20 mL)/benzene (1 mL) solution of 2,4,7-trinitrofluoren-9-one (0.2 g, 0.60 mmol). A dark brown precipitate formed, which after cooling of the reaction mixture to room temperature, filtration, and recrystallization from benzene/ethanol, yielded **48** as dark red needles (0.13 g, 41%), mp 202−204 °C; Anal. Calcd for $C_{28}H_{15}N_3O_7$: C, 66.53; H, 2.99; N, 8.32. Found: C, 66.72; H, 3.06; N, 8.60.

Reduction of 46 to 2,9*b*-Dihydrocyclopentafluorene (49). A mixture of **46** (0.083 g, 0.44 mmol), lithium aluminum hydride (0.020 g, 0.53 mmol), and Et_2O (15 mL) was refluxed for 15 min and then cooled to 0 °C. After dropwise addition of EtOAc (1 mL), the solution was washed with 10% aqueous HCl and brine, dried ($MgSO_4$), and concentrated. Column chromatography on silica gel with petroleum ether as eluent yielded **49** (~0.002 g, ~2%): ^{1}H NMR ($CDCl_3$) 1.80 (ddd, $J = 7.0$, 11.0, and 11.3 Hz, 1H), 2.79 (m, 1H), 2.96 (dd, $J = 7.1$ and 15.0 Hz, 1H), 3.57 (m, 1H), 4.24 (dd, $J = 6.8$ and 11.3 Hz, 1H), 7.0−7.55 (m, 6H), 7.7 (m, 1H); $M^+ = 192$ amu.

Pyrolysis of Spiro[indazol-3,1-indene] (50) to 46. Indene **50**[18] was sublimed into the furnace tube (Figure 1) at 265 °C/0.3 mm. Pyrolysis was incomplete after 2 h. The ^{1}H and ^{13}C NMR spectra of the product (**46**, no purification) exactly match those of **46** previously prepared from **11**.

Pyrolysis of 5-(9-Anthryl)tetrazole (12). Flash-vacuum pyrolysis of **12**[2] (0.050 g, 0.2 mmol) at 660 °C/10^{-3} mm yielded 3 products. By far, the major product was **13** (~90%). The 2 other products (~10%) were **11** and **46** in a 1:10 ratio as identified by their GC retention times and their MS ($M^+ = 190$ amu).

Thermal Isomerization of 11 to 46. Upon sublimation from a sample tube at 50 °C, pure **11** (0.030 g, 0.16 mmol) was pyrolyzed at 650 °C/10^{-3} mm. The condensate was passed through silica with hexanes as eluent. The major fraction collected (0.024 g, 80%) was shown by ^{1}H NMR to be a 1:1 mixture of **11** and **46**.

9-Bromo-10-deuterioanthracene (54). *n*-BuLi (1.4 M in pentane, 20 mL, 28 mmol) was added to 9,10-dibromoanthracene (10 g, 29.76 mmol) suspended in Et_2O (100 mL) at 0 °C. The mixture was stirred at room temperature for 30 min, and an orange solid precipitated. Upon addition of D_2O (2 mL, 100 mmol), the reaction mixture boiled gently. The solids were filtered, and the filtrate was dried ($MgSO_4$) and concentrated. The crude product was suspended in petroleum ether and filtered through a plug of silica. Fractional crystallization of the crude solid from ethanol yielded **54** (6.68 g, 79%); mp 96−99 °C, lit.[20b] mp 100−101 °C. Gas chromatography showed that **54** was 91% pure.

9-Deuterio-10-[methoxy(trimethylsilyl)methyl]anthracene (55). *n*-BuLi (20 mL, 1.4 M in pentane, 28.0 mmol) was added to **54** (6.68 g, 91%) in Et_2O (200 mL) at 0 °C. The resulting solution was stirred at ~25 °C for 30 min, and **39** (5.52 g, 28.0 mmol) was added. Reaction proceeded rapidly, and the dark gold solution was stirred for several minutes, washed with H_2O and brine, and dried ($MgSO_4$). Silica gel was added for sample adsorption. Column chromatography on silica gel was accomplished using petroleum ether, 10:1 petroleum ether/toluene, and 4:1 petroleum ether/toluene. Product isolation followed by recrystallization from hexanes yielded **55** (4.56 g, 66%): mp 92−94 °C; ^{1}H NMR ($CDCl_3$) 0.07 (s, 9H), 3.30 (s, 3H), 5.71 (s, 1H), 7.51 (m, 4H), 8.04 (m, 2H), 8.28 (m, 1H), 8.38 (s, 0.06H), 9.05 (m, 1H). ^{1}H NMR reveals that **55** is 94% deuterated at C-9.

Pyrolysis of 55 to 56, 57 and 58, 59. Pyrolysis of **55** (200 mg, 0.68 mmol) was effected at 650 °C/10^{-3} mm as for **7**. The pyrolysate was purified by MPLC using degassed hexanes as eluent. The following fractions were collected: (1) **56** and **57** (0.03 g, 23%); mp 60 °C (dec); ^{1}H NMR ($CDCl_3$) 5.05 (s with shoulder, 1.60H), 7.08 (d, 1H), 7.3−7.6 (m, 3H), 7.72 (d, 1H), 7.95 (dm, 1H), 8.11 (dm, 1H), 8.17 (s, 0.38H) and (2) **58** and **59** (0.085 g, 66%); mp 65−69 °C; ^{1}H NMR ($CDCl_3$) 4.08 (s with shoulder, 1.44H), 6.79 (d with shoulders, 0.67H), 7.3−7.5 (m, 4H), 7.60 (dd, $J = 1.6$ and 6.2 Hz, 1H), 7.83 (m, 1H), 7.87 (m, 1H).

Pyrolysis of 8 to 11 and 46. Pyrolysis of **8** (50 mg, 0.17 mmol) was effected at 560 °C/10^{-3} mm as previously described for **7**. The pyrolysate was purified by MPLC using degassed hexanes as eluent. The major reaction product, collected as a single fraction and analyzed by ^{1}H NMR, was a mixture of **11** (13 mg, 41%) and **46** (7 mg, 22%). At 660 °C/10^{-3} mm, decomposition of **8** yielded **11** (15%) and **46** (57%). Yields of **11** ranging from 49% to 52% were obtained upon distilling **8** (up to 1 g) into a vertical quartz-packed pyrolysis unit at 560−570 °C/0.02−0.07 mm.

9,10-Dibromo-9,10-dihydro-1*H*-cyclobuta[*de*]anthracene (94). Bromine (0.096 g, 0.6 mmol) in CCl_4 (2 mL) was added dropwise to **11** (0.076 g, 0.4 mmol) in CCl_4 (5 mL). The solution was stirred for 5 min and concentrated to a yellow solid. Trituration of the solid with benzene afforded **94** (0.087 g, 62% stereochemistry unknown): white solid, mp 150 °C (dec); ^{1}H NMR ($CDCl_3$) 4.03 (d, $J = 13.9$ Hz, 1H), 4.50 (d, $J = 13.9$ Hz, 1H), 5.98 (s, 1H), 7.00 (dd, 1H), 7.2−7.4 (m, 5H), 7.63 (m, 1H); ^{13}C NMR ($CDCl_3$) 42.3, 52.1, 55.0, 124.2, 124.3, 124.6, 128.2, 128.4, 128.7, 130.0, 130.1, 132.2, 137.2, 141.2, 142.1; exact mass calcd 347.9149, obsd 347.9129. The instability of **94** precludes its elemental analysis.

10-Bromo-1*H*-cyclobuta[*de*]anthracene (95). A solution of **94** in benzene (3 mL) was refluxed for 20 min. Concentration and purification by MPLC yielded **95** (19%): yellow crystals, mp 94−96 °C; ^{1}H NMR ($CDCl_3$) 5.01 (s, 2H), 7.09 (d, 1H), 7.5−7.6 (m, 3H), 7.74 (d, 1H), 7.92 (m, 1H), 8.60 (m, 1H); ^{13}C NMR ($CDCl_3$) 46.1, 114.9, 115.4, 120.9, 124.3, 125.1, 125.5, 125.6, 126.1, 127.1, 129.2, 132.3, 133.7, 141.0, 143.7; exact mass calcd 267.9888, obsd 267.9850. The product is too unstable for combustion analysis.

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Supporting Information Available: Experimental procedures and references for preparing anthracene-1-carboxylic acid, 1-anthracenemethanol, 9,10-dihydro-10-(methoxymethylene)-9-anthryl phenyl ketone (**21c**), 9,10-dihydro-10-(methoxymethylene)-α-methyl-9-anthracenemethanol (**21d**), 9,10-dihydro-10-(methoxymethylene)α-phenyl-9-anthracenemethanol (**21e**), 9,10-dihydro-10-(methoxymethylene)-α,α-dimethyl-9-anthracenemethanol (**21f**), and 1-(methoxymethyl)anthracene (**45**) and NMR spectra for **7**, **11**, **42**, **46**, **55**−**58**, **94**, and **95**. This material is available free of charge via the Internet at http://pubs.acs.org.

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