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Automerization of [4.2.2]Propella-2,4,7,9-tetraene. Intermediacy of a Cyclobutadiene Derivative and Its Trapping by Methanol

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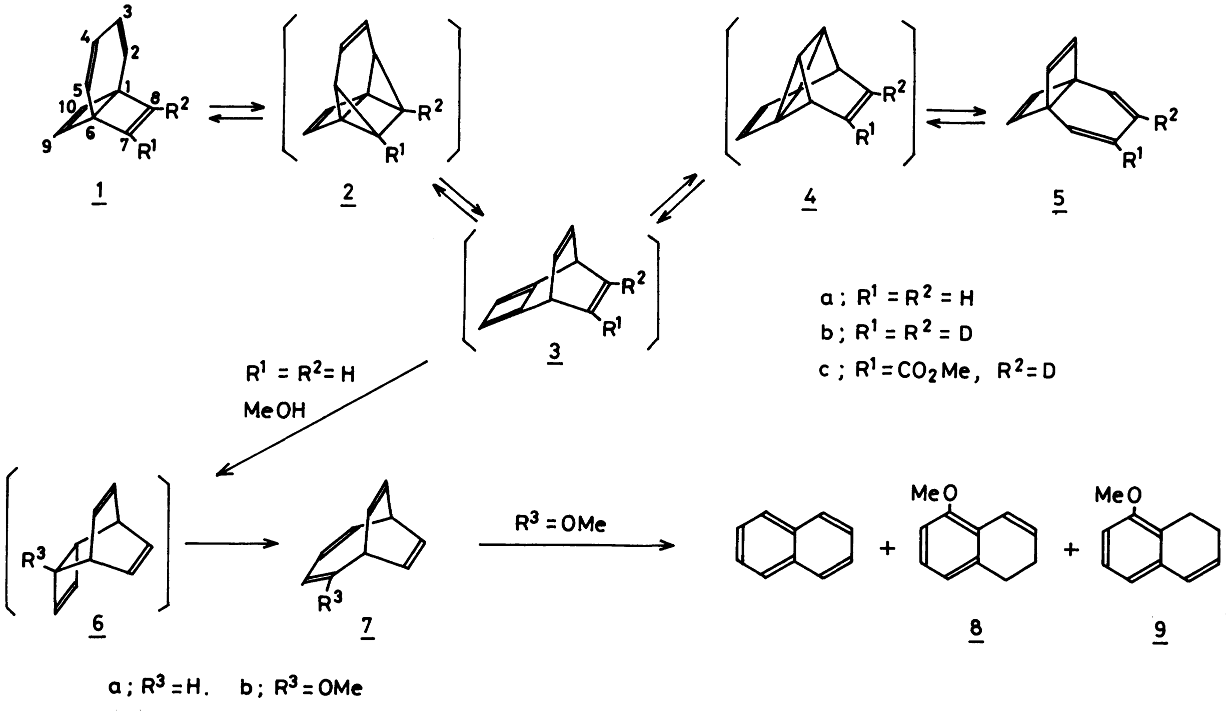
Automerization of [4.2.2]propella-2,4,7,9-tetraene system proceeds via a cyclobutadiene intermediate, which is trapped by methanol.

Molecular rearrangement, thermal reaction in particular, rarely takes pathway via such a highly energetic species as cyclobutadiene, which is electronically strongly destabilized and currently a subject of much interest, since less energetic alternative pathway is generally accessible. In the present letter, we report the remarkable observation that automerization of [4.2.2]propella-2,4,7,9-tetraene proceeds most probably by way of a cyclobutadiene intermediate which is trapped by methanol.

Thermal interconversion between 7-methoxycarbonyl[4.2.2]propella-2,4,7,9-tetraene (1c) and the 3-methoxycarbonyl derivative (5c) has previously been reported.1) To explore the generality of this type of automerization, 7,8-dideutero compound (1b)2) was prepared and heated at 200 °C for 40 h in degassed benzene. The recovered tetraene was converted to the Diels-Alder adduct of maleic

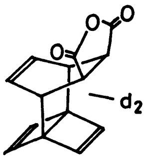


anhydride (11) to simplify the analysis of deuterium distribution by NMR. The examination of the adduct by ^{2}H-NMR unambiguously demonstrated the partial scrambling (11%) of the deuterium to the 3 and 4 positions of 1, but none of the deuterium was found in the 2 and 5 positions. Therefore, this type of thermal automerization in this ring system in which the 3 and 4 positions interchange with the 7 and 8 positions seems to be general.

For the automerization of 1c, we have previously proposed a few probable mechanisms including one via the cyclobutadiene intermediate (3c).1) The usual practice to prove generation of cyclobutadiene derivative is to carry out reaction in the presence of a dienophile or a reactive conjugated diene to trap the intermediate as a Diels-Alder adduct. This technique, however, cannot be applied to the present reaction since the substrate, 1, possesses both a 1,3-cyclohexadiene and dienophilic cyclobutene moieties. Recently it has been shown with isolable 1,2,3-tri-t-butylcyclobutadiene that its unsaturated bond system behaves as a fairly strong base owing to the high-lying π-MO and undergoes the addition of alcohol.3) Therefore, the reaction in methanol was examined to trap the possible cyclobutadiene intermediate. This scheme proved successful.

After heating a degassed methanolic solution of 1a (ca. 2 x 10^{-2} mol dm^{-3}) at 200 °C for a specified period, the solution was analyzed by GLPC and HPLC, which showed the formation of four methanol adducts as substantiated by the MS spectra, together with naphthalene and a small amount of 1-methoxynaphthalene (10). Two of them were readily identified as 5-methoxydihydronaphthalenes, 8 and 9 , by the comparison of spectra with those of authentic samples.4) For the third product, the structure of 2-methoxybicyclo[4.2.2]deca-2,4,7,9-tetraene (7b) was assigned on the basis of a well resolved 500 MHz NMR spectrum coupled with decoupling experiment.5) This product underwent secondary thermolysis under the reaction conditions with a half-life of 160 min to give a mixture of naphthalene, 8, and 9 in a ratio of ca. 2 : 1 : 1. This thermal behavior of 7b is also in accord with the structural assignment.6) The analysis of product composition at different reaction periods indicated that the major fraction of the naphthalene derivatives had derived from 7b (Fig. 1). The relatively minor fourth methanol adduct has not so far been identified.

The addition of methanol to unsaturated bond or strained σ bond is an acid-catalyzed reaction.7) However, the addition of triethylamine (2% to methanol) to the reaction mixture exerted no apparent effect on both the reaction rate and the product composition. In addition, 1,4-bridged Dewar benzene (12)8) was found to be stable under the reaction conditions and recovered quantitatively after heating at 200 °C for 50 h in methanol. Therefore, it will be safe to exclude the possibility that the methanol adducts somehow derived from the addition of methanol



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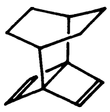

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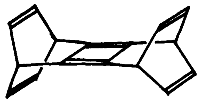

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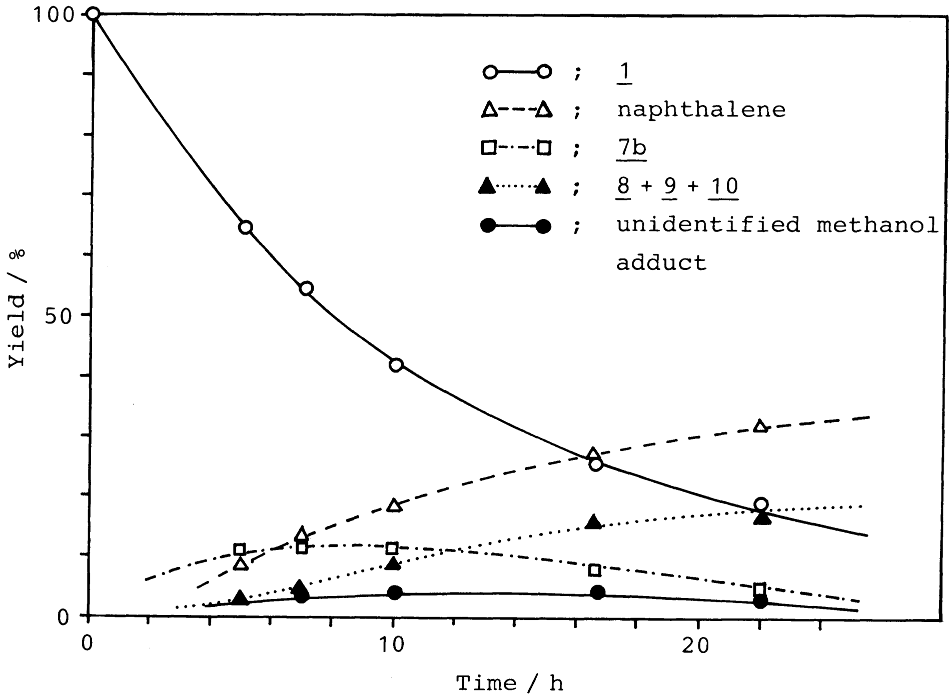

Fig. 1. Product yields vs. reaction time at 200 °C in methanol.

to 1a. It seems that the present results are best explained in terms of the methanol addition to the cyclobutadiene intermediate 3a to give 6b, which subsequently rearranged to 7b under the reaction conditions. The observation that the methanol adducts were produced at the rate comparable to that of the deuterium scrambling also supports the above mechanism in which the generation of 3a is rate-limiting.[10] The regioselectivity of methanol addition to 3a will be rationalized on the ground that 6b would be least strained among the possible adducts.[11] The thermal reaction of 6a has been extensively studied.[12] The extrapolation of the isomerization rate of 6a affording 7a to 200 °C gives a half-life of ca. 800 h for 6a. However, it has been well established that alkoxyl group facilitates adjacent carbon-carbon bond cleavage and, indeed, available kinetic data[14] indicates that 3-ethoxyl substituent accelerates the electrocyclic ring cleavage of cyclobutene by a factor of 5700. Therefore, it is not unreasonable that the initial methanol adduct 6b was not detected in the thermolysate.

The antiaromatic destabilization of cyclobutadiene has been estimated to amount to 88 kJ/mol.[15] In the present system, longicyclic interaction[16] among the π-bonds of 3 might facilitate access to 3 to some extent. Since cyclobutadiene possesses a high-lying HOMO as well as a low energy LUMO,[3] stabilization of 3 by this type of orbital interaction can be substantial. In this respect, the property of cyclobutadiene annelated by two 1,4-cyclohexadiene rings (13) is of considerable interest.

References

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