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On the Mechanism of the Diels-Alder Reaction between 1,3-Cyclopentadiene and 1,3-Cyclohexadiene

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Synopsis. The reaction of 1,3-cyclopentadiene with 1,3-cyclohexadiene, when carried out at 94—118 °C for 5—7 hr, gave tricyclo[4.4.0.1^{2,5}]undeca-3,7-diene rather than tricyclo[5.2.2.0^{2,6}]undeca-3,8-diene.

In the study of the Diels-Alder reaction, many investigations[1-5] have been carried out in an attempt to elucidate the bonding sequence of two new σ-bonds formed during the reaction. Recently, Salem[3] suggested a new transition structure with secondary attractive force (s.a.f.) like that of the Cope rearrangement and supported a two-stage mechanism postulated by Woodward and Katz.[4] On the other hand, Herndon[5] showed that the prefered *endo*-addition pathway can be interpreted principally in teams of a geometrical relationship rather than s.a.f. and then suggested a one-step mechanism in which the planes of the two reactants are assumed to intersect at an angle of 60°. In our previous work[6] concerning the reaction of 1,3-cyclopentadiene(CP) with 1,3-butadiene, we also imagined a one-step mechanism by considering that the transition state of this reaction is different from that of the Cope rearrangement of one product (*endo*-5-vinyl-2-norbornene) to another (*cis*-3a,4,7,7a-tetrahydroindene). The present work will presents some evidence for the one-step mechanism of the reaction between two different *s*-cisoid dienes, such as CP and 1,3-cyclohexadiene(CH).

The reaction of CP with CH was carried out under N_2 in a sealed tube at a fixed temperature. The reaction products were separated by fractionation into the following fractions; monomers(79—83 °C/760 mmHg), dimers(83—105 °C/66mmHg), trimers(105 °C/5mmHg), and higher polymers(residue). The dimer fraction was analyzed by glc. Two codimers, *A* and *B* (Fig. 1), were isolated from the dimer fraction by preparative glc. The structural assignment of *A* and *B* is based on the following data: *A* —NMR (60 MHz, CCl_4, δ), 1.41 (2H, k, m), 0.95—2.70(4H, a b, m), 2.45(2H, l e, m), 2.80(2H, f i, m), 5.56(2H, c d, m), 5.92(2H, g h, t); (NaCl), 1569 and 1676 cm^{-1}: *B* —NMR(60 HMz, CCl_4, δ), 1.32, 1.44(4H, j k, m), 1.02—2.35(3H, ai, m), 2.48(2H, e h, m), 3.01(1H, d, m), 5.43(2H, b c, t), 6.07(2H, f g, $J_{fg}=4.8$ Hz, $J_{ef}=J_{hg}=3.0$ Hz); IR (NaCl) 1610 and 1645 cm^{-1}.[7] The results of the reaction of CP with CH are shown in Table 1.

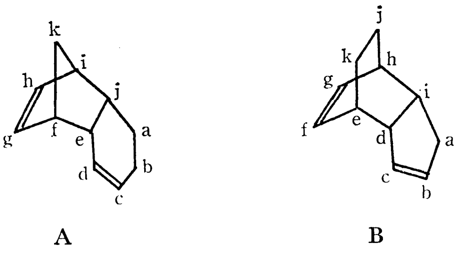


Fig. 1. Reaction products. (Codimer)

TABLE 1. REACTION OF CP WITH CH

Reaction temp.	(°C)	94.4	105.5	118.0	180.0
Reaction time	(hr)	5.0	24.0	5.0	5.0
Starting Material	CP (g)	5.5	7.0	5.0	5.0
	CH (g)	4.0	2.0	2.0	3.0
Yield (%)	Monomer	42.1	21.2	25.0	trace
	Homodimer	56.7	77.0	74.2	27.5
	Codimer	1.2	1.8	0.8	27.4
	Trimer	—	—	—	24.4
	Polymer	—	—	—	20.7
Codimer (%)	*A*	70.0	62.8	70.4	4.0
	B	20.1	23.4	16.0	84.2
	Unknown	9.9	13.8	13.6	11.8

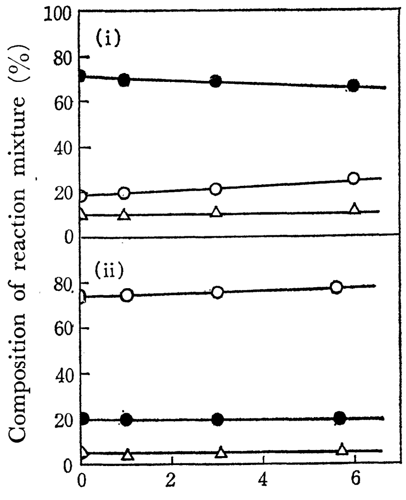
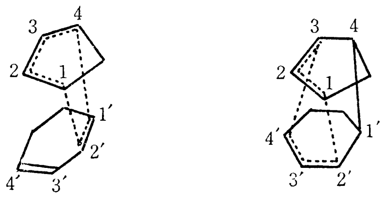


Fig. 2. Rearrangement of codimer.
—●— *A*, —○— *B*, —△— unknown
i) The reaction of *A*-rich fraction
ii) The reaction of *B*-rich fraction

A *n*-hexane solution(10 vol%) of an *A*- or *B*-rich fraction prepared from the reaction products was caused to react by heating at 139.0 °C. The results are shown in Fig. 2. Furthermore, in the reaction of the *A*-rich fraction with acryronitrile at 139.0 °C for 6 hr, no addition product with CH or CP was obtained. Consequently, the decomposition of *A* to CH and CP did not occur at this temperature.

The transition state of the reaction to produce an *A* or *B* codimer is considered to be I‡ for a one-step me-



$I^{\neq}$ $II^{\neq}$

Fig. 3. Hypothetical transition stats.

chanism and $II^{\neq}$ for a two-stage mechanism (Fig. 3). In the one-step mechanism, CP probably acts as a diene since the bond distance at C_1—C_4 is shorter than that at the C_1'—C_4' of CH. Therefore, the *A* product can be obtained through $I^{\neq}$. On the other hand, $II^{\neq}$ has σ-bond at C_4–C_1' and two weak bonds at C_1—C_2 and C_3—C_4'. As the latter two weak bonds are similar in their reactivity, $II^{\neq}$ may give both products, *A* and *B*. According to the additivity rule of strain, the relative stabilities of both *A* and *B* were calculated on the basis of the data estimated by Turner[8] and Alder;[9] *B* was found to be more stable than *A* by 11.4 kcal/mol. Consequently, when the reaction proceeds through the two-stage mechanism, *B* may be predominantly obtained in the products.

As was seen in Table 1 and Fig. 3, the results obviously show that *A* was initially produced and was then converted to *B*. Therefore, the reaction proceeds mainly along the following reaction course;

$$\mathrm{CP}+\mathrm{CH} \rightarrow I^{\neq} \rightarrow A \rightarrow II^{\neq} \rightarrow B$$

On the other hand, some portion of *B* may also be formed by the direct reaction of CP with CH, especially at higher temperatures.

Experimental

In glc, the colunms used were R-90(0.25 mmϕ) for analysis and PEG-20(25%, 8mm$\phi\times$3 m) for preparation. The measurements of the NMR and IR spectra were performed with JEOL-JNM-3H-60 and Shimadzu-IR-27G apparatuses respectively. All the reactions were carried out in sealed tubes maintained within ±0.1 °C.

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