Stereochemistry of 1,2-Dimethyl-3-isopropylcyclopentane

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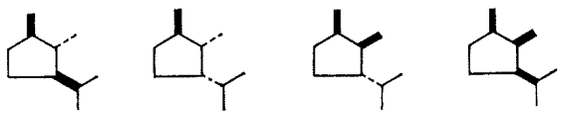
(+)-1,*trans*-2-Dimethyl-*trans*-3-isopropylcyclopentane (**1b**) and (±)-1,*cis*-2-dimethyl-*trans*-3-isopropylcyclopentane (**1c**) were prepared from (+)-isoiridomyrmecin (**3**) and (±)-dihydrophotocitral-A (**9**), respectively. A mixture of stereoisomers of (+)-1,2-dimethyl-3-isopropylcyclopentanes (**1a**, **1b**, and **1c**) was derived from crude (+)-iridodial (**5** with **6** and **7**). These products were compared with a mixture of stereoisomers of (±)-1,2-dimethyl-3-isopropylcyclopentanes synthesized from (±)-2-carbethoxy-5-methylcyclopentanone (**11**) *via* (±)-1-methyl-2-methylene-3-isopropylcyclopentane (**14**). The stereochemistry of these syntheses is discussed.

In a study of the fragrant flower constituents of *Osmanthus fragrans, Lour. var. aurantiacus (Makino)*, Isiguro and co-workers[1] obtained in a petroleum ether extract, a 0.002% yield of a hydrocarbon $C_{10}H_{20}$, which they named "osmane." The structure of "osmane" was shown to be 1,2-dimethyl-3-isopropylcyclopentane (**1**) by comparison of its physical properties including the infrared spectrum with those of a compound synthesized from thujone essentially according to Wallach.[2] "Osmane" was reported to be optically inactive, although this compound contains three asymmetric centers.

The present investigation was commenced in order to elucidate the configuration of "osmane" by the syntheses of all stereoisomers without considering the optical activity, since this compound constitutes a basic hydrocarbon of some natural monoterpenoids. Achmad and Cavill[3] as well as Strickler, *et al.*,[4] suggested that this hydrocarbon[5] would be named nepetane or iridane, respectively, without any stereochemical implications.

When, however, the extraction of flowers of *Osmanthus fragrans* collected on the campus of Kyôto University was repeated with carefully rectified petroleum ether (bp 40–60°), no hydrocarbon corresponding to 1,2-dimethyl-3-isopropylcyclopentane (**1**) was detected. Petroleum ether, bp 40–60°, commercially available in Japan, was found to contain 0.008% of a fraction, bp 158–160°, from which, by preparative gas chromatography, a hydrocarbon similar to 1,2-dimethyl-3-isopropylcyclopentane (**1**) was obtained. It was considered that the name "osmane" should be deleted from the literature.

Earlier reports[2,6-8] on the synthesis of 1,2-dimethyl-3-isopropylcyclopentane (**1**) gave no information about the stereochemistry. Pines, Hoffman, and Ipatieff[9] reported that 1,*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane (**1a**) was obtained from pinane. Recently, however, Crowley[10] suggested, by comparison of the compounds **1c** and **1a** prepared from alloocimene, that the hydrocarbon of Pines, *et al.*, was **1b**.



1a **1b** **1c** **1d**

The basic structure of 1,*trans*-2-dimethyl-*trans*-3-isopropylcyclopentane (**1b**) is present in iridomyrmecin[11] and isoiridomyrmecin[12] (**3**) so that these substances represent a source of isomer **1b**. Lithium aluminum hydride reduction of crystalline (+)-isoiridomyrmecin (**3**) obtained from (+)-citronellal (**2**) by the method of Robinson and co-workers[13] gave (−)-iridodiol[14] (**4**). Tosylation of this diol (**4**) followed by hydrogenolysis gave a hydrocarbon, $C_{10}H_{20}$, which was demonstrated by gas chromatography to consist of one isomer (peak b) (Table I). The structure (+)-**1b** was assigned to this compound.

TABLE I

STEREOISOMERS OF 1,2-DIMETHYL-3-ISOPROPYLCYCLOPENTANES. ANALYSIS BY GAS CHROMATOGRAPHY

($AgNO_3$–$C_6H_5CH_2CN$, 3 m × 4 mm; 75°; He, 35 ml/min)

Peak:	a	b	c	d
Retention time (min):	13.5	14.9	16.8	18.8
Material obtained from	Peak, %			
(+)-Isoiridomyrmecin	1	99	..	..
(+)-Iridodial by $LiAlH_4$	55	18	26	1
(+)-Iridodial by Huang-Minlon reduction	64	16	19	1
Citral	..	6	94	..
14 by hydroboration	1	72	6	22
14 by hydrogenation with diimide	6	62	14	18
14 by hydrogenation over palladium	78	3	12	6
14 by hydrogenation over Raney nickel	2	36	60[a]	1

[a] Contaminated with 1,2-dimethyl-3-isopropylcyclopentene-2.

It has been reported that (+)-iridodial (**5**) derived from (+)-citronellal (**2**)[13] is contaminated with small amounts of the stereoisomers (**6** and **7**).[15] When lithium aluminum hydride reduction was carried out with such an iridodial preparation, there was obtained a mixture of (+)-1,2-dimethyl-3-isopropylcyclopentanes, whose gas chromatogram showed four peaks, a major one (a), two minor ones (b and c), and a very

(1) T. Isiguro, N. Koga, and K. Nara, *Yakugaku Zassi*, **77**, 566 (1957); *Chem. Abstr.*, **51**, 15069*d* (1957).

(2) O. Wallach, *Ann.*, **323**, 333 (1902).

(3) S. A. Achmad and G. W. K. Cavill, *Australian J. Chem.*, **16**, 858 (1963).

(4) H. Strickler, G. Ohloff, and E. sz. Kováts, *Tetrahedron Letters*, 649 (1964).

(5) T. Ikeda and K. Wakatuki [*J. Chem. Soc. Japan*, **57**, 425 (1936)] described presumably the same hydrocarbon as tetrahydroplinolene.

(6) M. Godchot, *Compt. Rend.*, **158**, 1807 (1914).

(7) N. D. Zelinsky and B. A. Kasansky, *Ber.*, **60**, 1096 (1927).

(8) B. A. Kasansky, *ibid.*, **62**, 2205 (1929).

(9) H. Pines, N. E. Hoffman, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **75**, 6222 (1953); **76**, 4412 (1954).

(10) K. J. Crowley, *Tetrahedron Letters*, 2863 (1965).

(11) R. Fusco, R. Trave, and A. Vercellone, *Chim. Ind.* (Milan), **37**, 958 (1955).

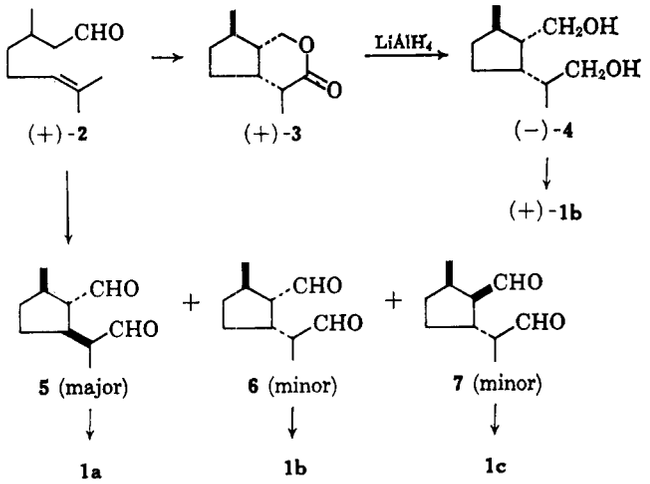
(12) G. W. K. Cavill, D. L. Ford, and H. D. Locksley, *Australian J. Chem.*, **9**, 288 (1956).

(13) K. J. Clark, G. I. Fray, R. H. Jaeger, and R. Robinson, *Tetrahedron*, **6**, 217 (1959).

(14) E. J. Eisenbraun, T. George, B. Riniker, and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 3684 (1960); E. J. Eisenbraun, A. Bright, and H. H. Appel, *Chem. Ind.*, 1242 (1962).

(15) G. W. K. Cavill and F. B. Whitfield, *Australian J. Chem.*, **17**, 1260 (1964).

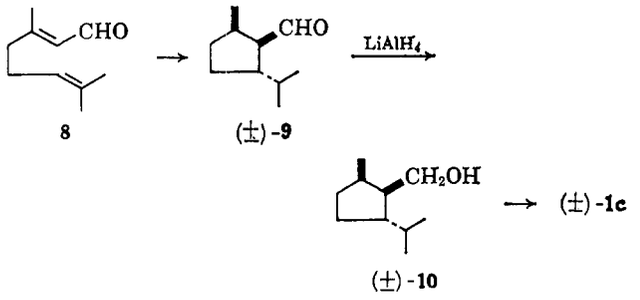
SCHEME I



small one (d) (Table I). The Huang-Minlon reduction of the crude dial (**5** with **6** and **7**) gave essentially the same results (Table I).

Structure **1a** is assigned to the major component (peak a). Since peak b is identical with that of **1b**, peak c should correspond to structure **1c** or **1d**. (See Scheme I.)

The basic structure of **1c** is present in photocitral-A[16] and dihydrophotocitral-A (**9**).[16,17] When lithium aluminum hydride reduction followed by the hydrogenolysis of dihydrophotocitral-A (**9**) prepared from citral[16] (**8**) was carried out as mentioned above, there were obtained (±)-1,2-dimethyl-3-isopropylcyclopentanes consisting predominantly of one isomer (peak c) accompanied by a small amount of a second isomer (peak b) (Table I).



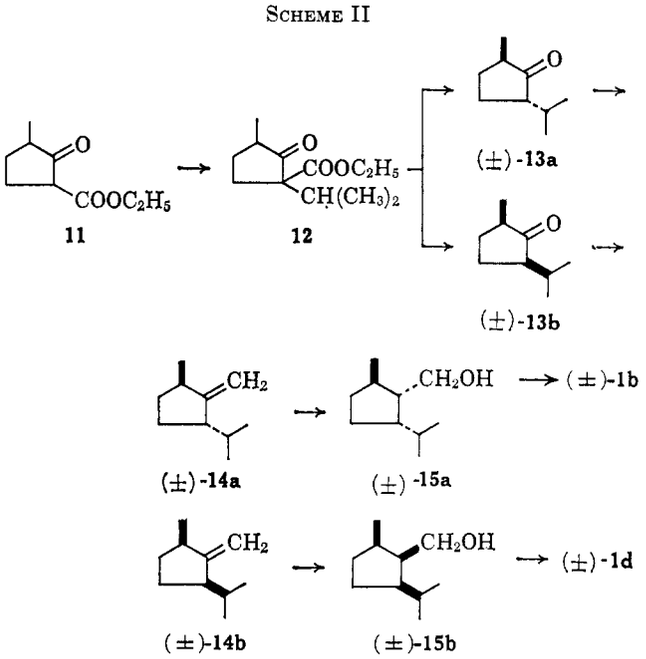
The structure **1c** was assigned to this major component as well as to the product from iridodial with peak c. The second isomer coincided with the structure **1b**, which would be derived from the epimer of **9**. Thus the fraction, showing peak d, derived from an iridodial preparation, could be assigned to the remaining structure **1d**.

As an alternative route for the synthesis of racemic 1,2-dimethyl-3-isopropylcyclopentane (**1**), a procedure similar to our previous synthesis of (±)-iridomyrmecin[18] was undertaken. The reaction of isopropyliodide with 2-carbethoxy-5-methylcyclopentanone (**11**)[19] gave, *via* **12**, 2-methyl-5-isopropylcyclopentanone (**13**), which showed two gas chromatographic peaks in a ratio of 7:3. The compound **13**, therefore, would consist of a mixture of *cis* and *trans* isomers with *trans* compound predominating for the reason given in the case of the synthesis of (±)-iridomyrmecin.[18] Since isopropyl iodide is less bulky than ethyl 2-bromopropionate,[20] the steric effect was not as strong in this case. This stereochemistry was proved as explained at the end of this article.

1-Methyl-2-methylene-3-isopropylcyclopentane (**14**) was obtained from **13** by the Wittig reaction.[21,22] Gas chromatography of this olefin (**14**) showed two peaks in a ratio of 3:1, which were considered to represent the *trans* (**14a**) and *cis* (**14b**) isomers (with respect to methyl and isopropyl), respectively.

Hydroboration[23] of **14** followed by oxidation gave 1-methyl-2-hydroxymethyl-3-isopropylcyclopentane (**15**), which furnished on tosylation and hydrogenolysis, a mixture of **1b** and **1d** in a ratio of about 3:1 (Table I). 1,2-Dimethyl-3-isopropylcyclopentanol-2 (**16**), an abnormal addition product of diborane, was less than 1% of the main product **15**. The reduction of **14** with diimide[24] gave products with essentially the same isomer distribution (Table I). (See Scheme II.) The presence of isomers **1a** and **1c** (Table I) indicated that the steric requirement of diimide seemed to be not so strong as that of diborane.

SCHEME II



The proposed configurational assignment supported the results of the hydroboration and diimide reduction. The *cis* addition of diborane or diimide occurred predominantly on the opposite side of the molecule from the isopropyl group due to the steric hindrance, thus putting the new hydroxymethyl or methyl group, respectively, on *cis* position with respect to the isopropyl group.[18] This problem is also treated at the end of the article.

(16) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. Whitear, *Tetrahedron Letters*, 79 (1962); *Tetrahedron*, **19**, 1995 (1963).
(17) G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **87**, 1589 (1965).
(18) K. Sisido, K. Utimoto, and T. Isida, *J. Org. Chem.*, **29**, 3361 (1964).
(19) K. Sisido, K. Utimoto, and T. Isida, *ibid.*, **29**, 2781 (1964).
(20) Similarly, a smaller steric effect was observed with ethyl bromoacetate than with ethyl 2-bromopropionate.
(21) G. Wittig and U. Schöllkopf, *Chem. Ber.*, **87**, 1318 (1954).
(22) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(23) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962; G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).
(24) A. Fust, R. C. Berlo, and S. Hooton, *Chem. Rev.*, **65**, 51 (1965).

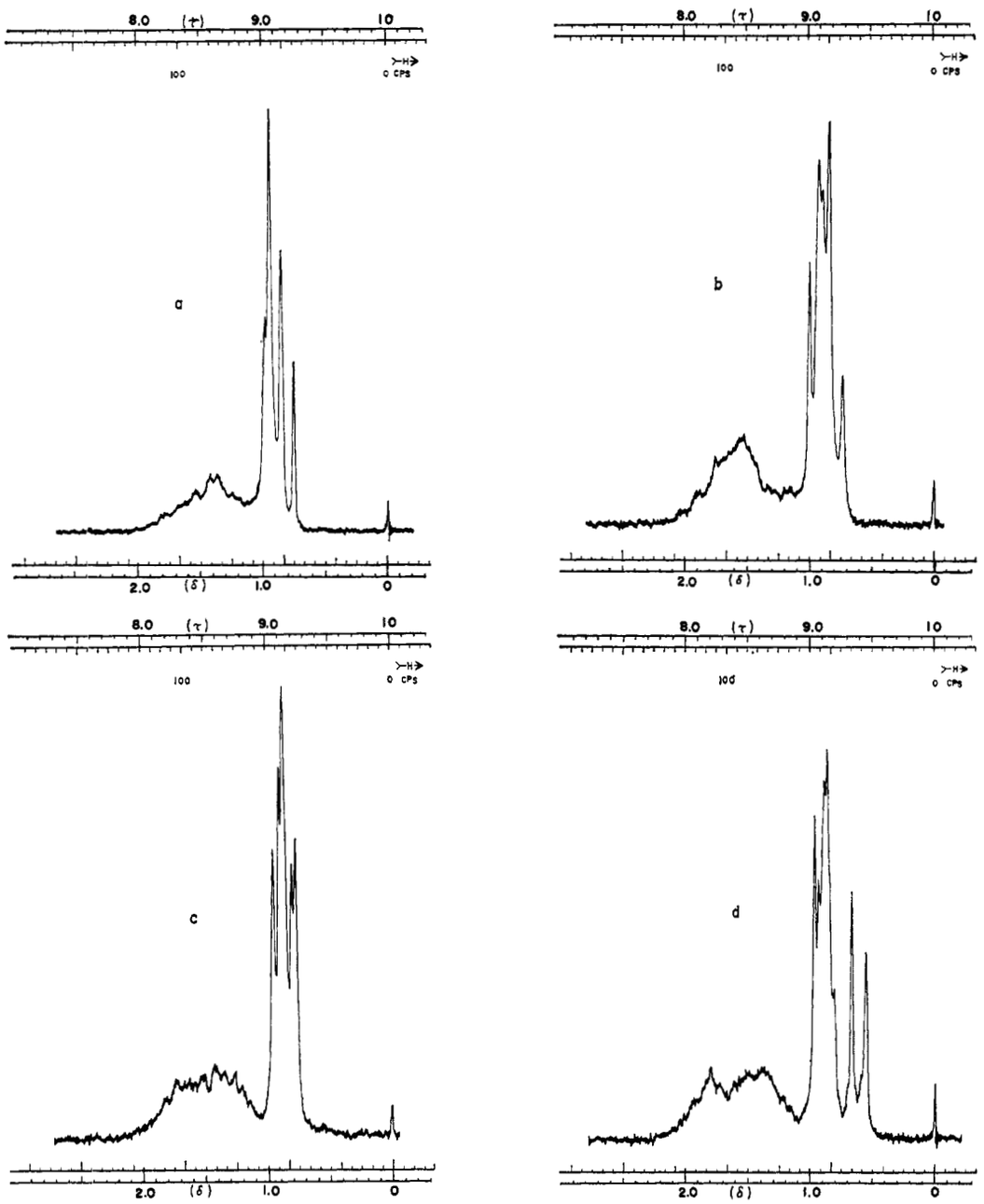
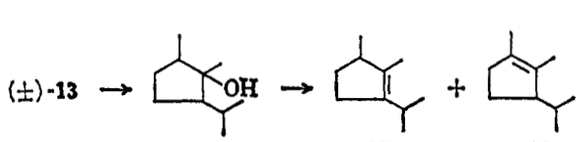


Figure 1.—The nmr spectra of (a) (±)-1,*trans*-2-dimethyl-*cis*-3-isopropylcyclopentane, (b) (±)-1,*trans*-2-dimethyl-*trans*-3-isopropylcyclopentane, (c) (±)-1,*cis*-2-dimethyl-*trans*-3-isopropylcyclopentane, and (d) (±)-1,*cis*-2-dimethyl-*cis*-3-isopropylcyclopentane at 60 Mc/sec in deuteriochloroform.

Hydrogenation of **14** over palladium–charcoal or with Raney nickel gave products showing predominantly peak a or c, respectively (Table I). The products of the Raney nickel hydrogenation contained, in addition, two products showing peaks other than those of **1**. Because an *exo* double bond, as that in **14**, readily isomerizes to an *endo* one on catalytic hydrogenation,[25] and because a tetrasubstituted ethylenic bond is not easily hydrogenated with Raney nickel,[26,27] it was considered that the extra peaks must correspond to cyclopentene derivatives.

Dehydration of 1,2-dimethyl-2-hydroxy-3-isopropylcyclopentane (**16**) prepared according to Kasansky[8] by the Grignard reaction yielded an olefinic mixture of

(25) S. Siegel and B. Dmuchovsky, *J. Am. Chem. Soc.*, **86**, 2192 (1964).
(26) G. Dupont, *Bull. Soc. Chim. France*, (5) **3**, 1021 (1936).
(27) Kasansky (reference 8) carried out this hydrogenation at 160–170°, *i.e.*, at a significantly higher temperature.



1,2-dimethyl-3-isopropylcyclopentene-2 (**17**) and 1,2-dimethyl-3-isopropylcyclopentene-1 (**18**) in a ratio of 1:1. Each of these *endo* olefins was isolated by preparative gas chromatography and the structure was determined by nmr spectra. The infrared spectra as well as the gas chromatograms of these olefins were different from those of the *exo* olefin **14**. The extra peaks coincided with those of **17** and **18**.

When the olefinic mixture of **17** and **18** was treated with hydrogen over Raney nickel catalyst, there was no marked change in the gas chromatograms. However, the mixture was slowly hydrogenated over pal-

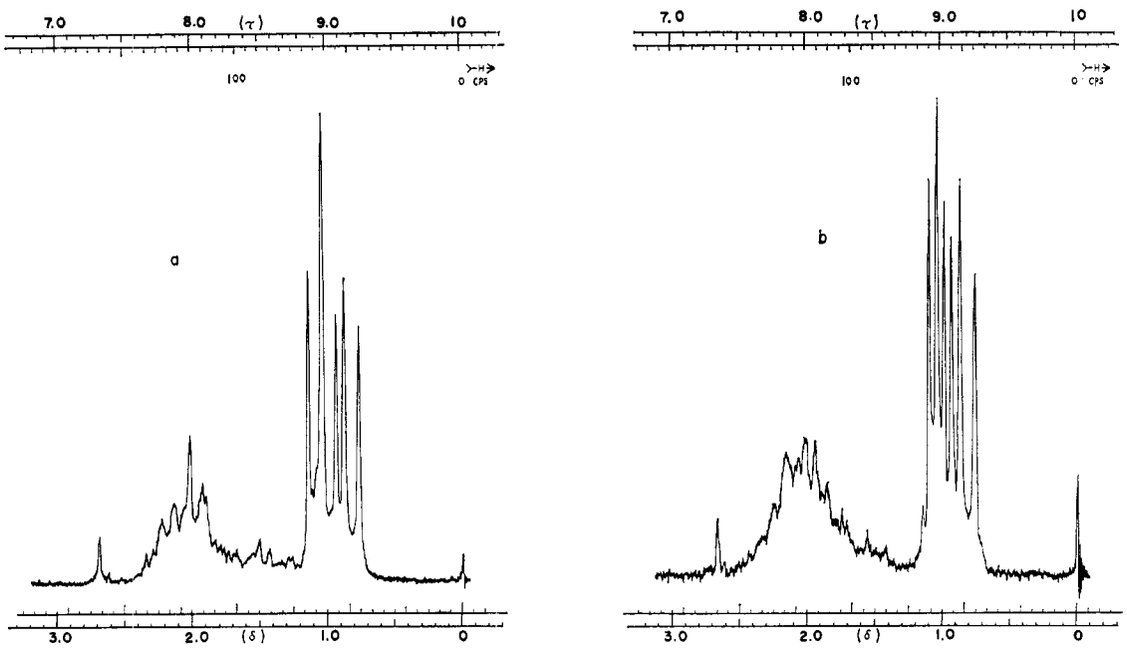


Figure 2.—The nmr spectra of (a) (±)-2-methyl-*trans*-5-isopropylcyclopentanone and (b) (±)-2-methyl-*cis*-5-isopropylcyclopentanone at 60 Mc/sec in deuteriochloroform.

ladium–charcoal catalyst to give a mixture of **1a** through **1d**. On catalytic hydrogenation of **14**, the abundant occurrence of **1a** which bears the isopropyl group on the *cis* position with respect to the 1-methyl group may account for such *endo* double-bonded intermediates and half-hydrogenated states.[28]

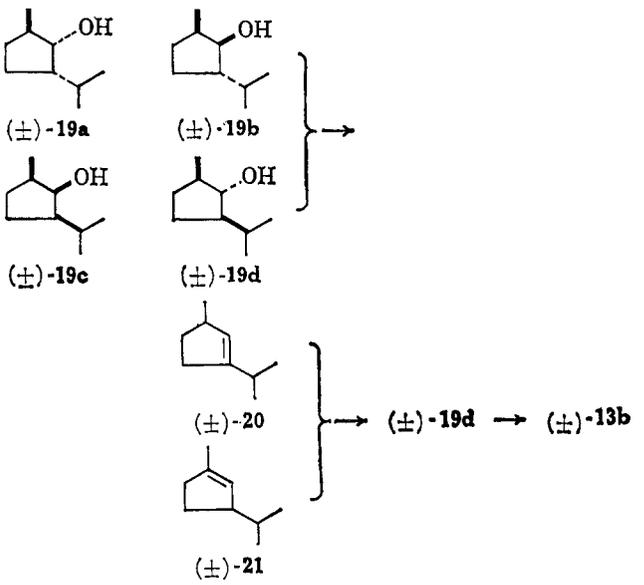
The infrared spectra of **1a**, **1b**, **1c**, and **1d** were different in the fingerprint region and CH deformation frequency bands (near 1380 and 1370 cm^{-1}) with each other. The identification of these compounds throughout the experiments were carried out by comparison of the infrared charts and by the peak enhancements of the gas chromatograms.

The nmr spectra of these four configurational isomers showed differences in the chemical shift of each one of the four methyl groups in the molecule (Figure 1). However, assignment of these signals was not feasible. The doublet (τ 9.38) corresponding to one methyl group found in nmr spectrum of **1d** seemed to correspond to the 2-methyl group suffering severe steric crowding by the *cis*-1-methyl group and the *cis*-3-isopropyl group.

The stereochemistry of 2-methyl-5-isopropylcyclopentanone (**13**) was verified by the following sequence of reactions.

Lithium aluminum hydride reduction of an isomeric mixture of **13a** and **13b** should give a mixture of four isomers, **19a–19d**. Since, however, the individual isomers could not be reliably characterized, the mixture was esterified with *p*-toluenesulfonyl chloride and then treated with potassium tertiary butoxide in dimethyl sulfoxide[29] to afford an olefinic mixture of 1-methyl-3-isopropylcyclopentene-2 (**20**) and 1-methyl-3-isopropylcyclopentene-1 (**21**) in a ratio of 3:2. The structures of **20** and **21** were determined by nmr spectra.[30] (See Scheme III.)

SCHEME III



Hydroboration followed by oxidation of a mixture of **20** and **21** should give an alcohol which would correspond to a structure **19d**, since diborane attacks the double bond predominantly from the less hindered side of the molecule,[18,31] *i.e.*, from the other side of the neighboring methyl or isopropyl group. The gas chromatography of this alcohol showed a broad peak and chromic acid oxidation, during which the retention of the configuration is assured,[32] afforded a mixture of two isomeric cyclopentanones in a ratio of 1:4. The major component of the products was **13b** and the minor one was **13a**. Considering that the steric effect

(28) I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(29) D. H. Froemsdorf and M. E. McCaln, *J. Am. Chem. Soc.*, **87**, 3983 (1965).

(30) The doublets of τ 9.02 (6.6 cps) and τ 8.98 (6.6 cps) found in **20** were assigned to the 1-methyl group and two methyls in 3-isopropyl groups, respectively, by double resonance technique. Two doublets of τ 9.13 (6.4 cps) and τ 9.17 (6.4 cps) found in **21** correspond to the isopropyl group. Nonequivalence between the methyl group in isopropyl was observed in this compound as in the case of **18**.

(31) D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. France*, 1662 (1965).

(32) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

of diborane was about 80% valid, the result supported the expectations.

Recently Varech, *et al.*,[31] reported that (+)- and (−)-**13b** were obtained from (+)-**20** and (+)-**21** and that **13b** was more stable than **13a**. It was observed, however, that the mixture of **13** with the *cis*:*trans* ratio of 4:1 changed to a ratio of 3:7 on treatment with sodium methoxide. No change was found on the same treatment of the mixture (*trans*:*cis* = 7:3). It was considered that the *trans* compound (**13a**) is more stable than the *cis* compound (**13b**).[33]

The infrared spectra of **13a** and **13b** differed in the fingerprint region. The nmr spectra clearly showed a different chemical shift of the 2-methyl group, the doublet signal of which was determined by double resonance technique (Figure 2).

A quantitative study of the effect of diborane attacking the least hindered side of the double bond was undertaken on some cyclopentene derivatives.

Lithium aluminum hydride reduction of a mixture of (±)-2,5-dimethylcyclopentanones (**22a** and **22b** in a ratio of 7:3) gave three configurationally isomeric alcohols, 1-*trans*-3-dimethyl-*trans*-2-hydroxycyclopentane (**23a**), 1-*cis*-3-dimethyl-*trans*-2-hydroxycyclopentane (**23b**), and 1-*cis*-3-dimethyl-*cis*-2-hydroxycyclopentane (**23c**) in a ratio of 6:3:1, respectively. The alcohol **23a** should be derived from **22a**, whereas **22b** should give a mixture of **23b** and **23c** with **23b** predominating. This result is supported by the "product stability control" reduction of monoalkyl-substituted cyclic ketones by lithium aluminum hydride proposed by Brown and Deck.[34] Hydroboration of 1,3-dimethylcyclopentene-1 (**24**) derived from the mixture of these three alcohols gave a mixture of two alcohols (**23b** and **23a**) in a ratio of 3:1. The latter alcohol mixture gave, on oxidation with chromic acid, *cis*- and *trans*-2,5-dimethylcyclopentanones (**22b** and **22a**) in a ratio of 3:1, respectively. This result shows that the attack by diborane occurs predominantly from the least hindered side. The same procedure was undertaken on compounds listed in Table II. (See Scheme IV.)

SCHEME IV

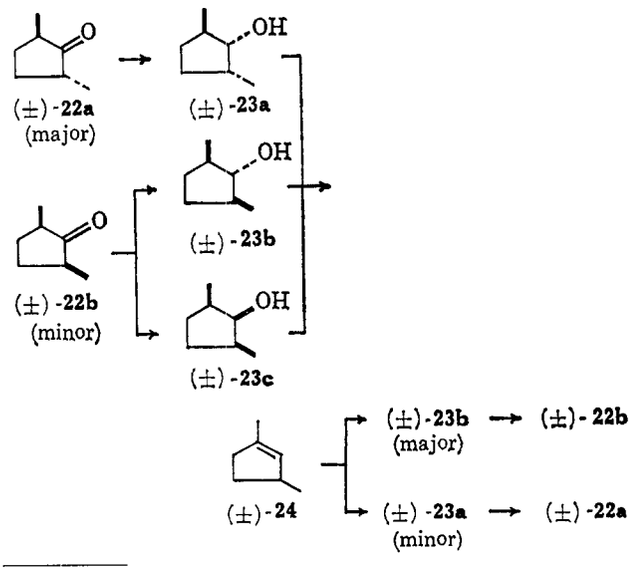
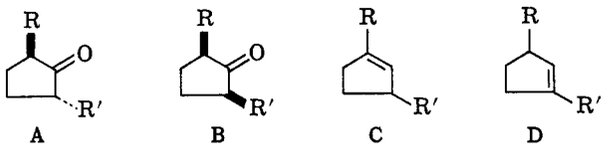


TABLE II

EFFECT OF α-ALKYL GROUP IN THE HYDROBORATION OF CYCLOPENTENES[a]

Starting materials (cyclopentenes)	Products (ketones)	Yields,[b] %	*cis*:*trans* ratios of ketones obtained by hydroboration
24	**22**	92	74:26
26	**25**	73	84:16
21	**13**	73[c]	88:12
32 + 33	**30**	85	78:22
20 + 21	**13**	81	79:21

Formulas of the compounds and the numerical designations



	A	B	C	D
R = R′ = methyl	**22a**	**22b**	**24** =	**24**
R = R′ = ethyl	**25a**	**25b**	**26** =	**26**
R = methyl, R′ = ethyl	**30a**	**30b**	**32**	**33**
R = methyl, R′ = isopropyl	**13a**	**13b**	**21**	**20**

[a] All compounds in this table are of (±) form. [b] The yields are based on the corresponding alcohols. [c] Calculated from gas chromatographic data.

Experimental Section

(+)-1,*trans*-2-Dimethyl-*trans*-3-isopropylcyclopentane (1b) from (+)-Isoiridomyrmecin (3).—Reduction of 1.45 g of crystalline (+)-isoiridomyrmecin (**3**) prepared according to the method of Robinson, *et al.*,[13] was carried out with 0.84 g of lithium aluminum hydride in 100 ml of ether by heating under reflux for 5 hr. The reaction mixture was worked up in the usual way and (−)-iridodiol (**4**) was obtained in quantitative yield, mp 80.5–81°, $[\alpha]^{20}D$ −7.8°. A solution of 1.45 g of the diol (**4**) in 10 ml of pyridine was added dropwise to a vigorously stirred solution of 3.9 g of *p*-toluenesulfonyl chloride in 10 ml of pyridine at 0° After being kept at 0° for 2.5 hr and an additional 2.5 hr at room temperature, the mixture was poured into ice–water and the crude ditosylate was isolated in 94% yield by extraction with ether followed by washing with dilute hydrochloric acid and water. A mixture of 3.80 g of dried ditosylate, 50 ml of ether, and 15 ml of benzene was added to a stirred suspension of 900 mg of lithium aluminum hydride in 40 ml of ether. After heating at reflux temperature for 13 hr and standing overnight, the mixture was worked up in the usual way. On removal of the solvent, 0.79 g (71% yield based on the crude ditosylate) of (+)-1,2-dimethyl-3-isopropylcyclopentane was obtained, bp 155–160°, $n^{25}D$ 1.4339, $[\alpha]^{20}D$ +12.8°. The infrared spectrum showed no typical functional groups. The gas chromatographic behavior is shown in Table I.

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.42; H, 14.09.

Isomer Mixture of (+)-1,2-Dimethyl-3-isopropylcyclopentanes (1a, 1b, and 1c) from Crude (+)-Iridodial (5 with 6 and 7) by Lithium Aluminum Hydride Reduction.—An isomer mixture of iridodial was obtained according to Robinson, *et al.*,[13] bp 86–88° (1 mm), $[\alpha]^{18}D$ +6.20°, infrared typical bands (liquid film): 2730 and 1725 cm^{-1}. The reduction with lithium aluminum hydride followed by tosylation and hydrogenolysis as described above gave (+)-1,2-dimethyl-3-isopropylcyclopentanes in 57% yield (from the crude ditosylate), bp 90–94° (100 mm), 153–155°, $[\alpha]^{20}D$ +3.6°, $n^{20}D$ 1.4358.

Huang-Minlon Reduction of Crude (+)-Iridodial (5 with 6 and 7).—A mixture of 4.0 g of the crude (+)-iridodial (**5** with **6** and **7**).[13] 9.8 g of potassium hydroxide, 7.4 ml of 85% hydrazine hydrate, and 18 ml of triethylene glycol was heated for 1 hr

(33) It was also demonstrated by gas chromatography that the *cis* isomer **13b** isomerizes very slowly to the *trans* isomer **13a** at room temperature. However, no isomerization in the gas chromatographic column during the measurement was observed.

(34) H. C. Brown and H. R. Deck, *J. Am. Chem. Soc.*, **87**, 5620 (1965).

at 130–135°. Then the reaction mixture was distilled, when the temperature inside the flask was increased to 210–220° and maintained at that level until the distillation ceased. The distillate was extracted with ether and the extract was washed with water and dried. On removal of ether, 0.42 g (13%) of 1,2-dimethyl-3-isopropylcyclopentanes was obtained, bp 90–92° (100 mm), $n^{20}D$ 1.4346. The components were separated by preparative gas chromatography (Table I). Analyses agreed with the calculated values.

(±)-1,*cis*-2-Dimethyl-*trans*-3-isopropylcyclopentane (1c) from (±)-Dihydrophotocitral-A (9).—Reduction of 4.8 g of (±)-dihydrophotocitral-A (9) prepared according to the method of Cookson, *et al.*,[16] was carried out with 1.2 g of lithium aluminum hydride in 40 ml of ether by heating under reflux for 3 hr. The reaction mixture was treated in the usual way and 3.9 g (81%) of (±)-1-methyl-*cis*-2-hydroxymethyl-*trans*-3-isopropylcyclopentane (10) was obtained, bp 139–142° (57 mm), $n^{20}D$ 14633, infrared typical bands (liquid film): 3330, 1030 cm^{-1}.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.87; H, 13.17.

Tosylation and hydrogenolysis of 3.3 g of 10 was worked up as described above. There was obtained 2.2 g (74% from the crude tosylate) of 1,2-dimethyl-3-isopropylcyclopentane, bp 159–160°, $n^{20}D$ 1.4374. The isomers were separated by gas chromatography (Table I).

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.35; H, 14.26.

2-Methyl-5-carbethoxy-5-isopropylcyclopentanone (12).—To 23.5 g of potassium dispersed in 400 ml of anhydrous toluene was added 102 g of 2-methyl-5-carbethoxycyclopentanone (11)[19] in the course of 1–2 hr, the temperature being kept below 45°. After an additional stirring for 1 hr at room temperature, 127 g of isopropyl iodide was added and heated to reflux for about 20 hr until the reaction mixture became a mobile solution. After addition of 30 ml of *t*-butyl alcohol, the reaction mixture was poured into ice-water and the organic layer was washed with water, 7% sodium carbonate solution, and water. The mixture was dried over anhydrous sodium sulfate and, after removing toluene, distilled to afford 83.1 g (65%) of 2-methyl-5-carbethoxy-5-isopropylcyclopentanone (12), bp 138–144° (25 mm), $n^{22}D$ 1.4493 [lit.[35] bp 123–124° (10 mm)], infrared typical bands (liquid film): 1760, 1735, 1390 and 1375 cm^{-1}.

2-Methyl-5-isopropylcyclopentanone (Dihydrocamphorone) (13).—A mixture of 200 ml of water, 100 ml of concentrated sulfuric acid, and 71.4 g of 2-methyl-5-carbethoxy-5-isopropylcyclopentanone (12) was heated under reflux for about 26 hr with vigorous stirring. By extraction with ether, 31.5 g (66.7%) of 2-methyl-5-isopropylcyclopentanone (13)[31,36–39] was obtained, bp 84° (31 mm) [reported bp 179.7° (*cis*-13),[36] 179.8° (*trans*-13),[36] 181–186° (740 mm)[37]], $n^{20}D$ 1.4370 [reported $n^{24.5}D$ 1.43821 (*cis*-13),[46] $n^{24.5}D$ 1.43801 (*trans*-13)[36]], infrared typical bands (liquid film): 1745, 1385 and 1370 cm^{-1}.

Semicarbazone, mp 194–195° (recrystallized from absolute ethanol) [reported mp 198° (*cis*-13),[36] 209° (*trans*-13),[36] 198–200° (*trans*-13),[38] 196°[39]].

2,4-Dinitrophenylhydrazone, mp 176–176.5° (absolute ethanol) (reported mp 170–171.5°,[36] 176–178° (*trans*-13)[38]).

Gas chromatography of 13 showed two peaks in a ratio of 7:3 (PEG-6000, 3 m × 3 mm; 110°; He, 30 ml/min). These compounds appear to be an equilibrium mixture of *trans* and *cis* isomers with *trans* isomer predominating.

trans isomer (13a) and *cis* isomer (13b) were isolated by preparative gas chromatography (triscyanoethoxypropane; 88°; He, 70 ml/min).

Nmr absorption of 13a: τ 9.19 (doublet, J = 6.5 cps) and τ 9.03 (doublet, J = 6.5 cps) (methyl groups of the isopropyl group); τ 8.92 (doublet, J = 6.4 cps) (2-methyl group).

Nmr absorption of 13b: τ 9.20 (doublet, J = 6.6 cps) and τ 9.02 (doublet, J = 6.5 cps) (methyl groups of the isopropyl group); τ 8.97 (doublet, J = 6.8 cps) (2-methyl group).

1-Methyl-2-methylene-3-isopropylcyclopentane (14).—To a solution of methylenetriphenylphosphorane[21] prepared from 6.0 g of sodium hydride, 40.4 g of methyltriphenylphosphonium iodide and 125 ml of 1,2-dimethoxyethane, 10.2 g of 2-methyl-5-isopropylcyclopentanone (13) was added at room temperature under nitrogen. After stirring for one-half hour at room temperature and an additional 3.5 hr at 60°, about 100 ml of the solvent was distilled off and, after addition of water, the product was extracted with petroleum ether (bp 40–70°). The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated. There was obtained 7.1 g (71%) of 1-methyl-2-methylene-3-isopropylcyclopentane (14), bp 84–86° (78 mm), $n^{25.5}D$ 1.4456, infrared typical bands (liquid film): 3060, 1650, 1385, 1370, and 880 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.67; H, 13.08.

Meinwald[37] obtained the same olefin by the other method in an analytically impure state.

When the solution of methylenetriphenylphosphorane in dimethylsulfoxide was prepared according to the directions of Corey, *et al.*,[22] the yield of 14 was 77%.

The gas chromatogram of 14 ($AgNO_3$–$C_6H_5CH_2CN$ column, 3 m × 4 mm; 75°; He, 35 ml/min) showed two peaks with retention times of 29.8 min and 30.9 min in a ratio of 74:26, respectively.

1,2-Dimethyl-3-isopropylcyclopentane from 1-Methyl-2-methylene-3-isopropylcyclopentane (14). (i) By Hydroboration.—To a solution of 2.5 g of 1-methyl-2-methylene-3-isopropylcyclopentane (14) in 20 ml of dried tetrahydrofuran, 8 ml of diborane solution of tetrahydrofuran (1.5 mole/l) was added at 0°, and the solution was stirred for 2 hr at room temperature. After adding 4.1 ml of 3 *N* aqueous sodium hydroxide solution and 4.1 ml of 30% hydrogen peroxide, the reaction mixture was heated under reflux for 1 hr and extracted with ether, washed with saturated sodium chloride solution, water, and dried over anhydrous sodium sulfate. There was obtained 2.1 g (74%) of 1-methyl-2-hydroxymethyl-3-isopropylcyclopentane (15), bp 108–110° (25 mm), $n^{20}D$ 1.4624, infrared typical bands (liquid film): 3330, 1030 cm^{-1}.

The gas chromatogram of this alcohol (15) showed a peak with a shoulder, whereas the alcohol (10) obtained from 9 showed only one peak (PEG-6000, 3 m × 3 mm; 165°; He, 50 ml/min).

Tosylation and hydrogenolysis of 2.0 g of 15 was worked up as mentioned above. There was obtained 1.2 g (66% based on the crude tosylate) of 1,2-dimethyl-3-isopropylcyclopentane, bp 155–160°, $n^{20}D$ 1.4362. Analyses gave correct values.

(ii) **By Diimide Reduction.**—A solution of 6.56 g of 14, 255 ml of 80% hydrazine hydrate and 1.0 g of cupric acetate dissolved in 150 ml of ethanol was vigorously stirred under passing through an air stream until the exothermic reaction was brought to completion (about 50 hr). The reaction mixture was extracted with *n*-hexane after addition of 250 ml of water and the extract was washed with water, dilute hydrochloric acid, saturated sodium hydrogen carbonate, 0.1 *N* sodium thiosulfate, and water. After drying over anhydrous sodium sulfate, removal of the solvent afforded 2.1 g (32%) of 1,2-dimethyl-3-isopropylcyclopentane, bp 95–100° (100 mm), $n^{20}D$ 1.4359. Though the infrared spectrum indicated a small amount of the starting material, the elemental analyses agreed with the calculated values for $C_{10}H_{20}$.

(iii) **By Hydrogenation over Palladium-Charcoal.**—A solution of 4.01 g of 14 in 40 ml of absolute ethanol was hydrogenated over 5% palladium-charcoal catalyst at room temperature under ordinary pressure. The calculated amount of hydrogen was absorbed during 3 hr. The reaction mixture was separated from the catalyst, and, on removal of the solvent, 3.41 g (85.3%) of 1,2-dimethyl-3-isopropylcyclopentane was obtained, bp 83–85° (80 mm) and 158–160°, $n^{20}D$ 1.4318. Analyses awarded correct values.

(iv) **By Hydrogenation over Raney nickel.**—Catalytic hydrogenation of 4.15 g of 14 over Raney nickel of W-4 type was carried out as in the foregoing experiment. No more than 51–54% of the calculated amount of hydrogen was absorbed under this reaction condition. There was obtained 3.76 g of a product, bp 86–88° (82 mm) and 157–159°, $n^{20}D$ 1.4420. Though infrared spectrum showed no typical functional groups, the gas chromatogram ($AgNO_3$-$C_6H_5CH_2CN$, 3 m × 4 mm; 75°; He, 35 ml/min) of this compound showed one extra peak (retention time: 23.4 min, 25% of the total amount) in addition to the four peaks, a, b, c, and d, corresponding to the four stereoisomers of 1. This extra peak was identified as that of 18 (see below).

(35) L. Bouveault and R. Locquin, *Compt. Rend.*, **146**, 82, 138 (1908); *Bull. Soc. Chim. France*, (4) **3**, 441 (1908).

(36) R. Calas, *Compt. Rend.*, **206**, 59 (1938); *Bull. Soc. Chim. France*, (5) **6**, 1493 (1939).

(37) J. Meinwald, *J. Am. Chem. Soc.*, **76**, 4571 (1954).

(38) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963).

(39) J. Golé, *Bull. Soc. Chim. France*, 894 (1949).

Dehydration of 1,2-Dimethyl-2-hydroxy-3-isopropylcyclopentane.—A 11.7-g sample of 2-methyl-5-isopropylcyclopentanone (**13**) was allowed to react with methylmagnesium iodide prepared from 2.7 g of magnesium and 15.9 g of methyl iodide to give 9.9 g of crude 1,2-dimethyl-2-hydroxy-3-isopropylcyclopentane (**16**). The crude product contaminated with the starting material was heated with a few drops of concentrated sulfuric acid and the reaction mixture was distilled out. There was obtained 6.4 g (73% yield calculated from the crude alcohol) of a product, bp 150–155°, n^{25}D 1.4472. 1,2-Dimethyl-3-isopropylcyclopentene-2 (**17**) and 1,2-dimethyl-3-isopropylcyclopentene-1 (**18**) were isolated from this olefinic product by preparative gas chromatography ("Apiezon" Grease L; 3 m × 4 mm; 145°; He, 34 ml/min): **17**, n^{20}D 1.4468; **18**, n^{20}D 1.4499 (lit.[40] bp 156°, n^{23}D 1.4490).

Nmr absorption of **17**: τ 9.04 (9H, doublet, J = 6.7 cps) and τ 8.43 (3H, multiplet). Nmr absorption of **18**: τ 9.36 (3H, doublet, J = 6.7 cps); τ 9.12 (3H, doublet, J = 6.7 cps) and τ 8.43 (6H, multiplet).

2-Methyl-5-isopropylcyclopentanol (19) from 2-Methyl-5-isopropylcyclopentanone (13).—To a suspension of 5.44 g of lithium aluminum hydride in 200 ml of ether, 40.0 g of 2-methyl-5-isopropylcyclopentanone (**13**) in 50 ml of ether was added dropwise during 30 min. After stirring under reflux for 5 hr, the reaction mixture was treated with 10% sulfuric acid, extracted with ether and washed with saturated sodium chloride solution and water. On drying over anhydrous sodium sulfate, there was obtained 38.1 g (94.1%) of 2-methyl-5-isopropylcyclopentanol (**19**), bp 87–88° (20 mm) [lit. bp 185–192°,[41] bp 82.3° (15 mm),[36] bp 80° (20 mm)[39]], n^{25}D 1.4501 (reported n^{20}D 1.4604,[41] n^{23}D 1.4496[36]), infrared typical bands (liquid film): 3350, 1040, 1020 cm^{-1}. Gas chromatogram of **19** ($AgNO_3$–PEG, 3m × 4 mm; 105°; He, 50 ml/min) showed only three peaks with retention times of 21.5, 27.4, and 29.0 min.

1-Methyl-3-isopropylcyclopentene-2 (20) and 1-Methyl-3-isopropylcyclopentene-1 (21).—Through a mixture of crude tosylate of **19**, prepared by the usual pyridine procedure from 9.0 g of **19** and 12.6 g of *p*-toluenesulfonyl chloride, 10.1 g of potassium *t*-butoxide, and 80 ml of dimethyl sulfoxide, a constant stream of dry nitrogen was bubbled under reduced pressure of 130 mm. The reaction flask was slowly heated to sweep the olefins which were collected into a trap immersed in an ice–salt mixture until the generation of the olefins was brought to completion (about 2 hr). The crude product was diluted with ether, washed with water, and dried over sodium sulfate. Removal of the solvent afforded 2.0 g (36% based on the crude tosylate) of a mixture of 1-methyl-3-isopropylcyclopentene-2 (**20**) and 1-methyl-3-isopropylcyclopentene-2 (**21**), bp 135–140°, n^{20}D 1.4390. Each of these olefins was separated by preparative gas chromatography ("High Vacuum Silicone Grease," 4.5 m × 4 mm; 113°; He, 180 ml/min).

20: n^{20}D 1.4358, infrared typical bands (liquid film): 3030, 1640, and 840 cm^{-1}. Nmr absorption: see footnote 30.

21: n^{20}D 1.4378 (reported bp 138–139°,[42] n^{18}D 1.44354[42]), infrared typical bands (liquid film): 3030, 1650, and 835 cm^{-1}. Nmr absorption: see footnote 30.

2-Methyl-*cis*-5-isopropylcyclopentanone (13b).—To a solution of 0.90 g of a mixture of 1-methyl-3-isopropylcyclopentene-2 (**20**) and 1-methyl-3-isopropylcyclopentene-1 (**21**) in 20 ml of tetrahydrofuran, 4.3 ml of diborane solution (1.85 mole/l) was added at 0° and the reaction mixture was stirred for 2 hr at room temperature. After adding 3.5 ml of 3 *N* sodium hydroxide and 3.5 ml of 30% hydrogen peroxide, the reaction mixture was heated under reflux, cooled, extracted with ether, washed with water, and dried. Removal of solvent gave 0.95 g (91%) of 2-methyl-5-isopropylcyclopentanol, bp 86–89° (20 mm), n^{20}D 1.4470, which showed a broad peak with a retention time of 28.7 min on gas chromatography (PEG–$AgNO_3$, 3 m × 4 mm; 105°; He, 50 ml/min).

Chromic acid oxidation of 0.68 g of this alcohol was undertaken according to Brown[32] and there was obtained 0.54 g (81%) of a *cis* predominant 2-methyl-5-isopropylcyclopentanone preparation (79% **13b**), bp 74–75° (20 mm), n^{20}D 1.4380.

Equilibrium of *trans*- and *cis*-2-Methyl-5-isopropylcyclopentanones (13a and 13b).—To a solution of 150 mg of sodium methoxide in 1.5 ml of methanol, 256 mg of the *cis* predominant isomer of **13** (79% **13b**) was added. The mixture was allowed to stand for 24 hr at room temperature under nitrogen atmosphere. It was then diluted with water, extracted with ether, washed with water, and dried over sodium sulfate. On gas chromatography (PEG–$AgNO_3$, 3 m × 4 mm; 86°; He, 65 ml/min), the ethereal solution showed two peaks in a ratio of 74:26. The same procedure as mentioned above was carried out on the *trans* predominant isomer of **13** (70% **13a**) obtained from **12** by saponification and decarboxylation with dilute sulfuric acid. On gas chromatography, this product showed two peaks in a ratio of 75:25 with no marked change in the ratio.

2,5-Dialkyl-5-carbethoxycyclopentanones.—Preparation of these keto esters was carried out in the same manner as that of **12**. Instead of potassium metal, sodium metal was used. Physical constants and yields are listed in Table III.

TABLE III

DIALKYLCYCLOPENTANE DERIVATIVES[a]

	R	R′	Yield, %	Bp, °C (mm)	n^{20}D	Ref
			2,5-Dialkyl-5-carbethoxycyclopentanones			
27	Me	Me	75	106–110 (14)	1.4450	*b*
28	Et	Et	88	131–132 (14)	1.4490	*c*
29	Et	Me	74	129–130 (27)	1.4447	...
			2,5-Dialkylcyclopentanones			
22	Me	Me	70	141–145 (760)	1.4280	*d*
25	Et	Et	72	182–184 (760)	1.4394	*c*
30	Et	Me	83	164–166 (760)	1.4345	*e*
			2,5-Dialkylcyclopentanols			
23	Me	Me	93	93–95 (83)	1.4488	*f*
34	Et	Et	90	128–129 (105)	1.4532	...
31	Et	Me	80	112 (97)	1.4510	...
			1,3-Dialkylcyclopentenes			
24	Me	Me	42	91–93 (760)	1.4276	*f*
26	Et	Et	50	148–150 (760)	1.4432	*g*
32	Me	Et	40	121–123 (760)	1.4381	...
33	Et	Me				

[a] All compounds in this table are of (±) form. [b] A. Haller and R. Cornubert, *Compt. Rend.*, **179**, 315 (1924). [c] I. Robert, D. Haworth, J. McKenna, and N. Singh, *J. Chem. Soc.*, 831 (1949). [d] A. Butenandt and L. A. Suranyi, *Ber.*, **75B**, 597 (1942). [e] R. Cornubert and C. Barrel, *Bull. Soc. Chim. France*, (4) **47**, 307 (1930). [f] G. Chavanne, *Chem. Zentr.*, **II**, 1845 (1926). [g] G. W. Barber and J. English, Jr., *J. Am. Chem. Soc.*, **73**, 746 (1951).

2,5-Dialkylcyclopentanones.—The same procedure as in the preparation of **13** was undertaken. Physical constants and yields are shown in Table III.

2,5-Dialkylcyclopentanols.—The same treatment as mentioned in the preparation of **19** gave 2,5-dialkylcyclopentanol (see Table III).

On gas chromatography (PEG–6000, 4.5 m × 6 mm; 123°; He, 150 ml/min) **23a**, **23b**, and **23c** had retention times of 42.6, 40.3, and 34.1 min, respectively.

1,3-Dialkylcyclopentenes.—Tosylation followed by elimination of 2,5-dialkylcyclopentanol was undertaken in the same manner as in the preparation of **20** and **21**. 1,3-Dimethylcyclopentene (**24**) was prepared according to the method of Brown and Zweifel.[43]

2-Alkyl-*cis*-5-alkylcyclopentanones.—Hydroboration followed by chromic acid oxidation of 1,3-dialkylcyclopentenes was carried out as mentioned in the preparation of **13b**. The gas chromatographic behavior of **22**, **25**, and **30** is listed in Table II.

Essential Oil from Flowers of *Osmanthus fragrans*.—According to Isiguro *et al.*[1] extraction of 26.7 kg of flowers[44] collected on the campus of Kyôto University in October 1965 was carried out with 40 l. of petroleum ether (bp 40–60°) carefully fractionated through a 50-cm. Vigreux column.

A fraction of bp 40–60° (80 mm) weighing 3.0 g and 1.04 g of a fraction of bp 84–100° (22 mm) were obtained. In both

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(41) F. W. Semmler and W. Schoeller, *Ber.*, **37B**, 237 (1904).

(42) R. Calas, *Bull. Soc. Chim. France*, 1505 (1939).

(43) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 2544 (1961).

(44) A crop of about 400 g of the flowers was obtained from a big tree, a flower weighing about 10 mg.

fractions no peak correpsonding to 1,2-dimethyl-3-isopropyl cyclopentanes was detected by gas chromatography.[45]

High-Boiling Hydrocarbons from Petroleum Ether.—Commercial petroleum ether (20 kg) of bp 40–60° was fractionated by a 50-cm Vigreux column and 1.58 g of a fraction, bp 158–160°, was obtained. On preparative gas chromatography, a peak corresponding to 1,2-dimethyl-3-isopropylcyclopentane was isolated, $n^{20}D$ 1.4375. The infrared spectrum of this peak was similar to 1. In the fingerprint region, however, the infrared spectrum was definitely different from those of **1a** through **1d**.

(45) In the essential oil of the flowers there were found and identified: γ-decano lactone, α- and β-ionones, *trans*- and *cis*-2,6,6-trimethyl-2-vinyl-5-hydroxytetrahydropyranes, linalool, *trans*- and *cis*-linalool oxides, nonanal, and leaf alcohol (*cis*-γ-hexenol). The details will be published elsewhere.

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Stereochemistry and the Mechanism of Catalytic Hydrogenation of Cycloalkenes. VII. Interaction Mechanisms Which Control the Ratio of Stereoisomers[1]

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The ratio of the *cis*- and *trans*-dialkylcyclohexanes obtained on hydrogenating a series of substituted methylenecyclohexanes and disubstituted cyclohexanes, over reduced platinum oxide, is a function of the hydrogen pressure. The results and further argument support previous conclusions that the limiting ratios are characteristic of different product-controlling reactions: the formation of 1,2-diadsorbed alkane at high pressures of hydrogen and the formation of the "half-hydrogenated state" at low pressure. Both inter- and intramolecular interaction mechanisms which may determine the proportion of saturated isomers are considered.

Explanations of the stereochemistry of catalytic hydrogenation have been dominated by ideas concerning the manner in which a given unsaturated compound may best be fitted onto a planar surface from which hydrogen is abstracted;[2] *cis* addition is a consequence. However, detailed studies of the reactions which occur when hydrogen (or deuterium) and unsaturated hydrocarbons interact upon metallic surfaces demonstrate that the net addition is the result of a complex system of reactions.[3] Accordingly, we have sought to interpret our stereochemical studies of the hydrogenation of cycloalkenes[4-8] in terms of the mechanistic proposals of Horiuti and Polanyi[9] and concluded that, on certain platinum catalysts, compounds such as 2,3-dimethylcyclohexene or alkyl-substituted methylenecyclohexanes give limiting ratios of the saturated stereoisomers at high hydrogen pressures which are characteristic of the formation of the 1,2-diadsorbed alkane,[10] while at low pressures the limiting ratio characterizes the formation of the "half-hydrogenated state."[9]

The present study provides additional data to support these views and the factors which determine the particular ratios of isomers are examined further.

Results

The results of this and some previous studies are shown in Tables I and II. Where comparisons are possible, the agreement with results obtained at 1 atm by Sauvage, Baker, and Hussey is satisfactory.[11] Clearly, the fraction of the *cis* isomer which is obtained is not only a function of the structure of the substrate but also of the pressure. However, the effect of changing the pressure differs for the various substances studied not only in magnitude but also in direction.

The alkyl-substituted methylenecyclohexanes yield mainly the axial–equatorial stereoisomer and the proportion, relative to its epimer, drops as the pressure of hydrogen is raised, Table I and Figure 1.

TABLE I

HYDROGENATION OF ALKYL-SUBSTITUTED METHYLENECYCLOHEXANES. VARIATIONS IN THE MOLE PER CENT OF THE *cis* ISOMER WITH THE PRESSURE OF HYDROGEN

	Pressure of hydrogen (atm)					
Substrate	0.25	0.50	1.0	3.0	50	100–200
2-Methyl[a]	70	70	70	69	69	68
3-Methyl	25	25	28	35[b]	43	46
4-Methyl	78	76	73[c]	70[b]	66	67
4-*t*-Butyl[d]	87	86	84	76	62	61

[a] Reference 4. [b] Our earlier report [S. Siegel and M. Dunkel, *Advan. Catalysis*, **9**, 15 (1957)] is in error. [c] Sauvage, Baker, and Hussey (ref 11) report that at 1 atm 4-methylmethylenecyclohexane gives 74% *cis*. [d] Reference 6.

The endocyclic alkenes show less regularity in their behavior with respect to both the principal stereoisomer formed at low hydrogen pressures and the direction of change, if any, when the pressure is raised, Table II.

Results that are recorded for pressures of 1 atm or less are obtained from experiments which were carried to less than 50% completion while those data obtained at higher pressures are for complete reductions. For certain of the substrates, the proportion of saturated stereoisomers may depend upon the stage at which the

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