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7-NORBORNENYLIDENE - A POTENTIALLY NONCLASSICAL CARBENE

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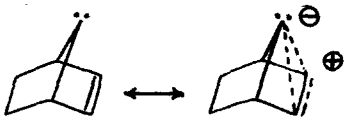
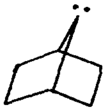
7-Norbornenylidene, I, is predicted to be a "singlet, stabilized, nonclassical methylene", its carbenic bridge ought to incline ~20° away from the vertical and toward the double bond.[1] No such stabilization is predicted for 7-norbornanylidene, II, which should have normal geometry and a triplet ground state.[1]

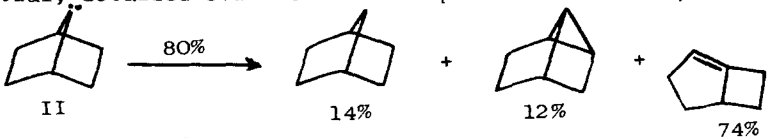


I



II

We have discussed the intramolecular chemistry of thermally-generated II[2] (summarized in eq. [1]), which should significantly differ from that of I. Now we report initial, detailed studies of the important carbene I, and we comment on



[1]

its intramolecular chemistry.

7-Norbornenone[3] tosylhydrazone (83%, mp. 156-157.5° decomp., from CH_3OH),[4] was converted to its Li salt with 1 equiv. of n-butyllithium in ether. After thorough vacuum drying, 5 g. of the salt was pyrolyzed in a previously degassed system at 0.05 Torr. and 190-191°. The approach to the rather sharp pyrolysis temperature was made at ~0.35°/min. from 179°, where the salt was stable for at least 15 min.[5] About a 50% yield of hydrocarbon product mixture was trapped at 77°K. Gc indicated 17 components, most of which were very minor (<1%). We used a 15', 0.25'', 15% SF-96 on 90/100 Anakrom ABS column at 50°, programmed to 160°, in stages, over 164 min. Injector and detector temperatures were 120° and 130°.

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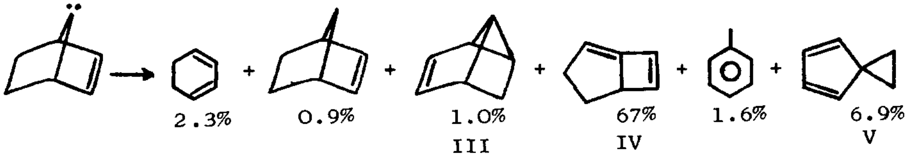
Gc isolation was carried out at a column temperature of 50°. The major identified products and their distribution (% of all products, uncorrected for gc detector response) are shown in eq. [2].

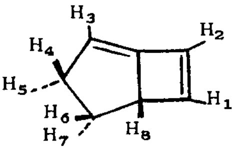


[2]

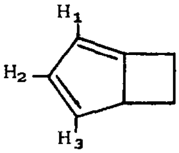
1,3-Cyclohexadiene, toluene, and spiro[2,4]heptadiene, V,[6] were identified by comparison of their nmr spectra and gc retention times with those of authentic samples. Norbornene and III[7] were identified only by retention times.

Bicyclo[3.2.0]heptadiene-1,6, IV, had M^+ at (m/e) 92 (30.3%), a base peak at 91, and a "carbon count" of 7 (m/e 93 was 2.4%).[8] A pure sample absorbed 2.0 equiv. of H_2 (10% Pd/C, -30°, ether), yielding bicyclo[3.2.0]heptane, identical (nmr) with a sample prepared by hydrogenation of bicyclo[3.2.0]heptadiene-2,6.[9]

Definitive spectral identification of IV[10] is based upon the 100 MHz. nmr spectrum (CS_2, -47°) and 60 MHz. double resonance experiments (CS_2, 32°). Eight distinct 1-proton signals (3 vinyl, 1 doubly allylic, 2 allylic, and 2 "isolated") were observed[14] and are assigned as follows: 6.71δ, d, J=1.5, H2; 6.40δ, t, J~2, H1; 4.96δ, q, spacings ~1.5, H3; 3.38δ, crude "t" (each branch further split), spacings 8, H8; 2.83δ, m (7 bands, each with further splitting), major separations ~5, H4; 2.27δ, octet, spacings 4, H5; 1.91δ, quintet, spacings ~6, H6; 1.53δ, m in 5 major sections (individual peaks at 1.72, 1.64, 1.62, 1.61, 1.54, 1.53, 1.51, 1.43, 1.42, 1.40, 1.31), H7. The spectrum is consistent with IV, but not with diene, VI. (VI is the most difficult-to-exclude alternative among the 9 other, non-allenic bicyclo[3.2.0]heptadienes). The chemical shift of H3 is not consistent with any of the cyclopentadiene protons of VI, but is reasonable for IV. (The analogous proton in bicyclo[3.2.0]heptene-1 occurs at 5.13δ).[2] Double resonance experiments show that H3 is coupled to H4 and H5 (by ~2 and 4 Hz.), but it is not coupled to either H2 or H1 (<1 Hz.), which are mutually coupled by ~2 Hz. These observations are consistent with IV.[15,16,17] In VI, however, each vinyl



IV

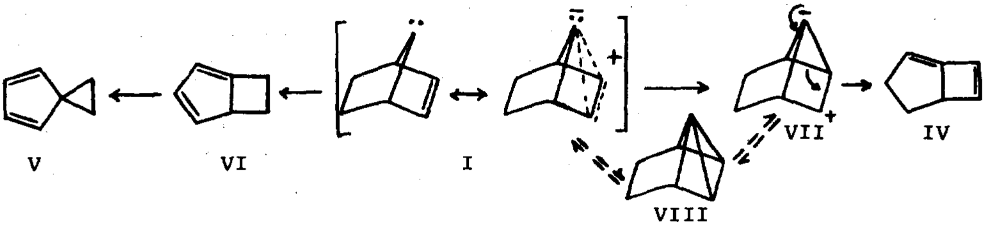


VI

proton should be coupled to at least one other vinyl proton (J_{12}~2, J_{23}~5 Hz.).[17] Allylic proton 5 can be readily analyzed giving J_{54}=16, J_{53}=4, and J_{57}=8 Hz. H5 is not coupled to H6. A model of IV, constructed to maximize p orbital overlap, indicates a dihedral angle of 90° between H5 and H6, predicting J=0.[17] Additional double resonance experiments, and a satisfactory computed spectrum, with associated, consistent J values, support the above assignments.[18]

Control pyrolyses experiments, over lithium toluene-p-sulfinate at 180-195° and 0.1 Torr., demonstrated the stability and independence of III, IV, and V. Gc experiments showed invariant product distribution at varying injector temperatures up to 185°. IV could be rearranged in a glass flow system at 170°, *15 seconds residence*, He stream, to toluene and benzene. No other products could be detected; V was stable under these conditions.[19]

Eq. [3] offers an attractive rationalization for the formation of products IV and V. IV could arise by fulfillment of the carbene-π interaction;[1] perhaps



[3]

via dipolar VII, which combines features of a cyclopropyl anion and a cyclopropylcarbinyl cation. (VII could be either a transition state or an unstable intermediate). The "foiled methylene" adduct,[1] VIII, could also be a fleeting intermediate.[21] Alternatively, IV could arise *via* a direct, 1,7-vinyl shift, favored[22] by the calculated, distinctive geometry of I.[1] Migration of the ethano bridge of I could afford unstable VI, and thence V. Dominance of IV over V (VI), and reduced insertion and abstraction (compared to II) may suggest special electronic and geometric features in I.[1] 1,3-Cyclohexadiene could stem from cycloreversion of I, accompanied by the release of C_1. This would resemble the behavior of 7-quadricyclanylidene.[23] Reversion of I to cyclopentadienylidene and ethylene, followed by cyclopropanation, constitutes an alternative route to V, which we will investigate.

Fisch and Pierce have recently described reactions of bicyclo[3.3.1]non-2-

en-9-ylidene, which they analyzed as suggestive of a "foiled methylene" (nonclassical carbene).[24] It remains to be seen whether the related intramolecular chemistry reported for this species,[24] and now for I, is diagnostic of a nonclassical carbene. We are searching for "nucleophilic" intermolecular chemistry of I, which could aid in this evaluation.

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