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# CYCLISATION MECHANISMS OF ω-ALKENYL-RADICALS

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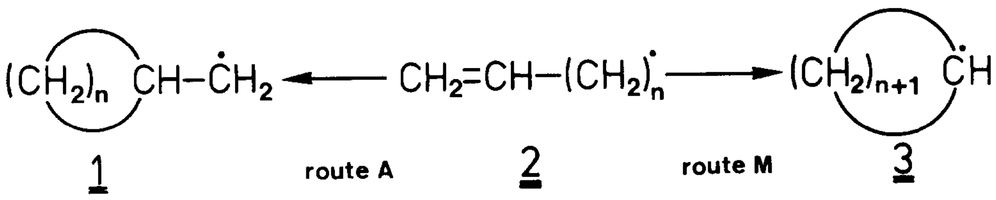
Addition of radicals to unsymmetrically substituted double bonds can in principle either lead to the thermodynamically more stable products ("Markownikow route", M) or the less stable products ("anti-Markownikow route", A).

Theory predicts,[1,2] that in case of bimolecular additions, the reaction follows the former pathway if the reactant radical consists of an alkyl radical, while charge control (in case of strongly electrophylic or nucleophilic radicals) should favour the latter course of reaction. Although experimental evidence is sparse,[2] this prediction is followed.[3]

On the other hand, the corresponding intramolecular radical cycloadditions of small ω-alkeny radicals (2) proceed via the anti Markownikow route A thus leading to cycloalkyl carbinyl radicals (1) and not to the more stable secondary cycloalkyl radicals (3):



This surprising observation has initiated a vast amount of experimental and theoretical investigations.[4)]

We have calculated the two possible reaction mechanisms A and M shown in scheme 1 for n=2 (homoallyl radical) to n=5 ($\omega$-heptenyl radical) using the MINDO/3-UHF[5)] method. The relevant structures were found by the standard procedures[5)] and will be given elsewhere. The calculated thermodynamical data are collected in the table.

Table:

Calculated thermodynamical data of $\omega$-Alkenyl radicals (2), their cyclisation products (1 and 3) and associated activation parameters. ($\Delta H$ in kJ/mole, entropies in J/Mole K).

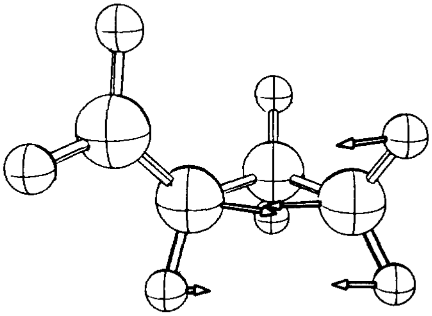
| n | 2 | | route A | | 1 | | route M | | 3 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta H_f$ | $S_{298}$ | $\Delta H^{\ddagger}_A$ | $\Delta S^{\ddagger}_{298}$ | $\Delta H_f$ | $S_{298}$ | $\Delta H^{\ddagger}_M$ | $\Delta S^{\ddagger}_{298}$ | $\Delta H_f$ | $S_{298}$ |
| 2 | 158 | 324 | 52 | -34 | 159 | 294 | 123 | -40 | 112 | 281 |
| 3 | 130 | 364 | 77 | -48 | 110 | 321 | 93 | -51 | 11 | 303 |
| 4 | 104 | 403 | 69 | -55 | 38 | 346 | 69 | -69 | -37 | 332 |
| 5 | 78 | 443 | 79 | -80 | 14 | 363 | 67 | -80 | -62 | 356 |

The entropies $S_{298}$ have been calculated by statistical thermodynamics[7)] based on the obtained structural data and calculated normal vibrations.[8)] Note, that $S_{298}$ cannot be calculated this way for the open chain radicals 2 because the exhaustive replacement of internal rotations by torsional vibrations leads to serious numerical errors. However, these values can be approximated by other means[6)] thus allowing to estimate the entropies of activation $\Delta S^{\ddagger}_{298}$ which are given in the table.

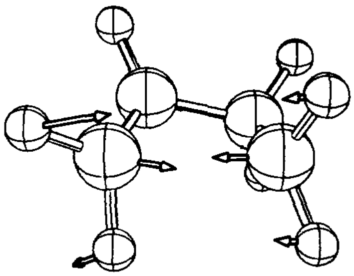
Apparently, the activation energies $\Delta H^{\ddagger}_A$ are considerably lower than $\Delta H^{\ddagger}_M$ for $n<4$, while for the $\omega$-hexenyl radical (n=4), both activation energies amount to the same value. However, the activation entropy $\Delta S^{\ddagger}_{298}$ for route A is considerably less negative than fo route M indicating a much larger preexponential factor and strongly favouring route A. We predict that the observed cyclisation proceeds along this route for entropic reasons only. This has been corroborated by experimental findings.[9)]

For n>4, the radicals again should behave "normal", thus favouring route M as in bimolecular additions.

*The calculated (and "observed") trend from route A to route M with increasing ring size* can be traced back to one common cause. The transition states $T_A$ and $T_M$ for the homoallyl radical (n=2) are shown in the figure below. The arrows indicate the nuclear displacements corresponding to the intrinsic reaction coordinates (IRC).[10] The IRC in $T_M$ indicates a dominant decoupling of the terminal double bond for this route which is associated with a large increase in energy. As n increases, this "decoupling angle" $\alpha$ decreases, since the radical center has more dynamic freedom to attack the double bond less costly. $\alpha$ has been calculated to be $28^0$ for n=2, $18^0$ for n=3, $9^0$ for n=4 and $5^0$ for n=5.[6]



$T_A$



$T_M$

It should be noted, that the cyclisation of the $\omega$-pentenyl radical is predicted to proceed **via** route A, although the reaction is expected to be much slower than the cyclization of the homoallyl radical and the $\omega$-hexenyl radical respectively. Experimental data concerning *the parent system* $C_5H_9$ *are absent and would be highly desirable.*

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