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PERI-METHANOARENES BY THERMOLYSIS OF [METHOXY(ARENYL)METHYL]TRIMETHYLSILANES

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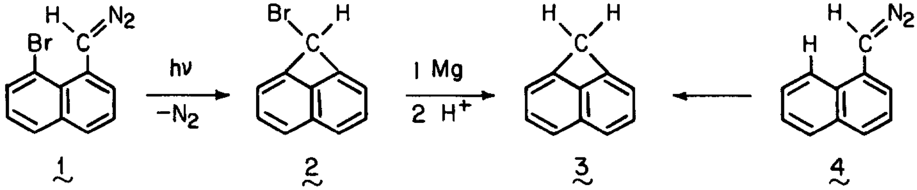
Abstract· Practical syntheses of varied *peri*-methanoarenes have been developed

8-Bromo-1*H*-cyclobuta[*de*]naphthalene (2), the initial arene to be bridged in *peri*-positions by a single carbon moiety, is formed (Eq 1) upon irradiation of 8-bromo-1-naphthyldiazomethane (1)[1a] and then convertable to 1*H*-cyclobuta[*de*]naphthalene (3) by hydrolysis of its Grignard reagent [1a] Recently 3 has been obtained (Eq 1) by flash-vacuum decomposition of salts of 1- or 2-naphthaldehyde *p*-tosylhydrazones or their subsequent 1(4)- or 2-naphthyldiazomethanes at 400-600°C/10^{-2}-10^{-4}Torr.[1b] We now report practical syntheses of *peri*-methanoarenes by pyrolytic elimination (525-675°C/0 05-0 1 mm Hg) of methoxytrimethylsilane from [methoxy(arenyl)methyl]-trimethylsilanes[1c,d] examples of which are illustrated in Equation 2 The method is advantageous because the initial silanes are readily prepared, conventional gas-phase thermolysis



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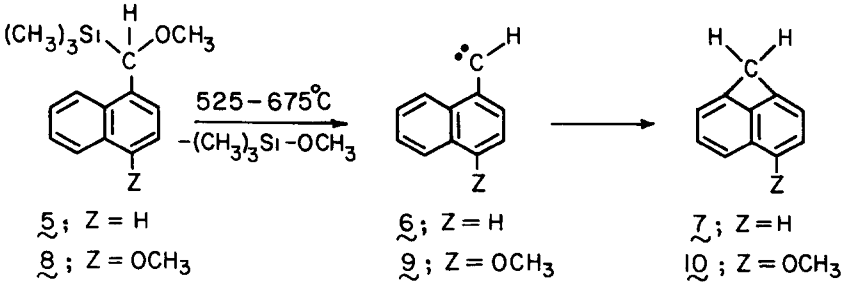
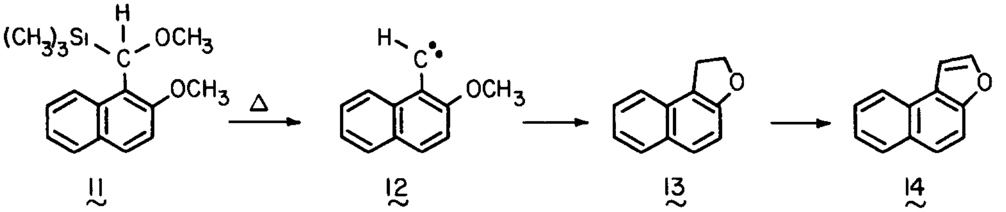


(2)

equipment is usable and varied cyclobutarenes can now be obtained preparatively [2a,b] This study also reveals synthesis of a number of *peri*-methanoarenes of interest and some remarkably extended isomerizations of arenylmethylenes to other arenylmethylenes and products thereof

Thus, volatization of [methoxy(1-naphthyl)methyl]trimethylsilane (5),[3a,b] prepared (100%) by deprotonation (*t*-butyllithium,tetramethylethylenediamine/ethyl ether at -78°C) and silylation (chlorotrimethylsilane) of 1-methoxymethylnaphthalene, through a packed quartz furnace at 650°C/0 05-0 10 mm yields 7 (39%, Eq 2) presumably via 1-naphthylmethylene (6) Minor products of the pyrolysis naphthalene (5%), 1-methylnaphthalene (3%), 1-methoxymethylnaphthalene (8%), 1-naphthaldehyde (9%) and α-methyl-1-naphthalenemethanol (7%) can be separated from 7 by column chromatography[3c] For much of the practical chemistry involving derivatization of 7, the pyrolysate can be used without purification.

Substituted-1*H*-cyclobuta[*de*]naphthalenes can also be prepared satisfactorily by pyrolysis of proper [methoxy(substituted-1-naphthyl)methyl]trimethylsilanes For example, 4-methoxy-1*H*-cyclobuta[*de*]naphthalene (10, Eq 2, 42%), is produced by decomposing [methoxy(4-methoxy-1-naphthyl)methyl]trimethylsilane (8) at 510°C/0 05-0 10 mm Thermolysis of [methoxy(2-methoxy-1-naphthyl)methyl]trimethylsilane (11, Eq 3) at 610°C/0 05-0.10 mm however yields 1,2-dihydronaphtho[2,1-*b*]furan (13, 64%) and naphtho[2,1-*b*]furan (14, 31%) presumably by insertion of 2-methoxy-1-naphthylmethylene (12) into a C-H bond of its *o*-methoxy group and then dehydrogenation of 13



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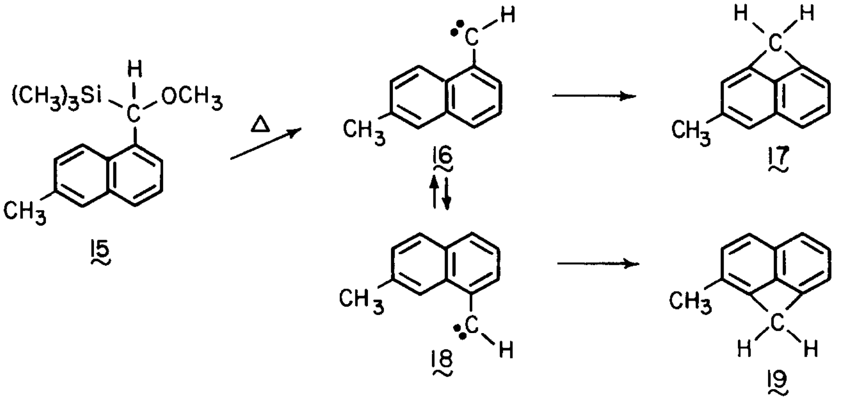
Of note is that pyrolysis (510°C/0 10-0 20 mm) of [methoxy(6-methyl-1-naphthyl)methyl]trimethylsilane (15, Eq 4 and 5) yields a 11 1 mixture of 3-methyl-1*H*-cyclobuta[*de*]naphthalene (17) and 2-methyl-1*H*-cyclobuta[*de*]naphthalene (19) in a combined yield of 25% Formation of 19 implies isomerization of 6-methyl-1-naphthylmethylene (16) to 7-methyl-1-naphthylmethylene



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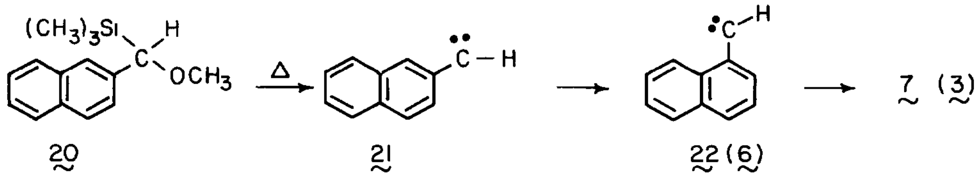
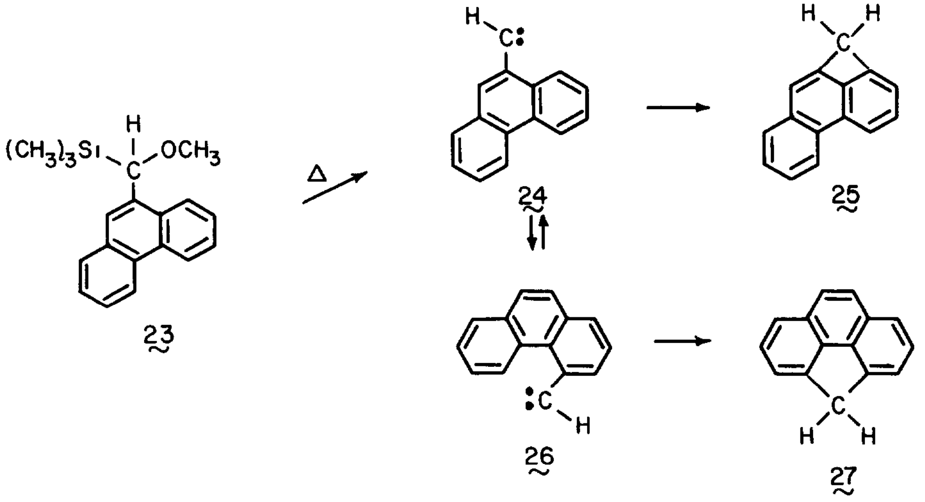


(6)

(18), carbene-carbene rearrangements of 1-naphthylmethylenes have not been previously observed[4] Since conversion to 19 is increased at higher temperatures (at 660-670°C the ratio of 17 19 is 1 9 1), pyrolysis of [methoxy(6-substituted-1-naphthyl)methyl]trimethylsilanes is of promise for preparing 2-substituted-1*H*-cyclobuta[*de*]naphthalenes Further, as expected, [methoxy(2-naphthyl)methyl]trimethylsilane (20) is converted to 7 at 640-650°C/0.20-0.30 mm) apparently upon rearrangement of 21 to 22 (Eq 6).[1b]

The pyrolytic method is also usable for preparing higher polycyclic *peri*-methanoarenes. Thus, [methoxy(9-phenanthryl)methyl]trimethylsilane (23, Eq 7 and 8) converts at 590°C/0.1 mm to 4*H*-cyclobuta[*jk*]phenanthrene(25, mp 87 5-88 5°C) and 4*H*-cyclopenta[*def*]phenanthrene (27) in a 9 1 ratio in a combined yield of 72%. Phenanthrene 27 apparently results from carbene-carbene rearrangement of 9-phenanthrylmethylene (24) to 4-phenanthrylmethylene (26) which then inserts into the C-H bond at C-5 Carbenic migration through a fused ring juncture as required for isomerization of 24 to 26 has not been previously reported Such an extended isomerization as involved in formation of 26 is of synthetic value since at 650°C, 23 decomposes to 25 and 27 in a 3 1 ratio and an overall yield of 70% Further, [methoxy(1-anthryl)methyl]trimethylsilane (28) decomposes at 560-570°C/0 02-0 07 mm with insertion into its *peri*-C-H bond at C-9 to give 1*H*-cyclobuta[*de*]anthracene (29, 52%), a light yellow solid which begins to decompose between 60-70°C before melting Even more impressively, 3*H*-cyclobuta[*cd*]pyrene (31), a white crystalline solid (mp 117-118°C from pentane), is obtained in 86% yield by thermolysis of [methoxy(1-pyrenyl)methyl]trimethylsilane (30) at 520-525°C/0.05-0 07 mm In cyclobuta[*de*]naphthalenes 2 and 3, the C(4)-C(9)-C(5) bond angles are 137-138°[5] That 31 forms efficiently from 30 and is such a well-behaved material would indicate that there is significant steric accommodation in its aft ring systems.



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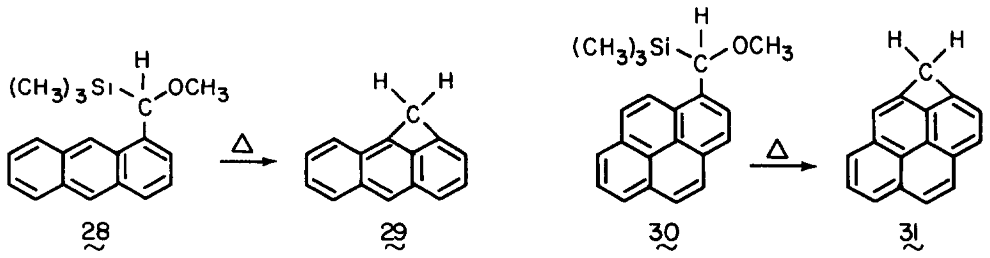

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Peri-methanoarenes **3**, **10**, **17**, **19** and **25** are stable, readily handled products. Cyclobutarenes **29** and **31** oxidize fairly rapidly, however, when exposed to the atmosphere at room temperature. Hydrocarbons **25**, **29** and **31** form air and thermally-stable, brightly-colored 1:1 complexes with 2,4,7-trinitrofluoren-9-one that are readily purified and then decomposed efficiently on silica gel (hexane eluent) to their parent molecules. Of particular value in identification of the cyclobutarenes are the ^{1}H and ^{13}C NMR of their methylene bridges at 4.69-5.19 and 45.95-52.97 ppm, respectively, relative to tetramethylsilane.[6] Investigation of the chemistry of the above *peri*-methanoarenes along with synthesis of other single atom, *peri*-bridged arenes are now in progress.

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1. (a) R. J. Bailey and H. Shechter, *J. Am. Chem. Soc.*, **96**, 8116 (1974). (b) C. Wentrup and J. Becker, *J. C. S., Chem. Comm.*, 190 (1980). (c) The low volatilities of *p*-tosylhydrazone and *p*-toluenesulfinate salts, the instabilities of aryldiazomethanes and their rapid conversions to azines, and the difficulties encountered in preparing and introducing large quantities of free-flowing solids into a pyrolysis tube at low pressures dictated the present development of more manageable carbene precursors. (d) During the present investigation, α-trimethylsilylbenzyl alcohols were reported to form carbenic products via thermal elimination of trimethylsilanol. A. Sekiguchi and W. Ando, *Tetrahedron Lett.*, 4077 (1979) and A. Sekiguchi and W. Ando, *J. Org. Chem.*, **45**, 5286 (1980).

2. (a) Entirely different methods for preparing **3** are described by T. Engler and H. Shechter, *Tetrahedron Lett.*, submitted 1982. (b) O. Chapman, Chemical and Engineering News, American Chemical Society, Sept. 18, 1978, p. 78 reports that matrix photolysis of (1) 2-diazoacenaphthenone at 8°K yields 1,8-naphthyleneketene and (2) 8-hydroxy-1-naphthylglyoxylic acid at -195°C gives 1*H*-cyclobuta[*de*]naphthalen-1-one.

3. (a) All new compounds or their derivatives gave proper analyses, exact masses and spectra. (b) The methoxyarenylmethylsilanes of this research were prepared by the method used for **5**. After completion of the present work, benzyl methyl ether was reported to be deprotonated at the benzyl position by *n*-butyllithium/tetramethylethylenediamine, M. K. Yeh, *J. Chem. Soc., Perkin 2*, 1652 (1981). (c) The apparent mechanisms of formation of these products will be discussed in a future publication.

4. See W. M. Jones, R. C. Joines, J. A. Meyers, T. Mitsuhashi, K. E. Karjca, E. E. Waali, T. L. Davis and A. B. Turner, *J. Am. Chem. Soc.*, **95**, 826 (1973), T. Mitsuhashi and W. M. Jones, *ibid*, **94**, 677 (1972), T. J. Coburn and W. M. Jones, *ibid*, **96**, 5218 (1974) and ref. 1b.

5. (a) M. Gessner, P. Card, H. Shechter and G. Christoph, *J. Am. Chem. Soc.*, **99**, 2371 (1977). (b) M. Gessner, M.S. Thesis, The Ohio State University, Columbus, Ohio, 1977.

6. The ^{1}H and the ^{13}C NMR of the methylene bridges of the indicated *peri*-methanoarenes (ppm relative to TMS) are **3**, 4.69, 47.3, **10**, 4.60, 45.95, **17**, 4.76, 47.10, **19**, 4.70, -, **25**, 4.80, 46.56, **29**, 4.98, 46.34, and **31**, 5.19, 52.97, respectively.

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