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endo-SELECTIVITY IN THE CYCLOADDITION REACTIONS OF TROPYLIUM ION

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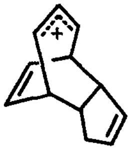
The presence of attractive diene-alkyl interactions in the transition state of cycloaddition reaction leading preferentially to the endo alkyl adduct appears to be established by a number of experiments (1,2). For the ionic cycloaddition reaction, a generalization was proposed by Bradsher with emphasis on the electrostatic repulsion in the transition state (3) in order to rationalize their result as well as our previous observation that tropylium ion and cyclopentadiene cycloadd with high peri- and stereoselectivity to give the endo-allylic ion I (and the tetracyclic ion formed therefrom) (4,5). Since tropylium ion of $D_{7}h$ symmetry is one of the simplest ionic (electron deficient) cycloaddend, and should lead to the exo- and endo-transition states of very similar steric environment, the ion is ideal to deduce the factors operating in the ionic cycloaddition reaction in general. We have carried out the reaction of the ion with simple olefines, cyclopropene and cyclopentene, anticipating the absence of the additional polarizable π-system should reduce the stereoselectivity of the reaction if the ionic repulsion is the predominating factor.

Cyclopropene was introduced into the 66% aqueous dioxane solution of tropylium perchlorate at room temperature to give an oily alcohol mixture in 20% yield (6). Chromic acid oxidation followed by a silica gel-$AgNO_3$ chromatography afforded two ketones, II and III, in 40% and 19% yield, respectively. While the first ketone II is identical (IR) with tricyclo[3.3.2.$0^{2,4}$]deca-7,9-dien-6-one (7), spectral data of the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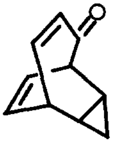
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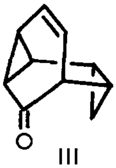
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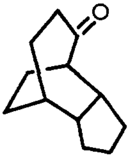
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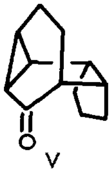
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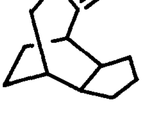
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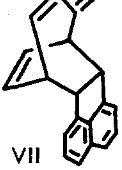
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second ketone III are in accord with the homobarbaralone structure shown (8). GLC of the crude ketone mixture exhibits only two peaks corresponding to II and III.

Cyclopentene reacted slowly with tropylium perchlorate under the same condition as above, to afford *a mixture of alcohols in 15% yield after 25 hrs. After Jones' oxidation, the corresponding ketone mixture* (ν^{CHCl_3} 1665, 1630 cm^{-1}) was subjected to catalytic hydrogenation without further separation. GLC of the hydrogenated ketone mixture consists of IV (contaminated by a small amount of V) and VI (4) in the ratio of 100:1.

These experiments, when coupled with our previous result (4), clearly demonstrated that the simple olefines cycloadd to tropylium ion with as much endo-selectivity as the more polarizable conjugated olefines; the fact inexplicable by the electrostatic repulsion (3) alone. More plausible explanation for the present *reactions is the attractive π-alkyl interaction as in the cases where only non-ionic addends are involved.*

For the reaction of cyclopropene to cyclopentadiene, theoretical calculation revealed that an allylic hydrogen in the former plays a crucial role and its interaction with π-system in the latter is the major factor for the second-order stabilization favoring endo arrangement and that these are the cases also in the approximated transition state although the first-order repulsion involving the same hydrogen prevents the molecules align parallel to each other (9). These general tendencies should also be valid for the reaction of cyclopentene in place of cyclopropene. Thus the result of the present reactions would be accounted *for by the same overall stabilization.*

We have also carried out the reaction using cycloaddend with no sp^3 type carbon: Thus acenaphthylene reacted with tropylium perchlorate under the same condition for 2 days to give colorless alcohol mixture in 40% yield, which after Jones' oxidation afforded the endo ketone VII (10) as the sole product. In this case, no serious steric factor is expected in either endo and exo transition state, and the preference of endo orientation should be ascribable to the stronger π-π interaction in endo transition state.

References and Footnotes

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5) The perispecificity there observed is in accord with the tendency found for the reaction of tropylium compounds, that is, the more tropylium ion character in the seven-membered ring, the more [4+2] adducts form. Cf. R.C. Cookson, B.V. Drake, J. Hudec and A. Morrison, Chem. Comm., 15 (1966). S. Itô, Y. Fujise, T. Okuda and Y. Inoue, Bull. Chem. Soc. Japan, 39, 1351 (1966). S. Itô, K. Sakan and Y. Fujise, Tetrahedron Letters, 775 (1969). Idem, ibid., 1873 (1970).
6) GLC (silicone SE-30, 120°) of the mixture discloses the ratio II:III as 64:36. Similar ratio (74:22) was obtained in the solvolysis of VIII (10).
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