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Novel *endo*- to *exo*-isomerization of dicyclopentadiene

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Abstract

Endo-dicyclopentadiene was isomerized to *exo*-isomer by thermal treatment at evaluated temperature and pressure. The reaction temperature and pressure are key factors for this novel isomerization. This result may have great potential for practical application.

Keywords: *Endo*-dicyclopentadiene; *Exo*-dicyclopentadiene; Isomerization

Dicyclopentadiene (DCPD) is generally formed from the combination of cyclopentadiene (CPD) molecules through Diels–Alder reaction. It is composed of two stereoisomers, namely *endo*- and *exo*-isomers, with the former about 99.5% and the later only 0.5% [1]. DCPD is an important chemical intermediate or monomer for many resins, rubbers, reaction injection molding materials, and high-energy fuels, in which *exo*-DCPD is expected to produce better polymers and fuels [2–6]. For example, the ring opening metathesis polymerization of *exo*-DCPD is much faster than that of *endo*-DCPD and the product is more rigid [4,5]. Hydrogenated *exo*-DCPD shows much better low temperature performance as high-energy fuels compared with hydrogenated *endo*-DCPD [6]. Therefore it is necessary to transfer *endo*-DCPD to *exo*-isomer. Bartlett et al. firstly disclosed a two-step method to produce *exo*-DCPD, including addition of *endo*-DCPD with hydrogen iodide, then elimination through a reaction with alcoholic potassium hydroxide [7]. Nelson et al. latter modified this method using HBr replacing of HI, which is now widely used for laboratory applications [8]. Bakke et al. presented a one-step catalytic gas-phase isomerization of *endo*-DCPD, but the yield of *exo*-isomer was relatively low [9]. To the author's knowledge, there is still no suitable method for this purpose.

Herndon et al. heated *endo*-DCPD in a sealed tube at 205 °C for 12–24 h and found that some *exo*-isomers was formed [10]. A dissociation-recombination mechanism was suggested in which *endo*-DCPD dissociates into CPD and re-dimerizes to *exo*-DCPD as shown in Scheme 1 [10,11]. Theoretical work of Jamróz et al. has shown that *exo*-DCPD is more stable than *endo*-DCPD [1]. These results suggest that the thermal isomerization of *endo*-DCPD to *exo*-isomer is possible. Here we present a novel isomerization of *endo*-DCPD to *exo*-DCPD at properly chosen pressure and temperature, which is simple and suitable for practical application.

Endo-DCPD (Sinopharm Chemical Reagent Co., self-distillated, 97.0%) was dissolved in decalin (Sinopharm Chemical Reagent Co., 98%) and the solution was continuously introduced into a tubular reactor heated by a tubular

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Scheme 1. Mechanism for the thermal isomerizaiton of *endo*-DCPD.

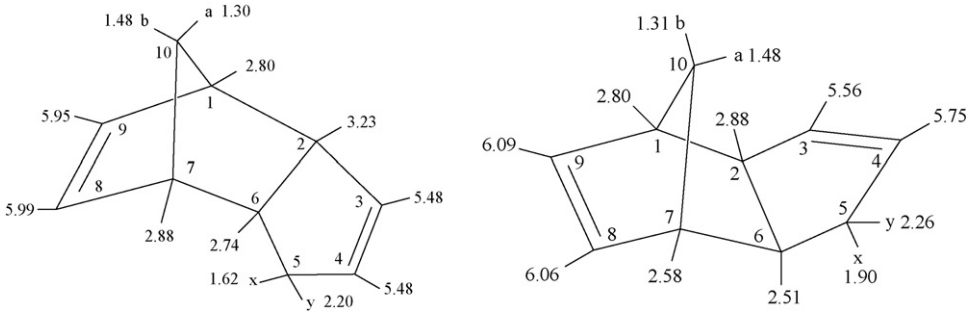

Fig. 1. The chemical shifts (ppm) of *endo*-DCPD (left) and *exo*-DCPD (right) in ^{1}H NMR.

oven. The reaction pressure was controlled by a downstream backpressure valve. The reaction effluent was cooled by water and collected. Portions of the reaction mass were analyzed using GC (Agilent 4890) equipped with a HP-5 capillary column (30 m × 0.53 mm × 1.5 μm) and a FID detector. Some samples were separated to obtain pure *exo*-DCPD. They were heated at 160 °C at ambient pressure to decompose *endo*-isomers into gaseous CPD [10]. Then the remained liquid was distilled at 80 °C with the pressure of 5.33×10^{-3} MPa to exclude the possible oligomers. Pure *exo*-DCPD and *endo*-DCPD was characterized using ^{1}H NMR. The ^{1}H NMR spectra were recorded at 25 °C in $CDCl_3$ with TMS as an internal reference on a Varian Unity INOVA spectrometer at 500 MHz.

Fig. 1 shows the chemical shifts of the *endo*- and *exo*-DCPD in ^{1}H NMR. The experimental results were coincident with the results reported in literature [1], confirming that the compound obtained in this work is *exo*-DCPD.

GC analysis showed that a significant amount of *exo*-DCPD was formed after the reaction. The *exo*/*endo* ratio can be as high as 1.46. Table 1 shows that the *exo*/*endo* ratio greatly depends on the reaction pressure and temperature.

Fig. 2 shows the effect of temperature on the isomerization reaction. At low temperature like 100 °C, no isomerization reaction took place. Since the first step of the isomerization reaction is the dissociation of *endo*-DCPD molecules, which needs higher temperature [1,7,8]. With the elevation of temperature, the conversion of *endo*-DCPD increased quickly. Meanwhile the highest selectivity for *exo*-isomers was 30.3% at 140 °C and the maximum yield was 18.3% at 160 °C. The amount of oligomers increased gradually as the temperature further increased. However, when the temperature was above 180 °C, *exo*-DCPD will be reversibly decomposed into CPD. As a result, the selectivity and yield of *exo*-DCPD dramatically decreased.

Table 1
The ratio of the isomers *exo*/*endo* under various reaction conditions

Temperature (°C)	Pressure (MPa)	*Exo*/*endo* ratio
100	4.0	0
140	4.0	0.15
150	4.0	0.35
160	4.0	1.34
180	4.0	1.46
200	4.0	0.84
160	0.1	0
160	0.2	0.20
160	0.6	1.02
160	2.0	1.09
160	4.0	1.34
160	5.0	1.19

Reaction time: 13.2 min.