Geometry of Olefins and Diolefins. I[1]

KENNETH W. GREENLEE AND VINCENT G. WILEY

Department of Chemistry, The Ohio State University, Columbus, Ohio

Received January 22, 1962

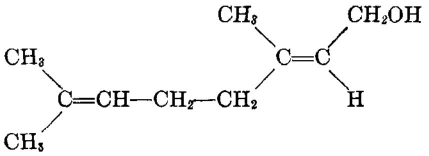
The *cis* and *trans* isomers of 2,6-dimethyl-2,6-octadiene have been made, by reduction (respectively) of nerol and geraniol, terpene alcohols of known geometric configuration. Study of these products suggests the tentative generalization that, among monoolefins of the 3-methyl-2-alkene type, the *cis* isomers have lower boiling points than their *trans* counterparts.

The assignment of geometric identity to numerous *cis* and *trans* pairs of *n*-alkenes (dialkylethylenes) is now accepted without question. In fact, the identification is done routinely by stereospecific synthesis[2–4] or by infrared spectra.[5,6] Some generalizations relative to physical properties and structure are possible within this group. For example, among the normal 2-alkenes the *cis* isomer always boils appreciably higher than the *trans.*

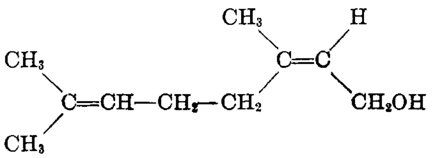
Until recently, no pair of geometrically isomeric trialkylethylenes had been proved as to structure, though a few pairs had been given tentative and conflicting assignments.[7–9] The very nomenclature of this group of olefins was uncertain until it was decided[10] that the geometry should be fixed with reference to the longest straight chain including the double bond. Moreover, it has not been possible to divide them into two distinct groups on the basis of infrared spectral characteristics. Now, however, a tentative generalization can be made that within the series of 3-methyl-2-alkenes the *trans* isomers boil higher than their *cis* counterparts.

In 1959, Cornforth, *et al.*,[11] reported the synthesis of both 3-methyl-2-pentenes, showing that the *cis* isomer boils at 67–68° and the *trans* at 70–71°. Their *cis* olefin was derived by straightforward reduction of the lactone of 5-hydroxy-3-methyl-3-pentenoic acid—a cyclic structure whose *cis* configuration cannot be doubted; their *trans* olefin was similarly derived from the isomeric (*trans*) acid which forms *no* lactone. In 1960, Onesta and Castelfranchi[12] reported the preparation of the two 3-methyl-2-pentenes and the related pair of 3,4-dimethyl-2-pentenes by the pyrolysis of the benzoates of appropriate tertiary alcohols. In both cases the higher boiling isomer predominated and was labeled *trans*, after a consideration of the pyrolysis mechanism. They postulated that a cyclic intermediate forms, which involves less strain in the *trans* yielding configuration than in the *cis.*

Before either of these reports appeared, the present authors had obtained relevant results in another way. Geraniol and nerol have long been known to be geometrically isomeric forms of 3,7-dimethyl-2,6-octadiene-1-ol.[13] In relatively recent years the structure of geraniol has been shown[14] by X-ray analysis to be *trans* with respect to the geometry around the double bond in the 2-3 position. (Note: Isomerism is absent around the double bond at the 6-7 position). Therefore, nerol is proved by elimination to be the *cis* isomer. If these alcohols could be obtained reasonably pure and deoxygenated without disturbing the geometry around the double bond, there would result two diolefins with definite structures differing only in the configuration around one triply substituted ethylenic group.



geraniol



nerol

The most promising method of converting these alcohols to the desired hydrocarbons seemed to be the reduction by sodium and alcohol in liquid ammonia discovered by Chablay.[15] He found that allylic alcohols in general are partly reduced to hydrocarbons and partly converted to alcoholates by sodium in ammonia, whereas reduction to the

---

[1] Presented before the American Chemical Society Organic Division at the 138th National Meeting, September, 1960. First submitted on January 1, 1959.

[2] K. N. Campbell and M. J. O'Connor, *J. Am. Chem. Soc.*, **61**, 2897 (1939).

[3] K. N. Campbell and L. T. Eby, *ibid.*, **63**, 217, 2683 (1941).

[4] A. L. Henne and K. W. Greenlee, *ibid.*, **65**, 2020 (1943).

[5] H. J. Hall and I. A. Mikos, *Anal. Chem.*, **21**, 422 (1949).

[6] L. J. Bellamy, The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, 1958, pp. 45–49.

[7] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

[8] G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Co., New York, 1939.

[9] Beilstein's "Handbuch der Organischen Chemie," Vol. I, 4th ed., 3rd Suppl., Springer Verlag, Berlin, pp. 813–814.

[10] American Chemical Society Official Reports, *Chem. Eng. News*, **27**, 1303 (1949).

[11] J. W. Cornforth, R. H. Cornforth, and K. K. Mathew, *J. Chem. Soc.*, 112 (1959).

[12] R. Onesta and G. Castelfranchi, *Chim. Ind.* (Milan), **42**, 735 (1960).

[13] J. L. Simonsen, "The Terpenes," Vol. I, 2nd ed., Cambridge University Press, 1947.

[14] G. A. Jeffrey, *Proc. Roy. Soc.* (London), **183A**, 388 (1945).

[15] M. E. Chablay, *Ann. Chim.*, (9), **8**, 145 (1917).

TABLE I

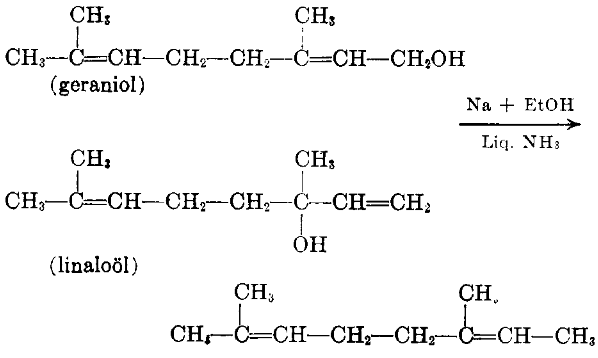
PROPERTIES OF NEROL AND GERANIOL

	Nerol		Geraniol	
	This work	Literature[a]	This work	Literature[a]
B.p./760	226.2°	224–227°	231°	230°
B.p./pressure	105–106°/10 mm.	105°/12	108–110°/10	107°/8
n^{20}_D	1.4749	1.4750[b]	1.4768	1.4766
d^{20}_4	0.8760	0.8813	0.8801	0.8894

[a] Heilbron, "Dictionary of Organic Compounds." [b] Corrected from 1.4795 (n^{11}_D) given in ref. 20.

hydrocarbon can be fairly complete if the allylic alcohol is mixed with a nonreducible alcohol (as proton donor) and added to a substantial excess of sodium dissolved in ammonia. Geraniol and its structural isomer linaloöl (3,7-dimethyl-1,6-octadiene-3-ol), but not nerol, were among those used to illustrate the method, and they were reduced with equal ease to what appeared to be the same hydrocarbon (b.p. 169–171°/764 mm., d = 0.775). Despite these properties (identical for the two) Chablay supposed that the product from geraniol was 2,6-dimethyl-2,6-octadiene and that from linaloöl was 2,6-dimethyl-2,7-octadiene, the products which would be formed if no double-bond shift occurred in either case; his attempts to prove these structures by oxidation failed, however. He did not discuss the geometric configuration of geraniol (not known until much later) or of the derived hydrocarbon.

Several investigators[16–19] have since repeated Chablay's reduction of geraniol and linaloöl and established the fact that the hydrocarbon products are identical,[20] being 2,6-dimethyl-2,6-octadiene (geometric configuration not mentioned). Obviously the terminal double bond of linaloöl becomes interior in the process of reduction, while the double bond of geraniol (being interior already) is unmoved.



$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2OH$

(geraniol)

$\xrightarrow[\text{Liq. NH}_3]{\text{Na + EtOH}}$

$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\underset{OH}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH=CH_2$

(linaloöl)

$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$

Considerable experience with this type of reaction[21] has proved that the double bond shifts one space whenever a more stable compound will result but remains substantially unmoved when it is already in the position of greatest stability. Thus, the shift will readily occur from a 1,2-position to a 2,3-position or from an unbranched position to a branched one, but only to a scant extent in the opposite direction. However, there was no basis for predicting whether the geometric configuration of the allylic double bond in geraniol would be retained or would be "racemized" during the process of reduction. It seemed quite possible that the molecule would pass through an intermediate mesomeric anion form as postulated by A. J. Birch[22] which might lead to a product with both geometric isomers present in substantial amounts. However, it seemed certain that in the reduction of linaloöl a mixture of products would be obtained.

Geraniol (99+%) and linaloöl (98%) were obtained from the Glidden Co. and used as such. Nerol was isolated from a commercial grade (containing about 50%) by lengthy and repeated distillations in which some pure geraniol was also obtained. Properties of the nerol and geraniol are given in Table I.

The reductions of nerol and geraniol were performed on 6.6 moles and 10.0 moles, respectively. Each product was roughly distilled (*ca.* 5-plate efficiency) under vacuum to eliminate any unchanged starting material, then was fractionated at around 30-plate efficiency. Both products had a small forerun containing α-olefin, presumably formed by the allylic shift. Each had one major component, quite distinct from the other in boiling point, etc. Pertinent data on these products are given in Table II; the physical properties were determined on heart cuts while the yields were calculated on material with 0.1 to 0.2° boiling ranges.

TABLE II

PROPERTIES OF 2,6-DIMETHYL-2,6-OCTADIENES

	From nerol (*cis* diene)	From geraniol (*trans* diene)	From geraniol[15]
B.p./760	166.41	169.22	169–171 (764 mm.)
n^{20}_D	1.4480	1.4502	1.4492
d^{20}_4	0.7713	0.7738	0.775
Yield	55%	58%	90–95%

It is obvious that two distinct products were formed. Gas-liquid chromatographic study showed that neither contained more than 0.2% of the other. The properties of the product from geraniol check

---

(16) G. Dupont, R. Doulou, and V. Desreux, *Bull. soc. chim. France* (5), **6**, 83 (1939).

(17) J. Douvre, *ibid.*, p. 882.

(18) R. F. Naylor, *J. Chem. Soc.*, 1532 (1947).

(19) A. J. Birch, *ibid.*, 430 (1944).

(20) D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard, and F. B. B. M. Sutherland, *ibid.*, 915 (1950).

(21) J. Hymon, M.S. thesis, The Ohio State University, 1955. J. Hymon and K. W. Greenlee, Abstracts of American Chemical Society Organic Division, 128th National Meeting, September, 1955.

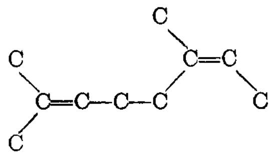
(22) A. J. Birch, *J. Chem. Soc.*, 430 (1944); 809 (1945).

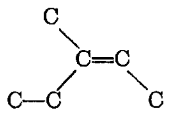
reasonably well with those reported in the literature by several authors, independently. The preparation of a dimethyloctadiene from nerol has not hitherto been reported. The purity of our products could not be determined cryoscopically, they would not crystallize. Infrared absorption spectrograms made with the purified materials had the smooth contours characteristic of pure compounds; they proved olefins of terminal and dialkylethylene types to be absent and were similar except for a few distinct variations. These spectra are being studied further and compared with those of other such pairs of isomers. Their NMR spectra were studied but could not be interpreted in terms of their known geometry.

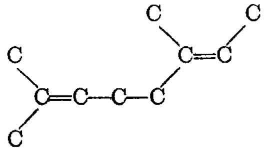
Since reduction of the two geometrically distinct alcohols yielded distinct and virtually pure dimethyloctadienes and since a quantitative geometric inversion in both cases is almost unthinkable, it is clear that the geometric configurations present in the alcohols have been carried intact into the derived diolefinic hydrocarbons. Thus, if a mesomeric intermediate[22] is formed in these reductions, an energy barrier to rotation around the C_2-C_3 bond must exist, preventing isomerization at the relatively low temperature employed.

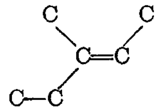
The reduction of linaloöl was done by essentially the same procedure as used for the other two alcohols. Gas-liquid chromatographic analysis showed that the product consisted chiefly of the two dienes already obtained from nerol and geraniol, present in about equal amounts.

The relative order of boiling points for the two pure diolefins (*trans* higher than *cis*) should be applicable to similar monoolefins—*e.g.*, the closely related *trans*- and *cis*-3,7-dimethyl-2-octenes. There is no reason to think that elimination of the "extra" double bond located far down the chain would reverse the effects of geometry around the other double bond. In skeletal formulas, it can easily be seen that the two diolefins differ from the two 3-methyl-2-pentenes only in addition of a remote isobutenyl group, and the boiling point differentials are 2.8° in each pair:


B.p. 166.4°


B.p. 67.7°


B.p. 169.2°


B.p. 70.5°

The present example at the C_{10} level, and the previous examples of the 3,4-dimethyl-2-pentenes (C_7) and 3-methyl-2-pentenes (C_6) appear to be adequate basis for the tentative generalization that among the 3-methyl-2-alkenes the *trans* varieties have higher boiling points than their *cis* isomers.

Experimental

2,6-Dimethyl-2,*trans*-6-octadiene.—An extra pure grade of geraniol was obtained from the Glidden Company, and was used as received; through infrared spectral and gas liquid chromatographic examination it appeared identical with the sample (see below) on which properties were reported in Table I. The apparatus for the reduction was an insulated 12-l., three-neck flask fitted with a Dry Ice-cooled reflux condenser of large capacity, a motor-driven Hershberg stirrer, and an addition funnel.

Ammonia (5 l.) was liquefied in the flask and 20 g.-atoms of sodium (460 g.) was dissolved in the ammonia. Geraniol (10 moles or 1545 g.) was mixed with methanol (10 moles or 320 g.) and the mixture was divided in two equal parts. One part was mixed with isoöctane solvent (1.0 l.) and added to the vigorously stirred sodium solution as rapidly as possible. Because of the vigor of the resulting reaction and a tendency toward foaming (presumably moderated by the isoöctane), the addition took about 1 hr. The second half of the geraniol and methanol mixture was added without admixed solvent, this taking another hour. At once, the addition of coarsely powdered ammonium chloride (20 moles or 1070 g.) was begun; it was added from a side-flask attached (in place of the funnel) by a flexible rubber sleeve and this required about 1 hr., also. The blue color of residual sodium disappeared midway through the addition of ammonium chloride which was sufficient in amount to form sodium chloride from all the sodium compounds present:

$$C_{10}H_{17}OH + CH_3OH + 2Na \longrightarrow C_{10}H_{18} + CH_3ONa + NaOH$$

$$CH_3ONa + NaOH + 2NH_4Cl \longrightarrow CH_3OH + H_2O + 2NH_3 + 2NaCl$$

The reaction mixture, still under reflux conditions, was then diluted with as much water as the remaining space in the flask would permit, whereupon the product plus isooctane separated as an upper layer. The lower layer (water, ammonia, etc.) was siphoned out with the help of applied air pressure, and the product layer was washed twice in *situ* with equal volumes of cold water. The product was transferred to a separatory funnel and washed with further small portions of cold water until the ammonia odor was gone.

The washed crude product was distilled free of solvent at atmospheric pressure, then distilled under reduced pressure at about 5-plate efficiency to separate the desired product (b.p. 64-66°/20 mm., n^{20}_{D} 1.4493-1.4501) from unchanged geraniol (150 g. or 10%).

The crude dimethyloctadiene, 1070 g. or 76.5% yield from geraniol consumed, was refractionated on a packed column operated at 30- to 35-plate efficiency. There was a small flat at 159-160° representing about 3% of the charge, then a quick rise to the main flat at 169.16-169.26°. The 159-160° material (n^{20}_{D} 1.438-1.439) had infrared spectral bands characteristic of the vinylic double bond, and was probably 2,6-dimethyl-2,7-octadiene formed by the allylic rearrangement. However, the material on the main flat (805 g. or 74% of charge) had no vinyl or dialkylethylene absorption in the infrared, and gas-liquid chromatographic examination revealed no significant impurities. Even the fractions between the two flats (6% of charge) were found to contain less than 1% of the nerol product (below). The 2,6-dimethyl-2,*trans*-6-octadiene was found to oxidize very readily, generating water and oxygenated impurities.

A center fraction, redistilled from molten sodium, was used for determination of its physical properties (Table II).

Anal. Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 86.92; H, 13.18.

2,6-Dimethyl-2,*cis*-6-octadiene.—The starting material was 4.43 kg. of a commercal "nerol" which was shown by gas-liquid chromatography to have two major components in about equal amounts. This material was fractionally distilled at reduced pressure (10 mm.) on a 3.5 × 100 cm. column packed with $^1/_8$ inch glass helices, which had been rated at 20-plate efficiency at atmosperic pressure. As it was difficult to get consistent boiling point data from the column-head thermometer, various fractions were studied in an ebulliometer at atmospheric pressure. The material boiling from 225 to 227.0° was taken as nerol concentrate (2463 g.) and that from 227.0 to 231° as geraniol concentrate (1442 g.).

The geraniol concentrate was redistilled on the same column and the last portion distilled was found quite pure; its properties are given in Table I. The nerol concentrate was similarly redistilled and the best fractions (1678 g.) had much improved properties (b.p. 225.8–226.2°, $n^{20}D$ 1.4748–1.4749). This portion was redistilled again, giving 1084 g. with a narrow boiling range (b.p. 226.15–226.23°) representing 24.5% of the original material.

The purified nerol (1015 g. or 6.57 moles) was reduced with sodium and methanol in liquid ammonia by the same procedure as used on geraniol, the amounts of all reagents being adjusted to suit. Preliminary distillation (under reduced pressure) removed the isoöctane solvent and showed that the amount of unchanged nerol was less than 5%. The product (b.p. 60–63°/20 mm., $n^{20}D$ 1.4473) amounted to 680 g. or 75% yield. When this was redistilled at about 30-plate efficiency, 5% distilled as a fraction at 158–162° ($n^{20}D$ 1.438–1.440) corresponding closely to the α-olefinic product obtained from geraniol. This was followed by intermediates (8%), the main product (82%) which had a narrow range of properties (b.p. 166.26–166.47°, $n^{20}D$ 1.4476–1.4480), and a small residue (4%) representing merely the holdup of the column. The main product would not crystallize, which precluded cryoscopic studies, but gas-liquid chromatography indicated that it contained only a trace of the diolefin which was the chief product from geraniol. The center portion of the main product was redistilled from sodium before it was used for determination of the properties seen in Table II. This sample was found pure by gas-liquid chromatography and gave an infrared spectrogram which was different in a few significant respects from that of the diene from geraniol.

Anal. Calcd. for $C_{10}H_{18}$: C, 86.87; H, 13.13. Found: C, 87.01; H, 13.12.

Reduction of Linaloöl.—The purity of the linaloöl was proved to be 98% or better by GLC analysis. One-half mole (77.1 g.) was reduced by the usual procedure except that a 50% excess of sodium was used and methanol was replaced by isopropyl alcohol which proved to eliminate foaming. The crude product was washed repeatedly with cold water and distilled at about 5-plate efficiency. The yield of dimethyloctadienes (b.p. range 158–169°, chiefly 167–169°) was 64.7 g., or 94%. Gas-liquid chromatographic analysis showed that this product had two major components, comprising 44% and 52%. They were identical to the major products from nerol and geraniol, respectively, according to their retention volumes. The product also contained 4% of a more volatile substance which corresponded to the α-olefinic by-product obtained from the other alcohols and must be the nonrearranged product, 3,7-dimethyl-1,6-octadiene.

Analyses.—The gas-liquid chromatographic studies were varied. For geraniol and nerol the substrate used was Triton X-100 on firebrick (in a 4 ft. by $^1/_4$ in. tube), the temperature was 120°, and the detector used was a Gow-Mae thermal conductivity cell in a home-made apparatus. For the dimethyloctadienes, the same system was used, but the tube length was increased to 12 ft. The dienes were also studied in a capillary apparatus.

Infrared Spectra.—The spectra of the two pure dimethyloctadienes were determined on a Perkin-Elmer Model 21 infrared spectrophotometer. Significant differences were noted in absorption bands of moderate intensity in three regions. A doublet occurring at 8.20 and 8.35 μ in the spectrum of the *cis* isomer is shifted to 8.3 and 8.4 μ in the *trans*, and the relative intensities are changed. A band at 9.35 μ in the *cis* appears to correspond to one at 9.20 μ in the *trans*. Also, a pair of bands found at 12.7 and 12.9 μ in the *trans* spectrum is missing in the *cis*. The spectrograms have been submitted to American Petroleum Institute Research Project 44 (A. and M. College of Texas) for inclusion in their catalog.

Acknowledgment.—The authors thank Dr. John M. Derfer, The Glidden Company, Jacksonville, Fla., for the special geraniol and linaloöl samples, and Dr. George Slomp, Jr., of the Upjohn Co. for the NMR studies. Financial support was provided by the American Petroleum Institute and the Goodyear Tire and Rubber Company.