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Double Bond Migration and Racemization During the Hydrogenation of Olefins

WILLIAM D. HUNTSMAN, NORMAN L. MADISON, AND
SHELDON I. SCHLESINGER

From the Department of Chemistry, Ohio University, Athens, Ohio

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Double bond migration and racemization during the hydrogenation of several optically active alkenes have been studied. Extensive double bond migration and racemization occur with supported and unsupported palladium catalysts. Most, if not all, of the racemization results from double bond migration. Racemization of the alkenes by other processes was not detected. The rate of double bond migration is reduced markedly by the presence of base.

INTRODUCTION

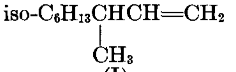
It is well known that double bond migration occurs readily during the hydrogenation of certain alkenes. From the many examples that have been reported, the following may be cited as illustrative.

The isomerization of 1-butene to 2-butene has been studied by several groups (*1–4*). With nickel catalysts, the rate of isomerization is approximately equal to the rate of addition at 60°; the rate of isomerization increases somewhat more rapidly than addition as the temperature is raised (*4*). Isomerization occurs even more rapidly in the presence of palladium. For example, when 1-butene is hydrogenated at $-8°$ over palladium on barium sulfate, 92% of the residual olefin at 20% saturation is 2-butene.

Double bond migration occurs during hydrogenation of oleic acid and its esters (*5–9*). β-Pinene isomerizes quantitatively to α-pinene in the presence of palladium and hydrogen (*10, 11*). Isomerization of various cycloalkenes has been observed with platinum, but to a much greater extent with palladium catalysts (*12–16*).

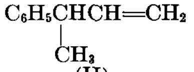
Cram observed that the 2-phenylbutane formed by hydrogenation of optically active 3-phenyl-1-butene was racemized to the extent of 1 to 11%, depending on the catalyst used (*17*). Racemization was greatest with palladium and least with Raney nickel catalysts. Cram postulated that racemization occurred by isomerization of active 3-phenyl-1-butene to inactive 2-phenyl-2-butene, which upon hydrogenation gives racemic 2-phenylbutane. Bonner and coworkers established that racemization is not due to phenyl migration (*18*).

We were interested in studying some of the factors that influence double bond migration and racemization, and the relationship of these processes to the addition reaction. For this purpose we chose these optically active alkenes: 3,7-dimethyl-1-octene (I), 3-phenyl-1-butene (II), and 3-methyl-1-hexene (III). Most of the experiments were carried out with (I) because it could be obtained easily from readily available starting materials.



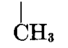
$\text{iso-}C_6H_{13}\underset{\displaystyle CH_3}{\underset{|}{CH}}CH{=}CH_2$

(I)



$C_6H_5\underset{\displaystyle CH_3}{\underset{|}{CH}}CH{=}CH_2$

(II)



$C_3H_7\underset{\displaystyle CH_3}{\underset{|}{CH}}CH{=}CH_2$

(III)

EXPERIMENTAL

Materials

(+)-3,7-Dimethyl-1-octanol. This alcohol was prepared by hydrogenation of citronellol over nickel-kieselguhr at 100° and 100 atm. Samples of citronellol from several different sources were used during the study, and the rotations were found to vary widely. It was necessary to fractionate both the citronellol and the hydrogenated material in an efficient column in order to obtain consistent results. The properties of a typical sample of 3,7-dimethyl-1-octanol are: b.p. 99–100° (8 mm), n_D^{25} 1.4340, d_4^{25} 0.8266, α_D^{25} 2.87°,* $[\alpha]_D^{25}$ 3.47°.

(−)-3,7-Dimethyl-1-bromooctane. Phosphorus tribromide (87 g, 0.32 mole) was added dropwise, with stirring, over a period of 1/2 hr to 63.2 g (0.4 mole) of 3,7-dimethyl-1-octanol, α_D^{25} 2.87°, in a 500-ml flask which was surrounded by an ice bath. The mixture was kept in the ice bath for an additional 1/2 hr, and then heated on the steam bath 1 hr, and allowed to stand at room temperature overnight. The mixture was poured into water, the organic layer was separated and washed repeatedly with water. After being dried over calcium chloride, the material was distilled to give 64.5 g, b.p. 99–101° (13 mm); final purification was effected by chromatography over alumina, and the purified product had these properties: n_D^{25} 1.4529, α_D^{25} −4.73°.

(+)-2,6-Dimethyloctane. A Grignard reagent was prepared from 13.0 g (0.059 mole) of the 3,7-dimethyl-1-bromooctane described above and 1.42 g of magnesium in 50 cc of ether. The reaction mixture was cooled in an ice bath and 35 cc of 5% HCl was added. The organic layer was separated, washed with water, and dried over magnesium sulfate. Fractionation in a spinning-band column gave 5.7 g of 2,6-dimethyloctane, b.p. 158.9°, n_D^{25} 1.4085, α_D^{25} 5.26°, d_4^{25} 0.7259, $[\alpha]_D^{25}$ 7.24°.

(−)-3,7-Dimethyl-1-octene: (a) By Hofmann elimination. A mixture of 12.0 g (0.054 mole) of the 1-bromo-3,7-dimethyloctane described above and 17 ml of a 25% solution of trimethylamine in anhydrous methanol was placed in a 125-ml glass-stoppered Erlenmeyer flask. The stopper was wired in place and the mixture was heated on the steam bath for 8 hr (*19*). The solvent was evaporated, and the crystals of trimethyl-3,7-dimethyloctylammonium bromide which separated (12.0 g) were washed with benzene, and dried in a vacuum desiccator.

Silver oxide was prepared by mixing 30.6 g of silver nitrate and 200 cc of 1 *N* sodium hydroxide. The precipitate was washed thoroughly with water. A solution of 22.0 g (0.0786 mole) of the quaternary bromide described above in 240 ml of water and 30 ml of methanol was added to the silver oxide and the mixture was shaken for 2 hr and allowed to stand overnight. The mixture was filtered, and the water was distilled from the filtrate. A slow stream of nitrogen was passed through the residue while the temperature was increased gradually. Decomposition began when the temperature reached 130°, and was essentially complete at 145°. Heating was continued until the temperature reached 200°. The distillate was taken up in pentane, washed with 120 ml of 5% hydrochloric acid, and finally with water until neutral. The pentane solution was dried over calcium chloride, and the pentane was stripped. Fractionation through a spinning-band column provided 7.3 g of (−)-3,7-dimethyl-1-octene, b.p. 86.1–86.7° (94 mm), n_D^{25} 1.4141, α_D^{25} −8.04°, d_4^{25} 0.7293, $[\alpha]_D^{25}$ −11.03°.

(b) By amine oxide pyrolysis. Dimethyl-3,7-dimethyloctylamine was prepared from 13.3 g (0.06 mole) of the 1-bromo-3,7-dimethyloctane described above and 12.9 g (0.29 mole) of dimethylamine according to the general procedure described by Cram (*20*). There was obtained 9.2 g of the amine, b.p. 89° (12 mm), n_D^{25} 1.4277, α_D^{25} −1.65°. This amine was converted to the oxide by treatment with 16.7 g of 30% hydrogen peroxide according to the general procedure. The excess hydrogen peroxide was destroyed by adding platinum black, and the methanol was evaporated at the water pump. The amine oxide which remained was heated under reduced pressure in an oil bath at 135–150°. The distillate was dissolved in pentane, washed thoroughly with dilute hydrochloric acid, and finally with water until neutral. After being dried

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* Throughout this paper, rotations refer to the observed value for the homogeneous liquid in a 10-cm tube.

over calcium chloride, the pentane asw stripped, and the residue was fractionated in a spinning-band column. There was obtained 5.1 g of (−)-3,7-dimethyl-1-octene, b.p. 87.5–87.8° (98 mm), n_D^{25} 1.4142, α_D^{25} −8.05°.

(c) **By acetate ester pyrolysis.** 3,7-Dimethyl-1-octanol (50 g, 0.35 mole; α_D^{25} 2.87°), 40 g (0.40 mole) of acetic anhydride and 3 cc of pyridine were mixed and allowed to stand overnight. The mixture was refluxed 1 hr, 4 ml of water was added, and refluxing was continued for 15 min. The mixture was cooled, diluted with water, and the organic layer was washed first with 10% sodium carbonate and then with water until neutral. After being dried over sodium sulfate, the material was fractionated in a 60-cm Fenske column. There was obtained 49.0 g of 3,7-dimethyloctyl acetate, b.p. 87.5° (4 mm), n_D^{25} 1.4243, α_D^{25} 1.21°, d_4^{25} 0.8612, $[\alpha]_D^{25}$ 1.41°.

This ester (43 g) was pyrolyzed by passing it through a 20 mm × 40 cm Pyrex tube packed with glass helices and heated at 500°. The pyrolysate was washed thoroughly with water and dried over sodium sulfate. Fractionation in a spinning-band column gave 18.4 g of 3,7-dimethyl-1-octene, b.p. 88.4–88.5° (100 mm), n_D^{25} 1.4144, α_D^{25} −8.01°.

3-Phenyl-1-butene. Partially resolved (−)-3-phenyl-1-butanol, b.p. 97–99° (5 mm), n_D^{25} 1.5188, α_D^{25} −14.6°, was prepared according to Cram (*20*). The acetate ester, prepared in 94% yield from 62.3 g of this alcohol and 45 g of acetic anhydride by the procedure described above for 3,7-dimethyloctyl acetate, had these properties: b.p. 92.5–99.5° (2 mm), n_D^{25} 1.4912. Although the optical rotation of this ester was not measured, another sample of the alcohol, α_D^{25} −15.54°, gave (−)-3-phenylbutyl acetate, α_D^{25} −20.94°. Pyrolysis of 74 g of the former ester at 500° gave, after the customary treatment of the pyrolysate, 35.5 g of (−)-3-phenyl-1-butene, b.p. 75–78° (3 mm), n_D^{25} 1.5067, α_D^{25} −2.14°. Vapor phase chromatographic (VPC) analysis indicated the presence of approximately 3% 2-phenyl-2-butene. (+)-3-Phenyl-1-butene was prepared by this same sequence of steps from (+)-3-phenyl-1-butanol. This alkene was fractionated in a spinning-band column and exhibited these properties: b.p. 86° (35 mm), n_D^{25} 1.5054, α_D^{25} 1.84°. VPC analysis indicated a purity of at least 99.5%.

It was observed that the rotation of 3-phenyl-1-butene changes quite rapidly with temperature. For example, these values were observed for a given sample: $\alpha_D^{20.7}$ 1.63°; $\alpha_D^{22.4}$ 1.72°; $\alpha_D^{25.3}$ 1.87°; $\alpha_D^{29.5}$ 2.15°. The rotation of 2-phenylbutane is much less sensitive to temperature, changing by less than 1% for a two degree change in the neighborhood of 25°.

Ozonolysis of (+)-3-phenyl-1-butene. A 6 g sample of (+)-3-phenyl-1-butene, α_D^{25} 1.85°, was dissolved in 60 ml of ether and ozonized at −40°. The end point was not sharp, and it is likely that the sample was over-ozonized. The ozonide was reduced with lithium aluminum hydride (6 g in 100 ml of ether) according to the procedure reported (*21*). There was obtained 4.3 g of material, b.p. 95–104° (14 mm), α_D^{25} 4.75°. VPC analysis showed this to consist of 92% 2-phenyl-1-propanol; 1-phenylethanol constituted most of the remainder.

(+)-3-Methyl-1-hexene. Ethyl 3-methylhexanoate was prepared by hydrogenation of ethyl 3-methylhexenoate (*22*) in the presence of platinum oxide. This ester was saponified, and the 3-methylhexanoic acid was partially resolved (*23*). Samples of acid with the following rotations were secured: α_D^{25} 1.68° and α_D^{25} −1.19°. The levorotatory acid (35.0 g) was reduced with 12.7 g of lithium aluminum hydride in 600 ml of ether. Upon hydrolysis and distillation of the reaction mixture, there was obtained 24.4 g of (−)-3-methyl-1-hexanol, b.p. 98–100° (50 mm), n_D^{25} 1.4168. The rotation of this alcohol was not measured, but from the dextrorotatory acid described above, there was obtained (+)-3-methyl-1-hexanol, α_D^{25} 1.04°. On this basis, the rotation of the levorotatory alcohol is estimated as α_D^{25} −0.73°.

A 22.0 g sample of (−)-3-methyl-1-hexanol was acetylated with 21.3 g of acetic anhydride and 2 ml of pyridine following the procedure described for 3,7-dimethyloctyl acetate. The resulting ester, 24.8 g, b.p.

82–85° (20 mm), n_D^{25} 1.4133, was pyrolyzed at 500° as described above. There was obtained 8.55 g of (+)-3-methyl-1-hexene, b.p. 82.5°, n_D^{25} 1.3941, α_D^{25} 9.17°.

Catalysts. The palladium-charcoal catalyst used in this study was obtained from Baker and Company, Newark, New Jersey, and contained 5% Pd. The platinum oxide and palladium oxide were also purchased from this source. The 0.5% $Pd(OH)_2$–$CaCO_3$ was prepared by the method of Busch and Stove (*25*) and the Lindlar catalyst was prepared according to Lindlar (*26*).

Hydrogenation Experiments

Apparatus. The vessel for atmospheric pressure reactions consisted of an Erlenmeyer flask with a ground-glass neck and with a side arm which was attached to the flask through a stopcock. A 1000-ml graduated burette, in which dibutyl phthalate served as the containing liquid, was used as the hydrogen reservoir. The reaction mixture was stirred magnetically, and the usual procedure for carrying out low pressure hydrogenations was followed. At the conclusion of a reaction, the catalyst was removed by filtration, and the filtrate was washed repeatedly with water to remove the ethanol. The product was dried over calcium chloride.

The results of studies in which the alkenes were hydrogenated to completion are summarized in Table 2.

Partial hydrogenation of (−)-3,7-dimethyl-1-octene. A 5-g sample of this alkene, α_D^{25} −8.49°, was dissolved in 8 ml of ethanol containing 0.041 g of KOH and hydrogenated in the presence of 0.07 g of Pd(C). Hydrogen uptake ceased at 90% of the theoretical amount. The product was washed thoroughly with water, dried, and combined with the product from a duplicate run. VPC showed that none of the original alkene remained. 2,6-Dimethyloctane, n_D^{25} 1.4080, α_D^{25} 5.57°, was isolated by chromatographing the mixture over silica gel. Calculated for no racemization, α_D^{25} 5.55°.

In another experiment a 7.5 g sample of (−)-3,7-dimethyl-1-octene, α_D^{25} −8.56°, was hydrogenated without solvent until the hydrogen consumption amounted to 25% of the theoretical volume. During the reaction, the flask was surrounded by a 25° water bath to prevent excessive temperature rise. The catalyst was removed and the filtrate was combined with the material from two duplicate runs. VPC analysis showed 50% 3,7-dimethyl-1-octene, 26.5% 2,6-dimethyloctane, and 23.5% isomeric alkenes. Careful fractionation of this material through a 60-cm MiniCal column afforded 3,7-dimethyl-1-octene, α_D^{25} −8.52°, n_D^{25} 1.4142.

Partial hydrogenation of (+)-3-phenyl-1-butene. For a study of possible racemization of the starting alkene, a 4.1-g sample of (+)-3-phenyl-1-butene, α_D^{25} 1.85°, was hydrogenated in the presence of 0.06 g of Pd(C) until 40% of the theoretical amount of hydrogen had been absorbed. The mixture was filtered, the filtrate was combined with the material from a duplicate run, and the mixture was ozonized as described above. The ozonide was reduced with a solution of 5.0 g of lithium aluminum hydride in 55 ml of ether. The mixture was hydrolyzed in the customary way, the ether was stripped, and the residue was chromatographed over alumina. The 2-phenylbutane was eluted with 500 ml of petroleum ether (30–60°), and the remaining material was eluted with methanol (1500 ml). The methanol was evaporated and the residue was distilled, b.p. 95–106° (14 mm), α_D^{25} 3.64°. VPC analysis indicated that 2-phenyl-1-propanol constituted 71% of this material, and 1-phenylethanol constituted the remainder.

Partial hydrogenation of 3-methyl-1-pentene. Samples of this alkene were partially hydrogenated and the composition of the mixtures was determined by VPC on a 4-m decyl phthalate column. The results are plotted in Fig. 1, where the term "isomeric olefins" refers to mixtures of *cis*- and *trans*-3-methyl-2-pentene and 2-ethyl-1-butene.

RESULTS

At the outset of this study, several routes from 3,7-dimethyl-1-octanol to 3,7-dimethyl-1-octene were considered. Acetate ester pyrolysis was the most attractive one, because of the ease with which it could be carried out, but we were concerned over the

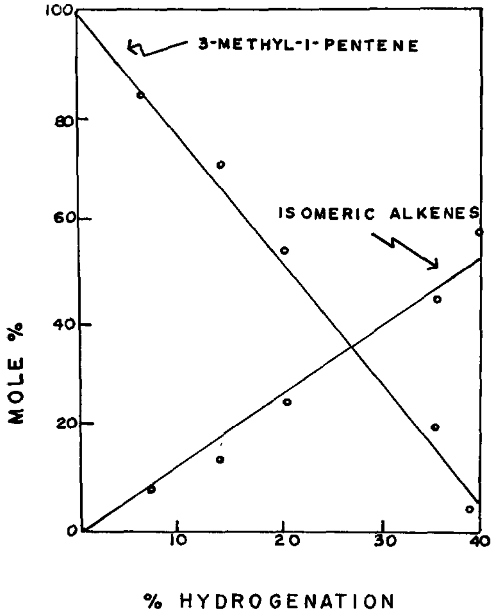

FIG. 1. Double bond migration during hydrogenation of 3-methyl-1-pentene.

TABLE 1
CORRELATION OF ROTATION OF ALKENES AND ALKANES

	$\mathrm{RCHCH{=}CH_2}$ $\mathrm{CH_3}$ (Rotation in °)[a]	$\mathrm{RCHCH_2CH_3}$ $\mathrm{CH_3}$ (Rotation in °)[a]
R = *iso*-$\mathrm{C_6H_{13}}$	−8.05	5.26
R = $\mathrm{C_6H_5}$	−2.22[b]	−8.81[c]
R = $\mathrm{C_3H_7}$	9.17	−4.5[d]

[a] Rotations refer to the homogeneous liquid in a 10-cm tube at 25°.

[b] Corrected for the 3% 2-phenyl-2-butene in the sample.

[c] Calculated from values given by Cram (*24*) for alkene and alkane of the same optical purity, and corrected to 25°.

[d] Estimated from values of Levene and Marker (*27*) who converted (−)-3-methylhexanoic acid, α_D^{26} −2.00° to (−)-3-methylhexane α_D^{21} −5.32°.

possibility that some racemization might occur, since the asymmetric center is an allylic position. The product obtained by this route, however, had essentially the same optical purity as those obtained from samples of the same alcohol by routes involving Hofmann elimination and amine oxide pyrolysis. No detectable double bond migration occurred during pyrolysis of 3,7-dimethyloctyl acetate, but the product from 3-phenylbutyl acetate contained approximately 3% 2-phenyl-2-butene.

Optical rotations of alkenes and the corresponding alkanes having the same optical purity are given in Table 1. The per cent racemization which occurred during hydrogenation was calculated as the per cent difference between the observed rotation of the alkane and the value given in Table 1, or a proportional value if alkene with rotation different from that in the table was used.

Results of the hydrogenation studies are summarized in Table 2. The amount of racemization is seen to be much greater with palladium catalysts than it is with platinum oxide (Run 1). Palladium-charcoal was used for most of the studies; with this catalyst under the usual conditions, approximately 52% racemization occurred, e.g., Run 4. This behavior was observed for several different batches of catalyst, although in the early phases of the study, one catalyst was encountered which gave a greater amount (57–62%) of racemization. Slightly less racemization occurred with palladium on calcium carbonate (Run 7) and still less with an unsupported palladium oxide catalyst (Run 8). When a Lindlar catalyst was used (Run 9), the rate of hydrogen uptake was very low, and the reaction required 12 days for completion. The amount of racemization observed (16%) with this catalyst was surprisingly small.

With palladium-charcoal, the amount of racemization seemed to be nearly independent of the catalyst–substrate ratio, unless the ratio was very small (Runs 2–6). Thus a change in ratio from 0.34 (Run 2) to 0.017 (Run 4) did not affect the amount of racemization. With the extremely small ratio of 0.001 (Run 6), a substantially smaller amount (32%) of racemization occurred.

Although not shown in Table 2, experiments were carried out in which it was found that the extent of racemization did not depend on the rate of stirring. It was also shown that racemization does not occur in the absence of hydrogen.

In Runs 10 and 11, in which hydrogen pressures of 2 atm and 100 atm, respectively,

TABLE 2
HYDROGENATION OF OPTICALLY ACTIVE OLEFINS

Run[a]	Catalyst Kind	Catalyst Wt. (g)	Alkene (g)	Racemization (%)
	(−)-3,7-Dimethyl-1-octene			
1	PtO_2[b]	0.10	2.9	3
2	Pd(C)[c]	1.09	3.2	52
3	Pd(C)	0.53	3.2	52
4	Pd(C)	0.05	3.0	52
5	Pd(C)	0.01	3.1	43
6	Pd(C)	0.003	3.4	32
7	Pd($CaCO_3$)	2.46	2.5	47
8	PdO	0.07	1.3	41
9	Lindlar	0.30	3.0	16
10	Pd(C)[d]	0.11	3.1	37
11	Pd(C)[e]	0.10	3.3	23
12	Pd(C)[f]	0.08	3.8	52
13	Pd(C)[g]	0.10	3.8	12
14	Pd(C)[h]	0.10	3.8	18
15	Pd(C)[b]	0.10	3.8	57
16	Pd(C)[i]	0.10	3.8	56
	(+)-3-Methyl-1-hexene			
17	Pd(C)[j]	0.11	3.3	63
	(−)-3-Phenyl-1-butene			
18	Pd(C)	0.02	2.0	10

[a] Absolute ethanol (ca. 10 ml) was used as solvent unless otherwise specified.

[b] Glacial acetic acid (10 ml) was used as solvent.

[c] In the early phases of the study, one batch of catalyst was found to give somewhat greater amounts (57–62%) racemization.

[d] Hydrogen pressure, 2 atm.

[e] Hydrogen pressure, 100 atm.

[f] No solvent used.

[g] KOH (0.03 g) was added to the reaction mixture. Hydrogen uptake ceased at 90% saturation. The catalyst was removed, PtO_2 and glacial HOAc were added, and the hydrogenation was completed.

[h] Pyridine (3 drops) was added. Hydrogen uptake practically ceased at 80% saturation. Completion of the reaction was achieved by adding PtO_2 and HOAc.

[i] Two drops of concentrated hydrochloric acid were added.

[j] The catalyst was from the batch that gave larger amounts of racemization with 3,7-dimethyl-1-octene. See footnote [c].

were employed, a substantial decrease in amount of racemization was observed.

The same per cent racemization occurs when the reaction is carried out without solvent (Run 12) as when ethanol is used. Slightly greater amounts of racemization occurred when acetic acid was used (Run 15) and when a small amount of hydrochloric acid was added to the ethanol. The differences are small, and may not be significant.

The most striking effect was observed when small amounts of potassium hydroxide or pyridine were added to the reaction mixtures (Runs 13 and 14). The rate of hydrogen uptake was lowered markedly by these bases, and reaction ceased before the theoretical amount of hydrogen had been absorbed. VPC analysis showed that the unsaturated material consisted entirely of double bond isomers of 3,7-dimethyl-1-octene. Saturation was achieved by removing the catalyst, adding platinum oxide and acetic acid, and reattaching the vessel to the apparatus.

In another experiment in which potassium hydroxide was present, the reaction was carried out until hydrogen uptake ceased. The 2,6-dimethyloctane, separated from the reaction mixture by chromatography over silica gel, was found to be unracemized.

The amount of racemization that occurred when (+)-3-methyl-1-hexene was hydrogenated (Run 17) was comparable to that observed with 3,7-dimethyl-1-octene. With (−)-3-phenyl-1-butene, however, the extent of racemization was substantially smaller (Run 18). The amount observed is in agreement with that found by Cram for this compound (*17*).

Experiments were carried out to determine whether or not the active alkenes might suffer substantial racemization by some process other than double bond migration. A sample of (−)-3,7-dimethyl-1-octene was hydrogenated to 25% completion, and the mixture was subjected to careful fractional distillation in an efficient column. Pure 3,7-dimethyl-1-octene of the same optical purity as the starting material was isolated.

We were not able to isolate 3-phenyl-1-butene from mixtures after partial hydrogenation, and consequently it was necessary to use an indirect method for checking racemization of this alkene. Unfortunately, the method chosen is not as clean-cut as could be desired. A sample of (+)-3-phenyl-

1-butene was ozonized and the ozonide was reduced with lithium aluminum hydride. One would expect to obtain 2-phenyl-1-propanol by this sequence, but VPC analysis showed this compound to be present to the extent of only 92%, with the principal contaminant being 1-phenylethanol. Acetophenone is the most likely precursor of the 1-phenylethanol, and consequently it is safe to assume that this alcohol is racemic. In separate experiments it was observed that some acetophenone was formed during ozonolysis of apparently pure 3-phenyl-1-butene. This was particularly noticeable when ozonolysis was carried beyond the end point. On this basis, one calculates that 3-phenyl-1-butene, α_D^{25} 1.85°, gives 2-phenyl-1-propanol, α_D^{25} 5.16°. Another sample of this alkene was hydrogenated to 40% completion and the mixture was ozonized. The ozonide was reduced and the mixture was chromatographed to remove 2-phenylbutane. The product obtained consisted of 71% 2-phenyl-1-propanol with 1-phenylethanol making up the remainder. Again assuming the latter to be inactive leads to a calculated rotation for 2-phenyl-1-propanol of α_D^{25} 5.12°. Thus, it appears that the optical purity of 3-phenyl-1-butene does not decrease appreciably during hydrogenation. When a sample of 3-phenyl-1-butene was hydrogenated to 50% completion, VPC analysis showed that the residual olefin consisted of 90% 3-phenyl-1-butene and 10% 2-phenyl-2-butene.

DISCUSSION

From the results of this study it is apparent that double bond migration is responsible for virtually all of the racemization that occurs during hydrogenation of the optically active alkenes. Other processes can account for not more than a few per cent of the racemization. Thus, when 3,7-dimethyl-1-octene was hydrogenated to 50% completion, 2,6-dimethyloctane was only 7% racemized; the residual olefin consisted entirely of optically inactive double bond isomers of the starting alkene. Approximately 55% racemization occurred with this catalyst when the hydrogenation was carried to completion. Therefore, nearly all of the racemized alkane must have arisen by hydrogenation of alkenes in which the double bond had shifted.

Rapid double bond migration appears to be general for purely aliphatic terminal alkenes. For example, approximately the same amount of racemization occurred with 3-methyl-1-hexene as with 3,7-dimethyl-1-octene, and the infrared spectrum of the material at 50% saturation showed the absence of starting alkene. Furthermore, at 40% hydrogenation of 3-methyl-1-pentene, 3-methyl-2-pentene along with a small amount of 2-ethyl-1-butene constituted practically all of the remaining olefin. (See Fig. 1.)

The slower rate of double bond migration and racemization with 3-phenyl-1-butene is interesting; intuitively one might expect double bond migration to occur faster with this compound than with simple alkenes since the double bond moves into conjugation with an aromatic ring. Indeed, in view of the extensive exchange observed when 3-phenyl-1-butene is treated with deuterium in the presence of palladium (*28*), rapid migration of the point of attachment to the catalyst surface must occur. However, as Burwell has pointed out, this process *per se* does not lead to racemization unless desorption occurs (*29*). Thus the difference between 3-phenyl-1-butene and purely aliphatic alkenes may result from differences in the extent to which desorption of isomerized species occurs.

The presence of base caused a reduction in the rate of the addition reaction, but caused an even greater decrease in the rate of double bond migration. Up to the point where addition ceased, the alkane which formed was unracemized; also, addition of hydrogen ceased when all of the terminal alkene was depleted and only double bond isomers remained. These facts suggest that there are certain sites on the catalyst surface which show enhanced activity for addition, but particularly for double bond migration. These sites are largely deactivated by base. The remaining ones show a low activity for double bond migration, and although capable of catalyzing the addition of hydrogen to terminal alkenes, they are ineffective for the saturation of trisubstituted double bonds.

The same explanation may hold for the decreased amount of racemization observed with the Lindlar catalyst. Possibly the "active sites" are deactivated by the lead ions used for poisoning the catalyst. Also, the smaller amount of racemization observed with very low catalyst-to-hydrocarbon ratio may be a result of partial deactivation by trace impurities in the alkene or by substances formed by a slow surface reaction.

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