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Abstract

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Some Transformations of Cyclododecatriene-1,5,9

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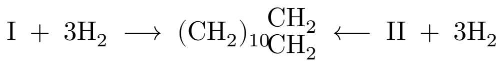
In the Willke cyclotrimerization of butadiene (1,2), two isomers of cyclododecatriene-1,5,9 were obtained, to which, on the basis of IR spectra, the structures cis-, trans-, trans-cyclododecatriene-1,5,9 (I) and trans-, trans-, trans-cyclododecatriene-1,5,9 (II) were assigned. In the present work we have studied some transformations of these isomers of cyclododecatriene. Both isomers are smoothly hydrogenated at atmospheric pressure and room temperature on Pt and Pd catalysts, and also on Raney Ni, giving cyclododecane in quantitative yield:



$$I + 3H_2 \longrightarrow (CH_2)_{10}\genfrac{}{}{0pt}{}{CH_2}{CH_2} \longleftarrow II + 3H_2$$

Hydrogenation of both isomers proceeds at practically the same rate. The rate of hydrogenation of the double bonds of I and II on $Pd/CaCO_3$ and $Pd/BaSO_4$ in alcoholic solution is almost identical. The rate of hydrogenation of the double bonds of I and II on Raney Ni in alcoholic solution gradually decreases.

On oxidation with potassium permanganate of the mixture of hydrogenation products of I, obtained upon uptake of 2 moles of hydrogen per mole of I, 1,10-decanedicarboxylic acid was isolated in 30% yield. On treatment of I and II with perbenzoic acid, the corresponding monooxides were obtained. I forms a liquid oxide (III), and II a crystalline oxide (IV). Opening of the oxide ring with formic acid followed by hydrolysis with alkali solution gave, from III, cis-, trans-cyclododecadiene-5,9-cis-diol-1,2, and from IV, trans-, trans-cyclododecadiene-5,9-cis-diol-1,2. Hydrogenation of both diols leads to the known cyclododecane-cis-diol-1,2 (3):

$$I \xrightarrow{C_6H_5CO_3H} III \longrightarrow \text{cis-, trans-cyclododecadiene-5,9-cis-diol-1,2}$$

$$II \xrightarrow{C_6H_5CO_3H} IV \longrightarrow \text{trans-, trans-cyclododecadiene-5,9-cis-diol-1,2}$$

$$\text{both} \longrightarrow (CH_2)_{10}CH(OH)CH(OH)$$

Thus, epoxidation of cis-, trans-, trans-cyclododecatriene proceeds selectively, leading to trans-oxide III. By reduction of the dou—

of the bonds of III gave trans-epoxycyclododecane, which on opening of the oxide ring gave cyclododecane-cis-diol-1,2.

The bromination of both isomers was studied. The best results were obtained on bromination in glacial acetic acid solution. On the action of three moles of bromine per mole of I, apparently a mixture of different geometrical isomers of hexabromocyclododecane is formed, from which it was possible to isolate crystalline hexabromide, m.p. 194-195°. On the action of bromine on II, hexabromocyclododecane, m.p. 177-178°, was isolated from the mixture. I and II give crystalline complexes with silver nitrate of composition $C_{12}H_{18} \cdot AgNO_3$.

Experimental Part

On addition of cis-, trans-, trans-cyclododecatriene to an alcoholic solution of silver nitrate, a crystalline adduct, m.p. 166-167° (from alcohol), was obtained.

$C_{12}H_{18}AgNO_3$. Found, %: C 43.62; 43.57; H 5.58; 5.45
Calculated, %: C 43.39; H 5.42

On addition of trans-, trans-, trans-cyclododecatriene to an alcoholic solution of silver nitrate, an adduct, m.p. 198-199° (from alcohol, decomposes), was obtained.

$C_{12}H_{18}AgNO_3$. Found, %: C 42.92; 42.93; H 5.37; 5.47
Calculated, %: C 43.39; H 5.42

Hydrogenation of cyclododecatriene-1,5,9. a) 20 g of cis-, trans-, trans-cyclododecatriene in 50 ml of ethyl alcohol were hydrogenated over 0.4 g of 5% Pd/$BaSO_4$ at atmospheric pressure and room temperature; 19.2 g of cyclododecane was obtained, m.p. 60-61° (from alcohol); b) 20 g of cis-, trans-, trans-cyclododecatriene in 50 ml of ethyl alcohol were hydrogenated over 2 g of Raney Ni at atmospheric pressure and room temperature; 18.7 g of cyclododecane was obtained, m.p. 60-61° (from alcohol); literature data (4): m.p. 60-61°; c) 320 g of cis-, trans-, trans-cyclododecatriene in 150 ml of ethyl alcohol were hydrogenated in a 2-liter autoclave over 20 g of Raney Ni at a hydrogen pressure of 100 atm and room temperature; 320 g of cyclododecane was obtained.

The hydrogenation of trans-, trans-, trans-cyclododecatriene proceeds analogously.

1,10-Decanedicarboxylic acid. 50 g of I in 100 ml of ethyl alcohol were hydrogenated over 20 g of 1% Pd/$CaCO_3$ until 14.8 liters of hydrogen had been absorbed. 50 g of a mixture of hydrogenated products was obtained. To 15 g of this mixture in 150 ml of water, a solution of 38.2 g of $KMnO_4$ in 725 ml of water was added gradually at 25-30°. After 2 hours, manganese dioxide was filtered off, the filtrate was evaporated to 200 ml and acidified with hydrochloric acid. The precipitate that separated was filtered off and recrystallized from water. 6.1 g of 1,10-decanedicarboxylic acid was obtained, m.p. 126-127°. Literature data (^{5}), m.p. 126.5-127°.

Epoxidation of cis-, trans-, trans-cyclododecatriene. To a solution of perbenzoic acid (from 100 g of benzoyl peroxide) in chloroform, 50 g of I was gradually added at 0°. The solution was left at 0° for 2 hours and then for 12 hours at 20°. The chloroform solution was washed with dilute sodium hydroxide solution, with water, and dried over calcium chloride. Distillation in vacuo gave 22.5 g of monoepoxide, b.p. 100-101° at 3 mm, n_D^{20} 1.5038; d_4^{20} 0.9743.

$C_{12}H_{18}O$. Found, %: C 81.07; 81.00; H 10.20; 10.01
Calculated, %: C 80.89; H 10.11

cis-, trans-Cyclododecadiene-cis-diol-1,2. 10 g of the epoxide from the preceding experiment were dissolved in 30 ml of 96% formic acid. The reaction proceeds with self-heating. After heating for 30 min at 45-55°, the formic acid was removed in vacuo; to the residue was added a solution of 15 g of caustic soda in 25 ml of water and 5 ml of alcohol. The mixture, with stirring, was heated for one hour at 60-70°. After cooling, water was added; the solid precipitate of the diol was filtered off, washed with water, and dried. 9.8 g of diol were obtained, m.p. 159-159.5° (from alcohol + benzene).

Found, %: C 73.39; 73.30; H 10.05; 10.12
$C_{12}H_{20}O_2$. Calculated, %: C 73.47; H 10.20

1 g of the diol in 10 ml of ethyl alcohol was hydrogenated over 0.2 g of $Pd/BaSO_4$. 1 g of cyclododecane-cis-diol-1,2 was obtained, m.p. 159-160° (aqueous alcohol). Literature data (^{3}): m.p. 159-160°.

Epoxidation of trans-, trans-, trans-cyclododecatriene. To a solution of perbenzoic acid (from 25 g of benzoyl peroxide) in chloroform, 14 g of II were added at 0°. The solution was left at 0° for 2 hours and at 20° for 12 hours. The chloroform solution was washed with dilute caustic soda solution and with water, and dried over calcium chloride. Distillation in vacuo gave 4.8 g of epoxide, b.p. 100-101° at 3 mm, m.p. 31-32° (from petroleum ether).

Found, %: C 80.72; 80.53; H 10.20; 9.98
$C_{12}H_{18}O$. Calculated, %: C 80.89; H 10.11

trans-, trans-Cyclododecadiene-cis-1,2-diol. 0.9 g of the epoxide from the preceding experiment was dissolved in 10 ml of 96% formic acid and heated at 45-55° for 2 hours. The formic acid was removed in vacuo; the residue was treated with 15 ml of 40% caustic soda solution at 50-60°. After dilution with water, the solid precipitate of the diol was filtered off, washed with water, and dried. 0.8 g of diol was obtained, m.p. 130-131° (from alcohol + benzene).

Found, %: C 73.39; 73.30; H 10.05; 10.12
$C_{12}H_{20}O_2$. Calculated, %: C 73.47; H 10.20

On hydrogenation of 0.5 g of the diol in 10 ml of ethyl alcohol with 0.2 g of $Pd/BaSO_4$, 0.5 g of cyclododecane-cis-diol-1,2 was obtained, m.p. 160°.

trans-Epoxycyclododecane. 8.6 g of trans-epoxy-cis-, trans-cyclododecadiene in a solution of 40 ml of methanol were hydrogenated with 3.2 g of 1% $Pd/CaCO_3$ until the calculated amount of hydrogen had been absorbed. Distillation in vacuo gave 5.3 g of trans-epoxycyclododecane, b.p. 100–102° at 3 mm, n_D^{20} 1.4775; d_4^{20} 0.9424.

Found, %: C 79.45; 79.56; H 11.97; 12.11
$C_{12}H_{22}O$. Calculated, %: C 79.12; H 12.08

On treatment of the epoxide obtained with formic acid and then with caustic soda solution, as described above in analogous experiments, cyclododecane-cis-diol-1,2 was obtained, m.p. 160°.

Bromination of cis-, trans-, trans-cyclododecatriene. To a solution of 16 g of I in 30 ml of acetic acid, with stirring at 10–12°, 44 g of bromine were gradually added. At the same time, a finely crystalline precipitate gradually separated; it was filtered off and washed with acetic acid. 14 g of product were obtained, m.p. 148–156°. After recrystallization from benzene, two bromides were obtained: hexabromocyclododecane with m.p. 194–195°.

Found, %: C 22.66; 22.88; H 2.84; 2.86; Br 74.54; 74.51
$C_{12}H_{18}Br_6$. Calculated, %: C 22.42; H 2.80; Br 74.76

and the tetrabromide with m.p. 162–163°:

Found, %:	C 29.91; 29.71;	H 3.83; 3.57;	Br 66.79; 66.43
$C_{12}H_{18}Br_4$. Calculated, %:	C 29.87;	H 3.73	Br 66.39

From the mixture of bromides dissolved in the acetic-acid mother liquor, which was a viscous oil that could not be distilled in vacuo without decomposition, no other crystalline compounds could be isolated.

Bromination of trans-, trans-, trans-cyclododecatriene. To a solution of 27 g of II in 80 ml of acetic acid, with stirring, 80 g of bromine was gradually added at 12–15°. At the end of the bromination the temperature was raised to 35–40°. The resulting solution was poured into water; the precipitated solid was filtered off and washed with water. To remove water, the bromide was triturated with methanol, then with ethanol, filtered, and dried in air. This gave 100 g of dry product, which on recrystallization from a benzene–ethanol mixture gave 37 g of hexabromocyclododecane. The remaining product was a smeary residue that could not be crystallized. The hexabromocyclododecane obtained had m.p. 177–178° (from acetic acid).

Found, %:	C 22.54; 22.67;	H 2.84; 2.86;	Br 74.71; 74.64
$C_{12}H_{18}Br_6$. Calculated, %:	C 22.42;	H 2.80;	Br 74.76

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