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STEREOCHEMISTRY OF THE ELECTROPHILIC OLEFINIC SUBSTITUTION OF 2-OXYALLYL—IRON(II) SPECIES. INSPECTION OF THE CONFORMATION OF THE ZWITTERIONIC INTERMEDIATES[1]

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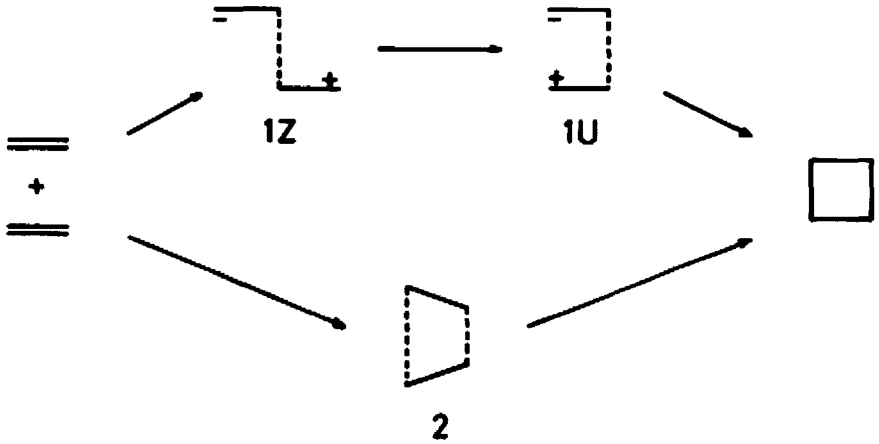
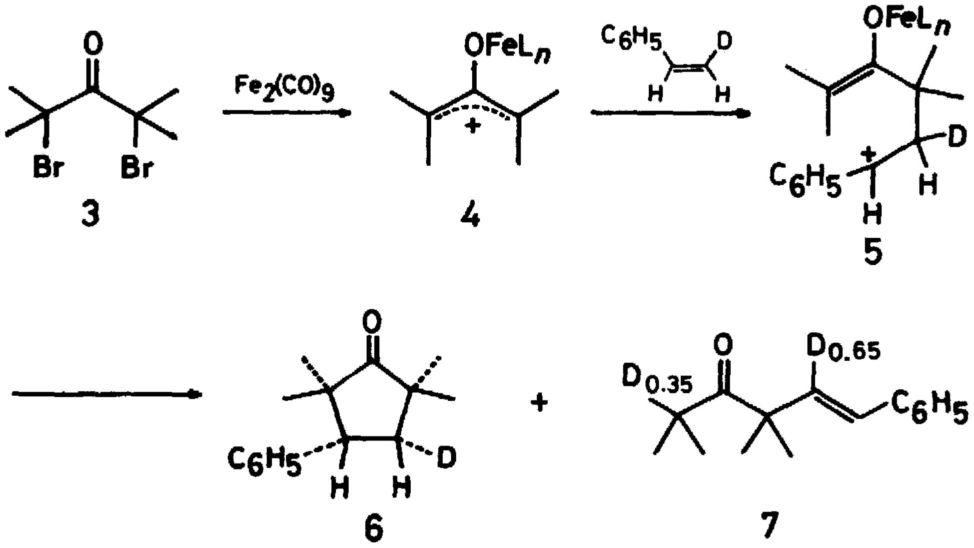
Intense attention has been paid in recent years on polar 2 + 2 cycloaddition of electron-deficient and -rich olefins.[2] Epiotis and coworkers predicted on the basis of the restricted Hartree—Fock type MO calculations that, since the transoid approach of such two olefins is energetically favored over the cisoid approach, the cycloaddition may occur through intermediates having two extreme types of conformations, 1Z and 1U.[3] They also suggested the alternative possibility that the reaction with high stereospecificity goes through an intermediates of type 2 in which the two cycloaddends achieve pericyclic bonding at a long distance. These theoretical analyses have prompted us to disclose some experimental findings related to this matter. We present here evidence indicative of the involvement of both U- and Z-shaped zwitterionic species in a reaction of certain 2π-electron components.



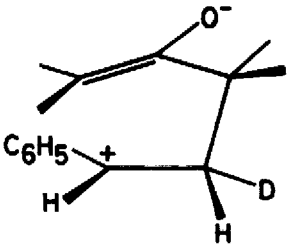
Reaction of α,α'-dibromo ketones and iron carbonyl generates reactive 2-oxyallyl—Fe(II) species (2π-electron system),[4] which in turn are trapped by certain olefinic substances giving



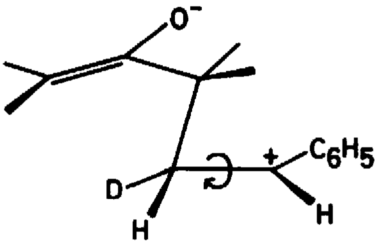
L = Br, CO, etc.

the corresponding cyclopentanone adducts.[5,6] It is known that the oxyallyl species 4 generated from the dibromo ketone 3 enters into stereospecific cycloaddition with (*Z*)-β-deuteriostyrene, affording the cyclopentanone 6.[6] Now it should be added that the reaction also produces as a by-product the open-chain adduct 7 having *E* olefinic configuration, contaminated with only trace of the *Z* isomer (<1%, if any). The structure was elucidated by comparing the spectral and chromatographic properties with those of its unlabeled protio derivative.[7] Location of deuterium atoms was determined by NMR analysis; 65% of deuterium atom which had been located in position cis, β to phenyl group was maintained at the vinylic position in the product but the remaining 35% was shifted to carbonyl α position during the reaction. Control experiments showed that (1) exposure of the *Z* isomer to the reaction conditions gives no or only very little *E* olefin (<1%), and (2) 6 is not convertible to 7 either. Thus notably, the keto olefin 7 has proved to form in a nonstereospecific manner with respect to the starting olefinic substrate. Both formal $[{}_{\pi}2 + {}_{\pi}2]$ cycloaddition, giving the cyclopentanone 6, and electrophilic olefinic substitution, leading to 7, may be simply considered to arise from the common intermediate 5, but full explanation of the contrasting stereochemical results displayed by these two reactions, *viz.*, stereospecific and nonstereospecific nature, requires the more detailed analysis of the reaction pathways.

The stereospecific formation of 6 is rationalized by assuming the U-shaped zwitterion 5U.[6,8] The strong attractive interactions inherently present between the enolate and cationic parts[2,9] prevent the structure from rotating around the $C_6H_5\overset{+}{C}H$—CDH bond that causes loss

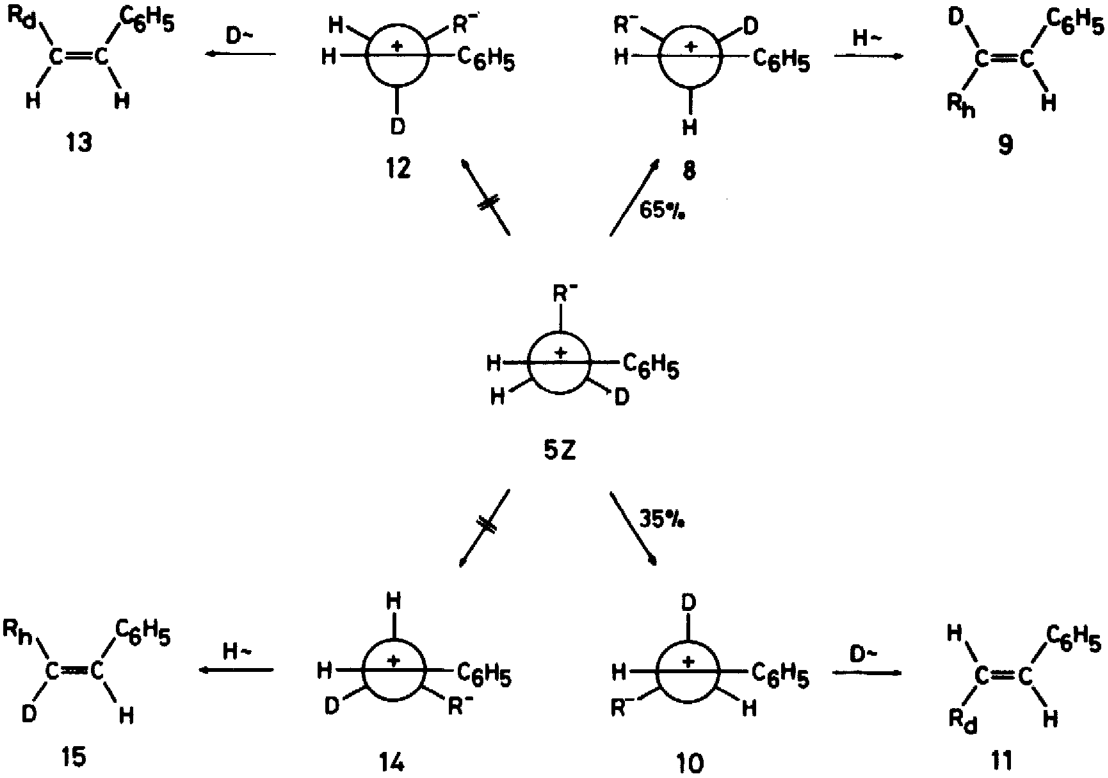


5U



5Z

Scheme I



$R^- = C(CH_3)_2C(O^-)=C(CH_3)_2$

$R_h = C(CH_3)_2COCH(CH_3)_2$

$R_d = C(CH_3)_2COCD(CH_3)_2$

of stereochemical integrity. On the other hand, the nonstereospecific nature of the electrophilic substitution reaction is best accounted for in terms of the Z-shaped intermediate **5Z**[8] undergoing transformations outlined in Scheme I. In this species electrostatic interaction between the charged moieties is of negligible significance in fixing the conformation. Here the 60° rotation, giving **8**, followed by proton transfer gives rise to the olefin **9** in which the stereochemistry of the starting styrene is retained, whereas deuterium elimination from **10**, derived via the 120° rotation, affords the product **11** where the starting olefin stereochemistry is inverted. Thus, mixing of these two pathways results in the overall nonstereospecific reaction. The *Z* olefins **13** and **15** are not produced, since formation of the sterically crowded precursors **12** and **14** is energetically unfavorable.[10]

REFERENCES AND NOTES

1. Carbon—Carbon Bond Formations Promoted by Transition Metal Carbonyls. XIV. Part XIII: Y. Hayakawa, M. Sakai, and R. Noyori, *Chem. Lett.*, 509 (1975).
2. Review: R. Gompper, *Angew. Chem., Int. Ed. Engl.*, **8**, 312 (1969).
3. N. D. Epiotis, R. L. Yates, D. Carlberg, and F. Bernardi, *J. Am. Chem. Soc.*, **98**, 453 (1976).
4. R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *J. Am. Chem. Soc.*, **94**, 7202 (1972).
5. R. Noyori, K. Yokoyama, S. Makino, and Y. Hayakawa, *J. Am. Chem. Soc.*, **94**, 1772 (1972).
6. R. Noyori, K. Yokoyama, and Y. Hayakawa, *J. Am. Chem. Soc.*, **95**, 2722 (1973).
7. (*E*)-2,4,4-Trimethyl-6-phenylhex-5-en-3-one: yield 3—23%, depending on the conditions; IR (CCl_4) 1704 (C=O) and 965 cm^{-1} (CH=CH); NMR (CCl_4, TMS) δ 1.03 (d, J = 7.0 Hz, $CH(C\underline{H}_3)_2$), 1.32 (s, $C(CH_3)_2$), 3.07 (seven lines, J = 7.0 Hz, $C\underline{H}(CH_3)_2$), 6.24 (d, J = 16.5 Hz, $C\underline{H}{=}CHC_6H_5$), 6.40 (d, J = 16.5 Hz, $CH{=}C\underline{H}C_6H_5$), 7.23 (m, C_6H_5). Its *Z* isomer: no IR absorption at 965 cm^{-1}; NMR signals due to olefinic protons at δ 5.69 and 6.46 (J = 12.5 Hz). These isomers were separable on GLC. No noticeable isomerization of the starting styrene took place during the reaction.
8. For **5U** and **5Z**, syn and anti structures are possible with respect to the phenyl (or deuterium) and enolate oxygen. Such difference in the diastereomeric relationship does not affect the argument described herein. It is difficult to distinguish experimentally between **5U** and an intermediate corresponded to **2**.
9. I. Karle, J. Flippen, R. Huisgen, and R. Schug, *J. Am. Chem. Soc.*, **97**, 5285 (1975).
10. D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963); H. C. Brown and M. Nakagawa, *ibid.*, **77**, 3614 (1955).