Diels-Alder Reaction between Cyclopentadiene and 1,3-Pentadiene

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The reaction between cyclopentadiene and commercially available 1,3-pentadiene was studied to yield principally 1:1 adducts; moreover, the stereochemistry of each component separated from the adducts was investigated with ^{13}C -NMR spectroscopy. The norbornene-type adducts were predominantly formed under mild reaction conditions, since 1,3-pentadiene served as a dienophile. The tetrahydroindene-type adduct gradually increased as reaction progressed owing partly to the Cope rearrangement of the norbornene-type adducts.

1. Introduction

Diels-Alder reactions of cyclopentadiene (CP) with butadiene and isoprene were reported in our previous papers^{1)~7)}. Although numerous products were expected from these reactions since such dienes also serve as a dienophile, a few adducts were predominantly produced due to the selectivity for cycloaddition. In continuation of our study, this paper deals with the reaction of CP and 1,3-pentadiene (PD) especially with their addition products and stereochemistry.

Previously, Duschek⁸⁾ has reported on stereochemistry of homo-dimers of *cis* and *trans*-PD's. However, the reaction products from CP and commercially available PD were very much complicated by the various addition reactions occurred concurrently. We will also describe the results of Diels-Alder reactions of *cis* and *trans*-PD's to reveal the addition products formed in cycloaddition of CP and PD.

2. Experimental

2.1 Materials

cis-PD was separated from a commercially available isomeric mixture of PD (*cis/trans*=35/65) by heating with 0.7 equivalent of maleic anhydride at 42°C for 2 hr followed by fractionation (bp 42°C). Purity of 98% can be attained without further purification. *trans*-PD obtained was 95% pure according to the Nazarov method⁹⁾. CP was obtained by destructive distillation of dicyclopentadiene before use.

2.2 Reaction

All Diels-Alder reactions were carried out by

using equimolar amounts of CP and PD in an autoclave under prescribed conditions. Reaction mixtures were fractionated into monomer, dimer, trimer, and polymer¹⁰⁾. Each component of the adducts was separated by repeated fractionations. But some components obtained as stereoisomeric mixture were used without difficulty to identify the individual components by ^{13}C -NMR spectroscopy.

The Cope rearrangement of some adducts was performed in a sealed glass tube of about 1 ml at 180°C for 3 hr.

2.3 Analysis

Gas chromatograms were recorded with a Shimadzu Model GC-3AF chromatograph employing a flame ionization detector and a 3 mm×3 m stainless column packed with Apiezone Grease L 10% and Squalene 20% on Chromosorb W. The weight percent of each peak was estimated directly from the peak area. Consequently, any substantial error could not be avoided for some peaks overlapping.

The ^{13}C -NMR spectra were recorded with a JNM-EC-100 Fourier transformation spectrometer (25.15 MHz) with the complete and half proton decoupling technique. The pulse width and repetition time were 11.5 sec (about $1/4\pi$ pulse) and 6 sec, respectively. Chemical shifts were determined in a CDCl_3 solution approximately 50 vol% using TMS as an internal standard. Quantitative analyses of dual stereoisomeric mixtures were performed by comparing the relative signal intensities of each corresponding signal.

3. Results and Discussion

Equimolar reactions of CP and commercially available PD gave a variety of adducts in about 60% yield at 160—180°C for 2 hr (**Table 1**).

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Structural Formula 1

The VPC of the adduct obtained at 180°C for 2 hr indicated numerous addition products (**Fig. 1-A**). In order to identify each component, the following reactions were carried out (**Table 2**). The VPCs of adducts obtained by various combinations of PD and CP are shown in **Fig. 1-B** to **Fig. 1-E**, and ^{13}C -NMR chemical shifts of some adducts are listed in **Table 3**.

3.1 Reaction of *trans*-PD

The dimer fraction gave four peaks in VPC (**Fig. 1-B**). Peaks *a* and *b* were in agreement with homo-dimers, **1** and **2**, respectively, by comparing the effluent sequence of VPC analysis with those reported by Duschek⁸⁾. In addition, hydrogenation of **1** gave a structurally symmetrical cyclohexane derivative exhibiting seven signals in NMR spectrum, while the number of signals in the spectrum of **2** remained unchanged after hydrogenation. However, detail configurations of **1** and **2** were not ascertained. Peaks *c* and *d* were revealed by means of ^{13}C -NMR to agree with **3** and **3'**, respectively. The identification of **3** and **3'** was accomplished by comparing the chemical shifts of their individual C-3 and C-4 carbons¹¹⁾.

3.2 Reaction of *cis*-PD and *trans*-PD

The adducts obtained from the reaction of *cis*-

A : Component of each peak is listed in Table 4

B : Peaks *a* (**1**) 5%, *b* (**2**) 6%, *c* (**3**) 51%, *d* (**3'**) 38%

C : Peaks *a* (**1**) 5%, *b* (**2**) 5%, *c* (**3**, **4**) 55%, *d* (**3'**) 19%, *e* (**4'**) 16%

D : Peaks *a* (**5**, **5'**) 7%, *b* (**6**, **6'**) 72%, *c* (**10**) 21%

E : Peaks *a* (**7**, **7'**) 4%, *b* (**1**) 2%, *c* (**2**) 2%, *d* (**3**, **8**) 16%, *e* (**8'**) 20%, *f* (**4'**) 9%, *g* (**10**) 19%, *h* (**9**) 28%

Fig. 1 Gas Chromatogram of 1 : 1 Adducts Obtained by Diels-Alder Reaction of CP and PD (Apiezone Grease L 10%, 3 mm $\times$ 3 m, 110°C)

PD with *trans*-PD showed five peaks in VPC (**Fig. 1-C**). Peaks *a*, *b*, *c*, and *d* were found to be in agreement with **1**, **2**, **3**, and **3'**, respectively, by comparing VPC retention times with those of the dimers obtained from *trans*-PD. However, NMR spectrum of peak *c* indicated to consist of two components having a signal intensity ratio of 7:3. The minor component agreed with **3**. The others gave a similar spectrum to that of **3** except for upfield shifts of C-4 and C-10 carbon signals which is considered to be due to the steric effect of *cis*-propenyl group. Thus, this was identified to **4**. Peak *e* which gave a similar spectrum to that of **4** was identified to **4'** by considering the upfield shifts of C-3 and C-4 carbons rather than those of **4** in a similar manner as described in the identification of **3** and **3'**.

3.3 Reaction of CP and *cis*-PD

The VPC analysis of the adducts yielded by the reaction of CP and *cis*-PD indicated three peaks (**Fig. 1-D**). Peak *a* was ascertained as consisting of two components **5** and **5'** having the

Table 1 Diels-Alder Reaction of CP and Commercial PD

Temp. (°C)	Time (hr)	Yield (%)			
		1 : 1 Adduct	1 : 2 Adduct	Polymer	Unchanged
160	2	60	7	2	31
180	2	61	8	16	15
200	2	39	20	32	9
220	2	33	27	33	7
240	2	22	20	55	3

Table 2 Diels-Alder Reactions of PD, and of CP and PD

Reactant	Molar ratio	Temp. (°C)	Time (hr)	Yield (%)	
				1 : 1 Adduct	Polymer
<i>trans</i> -PD		180	3*	63	12
<i>trans</i> -PD + <i>cis</i> -PD	1 : 1	180	3*	62	13
CP + <i>cis</i> -PD	1 : 1	180	2	52	17
CP + <i>trans</i> -PD	1 : 1	180	2	66	24

* Reaction time is prolonged, because the reaction without CP proceeded slowly to yield substantial amounts of products.

Table 3 ¹³C-NMR Chemical Shifts of Some 1 : 1 Adducts

Dimer	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9 or 3a	C-10 or 7a
1	125.4	132.6	35.6	54.6	32.4	34.3	20.5*	20.0*	141.8	115.6
2	124.9	133.5	33.3*	32.9*	49.7	28.3	20.2	16.7	141.2	114.8
3	125.8	133.0	35.9	45.3	29.2	25.1	20.1	136.0	124.2	18.0
3'	125.8	133.0	33.8	41.1	24.5	25.4	17.0	133.6	124.4	18.1
4	125.9	132.9	36.4	39.8	28.9	25.1	20.1	135.7	123.2	13.2
4'	125.9	132.9	33.2	35.1	32.9	26.0	17.1	132.4	123.6	13.0
5	48.5	135.5	135.2	48.0	37.9	49.5	49.4	15.6	141.0	114.8
5'	48.8	137.9	136.8	45.8	37.9	49.0	42.4	17.9	141.3	114.5
6	43.0	136.8*	132.8	48.5	36.1	34.1	49.8	136.4*	122.7	13.2
6'	42.2	137.1	136.0	47.4	35.7	34.1	45.7	136.4	122.7	13.2
7	48.9	137.4	134.1	47.7	40.8	51.8	47.2	18.3	142.8	112.7
7'	48.4	133.3	138.1	47.9	40.9	53.3	46.1	20.1	142.8	113.1
8	41.5	137.1	136.6	48.5	41.7	33.1	45.5	133.6	123.6	17.0
8'	42.9	137.0	132.9	48.2	42.2	33.1	49.6	136.8	123.6	17.0
9	41.7	131.2	131.5	35.4	134.8	127.3	28.8	18.7	50.2	31.1

* An alternative assignment is also possible.

signal intensity ratio of 3:7. Each configuration of **5** and **5'** can be determined by considering the steric compression effect of the bridged carbon C-7. The minor component indicating a bridged carbon signal at a higher field was identified as *exo*-isomer **5** and the others as *endo*-isomer **5'**. Peak *b* also consists of two stereoisomers **6** and **6'**, whose signal intensities are 4:6. They were identified by comparing each C-7 signal in the same manner as described above. Peak *c* was identified as dicyclopentadiene **10** by comparison of the authentic sample.

3.4 Reaction of CP and *trans*-PD

Reactions of CP and *trans*-PD resulted in many adducts, because both reactants served as diene and dienophile. The VPC analysis of adducts gave eight peaks (**Fig. 1-E**). The peaks *b*, *c*, *d*, *f*, and *g* were respectively identified as **1**, **2**, **3**, **3'** and **10** by comparison of their VPC retention

times and by means of ¹³C-NMR spectroscopy. Peak *a* was found to be the stereoisomeric mixture of **7** and **7'**, whose signal intensities were about 4:6 by comparing their spectra with those of **5** and **5'**. Peak *d*, corresponding to peak *c* in **Fig. 1-C**, contained **3** and one more component having equal signal intensity. The latter and the component of peak *e*, which showed analogous NMR spectra with each other, were established to be **8** and **8'**, respectively, by referring to the NMR spectra of **6** and **6'**. Peak *h* consists of a single component, whose NMR spectrum is apparently different from the ones described above and suggests evidence of some tetrahydroindene structure⁵⁾. In the reaction where CP serves as diene, two possible configurations, **9** and **9'**, are expected. From our previous reports^{5),6)} on the Cope rearrangement of norbornene-type adducts to tetrahydroindene ones, the reaction of **8** was expected

Table 4 The Component of 1 : 1 Adducts Obtained from CP and Commercial PD at Various Temperatures^{a)}

Temp. (°C)	Peak	Composition (%) ^{b)}								
		<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
	Com- ponent	7 7'	1	2	3 4 8	8'	3'	4'	10	9 unknown
160		1		1	16	21	1	1	54	5
180		2	1	1	20	24	7	2	31	12
200		1	1	1	9	18	9	4	10	47
220			1	1	14	10	7	5	7	53
240			1	1	18	8	7	6	8	49
										2
										2

a) The reactions of CP 14.1 g (0.21 mol) and PD 14.3 g (0.21 mol) were carried out in a 100 ml autoclave for 2 hr.

b) 1 : 1 Adducts separated by fractionation were examined by VPC analysis.

to give **9**. The product obtained by heating of **8** exhibited the same NMR spectrum as that measured on the component of peak *h*. Accordingly, the configuration of the adduct corresponding to the peak *h* was confirmed as **9**.

3.5 Reaction of CP and commercial PD

Reactions of CP and commercially available PD were carried out at various temperatures for 2 hr to elucidate the components of adducts. The VPCs of the adducts obtained at 180°C (**Fig. 1-A**) were compared with those of the reactions described above (**Fig. 1-B, 1-E**). Since the VPC pattern of **Fig. 1-A** is similar to that of **Fig. 1-E**, all peaks except for peak *g* are assigned to the corresponding peaks in **Fig. 1-E**. The peak *g* has also been assigned to **4'** by referring to the retention time of peak *e* in **Fig. 1-C**. The formation of **4'** indicates evidence of stereoisomer **4** which is probably induced in peak *d*. Thus, peak *d* is composed of three components **3**, **4**, and **8**.

In **Table 4**, the components of each peak and their yields at various temperatures are listed.

At low temperature, norbornene-type adducts for which CP serves as diene were predominantly obtained but they decreased gradually with rising temperature, and instead of the adducts, the tetrahydroindene-type adduct for which PD serves as diene was produced owing partly to the participation of the Cope rearrangement of a norbornene-type adduct. Especially, the remarkable decrease of **10** at around 180°C may be due to the retro-Diels-Alder reaction, and the CP thus generated further reacts with the dimers to give some trimers.

From these results, the following characteristics were observed in the Diels-Alder reactions of CP and PD:

i) CP reacts as diene considerably faster than PD, and hence norbornene-type adducts are likely produced at lower temperatures,

ii) *trans*-PD serves as both diene and dienophile and it is more reactive than *cis*-PD which behaves only as dienophile,

iii) the terminal double bond of PD undergoes cycloaddition more readily than the inner one,

iv) the tetrahydroindene-type adduct is more likely to be produced at higher temperatures and it is also formed by the Cope rearrangement of norbornene-type adduct.

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- 10) Various 1 : 1 and 1 : 2 or 2 : 1 adducts, involving homodimers and trimers, derived from CP and PD are called here dimers and trimers, respectively.
- 11) Conformations of **3** and **3'** are illustrated as follows:

Structural Formula 2

A stable conformation of 3 is a more energetically favorable $3ee$ in which two substituents are equatorial, while both conformers of $3'$ having one equatorial and one axial substituents undergo rapid interconversion between $3'ea$ and $3'ae$ owing to a similar stability. Thus, the chemical shifts of C-3 and C-4 carbons in $3'$ are observed at upper field than those in 3 by the steric compression effect of the axial substituent.

要 旨

シクロペンタジエンと 1,3-ペンタジエンの Diels-Alder 反応

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シクロペンタジエン (CP) と 1,3-ペンタジエン (PD) の Diels-Alder 反応から得られる 1:1 付加体の合成条件とそれらの立体構造について検討した。付加体の構造を明らかにするため、シスおよびトランス-PD 間の Diels-Alder 反応とそれぞれの環状付加反応、さらにシスおよびトランス-PD と CP を

反応させ、 ^{13}C -NMR よりそれぞれの付加体の構造を決定した。

180°C 付近の反応では PD のホモ二量体とノルボルネン骨格を持つ 1:1 付加物が多く得られた。反応温度の上昇とともにテトラヒドロインデンタイプの 1:1 付加物が次第に多く生成し、この増加にノルボルネンタイプ付加体の Cope 転位による異性化が寄与していることがわかった。

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Keywords

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