

CYCLOADDITION REACTION OF TROPYLIUM ION AND CYCLOHEPTATRIENE

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In a previous paper (1), we have shown that tropylium ion undergoes facile cycloaddition reaction with cyclopentadiene to result in the formation of the ion I with high degree of perispecificity and stereospecificity. In an extension of the study, we have carried out the reaction of the ion with cycloheptatriene. The result is described herein.

Tropylium perchlorate (II), when allowed to react at room temperature with 4 molar equivalents of cycloheptatriene (III) in 66% aq. dioxane for 21 hours, yielded a complex mixture of alcohols in 32% yield (2). Chromic anhydride (pyridine complex) oxidation of the mixture followed by careful chromatography using SiO₂ and SiO₂ impregnated with AgNO₃ afforded, besides two known ketones (3), IV (2%) and V (1%), four new isomeric ketones VI, m.p. 103-104° (3%), VII, m.p. 106° (9%), VIII, colorless liquid (1%), and IXa, m.p. 86-90° (1%) (4). That II is the reacting species is supported by the facts that the reaction proceeds only at low pH region where II is stable (2) and that ditropyl ether which might be in equilibrium with II failed to undergo cycloaddition reaction at room temperature.

The structures of the new ketones, VI, VII, VIII, IXa, were deduced on the basis of the physical

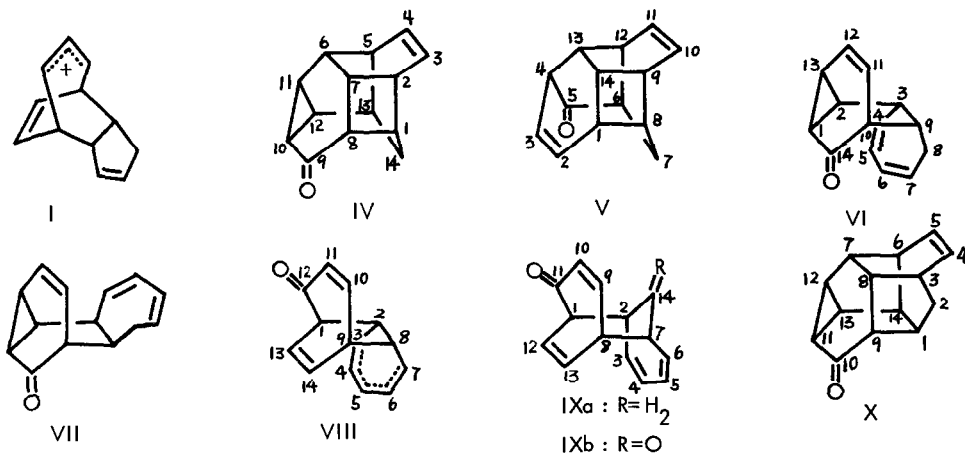


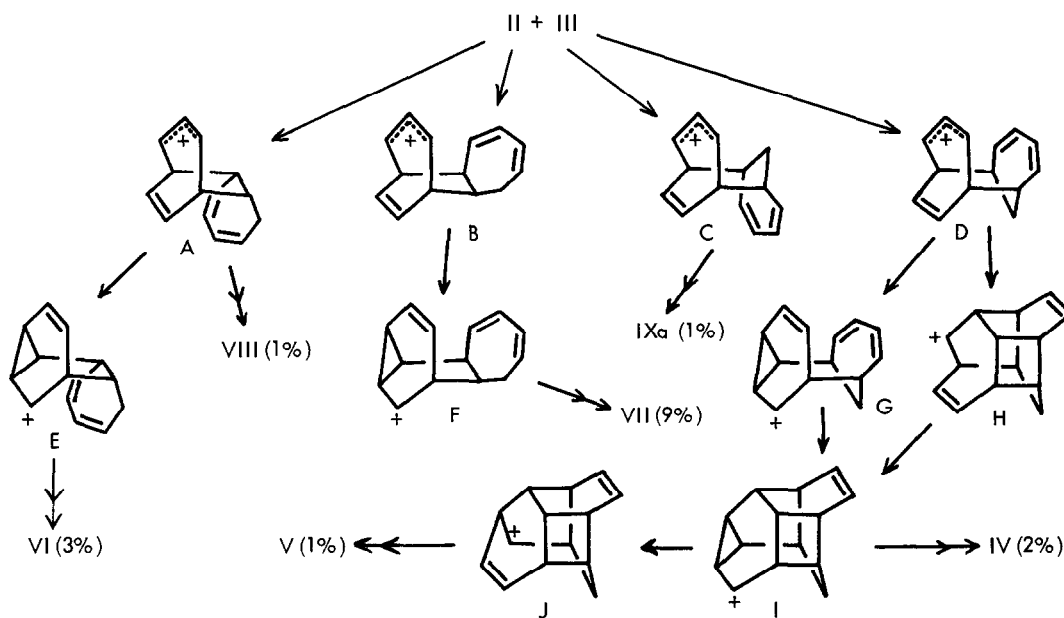
TABLE Physical Data of the Adducts

VI	VII	VIII	IXa
MS (m/e) 198 (M ⁺), 170 (M ⁺ -CO) 107 (C ₇ H ₇ O ⁺), 91 (C ₇ H ₇ ⁺)	198(M ⁺), 170, 107, 91	198 (M ⁺), 170, 107, 92, 91	198(M ⁺), 107, 91
$\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ nm (ϵ) 237 (4400), 293 (250)	255 (2500), 297 (85)	231 (6300), 250 (4400sh) 330 (130)	232 (9900), 255 (4900), 265 (3900), 290 (1800), 340 (130)
ν^{KBr} (cm ⁻¹) 3026, 1688, 880, 750, 716, 690	3026, 1690, 870, 830, 710, 660	3026, 1660, 750, 690*	3026, 1642, 855, 830, 700, 675
$\delta_{\text{CDCl}_3}^{100 \text{ MHz}}$ δ_1 : 1.91, δ_2 : 1.61 δ_3 : 3.06 δ_4 - δ_7 : 5.55-6.10 $\delta_{8\text{ex}}$: 3.06 (in C ₆ D ₆ 2.77) $\delta_{8\text{en}}$: 2.28 (in C ₆ D ₆ 2.00) δ_9 : 2.28, δ_{10} : 2.58 δ_{11}, δ_{12} : 5.55-6.10 δ_{13} : 2.14 $J_{1,2}=8$, $J_{1,10}=2$ $J_{1,13}=8$, $J_{2,3}=1$ $J_{2,13}=8$, $J_{7,8\text{en}}=5$ $J_{8\text{ex},8\text{en}}=12$, $J_{8\text{ex},9}=8$ $J_{9,10}=2$, $J_{10,11}=4$ $J_{10,12}=2$, $J_{11,13}=2.5$ $J_{12,13}=5$	δ_1 : 2.00, δ_2 : 2.25 δ_3 : 3.25 δ_4 - δ_7 : ~6.00 $\delta_{8\text{ex}}$: 2.49, $\delta_{8\text{en}}$: 1.75 δ_9 : 3.25, δ_{10} : 2.25 δ_{11}, δ_{12} : ~6.00 δ_{13} : 2.25 $J_{1,2}=8.5$, $J_{1,10}=2$ $J_{1,13}=7$, $J_{7,8\text{ex}}=4.5$ $J_{7,8\text{en}}=7.5$, $J_{8\text{ex},8\text{en}}=11.5$ $J_{8\text{ex},9}=3$, $J_{8\text{en},9}=4.5$	δ_3 - δ_6 (or δ_4 - δ_7): 5.8-6.1 δ_9 : 3.32, δ_{10} : 7.05 δ_{11} : 5.72, δ_{13} : 6.22 δ_{14} : 6.51 $J_{1,11}=2$, $J_{1,13}=6$ $J_{1,14}=1$, $J_{8,9}=2$ $J_{9,10}=8.5$, $J_{9,13}=1$ $J_{9,14}=6$, $J_{10,11}=10.8$ $J_{13,14}=8$	δ_1 : 3.49, δ_2 : 2.66 δ_3 - δ_6 : ~5.90 δ_7 : 2.85, δ_8 : 3.52 δ_9 : 6.92, δ_{10} : 6.31 δ_{12} : 5.55, δ_{13} : ~5.90 $\delta_{14\text{en}}$: 2.46 $\delta_{14\text{ex}}$: 1.54 $J_{1,2}=5$, $J_{1,12}=8.4$ $J_{1,13}=2$, $J_{2,7}=2$ $J_{2,14\text{en}}=5$ $J_{2,14\text{ex}}=2.5$ $J_{7,8}=5$, $J_{7,14\text{en}}=5$ $J_{7,14\text{ex}}=2.5$, $J_{8,9}=9$ $J_{8,10}=1.5$, $J_{8,12}=1.8$ $J_{8,13}=7.9$, $J_{9,10}=12$ $J_{12,13}=10$ $J_{14\text{en},14\text{ex}}=14$

* IR bands for liquid film.

data shown in the Table. The presence of cyclopropyl ketone in VI and VII is demonstrated in IR (ν 1688–1690 cm^{-1}) and NMR ($\delta_1, \delta_2, \delta_{13}$ and $J_{1,2}, J_{1,13}, J_{2,13}$). Stereochemistry of VI and VIII is based on the NMR (J s of the bridge head protons). The position of the methylene group in VII was revealed from NMR using EU(DPM)₃; H₉ adjacent to the methylene shifted twice as much as the allylic H₃. Stereochemistry of VII was concluded from the following observation: While VI was recovered from reflux in xylene for 20 hours, VII afforded the new isomeric ketone X, m.p. 116.5–118°, in 58% yield, MS m/e 198 (M^+), $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 280 nm ($\epsilon=60$), ν^{KBr} 1682, 890, 720 cm^{-1} , $\delta_{\text{CDCl}_3}^{300 \text{ MHz}}$ 1.68 (H_{2en}, d, $J=11.9$), 1.81 (H_{2ex}, ddd, $J_{2ex,2en}=11.9, J_{2ex,3}=9.3, J_{2ex,1}=4.8$), 1.99 (H₁₄, m, $w_{h/2}=16$), 2.03 (H₁₁, td, $J_{11,12}=J_{11,13}=7.5, J_{11,9}=2.0$), 2.19 (H₉, br. s, $w_{h/2}=9.5$), 2.34 (H₇, m, $w_{h/2}=13$), 2.40 (H₁₂, td, $J_{12,11}=J_{12,13}=7.5, J_{12,7}=5.4$), 2.53 (H₁₃, td, $J_{13,11}=J_{13,12}=7.5, J_{13,14}=5.4$), 2.72 (H₁, H₃, m, $w_{h/2}=13.1$), 2.90 (H₆, m, $w_{h/2}=13.2$), 3.00 (H₈, m, $w_{h/2}=18.0$), 5.93 (H₅, ddd, $J_{5,4}=8.5, J_{5,6}=7.5, J_{5,3}=1.8$), 6.50 (H₄, dd, $J_{4,5}=8.5, J_{4,3}=7.5$). The intramolecular nature of this cyclization was verified when no deuterated X was found in the reaction of VII in the presence of excess cycloheptatriene-7-d₁. Physical data of IXa are in close similarity with those of the tropone-photodimer IXb (5).

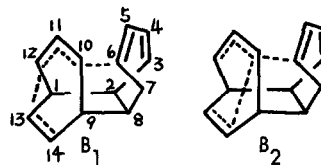
The entire course of the reaction can be summarized as follows:



The reduced reactivity of III toward II compared with that of cyclopentadiene (1), reflected in the slow reaction rate and the low total yield of the products, follows the general tendency of cycloaddition of these compounds. As is seen in the chart, II always reacts as 4 π component, demanding III to serve as either 2 π or 6 π reactant. Perispecificity, judged from the product ratio, is rather low ($[4\pi + 2\pi] : [4\pi + 6\pi] = \text{VI} + \text{VII} + \text{VIII} : \text{IV} + \text{V} + \text{IXa} = 3 : 1$). Stereospecificity, A : B = VI + VIII : VII = 4 : 9 for

$[4\pi + 2\pi]$ reaction and $C : D = IXa : IV + V = 1 : 3$ for $[4\pi + 6\pi]$ reaction, is also low, and further in the former reaction stereochemical preference ($A : B = 4 : 9$) is opposite to the case of cyclopentadiene (1) where the ratio, endo : exo is 40 : 1. This may indicate the complicated secondary effect operating in the transition states.

It is noteworthy that ions A and B form cyclopropane ring on the far side of the methylene group. Although the difference in internal strain at the bridge head carbons may be a reason for such a specificity, electronic factor should not be overlooked: Thus the ion B can have a conformation in which a terminus (C_6) of the diene system is situated closely ($\sim 2.2 \text{ \AA}$) to C_{10} , and which stabilizes B_1 more than B_2 by the transannular interaction. As the result of the greater contribution of B_1 than of B_2 , nucleophile would attack the ion B more at C_{14} than at C_{13} . Likewise in the ion A, a conformation in which C_6 is facing ($\sim 2.5 \text{ \AA}$) to C_{14} rather than C_{13} , would allow preferential attack of a nucleophile at C_{10} or at C_{13} . From this consideration, VIII is more likely to have 4,6-diene structure.



Although any conformation of A, B and F are incapable geometrically of further cycloaddition, the more symmetrical ions C and D have better geometry for the reaction. In fact, the ion D having better electron demand, proceeds to I through either G or H. Although symmetrical allylic ion is known to undergo the cycloaddition at both ends (6), the strong perturbation with the double bond in D would modify the situation and the ion H may result. The formation of I and J from H has been shown in our preceding paper (3). Intervention of G is supported by the formation of X from VII.

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References and Footnotes

- 1) S. Itô and I. Itoh, Tetrahedron Letters, 2969 (1971).
- 2) Addition of perchloric acid accelerates the reaction and increases the yield of alcohols up to 40%. The reaction at 60° accelerates the reaction, but the yield of alcohols remains constant (28-30%). The reaction under the constant acidity (pH 2.5) proceeds very slowly.
- 3) S. Itô, Y. Fujise, I. Saito and Y. Chonan, to be published.
- 4) The presence of a few more ketone was detected from the spectra of crude mixture. However, none of them were isolated pure because of the low yield, close Rf values in chromatography, and/or instability.
- 5) T. Tezuka, Y. Akasaki and T. Mukai, Tetrahedron Letters, 1397 (1967).
- 6) H. M. R. Hoffmann, D. R. Joy and A. K. Suter, J. Chem. Soc. B, 57 (1968).