

As a reflection of the difference between the chemical shifts of the two vinyl protons, the inner line separation of the *cis* adducts was usually larger than that of the *trans* adducts. The aromatic adducts in general showed smaller values than the aliphatic ones. In the case of the *trans*-4-chloro- and 4-bromo-benzenethiol adducts no inner line separation could be observed.

Infrared.—The infrared spectra were obtained using a Baird recording spectrophotometer. The out-of-plane —CH= deformation of the *trans*-benzenethiol adduct absorbed at 10.45μ , the *trans*-alkyl mercaptan adducts at 10.7μ . The vibrations of symmetrically disubstituted *trans*-ethylenes usually occurred at wave lengths between 10.2 and 10.4μ .^{33b} However, this absorption can be expected at a somewhat higher wave length in the case of our *trans* adducts since a higher wave length range, $10.5\text{--}11.2 \mu$, was also reported for bis(1,2-*p*-tolylmercapto)-ethenes.³¹ Alkylmercaptoethenes also absorb at higher wave lengths, $10.9\text{--}11.2 \mu$.⁴¹

The out-of-plane —CH= deformation vibrations of the *cis* adducts cannot be assigned because of the interesting —CH= deformation vibrations of the aromatics and the uncertainty of the wave length at which the absorption of such *cis* deformation vibrations occur.^{33e} However, it is apparent that the *cis* adducts have stronger absorption peaks than the *trans* adducts in the $12.75\text{--}15.2 \mu$ region. The *trans* adducts usually show wide absorption peaks, the *cis* adducts sharper peaks. Although it is known that *cis*-disubstituted olefins show this absorption between 13.75 and 14.8μ , little is certain about the effect of various substituents on the wave length of the absorption.

Another series of absorptions commonly employed for configurational information are the =C—H in-plane deformation vibrations. For *cis*- and *trans*-olefins, these appear near 7.1 and between 7.6 and 7.75μ , respectively.^{33e} It is apparent from Table VII that there is very little absorption in that region and that this absorption in our cases does not show relationship to the configuration of the compounds. It is interesting to note,

(41) H. J. Bonnstra and L. C. Rinzema, *Rec. trav. chim.*, **79**, 962 (1960).

however, that the *cis*- and *trans*-ethanethiol adducts show a definite difference in absorption at $7.30\text{--}7.35 \mu$. This absorption, however, is probably associated with the CH deformation of the methyl group.^{33d} In general, the spectra of the corresponding *cis* and *trans* compounds are almost identical in the fingerprint region, between 7.5 and 10μ . Similar observations were made by Truce and Groten³¹ in a study of the infrared spectra of 4-tolylmercaptoethenes.

The C=C stretching frequency of the aliphatic thiol adducts apparently occurs at 6μ . This is in the general range of the C=C stretching frequencies,^{33e} although absorptions in the $6.4\text{--}6.6 \mu$ region have been reported for mercaptoethenes.^{31,41} As expected, on the basis of the effect of the symmetry of the molecule at the double bond,^{33f} the *cis* adducts show C=C stretching absorptions of medium intensity. Neither the *cis* nor the *trans* isomers of the aromatic thiol adducts show any significant absorption at 6μ . It is possible that the disappearance of the C=C stretching absorption in these compounds is connected with the increased molecular symmetry.

In the aromatic thiol adducts there are three absorption peaks in the $6.2\text{--}6.4 \mu$ region due to aromatic C=C skeletal vibration,^{33g} while the aliphatic thiol adducts show only two absorption peaks in that region. It is believed that the extra peak of the aromatic thiol adducts is due to the second aromatic group in the molecule.

Like their parent compounds *cis*-sulfone oxidation products of the corresponding sulfide adducts showed no characteristic peaks which could be used to assign their configuration. The presence of the sulfone group, however, could be readily recognized by the strong absorption at about 7.8μ .^{33h}

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Photochemical Reactions. XIII.¹ A Total Synthesis of (\pm)-Thujopsene

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A total synthesis of (\pm)-thujopsene which corroborates the accepted structure is described.

The chemistry and structure of the sesquiterpene thujopsene has been the subject of considerable interest in recent years. The tricyclic hydrocarbon, which was isolated originally from the wood oil of Hiba,³ has been found to occur widely in genera of the natural order Cupressaceae.⁴ The structure of thujopsene (1) was first correctly deduced, in 1960, by Erdtman and Norin,⁵ who assigned the relative stereochemistry shown.⁶ The *cis* relationship of the angular methyl substituent and cyclopropane ring has subsequently been confirmed by a further degradative study⁷ and by a stereospecific total synthesis of thujopsene.⁸

(1) Part XII: J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb, *J. Am. Chem. Soc.*, **85**, 2257 (1963).

(2) Cabot Solar Energy Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow 1963–.

(3) M. Yano, *J. Soc. Chem. Ind. Japan*, **16**, 443 (1913); S. Uchida, *ibid.*, **31**, 501 (1928).

(4) H. Erdtman and B. R. Thomas, *Acta Chem. Scand.*, **12**, 267 (1958).

(5) H. Erdtman and T. Norin, *Chem. Ind. (London)*, 622 (1960); T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961); S. Forsén and T. Norin, *ibid.*, **15**, 592 (1961).

(6) Two other groups arrived at the same gross structure for thujopsene: T. Nozoe, H. Takeshita, S. Ito, T. Ozeki, and S. Seto, *Chem. Pharm. Bull. (Tokyo)*, **8**, 936 (1960), and K. Sisido, H. Nozaki, and T. Imagawa, *J. Org. Chem.*, **26**, 1964 (1961). Both, however, favored a *trans*-fused structure.

(7) T. Norin, *Acta Chem. Scand.*, **17**, 738 (1963).

(8) W. G. Dauben and A. C. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963).



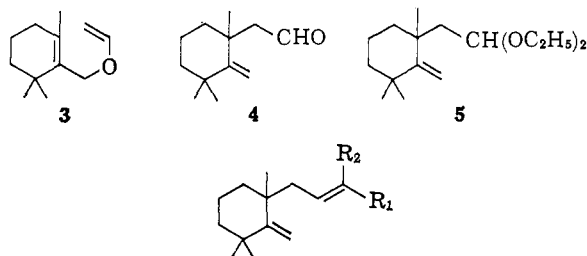
Although the formulation 1 for thujopsene rests secure, it was felt that the unusual tricyclic structure nevertheless constituted a legitimate target for further synthetic work. It was envisaged that decomposition of an intermediate such as 2 might afford a convenient synthesis of thujopsene by an intramolecular addition process, and efforts were therefore directed toward the acquisition of this intermediate.

β -Cyclogeraniol⁹ was chosen as the starting point for the synthesis and was prepared from β -cyclocitral¹⁰ by reduction with sodium borohydride. The vinyl ether 3 was obtained upon refluxing β -cyclogeraniol with an excess of ethyl vinyl ether in the presence of

(9) R. Kuhn and M. Hoffer, *Ber.*, **67**, 357 (1934).

(10) Prepared from citral by cyclization (L. Colombi, A. Bosshard, H. Schinz, and C. F. Seidel, *Helv. Chim. Acta*, **34**, 265 (1951)) followed by base-catalyzed isomerization of the resulting mixture of α - and β -cyclocitral (V. Prelog and H. Frick, *ibid.*, **31**, 417 (1948)). We are indebted to Chas. Pfizer and Co. for a generous supply of citral.

mercuric acetate,¹¹ and its nuclear magnetic resonance spectrum showed peaks at 3.5 (1 H, four lines, X of ABX), 5.9 (2 H, singlet), 6.05 (2 H, eight lines, AB of ABX), 8.0–8.6 (6 H, multiplet), 8.4 (3 H, singlet), and 9.0 τ (6 H, singlet). Pyrolysis of β -cyclogeranyl vinyl ether (**3**) in a continuous flow system at 320° resulted in its smooth conversion to the C₁₂-aldehyde **4**.¹² The infrared spectrum of **4** revealed the presence of both the aldehyde function (2730 and 1720 cm.⁻¹) and the exocyclic methylene grouping (3100, 1640, and 904 cm.⁻¹) and, in agreement with the structure **4**, the nuclear magnetic resonance spectrum of the pyrolysis product showed: 0.3 (1 H, triplet, J 3 c./sec.), 4.8 (1 H, singlet), 5.0 (1 H, singlet), 7.5 (2 H, two doublets,¹³ J 3 and 9 c./sec.), 8.7 (3H, singlet), and 8.8 τ (6 H, singlet).



- 6, R₁ = CH₃, R₂ = CHO
 7, R₁ = CHO, R₂ = CH₃
 8, R₁ = CH₃, R₂ = CH=NNHSO₂C₇H₇
 9, R₁ = CH=NNHSO₂C₇H₇, R₂ = CH₃

Condensation of acetals with vinyl ethers provides a convenient method for the extension of terpenoid side-chains and can be effected under conditions of extremely mild acid catalysis.¹⁴ The aldehyde **4** was accordingly transformed to the diethyl acetal **5** by treatment with ethyl orthoformate and a catalytic amount of *p*-toluenesulfonic acid in ethanol. The acetal was then allowed to react with ethyl propenyl ether in the presence of zinc chloride and the resulting ethoxy acetal, without isolation, was subjected to the action of a solution of sodium acetate in acetic acid. Two α,β -unsaturated aldehydes were obtained and these are assigned the *cis* and *trans* structures **6** and **7**. The major C₁₅-aldehyde, which constituted 92% of the mixture, possessed spectral properties in accord with either **6** or **7**, its configuration being left in doubt by the available evidence. The ultraviolet spectrum of this aldehyde showed $\lambda_{\text{max}}^{\text{isooctane}}$ 227 μ (ϵ 11,000) and its infrared spectrum confirmed the presence of an α,β -unsaturated aldehyde functionality (2720 and 1690 cm.⁻¹), isolated and conjugated C=C bonding (1640 and 1625 cm.⁻¹), and an exocyclic methylene grouping (903 cm.⁻¹). Its proton magnetic resonance spectrum showed absorption at 0.57 (1 H, singlet), 3.6 (1 H, triplet, J 7 c./sec.), 4.8 (1 H, singlet), 5.1 (1 H, singlet), 7.5 (2 H, symmetrical multiplet), 8.3 (3 H, singlet),

8.4–8.6 (6 H, complex multiplet), 8.8 (3 H, singlet), and 8.85 τ (6 H, singlet).¹⁵

The mixture of *cis*- and *trans*-C₁₅-aldehydes was converted to the corresponding tosylhydrazones **8** and **9** by treatment with tosylhydrazide in ethanol at 25°. It was expected that base-induced decomposition of one or both of these tosylhydrazones would lead initially to a diazo compound (**2**) and thence to products arising from an alkenyl carbene.¹⁶ The decomposition of tosylhydrazones has been accomplished under both photochemical¹⁷ and pyrolytic¹⁸ conditions, and in aprotic solvents affords products which may be ascribed to the intermediacy of carbenes. One product which might reasonably be anticipated from this sequence would be that derived from an intramolecular addition to the exocyclic double bond. The favored stereochemical result of such a process should be the *cis* structure **1** since addition with the side chain in an equatorial conformation (*cf.* **2**) would be expected to occur from the side opposite to that on which the 1,3-diaxial methyl substituents are situated. The conformer with axially oriented side chain can lead only to the desired stereochemistry.

The mixture of tosylhydrazones **8** and **9** was dissolved in isooctane containing 5% dry monoglyme and their sodium salts were prepared by addition of sodium hydride. When hydrogen evolution had ceased, the suspension was irradiated with a 450-watt high pressure mercury lamp, using a Pyrex filter. From the hydrocarbon fraction (18%) of the photolysate two components were isolated, the major constituent (10% based on tosylhydrazone) being assigned the cyclopropene structure **10** on the basis of its characteristic spectral properties. The unusually high C=C stretching frequency at 1780 cm.⁻¹ suggested the presence of a cyclopropene¹⁹ and the proton magnetic resonance spectrum confirmed this: 3.45 (1 H, symmetrical multiplet), 5.05 (1 H, singlet), 5.15 (1 H, singlet), 7.9 (3 H, unsymmetrical triplet, J 1 c./s.), 8.4–9.1 (9 H, broad), and 8.8 τ (9 H, singlet).²⁰ Formation of cyclopropenes by decomposition of tosylhydrazones of α,β -unsaturated aldehydes and ketones has been reported previously and evidence has been cited in support of the intervention of alkenyl carbenes in these cases.¹⁶ The second hydrocarbon component (4% based on tosylhydrazone) isolated from the photolysis products was identified as (\pm)-thujopsene by comparison of its

(15) Nuclear magnetic resonance has been shown to provide a basis for determining geometrical configuration in α,β -unsaturated carbonyl systems (L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960)), although unequivocal assignment in such cases can only be made when the spectra of both isomers are available. This possibility was precluded in the present instance by the poor vapor phase chromatographic separation of the two aldehydes and the inability of either chemical or photochemical methods to enrich the mixture in the minor isomer.

(16) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3796 (1963).

(17) W. G. Dauben and F. G. Willey, *ibid.*, **84**, 1497 (1962).

(18) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960).

(19) 1,3-Dimethylcyclopropene is reported to show infrared absorption at 1774 cm.⁻¹ (ref. 16).

(20) The low-field positions of the cyclopropenyl olefinic proton and methyl group are in accord with the proton magnetic resonance spectrum of 1,3,3-trimethylcyclopropene, in which the vinyl proton occurs as a partially resolved symmetrical multiplet at 3.35 τ and the methyl substituent on the double bond gives rise to a narrowly spaced doublet (J 1.1 c./sec.) at 8.0 τ (ref. 22). The diamagnetic anisotropy of the cyclopropene ring, which may account for the deshielding effect on protons lying in the plane of the ring, has been discussed: K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

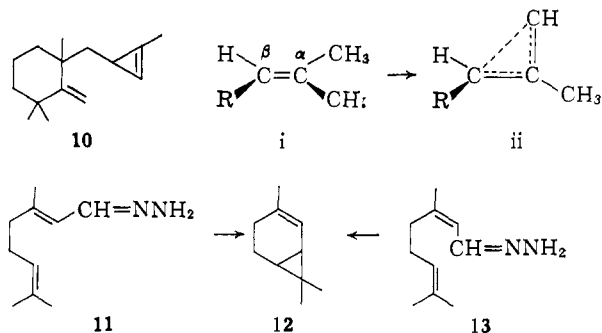
(11) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(12) Cf. A. W. Burgstahler and I. C. Nordin, *ibid.*, **83**, 198 (1961); R. F. Church, R. E. Ireland, and J. A. Marshall, *J. Org. Chem.*, **27**, 1118 (1962).

(13) The magnetic nonequivalence of the two methylene protons may be rationalized in terms of their proximity to a center of asymmetry: J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); G. M. Whitesides, F. Kaplan, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S. A.*, **48**, 1112 (1962).

(14) O. Isler and P. Schudel, "Advances in Organic Chemistry, Methods and Results," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1963, p. 128.

infrared, proton magnetic resonance, and mass spectra with those of the natural product.²¹



The question of whether the stereochemical integrity of the tosylhydrazones **8** and **9** is maintained in the course of their transformation to stable products remains open. However, the mechanism envisaged²² for formation of cyclopropenes from alkenyl carbenes involves rotation of the α,β -bond in **i** through 90° to a configuration (*e.g.*, **ii**) which can lead, in principle, to both configurations of the carbene.²³ Some support for the hypothesis that stereochemical integrity is at least partly lost in the decomposition of diazoalkenes comes from the observation that the hydrazone of geranial (**11**), as well as that of neral (**12**), furnished a low yield of Δ^4 -carene (**13**) on treatment with mercuric oxide followed by irradiation.²⁴

Experimental²⁵

β -Cyclogeraniol.—A solution of 87.0 g. (0.53 mole) of β -cyclocitral in 150 ml. of isopropyl alcohol was added slowly to an ice-cold suspension of 32.0 g. (0.84 mole) of sodium borohydride in 200 ml. of a 1:1 mixture of absolute ethanol and isopropyl alcohol. Stirring was maintained throughout addition. When addition was complete the mixture was allowed to warm to room temperature and stirring was continued for a further hour. The reaction mixture was poured into 1 l. of water and the unreacted borohydride was allowed to decompose. The aqueous phase was saturated with sodium chloride and extracted with ether. The ether extract, after drying (sodium sulfate) and removal of solvent, left a residue which was distilled through a spinning-band column to give 68.0 g. (78%) of β -cyclogeraniol, b.p. 101–103° (10 mm.). The alcohol solidified on standing (m.p. 40–42°) and was identical with β -cyclogeraniol prepared from β -cyclocitral by the method of Kuhn and Hoffer.⁹

β -Cyclogeranyl Vinyl Ether (3).—A solution of 130 g. (0.84 mole) of β -cyclogeraniol and 7.0 g. (0.02 mole) of mercuric acetate

in 2.5 l. of ethyl vinyl ether (distilled before use) was refluxed on the steam bath for 16 hr. Anhydrous potassium carbonate (15 g.) was added and the excess ethyl vinyl ether removed by distillation. The residue was filtered and the carbonate washed with pentane. The washings were added to the filtrate which was concentrated and distilled through a spinning-band column to give 77.0 g. (51%) of β -cyclogeranyl vinyl ether, b.p. 99–101° (15 mm.), and 37.3 g. of recovered β -cyclogeraniol, b.p. 107–109° (15 mm.).

A small amount of the cyclogeranyl vinyl ether was chromatographed on Woelm alumina (Activity III), eluting with hexane, and then distilled to yield an analytical sample, n_D^{25} 1.4783; $\nu_{\max}^{\text{liquid}}$ 1645, 1610, 1315, 1190, 1040, 980, and 809 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{20}\text{O}$: C, 80.07; H, 11.20. Found: C, 79.88; H, 11.18.

1,3,3-Trimethyl-2-methylenecyclohexylacetaldehyde (4).—The pyrolysis apparatus consisted of a vertical 1 cm. diameter Pyrex tube packed over an 18 cm. length with glass helices. The packed section of the tube was surrounded by an electrically heated oven equipped with a thermocouple. The pyrolysis tube was washed with dilute ammonium hydroxide before use and allowed to equilibrate at 320° under a slow stream of nitrogen. Addition of the vinyl ether **3** was accomplished by means of a capillary dropping funnel and the pyrolysate was collected in a trap immersed in a Dry Ice bath. β -Cyclogeranyl vinyl ether (**3**, 136 g., 0.76 mole) was pyrolyzed at 310–320° by continuous passage through the column under a slight positive pressure of nitrogen. The pyrolysate, after distillation, yielded 116 g. (85%) of the aldehyde **4**, b.p. 111–115° (13 mm.), n_D^{25} 1.4812; $\lambda_{\max}^{\text{noctane}}$ 297 m μ (ϵ 16), $\nu_{\max}^{\text{liquid}}$ 3100, 2730, 1720, 1640, 1105, 1045, 1025, 985, and 904 cm^{-1} .

The aldehyde readily afforded a semicarbazone by addition of 0.2 g. of **4** to a solution containing 0.2 g. of semicarbazide hydrochloride and 0.3 g. of sodium acetate in 1 ml. of water. A few drops of ethanol was added and the precipitated semicarbazone collected and recrystallized from ethanol to give colorless rosettes, m.p. 176–177°.

Anal. Calcd. for $\text{C}_{13}\text{H}_{23}\text{N}_3\text{O}$: C, 65.88; H, 9.78; N, 17.73. Found: C, 66.10; H, 9.91; N, 17.56.

1,3,3-Trimethyl-2-methylenecyclohexylacetaldehyde Diethyl Acetal (5).—A solution of 9.70 g. (0.054 mole) of **4**, 11.0 g. (0.075 mole) of ethyl orthoformate, and 25 mg. of *p*-toluenesulfonic acid in 250 ml. of absolute ethanol was allowed to stand at room temperature for 24 hr. The mixture was poured into 500 ml. of water and extracted with ether. The ether extract was washed several times with water, dried (magnesium sulfate), and concentrated. Distillation yielded 12.8 g. (94%) of the acetal **5**, b.p. 144–148° (12 mm.), n_D^{25} 1.4610; $\nu_{\max}^{\text{liquid}}$ 1635, 1350, 1160, 1120, 1100, 1055, 1000, 987, and 901 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{30}\text{O}_2$: C, 75.65; H, 11.91. Found: C, 75.87; H, 12.08.

***cis*- and *trans*-2-Methyl-4-(1,3,3-trimethyl-2-methylenecyclohexyl)crotonaldehyde (6 and 7).**—To 31.0 g. (0.12 mole) of **5** was added 3 ml. of a 10% suspension of zinc chloride (fused and dried under vacuum) in ethyl acetate. Ethyl propenyl ether²⁶ (16.0 g., 0.19 mole) was added dropwise with stirring to this mixture at 45°. After addition was complete the mixture was heated at 60–65° for 24 hr. A solution of 9.5 g. of sodium acetate in 75 ml. of glacial acetic acid and 12 ml. of water was added and the mixture, which consisted of two phases, was stirred at 95° under nitrogen until it became homogeneous (after about 45 min.). The reaction mixture was then poured into 250 ml. of water and extracted with pentane. The pentane extract was washed several times with water and sodium bicarbonate solution and dried (magnesium sulfate). Removal of solvent followed by distillation through a spinning-band column gave 9.10 g. of recovered C_{12} -aldehyde **4**, b.p. 65–69° (0.4 mm.), and 20.7 g. (76%) of the mixture of C_{15} -aldehydes as a pale yellow liquid, b.p. 99–107° (0.4 mm.). Examination of the mixture of C_{15} -aldehydes by thin layer chromatography revealed two spots, both of which gave an orange colored response to 2,4-dinitrophenylhydrazine reagent, with the major aldehyde possessing the larger R_f value. The vapor phase chromatogram of the mixture showed two poorly separated peaks in the ratio 12:1, the major component having the longer retention time.

The major aldehyde was obtained in pure form by prolonging the treatment with sodium acetate in aqueous acetic acid to 3 hr. or more. Work-up as before followed by distillation furnished

(21) In addition to thujopsene and the cyclopropane derivative **10**, five unidentified hydrocarbons were present in the photolysate in minor proportions.

(22) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85**, 99 (1963).

(23) The probability of a further 90° rotation occurring before ring closure to the cyclopropane will depend to some extent on the spin multiplicity of the photochemically generated carbene. As with the addition of methylene to olefins, any appreciable proportion of triplet species should favor a loss of stereospecificity. (See K. P. Kopecky, G. S. Hammond, and P. A. Leermakers, *ibid.*, **84**, 1015 (1962), and references cited therein.)

(24) E. P. Blanchard, Ph.D. Thesis, Massachusetts Institute of Technology, 1959; quoted by P. de Mayo, "Advances in Organic Chemistry, Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 411.

(25) Microanalyses were performed by Midwest Microlab., Inc., Indianapolis, Ind., and by Dr. S. M. Nagy and associates at the Massachusetts Institute of Technology. Melting points were determined on a hot-stage microscope and are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord; the bands listed include those relevant to the structural argument and others of medium or high intensity. Nuclear magnetic resonance spectra were obtained using a Varian A-60 instrument with carbon tetrachloride as solvent and tetramethylsilane as internal standard. Product mixtures were routinely analyzed by means of thin layer chromatography, using silica gel G as adsorbent and 2–6% methanol in benzene as eluent, or by vapor phase chromatography, using a Wilkens Autoprep instrument with column packings made up with either 5% Ucon Polar or 10% SE-30 as the liquid phase.

(26) M. G. Voronkov, *J. Gen. Chem. U.S.S.R.*, **20**, 2131 (1950).

pure aldehyde, b.p. 71–73° (0.05 mm.), n_{D}^{25} 1.5002; $\nu_{\max}^{\text{liquid}}$ 2720, 1690, 1640, 1625, 1210, 1180, 1080, 1005, and 903 cm^{-1} . This material was shown to be homogeneous by vapor phase chromatography and possessed a retention time identical with that of the major component of the mixture.

The major C_{15} -aldehyde, upon treatment with Brady reagent, yielded a 2,4-dinitrophenylhydrazone which was obtained (from ethanol) as orange colored prisms, m.p. 188–189°.

Anal. Calcd. for $C_{21}H_{32}N_4O_4$: C, 63.05; H, 7.06; N, 14.01. Found: C, 62.96; H, 7.24; N, 13.87.

cis- and *trans*-2-Methyl-4-(1,3,3-trimethyl-2-methylenecyclohexyl)crotonaldehyde Tosylhydrazones (8 and 9).—A solution of 5.06 g. (23 mmoles) of the mixture of 6 and 7 and 5.40 g. (29 mmoles) of tosylhydrazine in 100 ml. of ethanol was allowed to stand at room temperature for 24 hr. Water (150 ml.) was added and 7.12 g. (81%) of an oily mixture of the *cis*- and *trans*-tosylhydrazones 8 and 9 was collected. This mixture was taken up in hot aqueous ethanol which was allowed to cool slowly with seeding to precipitate the tosylhydrazone of the major C_{15} -aldehyde. Recrystallization from aqueous ethanol followed by drying *in vacuo* afforded the major tosylhydrazone as colorless prisms, m.p. 91–93° dec.; $\lambda_{\max}^{\text{EtOH}}$ 227 and 253 μ ; ν_{\max}^{CROH} 3230, 1640, 1605, 1500, 1365, 1320, 1165, 1095, 1045, 1025, 953, 909, and 817 cm^{-1} .

Anal. Calcd. for $C_{22}H_{32}N_2O_2S$: C, 68.10; H, 8.31; N, 7.22. Found: C, 67.88; H, 8.19; N, 7.27.

Chromatography of 1.20 g. of the oily mixture of tosylhydrazones on Merck acid-washed alumina yielded 920 mg. of pure major tosylhydrazone and 78 mg. of the minor isomer (*ca.* 90% pure). The infrared spectra of the two tosylhydrazones were similar, but differences of band position and intensity were apparent in the 800–1300 cm^{-1} region. Thin layer chromatography indicated that the major isomer possessed the larger R_f value on both silica gel and alumina.

Irradiation of the Sodium Salts of *cis*- and *trans*-2-Methyl-4-(1,3,3-trimethyl-2-methylenecyclohexyl)crotonaldehyde Tosyl-

hydrazones.—The irradiation apparatus consisted of a reaction vessel surrounding a quartz water-cooling jacket of slightly smaller diameter, leaving an annular space of 160-ml. capacity. The reaction vessel was equipped with a gas inlet at its base and a side-arm to which was attached a reflux condenser. A 450-watt Hanovia high pressure mercury arc surrounded with a Pyrex sleeve was placed in an immersion well in the water jacket.

A solution of 3.42 g. (8.8 mmoles) of the mixture of 8 and 9 in 150 ml. of isooctane (Fischer Spectranalyzed) containing 10 ml. of dry monoglyme was placed in the irradiation vessel and purged with a stream of dry nitrogen. Sodium hydride (0.5 g.) was added and the sodium salts of the tosylhydrazones formed as a yellow suspension with evolution of hydrogen. When hydrogen evolution had ceased (after 5 min.), the suspension, which was kept agitated with a brisk stream of nitrogen, was irradiated for 1 hr., during which a copious precipitate of the *p*-toluenesulfinate salt settled out. The photolysate was poured into 250 ml. of water and extracted with pentane. The pentane extract was dried (magnesium sulfate) and the solvent removed to yield 1.81 g. of a yellow oil which was chromatographed on Woelm neutral (Activity I) alumina. The first fraction to be eluted with hexane consisted of 171 mg. (10%) of virtually pure 10, $\nu_{\max}^{\text{liquid}}$ 3160, 1780, 1630, 1180, 1095, 978, 901, and 697 cm^{-1} . This hydrocarbon polymerizes rapidly at room temperature. Subsequent fractions were found to be mixtures and were combined (127 mg.) and subjected to vapor phase chromatographic analysis. The major component (51%, 4% based on tosylhydrazone) possessed a retention time identical with that of natural thujopsene and, when collected and distilled, had an infrared spectrum and mass spectral fragmentation pattern identical with those of the natural product.²⁷

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(27) A sample of natural thujopsene was kindly supplied by Drs. M. Stoll and E. Demole, Firmenich et Cie., Geneva, Switzerland.

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

The Condensation of Camphene and Phenol. Product Formation *via* a Direct 2,6-Hydride Transfer¹

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Reaction of *dl*-camphene and phenol at 0° with catalytic quantities of boron trifluoride etherate yielded isobornyl phenyl ether (1) in 80% yield. In contrast, treatment of camphene and phenol with boron trifluoride etherate under C-alkylation conditions (100°) afforded not only the *o*- and *p*-isobornylphenols (2 and 3) but also the *o*- and *p*-6-*exo*-hydroxyphenyl-*exo*-isocamphanes (4 and 5). Product formation was stereospecific as evidenced by absence of the bornylphenols 7 and 8, the camphenehydrophenols 9 and 10, and the 6-*exo*-hydroxyphenyl-*endo*-isocamphanes (11 and 12) in the reaction mixture. Reaction of *l*-bornyl acetate, $[\alpha]_D^{25} -38.3^\circ$, with phenol afforded the same completely racemic products in comparable yields. The corresponding 6-*exo*-acetoxy-*exo*-isocamphane (29) was not detected in the product mixture when camphene was treated with acetic acid under the same conditions. A mechanism to account for the observed facts is presented.

The formation of products from carbonium ions *via* a 1,3-hydride transfer is well documented for acyclic,² cyclic,³ and bicyclic systems.⁴ In each of these re-

(1) Presented at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

(2) (a) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **84**, 3962 (1962); (b) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962), and reference cited therein; (c) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950); (d) N. L. Wendler, R. P. Graber, and F. W. Bollinger, *Chem. Ind.* (London), 1312 (1956).

(3) (a) A. C. Cope, H. E. Johnson, and J. S. Stevenson, *J. Am. Chem. Soc.*, **78**, 5599 (1956), and references cited therein; (b) V. Prelog and W. Kung, *Helv. Chim. Acta*, **39**, 1394 (1956), and references cited therein.

(4) W. von E. Doering and A. P. Wolf, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, Abstracts, p. 437; *Perfumery Essent. Oil Record*, **42**, 414 (1951); *Chem. Abstr.*, **46**, 7080 (1952); (b) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); (c) P. de Mayo, "The Chemistry of Natural Products. Vol. II. Mono- and Sesquiterpenoids," Interscience Publishers, Inc., New York, N. Y., 1959, pp. 161–170; (d) J. A. Berson, "Carbonium Ion Rearrangements in Bridged Bicyclic Systems," Chapter 3 in "Molecular Rearrangements," edited by P. de Mayo, Interscience Publishers, Inc., New York, N. Y., 1963, pp. 139–155.

corded examples, however, the 1,3-hydride shift proceeds *via* transition from a less stable (higher energy) carbonium ion to a more stable ion (*i.e.*, primary ion \rightarrow secondary or tertiary ion; secondary ion \rightarrow tertiary ion) or by interconversion of two equienergetic secondary ions. We wish to report the first example of a reaction in which products are formed *via* a 1,3-hydride transformation involving conversion of a tertiary carbonium ion to a secondary ion⁵: the condensation of camphene and phenol.⁶ We have found in fact that

(5) Product formation *via* a 1,3-hydride transfer involving transition from a tertiary to a secondary carbonium ion does have a possible analogy in the Lewis acid catalyzed conversion of *endo*-tetrahydrodicyclopentadiene to adamantane. The driving force for this transformation has been postulated as relief of strain in the bicyclo[2.2.1]heptane ring. Since the over-all process is irreversible, the equilibrium is shifted from an initially formed tertiary carbonium ion to a secondary ion. P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).