

REACTIONS OF *cis*, *trans*, *trans*-1, 5, 9-CYCLODODECATRIENE

I. SELECTIVE OXIDATION WITH OSMIUM TETROXIDE
AND POTASSIUM PERMANGANATE

Masaji Ohno and Seiichi Torimitsu

Basic Research Laboratories, Toyo Rayon Co. Ltd.,

Kamakura, Japan

(Received 30 June 1964)

Among three stereoisomers of cyclododecatriene, *cis*, *trans*, *trans*-1, 5, 9-cyclododecatriene is not only most interesting because of the presence of one *cis* double bond and two *trans* double bonds in the same molecule, but also most easily available¹⁾.

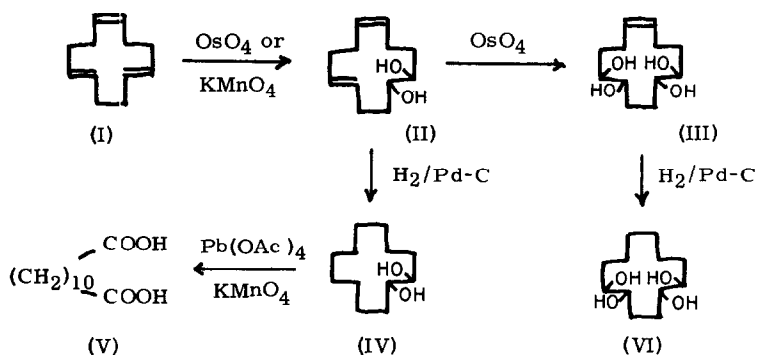
Various reactions utilizing the double bonds have been reported. A *trans* double bond is selectively oxidized with organo peracids to give *cis*-5, *trans*-9-cyclododecadiene-1, 2-epoxide^{2), 3)}, and more easily attacked by diethylborane⁴⁾.

However, addition reactions of halogen⁵⁾, hydrogen chloride⁶⁾, acetic acid⁶⁾ and silane⁷⁾ showed no selectivity in so far as the *cis* or *trans* configuration is concerned.

These results suggested us that the competitive reactivities

between the cis and trans double bonds must be greatly influenced by stereochemical stability at transition state, and led us to investigate the reactions of the cyclotriene with cis-addition reagents which might react preferentially with the trans double bond at transition state.

Oxidation of cis, trans, trans-1,5,9-cyclododecatriene with osmium tetroxide and potassium permanganate, well established as cis-addition reagents, showed a high selectivity to afford cis-5, trans-9-cyclododecane-trans-1,2-diol, and the results are shown below.

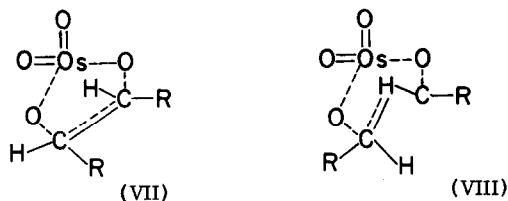


cis, trans, trans-1,5,9-Cyclododecatriene in aqueous acetone was treated with one mole equivalent of potassium permanganate under stirring and keeping at 20° (exothermic reaction). A colorless crystalline material, m. p. $168 - 169^\circ\text{C}$, was obtained in 59% yield and proved to be cis-5, trans-9-cyclododecadiene-trans-1,2-diol from analysis, infrared spectrum (Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}_2$: C, 73.43; H, 10.27. Found: C, 73.51; H, 10.47.), ($3300 - 3500\text{ cm}^{-1}$ for hydroxy group, 983 cm^{-1} for trans double bond and 707 cm^{-1} for cis double bond), and its quantitative conversion into known cyclo-

dodecane-trans-1,2-diol⁸⁾, m. p. 102 - 103^o, with catalytic hydrogenation and then known 1,10-decanedicarboxylic acid⁹⁾ by oxidation with lead tetraacetate and then potassium permanganate. The same cis-5, trans-9-cyclododecadiene-trans-1,2-diol was also obtained in 89% yield from a reaction with one mole equivalent of osmium tetroxide at room temperature.

These results clearly showed that the first attack by such cis-addition reagents took place at one of the trans double bonds and there was a considerable difference in reactivity between the cis and trans double bonds enough to control the product.

Such competitive reactivities might be reasonably explained by conformational stability at transition state as shown below, since there is no considerable difference in steric approach control between cis and trans double bonds of the starting material.



There are two eclipsing effects in form VII for the cis double bond but only one in form VIII for the trans double bond, therefore the latter is obviously more stable and hence reacts more rapidly¹⁰⁾.

It was also shown that further oxidation of cis-5, trans-9-cyclododecadiene-1,2-diol with osmium tetroxide gave cis-9-cyclododecene-1,2,5,6-tetrol, m. p. 212-4^o, in 60% yield. (Calcd.

for $C_{12}H_{22}O_4$: C, 62.58 ; H, 9.63. Found : C, 62.45 ; H, 9.63 .
I. R. only at 707 cm^{-1} for cis double bond). Catalytic hydrogenation
of the unsaturated tetrol yielded cyclododecane-1, 2, 5, 6-tetrol,
m. p. 169-170°. (Calcd. for $C_{12}H_{24}O_4$: C, 62.04 ; H, 10.41. Found :
C, 61.83 ; H, 10.49 . I. R. no absorption at 707 cm^{-1}).

Extension of the reaction with other cis-addition reagents are
now being surveyed and the results will be published soon.

References

- 1) G. Wilke, Angew. Chem., **69**, 397 (1957).
- 2) G. Wilke, J. Polymer Sci., **38**, 45 (1959).
- 3) L. I. Zakharkin and V. V. Korneva, Dokl. Akad. Nauk SSSR, **132**, 1078 (1960).
- 4) R. Koster and G. Griaznov, Angew. Chem., **73**, 171 (1961).
- 5) H. Takahashi and M. Yamaguchi, J. Chem. Soc. Japan. Pure Chem. Sect. **83**, 1042 (1962).
- 6) L. I. Zakharkin, V. V. Kornera, and A. V. Iogansen, Dokl. Akad. Nauk SSSR, **138**, 373 (1961).
- 7) H. Takahashi, H. Okita, M. Yamaguchi and I. Shiihara, J. Org. Chem., **28**, 3353 (1963).
- 8) V. Prelog and M. Speck, Helv. Chim. Acta, **38**, 1786 (1955).
- 9) J. Walker, J. Chem. Soc., 1940, 1304.
- 10) G. S. Hammond, J. Am. Chem. Soc., **77**, 334 (1955).