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The Thermal Isomerization of Pinane and Its Products

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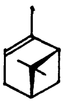
The stereochemistry of the reduced products of the iridenes was studied, and the main product produced by the thermal isomerization from pinane was confirmed to be 1-*trans*-2-dimethyl-*trans*-3-isopropenylcyclopentane, unlike as in the literatures. Moreover, the ozonolyses of the iridenes were reexamined in detail, and the following results were obtained: 1) When the ozonides were decomposed with Na_2CO_3-H_2O_2, the substituent on C-3 was epimerized. 2) On the other hand, when the ozonides were treated with Zn-CH_3COOH, no such epimerization occurred. Consequently, it was found that the former method when used for the confirmation of iridenes, did not give good results for assignments of these compounds.

l-cis-Pinane was isomerized at a high temperature to 3,7-dimethyl-1,6-octadiene (III)(=dihydromyrcene) and 1,2-dimethyl-3-isopropenylcyclopentanes (IVa—d) (=iridenes). The latter were the secondary products isomerized from the former. Those structures had been reported to be IVa and IVd.[2–5] Crowley,[6] however, reported that one of them was not IVa, but IVb, on the basis of his studies of the photochemical reactions of alloocimene. Furthermore, Ohloff[7] got plinols in which methyl on C-2 and isopropenyl on C-3 were *cis* configuration from ring-closure reactions of linalool.

In this paper, it will be reported on how, on the isomerization of pinane, the stereochemistry of iridenes was studied and IVb was obtained as the main product. Moreover, the determination of the structures through ozonolyses was reexamined, and the effect of epimerization on the process was reported.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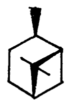
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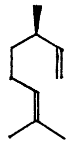
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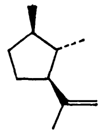
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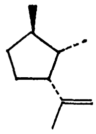
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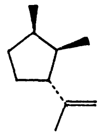
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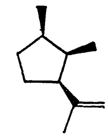
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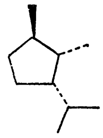
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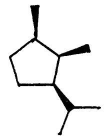
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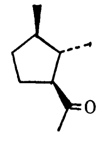
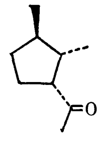

VIa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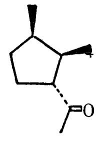
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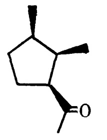
VId

Experimental

Measurements. The measurements were carried out after glc fractionations. The PMR spectra were recorded on a Hitachi-Perkin Elmer Model R-20, using tetramethylsilane as the internal standard and CCl_4 as the solvent at an ordinary temperature. A Perkin Elmer Model 337 infrared spectrometer was used for the measurements of the infrared absorption spectra in the 4000—400 cm^{-1} region.

Preparation of l-cis-Pinane(II). Into a 300-m*l* autoclave equipped with a magnetic stirrer, 100 m*l* of *l*-α-pinene(I) (bp 52—53°C/20 mmHg, n_D^{20} 1.4675, d^{25} 0.8537, $[\alpha]_D^{20}$ −39.1°), 10 g of Raney nickel W-6 and ethanol (40 m*l*) were added, and then hydrogen was introduced from a pressure bomb (150 kg/cm^2). Reduction was carried out at room temperature.[8] After the reaction, pinane (bp 60.5—62.0°C/20 mmHg, n_D^{20} 1.4630, $d^{12.5}$ 0.8592, $[\alpha]_D^{24.6}$−14.63. PMR; 8.85(s), 9.00(s), 9.01(d, J=6.5 Hz)) was obtained. These physical data corresponded to those for *l-cis*-pinane.[9]

Thermal Isomerization of II. II was isomerized in a silica tube (20 mm $\phi\times$300 mm) at a feed rate of 21 m*l*/hr in the range of 400—500°C with preheating (210°C). The isomerization products were carefully distilled, and two fractions, A (bp 160.5—161.0°C, n_D^{20} 1.4480) and B (bp 169.0—170.0°C, n_D^{20} 1.4550), were collected. The fraction A contained 84% of the peak 6, and the fraction B contained 83% of peak 8.

Ozonolyses of the Isomerized Products. A 2.0 g portion of each fraction (A and B) was dissolved in dichloromethane and saturated with ozone at −80°C, and then the solutions were warmed to −20°C. To each solution, the following two methods were applied: *Method 1*: Acetic acid (50 m*l*) and zinc powder (8 g) were then stirred into the solutions. After one hour, carbonyl compounds were obtained (A′ and B′). *Method 2*: Into the solutions, 5 m*l* of 10% aqueous Na_2CO_3 and 5 m*l* of 30% H_2O_2 were stirred. After three hours, these solutions were neutralized with 1 N HCl and extracted with ether.

Isomerization of the Carbonyl Compounds with Basic Reagents.

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1) Present address: The Research Institute of Nissan Chemical Industries, Ltd., Toshima, Kita-ku, Tokyo.

2) V. N. Ipatieff, W. D. Huntsman, and H. Pines, *J. Amer. Chem. Soc.*, **75**, 6222 (1953).

3) H. Pines, N. E. Hoffman, and V. N. Ipatieff, *ibid.*, **76**, 4412 (1954).

4) W. D. Huntsman and T. H. Curry, *ibid.*, **80**, 2252 (1958).

5) W. D. Huntsman, V. C. Solomon, and D. Eros, *ibid.*, **80**, 5455 (1958).

6) K. J. Crowley, *Tetrahedron Lett.*, **1965**, 2863.

7) H. Strickler, G. Ohloff, and E. sz. Kovats, *Helv. Chim. Acta*, **50**, 759 (1967).

8) A low-temperature reduction was desirable in obtaining a stereospecific product.

9) a) A. Lipp, *Ber.*, **56**, 2089 (1923). b) W. Cocker, P. V. R. Shanon, and P. A. Staniland, *J. Chem. Soc.*, *C*, **1966**, 41. c) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **86**, 393 (1964).

TABLE 1. THERMAL ISOMERIZATION OF *l-cis*-PINANE[a]

No.	Temp. (°C)	Yield (g)	Product Ratio by the Peak Area on the Glc[b]								
			1	2	3	4	5	6[c]	7	8[d]	9
1	400	3.0	—	0.9	2.7	—	15.3	5.6	73.1	2.4	—
2	425	3.0	—	3.1	3.8	—	29.0	3.3	57.3	3.3	—
3	455	2.9	—	1.2	5.2	—	44.2	21.3	18.6	5.0	4.1
4	480	2.8	—	4.8	5.7	—	31.9	38.4	2.7	13.7	2.3
5	500	2.8	0.5	2.3	2.8	3.7	25.5	42.8	2.3	14.8	5.3

a) 10 minutes feeding at the rate of 21 m*l*/hr. (*ca.* 3 g)

b) PEG 6000/celite, 120°C, H_2: 40 m*l*/min.

c) Peak 6: bp 160.5—161.0°C (lit.[3] for IVa; 161.1—161.4°C), n_D^{20} 1.4480 (lit.[3] for IVa; 1.4475), PMR 9.33 (3H, d, J=6.5 Hz), 8.99 (3H, d, J=4.8 Hz), 8.35 (3H, s), 8.70—7.20 (7H, m), 5.42 (1H, m), 5.30 (1H, m), IR 3080, 885 cm^{-1}.

d) Peak 8: bp 169.0—170.0°C (lit.[3] for IVd; 169—170°C), n_D^{20} 1.4550(lit.[3] for IVd; 1.4545—1.4560), PMR 9.50(3H, d, J=7.0 Hz), 9.08(3H, d, J=6.0 Hz), 8.31(3H, s), 8.70—7.30(7H, m), 5.42(1H, m), 5.28(1H, m), IR 3080, 885 cm^{-1}.

1) A mixture of A′ and B′ (1.5 g) was added to 30 m*l* of 10% aqueous Na_2CO_3 and refluxed for four hours with vigorous stirring. After the reaction, 1.0 g of an oily product was obtained.

2) A′ and B′ (0.5 g) were each dissolved in 20 m*l* of 1 N alcoholic potash, and the mixtures was refluxed for four hours. Then, a 60 m*l* portion of water was added to each solution and they were neutralized with 1 N HCl. The isomerized products were obtained by means of the usual treatment.

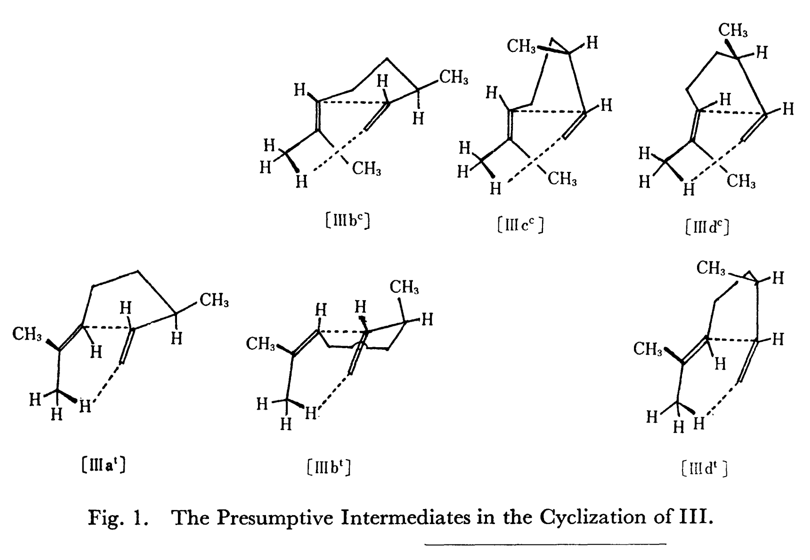
Results and Discussion

The results of the thermal isomerizations of II are listed in Table 1. The peaks 1,5, and 7 were identified as isoprene, III, and II respectively by reference to authentic samples. According to the literatures,[2,3] the peaks 6 and 8 seem to be iridenes, IVa and IVd respectively; this assignment is based on the physical constants listed in Table 1. When, however, the fraction A was reduced by the same way as II was, the PMR spectrum of the main product was identical with that of iridane Vb.[10] Therefore, the peak 6 may be identified as IVb, since, under our experimental conditions, the structure should be retained.

The formation of the iridenes has been considered to proceed through the polycenter-concerted mechanisms, and several 1,6-heptadienes have been cyclized intramolecularly at a high temperature to *cis*-products.[5,11,12] However, the iridenes obtained from III have been reported to be *trans* IVa mainly.[2–5] Therefore, Tabushi[12] considered that the primary product, IVd, was converted thermally to IVa, and Huntsman[5] presumed that the methyl group at the 3-position of III contributed to form IVa.

On the other hand, Ohloff and his coworkers[7] obtained *cis*-plinols as the main products on the cyclization of linalool, and they presumed a reaction mechanism.

Since the cyclization of III seems to be the same as in the case of linalool, the following intermediate structures are presumed (Fig. 1). In the [III^{c}] series, C-7 methyl and terminal methylene are *cis*, while in the [III^{t}] series they are *trans*. The IV's must be produced from the respective [III's]. Among these, the [III$^{c}_{e}$] and [III$^{t}_{d}$] structures are unstable because of the ecliptic arrangement of methyl on C-3 and terminal vinyl. (With regard to the latter, the interaction of methyls on C-3 and C-7 must also be con-



[IIIb^{c}] [IIIc^{c}] [IIId^{c}]

[IIIa^{t}] [IIIb^{t}] [IIId^{t}]

Fig. 1. The Presumptive Intermediates in the Cyclization of III.

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10) K. Sisido, S. Kurozumi, K. Utimoto, and T. Isida, *J. Org. Chem.*, **31**, 2795 (1966).

11) H. M. R. Hoffman, *Angew. Chem.*, **81**, 597 (1969).

12) I. Tabushi and K. Fujita, *Yuki Gosei Kagaku Kyokai Shi*, **25**, 10 (1967).

sidered). Hence, from the standpoint of stability and from that of the number of intermediates, the ease of the formation of iridenes seems to be the following sequence:

$$\text{IVb} > \text{IVd} > \text{IVa} > \text{IVc}.$$

TABLE 2. THE RESULTS OF OZONOLYSES OF IRIDENES

Reactant[a]	Method[b]	Product (%)[c]				
		VIa	VIb	VIc	VId	others
A	1	17.3	63.1	7.1	12.5	
B	1	—	4.4	—	95.6	
A+B	2	31.4	30.5	16.3	21.8	
A	2	47.8	45.8	4.8	1.0	
Iridene fraction from thermally isomerized product of II	1	15.1	48.0	6.6	24.7	5.6

a) Fraction A containing 84% of IVb, and B did 83% of IVd.
b) Methods were described in the experimental part.
c) Analyses were carried out by glc (PEG 6000/celite, 126°C, H_2: 41 m*l*/min).

This agrees with the experimental results.

Moreover, the results of the ozonolyses (Table 2) show that VIb and VId were produced from IVb and IVd respectively; therefore, in the former, the methyl groups on C-1 and C-2 are *trans*, and in the latter, *cis*. On the other hand, VIb and VId were isomerized partly into VIa and VIc respectively by the action of alkalis (Table 3), so it seems that, concerning the methyl on C-2 and the acetyl on C-3, VIa and VIc have more stable configurations than do VIb and VId. Therefore, these two groups may be considered to be *trans* in VIa and VIc, and *cis* in VIb and VId. That is, in the ozonolyses in which the ozonides are decomposed with Zn–CH_3COOH, the configurations do not change, but with alkalis epimerizations occur.

TABLE 3. ISOMERIZATION WITH BASIC REAGENTS[a]

Reactant[b]	Reagent	Product (%)[c]			
		VIa	IVb	VIc	VId
A′	1N-alc. potash	63.6	2.5	25.2	8.7
B′	1N-alc. potash	1.0	—	54.4	44.6
A′+B′ (1:1)	10% aq. Na_2CO_3	22.2	38.3	14.9	24.6

a) Reaction conditions; refluxing for four hours.
b) A′ was obtained from fraction A by means of method 1, and B′ was from B.
c) The analyses were same as Table 2.

Furthermore, the Cotton effects of VIa and VId were positive, and those of VIb and VIc were negative. According to Djerassi,[13] the Cotton effects of pregnan-3β-ol-20-one were negative in the case of the α configuration at C-17 acetyl and positive in the case of the β. Since, on the steroid, the steric effects of A, B, and C rings make contributions, the data may be not strictly suitable for our experiments. However, when we use these data in connections with those obtained in our studies, it can be deduced that the configuration of C-3 acetyl is α in VIb and VIc, and β in VIa and VId.

From these results, the decomposition of ozonides with Zn–CH_3COOH may be concluded to give the sterically-corresponding ketones. On the other hand, when the decomposition of ozonides is carried out with Na_2CO_3–H_2O_2, VIa and VIb are obtained from IVb, and VIc and VId from IVd. When the former workers[2,3] studied the structures of iridenes through ozonolyses, they used Na_2CO_3–H_2O_2 as the decomposing reagent of ozonides, they thus deduced that IVa, which is an epimer of IVb, was the main product from the thermal isomerization of II.

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[13] C. Djerassi, *Bull. Soc. Chim. Fr.*, **1957**, 741; C. Djerassi, O. Halpern, V. Schindler, and Ch. Jamm, *Helv. Chim. Acta*, **41**, 250 (1958); C. Djerassi, I. Fornaguera, and O. Mancera, *J. Amer. Chem. Soc.*, **81**, 2383 (1959).