Evidence for a "Foiled Methylene" in the Reactions of Bicyclo[3,3,1]non-2-en-9-ylidene†

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Summary. The carbene (**1**) reacts intramolecularly in a way strongly suggestive of preliminary interaction with the double bond; and, although cyclopropane formation is prevented by geometric factors, the "foiled methylene" determines the ultimate products.

HOFFMANN *et al.*[1,2] have recently reconsidered the reactions of singlet and triplet methylene on the basis of orbital correlation diagrams. In addition to rationalizing the stereospecificity of methylene additions to olefins,[3] they considered how a singlet ground state for methylene might be stabilized.[2] From these calculations, interaction of methylene with a double bond, a process calculated to have no activation energy,[1] ought to stabilize the singlet ground state, even if final cyclopropane formation is sterically impossible (the "foiled methylene"). Verifying this prediction is a two part problem: (i) is interaction with the double bond detectable; (ii) is the ground state of the foiled methylene a singlet? We report a test of the first of these points.

Consider bicyclo[3,3,1]non-2-en-9-ylidene (**1**) which can be generated by thermal decomposition of the tosylhydrazone sodium salt derived from bicyclo[3,3,1]non-2-en-9-one, (**2**).[4] In this species, attack on the double bond to form a cyclopropane would result in the extraordinarily strained (**3**), a structure which is well-nigh impossible to make, even with plastic tubular models.[5]

If one avoids eclipsing the hydrogens at C-4 and C-5 in (**1**), the axial C-H bonds (C-4, C-6, and C-8) are all in the proper relationship to the carbene centre for insertion.[6] Of these, the allylic bond may be the most reactive,[7,8] conformation permitting, and thus we would expect (**5**) to be the major cyclopropyl olefin among the products. In the event of rearrangement, migration of the allylic bond would presumably predominate to yield (**9**) rather than (**8**).

On the other hand, if interaction is important enough to attain "non-classical" stabilization,[2b] some deformation of the cyclohexene ring is expected so as to bring C-9 closer to the double bond. Models show the axial hydrogen at C-4 will then pivot toward an equatorial position, *i.e.* into the *wrong* stereochemistry for insertion, and favour the non-allylic cyclopropyl olefins (**6**) and (**7**) rather than (**5**). In addition, the interaction with the double bond may enhance the extent of migration by that bond (C-2) to yield (**8**).

The results permit a clear choice between these two

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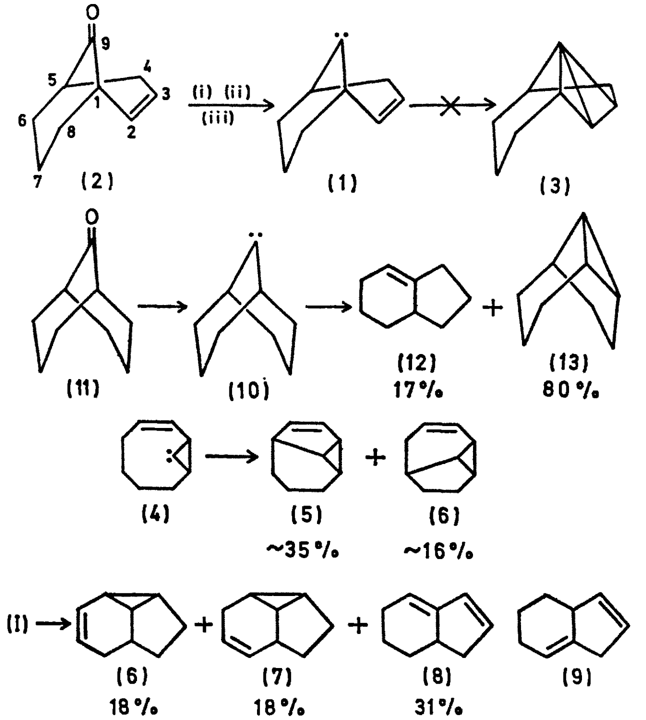
alternatives. Tosylhydrazone decomposition to (**1**) yields a mixture of hydrocarbons in an overall yield of 85%. The major component (31%) is a tetrahydroindene, as required by its hydrogenation to hydrindane and the presence of *three* vinylic protons in the n.m.r. [$CDCl_3$ with Me_4Si, AB pattern (2H) centred at δ 5·97 and a multiplet (1H) at δ 5·35]. The double bonds are conjugated and heteroannular [λ_{max} (Et_2O) 236 nm; calc. λ_{max} 234 nm] with the disubstituted double bond in the five-membered ring (*J* 6·0 Hz.).[9] Only (**8**) is consistent with all the data. The diene is homogeneous on all columns tried, from Silicone DC 550 to silver nitrate on Carbowax 20 M, and the n.m.r. shows no absorption in the region of δ 2·7—3·0, where one would expect the signal of the bisallylic protons in (**9**) if the allylic bond had migrated.[10]

The most important other products are two isomers formed in equal amounts (18% each). Both have the same carbon skeleton as shown by their hydrogenation to (**8**), and each has two vinyl hydrogens by n.m.r. Only three isomers, (**6**), (**7**), and (**8**) are possible. Following the method of Gardner,[7a] (**5**) and (**6**) were synthesized *via* (**4**) for direct comparison with the products (g.l.c., mass spectrum, and n.m.r.). In this way, one isomer was shown to be (**6**) and the other to be different from both the known compounds. The second product must be the unknown (**7**). We estimate our combined preparative g.l.c.–n.m.r. analysis would easily have detected 1% of (**5**) in the product mixture.



Reagents: (i) $TsNHNH_2$; (ii) NaH; (iii) Heat.

The remainder of the hydrocarbon product consisted of bicyclo[3,3,1]non-2-ene (11%), presumably arising *via* hydrogen abstraction from product diene or solvent by carbene (**1**), indane (8%), and a complex mixture of at least three unidentified compounds (13%).

The results are consistent with a controlling directive influence by a "foiled methylene." There is a high proportion of rearrangement to diene (**8**), equal amounts of (**6**) and (**7**), and essentially complete absence of both cyclopropyl olefin (**5**) and diene (**9**) from the products.

As an additional test of our predictions, we examined the saturated carbene (**10**) prepared from the tosylhydrazone of bicyclo[3,3,1]nonan-9-one (**11**). As expected, the major reaction pathway was C–H insertion to the known tricyclo-[4,3,0,0^{2,9}]nonane (**13**) (80%)[7] together with minor rearrangement to tetrahydroindane (**12**) (17%). A trace of bicyclo[3,3,1]nonane was also isolated. The overall yield was 60%. Tricyclo[4,3,0,0^{2,9}]nonane (**13**) was identified by direct comparison of its mass spectrum and n.m.r. with those of the known compound[7b] and bicyclo[3,3,1]nonane was identical in all respects with an authentic sample prepared by Wolff–Kishner reduction of bicyclo[3,3,1]-nonan-3-one. Proof of structure (**12**) rests upon its hydrogenation to hydrindane, mode of formation, and the presence in its n.m.r. spectrum of only one vinyl proton signal ($CDCl_3$ with Me_4Si, δ 5·38). From these results, it is clear that the predominant rearrangement observed in the olefinic system must be related to the presence of the double bond and is not characteristic of the bicyclo[3,3,1]nonane system itself.[11]

According to Hoffmann *et al.*[2b] the carbene, (**1**) ought to have a singlet ground state. Appropriate experiments to test this prediction will be reported in our full paper.

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