

# A Molecular Orbital Study of the Reduction Mechanism of Monoterpene, *p*-Mentha-1,3-dien-7-al, with Sodium in Aqueous Ammonia

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Recently, the author reported<sup>1-2)</sup> the reduction of  $\alpha\beta$ - and  $\alpha\beta, \gamma\delta$ -unsaturated monoterpene aldehyde. (-)-perillaldehyde (I) and *p*-mentha-1,3-dien-7-al (II)<sup>3a-3b)</sup> respectively, and also proposed the possible reduction mechanisms from the viewpoint of the structures of intermediates and reduction products.

In the present paper, the author deals with the theoretical studies for the mechanisms of the reduction of II with sodium in aqueous ammonia.

Formation of 1-*p*-menthen-7-al (VIII) in the early stage of the reduction shows that the reduction must involve the initial transference of an electron from the metallic sodium surface to the  $\alpha\beta, \gamma\delta$ -conjugated system of II, and that the

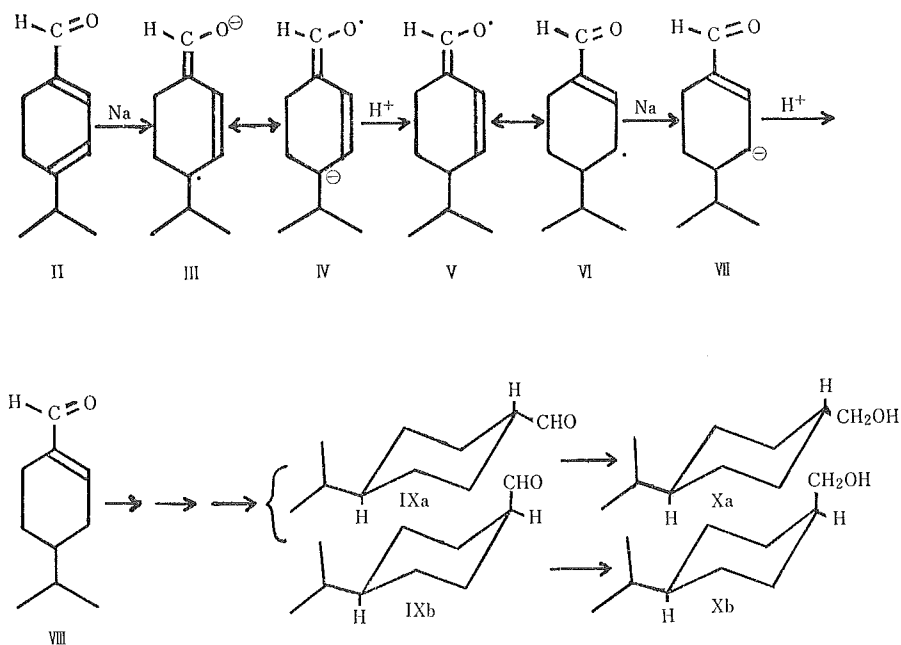


Fig. 1 Reduction Mechanism of *p*-Mentha-1,3-dien-7-al (II)

anion radical hybrid (III $\leftrightarrow$ IV) is formed as in the canonical form described in Figure 1. The canonical forms are theoretically possible, but it is not obvious which of the possible forms would be more stable. Subsequently, the anion radical abstracts a proton from water in solution to form the radical hybrid (V $\leftrightarrow$ VI) and again the transference of a second proton onto the radical hybrid leads to formation of the carbanion (VII). Protonation onto the carbanion (VII) may then occur in the reaction mixture, leading to 1-*p*-menthen-7-al (VIII).

The result which reinforces the above postulated mechanism was obtained from the molecular orbital study as an explanation of the initial 1,6-radical addition of the metallic hydrogen onto the conjugated system.

A study by the simple molecular orbital method may provide the information about the  $\pi$ -electron distribution in *p*-mentha-1,3-dien-7-al (II). The heteroatom parameters used in the calculation are described below:

$$\begin{aligned}\alpha_o &= \alpha + \beta \\ \beta_{c-o} &= \sqrt{2} \beta\end{aligned}$$

where  $\alpha_o$  is the coulomb integral of oxygen and  $\beta_{c-o}$  is the resonance integral between carbon and oxygen. The resulting molecular diagram was described in Figure 2.

It seems to be reasonably considered that the radical addition occurs at the position of the maximum value of the free valence. Therefore, the attack of the metallic hydrogen is assumed to take place at the position of both sides of the conjugated system. Though the limit of the calculated value is defined by the subjectivity of the experimentalist, on comparing the experimental results with the calculated results, it is satisfactory to consider that the reduction involves the initial 1,6-addition of the metallic hydrogen.

Although a conclusion cannot be drawn due to an insufficient number of the calculating sample, the value of the free valence seems to indicate the possibility of anticipating the position which allows to be reduced by the metallic hydrogen.

#### Calculation Procedure;

The secular determinant is rapidly set up as:

$$\begin{vmatrix} X & 1 & 0 & 0 & 0 & 0 \\ 1 & X & 1 & 0 & 0 & 0 \\ 0 & 1 & X & 1 & 0 & 0 \\ 0 & 0 & 1 & X & 1 & 0 \\ 0 & 0 & 0 & 1 & X\sqrt{2} & \\ 0 & 0 & 0 & 0\sqrt{2} & X+1 & \end{vmatrix} = 0 \dots\dots\dots(1)$$

$$X = \frac{\alpha \cdot E}{\beta}$$

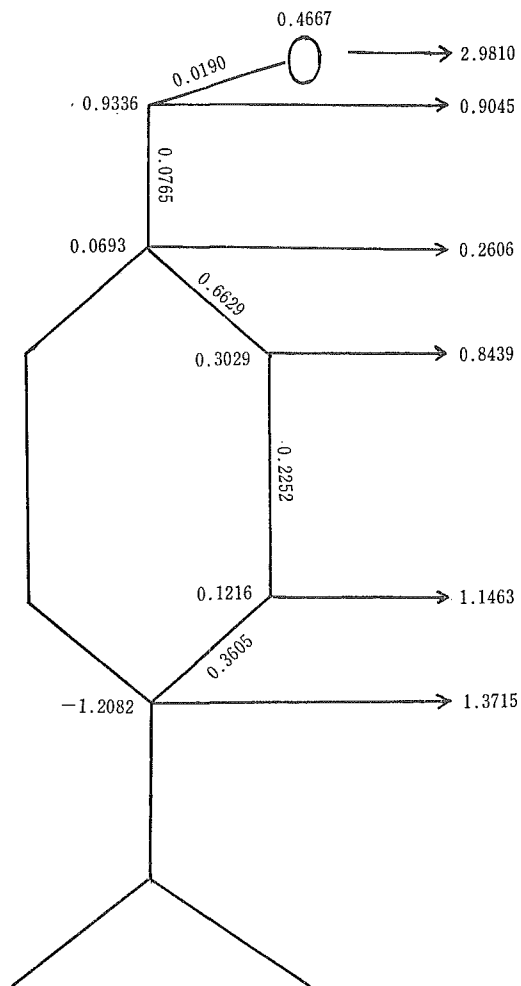


Fig. 2 Molecular Diagram of *p*-Mentha-1,3-dien-7-al (II)

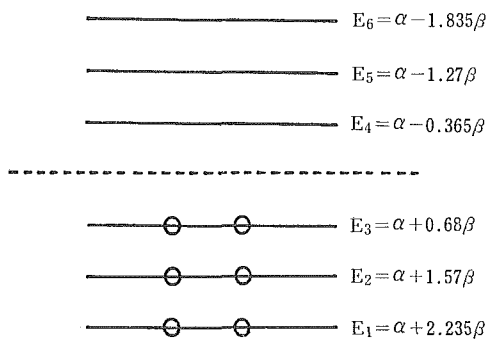


Fig.3 HMO $\pi$ -Energy Level Diagram of *p*-Mentha-1,3-dien-7-al (II)

Expansion of the determinant follows directly to give the secular polynomial:

$$X^6 + X^5 - 6X^4 - 4X^3 + 9X^2 + 3X - 2 = 0 \dots \dots \dots (2)$$

Since this equation is in the sixth form, the roots are found using the interpolation method and  $X = -2.235, -1.57, -0.68, 0.365, 1.27, 1.835$  or the resulting energy levels are  $E_1 = \alpha + 2.235\beta$ ,  $E_2 = \alpha + 1.57\beta$ ,  $E_3 = \alpha + 0.68\beta$ ,  $E_4 = \alpha - 0.365\beta$ ,  $E_5 = \alpha - 1.27\beta$ ,  $E_6 = \alpha - 1.835\beta$  (Fig. 3).

The six  $\pi$ -electrons are put into the first three MO's, giving  $6\alpha + 8.97\beta$ .

i) *Calculation of Coefficients and Wave Functions*

To find the coefficients ( $C_n$ ) and the wave functions ( $\psi_n^*$ ) for the molecular orbital corresponding to each energy, one returns to the original secular determinant (1) and must calculate the element ( $A_n$ ).

( $A_n$ ) is the determinant of the next lower order formed by striking out row and column of the original determinant:

$$\begin{aligned} A_1 &= X^5 + X^4 - 3X^3 - 2X^2 + 2X \\ A_2 &= -X^4 - X^3 + 4X^2 + 2X - 2 \\ A_3 &= X^3 + X^2 - 3X - 1 \\ A_4 &= -X^2 - X + 2 \\ A_5 &= X + 1 \\ A_6 &= -2 \end{aligned}$$

$E_1 = \alpha + 2.235\beta$ ,  $X = -2.235$ :

$$\begin{aligned} C_1 &= \frac{A_1}{A_1} = 1 & C_2 &= \frac{A_2}{A_1} = 0.02352 & C_3 &= \frac{A_3}{A_1} = 0.0394 \\ C_4 &= \frac{A_4}{A_1} = 0.0645 & C_5 &= \frac{A_5}{A_1} = 0.1048 & C_6 &= \frac{A_6}{A_1} = 0.1200 \end{aligned}$$

$$\psi_1 = \chi_1 + 0.02352\chi_2 + 0.0394\chi_3 + 0.0645\chi_4 + 0.1048\chi_5 + 0.1200\chi_6$$

Applying the normalization condition ( $N = 1.0157$ ), one find:

$$\psi_1^* = 0.9845\chi_1 + 0.0232\chi_2 + 0.388\chi_3 + 0.0635\chi_4 + 0.1032\chi_5 + 0.1181\chi_6$$

This procedure can be repeated for each wave function of the corresponding energy level.

Hence:

$$\begin{aligned} E_2 &= \alpha + 1.57\beta, \quad X = -1.57, \quad N = 62.6733; \\ \psi_2^* &= 0.0160\chi_1 + 0.5230\chi_2 + 0.4795\chi_3 + 0.2299\chi_4 - 0.1186\chi_5 - 0.2942\chi_6 \\ E_3 &= \alpha + 0.68\beta, \quad X = -0.68, \quad N = 2.7255; \\ \psi_3^* &= 0.3669\chi_1 + 0.4063\chi_2 - 0.3423\chi_3 - 0.6391\chi_4 - 0.0922\chi_5 + 0.4076\chi_6 \\ E_4 &= \alpha - 0.365\beta, \quad X = 0.365, \quad N = 9.4931; \\ \psi_4^* &= 0.1053\chi_1 - 0.2480\chi_2 - 0.5887\chi_3 + 0.4630\chi_4 + 0.4206\chi_5 - 0.4357\chi_6 \\ E_5 &= \alpha - 1.27\beta, \quad X = 1.27, \quad N = 4.2657; \end{aligned}$$

$$\begin{aligned} \phi^*_5 &= 0.2344\chi_1 - 0.5931\chi_2 + 0.2909\chi_3 + 0.2236\chi_4 - 0.5749\chi_5 + 0.3581\chi_6 \\ E_6 &= \alpha - 1.835\beta, \quad X = 1.835, \quad N = 1.1474: \\ \phi^*_6 &= 0.8715\chi_1 - 0.1996\chi_2 + 0.2514\chi_3 - 0.2647\chi_4 + 0.2344\chi_5 - 0.1169\chi_6 \end{aligned}$$

ii) *Bond orders*

Coulson<sup>4)</sup> introduced the partial mobile bond order  $P^j_{rs}$  for the r—s bond in the jth MO defined as:

$$P^j_{rs} = C_{jr}C_{js} \dots \dots \dots (3)$$

The corresponding bond order is:

$$P^j_{rs} = \sum_j^{\phi_{occ}} NC_{rs} \dots \dots \dots (4)$$

in which  $N$  is the number of electrons in the jth MO.

Hence:

$$P_{12} = 2 (0.9845 \times 0.0232 + 0.0160 \times 0.5230 + 0.3669 \times 0.4063) = 0.3605$$

Thus:

$$P_{23} = 0.2252, \quad P_{34} = 0.6629, \quad P_{45} = 0.0765, \quad P_{56} = 0.0190,$$

iii) *Electron Densities*

The total electron density at an atom  $Q_j$  is the sum of the electron densities contributed by each electron in each MO:

$$Q_j = 1 - \sum_j^{occ} NC_j^2$$

$C_j$  is the coefficient of the atom  $j$  in the jth MO, which is occupied by  $N$  electron.

Hence:

$$\begin{aligned} Q_1 &= 1 - 2(0.9845^2 + 0.0160^2 + 0.3669^2) \\ &= -1.2082 \end{aligned}$$

Thus:

$$Q_2 = 0.1216, \quad Q_3 = 0.3029, \quad Q_4 = 0.0693, \quad Q_5 = 0.9336, \quad Q_6 = 0.4667,$$

iv) *Free valence*

The free valence index  $F_i$  has been defined by Coulson<sup>5)</sup> as:

$$\begin{aligned} F_i &= N_{max} - N_i \\ &= 4.732 - \sum_j P^{\sigma}_{ij} - \sum_j P^{\pi}_{ij} \end{aligned}$$

in which  $N_i$  is the sum of the orders of all bonds joining the atom  $i$  and  $N_{max}$  is the maximum value.

Hence:

$$F_1 = 4.732 - 3 - 0.3605 = 1.3715$$

Thus:

$$F_2 = 1.1463, F_3 = 0.8439, F_4 = 0.2606, F_5 = 0.9045, F_6 = 2.9810$$

### Discussion

The concept of the bond order generally relates to the valency multiplicity between the atoms in molecules. Various definitions of the bond order based on the quantum mechanical theories have been proposed and the correlations with the bond distances have been suggested.<sup>6~7)</sup>

Nevertheless, this quantity has a rough physical significance, since the product of the coefficients of the adjacent atoms may be construed as a bond electron density.

The French workers have advocated particularly the use of the free valence for the radical reactions<sup>8)</sup> and Kooyman<sup>9)</sup> determined the relative reactivities of the trichloromethyl radical toward aromatic hydrocarbons and observed an excellent correlation with the highest free valence index of the hydrocarbon.

In the case of *p*-mentha-1,3-dien-7-al (II), the structure is assumed as so called "pseudo aromatic", and the free valence theory seems to provide a satisfying interpretation of the initial 1,6-radical addition of the metallic hydrogen onto the  $\alpha\beta, \gamma\delta$ -unsaturated system.

The significance of this study is to demonstrate that the attacking position of the metallic hydrogen in this type of the reduction is anticipated by using the simple MO method, although the other factors probably contribute to the finer details.

### References

- 1) H. Kayahara, H. Ueda, K. Takeo and C. Tatsumi; *J. Agr. Biol. Chem.* **33**(1) 86 (1969)
- 2) H. Kayahara, H. Ueda, I. Ichimoto and C. Tatsumi; *J. Agr. Biol. Chem.* **35**(4) 560 (1971)
- 3a) H. Kayahara, H. Ueda, I. Ichimoto and C. Tatsumi; *J. Org. Chem.* **33** 4536 (1968)
- 3b) H. Kayahara, H. Ueda, I. Ichimoto and C. Tatsumi; *J. Agr. Biol. Chem.* **34** (11) 1597 (1970)
- 4) C. A. Coulson; *Proc. Roy. Soc. A* **169** 413 (1939)
- 5) C. A. Coulson; *Discussions Faraday Soc.* **29** (1947)
- 6) L. Pauling, L. O. Brockway and J. Y. Beach; *J. Amer. Chem. Soc.* **57** 2705 (1935)
- 7) W. G. Penney; *Proc. Roy. Soc. A* **158** 306 (1937)
- 8) R. Daudel *et al*; *Advances in chemical physics*, Vol. 1, 165 (1958)
- 9) E. C. Kooyman and E. Farenhorst; *Trans. Faraday Soc.* **49** 58 (1953)

水溶液中における金属ナトリウムによるモノテルペン、  
*p*-メンタ-1,3-ジエン-7-アールの還元機構の  
分子軌道法的研究

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要 約

水溶液中における金属ナトリウムによるテルペン類の還元法は、飽和、不飽和ケトンおよびアルデヒド類に広く適用でき、優れた立体選択性のあることを報告してきたが、還元機構は未だ確立されていない。今回、一つの試みとしてラジカル反応の指標によく用いられる自由原子価指数をHMO法で計算し、実験データとの比較から本還元がラジカル的に進行する裏付けとなる知見を得ることが出来た。



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