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Catalytic Oxidation of Pentacyclo[6.6.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene. Syntheses of Novel Polyfunctional Half-Open Cage Compounds

Toshiaki Suzuki, Kazuo Iida, Kenji Wada, Teruyuki Kondo, and Take-aki Mitsudo*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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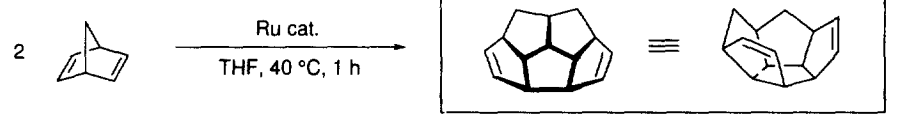
Abstract: Oxidation of pentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene, PCTD, with hydrogen peroxide catalyzed by methyltrioxorhenium selectively gave the *exo,exo*-diepoxide in high yield. Osmium tetraoxide catalyzed selective *syn-exo*-tetrahydroxylation or *syn-exo*-dihydroxylation of PCTD with *N*-methylmorphorine *N*-oxide. Ruthenium trichloride-catalyzed oxidative cleavage of the olefinic groups in PCTD with sodium periodate gave a derivative of tricyclodecanecarboxylic acid with two lactone rings. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: oxidation, epoxides, polyols, carboxylic acids and derivatives

Polyfunctionalyzed cage and half-open cage compounds are of interest in organic synthesis.[1] Recently, a synthetic method of a novel half-open cage hydrocarbon with two olefinic groups, pentacyclo-[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradeca-4,11-diene (PCTD, **1**), has been established (eq. 1).[2] Ru(η^6-cyclo-octatriene)(η^2-dimethyl fumarate)$_2$ was found to be an excellent catalyst for dimerization of 2,5-norbornadiene to PCTD. PCTD has five five-membered rings and two olefinic groups on both sides and is expected to be a novel starting dialkene for a cascade of polyfunctional half-open cage compounds. One important reaction is oxidation of the olefinic moieties of PCTD introducing oxygenated functional groups. Stoichiometric oxidation of **1** using $KMnO_4$ or ozonolysis was unsuccessful and mixtures of a number of oxidized products were formed. We found that complex-catalyzed stereoselective oxidation was successfully accomplished, the results of which we now report.



PCTD
1
96 %

(1)

For the epoxidation of PCTD, oxidation with *m*-chloroperbenzoic acid has been reported; however, the yield was unsatisfactory.[3,4] Oxidation of PCTD with an excess of hydrogen peroxide catalyzed by methyltrioxorhenium (MTO)[5] selectively gave the corresponding *exo,exo*-diepoxide **2**, *exo,exo*-4,5,11,12-diepoxypentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradecane, in excellent yields (eq. 2). With 1.1 equivalent of

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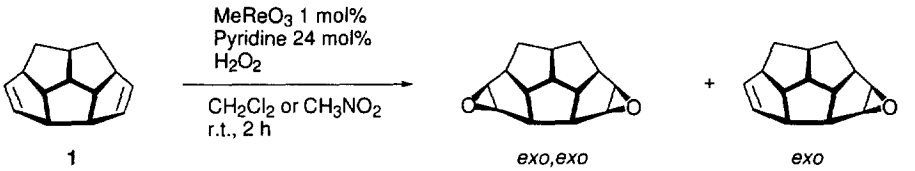
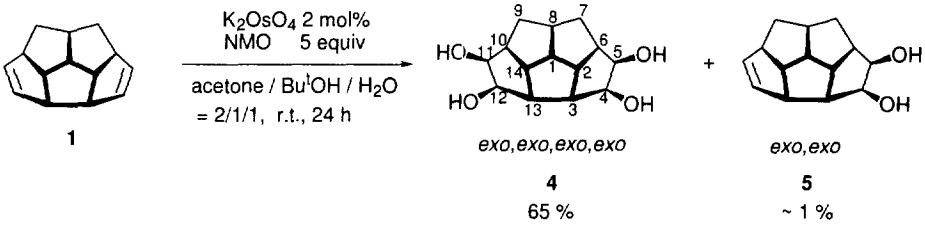
hydrogen peroxide, monoepoxide **3**, *exo*-11,12-epoxypentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradec-4-ene, and diepoxide **2** were formed in 65 and 20% yields, respectively.



(2)

Generally, alkenes can be vicinally dihydroxylated with a catalytic amount of osmium tetraoxide in the presence of an oxidant such as hydrogen peroxide, *N*-methylmorphorine *N*-oxide (NMO) or potassium ferricyanide (III).[6] The application of the osmium tetraoxide-catalyzed dihydroxydation with NMO to PCTD selectively gave a novel tetraol, *exo,exo,exo,exo*-4,5,11,12-tetrahydroxypentacyclo[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]-tetradecane (**4**),[7] in 65% yield with a small amount of diol **5**, *exo,exo*-11,12-dihydroxypentacyclo-[6.6.0.$0^{2,6}$.$0^{3,13}$.$0^{10,14}$]tetradec-4-ene (eq 3). Tetraol **4** is insoluble in most organic solvents, except for dimethyl sulfoxide, so it precipitated from the reaction mixture due to its poor solubility in the mixed solvent.

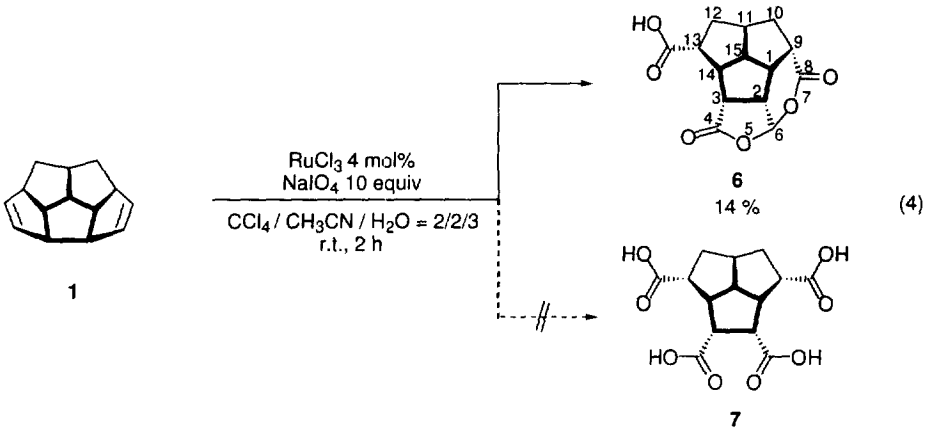


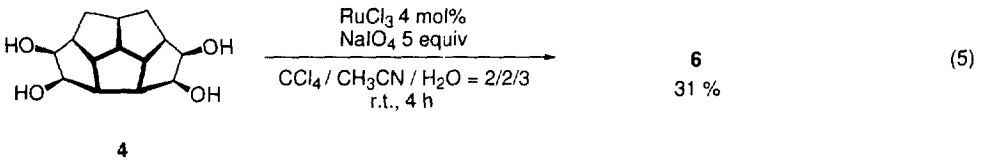
(3)

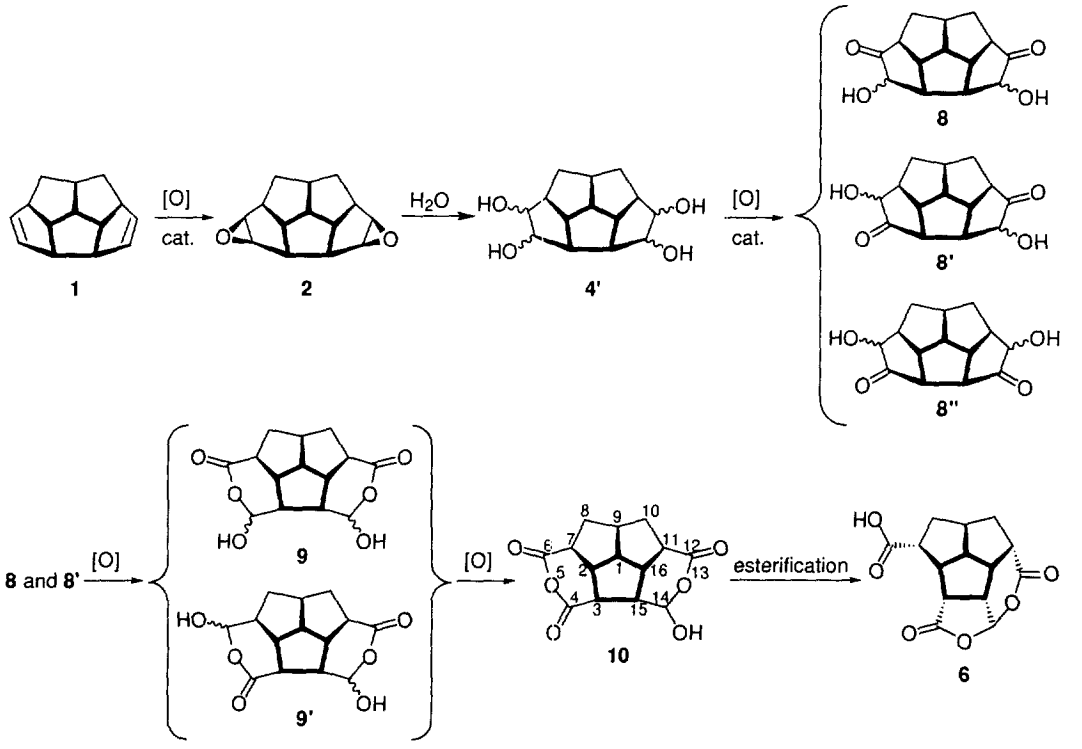
In the epoxidation (eq. 2) and dihydroxylation (eq. 3) of PCTD, there is a possibility that *endo*-isomers are formed. However, only *exo*-isomers were selectively formed because *endo* attack of the catalytically active species is suppressed by steric hindrance due to the characteristic cage structure.

For the oxidative cleavage of the olefinic groups, several efficient catalytic reactions have been developed.[8] Ruthenium trichloride has been known to give dicarboxylic acids from cycloalkenes in the presence of sodium periodate or sodium hypochlorite. This method was applied to the oxidation of **1**, and an unexpected monocarboxylic acid, 5,7-dioxa-4,8-dioxopentacyclo[7.6.0.$0^{2,6}$.$0^{3,14}$.$0^{11,15}$]pentadecane-13-carboxylic acid (**6**),[9] which is a derivative of tricyclodecanecarboxylic acid with two lactone rings, was obtained in 14% yield and no tetracarboxylic acid **7** was detected (eq 4). Bis(lactone) **6** is sparingly soluble in most organic solvents, but can be recrystallized from hot methanol without being converted into other derivatives. Tetraol **4** was transformed into **6** in 31% yield under similar reaction conditions (eq 5).

A plausible mechanism of the formation of **6** is shown in Scheme 1. PCTD **1** is oxidized to diepoxide **2** followed by hydrolysis to tetraols **4'**. The tetraols **4'** are oxidized to bis(α-ketol) **8**, **8'** and **8''**.[8e] The isomers **8** and **8'** would be converted into bis(hemiacylal) **9** and **9'** by Baeyer-Villiger oxidation.[8e] One of the hemiacylal groups of **9** is oxidized to carboxylic anhydride to give **10**,[8e] and esterification occurs to give **6**.







Scheme 1. A plausible mechanism for the formation of **6**.

The hydroxyl group at the 14-position in **10** could be very close to the carbonyl carbon at the 4-position. Thus, this reaction is specific to the half-open cage compound. Low yields of **6** are considered to be due to the formation of three isomers of **8** resulting in the formation of two isomers of **10**, one of which would be converted into unidentified compounds.

In conclusion, we have developed stereoselective syntheses of half-open cage compounds possessing oxygenated functional groups by transition metal-catalyzed oxidation of PCTD. Novel epoxides **2** and **3**, polyols **4** and **5** and the bis(lactone) **6** are useful starting compounds for further polyfunctional half-open cage compounds. These compounds are also expected to be functional monomers which control the character of polymers when they are introduced into polyesters or polyurethanes. Further studies on catalytic oxidations of PCTD are currently in progress.

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7. Tetraol **4**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.29 (d, 2H, OH, J = 4.4 Hz), 4.18 (d, 2H, OH, J = 5.4 Hz), 3.99 (br m, 2H, 4- and 12-H), 3.87 (br m, 2H, 5- and 11-H), 3.19 (q, 2H, 2- and 14-H, J = 9.8 Hz), 2.80 (q, 1H, 1-H, J = 9.8 Hz), 2.53 (m, 3H, 3-, 8- and 13-H), 2.31 (m, 2H, 6- and 10-H), 1.86 (dt, 2H, 7-*exo*- and 9-*exo*-H, J = 13.7, 9.3 Hz), 1.32 (dt, 2H, 7-*endo*- and 9-*endo*-H, J = 13.7, 5.9 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ 80.2 and 75.2 (C4, C5, C11 and C12), 57.2 (C3 and C13), 56.2 (C1), 52.3 (C2 and C14), 52.3 (C6 and C10), 47.4 (C8), 36.6 (C7 and C9).
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9. Bis(lactone) **6**. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.7 (br, 1H, CO_2H), 6.32 (d, 1H, 6-H, J = 6.6 Hz), 3.56 (dd, 1H, 3-H, J = 10.3, 8.8 Hz), 3.35 (td, 1H, 2-H, J = 10.3, 6.6 Hz), 3.27 (td, 1H, 13-H, J = 10.3, 7.3 Hz), 3.20 (dt, 1H, 15-H, J = 11.0, 8.8 Hz), 3.07 (dt, 1H, 9-H, J = 13.2, 8.8 Hz), 3.00 (td, 1H, 14-H, J = 8.8, 7.3 Hz), 2.91 (dt, 1H, 1-H, J = 10.3, 8.8 Hz), 2.66 (m, 1H, 11-H), 2.29 (dt, 1H, 10-H, J = 13.9, 8.8 Hz), 2.12 (dt, 1H, 12-H, J = 13.2, 10.3 Hz), 1.56 (ddd, 1H, 12-H, J = 13.2, 10.3, 5.5 Hz), 1.30 (dt, 1H, 10-H, J = 13.9, 13.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.4 (CO), 174.0 (CO), 170.3 (CO), 99.8 (C6, $J_{C\text{-}H}$ = 186 Hz), 59.1 (C15), 48.8 (C3), 48.0 (C14), 47.8 (C13), 45.0 (C9), 42.5 (C1), 41.4 (C2), 40.7 (C11), 38.3 (C10), 33.2 (C12).