

Dyotropic Hydrogen Rearrangement in the Molecular Ions of 8,9-Disubstituted Tricyclo[5.2.1.0^{2,6}]decenes as Supported by Field Ionization Kinetics

Els Kluff,[†] Nico M. M. Nibbering,^{**†} Heiner Kühn,[†] and Rainier Herzschuh^{*†}

Contribution from the Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands, and Sektion Chemie, Karl-Marx-Universität, DDR-7010 Leipzig, German Democratic Republic.
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Abstract: The molecular ions of the endo, but not exo, isomers of the title compounds eliminate C₅H₈ via a retro-Diels-Alder reaction. This highly stereospecific fragmentation requires a double hydrogen transfer in the molecular ions, which could take place in either a concerted or stepwise fashion. Field ionization kinetic experiments point to a concerted character of this double hydrogen transfer, which thus would be an example of a so-called dyotropic hydrogen rearrangement. Other fragmentations studied are the losses of C₅H₆ and C₅H₇[•]. These reactions are not stereospecific and most probably proceed via a common intermediate.

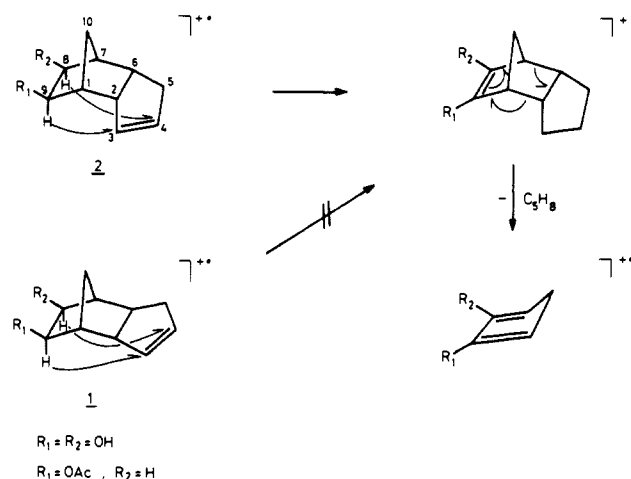
In an earlier publication,¹ one of us reported that the exo and endo isomers of the 8,9-disubstituted tricyclo[5.2.1.0^{2,6}]decenes **1** and **2**, respectively, fragment essentially differently upon electron impact. The ionized endo isomers **2** eliminate C₅H₈ via a retro-Diels-Alder reaction after migration of the hydrogen atoms from positions 8 and 9 to the double bond. This reaction is not observed for the exo isomers **1** where the distance between the hydrogen atoms of positions 8 and 9 and the double bond is too large for the hydrogen migration required to effect the retro-Diels-Alder reaction (Scheme I).

It is not known, however, whether the double hydrogen migration in ionized **2** occurs in a concerted or stepwise fashion. If the hydrogen atoms would migrate in a concerted fashion, then it is an example of a dyotropic reaction being defined as an uncatalyzed process in which two σ-bonds simultaneously, but not necessarily via a fully symmetrical mode, migrate intramolecularly.² Such a suprafacial dyotropic transfer of hydrogen is a thermally "allowed" [$\sigma_2s + \sigma_2s + \pi_2s$] pericyclic reaction³ and has been fully verified to occur in neutral *endo,endo*-11-oxatetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecenes.⁴ Double hydrogen migrations prior to a retro-Diels-Alder reaction have been reported before for gas-phase ions derived from adducts of *p*-benzoquinone⁵ and maleic anhydride.⁶ For the *p*-benzoquinone adduct ions it has been argued that the distance between the migrating hydrogen atoms and the carbonyl oxygen atoms is too large for a synchronous transfer.^{5,7} The double hydrogen transfer in the maleic anhydride adduct ions is nonstereospecific and occurs to a comparable extent in both endo and exo isomers as was shown by deuterium labeling.^{6,7} To our knowledge, therefore, no examples exist for experimentally supported dyotropic hydrogen rearrangements in gas-phase ions. There are also not many methods in mass spectrometry to examine the possible concertedness of double hydrogen migrations. Isotope effect measurements could, in principle, provide the required information but are difficult to interpret unambiguously. The most direct method to obtain insight in stepwise or concerted processes in gas-phase ions, which is presently available in mass spectrometry, is in our opinion field ionization kinetics (FIK). With this method⁸ decompositions of molecular ions occurring in the first 10⁻¹¹–10⁻⁹ s following ionization can be studied in a time-resolved way. In this paper we wish to report the results obtained by application of FIK to study the double hydrogen migration and accompanying retro-Diels-Alder reaction of molecular ions from the compounds mentioned in the title.

Experimental Section

The FIK experiments were performed with a Varian MAT 711 double-focusing mass spectrometer equipped with a combined EI/FI/FD ion source. The emitter, a 10-μm activated tungsten wire, was heated during

Scheme I. Double Hydrogen Transfer in the Ionized Endo Isomer **2** (Not Possible in the Ionized Exo Isomer **1**) followed by Elimination of C₅H₈ via a Retro-Diels-Alder Reaction



the experiments by passing a current of 30 mA through it. Most FIK experiments were obtained with the electric sector set to transmit ions with a kinetic energy of 8250 ± 45 V. For some of the FIK experiments and for the normalized rates measurements, however, the electric sector was set to transmit ions with an energy of 8250 ± 16 V. The sample pressure in the ion source was approximately 10⁻³ Pa. The samples were introduced into the ion source (150 °C) via a leak valve (150 °C). Spectral data were recorded on-line, stored, and then processed by the Varian Spectro System 100 as described earlier.⁹ The curves shown in all figures represent the average of seven to nine scans.

Results and Discussion

The following analogues of compounds **1** and **2**, having the carbon skeleton structure as given in the Introduction, have been studied by FIK: **1a**, R₁ = R₂ = OCH₃; **1b**, R₁ = R₂ = OH; **2a**, R₁ = R₂ = OCH₃; **2b**, R₁ = R₂ = OH; and **2c**, R₁ = OH, R₂ =

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(3) Woodward, R. B.; Hoffman, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: GmbH, Weinheim/Berstr., 1970; p 141.

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[†] University of Amsterdam.

^{**} Karl-Marx-Universität.

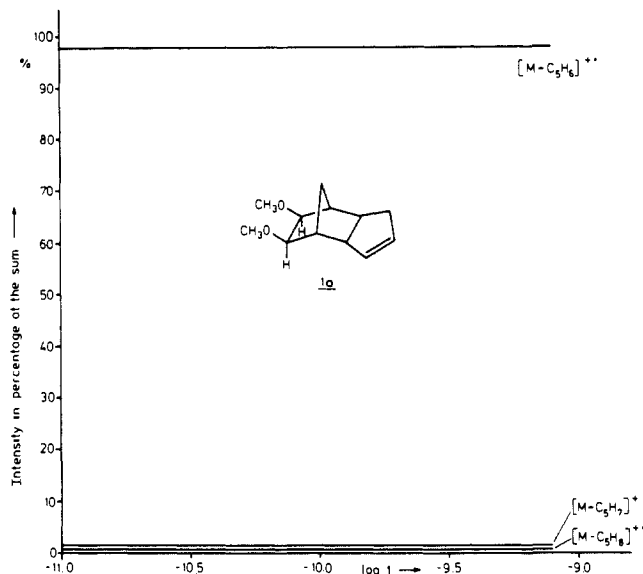


Figure 1. Losses of C_5H_6 , $C_5H_7^+$, and C_5H_8 , expressed in percentages of their sum, as a function of the lifetime of the molecular ion from compound **1a**.

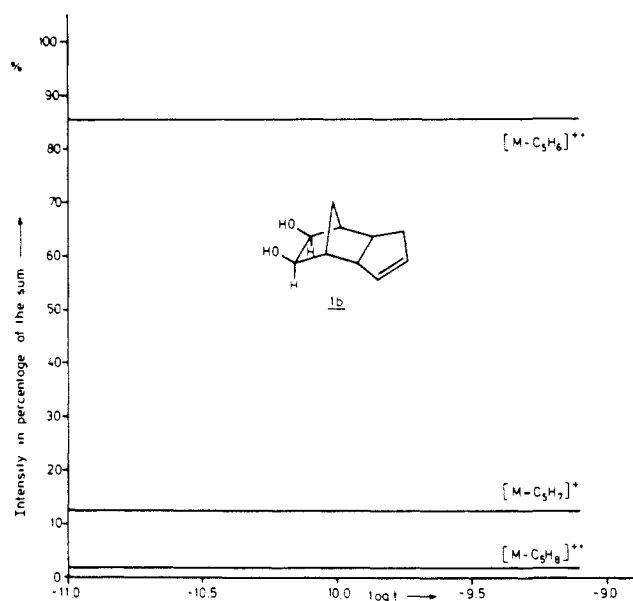


Figure 2. Losses of C_5H_6 , $C_5H_7^+$, and C_5H_8 , expressed in percentages of their sum, as a function of the lifetime of the molecular ion from compound **1b**.

OCH_3 . Figure 1 shows as a function of the molecular ion lifetime of compound **1a** the ion currents (abundances) of the $(M-C_5H_6)^{**}$, $(M-C_5H_7)^+$, and $(M-C_5H_8)^{**}$ ions. It can be seen that the abundances of the $(M-C_5H_7)^+$ and $(M-C_5H_8)^{**}$ ions are negligible, that is, at noise level, and that practically exclusively C_5H_6 is eliminated up to molecular ion lifetimes of 10^{-9} s. The same observations are made for molecular ions which decompose in the metastable time region of 10^{-7} – 10^{-6} s as evidenced from so-called linked B/E scans¹⁰ following field ionization (FI).

The abundances of the $(M-C_5H_6)^{**}$, $(M-C_5H_7)^+$, and $(M-C_5H_8)^{**}$ ions as a function of the molecular ion lifetime of compound **1b** are shown in Figure 2. Although the abundance of the $(M-C_5H_7)^+$ ions is now somewhat higher than in the case of compound **1a**, the $(M-C_5H_6)^{**}$ ions are again most abundant, whereas the $(M-C_5H_8)^{**}$ ions are generated to a negligible extent. Similar results have been obtained for the molecular ions which decompose in the metastable time region of 10^{-7} – 10^{-6} s on the

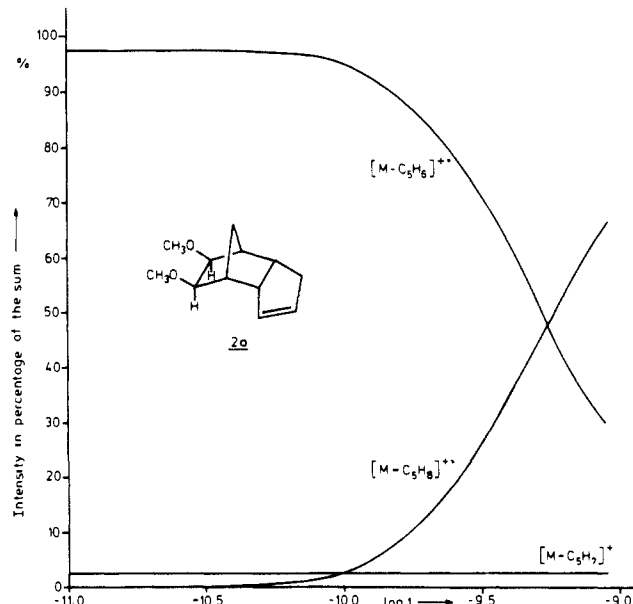
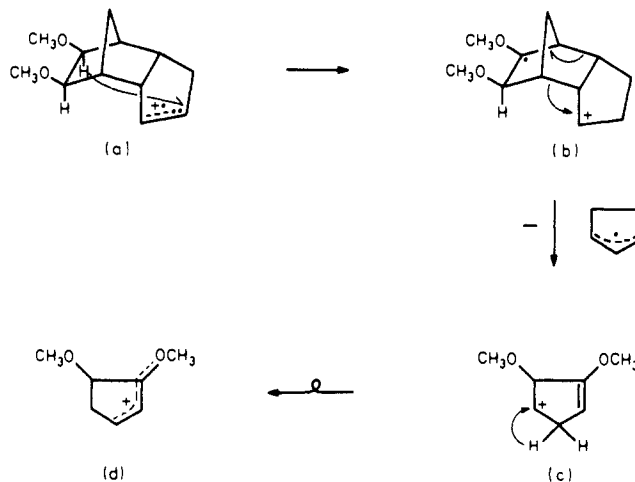


Figure 3. Losses of C_5H_6 , $C_5H_7^+$, and C_5H_8 , expressed in percentages of their sum, as a function of the lifetime of the molecular ion from compound **2a**.

Scheme II. Possible Pathway for the Elimination of a Resonance-Stabilized Cyclopentenyl Radical from the Molecular Ion of Compound **2a**



basis of linked B/E scans¹⁰ following FI.

These observations show that the endo stereochemistry as in compounds **2a–2c** is a prerequisite for the double hydrogen transfer and subsequent retro-Diels–Alder reaction which is in full agreement with the previously reported electron impact study.¹ It is also obvious from the observations made that such a stereochemical restriction is not imposed upon the eliminations of C_5H_6 and $C_5H_7^+$.

Figure 3 shows the eliminations of C_5H_6 , $C_5H_7^+$, and C_5H_8 as a function of the molecular ion lifetime of compound **2a** up to 10^{-9} s. For this compound the interesting observations are made that the elimination of C_5H_8 is a delayed process with respect to that of C_5H_6 and that the expulsion of $C_5H_7^+$ is negligible, that is, at noise level, if it occurs at all. Linked B/E scans¹⁰ following FI further show that the molecular ions of **2a** lose almost exclusively (>98%) C_5H_8 in the metastable time region of 10^{-7} – 10^{-6} s. The practical absence of loss of $C_5H_7^+$ from ionized **2a** could be due to the following: 1. The double hydrogen atom transfer prior to elimination of C_5H_8 from the molecular ion occurs indeed in a concerted process, i.e., via a dyotropic rearrangement. 2. The double hydrogen atom transfer takes place in a stepwise fashion, but there is no route available to the intermediate for expulsion of $C_5H_7^+$. The last possibility seems not so likely. Following

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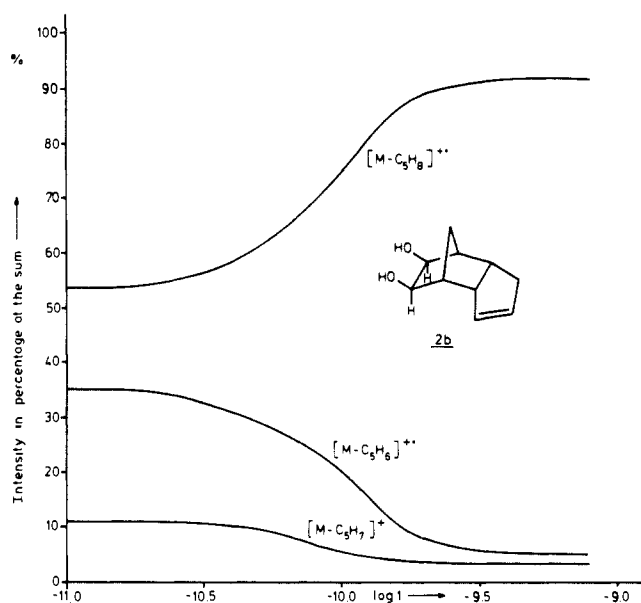


Figure 4. Losses of C_5H_6 , $C_5H_7^+$, and C_5H_8 , expressed in percentages of their sum, as a function of the lifetime of the molecular ion from compound **2b**.

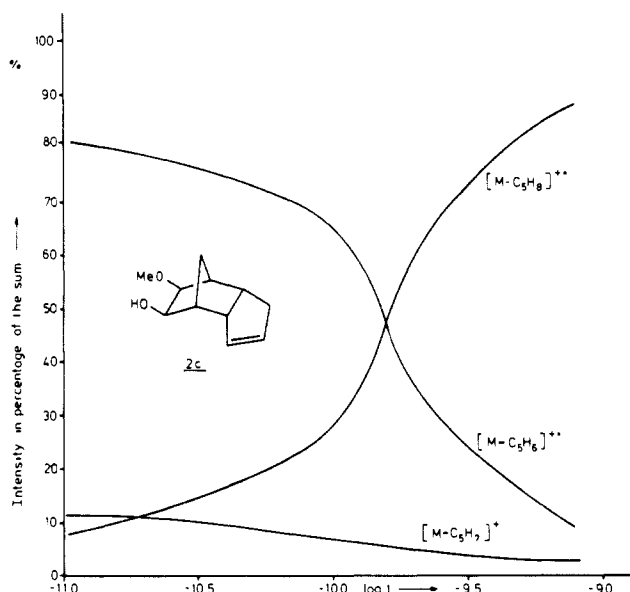


Figure 5. Losses of C_5H_6 , $C_5H_7^+$, and C_5H_8 , expressed in percentages of their sum, as a function of the lifetime of the molecular ion from compound **2c**.

transfer of one hydrogen atom to the double bond in ionized **2a**, a resonance-stabilized cyclopentenyl radical $C_5H_7^+$ can be lost as visualized in Scheme II. Of course, the resulting ion (c) needs further rearrangements to become better stabilized, but this, for example, can be achieved by a simple 1,2-H shift as shown in Scheme II by reaction $c \rightarrow d$.

The experimental fact that the elimination of $C_5H_7^+$ from ionized **2a** is negligible, if it occurs at all, over ion lifetimes spanning the range from 10^{-11} to 10^{-6} s following ionization therefore points in our opinion to a dyotropic rather than to a stepwise hydrogen atom transfer prior to elimination of C_5H_8 via a retro-Diels-Alder reaction.

Support for this point of view is further provided by Figures 4 and 5, which show the eliminations of C_5H_6 , $C_5H_7^+$, and C_5H_8 as a function of the molecular ion lifetime of compounds **2b** and **2c**, respectively.

It can be seen that the elimination of C_5H_8 is again a delayed process which becomes most dominant at longer molecular ion lifetimes. In these cases also a minor loss of $C_5H_7^+$ is observed, which further decreases in going from short to longer ion lifetimes.

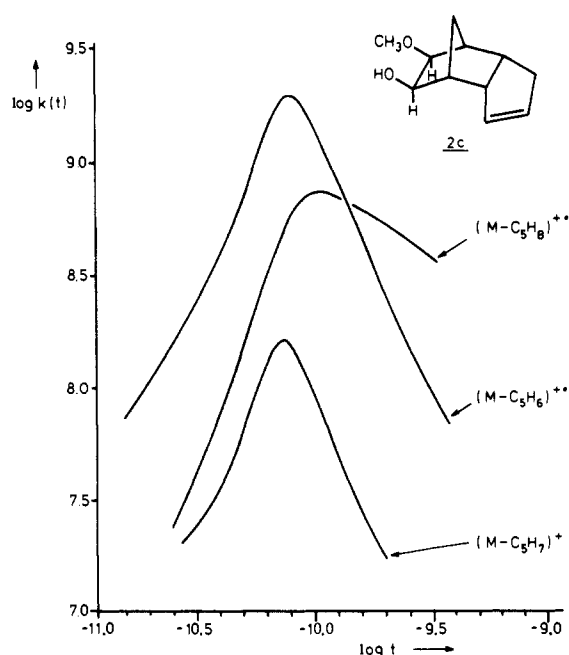
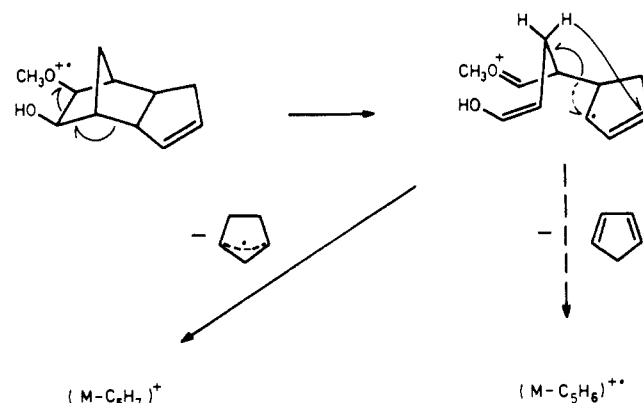


Figure 6. Normalized rates $k(t)$ for the eliminations of C_5H_6 , $C_5H_7^+$, and C_5H_8 from the molecular ion of compound **2c**.

Scheme III. Rationalization of the Loss of C_5H_6 and $C_5H_7^+$ from the Molecular Ion of Compound **2c** via a Common Intermediate



This reaction channel, however, is not related to the loss of C_5H_8 but to the loss of C_5H_6 . This is evident from the normalized rates¹¹ $k(t)$ for the eliminations of C_5H_6 , $C_5H_7^+$, and C_5H_8 , which for compound **2c** have been displayed in Figure 6.

Note, that the curves for loss of C_5H_6 and $C_5H_7^+$ are similar in shape and have their maximum at the same position, being in both aspects different from the curve for loss of C_5H_8 . In other words, the losses of $C_5H_7^+$ and C_5H_6 most probably occur via a common intermediate, as rationalized in Scheme III, but via a different route than the loss of C_5H_8 .

In conclusion, all experimental facts taken together point in our opinion to the occurrence of a dyotropic hydrogen rearrangement in the molecular ions of the endo isomers of 8,9-disubstituted tricyclo[5.2.1.0^{2,6}]decenes prior to the elimination of C_5H_8 via a retro-Diels-Alder reaction as visualized in Scheme I.

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Registry No. **1a****⁺, 104421-53-6; **1b****⁺, 104486-08-0; **2a****⁺, 104486-09-1; **2b****⁺, 104486-10-4; **2c****⁺, 104421-54-7.

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