# Synthesis and the Iodine-Catalyzed Rearrangement of Isohibaene

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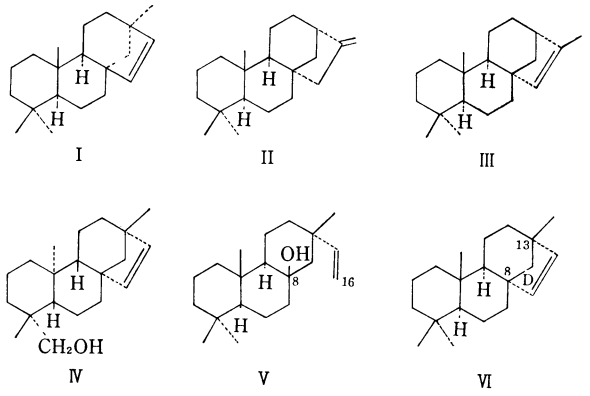
A partial synthesis of isohibaene (VI) starting with nezukol (V) has been accomplished. It involves, as the key step, the intramolecular insertion reaction of a ketocarbene generated by cuprous oxide-catalyzed decomposition of diazoketone (XI) under irradiation. It has been found that isohibaene undergoes rearrangement into a mixture of phyllocladene (XIV) and isophyllocladene (XV) by iodine catalytically.

In a previous paper[1] we (A. Y. and M. K.) reported on iodine-catalyzed skeletal rearrangement equilibrating among (−)-hibaene (I), (+)-kaurene (II), and (+)-isokaurene (III), in which we found hibaene as the most predominant component. The rearrangement was also utilized for the total synthesis of (±)-monogynol[2] (IV).

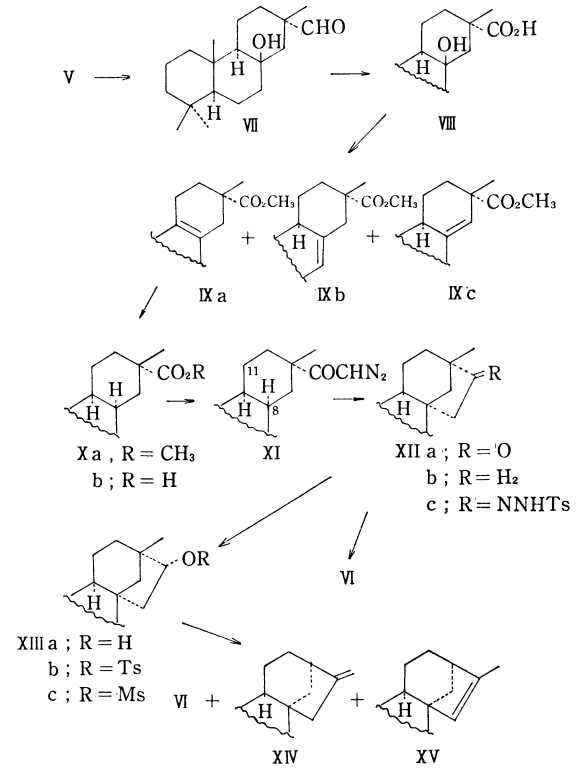
This paper deals with the transformation of nezukol[3] (V) into isohibaene[4] (VI) and the iodine-catalyzed rearrangement of the latter compound, which is a stereoisomer of hibaene concerning the $C_8$ and $C_{13}$ positions.




## Results and Discussion

*A. Synthesis of Isohibaene (VI).* For the construction of the five-membered ring (ring D) of isohibaene by forming a bond between $C_8$ and $C_{16}$ of isopimarane framework (formula V), a copper-catalyzed intramolecular insertion toward a C–H bond[5] as depicted by the step XI→XIIa was seen as a promising process (Scheme 1).

Ozonization of V followed by the reduction of the resulting ozonide with sodium iodide produced hydroxyaldehyde VII along with hydroxy-acid VIII. The former was oxidized with potassium permanganate to obtain VIII. More conveniently, V could be directly oxidized to acid VIII by potassium permanganate in warm acetone. This process gave a better yield. Attempted dehydration of VIII to an unsaturated acid with various dehydrating agents (*e.g.*, thionyl chloride, phosphorus oxychloride, or iodine) resulted in the formation of a complex mixture of products. When VIII was heated in methanol containing a catalytic amount of mineral acid, the acid-catalyzed esterification caused simultaneous dehydration which produced a mixture of the unsaturated esters IXa, IXb, and IXc in the ratio 7 : 2 : 1 (determined by glc). These unsaturated esters were separated by recrystallization and preparative glc, and their structures were assigned as follows. The crystalline ester IXa, the major product, showed no olefinic proton signals in the NMR spectrum and no absorption due to C=C in the IR spectrum. Provided no skeletal rearrangement occurs during the reaction, the double bond of IXa might be located on $\Delta^{8(9)}$. The oily ester IXb, formed in a ratio of 20%, showed a broad olefinic one-proton singlet and absorptions due to a trisubstituted double bond in the NMR and IR spectra, respectively. Hence the structure IXb was




Scheme 1

1) A. Yoshikoshi, K. Kitadani, and Y. Kitahara, *Tetrahedron*, **23**, 1175 (1965).

2) K. Mori, M. Matsui, N. Ikegawa, and Y. Sumiki, *Tetrahedron Lett.*, **1966**, 175; K. Mori and M. Matsui, *Tetrahedron*, **24**, 3095 (1968).

3) M. Kitadani, *Nippon Kagaku Zasshi*, **91**, 664 (1970).

4) For an alternate synthesis of this compound, see E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Amer. Chem. Soc.*, **86**, 2218 (1964).

5) E. Wenkert, B. L. Mylari, and L. L. Davis, *ibid.*, **90**, 3870 (1968).

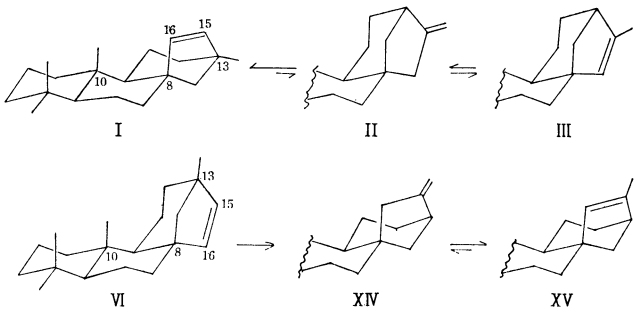
assignable as the ester. The NMR spectrum of the third ester exhibited a narrow olefinic one-proton singlet, and absorptions due to a trisubstituted double bond were shown in the IR spectrum. Thus, the structure IXc is likely to fit the last ester. The unsaturated ester IXa was hydrogenated in acetic acid over platinum under pressure, and the saturated ester Xa was obtained in 90% yield. Conclusive evidence was not available for the stereochemistry of the saturated ester at this stage. However, the fact that the final product of this synthesis was isohibaene (VI) indicated that the saturated ester had a *trans-anti-cis* stereochemistry. For the preparation of Xa, a mixture of the unsaturated esters IXa—c was similarly hydrogenated and gave a better yield of Xa.

The ester Xa, resistant to alkaline hydrolysis under standard conditions, was heated with potassium hydroxide in boiling ethylene glycol to obtain acid Xb. Treatment of Xb with thionyl chloride gave an acyl chloride, and the latter, without purification, was then converted into a diazoketone by the reaction with diazomethane. The IR spectrum of the product showed strong absorptions due to a diazoketo group at 2140 and 1620 $cm^{-1}$, and a sharp singlet due to the methine proton located between a carbonyl and a diazo group were observed at $\delta$ 5.5 in the NMR spectrum. These spectra supported the view that the product was the desired diazoketone XI.

The intramolecular ketocarbene insertion reaction was effected by addition of the diazoketone XI to boiling cyclohexane in which finely powdered cuprous oxide was suspended, while the reaction mixture was irradiated with a tungsten lamp. A ketone, whose carbonyl group showed absorption at 1740 $cm^{-1}$ in IR was obtained almost quantitatively. In XI, two C–H bonds, *i.e.*, $C_8$–H and $C_{11}$–H (axial), toward which the generated ketocarbene may intramolecularly be inserted to form five-membered ketone, were available. Participation of the former bond should lead to the formation of the desired ketone XIIa. The ketone was submitted to the Wolff-Kishner reduction under forced conditions, and the spectra of the resulting hydrocarbon were compared with those of an authentic specimen of isohibane[6] (XIIb). The results including the identity of optical rotation confirmed the hydrocarbon as isohibane. The melting point remained undepressed on admixture with the authentic sample. This demonstrates that the intramolecular ketocarbene insertion toward the *tert.* C–H ($C_8$–H) bond predominated the attack toward the *sec.* C–H bond ($C_{11}$-axial H), as has been generally observed in insertion reactions with other carbenes.[7]

Tosylhydrazone XIIc of the ketone was treated with excess methyl lithium to obtain isohibaene (VI), which was identified by comparison of its IR and NMR spectra with those of an authentic specimen. On the other hand, sodium borohydride reduction of ketone XIIa gave alcohol XIIIa, whose hydroxyl group was tentatively assigned to *endo*. Tosylate XIIIb or mesylate XIIIc of the alcohol was heated in collidine affording a mixture of isohibaene (VI), phyllocladene (XIV), and isophyllocladene (XV). XIV and XV were identified by comparison with authentic specimens.

*B. Iodine-catalyzed Rearrangement of Isohibaene (VI).* Heating isohibaene (VI), phyllocladene (XIV), or isophyllocladene (XV) with a catalytic amount of iodine in boiling xylene caused isomerization of the olefin, and each olefin finally gave a mixture of XIV and XV. In contrast to the rapid isomerization between XIV and XV,[8] isohibaene (VI) rearranged slowly and was exhausted after *ca.* 24 hr. The results on the hibaene-kaurene-isokaurene system[1] and those just mentioned concerning the isohibaene-phyllocladene-isophyllocladene system indicate that the ring system in which the $C_8$–$C_{16}$ bond is *cis* with regard to the $C_{10}$-methyl group is thermodynamically most favorable, *viz.*, in equilibrium, hibaene (I) and isophyllocladene (XV) are most stable in respective series (Scheme 2).




Scheme 2

## Experimental

Melting points were uncorrected. IR and UV spectra were run on JASCO Model IR-E and Hitachi Model 124 spectrophotometers, respectively. NMR spectra with carbon tetrachloride as solvent (unless otherwise stated) and tetramethylsilane ($\delta$=0 ppm) as internal standard were taken on a JEOL JNMC-60HL spectrometer, and coupling constants were given in Hz. Mass spectra were obtained by using a Hitachi RMU-6D spectrometer.

*Ozonization of Nezukol (V).* Excess ozonized air was passed through a solution of nezukol (8.5 g) in ethyl acetate (65 m*l*) at −75°C, and the ozonized solution was treated with sodium iodide (25.5 g) dissolved in acetic acid (85 m*l*). The mixture was allowed to stand overnight at room temperature. Liberated iodine was reduced by the addition of 3% aq. solution of sodium thiosulfate. The resulting solution was concentrated in a vacuum in a bath maintained below 50°C, and the residue was diluted with water. The product was extracted with ether, and the combined extracts were washed with aq. sodium carbonate solution, then with water, and dried over anhydrous magnesium sulfate. Evaporation of the ether left 5.6 g of a semisolid residue, which was recrystallized from ethanol - ether (5:1); 4.85 g (57%) of the hydroxy-aldehyde VII, mp 148—150°C, was obtained as colorless prisms. IR (KBr): 3550, 2725, 1725 $cm^{-1}$. NMR ($CDCl_3$): 7.33 (1H, s., CHO). $M^+$=292.

Found: C, 77.90; H, 10.71%. Calcd for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03%.

6) W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels, *J. Org. Chem.*, **30**, 1873 (1965).

7) W. Kirmse, "Carbene Chemistry," Academic Press, New York (1964).

8) The iodine-catalyzed isomerization of phyllocladene into isophyllocladene has been reported. L. H. Briggs, B. F. Cain, R. C. Cambie, and B. R. Davis, *J. Chem. Soc.*, **1962**, 1840.

The above sodium carbonate extracts were acidified with mineral acid, and liberated carboxylic acid was extracted with ether. From the extracts, 680 mg (7.6%) of the hydroxy-acid VIII, mp 187—189°C, was obtained as colorless leaflets. IR (KBr): 3560, ~2400, 1678 $cm^{-1}$.

Found: C, 73.98; H, 10.46%. Calcd for $C_{19}H_{32}O_3$: C, 74.02; H, 10.13%.

*Permanganate Oxidation of the Hydroxy-aldehyde VII.* To an acetone solution of the hydroxy-aldehyde VII (500 mg) was added potassium permanganate (250 mg) dissolved in water (5 m*l*) over a period of 30 min in an ice-bath. Stirring was continued for an additional 1 hr, and sulfur dioxide was passed through the solution to reduce precipitated manganese dioxide. The resulting solution was filtered and the filtrate was concentrated in a vacuum. The residue was diluted with water and extracted with ether. The extracts were combined, washed with water, and dried. Evaporation of the ether left crystals (500 mg), which were recrystallized from ether - *n*-hexane (1:5) giving hydroxy-acid VIII (498 mg; 94%) metling at 189—190°C.

*Permanganate Oxidation of Nezukol (V).* Powdered potassium permanganate (11 g) was added portionwise to a stirred solution of nezukol (5.0 g) in acetone (130 m*l*). The temperature of the solution rose gradually. Stirring was continued for an additional 13 hr while the temperature was maintained at 50°C. The reaction mixture was allowed to stand overnight at room temperature. Working up as described above for permanganate oxidation of hydroxy-aldehyde VII gave hydroxy-acid VIII (4.7 g; 90%) melting at 189—190°C.

*Unsaturated Esters IXa—c.* A suspension of hydroxy-acid VIII (1 g) in dry methanol (15 m*l*) containing concd. sulfuric acid (0.5 m*l*) was refluxed for 30 min. The reaction mixture was poured into water and extracted with ether. The combined extracts were washed with aq. sodium carbonate solution, then with water, and dried. Evaporation of the ether gave a semisolid residue (890 mg), whose glc (20% PEG-20M column) showed three peaks in the ratio of 7:1:2 in elution sequence. Most of the major product IXa, mp 90—91°C, was separated from the residue by recrystallization with methanol as colorless leaflets. IR (KBr): 1720, 1189 $cm^{-1}$. NMR ($CDCl_3$): 3.64 (3H, s.).

Found: C, 78.94; H, 10.74%. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.57%.

From the filtrate of the recrystallization, two minor esters were separated by preparative glc (20% PEG-20M column; $\phi$, 3 mm×2 m; column temperature, 225°C; hydrogen flow, 30 m*l*/min).

Ester IXb, an oil, corresponded to the last peak in glc. IR (liquid): 1663, 857, 835 $cm^{-1}$. NMR: 3.63 (3H, s.), 5.38 (1H, br. s., $W_{1/2}=10.5$).

Found: C, 78.65; H, 10.83%. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.57%.

Another ester IXc was also oily. IR (liquid): 1730, 856, 836 $cm^{-1}$. NMR: 3.64 (3H, s.), 5.50 (1H, s., $W_{1/2}=4.5$).

Found: C, 78.46; H, 10.89%. Calcd for $C_{20}H_{32}O_2$: C, 78.89; H, 10.57%.

*Hydrogenation of the Unsaturated Ester IXa.* Freshly prepared Adams' catalyst (1.48 g) suspended in acetic acid (100 m*l*) was activated by treatment with hydrogen in an autoclave. A solution of ester IXa (1.5 g) in acetic acid (100 m*l*) was added to the above suspension, and the mixture was shaken with hydrogen under 50 atm at 30°C for 24 hr. After the catalyst was separated, the solution was concentrated in a vacuum. The residue was dissolved in ether. The solution was washed with aq. sodium carbonate solution and then with water. Evaporation of the organic layer gave a crystalline residue (1.45 g) melting at 85—88°C, whose glc showed two peaks in the ratio of 19:1. Recrystallization of the crude crystals from the methanol solution afforded 1.35 g (90%) of the saturated ester Xa, mp 94—96°C. IR (KBr): 1723 $cm^{-1}$. NMR: 3.62 (3H, s.).

Found: C, 78.36; H, 10.92%. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18%.

A mixture of the unsaturated esters IXa—c provided the saturated ester Xa in 98% yield in a similar manner.

*Hydrolysis of the Saturated Ester Xa.* A solution of ester Xa (810 mg) and potassium hydroxide (6.4 g) in freshly distilled ethylene glycol (100 m*l*) was refluxed for 30 min. The solution was concentrated to a half volume by distillation, and then cooled down to room temperature. Water (50 m*l*) was added, and carboxylic acid Xb was extracted with chloroform. The crude carboxylic acid (770 mg) was recrystallized from ether - *n*-hexane (4:1) affording 750 mg (97.5%) of colorless prisms, mp 228—230°C. IR (KBr): ~2400, 1695 $cm^{-1}$.

Found: C, 78.10; H, 10.61%. Calcd for $C_{19}H_{32}O_2$: C, 78.03; H, 11.03%.

*Diazoketone XI.* A solution of acid Xb (1.012 g), thionyl chloride (20 m*l*), and pyridine (5 drops) in dry ether (45 m*l*) was allowed to stand at room temperature for 24 hr. The solvent and the excess reagent were distilled off in a vacuum, and the residue was redissolved in dry ether (20 m*l*). Excess ethereal diazomethane was added into the above solution over a period of 40 min, and the solution was stirred for 2 hr. After standing overnight the solvent was eliminated. The residue was dissolved in a small volume of ether, and the solution was filtered to remove insoluble substances. The filtrate was allowed to stand at room temperature giving 650 mg of pale yellow crystals, mp 118—121°C. The crystals were collected by filtration, and the filtrate was chromatographed on a silica gel column. An additional amount of diazoketone (400 mg), mp 119—122°C, was obtained by eluting with ether - *n*-hexane (1:4). The combined crystals were recrystallized from petroleum ether to give diazoketone XI (980 mg; 90%) as glossy pale yellow leaflets, mp 122—123°C. UV (cyclohexane): 251 nm (log $\varepsilon$ 3.75). IR (KBr): 3150, 2140, 1620 $cm^{-1}$. NMR ($CDCl_3$): 5.5 (1H, s., $COCHN_2$).

Found: C, 76.23; H, 10.14; N, 8.87%. Calcd for $C_{20}H_{32}ON_2$: C, 76.01; H, 10.21; N, 8.87%.

*Ketone XIIa.* To a stirred boiling suspension[9] of finely powdered cuprous oxide (5 g) in dry cyclohexane (150 m*l*) was added dropwise a hot solution of diazoketone (2.71 g) in dry cyclohexane (100 m*l*) over a period of 1.5 hr. Stirring was continued overnight at the same temperature. The catalyst was filtered off. Evaporation of cyclohexane left crystals (2.48 g). Recrystallization from *n*-hexane provided ketone XIIa (2.35 g; 95%), mp 145—146°C, as colorless long needles. IR (KBr): 1740 $cm^{-1}$.

Found: C, 83.65; H, 11.21%. Calcd for $C_{20}H_{32}O$: C, 83.40; H, 11.16%.

An experiment carried out without irradiation gave ketone in a lower yield.

*Isohibane (XIIb).* Sodium (60 mg) was dissolved in freshly distilled ethylene glycol (3 m*l*); ketone XIIa (280 mg) and anhydrous hydrazine (100 mg) were added to the above solution. The solution was refluxed for 2 days. Water was added, and the product was extracted with ether. The ether layer was washed with water and dried. Crystals (210 mg) obtained by evaporating the ether were chromatographed on an alumina column using petroleum ether - ether (9:1) as an eluting solvent giving isohibane (XIIb). Recrystallization

9) A 375 W tungsten lamp (National) was used for heating.

from *n*-hexane gave colorless needles melting at 76—77.5°C (lit,[6] 65—67°C). $[\alpha]_D$+63.4°C (*c* 0.83, methanol) (lit,[6] $[\alpha]_D$+56°).

Found: C, 87.38; H, 12.65%. Calcd for $C_{20}H_{34}$: C, 87.51; H, 12.49%.

The IR and NMR spectra of the hydrocarbon were identical with those of an authentic specimen.

*Tosylhydrazone XIIc.* A solution of ketone XIIa (72 mg) and *p*-tosylhydrazine (65 mg) in ethanol (3 m*l*) was refluxed for 1 hr. Water was added, and the product was extracted with ether and dried. A crystalline residue obtained by evaporation of the solvent was chromatographed on an alumina column, and tosylhydrazone (104 mg) was eluted with methanol - ether (1:20). Recrystallization from methanol - ether (5:1) gave crystals (100 mg; 90%) melting at 206—208°C. UV (methanol): 205 (log $\varepsilon$ 3.99), 228 (log $\varepsilon$ 3.93), 275 (sh.) nm. NMR ($CDCl_3$). 2.44 (3H, s.), 7.30, 7.88 (2H, d., $J$=8 each, an AB-type).

*Isohibaene (VI).* A large excess of methyllithium, prepared from methyl iodide and lithium in dry ether, was added to a suspension of tosylhydrazone XIIc (77.3 mg) in dry ether in an ice bath. The suspension changed into a clear solution after 30 min. Stirring was continued for an additional 2 hr at room temperature. The resulting solution was poured on crushed ice and extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate. The semisolid residue obtained by evaporating the ether was recrystallized from methanol. 40 mg (87%) of isohibaene, mp 83—84°C (lit,[5] mp 73—75°C), was obtained. In spite of the fact that the specific rotation observed for our sample, $[\alpha]_D^{25}$+93° (*c* 0.375, methanol) differs from the value reported for isohibaene ($[\alpha]_D$+8°),[5] the IR and NMR spectra of our sample were identical with those of an authentic specimen. IR (KBr): 751, 740 $cm^{-1}$. NMR: 0.85, 0.88 (3H, s. each), 1.01 (6H, s.), 5.36, 5.51 (1H, d., $J$=6 each; an AB-type). $M^+$=272.

Found: C, 88.25; H, 12.10%. Calcd for $C_{20}H_{32}$: C, 88.16; H, 11.84%.

*Alcohol XIIIa.* Ketone XIIa (628 mg) was dissolved in a 1:1 mixture (20 m*l*) of dry methanol and dry ether, and sodium borohydride (110 mg) was added into the stirred solution in an ice bath. After stirring for 5 hr at the same temperature, the reaction mixture was poured into ice water and extracted with ether. The ether layer was washed with 1N hydrochloric acid, then with water and dried. Ether was evaporated to leave crystals (630 mg), which were recrystallized from methanol to give alcohol XIIIa (625 mg; 96%), mp 130—131°C. IR (KBr): 3490 $cm^{-1}$. NMR: 3.82 (1H, q., $J$=10.2 and 5).

Found: C, 82.58; H, 11.80%. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80%.

*Tosylate XIIIb.* A solution of alcohol XIIIa (1 g) and *p*-toluenesulfonyl chloride (2 g) in dry pyridine (20 m*l*) was allowed to stand for 3 days at room temperature. The reaction mixture was poured into ice-cooled 0.5N hydrochloric acid and extracted with ether. The organic layer was washed with saturated sodium bicarbonate solution, then with water and dried. Evaporation of the solvent left a crystalline residue (1.5 g), which was poured into an alumina column. Elution with ether - petroleum ether (1:5) gave tosylate XIIIb. A pure sample was obtained from petroleum ether by recrystallization as colorless plates (1.35 g; 88%), mp 134—135°C. UV (methanol): 226 (log $\varepsilon$ 3.85), 262 (log $\varepsilon$ 2.42), 273 (log $\varepsilon$ 2.38)nm. IR (KBr): 1598, 1496, 1362, 1188, 1167 $cm^{-1}$. NMR ($CDCl_3$): 2.46 (3H, s.), 4.42 (1H, q., $J$=10 and 5), 7.4, 7.9 (2H, d., $J$=9 each, an AB-type).

Found: C, 73.23; H, 9.30%. Calcd for $C_{27}H_{40}O_3S$: C, 72.94; H, 9.07%.

*Mesylate XIIIc.* From alcohol XIIIa (450 mg) and mesyl chloride (460 mg), mesylate was obtained in 85% yield in the same manner as for tosylate. After recrystallization from chloroform - petroleum ether (1:5) a pure sample melted at 139—141°C. IR (KBr): 1355, 1180, 1170 $cm^{-1}$. NMR ($CDCl_3$): 3.0 (3H, s.), 4.61 (1H, q., $J$=10 and 4.8).

Found: C, 68.75; H, 9.85%. Calcd for $C_{21}H_{36}O_3S$: C, 68.44; H, 9.85%.

*Solvolysis of Sulfonates XIIIb and XIIIc.* A soultion of tosylate XIIIb (800 mg) and freshly distilled collidine (30 m*l*) was refluxed for 40 hr and then concentrated by distillation. The residue was poured into 1N hydrochloric acid and extracted with ether. The organic layer was washed with saturated sodium bicarbonate solution, then with water and dried. Evaporation of the solvent afforded an oily residue which crystallized on standing. Glc analysis (20% PEG-20M column; $\phi$, 3 mm×2 m; column temperature, 200°C; hydrogen flow, 8.3 m*l*/min) showed three peaks (1.4: 1.2: 1.0 in ratio) at the retention times of 4.0, 4.3, and 5.2 min. The reaction mixture was chromatographed on a 10% silver nitrate-impregnated silica gel column to separate each product. Petroleum ether - ether (9:1) eluted isohibaene (VI), mp 82—83°C (153 mg; 40%), (+)-isophyllocladene (XV; 130 mg; 33%), mp 109—111.5°C, $[\alpha]_D^{25}$+25.6° (lit,[10] mp 111—112°C, $[\alpha]_D$+23°) and (+)-phyllocladene (XIV; 110 mg; 28%), mp 94—96°C, $[\alpha]_D^{25}$+19.3° (lit,[11] mp 98°C, $[\alpha]_D$+16°) in order. Under the same conditions as described above, the retention times of isohibaene, isophyllocladene, and phyllocladene in glc were 4.0, 4.3, and 5.2 min., respectively. Each olefin was identified by comparison of its IR and NMR spectra with those of an authentic specimen.

A result in line with ours was obtained for the solvolysis of mesylate XIIIc.

*Iodine-catalyzed Isomerization of Isohibaene, Phyllocladene, and Isophyllocladene.* Each olefin was dissolved in dry xylene, and a piece of iodine was added. The solution was refluxed in an oil bath, while monitoring the reaction by 10% silver nitrate-impregnated silica gel tlc using *n*-hexane - ether - benzene (20: 1: 1) as an eluting solvent. Equilibrium between phyllocladene and isophyllocladene was attained in the predominant formation of the latter after about 2 hr, while isohibaene slowly rearranged into a mixture of phyllocladene and isophyllocladene under the same conditions and was exhausted after about 24 hr.

The reaction mixture of each run was vigorously shaken with mercury and then passed through a short alumina column to removed colored materials. The eluate was rechromatographed on a 10% silver nitrate-impregnated silica gel column affording phyllocladene and isophyllocladene in an approximate ratio of 1:3. These isomerization products were identified by their spectra and melting points on admixture with authentic specimens.

The authors would like to thank Professors Ernest Wenkert and Werner Herz for the identification of isohibaene and isohibane, respectively.

10) R. McCrindale and K. H. Overton, "Advances in Organic Chemistry," Vol. 5, p. 100, ed. by R. A. Raphael, E. D. Taylor, and H. Wynberg, Interscience Publishers, New York (1965).

11) A. W. Johnson, T. J. King, and R. J. Martin, *J. Chem. Soc.*, **1961**, 4420.