

## STEREOCHEMISTRY IN THE CYCLOADDITION OF OXYALLYL AND CONJUGATED DIENES

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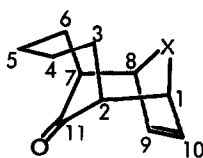
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Cycloaddition of allylic ions with dienes has attracted current interest (1) and its stereochemical course was proposed recently (1b). Although cyclopropanones (2) or halogenated ketones (3) are also known to undergo [ $\pi 4_s + \pi 2_s$ ] cycloadditions with dienes through the common intermediate, oxyallyl, and stereochemical course was implied in some cases (3b), definite proof is still lacking. We have investigated the reactions of a cyclic oxyallyl with furan and cyclopentadiene, where products have no possibility of epimerization, in order to clarify the stereochemistry of the reaction.

Reaction with furan 2,7-Dibromocycloheptanone was heated at 60° in acetonitrile for 52 hrs in the presence of excesses of zinc-copper couple and furan. After  $Al_2O_3$  chromatography of the reaction mixture, the 1:1 adduct Ia, colorless plates, m.p. 49-50°,  $\lambda_{max}^{hexane}$  260 ( $\epsilon$  19.2), 271 (22.3), 281 (25.8), 290 (31.4), 299.5 (34.7), 309.5 (29.2) and 321 nm (14.9),  $\nu^{KBr}$  1700, 714  $cm^{-1}$ , MS  $m/e$  178 ( $M^+$ ), 110, 107, 95, 82, 81 (base peak), 68, was obtained in 6.3 % yield (4). NMR spectrum (100 MHz in  $CCl_4$ ) exhibited the following signals:  $\delta$  1.10-2.20 (8H), 2.35 (2H, br. m,  $H_2, H_7$ ), 4.56 (2H, br s,  $H_1, H_8$ ), 6.22 (2H, s,  $H_9, H_{10}$ ). The assignment was confirmed by NMR, which also disclosed coupling constants  $J_{1,10} \approx 0.5$  Hz and  $J_{1,2} = 1.3$  Hz. The small  $J_{1,2}$  is compatible with the formula Ia but not with the stereoisomeric IIa (5). The stereoisomer IIa was failed to be detected.

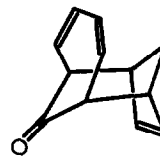
Reaction with cyclopentadiene 2,7-Dibromocycloheptanone was mixed at 0° in acetonitrile for 2 hrs in the presence of excesses of zinc-copper couple and cyclopentadiene. Chromatographic separation yielded two adducts, Ib, volatile liquid, and IIb, colorless needles, m.p. 183-190° (sealed tube), in 3.0 % and 4.4 % yield, respectively. They exhibit the following spectral data: Ib,  $\nu^{liq.}$  1700, 722  $cm^{-1}$ ,



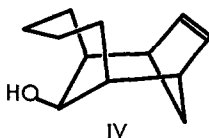
- I a X=O  
 b X=CH<sub>2</sub>  
 c X=CH<sub>2</sub> 9,10-dihydro



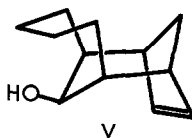
- II a X=O  
 b X=CH<sub>2</sub>  
 c X=CH<sub>2</sub> 9,10-dihydro



III



IV



V

$\delta^{\text{CDCl}_3}$  1.2-2.0 (8H, complex), 2.3-2.6 (4H, complex), 6.10 (2H, s), IIb,  $\nu^{\text{KBr}}$  1701, 784, 750  $\text{cm}^{-1}$ ,  
 $\delta^{\text{CDCl}_3}$  1.1-2.0 (8H, complex), 2.8 (4H, br.s), 6.41 (2H, s), MS  $m/e$  176 ( $M^+$ ), 110 (base peak), 91,  
 79, 66 55. Ib was further hydrogenated (Pd-C) to the known dihydro compound Ic (6a),  $\nu^{\text{liq}}$  1710  $\text{cm}^{-1}$ ,  
 which was obtained by the catalytic reduction of III (6) IIb, on the similar hydrogenation, yielded the  
 corresponding dihydro compounds IIc, colorless liquid,  $\nu$  1700  $\text{cm}^{-1}$ . Lithium aluminum hydride reduction  
 of IIb yielded the corresponding alcohol IV, colorless prisms, m.p. 180-190<sup>o</sup> (sealed tube),  $\nu$  3275, 1065,  
 760, 740  $\text{cm}^{-1}$ , MS  $m/e$  178 ( $M^+$ ), 160, 112, 67 (base peak) NMR spectrum [ $\delta^{\text{CDCl}_3}$  1.15-2.9 (14H,  
 complex), 4.70 (1H, t,  $J=6.5$ ), 6.30 (2H, br.s)] disclosed the presence of two equivalent protons at  $\beta$   
 positions A similar triplet [ $\delta$  4.16 (1H, t,  $J=5.5$ )] was observed for the alcohol V, colorless liquid,  
 corresponds to Ia.

Though the formation of two adducts from cyclopentadiene may be taken as the result of unconcerted nature of the reaction, the single product formation from furan suggests that the cycloaddition of oxyallyl in general is concerted reaction. Calculation of the stabilization energy in the transition state of each reaction (7) was therefore carried out using known molecular orbitals (8,9,10) of the reactants. The result for the latter reaction revealed that the p-orbital of oxygen rather than of C<sub>2</sub> of oxyallyl has larger 2nd order interaction with furan, and that the cis arrangement leading to the product Ia is ca 3 kcal/mol more stable than trans arrangement. Likewise, in the case of cyclopentadiene, the cis arrangement (leading to Ib) is ca 1.6 kcal/mol more stable than the trans arrangement (giving IIb). The smaller difference in

stabilization in the latter case, may be responsible for the poor stereospecificity (11)

#### References and Footnotes

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b. H. M. R. Hoffmann and D. R. Joy, ibid. (B), 1182 (1968).
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- 4) Similar reactions were once attempted by Cookson but no adduct was reported to be formed (3b).
- 5) With the Dreiding model of Ia, the dihedral angle between H<sub>1</sub> and H<sub>2</sub> is ca 55°, whereas the model of IIa has the dihedral angle of ca 20°. For the compound III, the coupling constants correspond to J<sub>1,10</sub> and J<sub>1,2</sub> in Ia are ~0.5 and 2.8 Hz, respectively (Y. Fujise, Ph.D. Thesis, Tohoku University, 1967).
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- 7) Cf. W. C. Herndon and L. H. Hall, Tetrahedron Letters, 3095 (1967). In our calculation, geometry of two reactants are taken from the literatures (8,9,10). They are assumed to arrange parallel to each other allowing the maximum overlap of the p-orbitals at the reacting centers. The distance of the reacting centers was assumed to be 2 Å. However, change of the distance does not make alternation of their relative stability.
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- 11) Because Ib is very volatile, the product ratio after isolation is not reliable for the quantitative evaluation. NMR spectrum of the crude ketonic fraction exhibits the signals δ 6.1 and δ 6.41 in the relative intensity ratio of 0.9-1.3.