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MULTIPLE THERMAL REARRANGEMENTS. III. THE PYROLYSIS OF 7-(3-BUTENYL)-CYCLOHEPTATRIENE

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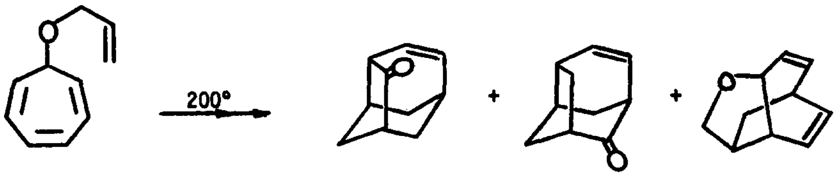
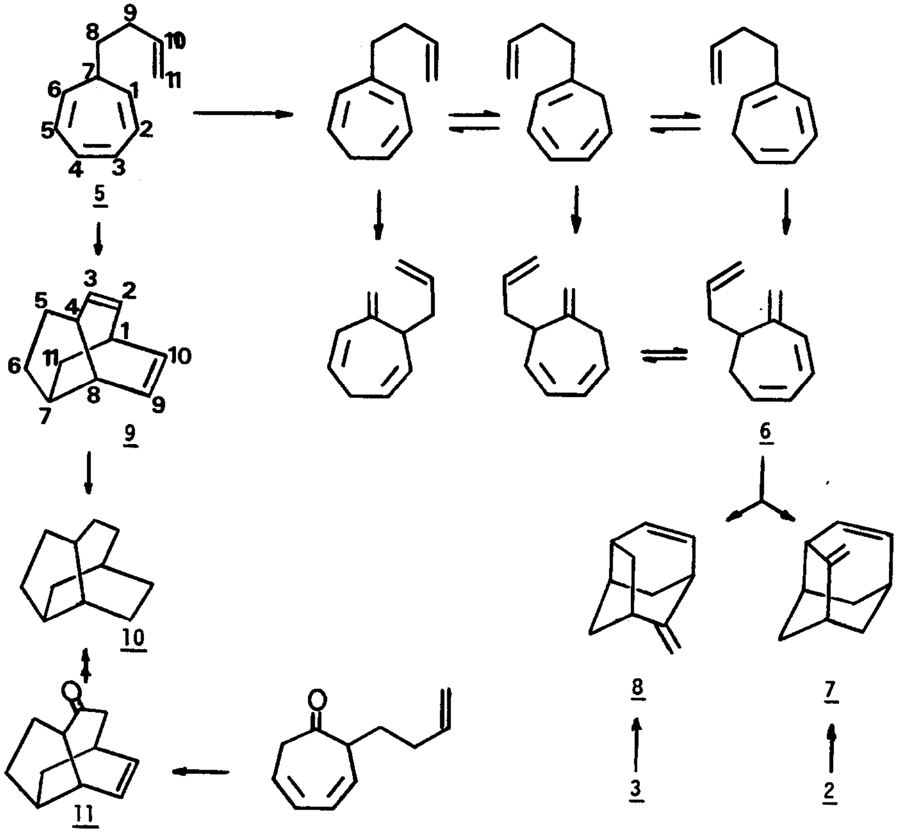
Mechanistic aspects of thermal sigmatropic rearrangements in cycloheptatrienes have been studied extensively.[2] In contrast, the synthetic potential of these isomerization reactions has been exploited only recently. For example, a facile entry to tricyclo[4.3.1.0^{3,8}]decane (protoadamantane) derivatives is provided by the rearrangement of 7-allyloxycycloheptatriene (1).[3]



1 46% 2 46% 3 8% 4

In continuation of our program concerned with developing routes to new bridged polycyclic hydrocarbon derivatives from the thermal rearrangement of appropriately substituted cycloheptatrienes and dihydrotropones,[4] we report here on the thermal behavior of the all-carbon prototype of 1, namely, 7-(3-butenyl)-cycloheptatriene (5).



Reaction of 7-methoxycycloheptatriene with 3-butenylmagnesium bromide gave 5 (89% yield; b.p. 45-46.5°/2.2 mm)[5a] which exhibited an NMR spectrum typical of 7-substituted cycloheptatrienes:[5b,6] τ 3.47 ("triplet," H_3, H_4); 3.94 (multiplet, H_2, H_5); 4.23 (multiplet, H_{10}); 5.00 (multiplet, H_1, H_6, and two terminal methylene H_{11}); 7.82 (multiplet, two allylic H_9); 8.0 - 8.5 (multiplet, preferentially equatorial H_7[6] and two H_8). Pyrolysis of 5 at 215±5° for four days (heptane solution) gave, in 58% yield, three tricyclic olefins:[7] 2-methylene tricyclo[4.3.1.$0^{3,8}$]dec-4-ene (7) (65%); 10-methylene tricyclo[4.3.1.$0^{3,8}$]dec-4-ene (8) (20%); and tricyclo[5.3.1.$0^{4,8}$]undeca-2,9-diene (9) (15%). Both 7 and 8 are formed from the dihydroheptafulvene intermediate 6 (generated by Cope rearrangement) by intramolecular $\pi_s^2 + \pi_s^4$ cycloaddition reactions analogous to those observed in the formation of 2 and 3. Wittig olefination of these latter ketones provided unambiguous independent syntheses for 7 and 8. The discerning feature of the NMR spectrum of 7 is the appearance of the terminal methylene protons as two singlets ($J_{gem} \cong 0$) at τ 5.50 and 5.70. In contrast, the *exo*-methylene protons of 8 are accidentally isochronous and appear as a singlet at τ 5.54. In addition the endocyclic olefinic protons of 7 and 8 appear as "triplets" (ABXY with small δ_{AB}) at τ 3.88, and the distinctly different aliphatic protons at τ 6.84 to 8.68 for 7 and 6.94 to 8.60 for 8.

The third tricyclic product obtained in the pyrolysis, 9, arises directly from 5, *via* $\pi_s^2 + \pi_s^4$ cycloaddition. This process is slightly more favorable than the similar formation of tricyclic ether 4 due to the slower rate of initial [1,5] hydrogen shift expected for 5 compared to 1.[8] The structure proof of 9 is based on the marked similarity of its NMR spectrum with that of 4[9] and on its hydrogenation to tricyclo[5.3.1.0^{4,8}]undecane (10)(mp 165-167°), which was identical to the material obtained upon Wolff-Kishner reduction and hydrogenation of keto-olefin 11.[4] The NMR spectrum of 9 shows for the pairs H_2, H_3 and H_9, H_{10} two overlapping ABXY patterns: thus H_{10} appears as a triplet ($J_{1,10} \cong J_{9,10}$) at τ 3.57, while H_2 and H_9 virtually overlap to give a triplet at τ 4.11, while H_3 gives a doublet of doublets at τ 4.88.

It is noteworthy that the rearrangement of 5 to 7 and 8 proceeds with some stereoselectivity in comparison to the rearrangement of 1 which under similar conditions produces equal amounts of the protoadamantenones. The factors responsible for this result along with other aspects of these thermal rearrangments are under investigation.

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5. (a) Satisfactory analyses were obtained for all new compounds; (b) NMR spectra were taken at 100 MHz on CCl_4 solutions with TMS as internal reference.
6. W. E. Heyd and C. A. Cupas, J. Am. Chem. Soc., 91, 1559 (1969), and references therein cited.
7. Separation of these liquid tricyclic olefins was achieved by preparative gas chromatography

on an 18% γ-methyl-γ-nitropimelonitrile column.

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9. We have obtained unambiguous structural assignment for **4** from extensive decoupling experiments at 100 MHz and the 300 MHz NMR spectrum of **4** in which all twelve protons show first order patterns! Details will be forthcoming in a full paper.