filtered and crystallized from acetonitrile–methanol (m.p. 238°).

Anal. Calcd. for $C_{17}H_{14}ClNO_7$: C, 53.8; H, 3.7; N, 3.7. Found: C, 53.5; H, 3.7; N, 3.4.

N-(1,4-Dioxo-3-methoxynaphthyl-2)4-styrylpyridinium perchlorate (XXVa) also was prepared in this manner, m.p. 287° (from acetonitrile).

Anal. Calcd. for $C_{24}H_{18}ClNO_7$: C, 61.7; H, 3.9; N, 3.0. Found: C, 61.4; H, 4.0; N, 3.0.

N-(1,4-Dioxo-3-methoxynaphthyl-2)isoquinolinium perchlorate (XXVIa) was prepared similarly, m.p. 210° (from acetonitrile–methanol).

Anal. Calcd. for $C_{20}H_{14}ClNO_7$: C, 57.9; H, 3.5; N, 3.5. Found: C, 58.1; H, 3.2; N, 3.4.

1-Acetyl-2,3-phthaloylpyrrocoline (III) was prepared from the hydrolysis of XV or XVI. A suspension of 2 g. of XV or XVI in 20 ml. of hydrochloric acid (*d* 1.18) was warmed to 95–100°. Complete solution occurred in about 5 min. The initially deep red colored solution changed to light red and the product separated. After 2 hr., 20 ml. of water was added. The product was filtered and crystallized from alcohol to give 1.1 g. of III (m.p. 206°) which was identified by comparison of its infrared spectrum with that of an authentic sample.

2,3-Bis(α-carbethoxy-α-cyanomethyl)-1,4-naphthoquinone (XXXI).—A mixture of 4.5 g. of 2,3-dichloronaphthoquinone, 5 ml. of ethyl cyanoacetate, and 4.5 ml. of 2,6-lutidine in 25 ml. of 1,2,3-trichloropropane was heated to 95–100° for 3 hr. A small amount of insoluble material was filtered off, the solvent was evaporated under reduced pressure, and the residue was crystallized from alcohol to give 3.5 g. of XXXI, m.p. 206°.[4]

Photosensitized Oxidation of Carvomenthene[1]

ROBERT L. KENNEY AND G. S. FISHER

Naval Stores Laboratory, Olustee, Florida[2]

Received June 10, 1963

Carvomenthene (1-*p*-menthene) sensitized with chlorophyll absorbed oxygen rapidly when exposed to intense light. Yields of hydroperoxide based on oxygen absorption were good. The hydroperoxides were reduced to alcohols with sodium sulfite for separation by gas–liquid chromatography. The individual g.l.c. peaks were identified on the basis of physical properties, infrared spectra, and hydrogenation to the saturated alcohols. The products in order of emergence were: carvomenthene epoxide (3%), *trans*-2-*p*-menthen-1-ol (29%), *cis*-2-*p*-menthen-1-ol (9%), *cis*-piperitol (2%), 1(7)-*p*-menthen-*trans*-2-ol (17%), *trans*-carvotanacetol (15%), 1(7)-*p*-menthen-*cis*-2-ol (25%). The *cis*-piperitol is attributed to isomerization of the 2-*p*-menthen-1-ols and the epoxide formation to reaction of a peroxide radical with carvomenthene. The relative yields of the other products are in accord with a nonconcerted reaction mechanism involving random attachment of the oxygen at one end of the double bond, migration of an allylic hydrogen to the oxygen from an "axial" position *cis* to the initial point of attack, and concurrent shifting of the double bond. Hydrogen transfer and bond migration probably occur through a cyclic intermediate.

Photosensitized oxidation is a very useful synthetic tool which would be even more useful if its mechanism were sufficiently well defined to permit prediction of the products obtained from a given olefin. Schenck, *et al.*,[3] proposed the general mechanism in which the activated sensitizer forms a complex with oxygen which then "adds to one C-atom of the double bond, whereupon an H-atom migrates from the allylic position to the oxygen and the double bond is shifted." More recently it has been shown that in condensed ring systems the migrating hydrogen comes from a quasi-axial position *cis* to the newly formed C–O bond.[4,5] Both groups picture a cyclic intermediate in which the initial double bond is essentially intact and the oxygen is partially bonded to a double bond carbon and to an allylic hydrogen; but the available evidence was not considered adequate to support uniquely a concerted mechanism.[5] A somewhat different mechanism has been proposed by Sharp[6] who suggested the initial formation of a perepoxide ion by electrophylic attack of an activated oxygen molecule on the double bond. Product ratios in the case of unsymmetrical olefins with several allylic hydrogens should be of help in deciding among these mechanisms because the different mechanisms would lead to different product ratios.

The available data is meager and somewhat conflicting. Photosensitized oxidation of α-pinene has been reported to yield only *trans*-pinocarvyl hydroperoxide.[3] This implies a selective, stereospecific attack on the monosubstituted end of the trisubstituted double bond. On the other hand, the isolated trisubstituted double bond in myrcene is attacked predominantly but not exclusively at the disubstituted end.[7] Without giving any experimental details, Schenck further reported that 1-methylcyclohexene yielded a mixture of secondary and tertiary hydroperoxides but that carvomenthene (1-*p*-menthene) (I) and limonene yielded only tertiary hydroperoxides.[8]

Carvomenthene (I) was selected as the substrate for the present investigation because it is easily prepared by hydrogenation of commercial citrus limonene or of dipentene obtained by isomerization of the pinenes; its structure is well suited to the purpose; and the exclusive formation of the tertiary isomers as suggested by Schenck, if correct, would offer a very attractive route to synthetic menthol.[9] Carvomenthene has been shown to exist chiefly in the half-chair form with the isopropyl group in the equatorial position.[10] This conformer has quasi-axial hydrogens on C-3 *cis* to the isopropyl group and on C-6 *trans* to the isopropyl group. In addition the methyl group is free to rotate giving the equivalent of an axial hydrogen both *cis* and

---

[1] Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, Abstract, p. 79P.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] G. O. Schenck, H. Eggert, and W. Denk, *Ann.*, **784**, 177 (1953).

[4] W. H. Schuller and R. V. Lawrence, Southeastern Regional Meeting of the American Chemical Society, Richmond, Va., November 6, 1959; *Chem. Ind.* (London), 105 (1961).

[5] A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **81**, 1630 (1959); **83**, 1498 (1961).

[6] D. B. Sharp, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 79P.

[7] R. L. Kenney and G. S. Fisher, *J. Am. Chem. Soc.*, **81**, 4288 (1959).

[8] G. O. Schenck, *Angew. Chem.*, **64**, 12 (1952).

[9] J. P. Bain, A. B. Booth, and W. Y. Gary (to The Glidden Co.). U. S. Patent 2,894,040 (1959).

[10] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959).

trans to the isopropyl group. Stereomodels of this compound indicate that there is no hindrance of oxygen attack from either side of the molecule or at either end of the double bond.

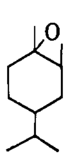
In general, the photosensitized oxidations were carried out in the same way as those previously reported for myrcene.[7] The hydroperoxides in the crude oxidates were reduced to the corresponding alcohols with sodium sulfite for separation and identification. Both quantitative analyses and preparative separations were accomplished by gas–liquid chromatography. The following seven products, in order of g.l.c. emergence times, were found to be present in significant amounts and were identified chiefly by reduction to the corresponding saturated alcohols: carvomenthene epoxide (II), 2-*trans*-*p*-menthen-1-ol (III), 2-*cis*-*p*-menthen-1-ol (IV), *cis*-piperitol (V), 1(7)-*p*-menthen-*trans*-2-ol (VI), *trans*-carvotanacetol (VII), and 1(7)-*p*-menthen-*cis*-2-ol (VIII). As shown in Table I, the product ratios were substantially unchanged by changes in temperature, substrate concentration, degree of oxidation, or nature of the photosensitizer.

TABLE I

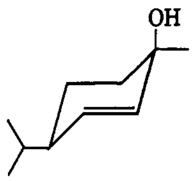
COMPOSITION OF THE REDUCED OXIDATES FROM THE VARIOUS PHOTOSENSITIZED OXIDATIONS OF CARVOMENTHENE (%)

Compound[a]	Large scale,[b] neat, chl.,[c] 20°	Neat, chl.[c] 16°[f]	Neat, chl.[c] 70°[g]	Neat, chl.[c] 70°[e,h]	30% in ethanol[d,e] Chl.[c] 15°	30% in ethanol[d,e] RB[i] 15°	30% in ethanol[d,e] MB[j] 15°
II	4	3	3	10	9	8	9
III	27	33	26	25	27	30	29
IV	8	8	7	9	10	8	8
V	2	<1	<1	2	2	<1	2
VI	18	19	18	16	15	13	14
VII	15	11	19	16	17	15	11
VIII	28	26	27	22	19	25	25

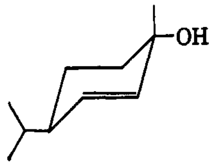
[a] See text. [b] Absorbed 46 mole % O_2. [c] Chlorophyll. [d] 14 mole % O_2. [e] These runs were made using carvomenthene with preformed II and should not be compared with the others. [f] 44 mole % O_2. [g] 51 mole % O_2. [h] 17 mole % O_2. [i] Rose bengal. [j] Methylene blue.



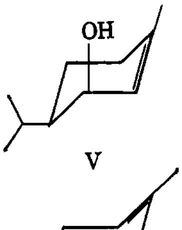
II



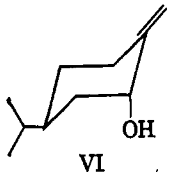
III



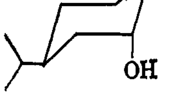
IV



V



VI



VII

VIII

Contrary to our previous conclusion,[2] the relative amounts of III, VI, VII, and VIII (34:19:18:29) are in better accord with a nonconcerted mechanism than with a concerted one. Nonselective attack of oxygen on one end of the double bond followed by nonselective transfer of a *cis*-axial hydrogen would lead to a 33:17:17:33 ratio of these products, while a nonselective concerted attack on a double bonded carbon and the hydrogen being transferred would lead to a 25:25:25:25 ratio of products.[11]

Further support for the nonconcerted mechanism is provided by the recent work of Schenck[12] on the photosensitized oxidation of 3-carene. The 50:25:25 ratio found for 2-caren-4-ol-4-caren-3-ol-4(8)-caren-3-ol (the only products) is exactly in accord with the nonconcerted, nonselective reaction mechanism. Formation of this product ratio by a concerted mechanism would require a strong preference for formation of the tertiary hydroperoxide which is not indicated by the ratio of III to VIII in the present case.

Formation of IV and II can be accomodated in the nonconcerted mechanism if it is assumed that the alkylperoxy diradical formed by *trans* attack of oxygen at C-1 has an appreciable life. The amount of IV formed corresponds to inversion of about one-third of the diradical or about a 2:1 ratio for rate of decomposition to rate of inversion. Reaction of this same diradical with another mole of carvomenthene would yield II. Analogous oxidation of an olefin by a peroxy radical to give an epoxide and an alkoxy radical is a generally accepted mechanism for the formation of epoxides during autoxidation. In the present case, the resultant alkylalkoxy diradical should cyclize to give a second mole of epoxide. By such a mechanism, the epoxide which came from the diradical would be *trans*, while that coming from the secondary oxidation of carvomenthene would be about half *cis* and half *trans*. Hydrogenation of the epoxide yields 70% of products having the oxygen attached *trans* to the isopropyl group.

Formation of IV by concerted attack on the less stable conformer of carvomenthene cannot be ruled out,[13] but, by analogy to the formation of VIII as well as III from the stable isomer, its formation by this mechanism would have been accompanied by the formation of about 7% of VI from this conformer. This would further reduce the amount of VI coming from the more stable conformer, an amount which is already too low to support the concerted mechanism.

Although II is formed in greater proportion by

---

(11) Formation of VI and VIII in the observed 40:60 ratio would require that the side of the carvomenthene molecule *trans* to the isopropyl group be more hindered than the *cis* side. The available data on the steric interactions involved (E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, N. Y., 1962, pp. 125, 126, 134, and 236) do not support such a hypothesis. *cis* Attack at C-2 involves an essentially eclipsed H-OO interaction with the quasi-axial H at C-3. No value for the potential energy of this interaction is given, but it should be at least as great as that for the corresponding H-H interaction (1 kcal./mole). Interaction with the axial H at C-5 would presumably be small. *trans* Attack at C-2 involves H-O interactions with the axial H on C-4 and the quasi-axial H on C-6, but such interactions involve energies of only 1 kcal./mole or less even when both hydrogens are fully axial.

(12) G. O. Schenck, S. Schroeter, and G. Ohloff, *Chem. Ind.* (London), 459 (1962).

(13) Although an axial isopropyl group on a cyclohexyl ring is unstable by about 3.5 kcal./mole [D. S. Noyce and J. Dolby, *J. Org. Chem.*, **26**, 3619 (1961)], only one H-C_3H_7 interaction occurs in the less stable conformer of carvomenthene, and the H is only quasi-axial. Hence the two conformers probably differ by less than 1.8 kcal./mole and as much as 5% of the less stable conformer may be present.[11]

autoxidation than by photosensitized oxidation[14] and can be formed by thermal decomposition of the crude photosensitized oxidate (Table II), failure to get increased yields at higher temperatures (Table I) rules out such side reactions as the source of II. Similarly autoxidation as a source of V is ruled out by its low concentration in the thermal oxidate. It is probably formed from III or IV during isolation, because simple heating of these compounds in the presence of water has been reported to bring about this isomerization.[9]

TABLE II

EFFECT OF THERMAL AUTOXIDATION AND DECOMPOSITION ON THE COMPOSITION OF THE REDUCED OXIDATES

	Compound,[a] %						
Run no.	II	III	IV	V	VI	VII	VIII
21A-1[b]	3	33	8	<1	19	11	26
21A-2[c]	12	29	7	<1	16	12	23
23-2[d]	14	12	6	1	[e]	[e]	[e]

[a] See text for compound identification. [b] This run was made at 16° with chlorophyll as catalyst. [c] A sample of the hydroperoxide mixture from 21A-1 which was heated at 70° for 8 hr. under nitrogen in a sealed tube. [d] This sample was thermally oxidized at 70°. [e] The higher boiling components amounting to 67% of the reduced oxidate were not investigated further.

Experimental

Carvomenthene (I).—The carvomenthene used in this work was prepared by the careful fractionation of a commercial sample. This material was the fraction distilling at 69.2° at 20 mm. and having the following properties: $d^{20}{}_{4}$ 0.8238, $n^{20}\mathrm{D}$ 1.4570, $[\alpha]^{22.6}\mathrm{D}$ +95.81°.[15] Gas–liquid chromatography indicated the samples used were at least 95% pure.

Oxidation Conditions.—In general the oxidations were carried out in a 250-ml. reactor with an internal light source (300-w., incandescent) immersed in a running water bath at 16 to 20°. The reaction zone was 0.65 cm. thick, 7 cm. long, and 5.2 cm. in diameter. Adequate stirring and contact with oxygen was obtained by circulating oxygen through the reactor at the rate of about 100 l./hr. Oxygen absorbed was replaced from a cylinder through a wet test meter. The meter reading was corrected for water vapor pressure and temperature.

In a typical case, 168.3 g. (1.2 moles) of carvomenthene containing 0.5 g. of crude chlorophyll (4% in oil) absorbed 0.56 mole of oxygen when illuminated for 185 min. The oxidation was stopped at this point to avoid excessive side reactions. The product had a peroxide number of 4900 mequiv./kg., which represented 0.48 mole of hydroperoxide or 0.86 mole of hydroperoxide per mole of oxygen absorbed. Small scale runs were made similarly to those reported previously.[7]

Chemical Reduction of the Hydroperoxide.—The hydroperoxide mixture (195.5 g.) was dissolved in 200 ml. of ethanol and added dropwise, with stirring, to 82.8 g. (0.66 mole, 45% excess) of sodium sulfite in 600 ml. of a 5:1 water–ethanol mixture. Stirring was continued overnight or until the mixture gave a negative peroxide test. The product was extracted with pentane, washed with water, dried with anhydrous sodium sulfate, and the solvent evaporated under vacuum. The yield was 164.6 g. Gas–liquid chromatography indicated that the product was a mixture of unchanged carvomenthene and, at least, six other compounds.

Gas–Liquid Chromatography.—The samples were chromatographed through a 0.25-in. o.d. copper column 9 ft. long packed with either alkaline Carbowax 20,000 or Craig polyester succinate on Chromosorb-W. Analytical runs were made using 0.5 to 3-μl. samples and preparative runs using 20- to 30-μl. samples.

Isolation of Components.—In order to simplify the collection of each g.l.c. peak for characterization and identification, the mixture was fractionally distilled through a column rated at 100 plates. The unchanged carvomenthene was distilled at 10 mm., and the residue was distilled at 4 mm. The residue was redistilled bulb-to-bulb at 2 mm. to give three more fractions. By determining the properties and making the g.l.c. analysis of each fraction, those having the highest concentration of each component were selected, and the individual products were collected by making preparative scale runs on the appropriate fraction. Purities of the collected materials were checked by g.l.c. analysis, rechromatographing if necessary to obtain a pure product.

Carvomenthene Epoxide (II).—The compound isolated from the fraction boiling at 70° (4 mm.) had the following properties: $d^{25}{}_{4}$ 0.8943, $n^{25}\mathrm{D}$ 1.4492, and $[\alpha]\mathrm{D}$ +44.8° (*c* 3.3, carbon tetrachloride), +50.7° (*c* 5.8, ethanol). Its infrared spectrum[16] shows no characteristic absorption below 8 μ and its largest absorption band at 11.95 μ suggests the presence of *cis*-epoxide.[17] Pigulevskii and Kozhin[18] give the following properties for carvomenthene oxide (II): d_{20} 0.9059, $n^{20}\mathrm{D}$ 1.4509, and $[\alpha]\mathrm{D}$ +57.53°. Catalytic hydrogenation (PtO_2) yielded products which as indicated by g.l.c. analysis were 9.6% *cis-p*-menthan-1-ol, 11.1% carvomenthol, 41.9% neocarvomenthol, 17.5% isocarvomenthol, and 20.0% neoisocarvomenthol. One would expect carvomenthene epoxide to yield these products.

2-*trans-p*-Menthen-1-ol (III).—A compound, f.p. 20°, $d^{25}{}_{4}$ 0.9070, $n^{25}\mathrm{D}$ 1.4696, and $[\alpha]\mathrm{D}$ −12.0° (*c* 4, carbon tetrachloride), 0.0° (ethanol), was obtained from the fraction boiling at 73.6° (4 mm.). It had strong infrared absorption at 3.02 and 8.57 μ which indicates that the compound is a tertiary alcohol. Strong absorption at 13.65 μ suggests the presence of a symmetrically disubstituted double bond.[17] On catalytic reduction (PtO_2) this material yielded essentially one compound, f.p. 13.9°, $d^{25}{}_{4}$ 0.8918, and $n^{25}\mathrm{D}$ 1.4571. Its infrared spectrum was identical with that of authentic *trans-p*-menthan-1-ol (*trans*-dihydro-*β*-terpineol).[19,20] Hence, the unsaturated alcohol is 2-*trans-p*-menthen-1-ol (III). Bain, *et al.*,[9] give the properties of 2-*trans-p*-menthen-1-ol as f.p. 6–8°, $d^{25}{}_{4}$ 0.915, $n^{25}\mathrm{D}$ 1.4698, and $[\alpha]^{25}\mathrm{D}$ −17.2°.

2-*cis-p*-Menthen-1-ol (IV).—A compound having the properties, $d^{25}{}_{4}$ 0.9128, $n^{25}\mathrm{D}$ 1.4710, and $[\alpha]\mathrm{D}$ +80° (*c* 4, ethanol), was obtained from the fraction boiling at 79.4° (4 mm.). It gave strong absorption at 3.02, 8.67, and 13.47 μ indicating that it is a tertiary alcohol with a symmetrically disubstituted double bond.[17] Catalytic reduction (PtO_2) yields essentially one compound melting 43.3 to 44.6°. Henbest and McElhinney[20] give the melting point of *cis-p*-menthan-1-ol as 43 to 44°. Its infrared spectrum was identical with that of the authentic material.[19] Hence, the unsaturated alcohol is 2-*cis-p*-menthen-1-ol (IV). Bain, *et al.*,[9] give the properties of 2-*cis-p*-menthen-1-ol as $d^{25}{}_{4}$ 0.915, $n^{25}\mathrm{D}$ 1.4729, $[\alpha]^{25}\mathrm{D}$ +69.2°.

***cis*-Piperitol (V).**—A minor component, not readily detectable in the chromatogram of the mixture, was obtained from the fraction boiling at 79.4° (4 mm.). It was identified as *cis*-piperitol (V) by comparison of its infrared spectrum with that of an authentic sample. It had the following properties: $d^{25}{}_{4}$ 0.9196, $n^{25}\mathrm{D}$ 1.4771, and $[\alpha]\mathrm{D}$ +155.95° (*c* 1.1, ethanol). Read and Story[21] give the properties of *d*-neopiperitol as $d^{25}{}_{4}$ (vac.) 0.9119, $n^{25}\mathrm{D}$ 1.4729, and $[\alpha]^{16}\mathrm{D}$ +21.22°. Bain[22] gives $[\alpha]^{25}\mathrm{D}$ −255° for 1-*cis*-piperitol. A catalytic hydrogenation (PtO_2) yielded primarily neomenthol (*trans-p*-menthan-*cis*-3-ol) which is the expected product from *cis*-piperitol.

1(7)-*p*-Menthen-*trans*-2-ol (VI).—This material obtained from the fraction boiling at 81.6° (4 mm.) had the following properties: $d^{25}{}_{4}$ 0.9180, $n^{25}\mathrm{D}$ 1.4755, and $[\alpha]\mathrm{D}$ +94.9° (*c* 12, ethanol). Its infrared spectrum shows strong absorption at 3.02 and in the 9.5 μ region indicating a secondary alcohol and strong absorption at 3.28, 6.05, 11.15 and 11.48 μ indicating an unsymmetrically disubstituted double bond.[17] Catalytic reduction (PtO_2) yields a mixture giving two major g.l.c. peaks which correspond to those of neocarvomenthol (*trans-p*-menthan-*trans*-2-ol) and isocarvo-

---

[14] J. P. Bain, A. B. Booth, and E. A. Klein (to the Glidden Co.), U. S. Patent 2,863,882 (1958).

[15] H. A. Smith, J. F. Fuzek, and H. T. Meriwether, *J. Am. Chem. Soc.*, **71**, 3765 (1949), give $n^{20}\mathrm{D}$ 1.4572, $[\alpha]^{20}\mathrm{D}$ +96°.

[16] All spectra were obtained using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Liquids were run neat, solids in carbon tetrachloride.

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 34, 96, 118.

[18] G. C. Pigulevskii and S. A. Kozhin, *Zh. Obschch. Khim.*, **27**, 803 (1957); *Chem. Abstr.*, **51**, 16357*i* (1957).

[19] J. S. Stinson, G. S. Fisher, and J. E. Hawkins, *J. Org. Chem.*, **24**, 1084 (1959).

[20] H. B. Henbest and R. S. McElhinney, *J. Chem. Soc.*, 1834 (1959), give $n^{25}\mathrm{D}$ 1.4568.

[21] J. Read and R. A. Story, *J. Chem. Soc.*, 2770–83 (1930).

[22] J. P. Bain (to The Glidden Company), U. S. Patent 2,935,526 (1960).

menthol (*cis-p*-menthan-*trans*-2-ol). This material is identified as 1(7)-*p*-menthen-*trans*-2-ol (VI) which would be expected to yield these carvomenthols.

trans-**Carvotanacetol (VII).**—The material obtained from the fraction boiling at 89.2° (4 mm.) had the following properties: d^{25}_{4} 0.9215, n^{25}_{D} 1.4757, and $[\alpha]_D$ −113.9° (*c* 4.1, ethanol). Its infrared spectrum shows strong absorption at 3.03 and 9.56 to 9.7 μ indicating a secondary alcohol, and at 12.43 μ indicating a trisubstituted double bond.[17] Catalytic reduction (PtO_2) yields a mixture giving two major g.l.c. peaks which correspond to those of neo- and isocarvomenthol with the former being the major component. These products and the infrared spectrum are those predicted for 1-*p*-menthen-*trans*-6-ol (*trans*-carvotanacetol) (VII). Jefferies and Milligan[23] give the properties of *dl-trans*-carvotanacetol as d_{20} 0.9290 and n^{20}_{D} 1.4786.

1(7)-*p*-Menthen-*cis*-2-ol (VIII). This material, the major component of the fraction boiling at 78° (2 mm.), had the following properties: d^{25}_{4} 0.9262, n^{25}_{D} 1.4803, and $[\alpha]_D$ +8.5° (*c* 8.25, ethanol). Its infrared spectrum shows strong absorption at 3.02 μ and in the 9.2 to 9.5 μ region indicating a secondary alcohol, and at 3.27, 6.05, 11.2 and 11.5 μ indicating an unsymmetrically disubstituted double bond.[17] Catalytic reduction (PtO_2) yields a mixture giving two major g.l.c. peaks corresponding to carvomenthol (*trans-p*-menthan-*cis*-2-ol) and neoisocarvomenthol (*cis-p*-menthan-*cis*-2-ol), the latter being the major component. These data are that predicted for 1(7)-*p*-menthen-*cis*-2-ol (VIII).

Preparation of the Carvomenthols.—Carvomenthol was obtained by g.l.c. purification of the products obtained by the anti-Markovnikov hydration of carvomenthene effected by the procedure by Brown.[24] Isocarvomenthol was obtained similarly from the catalytic reduction (PtO_2–HOAc) of isodihydrocarveol. Neo- and neoisocarvomenthols were obtained similarly from the products of the catalytic reduction (PtO_2–HOAc) of carvomenthone. The physical properties of the carvomenthols are given in Table III. The optical rotations were determined in ethanol at concentrations ranging from 3 to 10%.

TABLE III

PROPERTIES OF THE CARVOMENTHOLS

Compound	d^{25}_{4}		n^{25}_{D}		$[\alpha]_D$	
Carvomenthol	0.891	0.896[a]	1.4597	1.4595[a]	−21°	+26°[a]
Neocarvomenthol	.899	.897[a]	1.4611	1.4610[a]	+30°	−42°[a]
Isocarvomenthol	.906	.907[a]	1.4634	1.4640[a]	+16°	−18°[a]
Neoisocarvomenthol	.911	.908[a]	1.4652	1.4654[a]	+32°	−35°[a]

[a] R. G. Johnson and J. Read, *J. Chem. Soc.*, 1139 (1935). Original values were recalculated to 25°.

Acknowledgment.—The authors wish to express their appreciation to H. E. McLaughlin, Newport Industries, for supplying the carvomenthene used in this work; to Dr. J. P. Bain, The Glidden Company, for various reference compounds; and to Dr. J. C. Braun of this laboratory, for the reference sample of carvomenthol.

---

[23] P. R. Jefferies and B. Milligan, *J. Chem. Soc.*, 4348 (1956).

[24] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6423 (1959).

Stereoisomerism. I. The Synthesis of Some *cis*- and *trans*-1,3-Cyclohexanedialkanoic Acids. The Assignment of Configuration by Nuclear Magnetic Resonance[1]

THOMAS L. WESTMAN, RODRIGO PAREDES, AND WALLACE S. BREY, JR.

Department of Chemistry, University of Florida, Gainesville, Florida

Received June 17, 1963

The *cis*- and *trans*-1,3-cyclohexanediacetic and dipropionic acids were prepared by consecutive Arndt–Eistert homologation of the isomeric 1,3-cyclohexanedicarboxylic acids. The 1,3-cyclohexanedipropionic acids were also prepared by double addition of ethyl acrylate to the piperidine enamine of cyclohexanone, followed by Wolff–Kishner reduction of the intermediate keto diester. The major product isolated from this reduction was the *trans*-1,3-cyclohexanedipropionic acid. The nuclear magnetic resonance spectra of these isomeric diacids allow assignment of *cis* or *trans* configuration.

There are numerous reported studies on the stereochemistry of various substituted cyclic systems. However, for the most part, these studies have been devoted to considerations of alkylated cyclic systems or where functional groups are attached directly to the ring.[2] In connection with studies devoted to the stereochemistry of cyclic systems, where functional groups are attached to alkyl side chains, it was necessary to prepare a series of such isomeric derivatives and to be able to assign configurations readily to these types of systems. This paper reports the synthesis of the *cis*- and *trans*-1,3-cyclohexanediacetic and dipropionic acids and an examination of their nuclear magnetic resonance spectra.

A relatively straightforward approach to the synthesis of these compounds was the Arndt–Eistert homologation of the known and readily available *cis*- and *trans*-1,3-cyclohexanedicarboxylic acids (**1** and **2**).[3] This route appeared particularly attractive in view of the reported stereospecificity of this reaction with the corresponding half esters.[4]

Using the Newman–Beal modification of the Arndt–Eistert reaction (silver benzoate–triethylamine in absolute methanol),[5] the *cis*- and *trans*-1,3-cyclohexanedicarboxylic acids (**1** and **2**) were converted to the corresponding *cis*- and *trans*-1,3-cyclohexanediacetic acids (**3** and **4**), m.p. 138–139° and 118–119°, respectively, in 55 and 30% yields. Similarly, homologation of the diacetic acids gave the *cis*- and *trans*-1,3-cyclohexanedipropionic acids (**5** and **6**), m.p. 97–98° and 94–95°, respectively, in 55 and 21% yields. The homologation reactions in the *cis* series utilized N,N′-dinitroso-N,N′-dimethylterephthalamide (Du Pont EXR-101) as diazomethane precursor, while those in the *trans* series utilized *p*-tolylsulfonylmethylnitrosoamide. The dif-

---

[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] For general references to these studies, *cf.* E. L. Eliel, "The Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] A. Skita and R. Rossler, *Chem. Ber.*, **72B**, 265 (1939).

[4] F. Ramirez and J. W. Sargent, *J. Am. Chem. Soc.*, **74**, 5785 (1952).

[5] M. S. Newman and D. F. Beal, *ibid.*, **72**, 5163 (1950).