

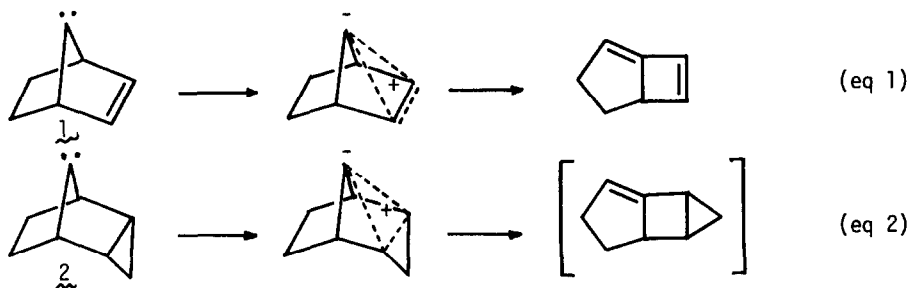
ENDO-TRICYCLO[3.2.1.0^{2,4}]OCT-6-EN-8-YLIDENE AND BICYCLO[3.2.1]OCTA-2,6-DIEN-8-YLIDENE.
 QUANTITATIVE ASSESSMENT OF HOMOALLYLIC CONJUGATION.

Kazuo Okumura and Shun-Ichi Murahashi*

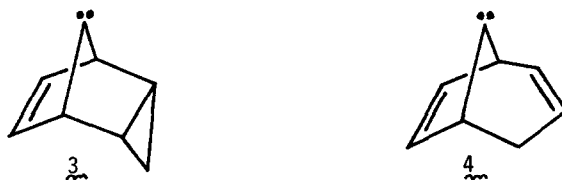
Department of Chemistry, Faculty of Engineering Science, Osaka University,
 Machikaneyama, Toyonaka, Osaka, 560, Japan.

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The interaction between the vacant p-orbital of the divalent carbon and the p-orbital of the carbon-carbon double bond (eq 1) or the Walsh orbital of a cyclopropane ring (eq 2) to stabilize sp² hybrid of the singlet state¹ has been demonstrated in foiled methyenes such as 7-norbornenylidene (1)^{2,3}, bicyclo[3.3.1]non-2-en-9-ylidene⁴, bicyclo[3.2.1]oct-2-en-8-ylidene⁵, endo-tricyclo[3.2.1.0^{2,4}]oct-8-ylidene (2)^{3,6,7}, bicyclo[4.2.1]nona-2,4,7-trien-9-ylidene⁸. In order to obtain quantitative assessment of such interaction, we investigated endo-Tricyclo-

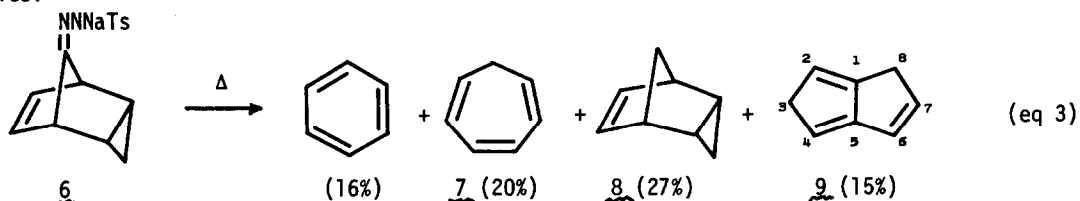


[3.2.1.0^{2,4}]oct-6-en-8-ylidene (3) and bicyclo[3.2.1]octa-2,6-dien-8-ylidene (4), since each of them has two possible features of the homoallylic interaction.

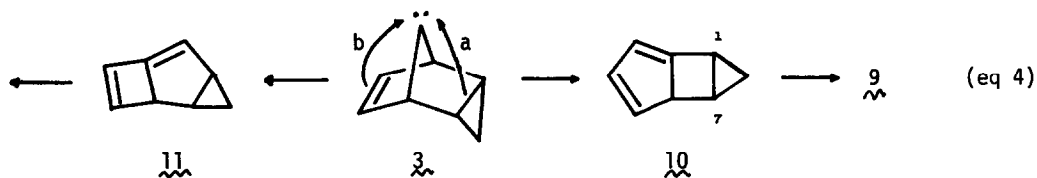


The reaction of endo-tricyclo[3.2.1.0^{2,4}]oct-6-en-8-one⁹ with tosylhydrazine in chloroform at 0° for 3 days in the presence of anhydrous magnesium sulfate gave the corresponding tosylhydrazone (5)^{10,11}, (22%, mp 145.5-146° (decomp)). After through vacuum drying, the sodium

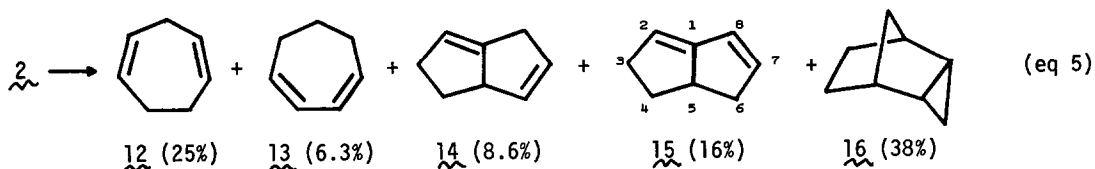
salt (6), prepared from 5 on treatment with sodium hydride in THF, was pyrolyzed in a previously degassed system at 5 mmHg and 180°¹². A hydrocarbon product mixture (60%) was trapped at 77 K. The glpc analysis (10% KF-96 on Celite 545 AW, 2m, 80°) showed that the pyrolysate consisted of four main hydrocarbons as shown in eq 3. These were readily assigned to benzene (16%), cycloheptatriene (7, 20%), endo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (8, 27%)¹³, and bicyclo[3.3.0]octa-1,4,6-triene (9, 15%)¹⁴ by comparison of their IR and NMR spectra with those of the authentic samples.



Dihydropentalene 9 can be formed by bond cleavage between C₁-C₇ bond of a highly strained intermediate of 10 derived from symmetrical interaction of olefin like cyclopropyl ring orbitals with p-orbital of the divalent carbon as indicated in eq 4. An alternative pathway to give 11



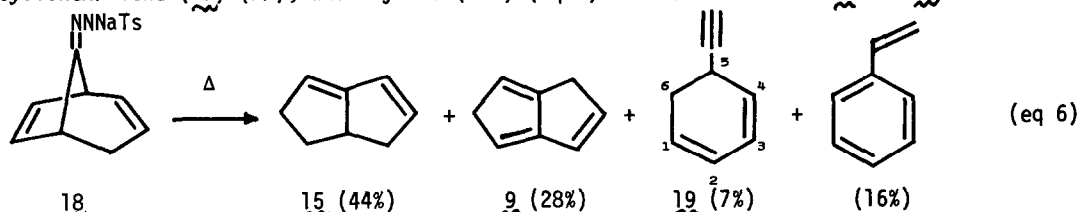
seems not to be operative, since 11 or its related products could not be detected among the pyrolysate. Interestingly, the distribution of the products from 3 (7 : 8 : 9 = 1 : 1.3 : 0.7) is closely related with that from 2^{3,6} (12 + 13 : 14 + 15 : 16 = 1 : 1.2 : 0.8) (eq 5).



Consequently, the homoconjugative interaction of the carbenic p-orbital with the Walsh orbital is much stronger than that with the p-orbital of the carbon-carbon double bond. This is consistent with the result of the corresponding carbonium ion, where the homoconjugation with a cyclopropane is 1.3×10^3 times stronger than that with the carbon-carbon double bond¹⁵.

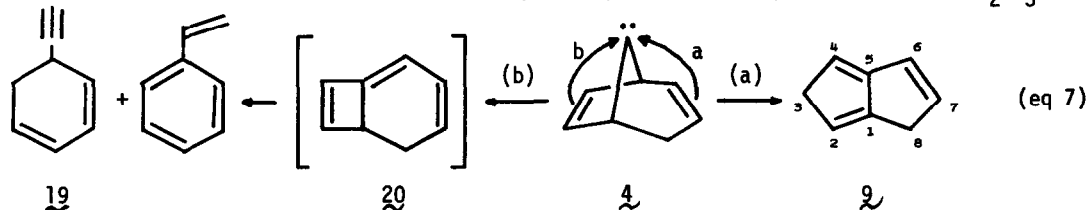
Bicyclo[3.2.1]octa-2,6-dien-8-one tosylhydrazone (17) was prepared from the reaction of the corresponding ketone¹⁶ with tosylhydrazine in chloroform, mp 154.5-155.5° (decompt)¹¹ (86%). On vacuum pyrolysis of the sodium salt (18) of 17 at 180°, hydrocarbon products (70%) were

collected in a trap at 77 K. Glpc analysis (20% KF-96 on Celite 545 AW, 1m, 80° and 20% Ucon oil on Celite 545 AW, 1m, 80°) showed that the pyrolysate consists of 15 (44%), 9 (28%), 5-ethynyl-1.3-cyclohexadiene (19) (7%), and styrene (16%) (eq 6). The structures of 9 and 15¹⁷ were



established by comparison of the spectral data with those of authentic samples. The highly unstable 19¹⁸ was assigned by the following data. m/e 104; $\lambda_{\text{max}}^{\text{hexane}}$ 256 nm; ir (liquid film) 3305, 2117 cm^{-1} ; nmr (δ , CCl_4) 5.84 (broad singlet, 4H) 3.25 (broad triplet, $J=10.6$ Hz, 1H) 2.6-2.2 (m, 2H) 1.91 (doublet, $J=2.8$ Hz, 1H). Similar vacuum pyrolysis of the sodium salt of bicyclo[3.2.1]octa-2,6-dien-8-one-4,4- d_2 tosylhydrazone gave bicyclo[3.2.1]octa-2,6-diene-4,4- d_2 (5%), 15-6,6- d_2 (11%)¹⁷, 9- d_2 (35%), 19- d_2 (5%), styrene- d_2 (17%). The deuterium scrambling can be seen in the latter three products.

The formation of 9 can be explained in terms of a carbene-carbene rearrangement (path a), whereas 19 and styrene can be rationalized by assuming an initial carbene-carbene rearrangement (path b) to 20, followed by ring opening of cyclobutane ring (eq 7). The product ratio of 9 / 19 + styrene is 1.2 ~ 1.7, indicating that the participation of the p-orbital of the $\text{C}_2\text{-C}_3$ bond



towards the divalent carbon is stronger than that of the $\text{C}_6\text{-C}_7$ bond. The transformation of 4 to 9 was recently indicated in the reaction of 8,8-dibromobicyclo[5.1.0]octa-2,4-diene with methyl lithium, where bicyclo[5.1.0]octa-2,4-dien-8-ylidene rearranges to 4 which undergoes rearrangement to 9¹⁹. The molecular model of 4 shows that the overlapping of the carbenic p-orbital with the $\text{C}_2\text{-C}_3$ double bond is larger than that with $\text{C}_6\text{-C}_7$ double bond. The stronger homoallylic interaction with the $\text{C}_2\text{-C}_3$ double bond in 4 is in contrast with that with the $\text{C}_6\text{-C}_7$ double bond in exerting anchimeric assistance in the solvolytic reaction of endo-bicyclo[3.2.1]octa-2,6-dien-8-yl tosylate¹⁶.

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