washed with water to give 104 mg, mp 229–234° dark red melt. The crude product was placed on two preparative thin layer chromatography plates (silica gel, 20 × 20 cm × 0.5 mm) and developed in the system benzene–acetone–water (2:1:2) (upper phase). After 55 min the plates were removed, dried, and redeveloped for 50 min. The bands containing the product (*ca.* 12.5–15 cm from the origin) were scraped from the plates and eluted with acetone to afford 80 mg of crystalline solid. Crystallization from acetone–hexane and methanol–water gave an analytical specimen of XXIVb, mp 233.5–238° red melt; λ_{max} 240 mμ (ϵ 54,000), 291 (4490), 302 (6600), 316 (8170), 343 (3680), and 356 (3720); $[\alpha]^{25}D$ +229° (acetone).

Anal. Calcd for $C_{18}H_{16}O_2$ (264.31): C, 81.79; H, 6.10. Found: C, 81.30, 82.15, 81.73; H, 6.41, 6.46, 6.83.

Hydroboration of Terpenes. III. Isomerization of (+)-3-Carene to (+)-2-Carene. Hydroboration of (+)-2-Carene (Δ^4-Carene). Nuclear Magnetic Resonance Spectra with Absolute Configurational and Conformational Assignments for the 2-Caranols and 2-Caranones

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Abstract: (+)-3-Carene (**1**) isomerizes to an equilibrium mixture of 40% (+)-2-carene (**2**) and 60% (+)-3-carene (**1**) under the influence of potassium *t*-butoxide in dimethyl sulfoxide. This unfavorable equilibrium is attributed to steric congestion present in both of the possible conformations (**2A**) and (**2B**) for (+)-2-carene. (+)-2-Carene on hydroboration–oxidation gives (−)-2-isocaranol (**10**), which on oxidation gives (−)-2-isocaranone (**7**). In the presence of base, this ketone epimerizes readily to an equilibrium mixture containing (−)-2-caranone (**8**) predominantly (83%). The recent assignment of the absolute configuration for (−)-dihydrocarvone, previously converted into (+)-2-caranone, permits assignment of the absolute configuration of (+)-2-carene and all other derivatives examined in this study. The reduction of (−)-2-isocaranone (**7**) with lithium trimethoxyaluminohydride gives (+)-2-neoisocaranol (**9**) of 96% purity. The other two epimeric alcohols, (−)-2-caranol (**11**) and (+)-2-neocaranol (**12**), have been prepared from (−)-2-caranone by reductions with lithium aluminum hydride and aluminum isopropoxide, respectively. The nmr spectra of the four alcohols and two ketones were subjected to detailed examination. This study revealed that the major alcohol obtained in the lithium aluminum hydride reduction of 2-caranone is 2-caranol (**11**) and not 2-neocaranol (**12**) as reported in the literature. (+)-2-Carene (**2**), like (+)-3-carene (**1**), gives on hydrogenation mainly *cis*-carane (**3**), which is readily distinguishable from the *trans*-carane (**4**) obtained by the Huang–Minlon reduction of (−)-2-caranone. These two hydrocarbons can be distinguished by glpc as well as nmr. Attempts to protonolyze the organoborane from (+)-2-carene (**2**) both in acidic and basic media or by the reduction of the tosylhydrazones from (−)-2-isocaranone and (−)-2-caranone failed to yield pure caranes. The ketones and alcohols have been characterized through their tosylhydrazones and *p*-nitrobenzoates, respectively. It is concluded that 2-carene resembles α-pinene in undergoing hydroboration practically exclusively from the side away from the *gem*-dimethyl groups to provide an entry into the 2-isocaranone series, with a ready entry into the carane series by epimerization of the (−)-2-isocaranone. In the latter respect 2-carene differs markedly from 3-carene, where the 4-isocaranone obtained *via* hydroboration–oxidation is the more stable isomer and cannot be epimerized into 4-caranone.

The report in 1960 that the hydroboration–oxidation of 3-carene (**1**) (Δ^3-carene) yields 4-neocaranol (**15**),[2] with a *trans* addition of the elements of water to the double bond, was startling and prompted an investigation[3] of this proposed exception to the stereochemical characteristics of this hydration procedure.[4,5] In the course of this investigation we came to the conclusion that the assigned configurations[6] of the 4-caranols (**13**, **14**, and **15**) and 4-caranones (**16** and **17**) were in error. However, the unusual stability of 4-isocaranone (**16**) in the epimerization reaction[3] and the flexibility of (+)-3-carene (**1**)[7] introduced a measure of uncertainty into our conclusion that hydroboration was proceeding on the side of the molecule away from the *gem*-dimethyl group (A, Figure 1). It was conceivable that the hydroboration would involve the alternate conformation and takes place preferentially on the side of the *gem*-dimethyl group (B, Figure 1). This ambiguity had been absent in our previous study of the hydroboration of α-pinene.[8] The greater rigidity of the 2-carene (**2**) (C, Figure 1) suggested the essential absence of such an ambiguity in this derivative. Consequently, we undertook a study of the hydroboration of

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(1) Postdoctoral Research Associate, 1965–1966, on Contract No. 12-14-100-7152(72) supported by the Southern Utilization Research and Development Division of the U. S. Department of Agriculture and on Grant No. 5ROI-GM-10937 of the National Institutes of Health.

(2) W. Kuczynski and A. Andrezejak, *Roczniki Chem.*, **34**, 1189 (1960).

(3) H. C. Brown and A. Suzuki, *J. Am. Chem. Soc.*, **89**, 1933 (1967).

(4) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(5) Recently, it has been suggested that the product is not 4-neocaranol, but 4-neoisocaranol (**13**), also involving a *trans* hydration: K. Piatkowski, H. Kuczynski, and A. Kubik, *Roczniki Chem.*, 40, 213 (1966).

(6) H. Kuczynski and Z. Chabudzinski, *ibid.*, **29**, 437 (1955).

(7) S. P. Acharya, *Tetrahedron Letters*, 4117 (1966).

(8) G. Zweifel and H. C. Brown, *J. Am. Chem. Soc.*, **86**, 393 (1964).

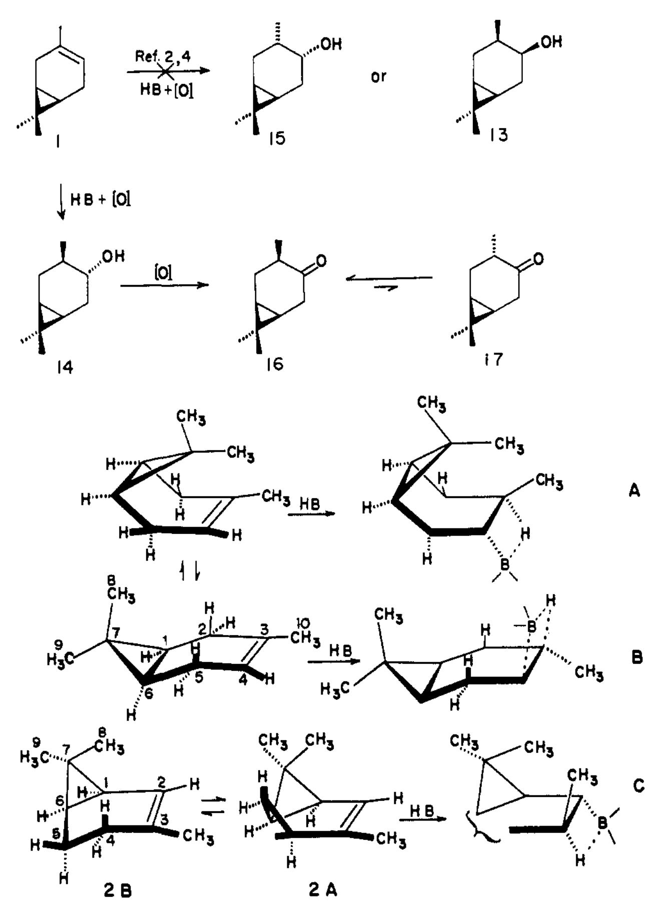

Figure 1. Ambiguities in the hydroboration–oxidation of 3-carene and the conformations of 2-carene.

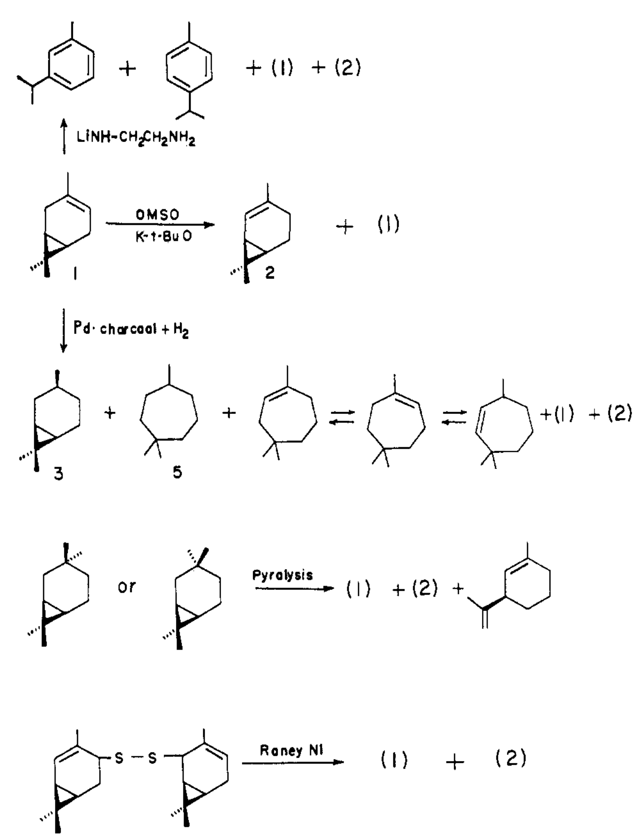

Figure 2. Conversions of 3-carene to 2-carene.

(+)-2-carene (**2**) in the hope that this might lead to derivatives which could be compared directly with the compounds prepared *via* the hydroboration of (+)-3-carene (**1**) and thus resolve the ambiguity.

Accordingly, we deferred publication of our investigation involving (+)-3-carene until we could complete the related study of (+)-2-carene (**2**). Recently, others have reported on this problem.[9,10] Fortunately, the experimental approaches in these studies differ considerably from those we utilized, so the overlap is not significant. However, these studies are in agreement with our conclusion that the original configurational assignments are in error and must be revised.

(+)-3-Carene (**1**) has been isomerized to (+)-2-carene (**2**) by a strong base like ethylenediaminolithium[11] or by palladized charcoal[12] under a hydrogen atmosphere (Figure 2). Both methods invariably yield side products. Thus, the former method gives, from our own experience, both *m*- and *p*-cymenes, the precise amount depending upon the temperature and the time of the reaction (see Experimental Section) whereas the latter method is reported to give a mixture of *cis*-carane (**3**) and 1,1,4-trimethylcycloheptane (**5**) (22%), 2-carene (30%), and 1,1,4-trimethyl-2- (or -3- or -4-) cycloheptene (2.6–6%). The present method involving potassium *t*-butoxide in dimethyl sulfoxide is both simple and rapid and yields an equilibrium of 40% (+)-2-carene (**2**) and 60% (+)-3-carene (**1**) without evidence of any side products to complicate the isolation of the pure sample of (+)-2-carene (**2**).

(+)-2-Carene (**2**) has also been prepared by the pyrolysis of the phenylurethan[5] (see Figure 2), benzoate,[13] or acetate[13] of *trans*-3-caranol and *cis*-3-caranol, or by desulfurization[14] of bis(2-carenyl-4) disulfide with Raney nickel. These methods yield 56–60% (+)-2-carene (**2**), 40% (+)-3-carene (**1**), and the pyrolysis products[13] of 2-carene such as *trans*-$\Delta^{2,8}$-*p*-menthadiene, depending upon the temperature of the pyrolysis.

It is, however, surprizing that equilibration of either (+)-3-carene or (+)-2-carene with a base gives an equilibrium mixture (60:40) containing (+)-3-carene preferentially, in spite of the fact that the double bond in (+)-2-carene (**2**) is in position to conjugate with the cyclopropane ring which should have served to increase its relative thermodynamic stability. This unexpected behavior of (+)-2-carene can be rationalized in terms of the steric interactions present in both of the possible conformations[7] of the olefin (C, Figure 1). Conformation **2B** permits maximum overlap between the cyclopropane ring and the double bond. However, it introduces severe nonbonded interactions between the 8-Me and 4-β-H with an indicated interatomic distance of only 0.2 A. Consequently, conformation **2A** should be more favorable sterically. However, this will be

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(9) W. Cocker, P. V. R. Shannon, and P. A. Staniland, *Tetrahedron Letters*, 1409 (1966).

(10) F. Fringuelli and A. Taticchi, *Farmaco* (Pavia) *Ed. Sci.*, **21**, 476 (1966).

(11) G. Ohloff, K. H. Schulte-Elte, and W. Giersch, *Helv. Chim. Acta*, **48**, 1665 (1965).

(12) W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc., Org.*, 41 (1966).

(13) K. Gollnik and G. Schade, *Tetrahedron*, **22**, 123 (1966).

(14) J. Krupowicz and E. Myslinski, *Roczniki Chem.*, **36**, 1575 (1962).

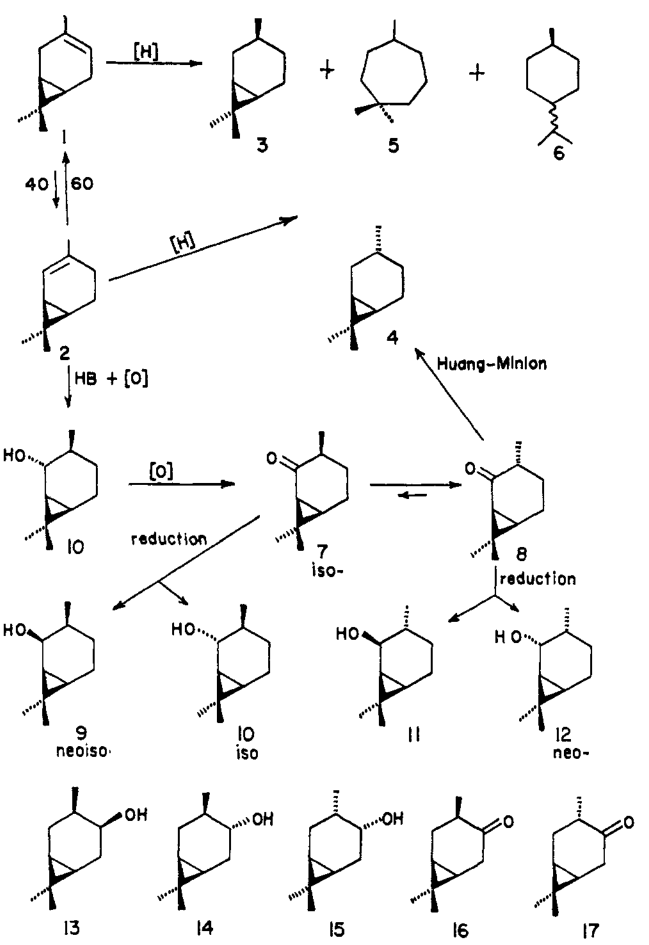

Figure 3. Conversion of 2-carene into the caranones, 2-caranone, 2-isocaranone, and their respective alcohols.

at the expense of the conjugation, since the π orbitals of the double bond make an angle of 15° with the plane of the cyclopropane ring.

(+)-2-Carene (**2**) was separated from the (+)-3-carene (**1**) in the equilibrium mixture by fractional distillation, followed by preparative glpc over a silver nitrate–ethylene glycol–firebrick column. The purified olefin exhibited the following properties: bp 60–61° (24 mm), $n^{20.8}$D 1.4762, α^{28}D +76.36° (neat). The low value of the optical rotation of the (+)-2-carene (**2**) as compared to literature values[11,12] may be due to the use of optically impure (+)-3-carene (**1**) which exhibited α^{20}D +13.51° (neat), indicating 80% optical purity.[12]

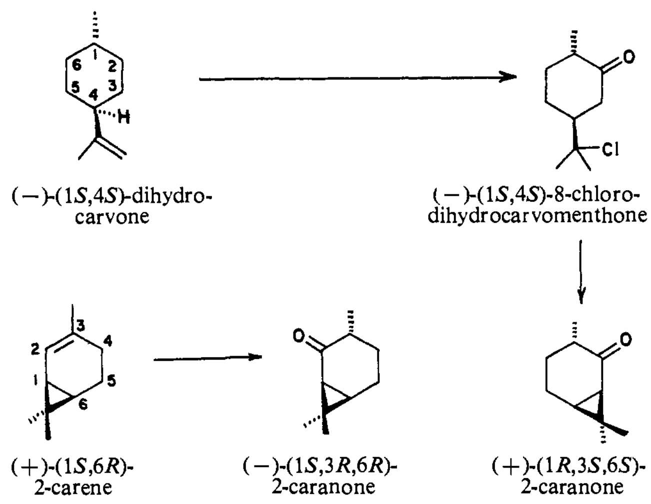

Figure 4. Absolute configurational assignments for (−)-2-caranone and (+)-2-carene.

(+)-2-Carene (**2**) was hydroborated with diborane in tetrahydrofuran at 0° and then oxidized *in situ* in the usual manner with alkaline hydrogen peroxide. There was obtained a single product (−)-2-isocaranol (**10**)[15] (Figure 3), confirmed by glpc on 150-ft, capillary Golay R, Carbowax 20M, Carbowax 1540M, Quadrol, and Apiezon L columns, in essentially quantitative yield. This establishes that there is no unusual difficulty in the hydroboration of a double bond conjugated with a cyclopropyl ring.[16] Oxidation of the alcohol by the ether–chromic acid procedure[17] yielded essentially pure (−)-2-isocaranone (**7**) in 94% yield by glpc and 87% by isolation. At room temperature, sodium ethoxide rapidly isomerized the ketone to a 83:17 mixture of (−)-2-caranone (**8**) and (−)-2-isocaranone (**7**). This is quite similar to the behavior of isopinocamphone,[8] obtained *via* the hydroboration–oxidation of α-pinene, but very different from that of 4-isocaranone[3] (**16**). A pure sample of (−)-2-caranone (**8**) was obtained by preparative glpc using a TCEP–Chromosorb W column. Comparison of the optical properties of these two ketones (**7** and **8**) with those obtained by the base-catalyzed cyclization of (−)-8-chlorocarvomenthone,[18] obtained from (−)-dihydrocarvone,[19] in Figure 4, reveals that these are optical antipodes. Hence the absolute configuration of (+)-2-carene (**2**) and (+)-3-carene (**1**), the ketones **7** and **8**, and all other alcohols **9**, **10**, **11**, and **12** are as represented in Figure 3.

Reduction of 2-isocaranone by lithium trimethoxyaluminohydride, a reagent sensitive to the steric environments of the carbonyl group,[20] yielded 96% of (+)-2-neoisocaranol (**9**) with 4% of the hydroboration–oxidation product, (−)-2-isocaranol (**10**). Reduction of (−)-2-caranone (**8**) with aluminum isopropoxide yielded two epimeric alcohols, (−)-2-caranol (**11**) and 2-neocaranol (**12**) in the ratio 21:79, whereas reduction with lithium aluminum hydride and lithium trimethoxyaluminohydride yielded the same two alcohols in a ratio of 88:12. We propose that the major alcohol produced in the reduction by the two complex hydrides is (−)-2-caranol on the basis of the nmr spectra, although this alcohol has been recently assigned the structure[18] 2-neocaranol (**12**) on the basis of a study of the rates of hydrolysis of the *p*-nitrobenzoates of the two alcohols **11** and **12**. We believe, that the alternate assignment is based on a misinterpretation of Barton's rule.[21] The *p*-nitrobenzoate of the major alcohol

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(15) The numbering system followed is in accordance with that used by *Chemical Abstracts*. The prefix iso is used to indicate that the cyclopropyl and 10-Me are *cis* to each other, and neo is used to indicate that the hydroxyl and 10-Me are *cis* to each other. See also S. H. Schroeter and E. L. Eliel, *J. Org. Chem.*, 30, 1 (1965).

(16) P. Pesnelle and G. Ourisson, *ibid.*, 30, 1744 (1965); B. Rickborn and S. E. Wood, *Chem. Ind.* (London), 162 (1966).

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

(18) A. Hendrick and H. Kuczynski, *Roczniki Chem.*, **39**, 7 (1965).

(19) E. E. Royals and J. C. Leffingwell, *J. Org. Chem.*, **31**, 1937 (1966), have established the absolute configuration of (+)-dihydrocarvone, whereas (+)-2-caranone (Figure 4) is related to (−)-dihydrocarvone: A. J. N. Hope and S. Mitchell, *J. Chem. Soc.*, 4215 (1954).

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

(21) D. H. R. Barton, *J. Chem. Soc.*, 1033 (1953).

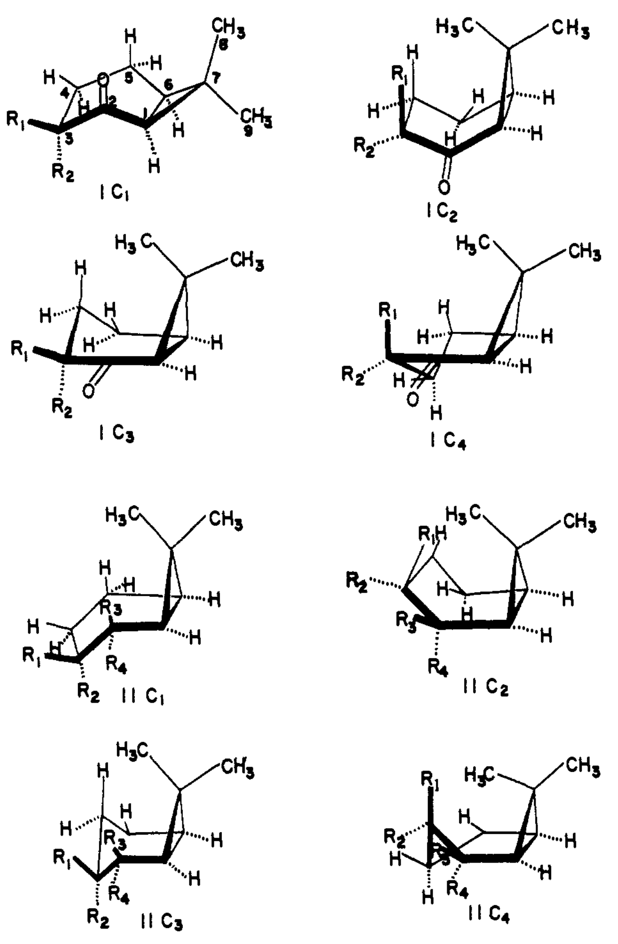

Figure 5. Possible conformations for the 2-caranones and 2-caranols.

obtained from the reduction of (−)-2-caranone (**8**) by lithium aluminum hydride exhibited $k = 1.60 \times 10^{-1}$ and that of the minor one, $k = 6.97 \times 10^{-1}$. On the basis of Barton's rule that cyclohexyl esters having an axial disposition saponify faster than the corresponding equatorial esters, the major alcohol should possess an equatorial -OH and the minor alcohol should have an axial -OH, which correspond to (−)-2-caranol (**11**) and (+)-2-neocaranol (**12**), respectively, in their most favorable conformations (II C₂, II C₄, Figure 5), assigned on the basis of the nmr data. The results of the reduction of (−)-2-isocaranone (**7**) and (−)-2-caranone (**8**) with various reducing agents are summarized in Table I. Pure samples of (+)-2-neoisocaranol (**9**) and (−)-2-caranol (**11**) were obtained by preparative glpc with a Quadrol column.

Table I. Reduction of (−)-2-Isocaranone (**7**) and (−)-2-Caranone (**8**)

Ketone	Reducing agent	Alcohol yield, %	Caranol distribution, % Neo-iso- **9**	Iso- **10**	**11**	Neo- **12**
7	$LiAl(OCH_3)_3H$	89	96	4	..	..
7	$LiAlH_4$	..	33	67	..	..
8	$LiAl(OCH_3)_3H$	86	..	..	88	12
8	$LiAlH_4$	..	..	..	88	12
8	$(i\text{-}PrO)_3Al$	..	..	..	21	79

Hydrogenation of (+)-2-carene (**2**) over borohydride reduced platinum catalyst[22] produced 84% *cis*-carane (**3**) with minor amounts of *trans*-carane (**4**) (12%) and an unidentified product (4%), whereas (+)-3-carene (**1**) gives *cis*-carane and *trans*-carane in the ratio 94:4 and an unidentified product (2%), with the following properties for the carane: $n^{20}\text{D}$ 1.4535, $[\alpha]\text{D}$ −13.0° (benzene). Protonolysis of the organoborane from (+)-3-carene[3] gave pure *cis*-carane: $n^{20}\text{D}$ 1.4542, $[\alpha]\text{D}$ −17.8° (benzene). Pure *trans*-carane (**4**) was obtained by Huang-Minlon reduction of 2-caranone (**8**) and showed $n^{20}\text{D}$ 1.4568, $\alpha^{24}\text{D}$ +55° (neat). These two caranes could be readily distinguished by glpc on a 150-ft, Golay squalene column. Recently, these two caranes have been prepared in a number of ways. Cocker[12,23] reports that *cis*- and *trans*-caranes are indistinguishable[23] by glpc on different columns they tried and that the hydrogenation of (+)-3-carene gives (−)-*cis*-carane (**3**) and 1,1,4-trimethylcycloheptane (**5**) without any traces[12] of *trans*-carane (**4**).

Attempts to prepare (−)-*cis*-carane (**3**) by protonolysis of the hydroboration product from (+)-2-carene both in acidic and basic medium or by the reduction of tosylhydrazone from (−)-2-isocaranone (**7**) with lithium aluminum hydride[24a] or sodium borohydride[24b,c] failed to yield pure *cis*-carane. Pure (+)-*trans*-carane (**4**) also could not be obtained by the reduction of tosylhydrazone from (−)-2-caranone. Evidently, the cyclopropane ring in the adjacent position interferes with these reactions.

In Table II are summarized our data for the ketones and alcohols (and their derivatives) derived from (+)-2-carene.

Spectroscopic Evidences and the Preferred Conformations of 2-Caranones and 2-Caranols

There are four possible conformations for the 2-caranones, one pair being derived from an arrangement in which C-1, C-2, C-3, C-5, and C-6, lie in one plane with C-4 above the plane as in I C₃, or below the plane, as in I C₄, and the other pair being derived from two possible boat forms, as in I C₁ and I C₂.

When the 3-Me has the β configuration, conformations I C₂ and I C₄ are to be neglected because of severe nonbonded interactions between the 8-Me and the 3-β-Me. In conformation I C₃, the distance between the 8-Me and the 4-β-H is less than 0.5 A. Therefore, it appears that the most favorable conformation for 2-isocaranone (**7**) would be one representing a compromise somewhere between I C₃ and I C₁.

When the 3-Me has an α configuration, *i.e.*, when the 3-Me and *gem*-dimethyl are *trans* related, the most favorable conformation would be I C₄, in which the 3-Me is equatorial. The conformation I C₂ is to be neglected because of serious nonbonded interactions present in the boat form. If these considerations, which were based on a close inspection of Dreiding models, are valid,

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[22] H. C. Brown and C. A. Brown, *Tetrahedron Suppl.*, **8**, 149 (1966). We used a commercial model of the automatic hydrogenator now available from the Delmar Scientific Laboratories, Inc., Maywood, Ill.

[23] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc., Org.*, 946 (1966).

[24] (a) L. Caglioti and M. Magi, *Tetrahedron*, **19**, 1127 (1963); (b) L. Caglioti, *ibid.*, **22**, 487 (1966); (c) M. Fischer, Z. Pelah, D. H. Williams, and C. Djerassi, *Chem. Ber.*, **98**, 3236 (1965).

Table II. Properties of 2-Caranols and 2-Caranones

Compound	Bp (mm) or mp, °C	$n^{20}D$	α, deg	t, °C	Concn	Soln
(−)-2-Isocaranol (**10**)	71–72 (2)	1.4778	−30.2	26	Neat	1 dm
p-Nitrobenzoate	86.5–87	...	0	27	14.16	CCl_4
(+)-2-Neoisocaranol (**9**)	63–64 (1)	1.4812	+86.3	28	Neat	1 dm
p-Nitrobenzoate	55.5–56		−128.4	26	7.7	CCl_4
(−)-2-Caranol (**11**)	65 (1)	1.4828	−60.9	26	Neat	1 dm
p-Nitrobenzoate	109.2–110		−99.8	26	16.5	CCl_4
(−)-2-Neocaranol (**12**)[a]	86–87 (6)	1.4828	−18.9	20	...	...
p-Nitrobenzoate	52–54		−12.9	20	4	$CHCl_3$
(−)-2-Isocaranone (**7**)	63–65 (1.5)	1.4740	−62.5	26	Neat	1 dm
Tosylhydrazone	114–115		−43.6	24	7.2	MeOH
(−)-2-Caranone (**8**)	65–66 (1.5)	1.4762	−160	26.2	Neat	1 dm
Tosylhydrazone	114–115		−189.3	24	7.2	MeOH

[a] Values as reported by Kuczynski, *et al.*,[18] but with sign of rotation changed to correspond to (+)-2-carene used in present study.

the following spectral properties could be predicted for the two ketones.

In 2-caranone (**8**) maximum overlap between delocalized electronic system lying in the plane of the three-membered ring[25] and the electronic system (π orbitals) of the carbonyl group is possible, whereas in 2-isocaranone (**7**), with a conformation between I C_1 and I C_3, the situation is much less favorable for coupling between the electronic systems since they make an unfavorable angle, 15–20°, with each other. Therefore 2-caranone (**8**) should have a higher ϵ value in the ultraviolet and a lower carbonyl stretching frequency in the infrared. In the nmr spectrum both the 8-Me and 9-Me should be expected to exhibit a downfield shift owing to the paramagnetic deshielding effect[26] of the carbonyl group or the tosylhydrazone group, but the upfield shift of the 8-Me absorption should be greater in 2-isocaranone (**7**) than in 2-caranone and in their related derivatives. Indeed, these predictions are in excellent agreement with the observed facts, as is evident in Table III.

Table III. Spectral Properties of 2-Caranone and 2-Isocaranone

Compound	Infrared, cm^{-1}	Ultraviolet, λ_{max}[a] 207.5 mμ ϵ	211 mμ ϵ	Nmr, cps (δ 9-Me) − (δ 8-Me)
2-Caranone (**8**)	1682[b]	4430	...	1.5
Tosylhydrazone	1607[c]	...	...	22
2-Isocaranone (**7**)	1695[b]	...	2510	3
Tosylhydrazone	1626[c]	...	...	26

[a] See ref 18. [b] $\nu_{C=O}$. [c] $\nu_{C=N-}$.

This seems to prove conclusively that the ketone, obtained from the alcohol realized in the hydroboration oxidation of 2-carene, has the methyl and *gem*-dimethyl groups in a *cis* relationship, whereas the epimeric ketone has the methyl and *gem*-dimethyl groups in a *trans* relationship and confirms the conclusion that there is no epimerization of the 3-Me group during the formation of the tosylhydrazones.

There are four possible conformations for the 2-caranols, II C_3 and II C_4, both being derived from half-chair forms, and II C_1 and II C_2, both derived from boat forms (Figure 5). The most stable conformations for the two 2-caranols would appear to be those involving neither the two boat forms nor the two half-chair forms exactly, but conformations between the extremes represented by II C_1 and II C_3 when R_1 is methyl and by II C_2 and II C_4 when R_2 is methyl, respectively. Neither R_1, as in II C_4, nor 4-β-H, as in II C_3, is perfectly axial, but each exists in a quasi-axial arrangement to minimize interactions with the 8-Me group. These considerations, which were based entirely on a careful study of Dreiding models, are borne out by the results of infrared and nmr examination of the 2-caranols.

It is known that C–OH stretching in the case of an equatorial hydroxyl group (in the direction of the ring) requires a higher energy[27] than for an axial group (perpendicular to the ring). So equatorial C–OH stretching appears at a higher frequency than axial. Hence, 2-caranol and 2-isocaranol, which have C–OH stretching at 1015 and 1036 cm^{-1}, respectively, should possess equatorial hydroxyl groups, whereas 2-neoisocaranol, with an absorption at 975 cm^{-1} should have an axial OH group.

Owing to paramagnetic currents associated with the hydroxyl group,[3,8] the chemical shift of protons in the immediate vicinity of the hydroxyl group is shifted downfield. So, if the preferred conformations proposed for the various 2-caranols were correct, the chemical shift of the 8-Me should decrease from 2-neoisocaranol (**9**) to 2-caranol (**11**), to 2-isocaranol (**10**), and to 2-neocaranol (**12**), whereas the 9-Me group should be practically unaffected. On the other hand, in the *p*-nitrobenzoates free rotation is possible for the *p*-nitrobenzoate group in the proposed preferred conformations for 2-isocaranol (**10**) and 2-caranol (**11**) resulting in a deshielding of the 8-Me group by the *p*-nitrobenzoate group. In the case of 2-neoisocaranol (**9**) the ester group is sandwiched between the 8-Me and the 3-β-Me thus forcing it to exist in a plane parallel to and facing the 8-Me group. Consequently, free rotation of the *p*-nitrobenzoate group is not possible in this derivative. As a result, the 8-Me group is shielded. That there is a less hindrance for the free rotation of the *p*-nitrobenzoate group as one passes through 2-neoisocaranol, 2-caranol, and 2-isocaranol is supported by the nmr spectra for the aromatic protons. The results are summarized in Table IV.

The data on the nmr spectra for the carbinyl proton also supports the proposed configurational and conformational assignments. It has been established that

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(25) C. Djerassi, W. Klyne, T. Norin, G. Ohloff, and E. Klein, *Tetrahedron*, 21, 163 (1965).

(26) L. M. Jackman, "Applications of Nmr Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1962, p 124.

(27) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 33.

Table IV. Chemical Shift (δ from TMS) of the 8-Me, 9-Me, Hydroxyl, and Aromatic Protons in Carane Derivatives

	δ				
Name	8-Me	9-Me	(8-Me) − (9-Me)	OH proton	Aromatic protons
cis-Carane[a] (**3**)	58	59.5	−1.5	...	...
trans-Carane[a] (**4**)	58	59.5	−1.5	...	...
3-Carene (**1**)	48	64	−16	...	...
2-Carene (**2**)	52.5	63	−10.5	...	...
2-Isocaranone (**7**)	64	67	−3	...	...
2-Caranone (**8**)	70.5	72	−1.5	...	...
2-Neoisocaranol (**9**)	76.5 (1.2)[b]	61 (4.1)[b]	+15.5	103	...
p-Nitrobenzoate	57.5	64	−6.5	...	488[c]
2-Isocaranol (**10**)	58.5 (3.6)[b]	63 (4.5)[b]	−4.5	216	...
p-Nitrobenzoate	68	63	+5	...	493[d]
2-Caranol (**11**)	70 (2.8)[b]	62.5 (4.2)[b]	+7.5	145	...
p-Nitrobenzoate	72.5	60	+12.5	...	491[e]
2-Neocaranol (**12**)	58.5 (3.8)[b]	63 (4.5)[b]	−4.5	175	...

[a] When nmr was run with a 50:50 mixture of *cis*-carane and *trans*-carane at 500 sweep width, the 8-Me and 9-Me were indistinguishable. However, when the spectrum was run at 100 sweep width, a distinct hump was obtained. [b] Distance from OH group in angstroms. [c] Distinct AB pattern, $J_{AB} = 9$ cps. [d] Single peak. [e] Almost merged to a single peak.

Table V. Chemical Shift (δ) of the Carbinyl Proton from TMS in Cps and the Coupling Constant

2-Caranols	Peak position, cps	Preferred conformation	Coupling atoms	Dihedral angle, deg	Coupling constant Calcd[e]	Coupling constant Obsd
Neoiso- (**9**)	256.5[b]	II C$_1$–II C$_3$	ΔH_1–2αH[a]	0 ± 5	9.5	9
			2αH–3αH	60 ± 5	1.8–2.5	2
p-Nitrobenzoate	325[b]	...	...	...	...	...
Iso- (**10**)	175[b]	II C$_1$–II C$_3$	$\Delta\alpha$H–2βH	110 ± 5	1.8–2.5	2
			2βH–3αH	135 ± 5	7–9	8
p-Nitrobenzoate	262.5[b]	...	...	...	...	...
(**11**)	220[c]	II C$_2$–II C$_4$	$\Delta\alpha$H–2αH	30 ± 5	6.2–7.8	6
			2αH–3βH	135 ± 5	7–9	6
p-Nitrobenzoate 307	307	...	...	...	...	...
Neo- (**12**)	218[d]	II C$_2$–II C$_4$	...	...	...	...

[a] Δ means cyclopropane. [b] Broad quartet. [c] Broad triplet. [d] Broad peak. [e] Calculated using modified Karplus equation: K. L. Williamson and W. S. Johnson, *J. Am. Chem. Soc.*, **83**, 231 (1961).

nmr absorption of an axial proton in substituted cyclohexanols occurs at a higher field than that of the equatorial proton.[28] So the peak at 256.5 cps (See Table V) for 2-neoisocaranol indicates that it possesses an equatorial carbinyl proton, while 2-isocaranol (175 cps) has an axial proton, in agreement with assignments. On the other hand, the close similarity in the absorption of the carbinyl protons for 2-neocaranol and 2-caranol makes it impossible to utilize the information for the structural assignments. However, in all four of the alcohols the excellent agreement between the calculated and the observed coupling constants can be considered to provide support for the conformational preference proposed for each of the caranols.

Experimental Section

Materials. (+)-3-Carene, $\alpha^{28.5}\text{D}$ +12.2°, $n^{20}\text{D}$ 1.4732, was a sample generously made available by the Dragoco Co. This was purified by distillation from 96 to 99% purity and was stored under nitrogen in a cold room, bp 170–171 (745 mm), $\alpha^{28.5}\text{D}$ +13.51°, $n^{20}\text{D}$ 1.4732. Dimethyl sulfoxide (100 ml) was refluxed over calcium hydride for 2 hr and then distilled, bp 62° (5 mm). Potassium *t*-butoxide (M.S.A. Co.) was obtained as the sublimed product. Hydrogen peroxide (Mallinckrodt), silver nitrate and platinum chloride (Engelhard Industries), firebrick and Chromosorb W (Wilkens), 1,1,1-tris(2-cyanoethoxymethyl)propane (TCEP) (Eastman), Quadrol (Micro-Tech), squalene (Eastman), lithium aluminum hydride and sodium borohydride (Metal Hydrides), decolorizing carbon, Darco (Atlas), hydrazine hydride (Matheson Coleman and Bell), lithium (Lithium Co.), ethylenediamine (Fischer Scientific), and *p*-tolylsulfonyl hydrazine (Aldrich) were used as such. Diborane in tetrahydrofuran was prepared according to the method described earlier.

Isomerization of (+)-3-Carene with Ethylenediaminolithium. A three-necked flask (100 ml), with a side arm stoppered with a serum cap, was fitted with a thermometer, a reflux condenser with nitrogen inlet, a mercury sealed outlet, and a magnetic stirring bar. The apparatus was flushed with nitrogen and flame-dried. Ethylenediamine (30 ml) was added through a hypodermic syringe and heated to 90–100°; 0.7 g of lithium dissolved to give the reagent. (+)-3-Carene (6.8 g, 50 mmoles) was added, the reaction mixture maintained at constant temperature (20, 50, and 75°), and the course of the isomerization followed by taking a 2-ml aliquot of the reaction mixture periodically and ascertaining its content of (+)-2-carene, (+)-3-carene, and *m*- and *p*-cymene. In no case was it possible to achieve conversion of 3-carene to 2-carene without the concurrent formation of the cymenes (Table VI). Consequently, this procedure was abandoned in favor of that utilizing potassium *t*-butoxide in dimethyl sulfoxide.

Isomerization of (+)-3-Carene by Potassium *t*-Butoxide in Dimethyl Sulfoxide. Using an assembly essentially similar to that above, dimethyl sulfoxide (50 ml) was heated to 50°. Potassium *t*-butoxide (4.6 g) was added through the side arm, followed by the addition of (+)-3-carene (4.76 g), so that the solution was 0.8 *M* in potassium *t*-butoxide and 0.7 *M* in 3-carene. Periodically, 2-ml aliquots of the reaction mixture were taken out and analyzed by glpc. The results at 50, 75, and 100° are given in Table VII.

(+)-2-Carene (2). A three-necked flask, with a side arm stoppered with a serum cap, was fitted with a mechanical stirrer at the center, condenser and the thermometer well at the sides. It was flamed and flushed with nitrogen and then mounted over a heating mantle. Potassium *t*-butoxide (100 g, 0.9 mole) and dimethyl sulfoxide (250 ml) were introduced. When a clear solution had been formed, (+)-3-carene (**1**) (136 g, 142 ml, 1 mole) was added through a hypodermic syringe within 10 min, the reaction mixture

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[28] E. L. Eliel, M. H. Gianne, and T. H. Williams, *Tetrahedron Letters*, 741 (1962).

Table VI. Isomerization of (+)-3-Carene (1) with Ethylenediaminolithium

	Temp, °C					
	20		50		75	
Time, hr	(+)-2-Carene, %	*m*-, *p*-Cymene, %	(+)-2-Carene, %	*m*-, *p*-Cymene, %	(+)-2-Carene, %	*m*-, *p*-Cymene, %
0.17	1	0	23	0	42	0
0.3	4	0.6	..	...	..	..
0.5	..	...	37	..	41	8
1.0	5	0.7	40	3	40	6
1.5	..	...	40	6	38	8
3.3	21	0.7	40	5	37	9
6.0	23	1	40	7	36	10
22.0	36	3	35	8	24	23

Table VII. Isomerization of (+)-3-Carene (1) with Potassium *t*-Butoxide in Dimethyl Sulfoxide

	Temp, °C					
	50		75		100	
Time, hr	(+)-2-Carene, %	*m*-, *p*-Cymenes, %	(+)-2-Carene, %	*m*-, *p*-Cymenes, %	(+)-2-Carene, %	*m*-, *p*-Cymenes, %
0.17	1	0	8	0	21	0
0.3	2	0	21	0	38	0
0.5	4	0	36	0	40	0
1.0	6	0	40	0	40	0
1.5	9	0	40	0	40	0
6.0	21	0	40	0	40	0
22.0	31	0	40	0	40	0

being kept stirred throughout the addition. The solution was heated to 100° and maintained at that temperature for 3 hr, with stirring. A deep pink color developed initially, turning to a dirty green and yellow at the end of the reaction period. (These color changes may be utilized as a criterion for the completion of the reaction.) The reaction mixture was cooled to 20°, petroleum ether (35–37°, 100 ml) was added, and the mixture stirred vigorously. The minimum quantity of water (50–60 ml) was added slowly to dissolve the precipitated potassium *t*-butoxide. Three distinct layers were observed. The lower two layers were separated and extracted with 20 ml of petroleum ether. The combined extracts were washed twice with 10 ml of water, dried over sodium sulfate, and distilled. There was obtained 128 g (98%) of the equilibrium mixture of 2- and 3-carenes, bp 60–61° (24 mm), $\alpha^{28}\text{D}$ +38.25°, $n^{20}\text{D}$ 1.4744. Glpc analysis of the product on a 150-ft, capillary Golay R column indicated that it is a mixture of 59% 3-carene and 41% 2-carene. A pure sample of (+)-2-carene was obtained at 50° by the preparative glpc on an 8-ft column packed with a saturated solution of silver nitrate in ethylene glycol, supported over firebrick 60–80. It had the following properties; bp 60–61 (24 mm), $\alpha^{28.5}\text{D}$ +76.36°, $n^{20.5}\text{D}$ 1.4762.

Isomerization of (+)-2-Carene (2). Potassium *t*-butoxide (1 g) was dissolved in dimethyl sulfoxide (3 ml) and 1 ml of the solution was transferred to a vial and maintained under nitrogen. 2-Carene (0.1 ml) was then added and subjected to isomerization at 100° for 1 hr. Under identical conditions, (+)-3-carene, in a duplicate vial, was subjected to isomerization. Analysis of the two reaction mixtures showed that an identical equilibrium distribution of 60% of (+)-3-carene and 40% of (+)-2-carene had been reached in both cases.

(−)-2-Isocaranol (10). (+)-2-Carene (3.26 g, 23.2 mmoles) was dissolved in tetrahydrofuran (10 ml) and maintained at 0.5° in a round-bottomed flask, previously flame dried and flushed with nitrogen, fitted with a side arm stoppered by a serum cap, a thermometer, and a reflux condenser fitted at the top with a nitrogen inlet and outlet connected to a gas-measuring buret. Diborane solution, in tetrahydrofuran (3.9 ml, 3.44 *M* in BH_3, 40 mmoles of active hydride), was added over a period of 20 min with stirring. It was kept stirring for 2 hr at 0° and 3 hr at room temperature. Excess of hydride was decomposed by adding 0.5 ml of water dissolved in 2 ml of tetrahydrofuran. From the hydrogen evolved, 24 mmoles of hydride had been utilized by the 23.2 mmoles of 2-carene. Thus, the cyclopropane ring had not been attacked. Oxidation with sodium hydroxide (4.0 ml, 3 *M*) and hydrogen peroxide (4.0 ml, 30%) produced only a single isomer, 92% yield by vpc. Distillation yielded 3.0 g (84%) of 2-isocaranol, bp 85–86° (5 mm), $[\alpha]^{26}\text{D}$ −35° (*c* 8, CCl_4), αD −30.23° (neat).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.89; H, 11.80.

***p*-Nitrobenzoate of 2-Isocaranol.** The following procedure was used to prepare the *p*-nitrobenzoates. Tetrahydrofuran (1.5 ml) was placed in a previously flame-dried flask, flushed with nitrogen, and cooled to 0°. 2-Isocaranol (0.233 g, 1.5 mmoles) was added and treated with an equivalent quantity of *n*-butyllithium in ether, followed by *p*-nitrobenzoyl chloride in ether (1.5 ml, 1.5 mmoles). After 2 hr, at room temperature, the reaction mixture was chromatographed through alumina (3 ml) with ether. The solvent was removed, and the product was dissolved in 1.2 ml of *n*-hexane and allowed to crystallize in ice-cold water. The *p*-nitrobenzoate was obtained in a yield of 95%, mp 86.5–87°, $[\alpha]^{27}\text{D}$ 0° (*c* 14.6, CCl_4).

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.41; H, 6.93.

(−)-2-Isocaranone (7). In a four-necked flask (500 ml) fitted with a mechanical stirrer at the center, a condenser, a dropping funnel, and a thermometer well at the sides, was placed ether (50 ml) and 2-isocaranol (3.01 g, 20 mmoles). To this vigorously stirred solution, maintained at 0°, was added over 10 min 25 ml of a chromic acid solution (0°), prepared from 4.0 g of sodium dichromate dihydride (13.5 mmoles), 5.4 g of sulfuric acid (55 mmoles), and sufficient water to make 25 ml of solution. The temperature rise was 5°. After stirring the solution for 5 min, 25 ml of water, previously cooled to 0°, was added, and the lower layer was siphoned out into another flask containing 25 ml of ether maintained at 0°. Siphoning helps to distinguish the two layers and to maintain the temperature at 0° throughout the extraction process. (This was not possible in a separatory funnel.) The ether layer was washed twice with cold water (10 ml), and the aqueous layer was siphoned out. The combined ether layer was washed twice with 5-ml portions of bicarbonate solution, dried over Na_2SO_4, filtered, evaporated, and distilled under reduced pressure to yield (−)-2-isocaranone (7), 2.64 g, 88%. The ketone was 95% pure, as indicated by glpc using TCEP (30%) over Chromosorb W. The other impurities were 3-isocaranone (due to the presence of (+)-3-carene as an impurity in the starting material) and less than 1% 2-caranone. This product exhibited the following properties: bp 63–65° (1.5 mm), $n^{20}\text{D}$ 1.4740, $\alpha^{26}\text{D}$ −62.05°. Attempts to purify the compound by preparative glpc resulted in the isomerization of 2-isocaranone to 2-caranone.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.86; H, 10.58.

***p*-Tolylsulfonylhydrazone of 2-Isocaranone.** 2-Isocaranone (0.5 ml, 0.475 g, 3.125 mmoles), dissolved in dry methanol (2 ml) and *p*-tolylsulfonylhydrazine (1 *M*, 3.12 ml) in tetrahydrofuran, was added and stirred for hours at room temperature under a static pressure of nitrogen. Periodically 10 μl of the solution was picked up and tested for the content of unreacted ketone by glpc on a TCEP column. The reaction was complete after 12 hr. The solution was cooled to −20°, and the tosylhydrazone of the ketone crystallized to yield 0.582 g (58.2%). A further yield of 20% can be obtained by concentrating the volume to half. The product exhibited mp 114–115°, $[\alpha]^{24}\text{D}$ −43.6° (*c* 7.2, MeOH).

Anal. Calcd for $C_{17}H_{24}N_2SO_2$: C, 63.75; H, 7.5; N, 8.75. Found: C, 63.76; H, 7.35; N, 8.75.

(−)-2-Caranone (8). (−)-2-Isocaranone (7) (5.5 g, 36 mmoles) was added dropwise to a stirred solution of 1.24 g of sodium in 25 ml of alcohol at 0° over 5 min and then permitted to come to room temperature overnight. It was diluted with water, acidified with dilute phosphoric acid, and saturated with sodium chloride. After extraction four times with pentane (35–37°), the extract, dried over Na_2SO_4, evaporated and distilled, yielded 5 g of the epimerized ketone, containing 86.5% of 2-caranone and 13.5% of 2-isocaranone. In a separate experiment, when the epimerization was followed at room temperature, it reached the above equilibrium distribution in a matter of minutes. A pure sample of 2-caranone was obtained by the preparative glpc on an 8-ft TCEP (30%)–Chromosorb W column. It showed bp 65–66° (1.5 mm), $n^{20.8}\text{D}$ 1.4762, $\alpha^{26}\text{D}$ −160.05°.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.47; H, 10.69.

***p*-Tolylsulfonylhydrazone of 2-Caranone.** This was prepared as described above, but the reaction was over within 6 hr; the yield in the first crop was 72%, mp 114–115°, $[\alpha]^{24}\mathrm{D}$ −189.3° (*c* 7.5, MeOH). There was no depression in the mixture melting point of the two tosylhydrazones. However, they were established to be different tosylhydrazones by the different values of their rotations and their distinct infrared and nmr spectra.

Anal. Calcd for $C_{17}H_{24}N_2SO_2$: C, 63.75; H, 7.5; N, 8.75. Found: C, 63.69; H, 7.49; N, 8.86.

(+)-2-Neoisocaranol (9). The reagent was prepared as follows. A three-necked flask (300 ml) equipped with a magnetic stirring bar, thermometer, a serum cap attached to a side arm, and a condenser with a nitrogen inlet was flame dried and flushed with nitrogen. To a solution of lithium aluminum hydride in tetrahydrofuran (1.04 *M*, 9.8 ml, 10 mmoles) taken in the above assembly was added dry methanol (0.980 g, 1.35 ml, 30.6 mmoles) dissolved in dry tetrahydrofuran (2 ml) over a period of 1 hr. When a little gel appeared, the addition of methanol was stopped, and the mixture was vigorously stirred until the gel was dissolved. During addition of methanol, hydrogen [875 ml, at 24° (752 mm)] was evolved [theoretically required 867 ml at 24° (752 mm)].

To the above solution of lithium trimethoxyaluminohydride, (−)-2-isocaranone (0.612 g, 4.28 mmoles) dissolved in tetrahydrofuran (2 ml) was added over 15 min at 0.5° with stirring. No hydrogen evolved during addition of the ketone solution. The mixture was then stirred at 23° overnight. Water (0.5 ml) in tetrahydrofuran (1 ml) was then added carefully to destroy the excess of the reducing agent. The thick white precipitate of aluminum hydroxide was treated with a saturated solution of potassium sodium tartarate, the upper layer of tetrahydrofuran was removed, and the lower layer was extracted with ether. The tetrahydrofuran layer and the ether layer were mixed and washed with saturated brine solution, dried over Na_2SO_4, evaporated, and distilled under reduced pressure, yielding 0.543 g, 3.49 mmoles, 88%, bp 63–64° (1 mm). This sample on a Quadrol (30%)–Chromosorb W column was found to contain 95.4% 2-neoisocaranol and 4.6% 2-isocaranol. A pure sample of 2-neoisocaranol was obtained by the preparative glpc over an 8-ft Quadrol (30%)–Chromosorb W column. It showed bp 63–64° (1 mm), $\alpha^{28}\mathrm{D}$ +86.31°, $n^{20}\mathrm{D}$ 1.4812.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.82; H, 11.94.

***p*-Nitrobenzoate of 2-Neoisocaranol.** This was prepared as described above for 2-isocaranol, mp 55.6–56°, $[\alpha]^{26}\mathrm{D}$ −128.41° (*c* 7.72, CCl_4).

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.29; H, 7.10.

(−)-2-Caranol (11). 2-Caranone (0.604 g, 3.97 mmoles) was reduced by the procedure described for 2-neoisocaranol. The yield of the isomeric alcohols was 0.524 g (85.6%) with a distribution of 2-caranol (**11**) to 2-neocaranol (**12**) of 88:12. A pure sample of 2-caranol was obtained by glpc on a Quadrol column, bp 65° (1 mm), $\alpha^{26}\mathrm{D}$ −60.90°, $n^{20}\mathrm{D}$ 1.4828.

Anal. Calcd for $C_{10}H_{16}O$: C, 77.87; H, 11.76. Found: C, 77.79; H, 11.86.

***p*-Nitrobenzoate of 2-Caranol.** It was prepared by the procedure described earlier, mp 109.5–110°, $[\alpha]^{26}\mathrm{D}$ −99.8° (*c* 16.54, CCl_4).

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98. Found: C, 67.48; H, 7.03.

Reduction of 2-Isocaranone (7) and 2-Caranone (8) with Lithium Aluminum Hydride. To a solution of lithium aluminum hydride in tetrahydrofuran (0.5 ml, 1.04 *M*) was added at 0°, 40 μl of 2-isocaranone or 2-caranone, previously dissolved in tetrahydrofuran (0.2 ml) over a period of 5 min and allowed to stand overnight with stirring under nitrogen atmosphere. The reaction mixture was worked up as described above for the reduction by lithium trimethoxyaluminohydride and examined for the content of 2-neoisocaranol, 2-neocaranol, 2-caranol, and 2-neocaranol by glpc on a Quadrol (30%)–Chromosorb W column. The results are summarized in Table I.

(+)-2-Neocaranol (12). A test tube with a side arm, stoppered by a rubber serum cap, was fitted with a 6-in. Vigreux column and a distillation unit. The apparatus was immersed in an oil bath and flushed with nitrogen. To a solution of aluminum isopropoxide (0.4 g, 2.00 mmoles) in anhydrous isopropyl alcohol (10 ml) in the above assembly was added 2-caranone (0.282 g, 1.85 mmoles). The temperature of the oil bath was raised to 90° and the distillation of isopropyl alcohol begun. As the distillation proceeded, additional alcohol was added to the reaction flask through a hypodermic syringe. Isopropyl alcohol (25 ml) was collected in 12 hr. To the residue (2 ml) remaining at the end of the reaction was added pentane (5 ml) and water (0.5 ml), and dilute hydrochloric acid (10%) was added to dissolve the gelatinous precipitate of aluminum hydroxide. The aqueous portion was saturated with NaCl and extracted four times with pentane. The pentane layer was washed twice with brine, concentrated, dried over $MgSO_4$, and distilled. There was obtained 0.192 g of the compound. The product, analyzed by glpc using 8-ft ethylene glycol adipate on a Chromosorb W column, contained 14% 2-caranone, 18% 2-caranol, and 68% 2-neocaranol. If the unreduced 2-caranone is neglected, the ratio of the isomer distribution, 2-neocaranol to 2-caranol, becomes 79:21. The major alcohol obtained in this experiment corresponds to the minor alcohol obtained in the lithium aluminum hydride reduction both by retention time or by the increase in peak height observed when admixed with the pure product. No attempt was made to isolate the pure product. However, the mixture was adequate to observe the nmr spectra of the major component.

Hydrogenation of (+)-2-Carene. In a 125-ml hydrogenation flask[22] were placed absolute ethanol (10 ml), chloroplatinic acid (0.2 *M*, 0.5 ml) in ethanol, and Darco carbon (0.5 g). With vigorous stirring a sodium borohydride solution (1.0 *M*, 3 ml) in ethanol was added as rapidly as possible. After 1 min glacial acetic acid (2 ml) was added. 2-Carene (0.805 g, 6.10 mmoles) was injected and the hydrogenation permitted to proceed to completion. The hydrogenation required 200 min and consumed 25% excess of hydride. The product was analyzed using a 150-ft Golay squalene column and showed three products, identified as 10.8% 1-methyl-4-isopropylcyclohexane (*cis* and/or *trans*) (identified by the increase in the peak height when completely reduced limonene was admixed), 78.9% of *cis*-carane, and 10.3% of a third component, probably *trans*-carane (the peak increases when authentic *trans*-carane was admixed), but possibly 1,1,4-trimethylcycloheptane.[23]

(−)-*cis*-Carene (3). Hydroboration–protonolysis of 3-carene[3] (100 mmoles) yielded 5.6 g of (−)-*cis*-carane, bp 58° (24 mm), free from the impurities present in the hydrogenation product, $n^{20}\mathrm{D}$ 1.4542, $[\alpha]\mathrm{D}$ −17.8° (*c* 2.92, benzene).

(+)-*trans*-Carane (4). 2-Caranone (1.04 g, 6.48 mmoles), hydrazine hydrate (1.7 g, 34.2 mmoles), potassium hydroxide (0.383 g, 6.84 mmoles), and diethylene glycol (freshly distilled, 5 ml) were mixed under anhydrous conditions and heated in a tube fitted with a reflux condenser and a guard tube for 4 hr at 135°. A yellow color, which developed initially, vanished after 2 hr. Diethylene glycol (8 ml) was added, followed by the addition of potassium hydroxide (3.83 g) pellets. The mixture was refluxed for 40 hr at 240° and allowed to cool. The product was taken up in pentane. The pentane layer was removed, passed through alumina (10 g of grade 1), and then eluted with pentane (250 ml). Evaporation of the pentane yielded 0.382 g, 2.77 mmoles, of pure *trans*-carane, bp 78° (35 mm), $\alpha^{24.2}\mathrm{D}$ +55.3°, $n^{20}\mathrm{D}$ 1.4568 The compound showed a single peak on a 150-ft Golay squalene column and the peak appears just after (−)-*cis*-carane.

Attempted Hydroboration–Protonolysis of 2-Carene. 2-Carene was hydroborated in tetrahydrofuran following the procedure described for the preparation of 2-isocaranol. Glacial acetic acid was added. No reaction occurred at room temperature. On heating under reflux, vpc examination revealed 16 different peaks.

Reduction of Tosylhydrazones from 2-Isocaranone and 2-Caranone. The poor solubility of sodium borohydride in dioxane and the poor yield of *cis*-carane from 4-isocaranone prompted us to use lithium aluminum hydride in tetrahydrofuran as the reducing agent to obtain *cis*- and *trans*-caranes from the corresponding tosylhydrazones from 2-isocaranone and 2-caranone. To the lithium aluminum hydride solution (2.4 ml, 3 mmoles), was added the *p*-tosylhydrazone of 2-isocaranone (**7**), or 2-caranone (**8**), or 4-isocaranone (**16**) (0.48 g) dissolved in tetrahyrofuran (1 ml) over a period of 15–20 min. After 2 hr at room temperature, the reaction mixture (50 μl) was removed and centrifuged with water (10 μl), and the supernatant liquid tested for the progress of the reaction by glpc on a 150-ft Golay squalene column. The products so obtained had the composition 73% 4-carene, 19% *cis*-carane, and 8% 3-carene in the case of the tosylhydrazone from 4-isocaranone. The tosylhydrazone of 2-isocaranone yielded 26% *cis*-carane, 44% 2-carene, 16% 3-carene, and 13% of an unknown. Finally, the tosylhydrazone of 2-caranone yielded 19% *trans*-carane, 10% 2-carene, 19% 3-carene, and 52% of two unidentified products. However, when the reaction was repeated with sodium borohydride in dioxane, *cis*- or *trans*-carane to an extent of 20% was obtained together with some unidentified products. It would appear that the cyclopropane ring interferes with this reduction.