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THE REACTIONS OF EXO- AND ENDO-TRICYCLO[3,2,1^{2,4}]OCTAN-8-YLIDENES

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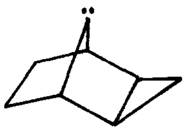
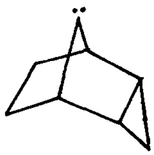
7-Norbornenylidene (1) and bicyclo[3,3,1]non-2-ene-9-ylidene (2) can be considered to be a singlet stabilized nonclassical methylene (3), and its carbenic bridge interacts with the p-orbital of the double bond. In connection with this, the reactions of exo- (**1**) and endo-tricyclo[3,2,1,0^{2,4}]octan-8-ylidenes (**2**) are of interest, since significant homoconjugative interaction between the p-orbital of the divalent carbon and the symmetric Walsh orbital of the cyclopropane ring can be expected. At a developing carbonium ion center, cyclopropyl homoconjugative participation has been clearly demonstrated (4). Further, the kinetic results (4) as well as extended Hückel calculations (5) on 8-tricyclo[3,2,1,0^{2,4}]-octenyl cation definitively indicated primary stabilization of the bridge cation from interaction with the cyclopropane ring rather than the double bond.

The interesting results on the chemistry of **1** and **2** recently communicated by Freeman (6) stimulated us to report our own closely related results which are somewhat different from those of Freeman but clearly demonstrate the presence of trishomocyclopropenyl interaction in endo-carbene **2**.

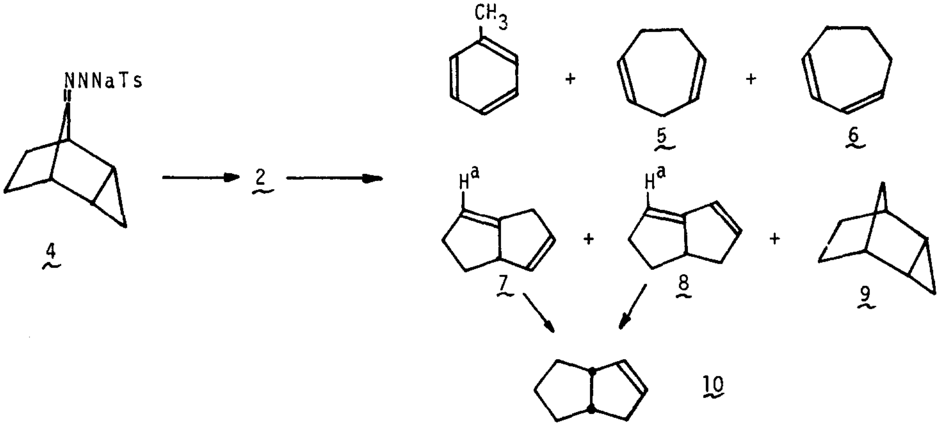


1



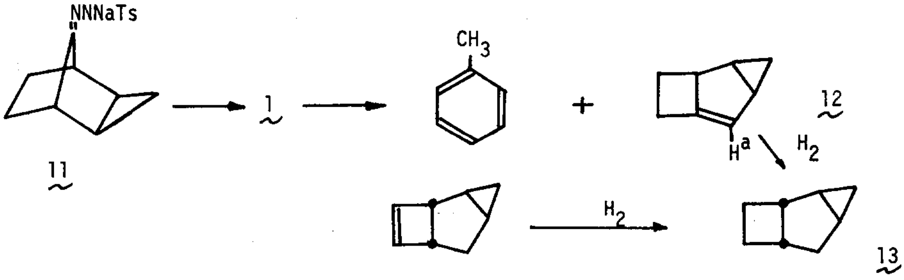
2

endo-Tricyclo[3,2,1,$0^{2,4}$]octan-8-one tosylhydrazone (3, mp 171-172°, decomp) (7) was converted to the sodium salt (4) on treatment with sodium hydride. On vacuum pyrolysis of 4 at 180°, hydrocarbon products (56 %) were collected in a trap at 77 °K. Vpc analysis (KF-96, 60°) indicated the products consisted of six hydrocarbons as shown in eq. 1; toluene (6.9 %), cyclohepta-1,4-diene (5, 25 %), cyclohepta-1,3-diene (6, 6.3 %), bicyclo[3,3,0]octa-1,6-diene (7, 8.6 %), bicyclo[3,3,0]octa-1,7-diene (8, 16 %) and endo-tricyclo[3,2,1,$0^{2,4}$]octane (9, 38 %). The structures of 5-6 (8) and 9 (7) were established by comparison of these spectral data with those of authentic samples. The highly unstable olefins 7-8 were determined by the following data. The 1,6-diene 7 (9), m/e 106, $\lambda_{max}^{n\text{-}hexane}$ 2.18 nm, nmrδ5.43 (m, H^a), 5.83 (s, 2H), 3.75-3.27 (m, H), 2.87-2.5 (m, 2H), 2.60-0.90 (m, 4H). Careful hydrogenation over palladium in carbon tetrachloride gave cis-bicyclo[3,3,0]oct-2-ene (10) (10). The 1,7-diene 8, m/e 106, $\lambda_{max}^{n\text{-}hexane}$ 246 nm, nmrδ5.27 (m, H^a), 6.23 (s, 2H), 3.38-2.83 (m, H), 2.83-0.56 (m, 6H). Similar hydrogenation of 8 gave 10.



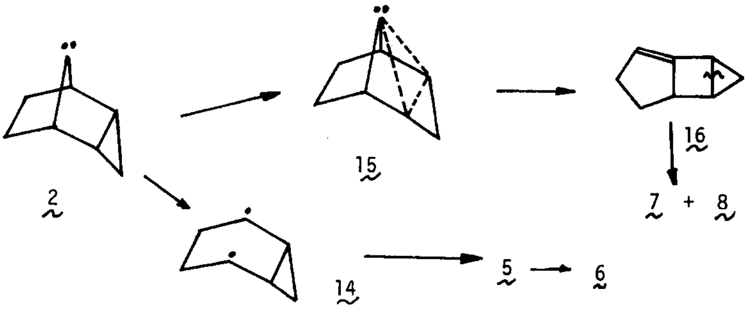
eq. 1

In sharp contrast, vacuum pyrolysis of the sodium salt (11) of exo-tricyclo-[3,2,1,$0^{2,4}$]octan-8-one tosylhydrazone (mp 165-166°, decomp) gave hydrocarbons (60 %), which consisted of tricyclo[5,1,$0^{1,7}$,$0^{3,6}$]oct-2-ene (12, 95.3 %), and toluene (2.5 %). The nmr spectrum of 12 reveals a multiplet at δ5.13 (m, H^a) and multiplets at 3.23-2.63 (3H), 2.35-1.53 (4H), 1.18-0.95 (H) and 0.55-0.35 (H). Careful hydrogenation of 12 over palladium black at -30~-20° absorbed one equivalent of hydrogen, yielding trans-tricyclo[5,1,$0^{2,5}0^{1,7}$]-octane (13), m/e 108, nmrδ 2.77-1.00 (m, 10H), 0.64-0.24 (m, H), -0.19~-0.44 (m, H), which was independently prepared by hydrogenation of trans-tricyclo[5,1,$0^{2,5}$,$0^{1,7}$]oct-3-ene(11) over palladium black in methanol.



The products of the above reactions are paralell with those from free carbenes (1-2, 12), however, they are quite different from those derived from thermal decomposition of 4 as well as 11 prepared by using sodium methoxide in diglyme (6). Thus, tetracyclo[3,3,0,$0^{2,8}0^{4,6}$] octane, which is a main product on decomposition of 4 in diglime, could not be detected among the products of the vacuum pyrolysis of 4. Under the former condition, two major reaction routes, a carbonium ion pathway as well as a carbene pathway can be involved, and real chemical difference between 1 and 2 can not clearly discussed, since carbon-hydrogen and carbon-skelton rearrangements can be derived from a highly energetic cation (13).

Attractive reaction-pathway affording 5-8 is shown in Scheme 1. Diene 7-8 can be formed by bond cleavage between C-1 and C-7 of a highly strained intermediate 16 derived from symmetrical interaction of the olefinlike cyclopropyl ring orbitals with the p-orbital of the divalent carbon (15). This would resemble the behavier of norbornenylidene (1) and bicyclo[3,3,1]nonen-9-ylidene (2), and clearly suggests the nonclassical stabilization of singlet carbene of 2. Cycloheptadiene 5 can stem from cycloreversion (8) of 2 via a biradical intermediate 14, accompanied by the release of C_1 (1, 14). Diene 6 is an isomerization-product of 5, while 9 is an hydrogen-abstraction product of 2.



Scheme 1

On the contrary, in exo-carbene **1**, participation of the cyclopropane ring to stabilize **1** can be completely eliminated, and presumably on steric reason, migration of C-2 (**17**) affording **12** is a exclusive pathway. Analogous 1,2-alkylation is a main pathway of 7-norbornanylidene (12).

11 **12**

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