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# THERMAL REARRANGEMENTS OF *EXO*- AND *ENDO*-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE

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The study of transition metal catalyzed isomerization reactions of *exo*- and *endo*-tricyclo-[3.2.1.$0^{2,4}$]octene (1 and 2, respectively) has received recent attention.[1] Photochemical reaction of either isomer affords the $[{}_{\sigma}2_{s} + {}_{\pi}2_{s}]$ cycloaddition product, tetracyclooctane 4.[2] Thermal rearrangements of derivatives of the parent system afford a variety of products which have been rationalized in terms of diradical mechanisms.[3]

We wish to report that 1 rearranges quantitatively to a 4:1 mixture of bicyclo[3.2.1]octa-2, 6-diene (3) and tetracyclo[3.3.0.$0^{2,8}$.$0^{4,6}$]octane (4) upon pyrolysis in the gas phase at 290°. By contrast, the *endo* isomer 2 rearranges quantitatively to a 98:2 mixture of 4 and 3, respectively. Product stability studies indicate that 4 slowly rearranges to 3 upon heating to 290°. Thus, it appears that 4 is the sole primary product from the *endo* isomer.[4] Interestingly, the rate of formation of 4 for the *endo* isomer is approximately 45 times the rate for the *exo* isomer (Table 1). The difference can be accounted for largely by the larger torsional interactions between the hydrogens at C-1 and C-2 and at C-4 and C-5 in the *endo* isomer. These forces are relieved by cleavage of the C-2, C-4 carbon bond to afford a diradical, which then undergoes cyclization. Torsional arguments have been used to explain the preference for *exo* hydride migration in the norbornyl cation,[5] and the preference seems to manifest itself in a similar rate difference (*exo:endo* hydride migration > 100).

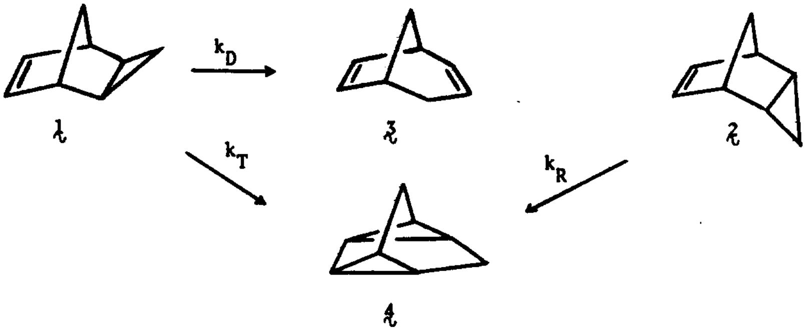
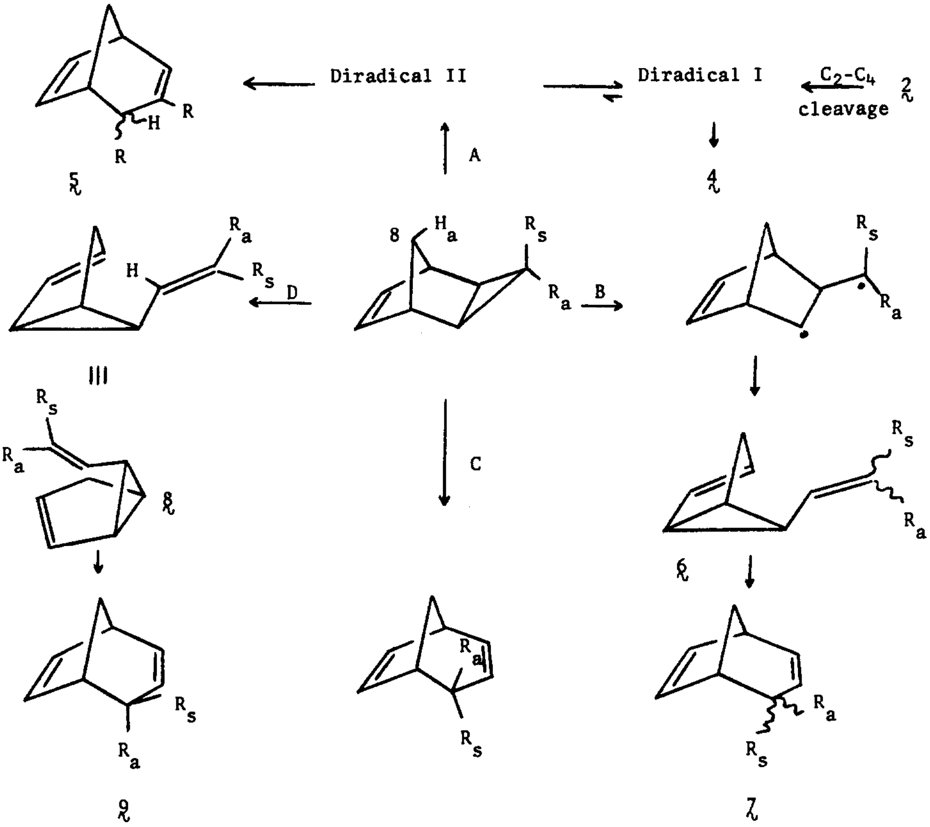


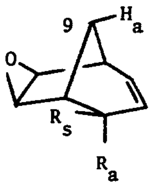
Table 1. Rates for Thermolysis of the Tricyclooctenes

| | k at 287.5° x $10^5$ $sec^{-1}$ |
|---|---|
| $k_T$ | 0.33 ± 0.015 |
| $k_D$ | 1.3 ± .15 |
| $k_R$ | 15 ± 1.5 |

The mechanism for the formation of **3** in the pyrolysis of **1** can be rationalized in several ways. Fission of the $C_2$-$C_4$ bond with generation of a diradical, necessarily different from that from **2**, followed by hydrogen shift to form **5** represents one alternative (pathway A). A second possibility consists of cleavage of the $C_2$-$C_3$ bond to a diradical, followed by bond reorganization to divinylcyclopropane **6** which is known to rearrange to bicyclooctadiene **3** [6] (pathway B). The intermediate radical center at $C_3$ should have a lifetime sufficiently long to permit stereochemical equilibration at that center,[7] resulting in scrambling of $R_s$ and $R_a$ in **6** and **7**. Diradical pathways may be avoided in a concerted rearrangement $[_{\sigma}2_s + _{\sigma}2_a]$[8] leading directly to bicyclo[3.2.1]octadiene (pathway C) or in a $[_{\pi}2_s + _{\sigma}2_a + _{\sigma}2_a]$ cycloreversion (pathway D) to the divinylcyclopropane derivative **8** which then rearranges stereospecifically[9] to **9**.



A sample of 1, deuterated at $C_3$, whose $d_{syn}/d_{anti}$ ratio was determined to be 2.0 ± 0.1 and whose total deuterium content was 88.5 ± 2.0%,[10] was pyrolyzed. The bicyclooctadiene formed was isolated and converted into monoepoxide 10.[12] Addition of $Eu(fod)_3$ resulted in separation of all hydrogens. Analysis of the spectrum[13] revealed that all the deuterium(88.2 ± 2.6%) was at $C_4$ and that the $d_{exo}/d_{endo}$ ratio was 2.0 ± 0.1. It is clear that these results support only the concerted $[{}_{\pi}2_s + {}_{\sigma}2_a + {}_{\sigma}2_a]$ alternative. This particular process would require considerable interaction of the π-system with the cyclopropyl group in the developing transition state; such an interaction not only seems reasonable, but has been demonstrated in 1 and not in 2 by photoelectron spectroscopy.[14]



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4) The reactions are sensitive to the presence of trace impurities on the glass surface, which can result in a less clean reaction and some polymerization. The most consistent results were obtained by washing the pyrolysis tubes with dilute ammonia.

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9) B. C. Cantello, J. M. Mellor and G. Scholes, *J. Chem. Soc. C*, 2915 (1971).

10) The *syn/anti* ratio could be estimated by conversion to the epoxide[11] and conducting a chemical shift study using Eu(fod)$_3$. Protons $R_s$, $R_a$ and $H_{8a}$ were isolated on a 250 Hz scan. Percentage deuterium and $d_{syn}/d_{anti}$ were estimated using $H_{8a}$ as a standard.

11) G. D. Sargent, M. J. Harrison and G. Khoury, *J. Amer. Chem. Soc.*, 91, 4937 (1969).

12) Epoxidation with m-chloroperoxybenzoic acid afforded a major and a minor epoxide which were easily separated using glc. A chemical shift study on the undeuterated epoxide is consistent only with the 7-oxatricyclo[3.3.1.0$^{6,8}$]oct-2-ene. The infrared spectrum is also in agreement.

13) Two hydrogens (deuteriums) at $C_4$ in 10 and the hydrogen at $C_{9a}$ were isolated on a 250 Hz scan. Integration was carried out using the $C_{9a}$ hydrogen as a standard.

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