

$$\begin{aligned} \text{Rate} &= k_3\text{III} \\ d\text{III}/dt = 0 &= -k_3\text{III} - k_{-2}\text{III} + k_2\text{II} (a_{\text{HOH}})^3 \\ &\quad \text{III} = \frac{k_2}{k_{-2} + k_3} [\text{II}(a_{\text{HOH}})^3] \quad (1) \\ \text{If } k_{-2} \gg k_2, \text{ III} &= (k_2/k_{-2})\text{II} (a_{\text{HOH}})^3 \\ d\text{II}/dt &= k_1\text{I}(a_{\text{HOH}}) - k_{-2}\text{III} + k_2\text{II}(a_{\text{HOH}})^3 - k_{-1}\text{II} \\ &\quad \text{and II} = (k/k_{-1})\text{I} (a_{\text{HOH}}) \quad (2) \\ \text{rate} &= k_1\text{III} = k, k_2k_1/k_{-1} (a_{\text{HOH}})^4\text{I} \\ &= k'\text{I}(a_{\text{HOH}})^4 \quad (3) \end{aligned}$$

One further deduction may be made from the mechanism given. If the halogen-carbon bond is broken after the O-H bond is broken, electronegative halogen should weaken this O-H<sup>+</sup> and hence increase the reaction rate. This argument is analogous to the greater acid strength of chloroacetic acid as compared to acetic acid. Further, the more electronegative halogen, Cl, should have a greater effect than I, as is observed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

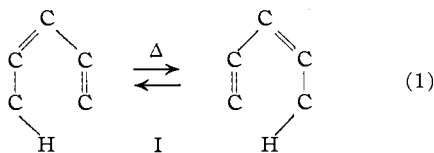
## Thermal Rearrangement of 1,3-Dienes

BY JOSEPH WOLINSKY, BRYAN CHOLLAR<sup>1a</sup> AND M. D. BAIRD<sup>1b</sup>

RECEIVED JANUARY 18, 1962

It is demonstrated that 1,3-dienes, in which a vinyl and alkyl group are *cis*, undergo a reversible thermal isomerization involving the over-all 1,5-transfer of a hydrogen with concomitant migration of both carbon-carbon double bonds. At 350–450°, depending on the nature of the dienes on hand, an equilibrium mixture is approached in which the more thermodynamically stable isomer predominates. Dienes in which a vinyl group and alkyl group are *trans* appear to be thermally stable. A means for distinguishing between isomeric *cis*- and *trans*-1,3-dienes is suggested on the basis of this difference in thermal behavior. In this manner, geometric configurations have been assigned to  $\alpha$ - and  $\beta$ -ocimene.

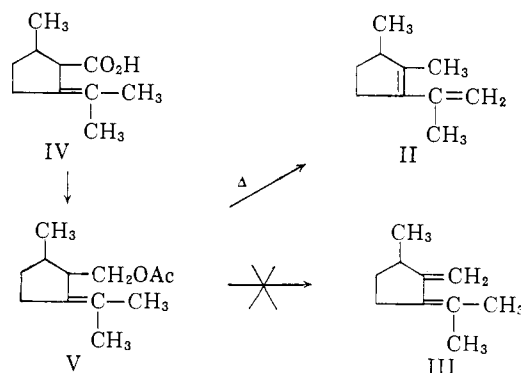
Thermal rearrangements of the type described in eq. 1 have occasionally been observed. It is well known that ocimene on being heated above 200°



is transformed into alloöcimene.<sup>2,3</sup> Pines<sup>4,5</sup> has shown that the shifting of double bonds in a number of substituted 1,3-cyclohexadiene derivatives occurs at 300–400°. Furthermore, it has been recognized that calciferol (Vit. D) is produced by the thermal isomerization of precalciferol.<sup>6</sup> However, the generality of such thermal isomerizations has not, hereto, been recognized.<sup>7,8</sup> In this communication the generality of the reversible thermal rearrangement of 1,3-dienes according to eq. 1 is demonstrated. Such transformations have considerable synthetic and theoretical application and, in addition, provide an important diagnostic method for distinguishing between isomeric *cis*- and *trans*-dienes.

This investigation was prompted by the observation that 2-isopropenyl-1,5-dimethyl-1-cyclopentene

(II), rather than the expected 3-isopropylidene-2-methylene-1-methylcyclopentane (III), was produced by the pyrolysis of 2-acetoxymethyl-3-isopropylidene-1-methylcyclopentane (V). Acetate V was prepared from pulegone *via* the pulegone acids (IV) as described in the Experimental section.



The constitution of diene II was indicated by a peak at 11.28  $\mu$  which is characteristic of a terminal methylene group, by absorption at 237 and 243  $m\mu$  ( $\epsilon$  10,130 and 9,860) in the ultraviolet, by its n.m.r. spectrum, determined at 60 mc. and related to tetramethylsilane, which exhibited signals at  $-\dot{5}7$  and  $-64$  c.p.s. (one methyl group spin coupled with an adjacent proton),  $-100.6$  and  $-107.6$  c.p.s. (two methyl groups attached to unsaturated carbon atoms), and  $-280.8$  and  $-289.6$  c.p.s. (two hydrogens of a terminal methylene group), and by reductive ozonolysis which afforded formaldehyde and only a trace of acetone.

The assumption that diene III had formed initially during the pyrolysis of acetate V, but then rearranged to the observed product, diene II, appeared well founded. In order to verify this hypothesis, diene III was prepared from the amine VI by employing the mild elimination procedure

(1) (a) Participant in the National Science Foundation Undergraduate Research Program, 1960. (b) 1961.

(2) C. J. Enklaar, *Rec. trav. chim.*, **26**, 171 (1907).

(3) J. E. Hawkins and H. G. Hunt, *J. Am. Chem. Soc.*, **73**, 5379 (1951).

(4) H. Pines and R. H. Kozlowski, *ibid.*, **78**, 3776 (1956).

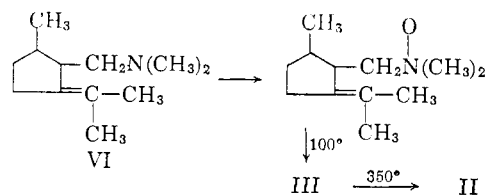
(5) H. Pines and C. T. Chen, *ibid.*, **81**, 928 (1959).

(6) L. Velluz, G. Amiard and B. Goffinet, *Bull. soc. chim. France*, 1341 (1955).

(7) K. Alder and M. Schumacher, *Fort. Chem. Org. Naturf.*, **10**, 8 (1953), have postulated a general reaction in the sense of eq. 1 but their basis for this postulate can hardly be regarded as compelling.

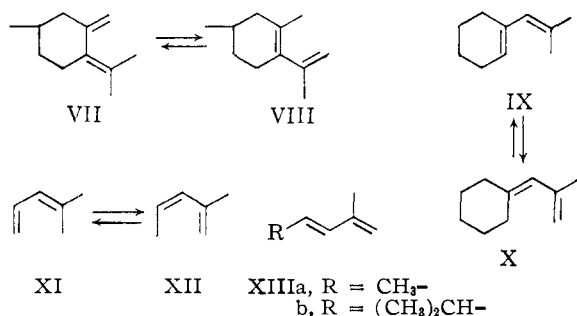
(8) Thermal isomerization of dienes should be distinguished from acid-catalyzed processes which, for example, are known for the abietic acids (N. M. Joye and R. V. Lawrence, *J. Org. Chem.*, **26**, 1024 (1961)) and from rearrangements observed during vigorous Diels-Alder condensations (I. N. Nazarov and M. V. Mavrov, *Proc. Acad. Sci. U.S.S.R.*, **120**, 325 (1958)).

developed by Cope.<sup>9</sup> The structure of III was indicated by its n.m.r., infrared and ultraviolet spectra (see Experimental) and by reductive ozonolysis which gave acetone and formaldehyde.



The thermal behavior of diene III was examined using the injector of a Gas Chromatograph as a pyrolysis chamber. The diene was found to be stable using an injection temperature below 200° and a Uconpolar or Carbowax 20M column maintained, in all instances, at 90–110°; however, at an injection temperature of 260° a 15% conversion to diene II was noted, while at 360° the transformation to II, free of any side reaction, was essentially quantitative.<sup>10</sup> Thus a sample of diene III could be injected at 360° and diene II collected.

Having made this interesting observation we decided to examine the scope and mechanism of this isomerization by studying the thermal behavior of the systems outlined below.



4-Isopropylidene-3-methylene-1-methylcyclohexane (VII) and 3-isopropenyl-1,5-dimethyl-1-cyclohexene (VIII) were prepared by the reaction of pulegone with triphenylmethylene phosphorane and methylmagnesium iodide, respectively.<sup>11</sup> 1-(1-Cyclohexenyl)-2-methyl-1-propene (IX) was obtained by prolonged heating of excess methylmagnesium iodide with cyclohexenylacetic acid. 3-Cyclohexylidene-2-methyl-1-propene (X) and *trans*-2,5-dimethyl-1,3-hexadiene (XIIIb) were synthesized by the heating the phosphorane produced from triphenylmethylphosphonium chloride with cyclohexanone and isobutyraldehyde, respectively. The infrared, ultraviolet and n.m.r. spectra of dienes IX, X and XIIIb were consistent with their structural assignments.

Evaluation of the results presented in Table I clearly demonstrate that 1,3-dienes, in which a vinyl group and alkyl group are *cis*, undergo a reversible thermal isomerization involving an over-

(9) A. C. Cope, D. C. McLean and N. A. Nelson, *J. Am. Chem. Soc.*, **77**, 1630 (1955).

(10) The fact that the rearrangement is dependent only on the injector temperature demonstrates this is a thermal process and cannot involve an acid- or base-catalyzed isomerization brought about by the column packing.

(11) J. Wolinsky and D. Chan, unpublished work.

all 1,5-hydrogen transfer with concomitant migration of two carbon-carbon double bonds. At 350–450°, depending upon the nature of the dienes on hand, an equilibrium mixture is approached in which the more thermodynamically stable isomer predominates. *trans*-1,3-Dienes are stable under these conditions; thus, *trans*-2-methyl-1,3-pentadiene (XIIIa) and *trans*-2,5-dimethyl-1,3-hexadiene (XIIIb) give rise to only trace amounts, <1.0%, of rearrangement products at 450°.

TABLE I

THERMAL REARRANGEMENT OF 1,3-DIENES<sup>a</sup>

Starting diene	Temperature of injector, °C.	Products, %	
III	260	85.5 (III)	14.5 (II)
	310	40	60
	360	5	95
VII	260	97.7 (VII)	2.3 (VIII)
	360	66.8	33.2
	450	20.7	79.3
VIII	360	0 (VII)	100.0 (VIII)
	400	3.8	96.2
	450	6.3	93.7
IX	360	99.0 (IX)	1.0 (X)
	450	93.8	6.2
X	260	35.7 (IX)	64.3 (X)
	360	94.3	5.7
	400	95.5	4.5
XI	320	95 (XI)	2.4 (XII) 2.4 (XIIIa)
	400	80	14 5.8
	450	78	16.4 5.5
XII	450	74 (XI)	21 (XII) 4.4 (XIIIa)
XIIIa	450	99	XIIIa
XIIIb	450	99	XIIIb

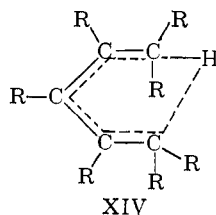
<sup>a</sup> Each pure diene, 1 to 2  $\mu$ l., was injected into a Gas Chromatograph using the designated injector temperature and a column temperature ranging from 25–100° depending on the diene on hand. Contact times were extremely low, mere fractions of a second. The composition of the products was determined from peak ratios. Products were also collected and identified by their infrared spectra.

In the case of the methylpentadienes a small, but significant, amount of XIIIa is always produced from XI and XII. It is suggested that XIIIa is formed by a slow *cis*  $\rightarrow$  *trans* isomerization of XII.

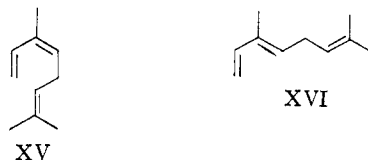
The selective isomerization of *cis*-1,3-dienes suggests the involvement of a six-membered transition state (XIV)<sup>12</sup> in which five carbon atoms lie in a plane or near plane with the migrating hydrogen above or below this plane. In this regard, it is of interest to note that the planar dienes II and III require a temperature of 350° to approach equilibrium, whereas an equilibrium mixture was never completely reached at 450° with the non-planar dienes VII and VIII.<sup>11</sup>

In addition to providing a general synthetic method for 1,3-dienes of type I, e.g., *cis*-2-methyl-1,3-pentadiene (XII), II and IX, the specific thermal isomerization of *cis*-dienes suggests a convenient method for differentiating between related

(12) This transition state is in a sense analogous with the transition states pictured for the Claisen and Cope rearrangements and for thermal eliminations such as acetate and xanthate pyrolysis.



pairs of geometric isomers. Two ocimenes are known and possess either structure XV or XVI. One isomer,  $\alpha$ -ocimene, can be obtained by pyrolysis of  $\alpha$ -pinene,<sup>6,13</sup> while the other isomer,  $\beta$ -



ocimene, has been recently isolated from *Tagetes minuta* L.<sup>14</sup> We have examined the thermal behavior of the ocimenes using samples, provided by Dr. H. Bayer,<sup>15</sup> which were separated from the hydrocarbons arising from mixed hydride (Li-AlH<sub>4</sub>-AlCl<sub>3</sub>) reduction of linalool.<sup>16,17</sup> We find that at 400°  $\alpha$ -ocimene is transformed into a complex mixture of the alloocimenes and pyronenes,<sup>18</sup> whereas  $\beta$ -ocimene is thermally stable, even at 450°. We conclude, therefore, that  $\alpha$ -ocimene and  $\beta$ -ocimene have the constitutions represented by XV and XVI, respectively.

It was hoped that information relative to the geometric configuration of trienes might be obtained in a similar fashion, but this did not prove to be the case. Pure samples of *cis*- and *trans*-alloocimene<sup>19</sup> gave essentially the same mixture of products over a temperature range of 350–450°.

### Experimental Part<sup>20</sup>

#### 2-Hydroxymethyl-3-isopropylidene-1-methylcyclopentane.

—To a stirred slurry of 3.0 g. (0.079 mole) of lithium alu-

(13)  $\alpha$ -Pinene, 1–10  $\mu$ , injected at 450° into a Gas Chromatograph gave in order of increasing retention time, unaltered  $\alpha$ -pinene, the three pyronenes, limonene and  $\alpha$ -ocimene, which were not separated by a Carbowax 20M preparatory column, but were separated on a Carbowax 20M analytical column, *cis*-alloocimene and a small amount of *trans*-alloocimene.

(14) Y. R. Naves and P. Tullen, *Helv. Chim. Acta*, **44**, 316 (1961).

(15) We wish to express our appreciation to Dr. J. H. Brewster and Dr. Bayer for making these samples available.

(16) H. Bayer, Ph.D. Thesis, Purdue University, 1961.

(17) Dehydration of linalool with iodine has been reported to yield myrcene (B. A. Arbusow and W. S. Abramow, *Ber.*, **67**, 1942 (1934)). In our hands this dehydration was extremely slow and never complete; while myrcene was the major product, *ca.* 55% of the hydrocarbon mixture, appreciable amounts of  $\beta$ -ocimene and dipentene, as well as smaller amounts of  $\alpha$ -ocimene and the alloocimenes were also produced. Dehydration of linalool with phosphorus oxychloride in pyridine proceeds smoothly to afford a similar hydrocarbon mixture from which  $\beta$ -ocimene can be readily separated by v.p.c.

(18) R. E. Fugitt and J. E. Hawkins, *J. Am. Chem. Soc.*, **67**, 242 (1945).

(19) These isomers are readily separated by v.p.c. Both isomers yield the same maleic anhydride adduct which is in agreement with the report by J. J. Hopfield, S. A. Hall and L. A. Goldblatt, *J. Am. Chem. Soc.*, **66**, 115 (1944), but in disagreement with the observation of K. Alder, H. Dreike, H. Erpenbach and V. Wicker, *Ann.*, **609**, 1 (1957).

(20) All boiling and melting points are uncorrected. Vapor phase chromatographic separations and analyses were conducted with a Carbowax 20M column unless otherwise noted. Infrared spectra were determined by Mrs. W. Dilling on a Perkin-Elmer double beam

minimum hydride and 50 ml. of ether was added slowly an ether solution of 9.03 g. (0.054 mole) of a mixture of *cis*- and *trans*-pulegenic acids.<sup>21,22</sup> After stirring 1 hour, 30 ml. of water was added dropwise and the resulting white precipitate removed by filtration. The ethereal solution was dried and distilled affording 6.15 g. (74.4%) of a mixture of *cis*- and *trans*-alcohols, b.p. 69–70° (2 mm.). Vapor phase chromatography of this mixture gave two fractions,  $n_D^{20}$  1.4850 and 1.4698, whose infrared spectra showed slight differences in the region 8.4–9.8  $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>O: C, 77.87; H, 11.76. Found: C, 78.07; H, 11.73.

**2-Acetoxyethyl-3-isopropylidene-1-methylcyclopentane (V).**—A solution of 6.17 g. (0.04 mole) of *cis*- and *trans*-2-hydroxymethyl-3-isopropylidene-1-methylcyclopentane in 15 ml. of acetic anhydride and 1 ml. of pyridine was kept overnight and then distilled to yield 6.66 g. (85%) of a mixture of *cis*- and *trans*-acetates V, b.p. 103–105° (1 mm.). Vapor phase chromatography of this mixture gave pure *cis* and *trans* isomers,  $n_D^{21}$  1.4608 and  $n_D^{20}$  1.4676, respectively, whose infrared spectra were identical except for the presence of very weak peaks at 7.55 and 8.65  $\mu$  in the *trans* isomer and a weak peak at 8.93  $\mu$  in the *cis* isomer. The assignment of configuration to these acetates is based on a difference in n.m.r. signals attributed to the -CH<sub>2</sub>OAc protons; a doublet at -231 and -237 c.p.s. appeared for the first fraction isolated from v.p.c., whereas the second fraction showed an octet ranging from -208 to -254.1 c.p.s. Molecular models of the *trans* isomer indicate that free rotation about the C-CH<sub>2</sub>OAc bond is possible; the acetoxyethyl protons are, therefore, equivalent and their resonance should appear as a doublet owing to spin-spin coupling with an adjacent proton attached to the cyclopentane ring. Models of the *cis* isomer indicate restricted rotation about the C-CH<sub>2</sub>OAc bond which results in non-equivalence of the acetoxyethyl protons; an octet should, therefore, be observed due to one acetoxyethyl proton coupling with the other in addition to coupling with the adjacent proton on the cyclopentane ring.

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>: C, 73.43; H, 10.27. Found for *cis*-V: C, 73.40; H, 10.11. Found for *trans*-V: C, 73.17; H, 10.07.

**2-Isopropenyl-1,5-dimethyl-1-cyclopentene (II).**—2-Acetoxyethyl-3-isopropylidene-1-methylcyclopentane (6.15 g., 0.0314 mole) was passed through a glass-bead packed Pyrex tube at 500 ± 10°. The yellow pyrolysate was washed with water, aqueous sodium carbonate and dried. Vapor phase chromatographic analysis, using a Uconpolar column, of the crude pyrolysate indicated the presence of a single diene as the major product, *ca.* 85% of the mixture, together with 10–15% of several lesser substances, including unaltered acetate. The diene was collected and rechromatography indicated a purity of greater than 99%,  $n_D^{20}$  1.4802,  $\lambda_{\text{max}}^{\text{acetone}}$  237, 243 and inf. 253,  $\epsilon$ , 10,130, 9,859 and 5,800;  $\gamma$  3.26, 3.45, 3.52, 5.65, 6.18, 6.30, 6.97, 7.32, 7.60, 7.90, 8.38, 8.60, 9.32, 9.53, 9.82, 10.04, 11.28 and 11.40  $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>: C, 88.16; H, 11.84. Found: C, 88.44; H, 11.80.

The tetracyanoethylene adduct of diene II showed m.p. 137–137.5° after three recrystallizations from ether.

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>4</sub>: C, 72.70; H, 6.10. Found: C, 72.88; H, 5.98.

**Ozonolysis of Diene II.**—A solution of 165.6 mg. (1.22 mmoles) of diene II in 15 ml. of acetic anhydride was ozonized at -78° for 30 minutes. The ozonide solution was added to a stirred slurry of zinc dust and water and after 1 hour the mixture was distilled directly into a solution of 2,4-dinitrophenylhydrazine reagent. The resulting solid, 90 mg., m.p. 128–140°, was chromatographed on silica gel, using 4% ether in petroleum ether as an eluent, to give after the elution of *ca.* 10 mg. of a red oil, 5 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 123–124° after

spectrometer, model 21. The microanalyses were performed by Dr. C. S. Yeh and Mrs. V. Kebly. The n.m.r. spectra were obtained at 60 Mc. with the Varian Associates high resolution spectrometer (V-4300 B). The shift values were measured with reference to tetramethylsilane as an internal standard.

(21) O. Wallach, *Ann.*, **289**, 349 (1895); **414**, 233 (1918).

(22) The stereochemistry of the pulegenic acids will be discussed in a later publication.

recrystallization from ethanol, and 42 mg. of formaldehyde 2,4-dinitrophenylhydrazone, m.p. 161–163° after recrystallization from ethanol.

**N,N-Dimethyl-2-isopropylidene-5-methylcyclopentane-carboxamide.**—Pulegenic acid,<sup>21</sup> (8.78 g., 0.052 mole) was heated with 4.5 ml. of phosphorus trichloride for 5.5 hours. Petroleum ether was added and decanted from the small amount of yellow oil which separated. The solvent and excess phosphorus trichloride were distilled under diminished pressure. The resulting residue was dissolved in petroleum ether and slowly added to a solution of ca. 20 g. of dimethylamine in petroleum ether. A white precipitate, dimethylamine hydrochloride, was removed from the resulting yellow solution and the solvent and excess amine were removed. Distillation of the residue gave 6.44 g. (63%) of the amide, b.p. 92° (3 mm.),  $n_D^{20}$  1.4903,  $\lambda_{\max}$  6.10  $\mu$ . *Cis* and *trans* isomers could not be resolved by v.p.c.

*Anal.* Calcd. for  $C_{12}H_{21}NO$ : C, 73.79; H, 10.84; N, 7.27. Found: C, 73.72; H, 11.05; N, 7.31.

The n.m.r. spectrum of the amide exhibited signals at  $-58.8$ ,  $-64.3$  (one  $CH_3-C-H$ ),  $-86.6$ ,  $-97.7$  ( $(CH_3)_2C=C$ ),  $-106$ ,  $113.3$ ,  $-133$  ( $-CH_2-$  and  $-CH-$ ) and  $-177.6$  c.p.s. ( $-N(CH_3)_2$ ).

**2-N,N-Dimethylaminomethyl-3-isopropylidene-1-methylcyclopentane (VI).**—A solution of 6.67 g. (0.034 mole) of the above amide in 100 ml. of ether was added slowly to 2.34 g. (0.062 mole) of lithium aluminum hydride in 150 ml. of ether. The mixture was heated for 5 hours and allowed to stand at room temperature for 2 days. Water was added, the resulting precipitate was removed, and the ether solution dried over anhydrous magnesium sulfate. Distillation gave 4.37 g. (70.5%) of an amine mixture, b.p. 93–95° (20 mm.). Vapor phase chromatography of this product gave two fractions: (a)  $n_D^{20}$  1.4582 and (b)  $n_D^{20}$  1.4673.

*Anal.* Calcd. for  $C_{12}H_{23}N$ : C, 79.49; H, 12.79. Found for fraction a: C, 79.60; H, 12.80. Found for fraction b: C, 79.35; H, 12.57.

The n.m.r. spectrum of fraction b was consistent with that expected for amine VI:  $-50.2$ ,  $-56.2$  (one  $CH_3-C-H$ ),  $-95.2$  ( $(CH_3)_2C=C$ ) and  $-128.7$  c.p.s. ( $(CH_3)_2N-$  superimposed upon  $-CH_2-$  and  $-CH-$ ). The spectrum of fraction a was not consistent with structure VI; rather, suggested its assignment as 1-N,N-dimethylaminomethyl-2-isopropyl-5-methyl-1-cyclopentene<sup>23</sup>;  $-53.7$ , (*three*  $CH_3-C-H$ ),  $125$  ( $-N(CH_3)_2$ ) and  $-166.4$  c.p.s. ( $C=C-CH_2-N$ ).

**3-Isopropylidene-2-methylene-1-methylcyclopentane (III).**—Eight milliliters of 30% hydrogen peroxide was added slowly to a Dry Ice-cooled solution of 4.37 g. (0.0241 mole) of the amine mixture obtained above in 9.0 ml. of methanol. The solution was allowed to warm to room temperature and was left for 25 hours. Platinum black, 18.6 mg., and 10 ml. of water were added and the mixture was stirred for 24 hours. The solvents were removed at room temperature under diminished pressure. The viscous residue was heated to 70–80° at 200 mm. affording an initial distillate, composed largely of dimethylhydroxylamine, which was collected in two Dry Ice traps. The pressure was then lowered to 3–5 mm. and the temperature raised to 80–90° resulting in the distillation of a liquid, b.p. 35–41°, which was collected in the ice-cooled receiver of the distillation apparatus. Vapor phase chromatography, using a Ucon-polar column, gave a main fraction composed of diene III,  $n_D^{20}$  1.4922,  $\lambda_{\max}^{EtOH}$  249  $\mu$ ;  $\gamma_{\max}^{(strong)}$  3.43, 6.10, 6.92, 7.34, and 11.40  $\mu$ ;  $\gamma_{\max}^{(weak)}$  3.27, 3.52, 5.72, 7.8, 8.0, 8.27, 8.52, 8.92, 9.26, 9.72, 9.88, 10.13, 11.96 and 12.50  $\mu$ . The n.m.r. spectrum of III displayed signals at  $-60.1$ ,  $-66.3$  (one  $CH_3-C-H$ ),  $-106.2$ ,  $-115.4$  ( $(CH_3)_2C=C$ ),  $-139.2$  ( $-CH_2-$  and  $-CH-$ ) and  $-293$  c.p.s. ( $CH_2=C$ ).

*Anal.* Calcd. for  $C_{10}H_{16}$ : C, 88.16; H, 11.84. Found: C, 88.30; H, 11.96.

In addition to diene IV, three other fractions, ca. 20–30% of the crude mixture, were isolated by v.p.c. The fraction eluting most closely to diene III displayed an

infrared spectrum identical with that of 1-N,N-dimethylaminomethyl-2-isopropyl-5-methyl-1-cyclopentene. The last two fractions were not investigated further; however, the infrared spectrum of the last fraction contained all the peaks exhibited by amine VI.

**Ozonolysis of Diene III.**—A solution of 100 mg. (0.736 mmole) of III in acetic anhydride was ozonized at  $-78^\circ$  for 1 hour. The 2,4-dinitrophenylhydrazone which resulted following the usual work up was chromatographed on silica gel, using 4% ether–petroleum ether as an eluant, to give 75.4 mg. of acetone 2,4-dinitrophenylhydrazone, m.p. 123.5–124°, and 37 mg. of formaldehyde 2,4-dinitrophenylhydrazone, m.p. 160–162°.

**1-(1-Cyclohexenyl)-2-methyl-2-propanol and 1-(1-Cyclohexenyl)-2-methyl-1-propene (IX).**—To the solution resulting from the reaction of 16.35 (0.115 mole) of methyl iodide with 2.8 g. (0.115 g. atom) of magnesium in 100 ml. of ether was added 6.44 g. (0.385 mole) of ethyl 1-cyclohexenylacetate. After 30 minutes dilute hydrochloric acid was added. The ether layer was separated, dried and distilled affording 0.155 g. of a mixture of IX and 1-(1-cyclohexenyl)-2-methyl-2-propanol, b.p. 70–87° (13 mm.), and 3.65 g. of the alcohol, b.p. 87–91° (13 mm.).

Vapor phase chromatography of the first fraction afforded the diene IX,  $n_D^{20}$  1.4928,  $\lambda_{\max}$  234  $\mu$ ,  $\epsilon$  9,830;  $\gamma_{\max}$  3.43, 6.09, 6.96, 7.30, 7.54, 7.92, 8.10, 8.41, 8.60, 8.88, 9.31, 9.50, 9.63, 10.20, 11.46, 11.60, 12.16, 12.50, 13.10 and 14.25  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_{16}$ : C, 88.16; H, 11.84. Found: C, 88.55; H, 12.09.

The alcohol, purified by gas chromatography showed  $n_D^{20}$  1.4972,  $\gamma_{\max}$  2.95  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_{18}O$ : C, 77.86; H, 11.76. Found: C, 77.70; H, 12.03.

The n.m.r. spectra of diene IX,  $-95.4$  ( $(CH_3)_2C=C$ ),  $-122.4$  (4  $-CH_2-$ ) and  $-327.6$  c.p.s. (2  $H-C=C-$ ), and the propanol,  $-69.5$  (2  $CH_3-C$ ),  $-92.8$ ,  $-94.4$ ,  $-97.4$ ,  $-100.4$ ,  $-106$ ,  $-122.5$  and  $-326.2$  c.p.s. (1  $H-C=C$ ), were consistent with their assigned structures.

The tetracyanoethylene adduct of diene IX melted at 100–101° after several recrystallizations from ether at  $-78^\circ$ .

*Anal.* Calcd. for  $C_{16}H_{18}N_4$ : C, 72.70; H, 6.10. Found: C, 73.34; H, 6.19.

**The Reaction of Cyclohexylideneacetic Acid with Methylmagnesium Iodide.**—An ether solution of 10.0 g. of cyclohexylideneacetic acid (0.071 mole), m.p. 90–92°, was added to an ether solution of methylmagnesium iodide, prepared from 51.2 g. (0.36 mole) of methyl iodide and 8.8 g. (0.366 g. atom) of magnesium. After heating for 19 hours, dry benzene was added and the solvent slowly distilled until the boiling point of the distillate rose to 65°. Dilute hydrochloric acid was added and the organic layer was separated, washed with aqueous sodium carbonate, dried and then distilled to give 3.2 g. of diene IX, b.p. 32–38° (1.5 mm.). A small amount of higher boiling ketonic material was obtained but was not examined further.

Acidification of the sodium carbonate extract mentioned above afforded 2.7 g. of solid, m.p. 88–89°, whose infrared spectrum was identical with that of cyclohexylideneacetic acid.

**Triphenylmethallylphosphonium Chloride.**—A solution of 20 g. of triphenylphosphine and 7 g. of methallyl chloride in benzene was heated at reflux for 7 days affording 18 g. of a white crystalline salt, m.p. 214–216°.

*Anal.* Calcd. for  $C_{22}H_{22}ClP$ : Cl, 10.0. Found: Cl, 9.50.

**3-Cyclohexylidene-2-methyl-1-propene (X).**—To a slurry of 17 g. (0.047 mole) of triphenylmethallylphosphonium chloride and 50 ml. of tetrahydrofuran was added an ethereal solution of phenyllithium, prepared from 7.6 g. (0.048 mole) of bromobenzene. The solution immediately became deep red and all but a small amount of the salt dissolved. After stirring for an hour, 5 g. (0.051 mole) of cyclohexanone was added; a flocculant precipitate deposited instantaneously. The ether was slowly distilled from the reaction mixture over a 4-hour period during which time the orange-red color gradually faded and finally disappeared. The salts were removed by filtration and washed thoroughly with ether. The filtrate was washed with water, dried and distilled to give 1.1 g. of crude diene X, b.p. 53–85° (19 mm.). A pure sample of X was obtained by gas chroma-

(23) This is the only instance, to date, where we have observed a product derived from pulegenic acid in which the exocyclic double bond has migrated into the ring.

tography and showed  $n_D^{25}$  1.4885,  $\lambda_{\max}$  233  $m\mu$  ( $\epsilon$  11,300);  $\gamma_{\max}$  (strong) 3.45, 3.50, 6.14, 6.94, 11.30 and 11.82  $\mu$ ; (weak) 3.24, 5.60, 6.10, 6.26, 7.32, 7.48, 7.68, 7.90, 8.0, 8.2, 8.9, 9.12, 10.07, 10.39, 10.73 and 12.90  $\mu$ . The n.m.r. spectrum of X displayed signals at  $-92.2$  ( $-\text{CH}_2-$ ),  $-105.7$  ( $\text{CH}_3-\text{C}=\text{C}$ ),  $-123.7$  and  $-137.2$  ( $-\text{CH}_2\text{C}=\text{C}$ ),  $-280.5$  and  $-295.5$  ( $\text{CH}_2=\text{C}$ ) and  $-330.7$  c.p.s. ( $\text{CH}=\text{C}$ ).

*Anal.* Calcd. for  $\text{C}_{10}\text{H}_{16}$ : C, 88.16; H, 11.84. Found: C, 88.44; H, 11.69.

*trans*-2,5-Dimethyl-1,3-hexadiene (XIIIa).—This diene was obtained from isobutyraldehyde by the use of the procedure described above. Pure *trans*-2,5-dimethyl-1,3-hexadiene showed  $n_D^{20}$  1.4432,  $\lambda_{\max}$  228  $m\mu$  ( $\epsilon$  22,100);  $\lambda_{\max}$  3.29, 3.40, 3.50, 6.10, 6.24, 6.88, 7.26, 7.33, 7.52, 7.68, 8.22, 8.38, 9.10, 10.33, 11.24 and 11.80  $\mu$ . The n.m.r. spectrum showed signals at  $-55.8$  and  $-61.9$  ( $(\text{CH}_3)_2\text{C}-\text{H}$ ),  $-100.5$  ( $\text{CH}_3-\text{C}=\text{C}$ ), a sextet centered at *ca.*  $-123$  ( $\text{C}-\text{H}$ ),  $-263.4$  ( $\text{CH}_2=\text{C}$ ) and a complex set of six peaks from  $-298.8$  to  $-349$  c.p.s. ( $\text{CH}=\text{CH}$ ).

**Methylpentadienes.**—A mixture comprised of 22% 4-methyl-1,3-pentadiene (XI) and 78% *trans*-2-methyl-1,3-pentadiene (XIIIa) was obtained by the dehydration of 2-methyl-2,4-pentane diol.<sup>24</sup> These dienes were readily separated using an adiponitrile column; XI displayed a

longer retention time than XIIIa. The infrared spectra of these pure dienes were identical with those recorded in the API catalogue.<sup>25</sup>

*cis*-2-Methyl-1,3-pentadiene (XII) was obtained by thermal isomerization of 4-methyl-1,3-pentadiene (XI) and showed  $\lambda_{\max}$  222  $m\mu$  (5,000);  $\gamma_{\max}$  3.25, 3.42, 5.61, 6.13, 6.25, 6.95, 7.35, 8.05, 9.70, 9.95, 10.35(w), 10.85, 11.25, 13.20 and 14.85  $\mu$ . The n.m.r. spectrum was also consistent with the assigned structure,  $-103.4$  (2  $\text{CH}_3-\text{C}=\text{C}$ ),  $-270.8$ , 279.8 and  $-322.5$  c.p.s. (4 olefinic hydrogens).

**Acknowledgment.**—This work was supported in part by a grant from the Purdue Research Foundation. The authors are indebted to Mr. William E. Baitinger for determining the nuclear magnetic resonance spectra.

(24) According to M. G. Dupont and M. Darmon, *Bull. soc. chim. France*, **6**, 1208 (1939), the 2-methyl-1,3-pentadiene so produced is a mixture of *cis* and *trans* isomers. We, however, find that there is less than 0.2% of the *cis* isomer present.

(25) "Catalogue of Selected Infrared Absorption Spectrograms," American Petroleum Institute Research, Project 41, National Bureau of Standards, Washington, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

## Stereochemistry of Allylic Rearrangements. XII. Oxygen Exchange Associated with the Acid-catalyzed Rearrangement of *cis*- and *trans*-5-Methyl-2-cyclohexenol<sup>1,2</sup>

BY HARLAN L. GOERING AND ROY R. JOSEPHSON

RECEIVED JANUARY 29, 1962

The acid-catalyzed isomeric rearrangement of *cis*- (I) and *trans*-5-methyl-2-cyclohexenol (II) in aqueous acetone results in interconversion of enantiomers (racemization) and geometric isomers (isomerization). With each isomer the rate of racemization ( $k_{\text{rac}}$ ) is several times that of isomerization ( $k_i$ ). Experiments with <sup>18</sup>O-labeled alcohols show that in the *cis* system most of the racemization is intramolecular, *i.e.*, little exchange is associated with the interconversion of enantiomers. On the other hand, in the *trans* system interconversion of enantiomers results in almost complete exchange. The stereochemical and exchange results are interpreted in terms of conformational considerations. The symmetrical 5-methyl-2-cyclohexenyl carbonium ion can exist in two conformations. Presumably the isomeric alcohols react *via* the quasi-axial conformers and give rise to carbonium ions which differ conformationally and in the way they are solvated.

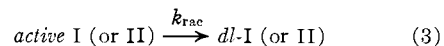
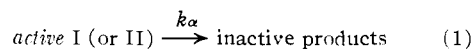
### Introduction

The acid-catalyzed ( $\text{HClO}_4$ ) isomeric rearrangement of optically active *cis*-(I) and *trans*-5-methyl-2-cyclohexenol (II) in aqueous media results in formation of two products, racemic I and II—in this symmetrical system rearrangement without geometric isomerization results in interconversion of enantiomers (racemization). In an earlier investigation<sup>3</sup> it was found that in 35% aqueous acetone, both loss of optical activity (eq. 1) and isomerization (eq. 2) are pseudo first order, and for each isomer  $k\alpha$  is several times larger than  $k_i$ . This means that there is "excess" racemization, or in other words there is a tendency for preservation of geometric configuration during the rearrangement.

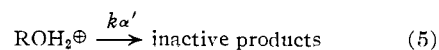


Since loss of activity and isomerization are cleanly pseudo first order, the difference between

$k\alpha$  and  $k_i$  for each isomer is the pseudo-first-order constant for racemization (eq. 3), *i.e.*,  $k_{\text{rac}} = k\alpha - k_i$ . Thus the total rate of rearrangement (disappearance of substrate) is measured by  $k\alpha$  and rates of formation of the two products (isomerization and racemization) are measured by  $k_i$  and  $k_{\text{rac}}$ .



From the kinetic behavior—the rate of rearrangement ( $k\alpha$ ) is proportional to the acid concentration<sup>3</sup>—it is clear that rearrangement involves reversible protonation of the substrate (eq. 4;  $\text{SH}^\oplus$  is lyonium ion) followed by first-order rearrangement of the alcohol conjugate acid (eq. 5). The latter is the sum of the first-order rates of isomerization (eq. 6) and racemization (eq. 7).



(1) This work was supported by a grant (G-6285) from the National Science Foundation.

(2) First reported as a Communication, H. L. Goering and R. R. Josephson, *J. Am. Chem. Soc.*, **83**, 2585 (1961).

(3) H. L. Goering and E. F. Silversmith, *ibid.*, **79**, 348 (1957).