Tetrahedron Letters No. 31, pp. 2969-2972, 1971. Pergamon Press. Printed in Great Britain

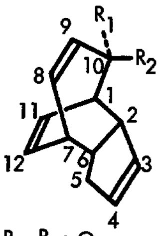
CYCLOADDITION REACTION OF TROPYLIUM ION AND CYCLOPENTADIENE

Shô Itô and Isamu Itoh
Department of Chemistry, Tohoku University
Sendai, Japan

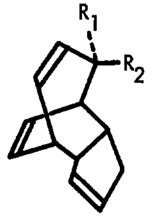
Although organic cations are known to undergo cycloaddition reactions with olefines and their reactions were ingeniously rationalized in terms of the conservation of orbital symmetry (1), information about the secondary effect, which reflects on the stereospecificity of the reaction, is still limited. We have found that the tropylium ion undergoes facile cycloaddition reactions highly-stereospecifically with conjugated olefines. This paper deals with its reaction with cyclopentadiene.

Tropylium perchlorate (I), when allowed to react at room temperature with 5 molar equivalents of cyclopentadiene (II) in 66% aq. dioxane for 10 hours, yielded a complex mixture of alcohols in 90% yield. Although complete separation of the mixture failed, chromic anhydride oxidation in pyridine of the partially separated alcohols followed by careful chromatography using SiO_2 and SiO_2 impregnated with $AgNO_3$ afforded three previously known ketones, III (25%), IV (37%) and V (2%) (2), and two new isomeric ketones VI (7%), m.p. 57.5-58.5°, Mass m/e 172 (M^+), 107 (base peak, C_7H_7O), λ_{max} 230 (sh, ϵ=1181), 297 nm (100), ν 1690, 910, 750 cm^{-1} , and VII (11%), m.p. 75.5-77°, Mass m/e 172 (M^+), 107 (base peak, C_7H_7O), λ_{max} 230 (sh, ϵ=1185), 297 nm (150), ν 1690, 908, 734 cm^{-1} (3).

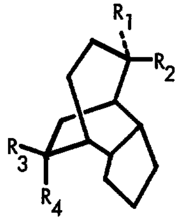
Structures of VI and VII were established in the following way. On catalytic reduction, both VI and VII yielded a mixture of VIII, liq., Mass m/e 178 (M^+), ν 1715, 1408 cm^{-1} (67% yield), 2,4-dinitrophenylhydrazone (DNP) m.p. 165°, and IX, liq., Mass m/e 176 (M^+), ν 1690, 923 cm^{-1} (26% yield). Although VIII is different from X, DNP m.p. 131° (2), their Huang Min-Lon reduction product XI was identical (VPC, IR). Complete structures of VI and VII, especially the positions of the double bonds in the 5-membered ring were established by extensive NMDR studies. NMR parameters obtained are as follows:



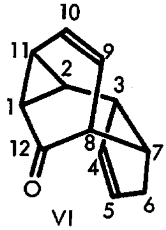
III R_1,R_2=O
XII R_1=OH, R_2=H
XIII R_1=H, R_2=OH



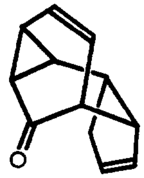
IV R_1,R_2=O
XIV R_1=OH, R_2=H
XV R_1=H, R_2=OH



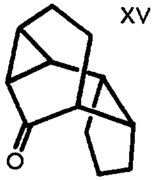
VIII R_1=R_2=H, R_3,R_4=O
X R_1,R_2=O, R_3=R_4=H
XI R_1=R_2=R_3=R_4=H
XVI R_1=OH, R_2=R_3=R_4=H
XVII R_2=OH, R_1=R_3=R_4=H



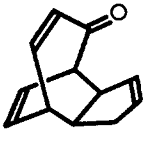
VI



VII



IX



V

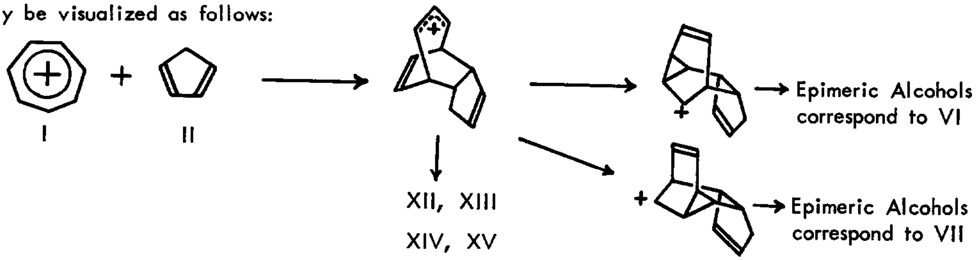
For VI, δ_1: 2.2, δ_2: 1.89, δ_3: 3.17, δ_4: 5.70, δ_5: 5.72, $\delta_{6\alpha}$: 2.18, $\delta_{6\beta}$: 2.42, δ_7: 2.92, δ_8: 2.73, δ_9: 5.88, δ_{10}: 5.88, δ_{11}: 1.95, $J_{1,2}$: 8.0, $J_{1,8}$: 2.0, $J_{1,11}$: 8.0, $J_{2,3}$: 1.0, $J_{2,11}$: 8.0, $J_{3,4}$: 1.7, $J_{3,5}$: 0.7, $J_{3,6\alpha}$: 2.5, $J_{3,6\beta}$: 1.5, $J_{3,7}$: 8.5, $J_{4,5}$: 7.0, $J_{4,6\alpha}$: 1.2, $J_{4,6\beta}$: 1.8, $J_{5,6\alpha}$: 1.2, $J_{5,6\beta}$: 1.8, $J_{6\alpha,6\beta}$: 16.0, $J_{6\alpha,7}$: 2.5, $J_{6\beta,7}$: 8.0, $J_{7,8}$: 3.0, $J_{8,9}$: 4.0, $J_{10,11}$: 3.0, and for VII, δ_1: 1.91, δ_2: 1.72, δ_3: 2.8, $\delta_{4\alpha}$: 2.36, $\delta_{4\beta}$: 2.91, δ_5: 5.42, δ_6: 5.75, δ_7: 3.38, δ_8: 2.77, δ_9: 5.88, δ_{10}: 5.88, δ_{11}: 2.13, $J_{1,2}$: 8.0, $J_{1,8}$: 2.0, $J_{1,11}$: 8.0, $J_{2,3}$: 0.5, $J_{2,11}$: 8.0, $J_{3,4\alpha}$: 5.5, $J_{3,7}$: 10.0, $J_{4\alpha,4\beta}$: 15.0, $J_{4\alpha,5}$: 2.0, $J_{4\alpha,6}$: 1.8, $J_{4\alpha,7}$: 3.0, $J_{4\beta,5}$: 1.8, $J_{4\beta,6}$: 1.8, $J_{5,6}$: 6.0, $J_{5,7}$: 2.0, $J_{6,7}$: 2.0, $J_{7,8}$: 3.0, $J_{8,9}$: 3.0, $J_{10,11}$: 3.5.

$LiAlH_4$ reduction of III yielded two epimeric alcohols XII, liq., ν 3330, 1035, 710 cm^{-1}, 3,5-dinitrobenzoate (DNB) m.p. 156-157°, and XIII, liq., ν 3310, 1021, 710 cm^{-1}, benzoate m.p. 68-69.5°, in 30 : 70 ratio. Configurations of the hydroxyl groups in XII and XIII were determined by an NMR method using the "shift reagent" $Eu(DPM)_3$ (4). The shift of the pertinent hydrogens are listed in TABLE I.

TABLE I. The Paramagnetic Induced Shift of XII and XIII for $CDCl_3$ Solution in the Presence of 1/2 Molar Equivalent of $Eu(DPM)_3$ (ppm)

Compds.	H-2	H-6	H-11	H-12
XII	2.95	2.07	4.67	2.74
XIII	8.02	3.24	1.99	1.70

The paramagnetic induced shift is definitely larger at hydrogens on one side of the three carbon bridge (H-11 and H-12 in XII,and H-2 and H-6 in XIII) compared with the ones located on the other side (H-2 and H-6 in XII, and H-11 and H-12 in XIII), revealing the orientation of the hydroxyl groups (5). Both XII and XIII are present in the original mixture of cycloaddition products. So are the epimeric alcohols XIV, liq., ν 3330, 1021, 716 cm^{-1}, 3,5-dinitrobenzoate, m.p. 148-149.5°, and XV, liq., ν 3310, 1018, 746 cm^{-1}, benzoate, m.p. 85-86°, which were produced by the LiAlH$_4$ reduction of IV. Catalytic reduction (PtO$_2$) of XIV and XV yielded the saturated alcohols, XVI, m.p. 76-77° and XVII, liq., DNB, m.p. 140.5-141.5°, respectively. Since these alcohols, XVI and XVII, were also obtained by the respective reduction of XII and XIII, the structures of XIV and XV are confirmed. Although the separation of the alcohols formed by the LiAlH$_4$ reductions of VI and VII was incomplete, the presence of all four alcohols which correspond to VI and VII in the original alcohol mixture were ascertained by TLC and NMR. Thus, the cycloaddition reaction in question afforded all of eight possible isomeric alcohols and probably the ones which correspond to V. The major course of the reaction can therefore easily be visualized as follows:



The participation of I in the reaction was supported by the fact that the reaction proceeds only at a low pH region in which I is stable, and that the cycloaddition reaction of ditropyl ether or methoxytropylidene and II does not take place under the conditions employed for the reaction of I and II.

The high perispecificity (6) (only [4+2] adducts were formed) and the high stereospecificity (endo/exo = (III+IV+VI+VII)/ V= 80/2) clearly demonstrated in this reaction are rather surprising if one considers that the calculation of the perturbation energy in the transition state, which rationalized the dimerization of cyclopentadiene (7), leads to no such preference in this reaction (8).

The reactions of I with other olefines are in progress and will be published shortly (9).

We are deeply indebted to Professor T. Nakajima for his suggestions, to Dr. A. Mori for the calculations and to Mr. K. Sasaki for his technical assistance.

References and Footnotes

1) R. B. Woodward and R. Hoffmann, *Angew. Chem. Intern. Ed.*, **8**, 781 (1969).

2) S. Itô, K. Sakan and Y. Fujise, *Tetrahedron Letters*, 775 (1969). *Idem*, *ibid.*, 2873 (1970).

3) All new compounds gave satisfactory elemental analyses. UV and IR spectra were taken for methanol solution and liquid film or KBr disc, respectively. NMR spectra were measured at 100 MHz for $CDCl_3$ solution.

4) C.C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969), J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 422 (1970).

5) Application of the shift-reagent to the related system will be published separately.

6) K. N. Houk, L. J. Luskus and N. S. Bhacca, *J. Amer. Chem. Soc.*, **92**, 6392 (1970).

7) W.C. Herndon and L.H. Hall, *Tetrahedron Letters*, 3095 (1967).

8) In this calculation, tropylium ion was assumed to be bent in the transition state.

9) S. Itô, A. Mori, I. Saito, K. Sakan and H. Ishiyama, to be published.