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Intramolecular Behaviors of Anthryldicarbenic Systems: Dibenzo[*b,f*]pentalene and 1*H*,5*H*-Dicyclobuta[*de,kl*]anthracene

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9,10-Bis[methoxy(trimethylsilyl)methyl]anthracenes (**24**), synthesized from 9,10-dilithioanthracene (**26**) and bromomethoxytrimethylsilylmethane (**27**, 2 equiv), decompose (550−650 °C/10^{-3} mmHg) carbenically to dibenzo[*b,f*]pentalene (**28**, >48%). 9,10-Anthryldicarbenes **39** or their equivalents convert to pentalene **28** rather than di-*peri*-cyclobutanthracenes **30** and **31**, benzobiphenylene **32**, or extended rearrangement products **33**−**38**. Formation of **28** from **24** raises questions with respect to the behavior of 1,3,4,6-cycloheptatetraenyl-1-carbenes **49**, 2,4,5,7-cyclooctatetraenylidene **51**, 2,5,7-cyclooctatriene-1,4-diylidene **52**, 1,2,4,5,7-cyclooctapentaene **53**, and bicyclo[4.1.0]heptatrienyl-1-carbenes **54** and to carbon-skeleton and hydrogen rearrangements of anthryldicarbenes **39** and/or their equivalents at various temperatures. 1,5-Bis[methoxy(trimethylsilyl)methyl]anthracenes (**25**), prepared from 1,5-diiodoanthracene (**63**) and methoxytrimethylsilylmethylzinc bromide (**57**, 2 equiv) as catalyzed by $PdCl_2(PPh_3)_2$, yield the di-*peri*-carbenic reaction product 1*H*,5*H*-dicyclobuta[*de,kl*]-anthracene (**30**, >40%) on pyrolysis at 550−650 °C/10^{-3} mmHg. Proof of structure and various aspects of the mechanisms of formation of **30** are discussed.

Introduction

The products and mechanisms of thermal and photolytic rearrangements of arylmonocarbenes (ArCH) are subjects of intense interest.[1−3] As important examples of such rearrangements, 2-naphthylcarbenes (**1**) isomerize via 4,5-benzocyclohepta-1,2,4,6-tetraene (**3**) to 1-naphthylcarbenes (**5**) that then convert to cyclobuta[*de*]naphthalene (**6**), 1-vinylideneindene (**12**), and 1*H*-cyclobuta[cd]indene (**13**) as stable products possibly as formalized in Scheme 1.[2,4−6] Although little investigated, arylpolycarbenic systems undergo rearrangements that are dramatic extensions of that of monocarbenic analogues. Thus, thermolyses of bis(methoxysilylmethyl)binaphthyls **14** (Scheme 2)[7] give the di-*peri*-cyclobuta derivative **15**, which is dehydrogenated to di-*peri*-cyclobuta product **16**.[8]

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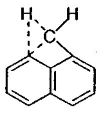
(1) (a) For details, discussions, and further references to studies of the products and mechanisms of rearrangements of phenylcarbene ($C_6H_5−\ddot{C}$-H), a member of the C_7H_6 energy surface, see ref 1b−j. (b) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, M., Jr. *Tetrahedron* **1985**, *41*, 1479. (c) Wentrup, C.; Mayor, C.; Becker, J.; Lindner, H. J. *Tetrahedron* **1985**, *41*, 1601. (d) McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J. P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.* **1987**, *109*, 2456. (e) Miller, P. C.; Gaspar, P. P. *J. Org. Chem.* **1991**, *56*, 5101. (f) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535. (g) Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1996**, *61*, 7022. (h) Schreiner, P. R.; Karney, W. L.; Schleyer, P. v. R.; Borden, W. T.; Hamilton, T. P.; Schaefer, H. F., III. *J. Org. Chem.* **1996**, *61*, 7030. (i) Patterson, E. V.; McMahon, R. J. *J. Org. Chem.* **1997**, *62*, 4398. (j) Investigations of and prior references to the various intramolecular reactions of substituted phenylcarbenes are included in ref 1b−i.

(2) (a) The rearrangements of naphthylcarbenes **1** and **5** as summarized in Scheme 1 are based on studies in refs 1b, 2b−g, and references therein. (b) West, P. R.; Mooring, A. M.; West, P. R.; McMahon, R. J.; Chapman, O. L. *J. Org. Chem.* **1986**, *51*, 1316. (c) Albrecht, S. W.; McMahon, R. J. *J. Am. Chem. Soc.* **1993**, *115*, 855. (d) Xie, Y.; Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1997**, *119*, 1370. (e) Engler, T. A.; Shechter, H. *J. Org. Chem.* **1999**, *64*, 4247. (f) Zheng, F.; McKee, M. L.; Shevlin, P. B. *J. Am. Chem. Soc.* **1999**, *121*, 11237. (g) Bonvallet, P. A.; McMahon, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 9332.

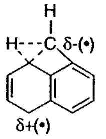
(3) (a) For investigations of the rearrangements of substituted-naphthyl and more complicated arylmonocarbenes see refs 1b,d, 2c,e, and 3b,c and references therein. (b) Bailey, R. J.; Shechter, H. *J. Am. Chem. Soc.* **1974**, *96*, 8116. (c) Kendall, J. K.; Engler, T. A.; Shechter, H. *J. Org. Chem.* **1999**, *64*, 4255.

(4) (a) The C⌇H notation in **1** and in other carbenes in this manuscript indicate that the species illustrated may exist in (*E*)- and (*Z*)- forms in their singlet and triplet states.[4b] (b) Trozzolo, A. M.; Wasserman, E.; Yager, W. A. *J. Am. Chem. Soc.* **1965**, *87*, 129.

(5) The questions as to intramolecular conversion of **5** to **6** by (1) direct *peri*-C−H insertion as in **A**, (2) *peri*-C−H insertion as a singlet or/and a triplet to give **B** with polar or (and) radical delocalization, (3) addition as a singlet or (and) a triplet to C_8 to give **C** or (and) **D**, stabilization therein followed by hydrogen migration, (4) addition to give **E** or (and) **F** and then hydrogen rearrangement, (5) carbenic abstraction to give **G** or (and) **H** and then ring-closure, and (6) spiroconjugative paths as in **10** will be discussed in future publications from this laboratory and by associates. Similar questions may be raised with respect to the conversions of **11** to **13** and of **64** and/or **67** to **30**.



A



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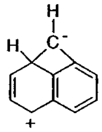
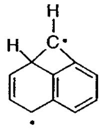
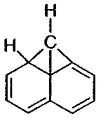


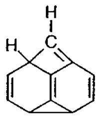
C



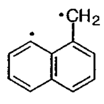
D



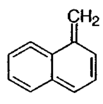
E



F



G

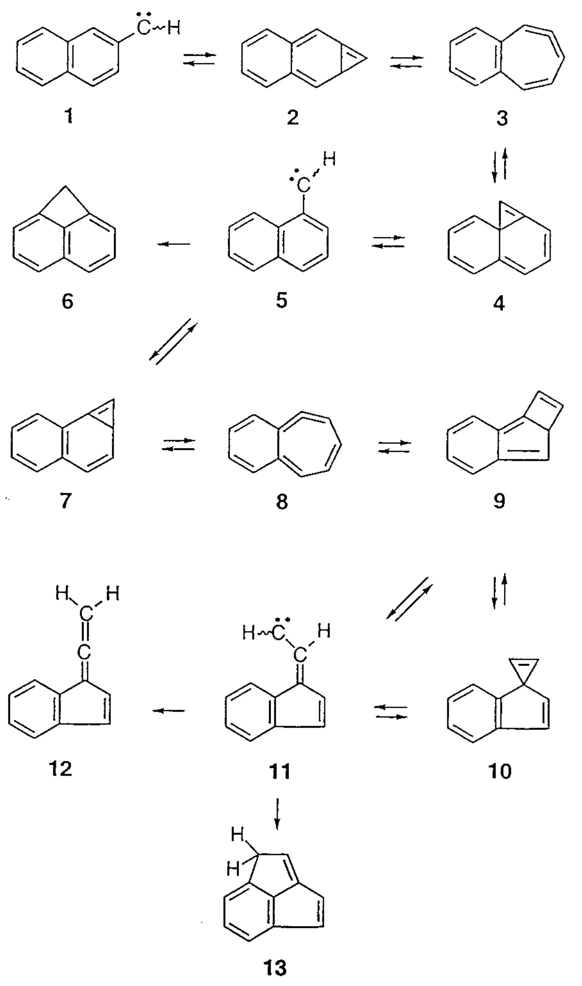


H

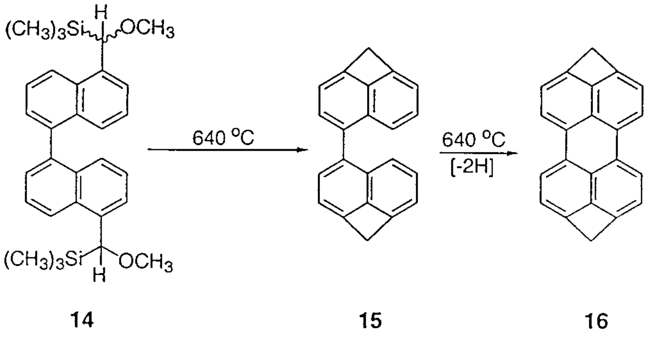
(6) (a) Spiro[2,4]heptatriene intermediates such as **10** (Scheme 1) in rearrangements of arylcarbenes have been considered (Brown, W. T.; Jones, W. M. *J. Org. Chem.* **1979**, *44*, 3092 and ref 1e) and may be highly involved in carbenic conversions of 9-deuterio-10-[methoxy-(trimethylsilyl)methyl]anthracene to 10(49%)- and 1(51%)-deutero-1*H*-cyclobutanthracene at 650 °C/10^{-3} mm.[3c] (b) Syntheses, properties, and the effects of spiroconjugation in spiroheptatrienes have been reviewed in ref 6c−f and references therein. (c) Dürr, H.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 559. (d) Dürr, H.; Albert, K.-H.; Kausch, M. *Tetrahedron* **1979**, *35*, 1285. (e) Maksic, Z.; Kovacevic, K.; Mogus, A. *Theochem* **1982**, *2*, 9. (f) Galasso, V. *THEOCHEM* **1992**, *89*, 181.

10.1021/jo010404p CCC: $20.00

Scheme 1



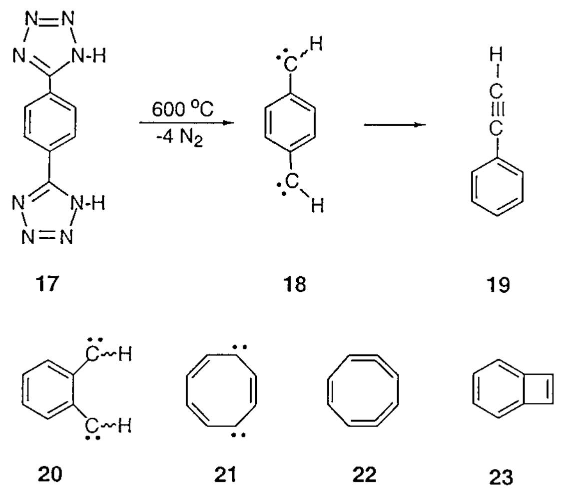
Scheme 2

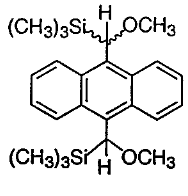


Further, *p*-phenylenedicarbenes **18** (Scheme 3) or their precursors, as generated thermally from bis-tetrazole **17**,[9] convert to phenylacetylene (**19**, 3%) in low yield possibly by degenerate rearrangement of cyclobutabenzene (benzocyclobutadiene, **23**) upon eventual formation and ring closures of *o*-phenylenedicarbenes **20**, cyclooctatrienyl-1,4-dicarbene **21**, and/or cyclooctapentaene **22**.[9,10]

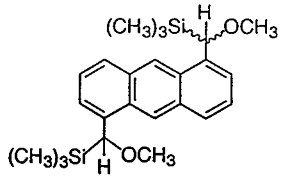
Study is now reported of syntheses and flash-vacuum pyrolyses of bis(methoxysilylmethyl)anthracenes **24**[7] and **25**.[7] The present thermolysis experiments result in formation of impressive products by efficient multiple carbenic processes and raise significant mechanism questions with respect to preferred reaction routes and transannular paths in single and multiple arylcarbene rearrangement systems.

Scheme 3





24



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Results and Discussion

Preparation and Pyrolysis of 9,10-Bis[(methoxymethyl)silanes] 24. 9,10-Bis(silanes) **24** are obtained by displacement reactions of bromo(methoxy)silylmethane

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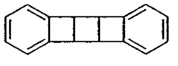
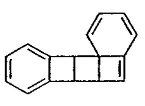
(7) Silanes **14**, **24**, and **25** are presumed to have been prepared as mixtures of stereoisomers.

(8) Jaworek, W.; Vögtle, F. *Chem. Ber.* **1991**, *124*, 347.

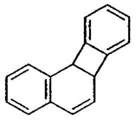
(9) (a) Baum, M. W.; Font, J. L.; Meislich, M. E.; Wentrup, C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2534.[9b] (b) Pyrolysis of bis-tetrazole **17** at 600 °C/0.01 Torr also yields dibenzotricyclooctadiene **I** (<0.5%, stereochemistry unassigned)[9a] apparently as formed by selective dimerization of **23**.[9c] (c) Rieke, R. D.; Hudnall, P. M. *J. Am. Chem. Soc.* **1973**, *95*, 2640. (d) Cyclobutabenzene (benzocyclobutadiene, **23**) has been kept as a monomer at low temperature in an argon-matrix. In solution **23** converts rapidly to **K** presumably after formation of **J**.[9e–i] (e) Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261. (f) Trahanovsky, W. S.; Arvidson, K. B. *J. Org. Chem.* **1996**, *61*, 9528. (g) Gandhi, P. J. *Sci. Ind. Res.* **1982**, *41*, 495. (h) Cava, M. P.; Mitchell, M. J. *J. Am. Chem. Soc.* **1959**, *81*, 5409. (i) References in ref 9e–h and: Wang, K. W.; Liu, B.; Peterson, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6860.



I

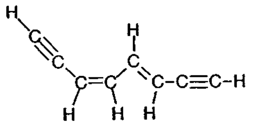


J



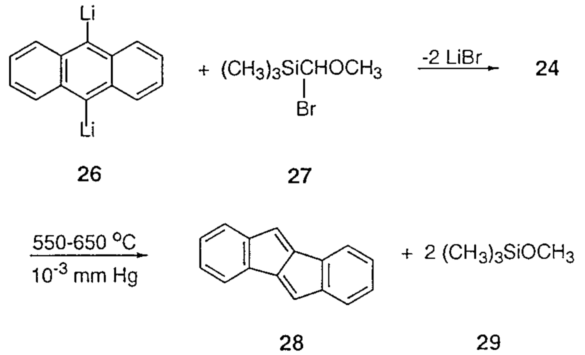
K

(10) (a) *o*-Phenylenedicarbenes (**20**) are calculated to (1) have isomeric (*Z,Z*-, *E,Z*-, and *E,E*) ground-state, quinoidal, singlet structures and (2) undergo cyclization to cyclobutabenzene (**23**) in preference to ring-opening to octadienediyne **L**.[10b] (b) Nicolaides, A.; Nakayama, T.; Yamazaki, K.; Tomioka, H.; Koseki, S.; Stracener, L. L.; McMahon, R. J. *J. Am. Chem. Soc.* **1999**, *121*, 10563.

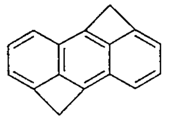


L

Scheme 4



27[11a,b] (Scheme 4, 2 equiv) with 9,10-dilithioanthracene (**26**)[12] as generated from 9,10-dibromoanthracene and *n*-BuLi (2 equiv) in hexane.[13] Flash-vacuum pyrolyses of **24**[2e,3d] at 550−650 °C/10^{-3} mmHg give dibenzo[*b*,*f*]pentalene (indeno[2,1-*a*]indene, **28**, Scheme 4, >48%),[14,15] a bronze-red, volatile solid ($C_{10}H_{16}$). Pentalene **28** is assigned from its exact mass and upon comparison of its color, fluorescence, decomposition temperatures, mass spectra (including its cracking patterns), detailed ^1H and ^{13}C NMR spectra, IR and UV absorptions, and chemical behavior with that previously reported.[14,15] Further, the $C_{16}H_{10}$ thermolysis product from **24** exhibits no ^1H NMR at ~5 ppm for cyclobuta protons[2d] or any other evidence for di-*peri*-cyclobutanthracene **30**, its more strained di-*peri*-cyclobuta isomer **31**, or any other cyclobutarene structure. Of importance also is that the $C_{16}H_{10}$ reaction product did not contain benzobiphenylene **32**,[16a−e] cyclobutanthracenes **33**[16e] or **34**,[16e] anthrylacetylenes **35**,[16f] **36**,[16g] or **37**,[16h] or aceanthrylene (**38**),[16i,j] products that might be formed by rearrangements of anthryldicarbenes **39** or their equivalents via sequences that are extensions of Schemes 1 and 2 or as previously proposed for phenylenedicarbenes **18**[9a] (Scheme 3).



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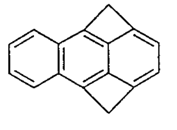

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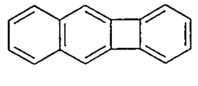

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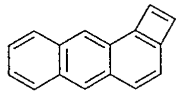

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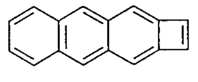

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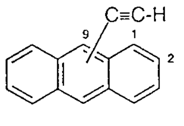
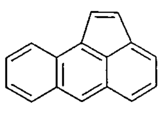


35; C_9, C≡CH
36; C_1, C≡CH
37; C_2, C≡CH



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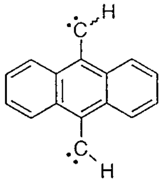

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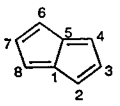
Thermolyses of **24** (Scheme 4) to give pentalene derivative **28** rather than its benzobiphenylene isomer **32** is important for synthesis and with respect to theory[9a] and to mechanisms of rearrangements of anthrylmono- and dicarbenes. Of relevance are that pentalene (**40**, C_8H_6) is more stable thermodynamically than cyclobutabenzene (**23**)[17] and 2,4,5,7-cyclooctatetraenylidene (**41**) is a simple ring-opened isomer of **40**. Further, biphenylene (**42**) rearranges at 940 °C in the gas-phase to benzo[*a*]pentalene (**44**, Scheme 5).[18] The mechanism proposed for isomerization of **42** to **44** involves 1,2-hydrogen migration and ring-expansion (Scheme 5) to the developing carbenic center as in **43**.[18,19]



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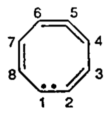

41

Recently benzobiphenylene **32** (Scheme 6) has been reported[19] to rearrange at 900−1100 °C to dibenzopentalene **28** as in Scheme 6. Of interest now are how bis-silanes **24** are converted carbenically at 550−650 °C to

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(11) (a) Christiansen, M. L.; Benneche, T.; Undheim, K. *Acta Chem. Scand.* **1987**, *B41*, 536. (b) John E. Strode is thanked for suggesting the use of **27** for preparing **24** and **25**.

(12) Duerr, B. F.; Chung, Y.-S.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 2120.

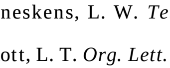
(13) (a) Present efforts to prepare **24** by treatment of 9,10-bis-(methoxymethyl)anthracene[13b] with *t*-BuLi (2.2 equiv) in pentane at −100 °C followed by chlorotrimethylsilane (4.5 equiv) and allowing the mixture to warm to room temperature failed. (b) Miller, M. W.; Amidon, R. W.; Tawney, P. O. *J. Am. Chem. Soc.* **1955**, *77*, 2845.

(14) (a) Blood, C. T.; Linstead, R. P. *J. Chem. Soc.* **1952**, 2263. (b) Chuen, C. C.; Fenton, S. W. *J. Org. Chem.* **1958**, *23*, 1538. (c) Eliasson, B.; Edlund, U. *Org. Magn. Reson.* **1983**, *21*, 322. (d) Anderson, M. J.; Brown, R. F. C.; Coulston, K. J.; Eastwood, F. W.; Ward, A. *Aust. J. Chem.* ***1990***, *43,* 1137. (e) Brown, R. F. C.; Eastwood, F. W.; Wong, N. R. *Tetrahedron Lett.* **1993**, *34*, 3607.

(15) (a) The product assigned as dibenzopentalene **28** also exhibits C−H IR absorptions at (1) ~3047 cm^{-1} for aryl and olefinic protons, (2) 746 (s) cm^{-1} for out of plane C−H bending vibration of the 4 adjacent aromatic hydrogen atoms, and (3) none for cyclobuta or acetylenic hydrogens. (b) Further, the ^1H and the ^{13}C NMR chemical shifts of the product presently assigned as **28** correspond excellently with that of the ring protons and carbon atoms in 5, 10-dimethylindeno-[2,1-*a*]indene[14c] (see the Experimental Section).

(16) (a) Jensen, F. R.; Coleman, W. E. *Tetrahedron Lett.* **1959**, 7. (b) Baker, W.; Barton, J. W.; McOmie, J. F. W.; Searle, R. J. G. *J. Chem. Soc.* **1962**, 2633. (c) Barton, J. W.; Rowe, D. J. *Tetrahedron* **1985**, *41*, 1323. (d) Barton, J. W.; Shepherd, M. K.; Willis, R. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 967. (e) Dewar, M. J. S.; Gleicher, G. J. *Tetrahedron* **1965**, *21*, 1817. (f) Akiyama, S.; Ogura, F.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3443. (g) Akiyama, S.; Nakagawa, M. *Bull. Soc. Chem. Jpn.* **1960**, *33*, 1291. (h) Moroz, A. A.; Piskunov, A. V.; Shvartsberg, M. S. *Izv. Akad. Nauk SSSR. Ser. Khim.* **1981**, 368. (i) Plummer, B. F.; Al-Saigh, Z. Y.; Arfan, M. *J. Org. Chem.* **1984**, *49*, 2069. (j) Becker, H.-D.; Hanson, L.; Anderson, K. *J. Org. Chem.* **1985**, *50*, 277.

(17) (a) Dewar, M. J. S.; Merz, K. M. Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6175. (b) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 11153. (c) Bally, T.; Zhu, Z.; Neuenschwander, M.; Chai, S. *J. Am. Chem. Soc.* **1997**, *119*, 1869 and references therein. (d) References in ref 17b,c. (e) Pentalene (**40**) may be kept as a monomer in matrix at low temperature, dimerizes in solution to **M**, and has been trapped with various reagents.[17c]

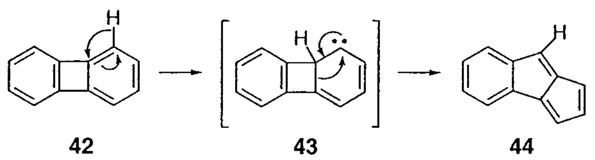


M

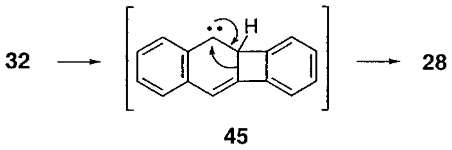
(18) (a) Wiersurn, U. E.; Jenneskens, L. W. *Tetrahedron Lett.* **1993**, *34*, 6615. (b) Brown, R. F. C.; Choi, N.; Coulston, K. J.; Eastwood, F. W.; Wiersurn, U. E.; Jenneskens, L. W. *Tetrahedron Lett.* **1994**, *35*, 4405.

(19) (a) Preda, D. V.; Scott, L. T. *Org. Lett.* **2000**, *2*, 1490.[19c] (b) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113,* 9692. (c) Further, **28** undergoes ring-opening, phenyl rearrangement, and ring-closure at 900−1100 °C to give fluoranthene.[19a] (d) Rearrangement of **28** to fluoranthene is not observed in the present thermolyses of **24** at 550−650 °C. (e) In studies made prior to that in ref 19a, Hartree−Fock calculations (6−31 G) were found to reveal that **28** is of lower energy [$\Delta(\Delta E°)$ = 16.3 kcal/mol] than **32**. Dr. O. Alekseeva is thanked for these calculations.

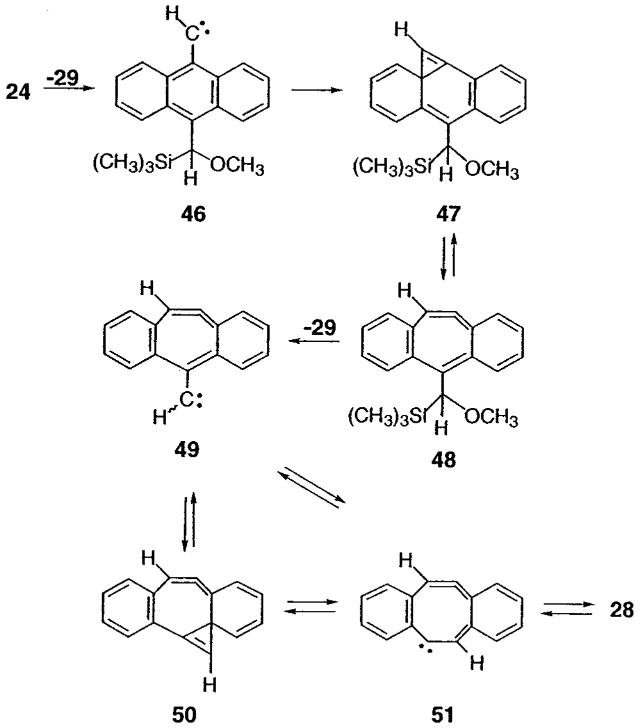
Scheme 5



Scheme 6



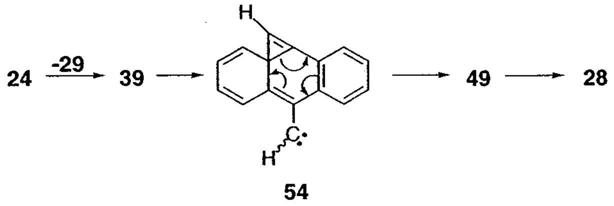
Scheme 7



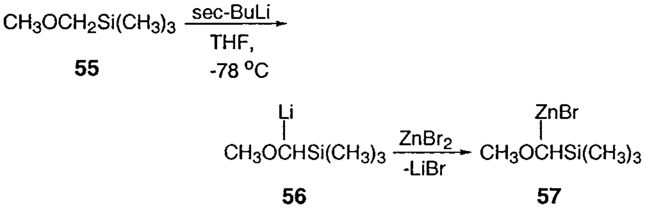
28 and the relation of the reaction mechanisms with that in Scheme 6.

In the present experiments, pentalene **28** might be formed from bis-silanes **24** (Scheme 7) upon (1) loss of $(CH_3)_3SiOCH_3$ (1 equiv), rearrangement of the initial carbene (**46**) generated, further elimination of $(CH_3)_3SiOCH_3$ (1 equiv), and isomerization of **51** and/or (2) complete elimination of $(CH_3)_3SiOCH_3$ (2 equiv) to give dicarbenes **39** and then rearrangements as will be explained. Scheme 7 illustrates a monocarbenic sequence by which **24** is converted to **28** by mechanisms involving only carbon skeleton rearrangements.[20,21] The monocarbenic rearrangments in Scheme 7 are similar to or extensions of that in Scheme 1.[20] Scheme 7 includes

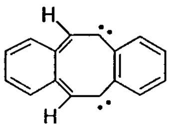
Scheme 8



Scheme 9



allenic intermediates **48**−**50** and, in particular, benzocycloocta-2,4,5,7-tetraenylidene **51** which converts to pentalene **28** simply by 1,5-transannular ring-closure (as for **41** to **40**).[20] Because of the eventual cyclobutadienic character and the strain in the reaction transition states, rearrangements of **49**, **50**, and **51** to **52** and/or **53** and then benzobiphenylene **28** are expected to be repressed.[17,19−21] Whether 9,10-anthryldicarbenes **39** are



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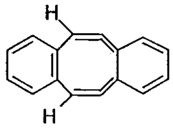

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generated in the present thermolyses of disilanes **24** is not known. However, carbon-skeleton monorearrangements in dicarbenes **39** as in Scheme 8 will give simply **54,** which may convert to 1,3,4,6-cycloheptatetraenylcarbene **49** (Scheme 7) and then pentalene **28**. Of further note is that the thermal carbenic behaviors of bis(methoxysilylmethyl)anthracenes **24** (Schemes 4, 7, and 8) are very different from that reported for bis-tetrazole **17** (Scheme 3).[9a] Studies should now be made of (1) whether various phenylenedicarbenic systems yield pentalene (**40**) and products thereof[17d,e] and (2) the products and mechanisms of rearrangements of varied arenyldicarbenes and hetarenyldicarbenes or their equivalents.

Synthesis and Thermolysis of 1,5-Bis[(methoxymethyl)silanes] 25. 1,5-Bis(silanes) **25** are prepared as in Schemes 9 and 10 from methoxytrimethylsilylmethylzinc bromide (**57**), 1,5-diiodoanthracene (**63**), and catalytic amounts of $PdCl_2(PPh_3)_2$.[22,23]

Thermolysis of bis(silanes) **25** at 550−650 °C/10^{-3} mmHg produces a pyrolysate that has a GC−MS trace with only one peak with a mass (202) for $C_{16}H_{10}$. Purification by MPLC/hexane yields di-*peri*-dicyclobutanthracene **30** (>40%), a white solid, presumably formed from monocarbenes **64** and **67** and (less likely) dicarbenes **66** as in Scheme 11. Effective synthesis of such a highly strained product as **30** at 550−650 °C by two *peri*-cyclobuta ring-closure processes is impressive. Sealed under argon, **30** turns red and decomposes rapidly at ~60 °C. Dicyclobuta derivative **30** is air-sensitive and yellows noticeably at room temperature under N_2. At −20 °C under argon, **30** is more stable. Pentalene **28** and possible isomers **31**−**38** are not found as products of thermal decompositions of bis-silanes **25**.

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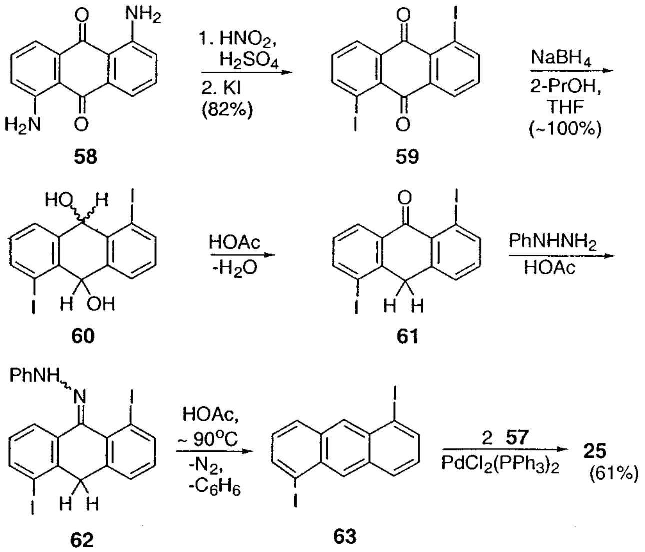
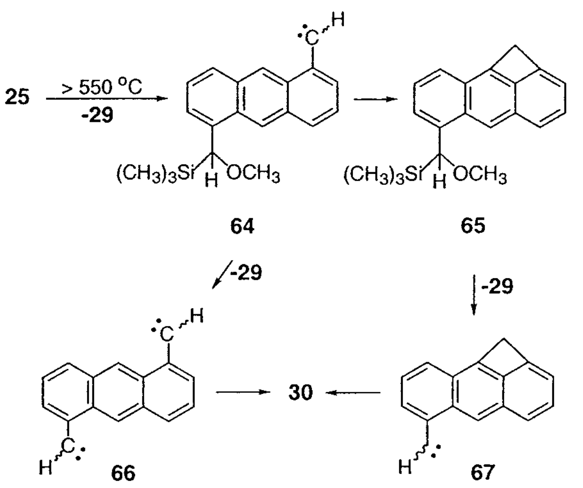
(20) The cycloheptatrienylidene possibly formed by ring-opening of **47** and leading to cycloheptatetraene **48** in Scheme 7 and the cycloheptatrienediylidene related to cycloheptatetraenylcarbene **49** in Scheme 7 have not been included in the sequences illustrated in order to save space and because the carbenes are expected to be of higher energies than their corresponding allenes.[1a−j]

(21) Dicarbene **52** and/or diallene **53**, if formed in thermolyses of **24** and of **32**, might convert to **51** by multiple 1,2-carbon-skeleton rearrangements or/and, as in ref 19a, by hydrogen migration. Pentalene **28** can then result upon ring-closure of **51** (Scheme 7). Study of the behavior of labeled **24** and **32** in the gas-phase at 550−1100 °C might allow further definition of the mechanism(s) of formation of **28**.[19a]

Scheme 10



Scheme 11



The structural assignment as **30** is based primarily on spectral data. The mass spectrum of the hydrocarbon gives $M^+ = 202$ amu. The IR, ^{1}H NMR, and ^{13}C NMR provide evidence for the symmetry of **30**. The GC−FTIR trace of **30** has three bands: aromatic C−H stretching at 3062 cm^{-1}, methylene C−H stretching at 2936 cm^{-1}, and C−H out-of-plane bending at 767 cm^{-1}. Since the anthryl ring hydrogens are not separated by any other substituent, **30** has only one out-of-plane IR C−H bending band. The ^{1}H NMR spectrum (Figure 1) of the product shows absorption expected for cyclobuta methylene hydrogens at 4.83 ppm (s, 4H),[2e] the hydrogens ortho to the methylene groups give a doublet at 7.05 ppm (2H, J = 5.97 Hz, AX system), the meta hydrogens absorb at 7.51 ppm (dd, 2H, J = 5.97, 8.86 Hz, AX and AB systems), and the para hydrogens give NMR at 7.60 ppm (d, 2H, J = 8.87 Hz, AB system). The ^{13}C NMR of **30** reveals absorption for the methylene carbons at 44.7 ppm. There are only six distinct peaks from δ 113−144 for the remaining seven carbon atoms. Apparently, two of these carbons have coincident chemical shifts. As yet it has been impossible to obtain satisfactory stable crystals of **30** for X-ray analysis. The chemistry of **30** and its derivatives is to be determined.

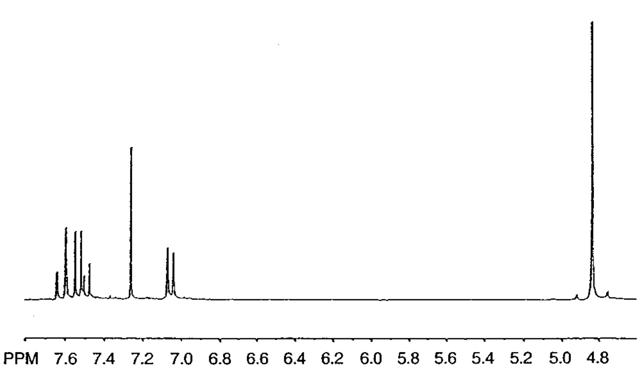


Figure 1. ^{1}H NMR of 1*H*,5*H*-Dicyclobuta[*de,kl*]anthracene (**30**).

Thermolyses of 1,5-bis(silanes) **25** to give the di-*peri*-cyclobuta product **30** (Scheme 11), whereas 9,10-bis(silanes) **24** yield the multiple rearrangment derivative pentalene **28** (Schemes, 4, 7, and 8), are also of interest with respect to preferred carbenic reaction mechanisms. 1-Anthrylcarbenes **64** (Scheme 11), as singlets or (and) triplets, are more energetic than 9-anthrylcarbenes **46** (Scheme 7) of corresponding spin states. Similarly, 1,5-anthryldicarbenes **66** have higher energies than 9,10-anthryldicarbene analogues **39**. Since pentalene **28** is more stable than di-*peri*-cyclobutanthracene **30**, on the basis of thermodynamic equilibrative control, thermal carbenic decompositions of 1,5-bis(silanes) **25** should yield **28** in preference to **30**. Mechanistic schemes (see the Supporting Information), however, for such carbenic conversions of **25** to **28** via **64** and/or **66** involve intermediates and/or transition states that do not have naphthalenoid, benzenoid, and other favorable structures for stabilization, and therefore, more preferable reaction routes to **30**, as will be proposed, are expected to be followed.

The double carbenic reactions of 1,5-bis(silanes) **25** to give the highly strained di-*peri*-cyclobuta derivative **30**, whereas 9,10-bis(silanes) **24** do not are of further interest

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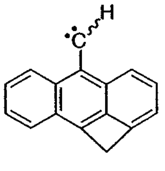
(22) (a) In the preparation of **56** by the method of Magnus and Roy (Magnus, P.; Roy, G. *Organometallics* **1982**, *1*, 533) in which *sec*-BuLi reacts with methoxysilane **55** and THF in a 1:10 ratio at −78 °C and the solution is warmed to −30 °C, $CH_3OCH_2Si(CH_3)_2CH_2Li$ is also formed in substantial yield. Synthesis of **56** has now been found to be greatly improved by using **55** and THF in a 1:2 ratio and lowering the reaction temperature. A reliable method for preparing **56** is to add **55** in THF to a solution of sec-BuLi and THF (the ratio of **55**/THF is 1:2) frozen by liquid nitrogen and allowing the mixture to warm to −30 °C. (b) In the preparation of halozinc reagents $[CH_3OCH(ZnX)Si(CH_3)_3]$ from **56** (Scheme 9), $ZnBr_2$ and ZnI_2 give comparable yields and better than that from $ZnCl_2$. $ZnBr_2$ is preferred in the present preparation because ZnI_2 decomposes extensively while drying. (c) In further development of this advantageous new synthetic methodology, (1) iodobenzene, **57**, and catalytic amounts of $PdCl_2(PPh_3)_2$ in dioxane have been found to give [methoxy(trimethylsilyl)methyl]benzene (>66%) and biphenyl (10%) and (2) 1-iodonaphthalene is converted by **57** and $PdCl_2(PPh_3)_2$ in dioxane to 1-[methoxy(trimethylsilyl)methyl]naphthalene (>39%) and 1, 1′-binaphthyl (25%). (d) For coupling of iodoarenes with other organozinc reagents using palladium chloride catalysts, see: Erdik, E. *Tetrahedron* **1992**, *48*, 9577 and Negishi, E.; Gulevich, Y. V.; Noda, Y. *Tetrahedron Lett.* **1993**, *34*, 1437.

(23) (a) The present method for converting diaminoquinone **58** to diiodoquinone **59** is simpler and more convenient than that by: Scholl, R.; Hass, S.; Meyer, H. K. *Chem. Ber.* **1929**, 107. (b) Syntheses of diiodide **63** and **25** from **59** as in Scheme 10 are completely new. (c) It is advantageous to reduce **59** with $NaBH_4$ in 2-propanol to diols **60**. Methanol, methanol/diglyme, and methanol/THF as solvents lead to extensive iodine removal during reactions of **59** with $NaBH_4$. (d) For other methodologies for reductions of 9,10-anthraquinones to anthracenes, see ref 23e−h. (e) Criswell, T. R.; Klandermann, B. H. *J. Org. Chem.* **1974**, *39*, 770, (f) Norves, S. *J. Org. Chem.* **1993**, *58*, 2414, (g) Marquardt, D. J.; McCormick, F. A. *Tetrahedron Lett.* **1994**, 1131. (h) Clark, K. J. *J. Chem. Soc.* **1956**, 1911.

in that the C−H bond strengths at C_{10} in monocarbenes **64** and **67** (Scheme 11), C_9 and C_{10} in dicarbenes **66** (Scheme 11), C_1 in monocarbenes **46** (Scheme 7), C_1 and C_5 in dicarbenes **39**, and C_1 and C_8 in monocarbenes **68**, are all expected to be similar.[24] Therefore, differences in the abilities of C−H bonds to undergo direct insertion or hydrogen abstraction-recombination do not explain the carbenic products from **24** and **25**.



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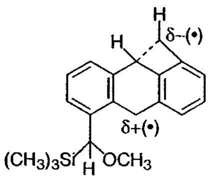
Of relevance with respect to differences in the carbenic behaviors of **24** and **25** is that attacks on the π-electron systems of anthracenes by unencumbering electrophilic, homolytic, and electron-transfer reagents usually occur much more rapidly at C_9 than at C_1 and C_2 positions.[25] Carbenic ring-closure reactions of 1-anthrylcarbenes such as **64** and **67** and (even) 1,5-dicarbenes **66** as singlets are thus expected to be significantly expedited by the stabilizing effects involving two phenyl groups as illustrated in dipolar transition states **69**−**71**.[26] Similar conclusions can be drawn for ring closures of **64**, **67**, and **66** to give diradical analogues of **69**−**71**.[26] In *peri* ring-closures of 9-anthrylcarbene **46**, cyclobut-9-anthrylcarbenes **68**, and 9,10-anthryldicarbenes **39**, the corresponding transition states **72**−**74** are stabilized by single naphthyl and olefinic interactions.[26] Since delocalization by two phenyl groups will be greater than for a naphthyl and an olefinic group, transition states **69**−**71** will be favored over that in **72**−**74**, respectively, and thus conversions to cyclobuta derivatives can occur more readily from **69**−**71** than from **72**−**74**. Of further note with respect to the above mechanisms of carbenic decompositions of **24** and **25** to **30** is that the transition states might develop earlier than represented in **69**−**74** and involve C−H insertive interaction on hydrogen on the carbon atoms, C_9 or C_1, at which cyclobuta bridging is occurring.[27] In such transition states, the stabilizations by two phenyl groups will continue to be more significant than that from a naphthyl and an olefinic group and be important in the conversion of **25** to the di-*peri*-cyclobuta product **30**.[27]



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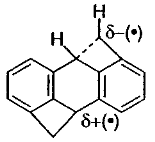

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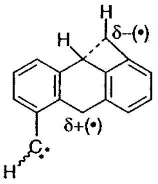

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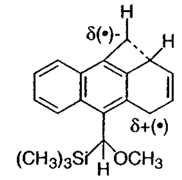

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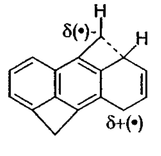

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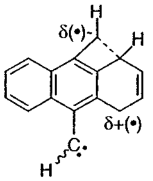

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The effects of substituents on the intramolecular reactions of anthrylcarbenes will be reported.[3c,28]

Experimental Section

Methods, Techniques, Reagents, and Analyses. The methods, techniques, handling of reagents, and the various analyses and spectral determinations used in the present experiments are essentially identical with that in ref 3c.

Bromo[methoxy(trimethylsilyl)]methane (27). Bromine (9.7 g, 60.6 mmol) in CCl_4 (50 mL) was added dropwise in 1 h to a solution of methoxy(trimethylsilyl)methane[29] (10 mL, 63.6 mmol) in dry CCl_4 (100 mL). The resulting mixture was stirred overnight. The solvent was removed, and the concentrate was distilled fractionally under reduced pressure to give **27** as a colorless oil: 4.3 g (34%); bp 41 °C/10.5 mmHg (lit.[11a] bp 40 °C/10 mmHg); ^1H NMR ($CDCl_3$) δ 0.18 (s, 9H), 3.52 (s, 3H), 5.76 (s, 1H).

9,10-Bis[methoxy(trimethylsilyl)methyl]anthracenes (24). *n*-BuLi in hexane (10.5 mL, 1.4 M, 15.0 mmol) was slowly added to 9,10-dibromoanthracene[30] (1.25 g, 3.75 mmol) in dry Et_2O (100 mL) at 0 °C. An orange solid formed, and the mixture was stirred for 30 min at room temperature. Bromomethoxysilylmethane **27** (2.95 g, 15.0 mmol) was added in one portion. The solution warmed as the solid reacted. The mixture was stirred for 2 h and then washed with H_2O and brine. Silica gel was added, and the mixture was concentrated. Column chromatography using petroleum ether−toluene as eluent yielded **24**. Recrystallization from hexane gave yellow crystals of **24** (0.70 g, 45%) apparently as an isomeric mixture:[7] the mp of **24** is broad,[7] mp 140−146 °C; ^1H NMR ($CDCl_3$) δ −0.05 (s, 9H), 0.01 (s, 9H), 3.23 (s, 3H), 3.29 (s, 3H), 5.70 (m, 2H), 7.45 (m, 4H), 8.30 (m, 2H), 9.05 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −1.5, −1.4, 59.2, 59.3, 76.8, 76.9, 123.4, 123.5, 123.5, 123.6, 124.3, 124.4, 124.4, 125.1, 127.7, 127.8, 128.5, 128.6, 128.6, 129.8, 130.1, 130.1, 130.2, 131.8, 131.9, 131.9 (several indistinguishable shoulder absorptions are not listed); exact mass calcd 410.2097, obsd 410.2101. Anal. Calcd for $C_{24}H_{34}O_2Si_2$: C, 70.19; H, 8.34. Found: C, 70.12; H, 8.30.

Pyrolysis of 9,10-Disilanes 24 to Dibenzo[*b*,*f*]pentalene (28). Flash-vacuum decomposition of **24** (200 mg, 0.49 mmol) was effected at 650 °C/10^{-3} mmHg in a horizontal quartz furnace filled with quartz chips as described in ref 3d. The pyrolysate upon trituration with degassed benzene gave **28**

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[24] (a) Calculated [B3LYP/6-31G(d)] bond dissociation energies (BDE, kcal mol^{-1}, 298 K) for cleavage of the C−H bonds at the indicated carbon atom in anthracene are: C_9 (111.4), C_1 (111.0), and C_2 (110.9). Such calculated BDEs for C−H in naphthalene are: C_1 (111.1) and C_2 (110.9). For benzene the calculated BDE is 110.8 kcal mol^{-1}.[24b] (b) Barckholtz, C.; Barckholtz, T. A.; Hadad, C. M. *J. Am. Chem. Soc.* **1999**, *121*, 491. (c) The BDE for C−H in benzene has been found experimentally to be 111.2 ± 0.8 [24d] and 113.5 ± 0.5[24e] kcal mol^{-1} at 300 K. The experimental BDE for C−H in naphthalene (gas-phase ion)[24f] is 111 ± 3 kcal mol^{-1}. (d) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744. (e) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590. (f) Kass, S. Private communication.

[25] (a) Various reactions and reactivities of anthracene have been reviewed by: (b) Sainsbury, M. *Rodd's Chemistry of Carbon Compounds*, 2nd. ed.; Elsevier Scientific Publishing Company: Amsterdam, 1979; Vol. III H, pp 1−91. (c) Bolton, R. *Rodd's Chemistry of Carbon Compounds*, 2nd. ed.; Elsevier Science Publishers B.V.: Amsterdam, The Netherlands, 1988; Vol. III, Supplement, pp 1−17. (d) For comprehensive summary and mechanistic interpretations of various electrophilic reactions of anthracenes, see: Taylor, R. *Electrophilic Aromatic Substitution*; J. Wiley & Sons: Chichester, 1990; pp 1−513.

[26] In **69**−**71**, there will be delocalization by two phenyl groups at C_{10} and by a phenyl group at the bridging carbenic (cyclobuta) carbon. Delocalization in **72**−**74** at C_4 will involve interaction with a single 2-naphthyl group and an olefinic group and at the cyclobuta carbon with a 1-naphthyl group.

[27] Such insertive-addition transition states are similar to **B** in footnote 5.

[28] (a) 9- and 1-anthrylcarbenes, upon generation at 500−600 °C, yield 1*H*-cyclobuta[*de*]anthracene[1c,3c,5,6a,28b,c] and other products. (b) Engler, T. A.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 2715. (c) The mechanisms of these reactions will be interpreted further.[6a]

[29] Speier, J. L. *J. Am. Chem. Soc.* **1948**, *70*, 4142.

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as a bronze solid:[14] 38 mg (40%); mp 300−310 °C dec (lit.[14c,d] mp >280 °C dec); IR (KBr) 3047 (w), 1582 (w), 1453 (w), 1428 (w), 1156 (w), 9.34 (w), 891 (w), 853 (m), 746 (s), 473 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 1H), 6.85−6.9 (m, 3H), 7.0−7.1 (m, 1H) [lit.[14c,d] ^{1}H NMR ($CDCl_3$) δ 6.40 (s, 1H), 6.85−6.9 (m, 3H), 7.0−7.1 (m, 1H)]; ^{13}C NMR ($CDCl_3$) δ 122.0, 123.0, 126.1, 127.1, 128.2, 134.6, 148.8, 150.1 [lit.[14c,d] ^{13}C NMR ($CDCl_3$) δ 122.1, 123.2, 126.3, 127.2, 128.3, 134.8, 149.0, 150.2]; $M^+ = 202$ amu; *m*/*z* 202 (M, 100), 200 (14), 101 (9), 100 (6) [lit.[14c,d] m/Z 202 (M, 100), 200 (14), 101 (11), 100 (6)]. The NMR chemical shifts of the ring hydrogens and carbons in 5,10-dimethylindeno[2,1-*a*]indene are as follows: [lit.[14c] ^{1}H NMR δ 6.9 (m, 3H), 7.1 (m, 2H); lit.[14c,15] ^{13}C NMR ($CDCl_3$) δ 120.5, 121.6, 126.9, 127.1, 135.5, 136.0, 143.0, 151.1]. (Pyrolysis of **24** at 550 °C/10^{-3} mmHg gave **28** in >48% yield).

1,5-Diiodo-9,10-anthraquinone (59). 1,5-Diamino-9,10-anthraquinone (**58**, 50 g, 210 mmol) was suspended in chilled concd H_2SO_4 (200 mL). Sodium nitrite (40 g, 580 mmol) was added over 30 min. The resulting thick brown mixture was stirred 3 h and poured into H_2O (2.5 L). After the mixture had been stirred for 30 min, the purple solids were filtered. To the filtrate was added KI (50 g, 310 mmol). The solution bubbled and turned black. After the mixture had stirred for 3 h, $NaHSO_3$ was added until the color of the solution changed to brown. The orange solid formed was washed with H_2O until acid free, oven-dried, and identified as **59** (6.68 g, 7%).

The purple solids filtered from the initial reaction mixture were suspended in H_2O (2.5 L) for 15 min. After filtering the dark diazonium salt solution, KI (50 g) was added portionwise. The solution bubbled vigorously, and the olive solid formed was washed with H_2O and oven-dried. Combination of the solid fractions gave gold-orange **59** (79.2 g, 82%): mp 250−260 °C dec (lit.[23a] mp 308−309 °C).

1,5-Diiodoanthracene (63) from 59. Finely ground **59** (5.0 g, 10.87 mmol) was suspended in a mixture of 2-propanol (50 mL) and THF (50 mL). After the stirred mixture was cooled to 0 °C, $NaBH_4$ (1 g, 26.32 mmol) was added. The red-brown suspension became homogeneous after 30 min. The mixture was stirred at room temperature for 30 min, and H_2O was added. The crude 9,10-dihydro-9,10-dihydroxy-1,5-diiodoanthracenes (**60**, mp 250−270 °C dec) collected were washed with H_2O, dried, and added to phenylhydrazine (3.0 mL, 30.6 mmol) in glacial acetic acid (50 mL). The mixture was heated at 80−95 °C for 7 h, cooled, and diluted with H_2O. The light brown solids were vacuum-filtered, washed with H_2O, oven-dried, and then purified by continuous extraction on silica gel with hexanes. (Sublimation of the product leads to substantial losses; conventional chromatography requires massive amounts of solvent because of the insolubility of diiodide **63**.) Concentration of the hexane mixture followed by recrystallization from THF-EtOH yielded light orange **63**: 0.84 g (18%); mp 236−238 °C; ^{1}H NMR ($CDCl_3$) δ 7.21 (t, 2H), 8.12 (t, 4H), 8.61 (s, 2H); ^{1}H NMR (DMSO-d_6) δ 7.32 (t, 2H), 8.27 (q, 4H), 8.66 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 126.7, 129.7, 132.3, 132.6, 137.9; exact mass calcd 429.8719, obsd 429.8713. Anal. Calcd for $C_{14}H_8I_2$: C, 39.10; H, 1.88. Found: C, 39.17; H, 1.89.

1,5-Bis[methoxy(trimethylsilyl)methyl]anthracenes (25) from 63. *sec*-BuLi in hexane (1.4 M, 2.1 mL, 2.88 mmol) was added to THF (1 mL) at −78 °C, and the resulting solution was frozen by liquid N_2. (Methoxymethyl)trimethylsilane (**55**, 0.45 mL, 2.9 mmol) was injected. The mixture was melted and warmed over 1 h to −10 °C. Addition of $ZnBr_2$ in THF (0.77 M, 3.7 mL, 2.85 mmol) and diglyme (5 mL) was followed by 5 min of stirring. Diiodide **63** (250 mg, 0.96 mmol, 0.33 equiv) and $PdCl_2(PPh_3)_2$ (22 mg, 3.3 mol % of **63**) were added to the **57** generated, and the orange mixture was then stirred for 4 h. During this time, the mixture became dark blue.

Et_2O (ca. 20 mL) and H_2O (ca. 20 mL) were added, and the mixture was vacuum-filtered over Celite. The Et_2O extract was washed with H_2O and brine, dried, concentrated on silica gel, and column chromatographed on silica with petroleum ether and petroleum ether−toluene as eluents to yield **25** (145 mg, 61%). The mp of **25** is broad and its NMR is complex as expected for stereoisomers: mp 147−166 °C (lit.[7] mp 147−166 °C); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 18H),3.40 (s, 3H), 3.41 (s, 3H), 4.96 (s, 1H), 4.98 (s, 1H), 7.49 (m, 4H), 7.92 (dd, 2H), 8.64 (d, 2H); ^{13}C NMR ($CDCl_3$) δ −2.4, 59.4, 78.0, 78.3, 122.6, 122.7, 123.6, 123.7, 125.0, 126.9, 127.0, 129.3, 129.3, 131.6, 137.0; exact mass calcd 410.2097, obsd 410.2108. Anal. Calcd for $C_{24}H_{34}O_2Si_2$: C, 70.21; H, 8.35. Found: C, 70.45; H, 8.35.

Pyrolysis of 1,5-Disilane 25 to 1*H*,5*H*-Dicyclobuta[*de*,*kl*]anthracene (30). Flash-vacuum decomposition of **25** (50 mg, 0.12 mmol) was conducted at 550 °C/10^{-3} mmHg in a horizontal quartz apparatus filled with quartz chips as described in ref 3c. MPLC (hexanes) of the pyrolysate yielded two yellow fractions and one colorless fraction. GC−IR−MS and ^{1}H NMR of the two yellow fractions indicated each to be complex mixtures containing incompletely pyrolyzed material. The colorless fraction on concentration gave white crystals of **30**: 10 mg (40%); mp (sealed capillary) 60−82 °C (dec, yellow-red); FTIR (gas phase) 3062, 2967, 2936, 2832, 1613, 1458, 984, 767, 729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.83 (s, 4H), 7.05 (d, 2H, $J = 5.97$), 7.51 (dd, 2H, $J = 5.97$, 8.86 Hz), 7.60 (d, 2H, $J = 8.87$ Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 44.7, 114.1, 118.8, 120.3, 130.6, 143.7; UV (λ, hexane) 228, 262, 352, 368, 370, 386; exact mass 202.0783, obsd 202.0788. The instability of **30** at room temperature has precluded elemental analysis. Many experiments as above gave **30** in ∼40% yield.

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Supporting Information Available: Discussion of mechanisms for possible conversions of **25** to **28** via **64** and/or **66**, ^{1}H and ^{13}C NMR of **24**, **25**, and **63**, ^{1}H NMR of **28**, and ^{13}C NMR of **30**. Also included are experimental details for (1) reaction of **55** with *sec*-BuLi in THF to give [(dimethyl(methoxymethyl)silyl)methyl]lithium (see ref 22a) and its reaction with $MgBr_2$ and then 1,5-dichloroanthracene/$NiCl_2$ dppp to yield 1,5-bis[(dimethyl(methoxymethyl)silyl)methyl]anthracene, (2) development methodology and advantageous synthesis of [methoxy(trimethylsilyl)methyl]benzene and 1-[methoxy(trimethylsilyl)methyl]naphthalene from iodobenzene and 1-iodonaphthalene, respectively, with **57** and $PdCl_2(PPh_3)_2$, (3) alternate synthesis of **63** by diazotization of 1,5-diaminoanthracene followed by KI, and (4) alternate preparation of **25** from anthracene-1,5-dicarboxylic acid upon conversion to dimethyl anthracene-1,5-dicarboxylate, 1,5-bis(hydroxymethyl)anthracene, and 1,5-bis(methoxymethyl)anthracene. This material is available free of charge via the Internet at http://pubs.acs.org.

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