

The *endo* to *exo* Isomerisation of Dicyclopentadiene

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*endo*-Dicyclopentadiene (**1**, *endo*-tricyclo[5.2.1.0<sup>2,6</sup>]deca-3,8-diene) is readily available, formed in the kinetically controlled dimerisation of cyclopentadiene. The thermodynamically more stable *exo*-dicyclopentadiene (**4**) is made from the *endo* isomer in a two-step process: addition of HBr to **1** followed by elimination of HBr from **3** gives *exo*-dicyclopentadiene (Scheme 1).<sup>1</sup> The yields are good (58 % overall<sup>1</sup>), but the two-step reaction and the use of HBr is a drawback for the preparation. The isomerisation takes place in the first step (Scheme 1), presumably after protonation of the 8,9-double bond. The carbocation (**2**) reacts with the bromide ion to give the product from this step (**3**). Two carbocations may be formed on protonation of **1** (at C<sup>8</sup> and C<sup>9</sup>). Only one is shown in Scheme 1. Both give **4** as the end product.

If the reaction were run in the presence of an acid with a non-nucleophilic anion, we might expect the cation **2** to eliminate a proton and thereby form the double bond. If such a reaction proved possible, a one-step isomerisation of *endo*- to *exo*-dicyclopentadiene would be the result.

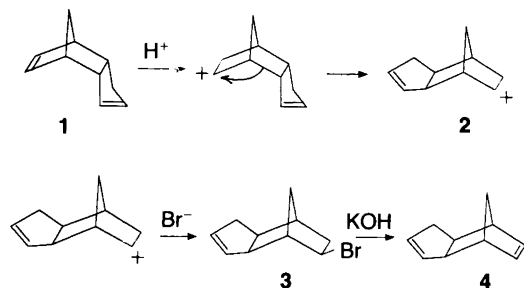
We have tested this idea with several acidic catalysts believed to be suitable for this purpose. In the introductory experiments the isomerisations were run in toluene solution at 100°C. With some acids, no reaction took place (*p*-TosOH, BF<sub>3</sub>/AcOH, Dowex 50, H-mordenite, ClSO<sub>3</sub>H). With others, a low degree of isomerisation was observed but polymerisation was the dominant reaction (Nafion-H, *endo/exo* 94/6; Amberlyst 15, 94/6). From these

results, intermolecular reactions, resulting in polymers (tars) were the major processes in the condensed phase. The isomerisation was therefore tried in the gas phase over acidic catalysts. The results are given in Table 1.

H-Mordenite is a strong acid which, e.g., catalyses the alkylation of aromatic compounds.<sup>2</sup> However, only a moderate degree of *endo/exo* isomerisation of dicyclopentadiene was observed with this catalyst (run 1). In addition, the activity was rapidly lost. The activity of zeolite catalysts towards hydrocarbon isomerisation often increases after ion exchange with multivalent cations. Lanthanum has proved particularly effective in this respect.<sup>3,4</sup> In run 2 the La<sup>+++</sup> mordenite showed a somewhat better catalytic effect than the H<sup>+</sup> form and the activity lasted somewhat longer. Increasing the feed rate, that is, decreasing the contact time, decreased the degree of isomerisation (run 3).

The clay mineral montmorillonite (run 4) was about as effective as H-mordenite and the reaction lifetime was again rather short. In an attempt to increase this, hydrogen was used as the carrier gas instead of nitrogen (run 5). This had no positive effect.

The best results were obtained with a silica–alumina catalyst containing platinum. In run 6, the observed *exo/endo* ratio was 62/38. To compare this with the equilibrium ratio at this temperature, *exo*-dicyclopentadiene was used as the starting material (run 7). In this run, the *exo/endo* ratio obtained was 77/23. It is thus reasonable to assume the equilibrium mixture of dicyclopentadiene at 120°C to consist of ca. 70 % *exo* isomer and 30 % *endo*. The isomerisation of **1** over the platinum containing silica–alumina catalyst thus gave a product with a composition close to this. Increasing the temperature in an attempt to increase the rate of equilibration resulted in partial decomposition of dicyclopentadiene (run 8, 11 % yield of cyclopentadiene). The total yield of *exo*- and *endo*-dicyclopentadiene in run 6 was ca. 50 %. The loss was mainly due to polymerisation in the catalyst. To prevent this reaction, *endo*-dicyclopentadiene was reacted together with water vapour (run 9). This technique is used to avoid coke formation in reformation reactions.<sup>5</sup> However, in our case it did not give any improvement (run 9, low degree of isomerisation, low yield).



Scheme 1.

Table 1. Isomerisation of *endo*- to *exo*-dicyclopentadiene over acidic catalysts in a continuous tubular reactor. Feed rate 0.50 mmol g<sup>-1</sup> h<sup>-1</sup>; carrier gas N<sub>2</sub> (9.0 l h<sup>-1</sup>); temperature 120 °C.

Run	Catalyst	Ratio <i>exo/endo</i> DCPD	Yield of <i>exo</i> -DCPD (%)	Remarks
1	H-Mordenite	12/88	8	Rapid decline in catalyst activity
2	La-Mordenite	20/80	14	
3	La-Mordenite	15/85	10	Feed rate 1.0 mmol g <sup>-1</sup> h <sup>-1</sup>
4	H-Montmorillonite	39/61	10	
5	H-Montmorillonite	30/70	11	H <sub>2</sub> as carrier gas, 10 l h <sup>-1</sup>
6	Silica–alumina 0.1 % Pt	62/38	31	
7	Silica–alumina 0.1 % Pt	77/23	52	Feed: <i>exo</i> -DCPD
8	Silica–alumina 0.1 % Pt	54/29	31	Temp. 150 °C, 11 % cyclopentadiene obtained
9	Silica–alumina 0.1 % Pt	12/88	2	H <sub>2</sub> O/ <i>endo</i> -DCPD reacted, 17 mol % water

The method presented here gives only a moderate yield of *exo*-dicyclopentadiene. This is partly due to the equilibrium composition at 120 °C (ca. 70/30) and partly due to polymerisation reactions. Nevertheless, the method is not without merit. The only published one-step isomerisation of *endo*- to *exo*-dicyclopentadiene is an equilibration at ca. 300 °C and 270 atm. That reaction gave only a 22 % yield of *exo*-dicyclopentadiene (*exo/endo* ratio at 310 °C 46/54).<sup>6</sup> The isomerisation via the bromide (Scheme 1) has an overall yield of 58%.<sup>1</sup> The *exo/endo* mixture obtained may be used as such for some purposes, e.g. as starting material for polymers.<sup>6</sup> The *exo* isomer can be isolated by the method of Nelson and Kuo: *endo*-dicyclopentadiene undergoes a retro Diels–Alder reaction at a high rate compared with that of the *exo* isomer. At 180 °C, the *endo* isomer decomposes to cyclopentadiene with the *exo* isomer remaining in the distillation flask. After decomposition of the *endo* isomer, *exo*-dicyclopentadiene is isolated by vacuum distillation.<sup>1</sup>

**Conclusions.** We have presented a simple one-step method for the isomerisation of *endo*- to *exo*-dicyclopentadiene at 120 °C over a platinum-containing alumina silica catalyst. The comparatively low yield of the *exo*-isomer was due partly to the equilibrium constant (ca. 70/30 *exo/endo*) at this temperature and partly to polymerisation reactions.

### Experimental

The heterogenous catalysts are all commercially available: H-mordenite: Zeolon 200H, Norton Co; H-montmorillonite: KA-2, Südchemie AG; silica–alumina, 0.1 % Pt: CK-303, Azko. The experimental set-up for the gas-phase reactions has been described.<sup>2</sup> The quantitative results in Table 1 were obtained by calibration of the GC (Perkin Elmer F33, column OV17) by runs of dicyclopentadiene with glass spheres in the reactor. No reaction took place at 120 °C (GC) and the starting material was recovered (98 %).

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