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Rearrangement of 5-Isopropenyl-2-norbornene to 5-Methyl-3a,4,7,7a-tetrahydro-1*H*-indene

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Synopsis. The Diels-Alder reaction between cyclopentadiene and isoprene gave predominantly *endo*- and *exo*-5-isopropenyl-2-norbornenes and also *cis*-5-methyltetrahydro-1*H*-indene produced from the *endo*-product by Cope rearrangement.

In a previous paper,[1] the present have reported the reaction of isoprene (IP) with cyclopentadiene (CP). However, the stereochemical structure has not yet been established because of certain difficulties in the assignments of the ^{1}H-NMR spectra. Here, the authors report the chemical structures of the above reaction products confirmed by means of ^{13}C-NMR spectroscopy.

Experimental

Preparation of the Addition Products.[1,2] The co-dimers obtained in the reaction of IP with CP are both of methylvinylnorbornene (MVN) and methyltetrahydroindene (MTI). After the equi-molar reaction mixture had been stirred for 3 h at 145 or 160 °C in an autoclave and then cooled, the MVN produced was isolated by means of distillation and preparative gas chromatography. Following a similar procedure, MTI was also obtained under the reaction conditions at 145—220 °C for 3 h.

The co-dimer of the reaction of butadiene with CP, employed as a reference was prepared by a previously reported method.[2]

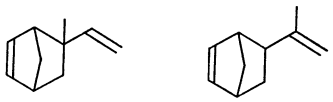
Rearrangement of MVN to MTI. The reaction of 0.1 ml of MVN was carried out in a 1-ml sealed tube in the range of the temperature from 145 to 170 °C. After the reaction had been completed and cooled, the product was analyzed by VPC.

Measurements. The ^{13}C-NMR spectra were recorded with a JNM-EC-100 Fourier transform spectrometer (25.15 MHz) with complete proton decoupling. The chemical shifts were determined in a CCl_4 solution of approximately 50 vol % using TMS as an internal standard. To all samples, the off-resonance proton decoupling technique was applied.

Preparative gas chromatography was carried out on a JEOL GC-750 with a 10 mmϕ × 3 m column packed with 25% silicon H. V. grease at 100 °C. The VPC analysis of the reaction products were made on a HITACHI KGL-2A gas chromatograph using a Golay column Q-90 (0.25 mmϕ × 90 m) at 134 °C.

Results and Discussion

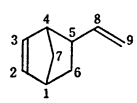
Stereochemical Structure of MVN. The two possible structures for MVN are presented as follows:



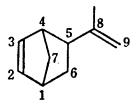
1 **2**

The result of the VPC analysis of the fractions of MVN showed the presence of the two components, **A** (R_t=22.4) and **B** (R_t=24.0). The molar ratio of **A** to **B** was found to be 14: 84 and 41: 59 in the fractions reacted at 145 and 160 °C, respectively. These two fractions were also examined by ^{13}C-NMR spectroscopy and the assignments of the signals in each fraction were easily determined. Furthermore, the numbers of protons attached to each carbon atom were obtained by means of the off-resonance proton decoupling technique. This result indicates that each of the components, **A** and **B**, has one nonprotonated sp^2 carbon atom. From this fact, the above structure **2** is in complete agreement with MVN, and thus **A** and **B** appear to be either the *endo*- or the *exo*-isomer of **2**.

TABLE 1. OBSERVED AND CALCULATED ^{13}C-NMR CHEMICAL SHIFTS[a] FOR VNB AND MVN



VNB

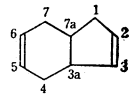


MVN

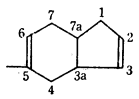
	Compound	C-2	C-3	C-6	C-7	C-8	C-9	CH_3	C-1, 4 or 5		
Calcd	VNB	137.2	134.2	36.5	37.0	145.3	114.9				
Obsd	*endo*-VNB	137.3 (d)	133.2 (d)	33.5 (t)	49.7 (t)	143.2 (d)	113.9 (t)		42.9 (d)	43.2 (d)	48.1 (d)
Obsd	*exo*-VNB	137.3 (d)	136.8 (d)	33.5 (t)	45.9 (t)	143.6 (d)	112.6 (t)		42.2 (d)	42.6 (d)	48.1 (d)
Calcd	MVN	136.2	134.5	33.9	37.0	149.5	112.4	20.1			
Obsd	*endo*-MVN	136.7 (d)	132.2 (d)	29.8 (t)	49.7 (t)	147.1 (s)	109.3 (t)	23.4 (q)	42.9 (d)	45.1 (d)	45.9 (d)
Obsd	*exo*-MVN	136.7 (d)	135.9 (d)	31.5 (t)	45.3 (t)	149.5 (s)	107.9 (t)	23.4 (q)	42.3 (d)	45.5 (d)	44.7 (d)

( ): off-resonance a) In ppm relative to internal TMS.

TABLE 2. OBSERVED AND CALCULATED ^{13}C-NMR CHEMICAL SHIFTS[a] FOR THI AND MTI



cis-THI



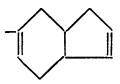
cis-MTI

Compound		C-1	C-2	C-3	C-3a	C-5	C-6	C-7a	C-4 or 7		CH_3
Calcd	THI	32.3	130.0	136.0	39.5	130.3	130.3	39.5	32.0		
Obsd	THI	40.2	129.5	136.2	43.1	128.1	128.1	35.6	27.8	28.7	
		(t)	(d)	(d)	(d)	(d)	(d)	(d)	(t)	(t)	
Obsd	MTI	40.1	129.5	135.9	43.5	135.5	121.4	34.9	32.8	29.1	23.8
		(t)	(d)	(d)	(d)	(d)	(d)	(d)	(t)	(t)	(q)

( ): off-resonance a) In ppm relative to internal TMS.

The selection of a suitable structure for **A** and **B** was governed by the following three factors: (i) by comparison with the ^{13}C-NMR spectra of *endo*- and *exo*-5-vinyl-2-norbornene(VNB),[2] (ii) by matching with the calculated chemical shifts according to parameter of Lindemann[3] for alkane and that of Roberts[4] for alkene and (iii) by referring to the off-resonance decoupling information. From this evidence, **A** and **B** were identified to be the *endo*- and *exo*-5-isopropenyl-2-norbornene (MVN), respectively. The data of the ^{13}C-NMR spectra are listed in Table 1.

Structure of MTI. The following two formulae are presented as possible structures of MTI.



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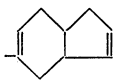

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From the results of the ^{13}C-NMR spectra data (in Table 2) and the VPC analysis, it was found that the fraction of MTI consists of only a single component. The determination of the stereochemical structure of MTI contained in the fraction was performed in the following section.

Rearrangement of MVN to MTI. The rearrangement of the fraction of MVN was carried out by a method similar to that reported in a previous paper.[2] In the case of the fraction (*endo*-MVN: *exo*-MVN= 59: 41) obtained from the reaction at 170 °C for 4 h, the *endo*-MVN was rearranged to MTI, while no *exo*-MVN reacted. This fact indicates that MTI was produced along with Cope rearrangement and its structure must be **4**.

Further, the rearrangement kinetics were examined using a fraction having a high content of the *endo*-product(*endo*: *exo*=86: 14), in the temperature range from 145 to 170 °C. The rate constants and the activation parameters are listed in Table 3.

The positive value of $\Delta S^{\ddagger}$ may also support the above mechanism where by the reaction proceeds through Cope rearrangement.[5]

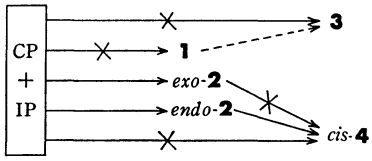
TABLE 3. RATE CONSTANTS FOR THE REARRANGEMENT OF *endo*-MVN TO MTI AT VARIOUS TEMPERATURES

Reaction temp (°C)	Rate constant ($\times 10^{-4}$ s^{-1})
145	0.22
155	0.38
165	1.13
170	2.25

$\Delta H^{\ddagger}$: 33.8 kcal/mol, $\Delta S^{\ddagger}$: 0.40 e.u. (at 150 °C) calculated from the Eyring equation.

The Diels-Alder reaction of the IP–CP equi-molar mixture gave products **2** and **4**, while neither the **1** nor the **3** compounds were obtained. The reason for the absence of **1** in the products may be illustrated by steric repulsion between the methylene protons of CP(diene) and the methyl group of IP(dienophile).

The reaction scheme is illustrated as follows:



References

1) S. Tsuchida, T. Maehata, and M. Ogawa, *Sekiyu Gakkai-shi*, **14**, 257 (1971).

2) T. Maeda, M. Muranaka, S. Hamanaka, and M. Ogawa, *Nippon Kagaku Kaishi*, **1974**, 1587.

3) L. P. Lindeman and J. Q. Adams, *Anal. Chem.*, **43**, 1245 (1971).

4) D. E. Dorman, M. Jautelate, and J. D. Roberts, *J. Org. Chem.*, **36** 2757 (1971).

5) The observed $\Delta S^{\ddagger}$ value differs widely in comparison with the value for the reaction of VNB with THI reported in a previous paper.[2] In that work, no explanation of this fact was presented.