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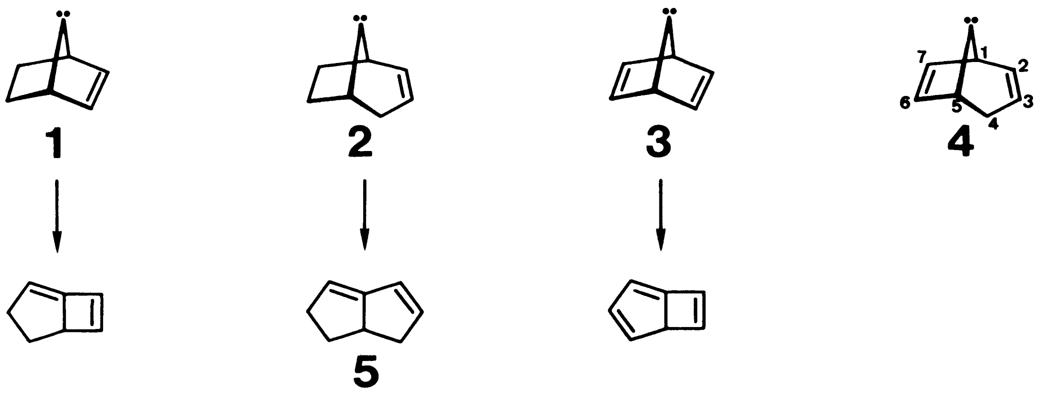
BICYCLO[3.2.1]OCTA-2,6-DIEN-8-YLIDENE (HOMO-7-NORBORNADIENYLIDENE), A "FOILED" CARBENE

Udo H. BRINKER*[1] and Lothar KÖNIG
Abteilung für Chemie der Ruhr-Universität, 4630 Bochum,
Federal Republic of Germany

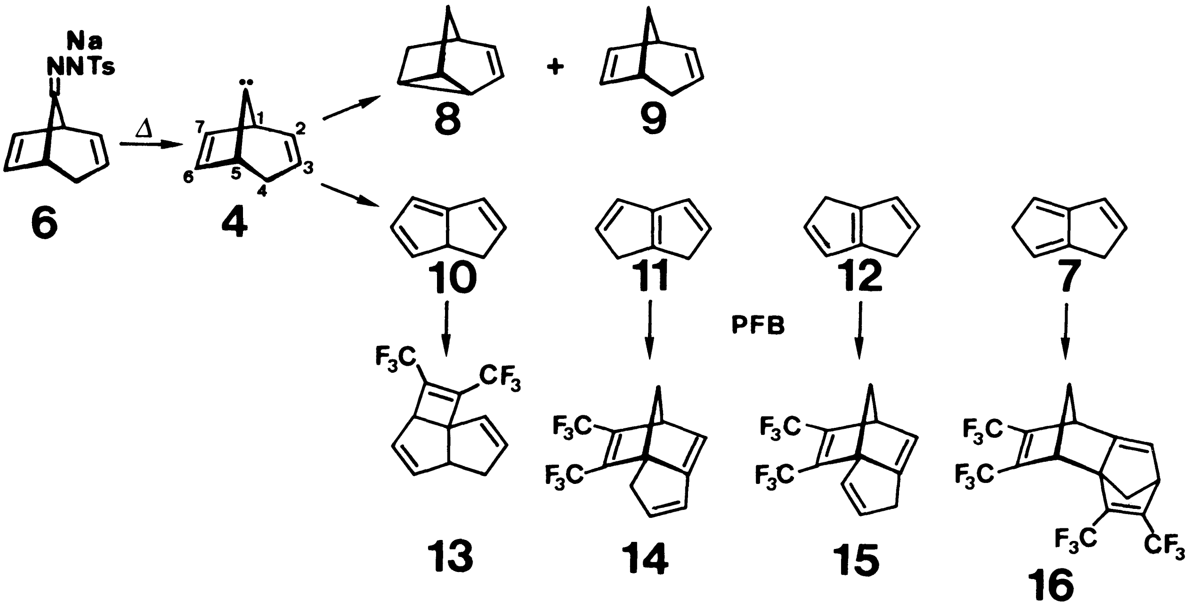
Bicyclo[3.2.1]octa-2,6-dien-8-ylidene nearly exclusively rearranges by 1,2-vinyl migrations. The interaction with the double bond of the six-membered ring dominates.

The reactive behavior of thermally generated 7-norbornenylidene (1),[2a,b,c] bicyclo[3.2.1]oct-2-en-8-ylidene (2)[3a,b,c] and 7-norbornadienylidene (3)[4] is clearly dominated by 1,2-vinyl migrations,[5] the typical reactions of the so-called "foiled" carbenes.[6] These species are foiled in their attempts to undergo intramolecular additions, which would result in extraordinarily strained structures.



In contrast to 1, 2, and 3, it has been reported that in bicyclo[3.2.1]octa-2,6-dien-8-ylidene (homo-7-norbornadienylidene) (4)[7] vinyl migration seems not to be the dominant reaction path. The decomposition of Bicyclo[3.2.1]octa-2,6-dien-8-one tosylhydrazone sodium salt (6) at 180 °C (2 Torr) led to bicyclo[3.3.0]octa-1,7-diene (5) (44%), 1,5-dihydropentalene (7) (28%), styrene (16%) and 5-ethynyl-1,3-cyclohexadiene (7%).[7] While there has been no explanation given for the formation of the main product 5 (a C_8H_{10}-isomer out of 4, a C_8H_8-carbene), 7 is thought to stem from a 1,2-vinyl migration by rupture of bond C-1-C-2 in 4.[7] Styrene and 5-ethynyl-1,3-cyclohexadiene are believed to derive from bicyclo[4.2.0]octa-1(2),-3,7-triene which is formed out of 4 by 1,2-vinyl migration (cleavage of bond C-1-C-7).

In connection with the potential carbene-carbene rearrangement with 1,3-carbon migration[3b,c,5,8] of bicyclo[4.1.1]octa-2,4-dien-7-ylidene[9] to 4, we studied the reactive behavior of 4 under conditions discussed previously.[10] Bicyclo[3.2.1]-octa-2,6-dien-8-one[11] was converted with p-toluenesulfonylhydrazide into the corresponding tosylhydrazone in a yield of 78% [mp: 172-173 °C (decomp); 154.5-155.5 °C (decomp)[7]] from which 6 was prepared in 82% yield. The pyrolysis of 6 at 220 and 250 °C/0.03 Torr[10] gave a mixture of hydrocarbons (55-65%) (see Table 1).



The major component was 1,5-dihydropentalene (7)[12] (52-74%). Tricyclo-[3.2.1.0^{2,7}]oct-3-ene (8) (5-12%) and bicyclo[3.2.1]octa-2,6-diene (9) (up to 1.5%) were also formed. Furthermore, benzene (0.9-1.7%), toluene (up to 1.3%) and styrene (up to 0.3%) were detected in the reaction mixture. Bicyclo[3.3.0]octa-1,7-diene, which has been claimed[7] to be the main product (44%) in the decomposition of 6, could not be detected. Also, under the above conditions, no direct evidence for the formation of 5-ethynyl-1,3-cyclohexadiene was found.

Table 1. Product Distribution from Decomposition of 6

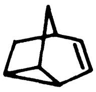
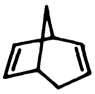
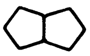
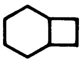
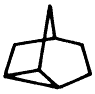
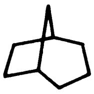
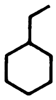
No.	T±5 °C	7	10-12						Total isolated yield/%
1	220	73.7	12.8	4.9	trace	-	trace	1.7	55
2	250	52.0	21.9	12.2	0.8	0.3	0.2	0.9	65

Table 2. Product Distribution from Decomposition of 6 in Presence of PFB

No.	13	14	15	16	Σ 13-16	Σ 13-16a) (%)
1b)	1.5	4.9	15.8	76.6	98.8	87
2c)	1.1	8.5	21.4	68.1	99.1	83

a) PFB-adducts = 100%; hydrocarbons, which were not trapped (Σ13% and Σ17%, respectively) are not listed. b) Addition of PFB after VPC analysis. c) Direct trapping.

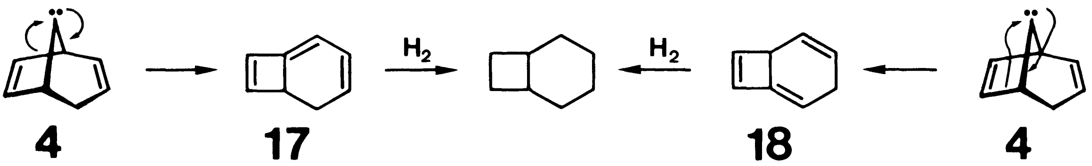
Table 3. Product Distribution from Decomposition of 6 after Hydrogenation (Pt/C)

No.						Σ(%)a)
1	83.0	9.5	0.8	0.2	1.2	94.7
2	91.3	4.9	0.3	0.1	0.5	97.1

a) Toluene and benzene were also present.

In order to trap dihydropentalenes which might have rearranged to the more stable 1,5-dihydropentalene (7)12) by 1,5-hydrogen migrations, the pyrolysate was allowed to react instantaneously with perfluoro-2-butyne (PFB) at -30 up to -40 °C (see Table 2). In a second experiment after VPC analysis the reaction mixture was diluted with $CDCl_3$ and treated with PFB. In all cases the adducts 13,14,15, and 16 were formed. The formation of 9 can be the result of a hydrogen abstraction process of 4 from the excess of sodium hydride present.13) Semibullvalene, which would result from the insertion of the divalent carbon of 4 into the C-H-bond of C-4, was not present even in trace amounts. Cycloheptatriene, the product expected from extrusion of carbon in 4, was not formed.

Three different 1,2-vinyl migrations can take place in 4. Cleavage of bond C-1-C-2 forms 1,6a-dihydropentalene (10),14) from which 1,5-hydrogen shifts lead to 11 and 12. Both rearrange by a further 1,5-H-migration to 1,5-dihydropentalene (7). The four isolated 1:1 and (or) 2:1-PFB adducts 13-16 15a-d) of the dihydropentalenes 10-12 and 7 make up ca. 85% of the total reaction mixture (see Table 2). There seems to exist a direct relationship between the thermal stability of dihydropentalenes 7 and 10-12 and the yields of PFB-adducts 13-16 (see Table 2). From 1,2-vinyl migrations by rupture of bond C-1-C-7 or C-5-C-6 in 4 bicyclo[4.2.0]octatrienes 17 and



18 would have been expected. These compounds, however, were not found. That vinyl migration(s) leading to 17 or (and) 18 is (are) involved can be concluded from the hydrogenation of the reaction mixture. Besides bicyclo[3.3.0]octane (91-83%) bicyclo[4.2.0]octane in 5-10% yield was formed (see Table 3).

Thus, in conclusion, in 4 1,2-vinyl migrations take place nearly exclusively (up to 96%). If the interaction of the carbene center with the C-2-C-3- and the C-6-C-7-double bonds are compared, the former is found to be much stronger. The preference for the formation of 1,6a-dihydropentalene (10) over the bicyclo[4.2.0]-octatriene(s) 17 or (and) 18 may be due to the fact that 10 contains less strain than 17 or 18.-4 is a valid member in the family of "foiled" carbenes.

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13) If for the preparation of 6 any excess of sodium hydride was avoided, the yield of 8 and 9 fell below 5%. 8 could originate from 9.- It has been demonstrated that if catalyzed by silicagel, 9 already rearranges to 8 at room temperature [I.I.Khochenko, E.M.Mil'vitskaya, A.F.Platê, and M.A. Pryanishnikova, J.Org.Chem., USSR 9, 2322 (1973)].
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