Diels-Alder Reaction of Allene and Isoprene

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Thermal reaction of allene and isoprene was examined and the exact ratio of the resulting isomers was determined. The *meta*-isomer was formed in a nearly 70% selectivity at 180–220°C. The mechanism of the reaction is discussed briefly in the light of the unusual orientation for Diels-Alder reaction and the concerted mechanism is preferred.

INTRODUCTION

It is well known that Diels-Alder reaction of monosubstituted dienes and dienophiles proceeds regiospecifically, giving mainly *o*- or *p*-disubstituted cyclohexenes from 1-substituted or 2-substituted dienes, respectively.[1] Since allene can be regarded as a kind of mono-substituted dienophiles, Diels-Alder reaction of allene and an unsymmetric diene is expected to give two structural isomers. Diels-Alder reaction of allene is, however, little studied and no detailed examination about the orientation of the reaction was ever reported.**

We have studied the reaction of allene and isoprene, and the ratio of the two isomers was determined exactly. It was found that *m*-isomer was formed in a nearly 70% selectivity. The mechanism of the reaction was discussed briefly based on the unusual result of orientation.

RESULTS AND DISCUSSION

The thermal reaction of allene and isoprene afforded two structural isomers, 1-methyl-4-methylene-1-cyclohexene (I) and 1-methyl-5-methylene-1-cyclohexene (II).
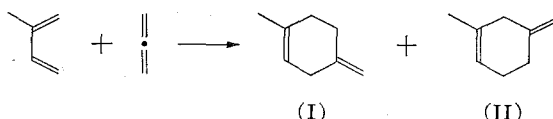
It was difficult to determine the ratio of the isomers directly from the reaction mixture. After they were converted to xylenes by dehydrogenation with chloranil, the ratio of

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** On the way of our study, a paper including a preliminary investigation of the orientation appeared.[2] But the result was qualitative and not confirmative.
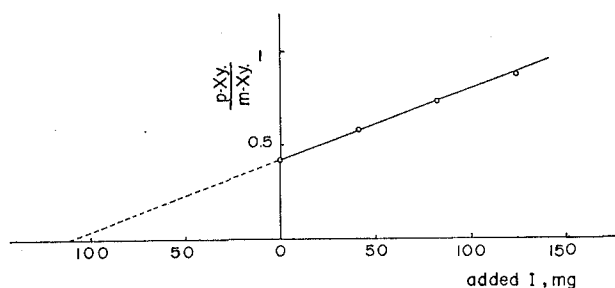
Fig. 1.　Isomer distribution in the dehydrogenation of the
mixture of Diels-Alder adduct (332 mg) and I.

the resulting p- to m-isomers was determined by gas chromatography (VPC).   But the
dehydrogenation reaction was not quantitative and therefore the ratio of p-xylene/m-
xylene was not necessarily equal to the ratio of I/II.   Then, various mixtures of the
Diels-Alder adducts and I, which was independently synthesized as an authentic sample,
were dehydrogenated, and the isomer distribution in the resulting products is shown in
Fig. 1.   As o-xylene was not found in the product and a linear relationship was observed,
it is evident that no migration of the methyl group occurred during the dehydrogenation.
The amount of I in the adduct 332 mg is estimated to be 112 mg from the intercept
of the extrapolated line on the x-axis in Fig. 1.   Eq. 1, which shows the correlation
between the two ratios, was obtained from these values.

$$\frac{I}{II} = \frac{p\text{--xylene}}{m\text{--xylene}} \times 1.22 \qquad\qquad \text{Eq. 1}$$

The results of the Diels-Alder reaction of allene and isoprene are shown in Table 1.
As shown in Table 1, the ratio of I/II was almost constant, 1/2.0, under the reaction
conditions examined.   That is, m-isomer is a major product.   The same ratio of the
isomers in Runs 2 and 3 suggests that there is no difference in the polymerization tend-
ency of both isomers.   As the products were apt to polymerize, high temperature and
short reaction time gave a better yield.

This is the first clear example of Diels-Alder reaction which gives m-isomer as a
major product.   From the view of the isomer distribution, some discussion was made
on the mechanism of Diels-Alder reaction.

The orientation of Diels-Alder reaction of unsymmetric diene and dienophile has

Table 1.　The Diels-Alder Reaction of Allene and Isoprene

Run No.	Allene/Isoprene	Temp (°C)	Time (hr)	Yield[a]	I/II
1	1/2	175–185	4.5	18	1/2.0
2	1/2	215–225	2	36	1/2.0
3	1/2	215–225	3	31	1/2.0

[a]　yield of I+II based on allene

(110)

been explained mainly by the two-step radical mechanism.[1] According to the mechanism, the following discussion is given on the reaction. When one new σ-bond is formed, four unstable intermediates may be produced.
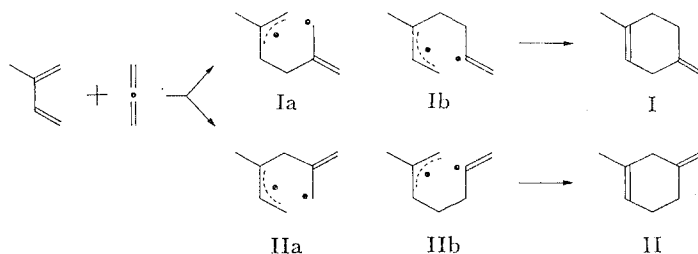

On appreciating the stability of them, it is a problem whether or not allylic resonance exists in allene side of Ia and IIa. As the cumulated double bonds of allene are orthognal to each other, a 90°C rotation of the C-C bond is necessary for the allylic resonance. It was known that most free radicals attack allene mainly at the two terminal carbon atoms.[3]
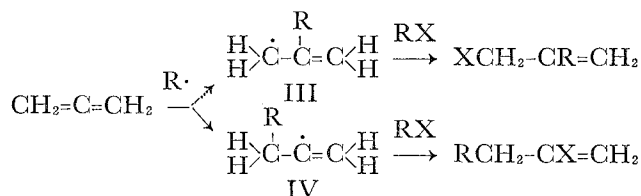
This fact supports that no allylic resonance would exist in radical III.

Moreover, it has been reported that during the thermal rearrangement of 1-isopropenyl-3-methylenecyclobutane to I, which is considered to proceed by the route described below, no fragmentation to allene and isoprene occurs.[2]
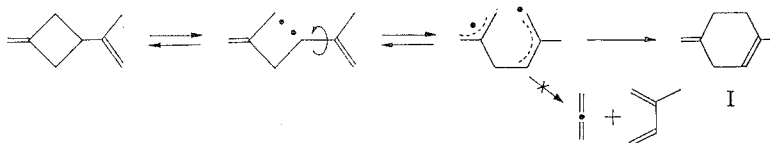
From this fact, even if allylic resonance exists at allene side of Ia, the species lies very near to the product side on the reaction co-odinate and would not concern itself with the orientation of the reaction.

It is better to take off consideration of the allylic resonance in Ia and IIa. Then in allene side, Ib and IIb (secondary radical) are more stable than Ia and IIa (primary radical), and in isoprene side, Ib and IIa are more stabilized than Ia and IIb by hyperconjugation of the methyl group. Since the order of the stability would be Ib>IIa≃IIb>Ia, p-isomer would be formed as a major product through the most stable intermediate Ib. This is not consistent with the experimental results.

For the concerted mechanism, the perturbation energy is given by the following formula,[4]

$$\Delta E = \left[2\sum_m^{occ} \sum_n^{vac} - \sum_n^{occ} \sum_m^{vac} \right] (a_{mr}b_{ns} + a_{mu}b_{nv})^2 \gamma^2 / (E_m - E_n)$$

where a and b are the coefficients of the atomic orbitals of isoprene and allene. Subscripts r, s and u, v refer to the two pairs of atoms in diene and dienophile at which bonds are formed, and γ is the interaction integral. The energies, ΔE, in the formation of two isomers can be obtained by using Hückel parameters.[*]

The results of calculations are:

$$\Delta E(I, p\text{-isomer}) = 1.304 \quad (\text{unit of } \gamma^2/\beta)$$

$$\Delta E(II, m\text{-isomer}) = 1.354 \quad (\text{unit of } \gamma^2/\beta)$$

These results show that m-isomer is more favored than p-isomer, and they are consistent with the experimental results.

The above discussion suggests the concerted mechanism is more favorable than the two steps bi-radical mechanism for the Diels-Alder reaction of allene. An ionic mechanism would be less probable for such a nonpolar system.

EXPERIMENTAL

Reaction of allene and isoprene: A mixture of allene 6.0 g, isoprene 20.4 g, n-pentane 24 ml, and hydroquinone 0.5 g was heated at the temperature for the time described in Table 1 in sealed tubes placed in an autoclave which contained petroleum ether. The resulting miture was flash-distilled to separate polymeric material, and analyzed by VPC (Apiezone grease L/Celite 545). Four components, A, B, C, and D, were detected and the ratio of peak areas were about 3.5, 2, 6, and 1, respectively. A blank test showed that B, C, and D were formed from isoprene only. The major components A, B, and C, were isolated by VPC.

Component A: (mixture of I and II) NMR (δ, ppm): 1.7 (3H, s), 2.2 (4H, m), 2.7 (2H, m), 4.75 (2H, s), and 5.4 (1H, m). $M^+/e = 108$. Found: C, 88.02; H, 11.32%, Calcd. for C_8H_{12}: C, 88.82; H 11.18%.[**]

Component B (yield anout 15%) was found to be a mixture of 1,4-dimethyl-4-vinyl-1-cyclohexene and 2,4-dimethyl-4-vinyl-1-cyclohexene by comparison of its NMR and IR spectra with the reported values.[5]

Component C (yield about 40%) was separated into two peaks by VPC of a Golay type column and found to be a mixture of 1-methyl-4-isopropenyl-1-cyclohexene and

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[*] Allene was considered as a monosubstituted ethylene and the Hückel parameters were chosen as follows:

$\alpha(-CH_3)$	$\alpha + 3\beta$
$\alpha(=CH_2)$	$\alpha + 2\beta$
α(carbon adjacent to$-CH_3$)	$\alpha - 0.1\beta$
α(carbon adjacent to$=CH_2$)	α
β(C to$-CH_3$)	β
β(C to$=CH_2$)	β

[**] The compounds did not give satisfactory analytical values possibly owing to their high volatilities. The ratios of carbon to hydrogen accord with the theoretical values within the experimental error.

1-methyl-5-isopropenyl-1-cyclohexene by comparison of its IR spectrum with a reported chart[6] and from the analysis of its NMR spectrum.

Dehydrogenation of the Diels-Alder adducts: A mixture of component A, independently synthesized I, and 10% excess chrolanil was heated at 115°C for 45 min. in anisole. After being cooled, the reaction mixture was filtered, and analyzed by VPC (Bentone 34+DIDP/Neopack 1A). Yields of the dehydrogenation products were about 60% and were nearly constant for all experiments.

1-Methyl-4-methylene-1-cyclohexene (I): NaH (52% dispersion in mineral oil) 5.08 g in a 200 ml three necked flask was washed with n-pentane to remove the mineral oil. The flask was equipped with a rubber stopper, a reflux condenser fitted with a three-way stopcock, and a magnetic stirrer. After the air in the flask was replaced with nitrogen, 50 ml of dimethylsulfoxide was introduced by a syringe, and the mixture was heated at 75–80°C untill the evolution of hydrogen ceased. After the mixture had been cooled, methylenetriphenylphosphonium bromide 42.8 g in dimethylsulfoxide 100 ml was added, and the solution was stirred at room temperature for 15 min., then 4-methyl-Δ^3-cyclohexenone[7] 11 g was added slowly. The mixture was immediately distilled under reduced pressure and from the lower boiling liquid than the solvent, I was collected by VPC.

NMR: (δ, ppm): 1.7 (3H, s), 2.2 (4H, m), 2.7 (2H, m), 4.75 (2H, s), 5.4 (1H, m). $m^+/e=108$, Found: C, 84.84; H, 10.55%. Calcd for C_8H_{12}: C, 88.82; H, 11.18%**.

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