

## REARRANGEMENT OF 4-METHYLDICYCLOPENTADIENE TO 2-METHYLDICYCLOPENTADIENE

Jiří Krupka

*Department of Organic Technology, Institute of Chemical Technology,  
Technická 5, 166 28 Prague 6, Czech Republic, e-mail: [Jiri.Krupka@vscht.cz](mailto:Jiri.Krupka@vscht.cz)*

Received May 17, 2011, Accepted September 1, 2011

### Abstract

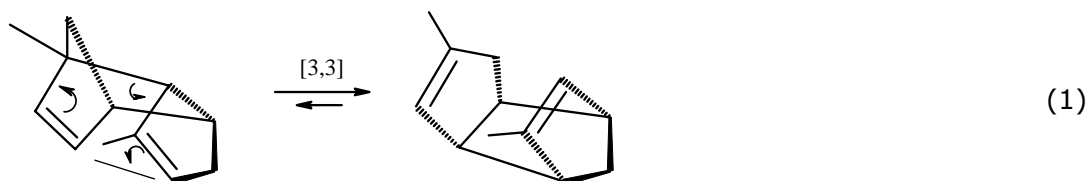
It was observed that 4-methyl-*endo*-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene, when heated at 100°C, isomerizes to a thermodynamically more stable isomer, 2-methyl-*endo*-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene, through [3,3]-sigmatropic rearrangement. The kinetics of this thermal rearrangement was studied in the liquid phase in the temperature range of 80 – 140°C and kinetic parameters were evaluated.

**Key words:** kinetics; methylcyclopentadiene; Cope rearrangement; activation energy.

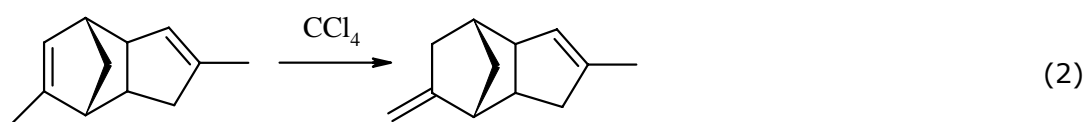
### 1. Introduction

Liquid products of steam cracking of petroleum fractions contain, in addition to many other unsaturated substances, also a certain amount of dicyclopentadiene (DCPD, 3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene) and some of its methyl derivatives (MDCPD), as well as dimethyl derivatives (DMDCPD). Namely it was found [1] that five positional isomers of methyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene are present in the steam cracking products, having the methyl group in the 2, 3, 4, 5, and 7 position. They originate from co-dimerizations of 1-methyl- and 2-methyl-1,3-cyclopentadiene with 1,3-cyclopentadiene, the kinetics of which was reported in the preceding study [2]. The application of technical mixtures of the isomers of MDCPD and DMDCPD in industry is similar to that of DCPD [3]. Due to their large-scale accessibility and low price, they are used to produce various types of resins (of hydrocarbon, polyester and epoxy nature) or auxiliary substances for plasticizing of rubber, modification of fusing adhesives, alkyd resins or varnishes. The MDCPD isomer mixture can be isolated from the steam-cracking condensates as a separate technical-grade fraction or incorporated either in technical multicomponent mixtures of the isomeric DMDCPDs or in low purity DCPD.

Thommen et al. [4] dealt with the structural analysis and thermal behavior of the DMDCPD mixture formed by the Diels-Alder reactions of the methyl-1,3-cyclopentadiene isomers and found that by heating the mixture at 110°C the content of 2,5-dimethyl-*endo*-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene (2,5-dimethyl-*endo*-DCPD) increases at the expense of 3,4-dimethyl-*endo*-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene (3,4-dimethyl-*endo*-DCPD), as a result of the reversible [3,3]-sigmatropic rearrangement. The equilibrium of this thermal rearrangement is shifted toward the thermodynamically more stable 2,5-dimethyl isomer.

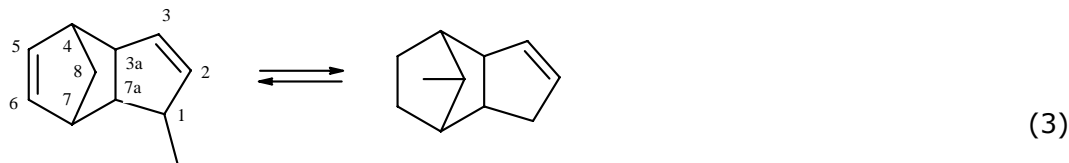


Also other isomerization reactions of methylcyclopentadiene dimers (DMDCPD) are known from the literature. In addition to isomerizations catalyzed by acid or basic agents, Diez *et al.* [5] described the isomerization of some dimers in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> a CCl<sub>4</sub>. This isomerization concerns those dimers which in their molecule contain the 2-methylnorbornene ring, yielding structures with 2-methylenenorbornane ring:



Unlike the starting isomers, the so-called "iso-dimers" formed are not included neither in the mixture of DMDCPD obtained by Diels-Alder reactions of methylcyclopentadiene isomers, nor in steam cracking condensates.

A thermal isomerization was observed also for methyldicyclopentadienes. According to Mironov *et al.* [6], 1-methyldicyclopentadiene isomerizes at 145°C to 8-methyldicyclopentadiene:



1-methyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene      8-methyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene

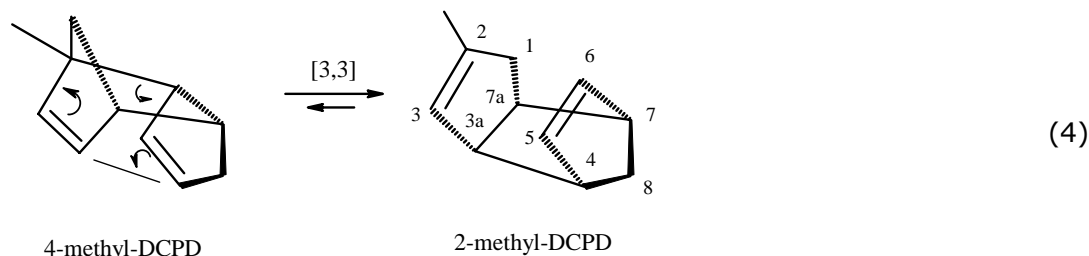
However, the isomers mentioned are not present in steam cracking condensates. Until now it was not known that, at temperatures applied to process steam cracking condensates, some of the MDCPD isomers present in these condensates would rearrange to another one.

## 2. Experimental

Fractions from efficient vacuum rectification of commercial mixture of the MDCPD isomers were the starting material for kinetic measurements. The kinetic of isomerization was measured in the liquid phase in stainless pressure vessels of 2.7 mL capacity. The regression analysis of the experimental data was performed by the ERA software [7] (Easy Regression Analysis). The kinetic measurement procedure, quantitative analysis of the reaction mixtures and kinetic data assessment were referred to in the preceding study [2]. The identification of the chemical structures of MDCPD isomers was the subject of another previous study [8].

## 3. Results and Discussion

During the study of the kinetics of the Diels-Alder reactions in a system consisting of 1,3-cyclopentadiene, 1-methyl-1,3-cyclopentadiene and 2-methyl-1,3-cyclopentadiene, as well as thermal behavior of the MDCPD mixtures, a new finding was revealed, namely, that 4-methyl-*endo*-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene (4-methyl-*endo*-DCPD) isomerizes to 2-methyl-*endo*-3a,4,7,7a-tetrahydro-1H-4,7-methanoindene (2-methyl-*endo*-DCPD). It is evident that this is a rearrangement analogous to the already described [4,9] reversible [3,3]-sigmatropic rearrangement of 3,4-dimethyl-*endo*-DCPD to a thermodynamically more stable 2,5-dimethyl-*endo*-DCPD. Using this analogy, the mechanism of the rearrangement of 4-methyl-*endo*-DCPD should be as follows:

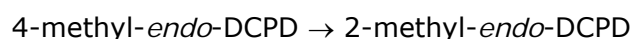


Kinetics of this rearrangement was studied in the range of 80-140°C. The measurements were performed at 80, 100, 120, and 140°C, the initial concentration of 4-methyl-*endo*-DCPD being ~20 or 10 wt.%. A pre-selected distillation cut containing 40 wt.% of 4-methyl-*endo*-DCPD was diluted by cyclohexane to the desired concentration and used for measurements. During the kinetic experiment, the content of other components present in the starting reaction mixture remained constant. The data obtained (temporal dependences of mole concentrations of isomers) are given in Table 1.

Table 1 Experimental data from the kinetic measurements of the 4-methyldicyclopentadiene rearrangement *Composition of the reaction mixtures in mmol/L in relation to the reaction time and reaction temperature*

<i>t</i> (min)	<i>T</i> (K)	<i>C</i> 4-methylDCPD (mmol.l <sup>-1</sup> )	<i>C</i> 2-methylDCPD (mmol.l <sup>-1</sup> )
0	353.15	1194.0	22.7
500	353.15	1157.5	56.8
3360	353.15	993.9	243.5
6050	353.15	824.6	366.3
15840	353.15	453.8	690.4
0	373.15	495.6	22.1
50	373.15	458.3	35.8
120	373.15	439.7	57.4
250	373.15	400.0	93.6
440	373.15	359.4	139.0
1400	373.15	219.7	312.3
0	393.15	440.4	41.6
20	393.15	411.6	87.9
40	393.15	384.6	136.8
110	393.15	276.8	261.8
275	393.15	156.1	391.9
480	393.15	110.7	414.8
0	413.15	349.5	220.0
20	413.15	188.8	369.8
40	413.15	138.9	409.5

When heating the concentrate of 2-methyl-*endo*-DCPD not containing 4-methyl-*endo*-DCPD in the temperature range of 80-140°C, no formation of 4-methyl-*endo*-DCPD was observed; it follows that, in this range, the equilibrium of the reaction (4) is markedly shifted to the product. Therefore, no reverse reaction was taken into an account in the kinetic model. The rate constant  $k_{(120^{\circ}\text{C})}$  and the activation energy  $E_a$  at a reference temperature 120°C for the forward reaction



were evaluated by a regression analysis. The results are presented in Table 2.

Table 2 Regression analysis results

Kinetic parameter	Value	95% confidence limits
$k_{(120^{\circ}\text{C})} \cdot 10^3$ [l.mol <sup>-1</sup> .min <sup>-1</sup> ]	4,32	3,92 - 4,77
$E_a$ [kJ.mol <sup>-1</sup> ]	124,5	121,2 - 127,8

The rate of isomerization of 4-methyl-*endo*-DCPD is relatively high. For the sake of comparison, the corresponding rate constant at 120°C,  $k_{(120^{\circ}\text{C})}$ , is 50 times as high as  $k_{(120^{\circ}\text{C})}$  of the Cope rearrangement of *endo*-5-isopropenyl-2-norbornene to 5-methyl-3a,7,7a-tetrahydro-1H-indene [10,11]. The two last mentioned isomers belong to the co-dimers of 1,3-cyclopentadiene with isoprene.

The new finding that 4-methyl-*endo*-DCPD isomerizes already at temperatures around 100 C to 2-methyl-*endo*-DCPD is important also for industrial practice, specifically for the technology of the isolation of DCPD from light pyrolysis gasoline by rectification. Using this technology, light pyrolysis gasoline is processed in a series of continuous rectification columns to yield technical dicyclopentadiene (purity 75 – 94 %) [12-14]. C6 to C9 hydrocarbons are separated as the first; and then dicyclopentadiene of various degree of purity is isolated by rectification under reduced pressure. The starting material contains several substances hardly separable from DCPD which are of key importance for its isolation. Also 4-methyl-*endo*-DCPD, having its boiling point by only 3.5°C higher than *endo*-DCPD, belongs to them. In contrast to that, boiling points of 2-methyl-*endo*-DCPD and other isomers with a methyl group on the double bonds of the *endo*-DCPD cycle are markedly higher than that of *endo*-DCPD (approx. by 10-17°C). Thus, the newly discovered isomerization of the hardly separable MDCPD isomer (4-methyl-*endo*-DCPD) to the easily separable isomer

(2-methyl-*endo*-DCPD) is favorable and improves the purity of DCPD. Due to the fact that the operation temperature in the boiler of the product column ranges between 100 and 120°C, the concentration of the key impurity (4-methyl-*endo*-DCPD) decreases with increasing time of retention of the mixture in the boiler. The extent of the decrease of this component with time is illustrated in Fig. 1 for initial concentrations 4 and 8 wt.% and temperatures 100 and 120°C.

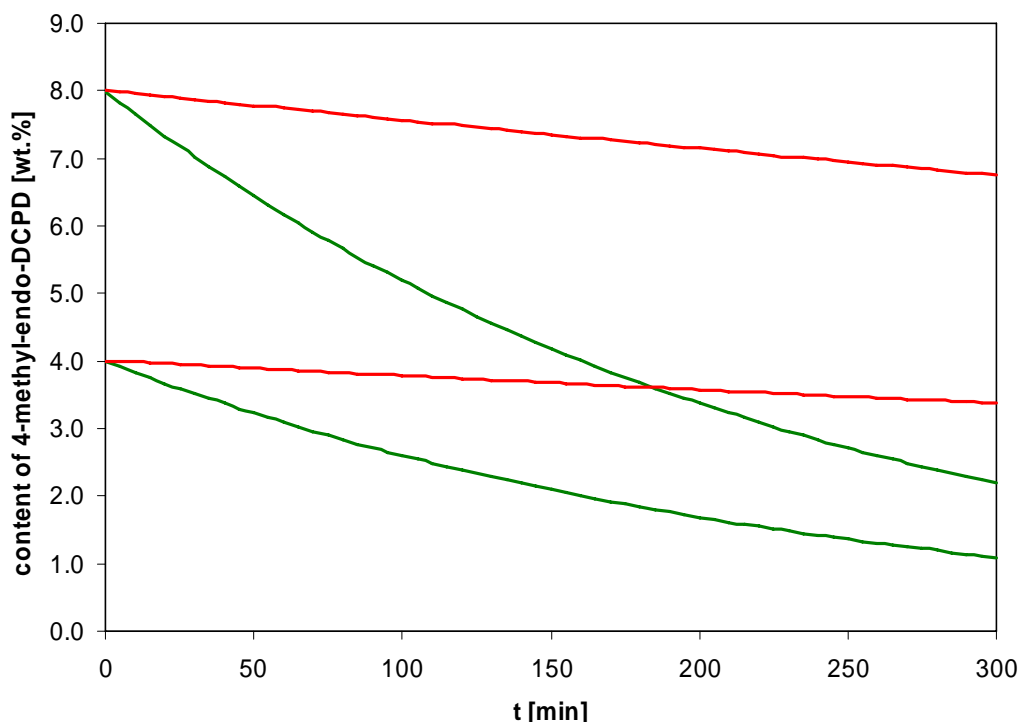


Fig. 1. The drop of the content of 4-methyl-*endo*-DCPD by action of thermal rearrangement (green curves: 120°C; red curves: 100°C; medium: liquid DCPD)

#### Acknowledgements

We would like to thank the Ministry of Industry and Trade of the Czech Republic for financial support through project FT-TA3/079, "Research on Progressive Chemical Products Based on Dicyclopentadiene".

#### 4. References

- [1] Lauer, J. C., Laurens, T., Schmit-Quiles, F., Nicole, D., Matlengiewicz, M., Henzel, N.: *Analisis* 1993, 21, 359.
- [2] Krupka, J.: *Petroleum and Coal* 2010, 52, 290.
- [3] Krupka, J., Štěpánek, K., Herink, T.: *Chem. Listy* 2008, 102, 1107.
- [4] Thommen, W., Pamingle, H., Schulte-Elte, K. H.: *Helv. Chim. Acta* 1989, 72, 1346.
- [5] Diez, M. S., Fannanas, F. J., Blanco, C. G., Bermejo J.: *J. Chem. Technol. Biotechnol.* 1990, 48, 173.
- [6] Mironov, V. A., Fadeeva, T. M., Stepanyanc, A. U., Akhrem, A. A.: *Izvestiya Akad. Nauk SSSR Ser. Khim.* 1967 (2), p. 434.
- [7] Zámotný, P., Bělohav, Z.: *Comput. Chem.* 1999, 23, 479.
- [8] Krupka, J., Pašek, J.: *Petroleum and Coal* 2010, 52, 227.
- [9] Woodward, R. B., Katz, T. J.: *Tetrahedron* 1959, 5, 70.
- [10] Iwase, S., Nakata, M., Hamanaka, S., Ogawa, M.: *Bull. Chem. Soc. Jpn* 1976, 49, 2017.
- [11] Krupka, J.: Doctoral thesis, 2008, Institute of Chem. Technology, Prague, Czech Rep.
- [12] Navara, M., Goppoldová, M., Zelenka, J.: patent CS 240664 (1987).
- [13] Galka, S., Tecza, W., Jamroz, M. Jakubowski, W.: Patent PL 192210 (2006).
- [14] Pašek, J.: *Chem. Listy* 2008, 102, 101.