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GENERATION OF BICYCLO[4.1.0]HEPTATRIENES.
CARBENE-CARBENE REARRANGEMENTS IN SOLUTION.

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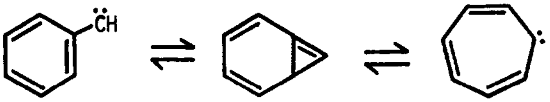
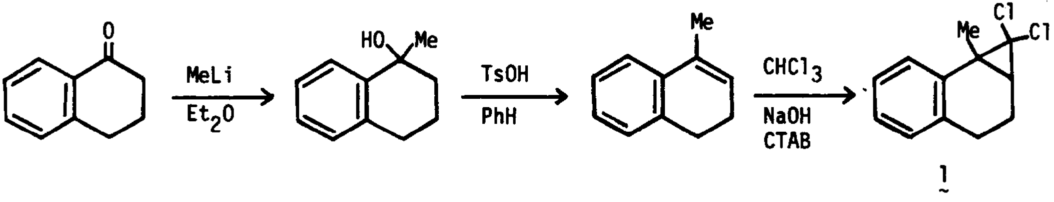
Since the initial discovery by Shechter and Vander Stouw[1] in 1965 of the multiple rearrangements associated with aryl carbenes, several groups[2] have investigated these rearrangements and evidence[2j,2k,3] has been presented for the discrete existence of bicyclo[4.1.0]heptatrienes in the interconversion of aryl and aromatic carbenes (eq. 1). Generation of the bicycloheptatrienes has been achieved primarily by the thermal (105° to 700°C, usually gas phase) or photochemical formation of either the aryl or aromatic carbene and subsequent rearrangement to the bicycloheptatriene. Alternatively, base induced dehydrohalogenation of suitably substituted halocyclopropanes[3] provides a nonphotochemical method for the generation of bicycloheptatrienes in solution, at or below room temperature, and under conditions which preclude any argument as to the vibrational or electronic state of the reactive intermediate. Another advantage of the latter method is that the bicycloheptatriene can be generated independently of either carbene and by choosing a suitable precursor, products derived by rearrangement through both paths of equation 1 can be observed.



(1)

Such a precursor is 1, whose synthesis was achieved in 48% overall yield as shown in Scheme I.

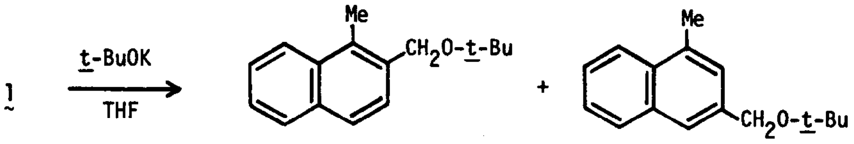
Scheme I



CTAB = cetyltrimethylammonium bromide

Compound 1 was purified by short path distillation (bp 77-80° / 0.07 mm), and displayed the following spectral properties: nmr ($CDCl_3$) δ 1.65 (s,3H), 1.66-2.80 (m,5H), 6.92-7.42 (m,4H); ir (neat) 740, 760, 820, 1010, 1130, 1380, 1445, 1480 cm^{-1}.

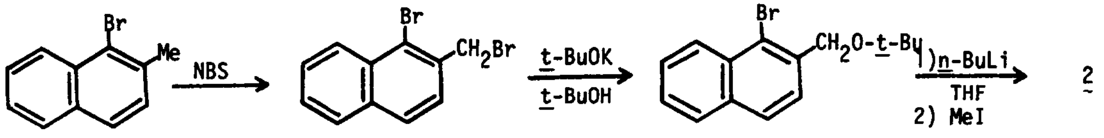
Treatment of 1 with KO*t*-Bu (15 equiv.) in THF at 15° for 23 hrs. gave a black viscous oil which was subjected to preparative TLC (silica gel, pentane-CH_2Cl_2) to yield unreacted starting material (38%) and *t*-butyl ethers 2 and 3 (43%) in a ratio of 1:2,[4a] respectively, (eq. 2). The nmr spectrum[4b] of the mixture left little doubt that it was two isomers of methyl (*t*-butoxymethyl)naphthalene. The high energy intermediates required for the formation of isomers other than 2 and 3 make their formation highly unlikely (*vide infra*).



2 3 (2)

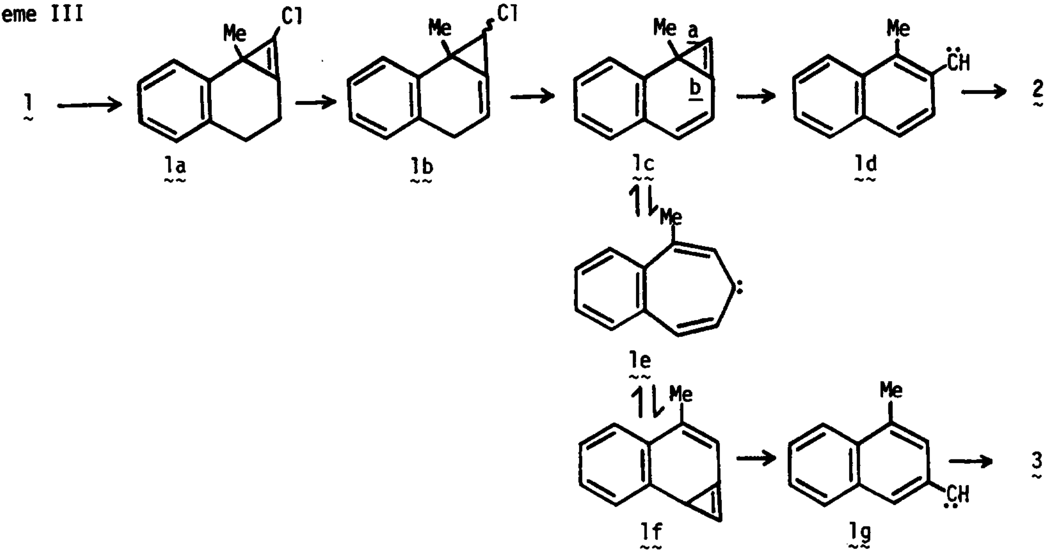
Separation of the ethers proved to be difficult; however, enriched samples of 2 (84:16)[5] and 3 (92:8)[5] were obtained by preparative TLC (silica gel, CCl_4). The compound eluting first was shown to be 2 by comparing its ir and nmr spectra and GC retention time with those of an authentic sample synthesized independently as shown in Scheme II. *t*-Butyl ether 2 (and the authentic sample) exhibited the following spectral properties: nmr ($CDCl_3$) δ 1.22 (s,9H), 2.52 (s,3H), 4.42 (s,2H), 7.05-7.90 (m,6H); ir (neat) 740, 765, 810, 860, 895, 1015, 1055, 1085, 1100, 1195, 1230, 1250, 1365, 1390, 1470, 1510, 1600 cm^{-1}. The spectral data of 3 are: nmr ($CDCl_3$) δ 1.35 (s,9H), 2.50 (s,3H), 4.72 (s,2H), 6.92-8.08 (m,6H); ir (CCl_4, CS_2) 735-805, 895, 1015, 1055, 1185, 1230, 1255, 1360, 1390, 1430, 1460, 1595, 1625, 1730, 1895, 1910, 1935 cm^{-1}.

Scheme II



The formation of 2 and 3 can be rationalized in terms of the mechanism shown in Scheme III.

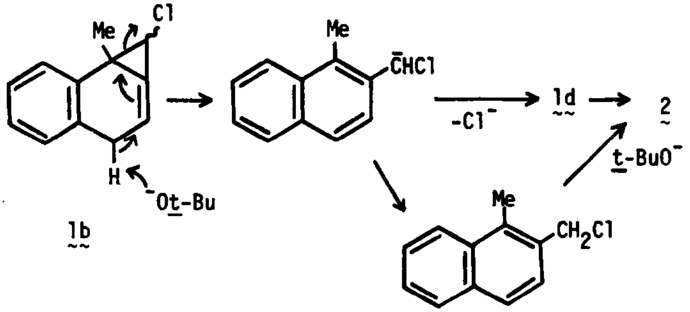
Scheme III



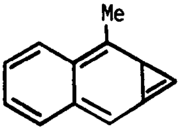
In this Scheme, base induced dehydrohalogenation of 1 leads initially to the cyclopropene 1a, but this compound isomerizes to 1b[6] under the basic conditions. *Syn* 1,4-elimination of HCl from 1b gives bicycloheptatriene 1c. Rearrangement of 1c may proceed by cleavage of bond a to give aryl carbene 1d or by cleavage of bond b to give aromatic carbene 1e. Reaction of the aryl carbene with t-BuO$^-$ followed by protonation results in ether 2, whereas 1e, due to the nucleophilicity of cycloheptatrienylidenes,[7] does not react with nucleophile but instead closes to give a new bicycloheptatriene, 1f, which leads to 3 via 1g. It is interesting that naphtho[a]-cyclobutene was not detected,[8] although it is the sole product when 1d is generated in the gas phase.[2g] This is attributed to the electrophilicity of 1d and the high concentration of t-butoxide that is present.

An alternate mechanism for the formation of 2, which bypasses 1c, is shown in Scheme IV. However, formation of ether 3 from 1d would still seem to require the intermediacy of bicycloheptatrienes 1c and 1f.

Scheme IV



Finally, isomers other than **2** and **3** and 1-vinylnaphthalene[2g] are precluded, because formation of the required intermediates, **4** and **5**, respectively, would result in loss of aromaticity, an unlikely rearrangement when lower energy paths can be followed.[2g,2i]



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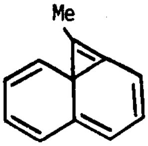

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4. (a) As determined by nmr spectroscopy. (b) There are 6 singlets, and the intensities and positions make it obvious that these are 2 sets of 3 each. Each set is in the ratio 9:3:2.
5. The relative ratio of *t*-butyl ethers **2** and **3** was determined by GLPC at 220°C on a 4'x0.25" column packed with Carbowax 20M on Anakrom ABS; compound **3** elutes first.
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8. As determined by GLPC co-injection with an authentic sample. We express our sincerest thanks to Dr. R. P. Thummel who provided the authentic sample of naphtho[a]cyclobutene.