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INTERMOLECULAR PROTON TRANSFER FROM BICYCLOOCTYL CARBONIUM ION TO CYCLOOCTADIENE

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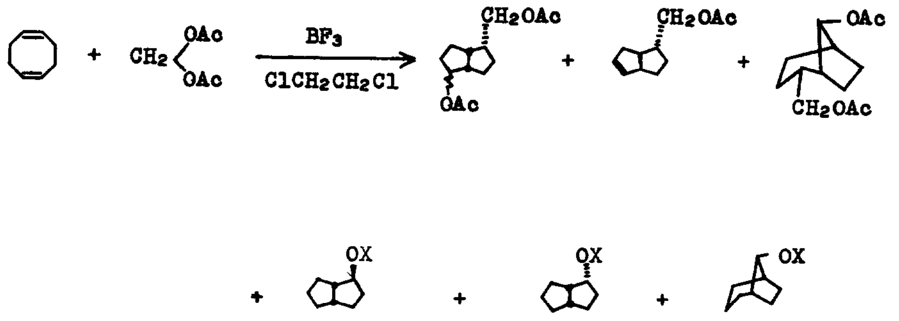
In our current study on π-π cyclization of cis, cis-1,5-cyclooctadiene by cationic addition(1), it is concluded that remarkable intermolecular proton transfer from 6-substituted bicyclo[3,3,0] oct-2-yl carbonium ion to the diene should be involved. Addition of diacetoxymethane to cyclooctadiene (equimolar amount) in the presence of Lewis acid such as $ZnCl_2$ or BF_3 (up to 20 mol% to the reactants) gave a considerable amount of monoacetate mixture (13.1% yield of bp 72°/7mmHg) together with normal addition-cyclization products(1a). The monoacetate mixture was consisted of exo- (I) and endo-cis-bicyclo[3,3,0]octyl -2-acetate (II) (49% and 34%, respectively) and exo-bicyclo[3,2,1]octyl-8 -acetate (III) (17%). Structural assignment of these was made on comparison of VPC and IR, and nmr spectra of these with those of authentic I(2), II(2) and III(3). Broad nmr of proton α to OAc is characteristic to the configuration ; centered at 5.40τ, relatively sharp, endo H of III(4), 5.30τ, broad and quartet -like, endo H of I ; or 4.90τ (broad and quartet-like, exo H of II(5). Other obsorptions are 9.0-7.0τ broad, twelve protons, ca. 8.07τ, singlet, three protons.

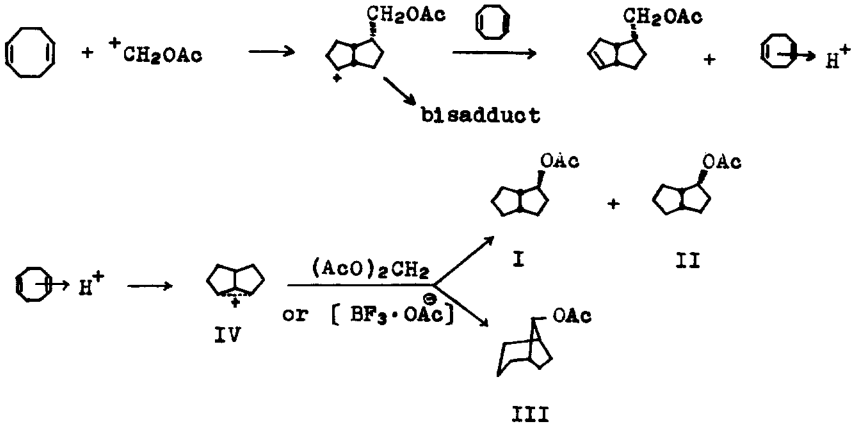


I a. X=Ac b. X=CHO c. X=H

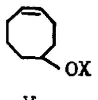
II a. X=Ac b. X=CHO c. X=H

III a. X=Ac b. X=CHO c. X=H

Formation of I, II and III are best explained by intermolecular proton transfer mechanism from intermediary bicyclooctyl carbonium ion to 1,5-cyclooctadiene. Possibility of acetic acid addition to the diene is evidently eliminated from the facts that acetic acid was not detected in diacetoxymethane and that formic acid addition to the diene gave cyclooctenyl formate as one of major products (see Table 1). Initial acetyloxyl cation addition to diene can not be reasonablly assumed and furthermore it may be eliminated on the stereochemical ground(6).



The present product ratio was very similar to that reported in cationic addition of formic acid (or acetic acid) to the diene (Table 1), which support the mechanism involving bicyclooctyl carbonium ion IV. Sole remarkable difference between both reactions is an absence of uncyclized ester V in our products. This may be attributable to much low nucleophilicity of $CH_2(OAc)_2$ or $(BF_3 \cdot OAc)^-$ compared with that of formic acid, and long-lived protonated cyclooctadiene would cyclize to IV exclusively.



V a. X=Ac

b. X=CHO

Table 1 Cation addition to 1,5-Cyclooctadiene (COD)

Reaction	Monoester Composition				
	I	II	III	VI d)	V
COD + $CH_2(OAc)_2$ + BF_3 a)	49	34	17	Not determined	Nill
COD + $HClO_4$ + HCO_2H b)	18.5	8.2	14.4 c)		59.0
+ AcOH c)	25.4	26.7		(18.9) f)	29.0 e)

a) present result b) ref. 7 c) unpublished result by the authors

d)  X=OAc or OCHO e) From prolonged reaction. (74 hrs refluxing in ethylene chloride, the same reaction time as disubstituted methane addition) f) including unknown product.

COD has a very high cyclizing tendency when it suffers attack by cationic reagent as seen in the reaction with disubstituted methanes(1) as well as in other cationic additions(7, 8). This tendency strongly suggests that π-π interaction in the diene or, at least, C^+-π interaction in the protonated diene is of great importance. The effective stabilization of cyclooctenium ion is in quite accordance with the strikingly facile proton transfer from the secondary carbanium ion to the diene. It has never been reported such a marked proton transfer from a carbonium ion to a unconjugated diene to the best of author's knowledge.

Kinetic investigation of the reaction is carring out where large excess amount of the diene or mixed olefins (cyclohexene, tetramethylethylene or isoprene were used as addenda) were used. Interestingly, preliminary results showed that a ratio "monoadducts" to "bisadducts"(9) of the diene was markedly increased in the condition. The finding is also in accord with the "proton transfer" mechanism. A detailed description of the results will appear in a separate paper.

References

1. a) A separate communication
   b) I.Tabushi, K.Fujita and R.Oda, Symposium on the Mechanism of Organic Reactions, *Chem.Soc.Japan*, 1966 October, Tokyo, Japan. (Abstr., p. 17-20)
2. I and II were prepared by means of Cope's prodedure (acetolysis of Δ^4-cyclooctenyl brosylate) ; A.C.Cope and P.E.Peterson, *J.Am.Chem.Soc*., **81**, 1643 (1959).
3. III was prepared via trifluoroacetolysis of Δ^4-cyclooctenyl brosylate, followed by saponification and acetylation ; A.C.Cope, J.M.Crisar and P.E. Peterson, *J.Am.Chem.Soc*., **81**, 4299 (1960).
4. This characteristic endo H absorption was general in our compounds. In these compounds, a bridge proton is nearly parpendicular to bridgehead proton so that the coupling constant is expected to be very small. In only one example was taken nmr spectrum of similar proton and singlet (τ 5.87) was observed for anti-bicyclo[3,2,1]oct-en-8-ol, N.A.LeBel, and L.A.Spurlock, *Tetrahedron*, **20**, 215 (1964).
5. All of exo- and endo derivatives in our hands show the same nmr characteristics (shape and chemical shift). $\Delta\tau$ is of the order of magnitude that is expected from different shielding by ring C-C bonds.
6. Cationic addition -π-πcyclization of 1,5-cyclooctadiene generally took place via initial exo-wise addition leading to endo [3,3,0] derivatives concerning with entering group. Similar stereochemistry was observed in the π-π cyclization of 1,6-cis, cis cyclodecadiene ; R.M.Gipson et al, *J.Am.Chem. Soc*., **88**, 5366 (1966).
7. A.C.Cope and P.E.Peterson, *J.Am.Chem.Soc*., **81**, 1640 (1959).

8. [3,3,0] Bicyclooctene-2 was reported as the product from phosphoric acid-silica gel cyclization of COD ; German Patent, 1, 167, 824 ; _Chem.Abstr._, **61**, 1776 (1964).

9. "monoadducts" include $^{+}CH_2X$ addition-H^{-} elimination products and H^{+} addition-Y^{-} addition products, while "bisadduct" include $^{+}CH_2X$ and Y^{-} addition products.