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Stereochemistry of Migrating Carbon in Wagner-Meerwein rearrangement

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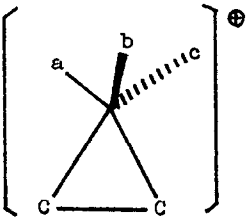
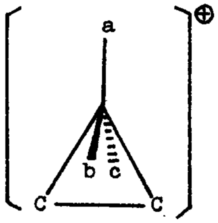
Mechanism of Wagner-Meerwein rearrangement$^{1)}$, especially the rearrangement of β-phenylethyl cation and norbonyl cation system, has been vastly studied on the basis of kinetics and stereochemistry of the migrating origin and terminus.

On the other hand, the rearrangement was scarcely discussed from the standpoint of the stereochemical behavior (retention or inversion) of the migrating carbon itself. From kinetic data, the migrating saturated carbon was suggested to attain a coordination number of five in the transition state[1a] (The typical examples seem to be **1** or **2**). Although the configuration retention of a substituted cyclohexyl group was observed in the rearrangement of the rigid system, **3**[1f], such a stereochemical result seems not to be general, since the migrating carbon was a member of a relatively rigid cyclic system. Thus, a direct and general study on the stereochemistry of the migrating carbon is considered to be necessary and interesting.

We wish to report the first observation of the retention of configuration of the migrating carbon in the rearrangement of a system where the configuration of the carbon skeleton is relatively free and the migrating site is asymmetric.



1



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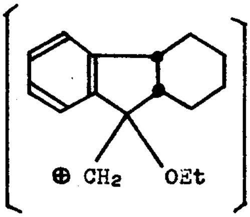

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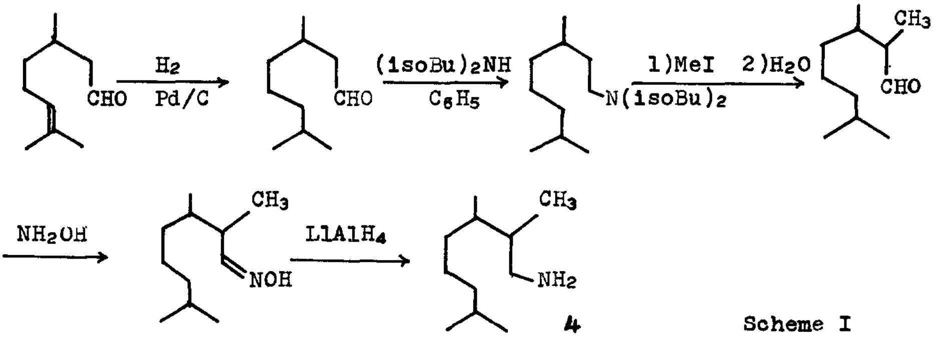


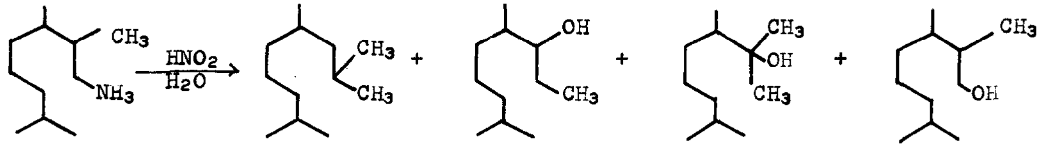
4

Scheme I

An optically active amine, 4[2], which was prepared from d-citronellal[3] (Scheme I) was deaminated by the treatment with nitrous acid. The result is summarized in Scheme II[4]. The product formation was easily explicable by the alkyl or hydrogen migration to the β-cation (Scheme III). The product, 5, yielded from the migration of the asymmetric carbon was oxidized by chromic acid to give a ketone, 9[5], which showed the same optical activity as an authentic ketone[6] which was prepared from d-citronellal (optical purity 81.3%) (Scheme IV). The result shows that the stereochemistry of the migrating carbon was completely (100%) retained and suggests that the Wagner-Meerwein rearrangement of an alkyl group involves neither the complete separation of the migrating group from both of the migrating origin and terminus nor the "pivot" type transition state, 2, which would bring about the inversion of asymmetry, but the partial bonded transition state such as I(the "slither" type).

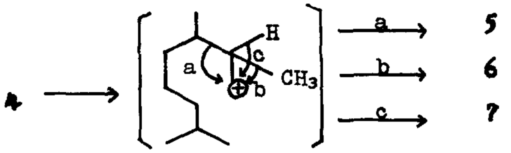
This seems to be the first direct and general evidence for the Hoffmann-Woodward prediction[7] that $[\omega 0s + \sigma 2s]$ (1) will be allowed while $[\omega 0s + \sigma 2a]$ (2) will be forbidden in the thermal reaction.

Further more, this result is consistent with the retention of stereochemistry of migrating carbon in Beckman rearrangement[8] or in Baeyer-Villiger oxidation[9]

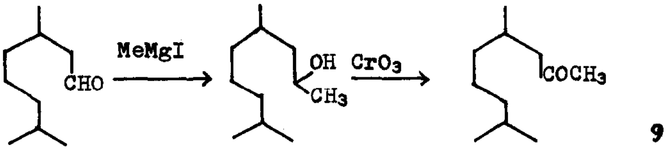


4 5 (11.8%) 6 (7.4%) 7 (7.4%) 8 (73.4%)

Scheme II



Scheme III



Scheme IV

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(2) 4: bp 59-61° (4mm) ; ν_{NH} (neat) 3500-3100 cm^{-1} : nmr (CCl_4) τ 7.58 (2H, multiplet) 8.17-8.95 (9H, multiplet), 9.11 (12H, doublet). The elemental analysis agreed with the calculated value. On the basis of the optical purity of the starting material (citronellal), the specific rotation of 4 was calculated to be 8.0° ($[\alpha]_D^{26°}$) (C=7.15, methanol).

(3) The starting material, citronellal, was compound of 81.3% of d-enantiomer and 18.7% of l-enantiomer.

(4) The product, **5** + **6** , **7** and **8**, were isolated by the preparative vapour phase chromatography (PEG 20M). **7**: ν_{OH} (neat) 3600-3100 cm^{-1} ; nmr (CCl_4) 6.58 (2H, doublet). 7.75 (1H, multiplet), 8.00-8.96 (9H, multiplet), 9.11 (12H, doublet); mass spectrum (m/e) 154 ($M^+ - H_2O$) (The molecular peak was not detected). **8**: ν_{OH}(neat) 3600-3150 cm^{-1} ; nmr (CCl_4) τ 8.13-8.97 (8H, multiplet), 8.90 (6H, singlet), 9.11 (9H, doublet); mass spectrum (m/e) 157 ($M^+ - CH_3$), 59 ($\overset{\oplus}{C}(CH_3)_2OH$) (The molecular peak was not detected). **5** and **6** could separated by the oxidation to the corresponding ketones (see a footnote (5)).

(5) The ketone, **9**, was separated from the ethyl ketone derived from **6** by the preparative vapour phase chromatography (PEG 20M). **9**: ν_{CO} (neat) 1715cm^{-1}: nmr (CCl_4) τ 7.58-7.87 (2H, multiplet), 7.97(3H, singlet), 8.03-8.94 (8H, multiplet), 9.11 (9H, doublet); mass spectrum(m/e) 170(M^+), 43 ($CH_3\overset{\oplus}{C}O$), $[\alpha]^{26°}_{350}$ 60.0° (C=4.50, methanol), $[\alpha]^{26°}_{370}$ 41.7°. The ethyl ketone derived from **6** showed :ν_{CO}(neat) 1715cm^{-1}; nmr(CCl_4) τ 7.30-7.83 (1H, multiplet), 7.60 (2H, quartet), 8.13-8.45(1H, multiplet), 8.45-9.37(12H, superimposed absorption), 9.06(6H, doublet) $[\alpha]^{26°}_{370}$- 43.8°, $[\alpha]^{26°}_{350}$-74.5(C=1.14, methanol).

(6) On the basis of the optical purity of the starting material(citronellal), the specific rotation of **9** was calculated to be 66.5° ($[\alpha]^{26°}_{370}$) or 95.8°($[\alpha]^{26°}_{350}$)

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