CHEMISTRY OF THE CAROTANE SESQUITERPENES V.[1, 2] BIOSIMULATED CONVERSIONS

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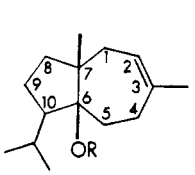
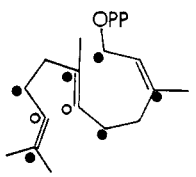
ABSTRACT.—The dehydration of carotol (**1**) by thionyl chloride in pyridine was reinvestigated and found to yield acoradiene **7**, in addition to the previously reported daucene (**6**), thus establishing the absolute configuration of this natural product. In addition, the isomeric acoradiene **11** was isolated from the product mixture. The dehydration of dihydrocarotol (**14**) was similarly studied and found to yield only unrearranged products. The reactions of carotol acetate (**26**) and dihydrocarotol acetate (**29**) with 90% formic acetate were investigated. As a result of these studies, the role of the C-3 double bond, in the carotane skeleton, in facilitating rearrangement to the acorane skeleton is discussed. The epoxidation of the isomeric dihydrodaucenes **15**, **16**, **17** was also studied.

The carotane (daucane) group of sesquiterpenes is a small one based on a novel skeleton as exemplified by the parent compound carotol (**1**). They have been



1 R=H

26 R=$COCH_3$



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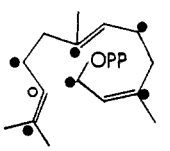

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found almost exclusively in the plant family Umbelliferae (1, 2, 3) and new members are slowly being added to the group (4, 5, 6, 7, 8). Of particular interest is the recent report of the first example of a carotane sesquiterpene isolated from fungal origin (4). The biogenesis of this novel group has been of interest for some time. In 1962 Souček (9) fed 1-^{14}C-acetate to the carrot plant and isolated the radioactive carotol. This carotol was degraded so as to yield C-3 and its attached methyl group as acetic acid (C-3 as carboxyl). Since the isolated acetic acid contained approximately one sixth of the molar activity of the carotane skeleton, it was postulated that a mechanism involving *trans*, *cis*-farnesol pyrophosphate folded as in **2** was consistent with the biogenetic origin of carotol, whereas farnesol pyrophosphate folded as in **3**, which would subsequently involve a methyl migration to give the C-3 methyl group and ultimately the isolation of

[1]The former papers in this series are:

IV. Carotol Chemistry: Formic Acid Catalyzed Rearrangements. L. H. Zalkow, M. G. Clower, Jr., M. Gordon, J. Smith, D. Van Derveer and J. A. Bertrand, Chem. Comm., 374 (1976).

III. The Absolute Configuration of a Vetiver Acoradiene. The Conversion of Carotol to Acoradienes. L. H. Zalkow and M. G. Clower, Jr., Tetrahedron Letters, 75 (1975).

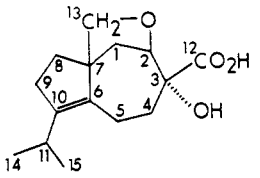
II. A Vapor Phase Chromatographic Analysis of Carrot Seed Oil. L. H. Zalkow, M. K. Park and J. W. Ellis, Essent. Oil Record, **55**, 507 (1963).

I. Structure of Carotol and Daucol. L. H. Zalkow, E. J. Eisenbraun and J. N. Shoolery, J. Org. Chem., **26**, 981 (1961).

[2a]Some of this work appeared in preliminary form in paper III above.

[2b]Taken in part from Marion Grove Clower, Jr., Ph.D. Dissertation, Georgia Institute of Technology, 1975.

inactive acetic acid from the above-described experiment, would not be appropriate. Tsudo *et al.* (4) have now simultaneously fed 2-^{13}C and 2-^{14}C acetate to *Aspergillus terreus* and isolated the labeled fungal carotane sesquiterpene aspterric



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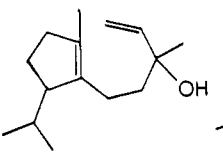

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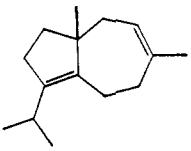

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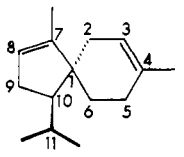
acid (**4**). From the ^{14}C content, it was determined that the incorporation was 1.32%, and the ^{13}C nmr spectrum indicated enrichment at C-2, -4, -6, -8, -10, -12, -14 and -15 as expected. In addition, ^{13}C-^{13}C coupling (42.7 Hz) was observed between C-6 and C-10; thus the cyclization of *trans, cis*-farnesyl pyrophosphate as in **2** was confirmed (C-6 and C-10 both arise from the labeled methyl group in $^{13}CH_3CO_2Na$).

In the past, the carotane sesquiterpenes have been considered to be an isolated biogenetic group arising directly from *trans, cis*-farnesol pyrophosphate and not closely related to any other sesquiterpenoid family (10). A recent report of biosynthetic interest describes the conversion of the synthetic isoprenoid **5**, prepared efficiently from racemic dehydrolinalool or optically active limonene, into daucene (**6**) and acoradiene **7** (10, 11). Another report describes the conversion of the



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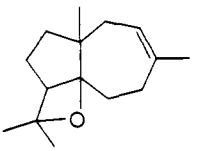
10 Δ^{11}



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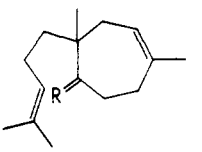
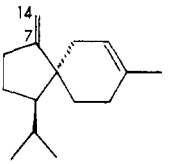
25 dihydro



9 R=O

24 R=<H/OH



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synthetic product "carotol-ether" (**8**), prepared by the [3,3] sigmatropic rearrangement of the isoprenoid **9** (itself synthesized from nerolidol) into acoratriene **10** as the major product and acoradiene **7** as the minor product with $HAlCl_2$(12).

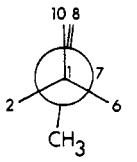
Kaiser and Naegeli (13) isolated a new acordiene from the essential oil of *Vetiveria zizanoides* (Stapf), which was synthesized, in the racemic form, as described above (10). It was assigned an absolute configuration enantiomeric to that indicated in **7**, based on its co-occurrence with (+)-α-cedrene, (+)-prezizaene and (+)-zizaene. We visualized by analogy to the co-formation of daucene (**6**) and acoradiene **7** from **5**, as described above, a stereospecific conversion of carotol (**1**) of known absolute configuration (14-18) into acoradiene **7**, thus unequivocally establishing the absolute configuration of the new acoradiene.

The relative configuration of carotol is known both from various chemical transformations (14) and from an X-ray analysis (18) of daucyl (±)-alaninate hydrobromide. Daucol is obtained easily from carotol on treatment of the latter with a peracid (14, 19). The absolute configuration of carotol is known from the circular dichroism curves of α-bromodaucone and daucone (14). The latter is simply the oxidation product of daucol while the former is obtained on bromina-

tion of the latter. In addition, carotol has been correlated with (−) dihydrocarvone (15, 16) and, finally, the latter was converted into (+)-daucene (**6**) which, in turn, was converted into carotol, albeit, in very low yield (17). However, carotol was reported to be converted into daucene (**6**) in good yield by treatment with thionyl chloride in pyridine (14). The synthesis of (−) daucene from R(+) limonene offers further substantiation to the assigned absolute configuration of carotol (11).

Initially, we reinvestigated the previously reported (14) dehydration of carotol (**1**) to give daucene (**6**), as mentioned above, and under the previously reported conditions. We found, in addition to daucene (65%), three other products, **A** (4%), **B** (11%) and **C** (20%), listed in order of increasing retention time by glc. Chromatography on silica gel impregnated with silver nitrate provided, first, an enriched fraction of **B**, then, a fraction containing **C** with daucene and, finally, pure daucene. Preparative gas chromatography was used to obtain analytically pure samples of **B** and **C**, while **A** has not been identified due to the small amount available. The ^{1}H nmr spectrum of **B** indicated that it contained two olefinic protons, an isopropyl group and two methyl groups attached to double bonds. These data, together with the ir spectrum (trisubstituted double bonds) and mass spectrum, indicated a bicyclic sesquiterpene. Thus, **B** could not contain the carotol skeleton since there was no quaternary methyl group present. Therefore, **B** had to arise by skeletal rearrangement. As mentioned above, we expected to obtain an acorane sesquiterpene by rearrangement of carotol. When **B** was compared with the acoradiene isolated by Kaiser and Naegeli (13), it was indeed found to be identical to the latter in every way including its ord spectrum, thus establishing that they were of the same absolute configuration. From the known absolute configuration of carotol and the method of preparation, **B**[3] and, therefore, the acoradiene of Kaiser and Naegeli (13) could be assigned the absolute configuration depicted in **7**.

The spectral properties of **C** were similar to those of **B** with the exception that in the nmr spectrum of **C** there appeared a single hydrogen attached to a trisubstituted double bond, a single methyl group attached to a double bond and a vinylidene grouping. The ir spectrum confirmed the presence of a vinylidene grouping. Thus, structure **11** could be assigned to **C**. It is of interest to note that **C** (**11**) shows a plain positive ord curve, whereas **B** (**7**) shows a plain negative curve of similar magnitude, even though the absolute configurations around the chiral centers C–1 and C–10 have not changed. This can be explained by the application of Brewster's rules (20) to C–1. Thus, if one looks down bond C–1, C–7 in **7** and **11**, it can be seen that the double bond has reversed its position in going from **7** to **11**, as indicated in **12** and **13**, respectively. According to Brewster's



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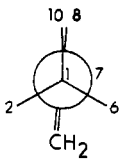

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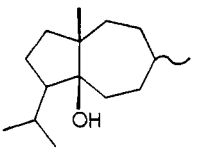

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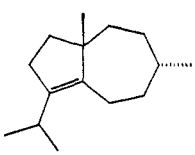
[3]A mechanistically related conversion of carotol oxide to an acoratriene has been described (12).

rules, the contribution of the double bond to the overall rotation at chiral center C–1 would also be expected to be reversed. In this case, this is the major contribution to the optical rotation of the molecules in question.

Carotol was unreactive toward phosphorous oxychloride at 0° and reacted only slowly with mesyl chloride in refluxing pyridine to give the same products as obtained with thionyl chloride. In order to learn more about the effect of the C–2 double bond in carotol (**1**) on the course of the dehydration reaction, carotol was hydrogenated as previously described (21) to give dihydrocarotol (**14**). The ^{13}C nmr spectrum immediately indicated that the hydrogenation had, in fact, given an epimeric mixture of isomers by the presence of two sets of 15 signals, the minor set being approximately one-third the height of the major set. On dehydra-



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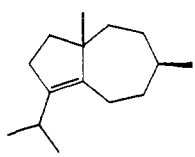

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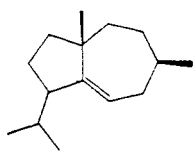

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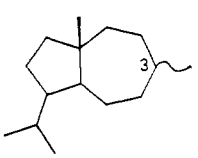
tion of dihydrocarotol (**14**) with thionyl chloride in pyridine under conditions similar to those used for carotol (**1**), the three products **16** (51%), **15** (28%) and **17** (20%) were obtained. The products were separated by chromatography on silica gel impregnated with silver nitrate; the structures could be readily assigned by spectroscopic analyses. Thus, the mass spectrum of each indicated a molecular formula of $C_{12}H_{26}$ (*m/e* 206) and, in each case, the base peak appeared at *m/e* 163 corresponding to the loss of an isopropyl group. The presence of an isopropyl group, an additional secondary methyl group and a tertiary methyl group were evident from the ^1H nmr spectra, and the ^{13}C nmr spectra showed that each substance contained a double bond. It was evident from the ^1H nmr spectra that the double bonds in **15** and **16** were tetrasubstituted, while that in **17** was trisubstituted. The structures of **15** and **16** were confirmed by their formation in a 1:1 ratio by the hydrogenation of daucene (**6**) in the presence of PtO_2. In the presence of Pd/C at 3 atm hydrogen pressure, daucene gave **15**, **16** and daucane (**18**). Daucane was also obtained, as previously described (22), by hydrogenation of carotol. This material, however, is undoubtedly a mixture of C–3 epimers, although this was not evident from a single glc analysis and the 60 MHz ^1H nmr spectrum.



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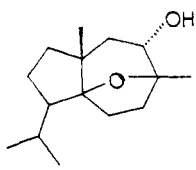

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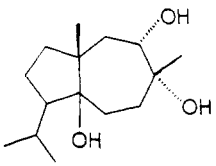

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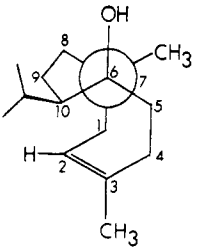
Equilibration of **15** and **16**, respectively, with formic acid left them unchanged; while, under these conditions, **17** was converted in 73% yield into **16**. Thus, the C–3 methyl groups in **16** and **17** must possess the same configuration. Reaction of dihydrocarotol (**14**) with formic acid, under the same conditions, gave a mix-

ture composed of **16** (70%), **15** (25%) and **17** (5%). This composition is almost identical to that obtained on treatment of dihydrocarotol with thionyl chloride in pyridine, after one takes into consideration the above-mentioned conversion of **17** into **16** in 51% yield on exposure to formic acid. The assignment of the C-3 configuration in **15**, **16** and **17** is based on inspection of molecular models. Thus, catalytic hydrogenation of carotol (**1**) would be expected to proceed predominantly by the addition of hydrogen from the α side, opposite to the β oriented C–7 methyl, C–6 hydroxyl and C–10 isopropyl groups. Dehydration of this epimeric mixture of dihydrocarotols would then be expected to give a mixture of dehydrodihydrocarotols (**15**, **16**, **17**) in which those isomers with the C–3 β methyl group predominate and, indeed, the ratio of C–3 β (**16**, **17**) to C–3 α (**15**) isomers is approximately 3:1. This ratio also corresponds roughly to the relative intensities of the two sets of lines in the ^{13}C spectrum of the dihydrocarotol mixture. Of course, caution must be exercised in utilizing the ^{13}C line intensities for quantitative evaluations due to long relaxation times and varying degrees of Nuclear Overhauser Enhancements. In the catalytic hydrogenation of daucene (**6**), a 1:1 ratio of **15** and **16** was produced. An inspection of a molecular model of daucene clearly shows that, as compared to carotol (**1**), more attack of hydrogen from the β side to give more of the C–3 α-methyl group should occur in this case since steric inhibition offered by the β-oriented C–6 hydroxyl and C–10 isopropyl groups of carotol are removed. Other examples of the preferred attack on the α-face of carotol can be found in its reaction with perphthalic acid in ether (21) and potassium permanganate (21) in acetone-ice to give daucol (**19**) and the triol **20**, respectively, (14–18).

The role of the double bond in carotol (**1**) thus appears to be essential for the formation of rearranged products such as acoradienes **7** and **11** since no such products are produced from dihydrocarotol (**14**). In the preferred conformation of carotol for concerted migration of the C–7, C–1 bond to C–6, as depicted in **21**, the



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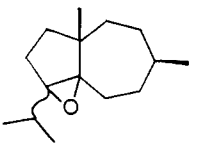

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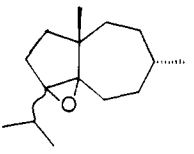
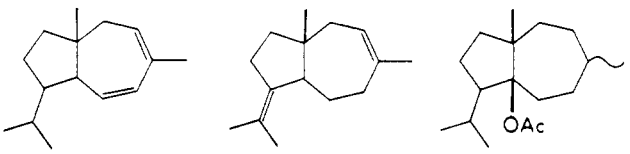


23

π orbital of the C–2, C–3 double bond may be able to provide anchimeric assistance to the departing hydroxyl group at C–6. In this conformation, the angle between the π orbital and the C–6 carbon and attached O–H group is about 40°, not the most ideal for good overlap. Of perhaps more significance, may be the observation that in this conformation the C–7, C–1 σ-bond and the π orbital at C–2, C–3 are only about 30° from planarity. Thus the π orbital could provide additional electron density to the C–7, C–1 bond enhancing its migratory capacity.

The conformations of the seven-membered rings in the dihydrodaucenes **15** and **16** were reflected in their reactions with *m*-chloroperbenzoic acid. Under identical conditions, the reaction with **16** was complete after 0.5 hr, whereas with **15**, the reaction was complete only after 3 hr. While an inseparable mixture of

epoxides was obtained in each case, **16** gave the two isomers (**22**) in a ratio of 2:1, while **15** gave an isomeric ratio of 1:1 (**23**). An inspection of Dreiding models shows that in the preferred conformation for **16** the seven-membered ring is a distorted chair conformation with the C–3 methyl group in a pseudo-equatorial position, and the less hindered face of the double bond is clearly the α face. This situation is analogous to that in Δ^4-cholestene (23). On the other hand, in what appears to be the preferred conformation of **15**, in which the seven-membered ring is again in a distorted chair conformation and the C–3 methyl group is pseudo-equatorial, the α-face is clearly more hindered than in **16**. Thus one observes a 1:1 ratio of epoxide isomers. On treatment with 90% formic acid or stannic chloride in benzene, both **22** and **23** gave complex mixtures; these procedures, therefore, did not seem a viable method of converting the carotane skeleton into the acorane skeleton.



27 **28** **29**

The synthesis of synthetic "carotol ether" (**8**) via the cycloheptenone **9** was mentioned earlier. We visualized an "in-vitro biosynthesis" of carotane and/or acorane sesquiterpenes via an intermediate such as **9**. Thus, the biogenesis of carotol via **2** would be expected to proceed by an intermediate such as **9** where R would represent a trigonal carbonium ion. We, therefore, prepared **9** as previously described (12) and reduced it with lithium aluminum hydride to get an inseparable mixture of alcoholic isomers **24**, in a 2:1 ratio as determined by ^{1}H nmr analysis of the quaternary methyl signal. When refluxed overnight in acetone containing a few drops of 90% formic acid, the alcohol mixture **24** remained unchanged. After 1.5 hr in refluxing 90% formic acid, 26% of unreacted **24** remained; whereas after 3 hrs at room temperature, a mixture containing over 15 products was obtained. The complexity of this mixture discouraged us from further analysis. We were unable to prepare the tosylate of **24** in order to study its solvolysis.

As previously mentioned, Demole *et al.* (12) reported that "carotol-ether" (**8**) gave acoratriene **10** in 70% yield and acoradiene **7** in 7% yield on treatment with $LiAlH_4/AlCl_3$ (1:2). In our hands, these conditions gave a much more complex mixture containing at least seven products with no particular major product. Stirring of a solution of "carotol-ether" in 90% formic acid at room temperature for three hours left 63% of the "carotol ether" unchanged. Heating at 50° for an additional three hours gave a product mixture still containing 21% "carotol ether" in addition to six more volatile products. Similar results were obtained by exposure of "carotol-ether" to 90% formic acid at room temperature for extended periods of time; after three days the composition of products was similar to that obtained at 50° for three hours, remaining essentially unchanged for up to 30 days. By contrast, when "dihydrocarotol-ether" (**25**) was exposed to 90% formic acid at room temperature for 30 days, greater than 90% of the ether remained unchanged. This again points out the dramatic effect of the double bond in the seven-membered ring. However, in the presence of stannic chloride in

benzene, "dihydrocarotol-ether" (**25**) quickly led to four volatile products with 15% unreacted ether remaining. The reaction products obtained from "carotol-ether" and "dihydrocarotol-ether" were not further investigated when the subsequent reaction of carotol with formic acid was found to yield a separable mixture of interesting compounds, as will be discussed in the next paper in this series.

Finally, we examined the reactions of carotol acetate (**26**) and dihydrocarotol acetate (**29**) with 90% formic acid at room temperature. Carotol acetate was prepared, as previously described (14), by reaction with acetyl chloride in *N*,*N*-dimethylaniline at 50°. Interestingly, these same conditions led to a complex mixture of at least six products in the case of dihydrocarotol acetate (**29**). When carotol acetate was passed through a silica gel column, it gave daucene (54%), acoradiene **7** (19%), acoradiene **11** (15%) and two minor dienes believed to possess the carotane skeleton. One of these has been tentatively assigned structure **27** based on its spectral properties. The ultraviolet spectrum of this diene is interesting because of the low intensities of the absorption maxima (λ^{CHCl_3} 253 nm, $\epsilon = 3470$; λ^{hexane} 275, $\epsilon = 2090$). We are unable to assign, at this time, any stereochemistry to C–6 of **27**, but an examination of Dreiding models reveals that the double bonds in **27** cannot be coplanar regardless of the stereochemistry at C–6 thus accounting for the low ϵ values. Structure **28** has been tentatively assigned to the second minor diene mostly on the basis of its ^{1}H nmr spectrum. This method of preparing acoradienes **7** and **11** is particularly facile and, interestingly, gives about a 1:1 ratio of the two acoradienes, whereas in the reaction of carotol with thionyl chloride in pyridine, the total yield was almost identical, but the ratio of **7** to **11** was about 1:2. Carotol acetate led to rearranged products even on distillation and could be distilled unchanged only when the glassware was washed in 1N sodium hydroxide and then with distilled water and then carrying out the distillation in the presence of potassium carbonate.

In the presence of 90% formic acid at room temperature, carotol acetate led within one minute to a mixture containing 83% daucene (**6**) and 17% acoradiene (**7**). Under similar conditions, carotol itself gave almost an identical product mixture, but in this case the reaction was somewhat slower. The reaction of carotol with formic acid has been studied in intensive detail and is the subject of the next paper in this series.

Dihydrocarotol acetate (**29**) was readily prepared as a mixture of C–3 isomers with one predominant (presumably the C–3 β-methyl) by hydrogenation of carotol acetate. On the other hand, an attempt to prepare dihydrocarotol acetate from dihydrocarotol under the conditions used successfully to prepare carotol acetate led instead to a complex mixture of products. Dihydrocarotol acetate reacted with formic acid at room temperature in a fashion similar to the reaction of dihydrocarotol to give a mixture of olefins **15** (16%), **16** (81%) and **17** (3%).

EXPERIMENTAL[4]

PURIFICATION OF CAROTOL (**1**).—Carrot seed oil (P. Robertet and Co., Grasse, France or Magnus, Mabee and Reynard, Inc., New York, N. Y.) was distilled with a Nester-Faust 24 x 0.5

[4]Mp's were taken on a Kofler hot stage or a Thomas-Hoover capillary apparatus and are uncorrected. Ir spectra were recorded with a Perkin Elmer 237 B spectrophotometer. ^{1}H nmr spectra were obtained with a Varian A-60D or T60 spectrometer, except where otherwise indicated, with Me_4Si as an internal standard (δ 0). ^{13}C nmr spectra were run on a JOEL-PFT-100 Ft spectrometer. Mass spectra were run on a Hitachi RMU-7 spectrometer. Gas chromatography was done with a F&M Biomedical Gas Chromatograph, model 402, and ord spectra were recorded with a Jasco ORD/UV-5 instrument. Microanalyses were done by Atlantic Microlabs, Atlanta, Georgia.

in annular teflon spinning band column to give carotol, bp 73–74°/0.35 mm; ν film 3600, 3500 cm^{-1}; ^1H nmr δ ($CDCl_3$) 0.95 (3 H, s), 0.96 (3 H, d, J=6 Hz), 1.02 (3 H, d, J=6 Hz), 1.18 (1 H, s), 1.65 (3 H, s), 5.40 (1 H, bm); ^{13}C nmr δ ($CDCl_3$) 137.7 (s), 121.5 (d), 84.0 (s), 48.8 (s), 52.2, 39.3, 38.5, 34.2, 29.3, 27.4, 25.1, 24.3, 23.9, 21.3; *m/e* 222 (M^+, 2), 204 (24), 179 (14), 162 (14), 161 (100), 151 (13), 140 (11), 139 (12), 138 (17), 137 (20), 136 (11), 123 (26), 121 (18), 120 (15), 119 (35), 110 (17), 109 (20), 107 (33), 106 (14), 105 (32), 97 (36), 96 (15), 95 (27), 94 (14), 93 (25), 84 (38), 81 (38), 79 (18), 69 (35%); ord (C, 3.02, $CDCl_3$): $[\theta]_{700}$=29.3, $[\theta]_{600}$=58.3, $[\theta]_{589}$=74.6 ($[\alpha]^{25}_{589}$=33.6), $[\theta]_{500}$=91.9, $[\theta]_{400}$=172.7, $[\theta]_{350}$=246.2, $[\theta]_{300}$=389.6°.

REACTION OF CAROTOL WITH THIONYL CHLORIDE. FORMATION OF DAUCENE (**6**), ACORADIENE **7** AND ACORADIENE **11**.—A solution prepared by dissolving 1.9 g of thionyl chloride in 16 ml of dry pyridine was slowly added, with stirring, to a solution prepared by dissolving 1.0 g carotol in 16 ml dry pyridine at ice bath temperature. After standing for 10 min at 0°, the solution was poured on to ice and extracted with ether. The ether extracts were washed with 10% HCl until acidic, then with water until neutral, dried over $MgSO_4$, filtered and evaporated *in vacuo* to give 0.88 g of a yellow oil. Glc analysis on a 6′ x ¼″, 10% XE-60 on 60/80 Gas Chrom Q column at 125° showed three products: R_t 3.1 min, daucene (**6**), 65%; R_t 4.2 min, unidentified, 4%; R_t 4.6 min, acoradiene **7**, 11%; R_t 5.2 min, acoradiene **11**, 20%. Chromatography of this product mixture on silica gel impregnated with silver nitrate (25%) gave, on elution with petroleum ether, in order of elution: 76% pure acoradiene **7**, a 10:1 mixture of daucene (**6**) and acoradiene **11** and finally pure daucene. The daucene showed the following properties: bp 100°/0.3 mm (air bath): ν film 3030, 830 cm^{-1}; ^1H nmr ($CDCl_3$) 0.90 (3 H, d, J=6 Hz), 0.90 (3 H, s), 1.00 (3 H, d, J=6 Hz), 1.40–2.90 (11 H), 5.47 (1 H, m); ^{13}C nmr δ ($CDCl_3$) 142.0 (s), 139.5 (s), 138.7 (s), 122.7 (d), 49.6 (s), 40.5, 38.7, 33.7, 27.3, 26.5, 25.8, 23.6, 22.6, 21.8, 21.2; *m/e* 204 (M^-, 7), 162 (18), 161 (100), 121 (46), 107 (14), 105 (15), 93 (20), 91 (12), 79 (10%); ord (C, 2.92, $CHCl_3$): $[\theta]_{700}$=62.9, $[\theta]_{600}$=66.3, $[\theta]_{589}$=69.0 ($[\alpha]^{25}_{589}$=34.2), $[\theta]_{500}$=94.3, $[\theta]_{400}$=150.2, $[\theta]_{350}$=178.1, $[\theta]_{300}$=337.3°.

Acoradiene **7** was obtained in >98% purity by preparative glc (6′ x ¼″, 3% SE-30 on 100/120 Gas Chrom Q at 108°) and showed the following properties: ν film 3035, 3020, 805, 795 cm^{-1}; ^1H nmr ($CDCl_3$), 0.80 (3 H, d, J=6 Hz), 0.90 (3 H, d, J=6 Hz), 1.57 (6 H, s), 1.40–2.20 (12 H), 5.30 (1 H), 5.37 (1 H); *m/e* 204 (M^+, 13), 161 (12), 136 (30), 121 (23), 105 (12), 95 (11), 94 (100), 93 (22), 91 (13), 79 (14), 78 (12), 77 (13%); ord (C, 1.51, MeOH): $[\theta]_{700}$=−27, $[\theta]_{600}$=−33.4, $[\theta]_{589}$=−33.8, ($[\alpha]^{25}_{589}$=−16.3), $[\theta]_{500}$=−60.8, $[\theta]_{400}$=−141.8, $[\theta]_{350}$=−249.9, $[\theta]_{300}$=−540.4°. *The nmr, ir, ord and mass spectra of this material were virtually identical to those of an authentic sample (13).*

Acoradiene **11** was obtained >99% purity by preparative gas chromatography (same column as above, 140°) and showed the following properties: ν film 1640, 885 cm^{-1}; ^1H nmr ($CDCl_3$) 0.84 (3 H, d, J=6.0 Hz), 0.94 (3 H, d, J=6.0 Hz), 1.65 (3 H, s), 1.15–2.70 (12 H), 4.79 (2 H, m), 5.41 (1 H, m); *m/e* 204 (M^-, 21), 162 (16), 161 (100), 133 (14), 121 (24), 119 (27), 107 (12), 105 (43), 95 (11), 94 (52), 93 (36), 91 (29), 81 (29), 79 (29), 77 (21%); exact mass Calc. for $C_{15}H_{24}$: 204.188, found: 204.187; ord (C, 1.35, CH_3OH): $[\theta]_{700}$=34.0, $[\theta]_{600}$=52.9, $[\theta]_{589}$=55.9, ($[\alpha]^{25}_{589}$=27.4), $[\theta]_{500}$=86.9, $[\theta]_{400}$=162.4, $[\theta]_{350}$=256.9, $[\theta]_{300}$=460.9°.

REACTION OF CAROTOL WITH PHOSPHORUS OXYCHLORIDE AND METHANESULFONYL CHLORIDE.—To a solution of 1.0 g carotol in pyridine (4 ml) at 0° was added 1.4 g of $POCl_3$, and the entire solution was stirred under N_2 at 0° for 3 hr, after which glc analysis indicated no reaction. The solution was then stirred at room temperature for 89 hr, after which glc analysis indicated less than 10% reaction. The solution was then poured on ice and extracted with ether: the ether extract was washed with 10% HCl until acidic, then with water until neutral and finally dried over $MgSO_4$. Evaporation yielded 0.95 g of a yellow oil, glc of which indicated 90% carotol. Chromatography on silica gel gave, in addition to carotol, small amounts of material with glc retention times corresponding to daucene and acoradiene **7**.

Methanesulfonyl chloride (120 mg) was added by syringe to a solution of carotol (210 mg) in dry pyridine (4 ml) under nitrogen. After 28 hr, glc analysis indicated no reaction, and an additional 1.06 g of methanesulfonyl chloride was added to the solution. Glc analysis again indicated no reaction after an additional 19 hr. The solution was then refluxed for 25 hr after which glc analysis (6′ x ¼″, 10% XE-60 on 60/80 Gas Chrom Q at 170°) showed: R_t 0.8 min, daucene, 41%; R_t 1.0 min, acoradiene **7**, 20%; R_t 1.1 min, acoradiene **11**, 10%; R_t 3.0 min, unidentified, 5%; R_t 3.5 min, carotol, 24%. Glc analyses were also run on a 4′ x ¼″, 3% SE-30 column at 141° and a 6′ x ¼″ 20% XF-1150 column at 108° with similar results.

HYDROGENATION OF CAROTOL. PREPARATION OF EPIMERIC DIHYDROCAROTOLS (**14**).—Hydrogen was added to 3.0 g of carotol in 35 ml of glacial acetic acid in the presence of 243 mg of 83.4% PtO_2 at 22° and 740 mm. Hydrogen uptake ceased after 2 hr when 415 cc had been taken up. The solution was filtered through Celite 545, concentrated *in vacuo*, taken up in ether, washed with saturated $KHCO_3$ until basic, then with water until neutral, and finally dried over $MgSO_4$. Filtration and evaporation gave a yellow oil which on fractional distilla-

tion gave 2.75 g of epimeric dihydrocarotols: bp 68–69°/0.075 mm; ν film 3610, 3515 cm^{-1}; ^1H nmr ($CDCl_3$) 0.88–1.03 (9 H, overlapping multiplets), 1.00 (3 H, s), 1.25 (1 H, s), 1.30–2.10 (15 H, complex); ^{13}C nmr ($CDCl_3$) 83.8, 87.8 (hydroxyl bearing carbons of each epimer); *m/e* 224 (M^+, 2), 206 (10), 191 (22), 163 (100), 140 (95), 139 (56), 121 (21), 107 (32), 97 (39), 95 (39), 81 (42), 69 (45%); Calc. for $C_{15}H_{25}O$: C, 80.36; H, 12.50; Found: C, 80.34; H, 12.50.

REACTION OF DIHYDROCAROTOL (**14**) WITH THIONYL CHLORIDE. FORMATION OF DEHYDRODIHYDROCAROTOLS **15**, **16** AND **17**.—A solution of thionyl chloride (2.0 ml) in dry pyridine (15 ml) was added dropwise to a solution of the epimeric dihydrocarotols (**14**, 1.0 g) in dry pyridine (15 ml) at 0°. After 10 min of stirring, the solution was poured into 10 g of ice/water, extracted with ether, washed with 10% HCl until acidic, then with water until neutral, dried over $MgSO_4$, filtered, and evaporated *in vacuo* to give 0.92 g of a pale yellow oil. Glc analysis (10% XE-60 column at 170°) showed three products: R_t 0.6 min, **15**, 28%; R_t 0.7 min, **16**, 51%; R_t 1.0 min, **17**, 21%. Chromatography on silica gel impregnated with silver nitrate (25%) gave, on elution with petroleum ether, in order of elution **15**, **16** and, finally, a 1:5 mixture of **16** and **17**, respectively. Rechromatography of the latter fraction, as above, gave analytically pure **17**.

1β, 4α-DIMETHYL-8-ISOPROPYLBICYCLO (5.3.0)DEC-7-ENE. (**15**).—The following data was obtained for compound **15**: bp 50–51°/0.07 mm; ν film 1445, 1360, 1345, 1175, 1100, 1060, 1010, 970 cm^{-1}; ^1H nmr ($CDCl_3$) 0.87 (3 H, s), 0.88 (3 H, d, J=6 Hz), 0.92 (3 H, d, J=6 Hz), 1.03 (3 H, d, J=6 Hz), 1.20–3.00 (14 H); ^{13}C nmr ($CDCl_3$) 141.9, 139.8 and 13 other higher field signals; *m/e* 206 (M^+, 12), 191 (50), 163 (100), 135 (11), 121 (26), 107 (19), 95 (19), 93 (14), 91 (15), 81 (15), 79 (11), 77 (10%); Calc. for $C_{15}H_{26}$: C, 87.37; H, 12.63; Found: C, 87.35; H, 12.62.

1β, 4β-DIMETHYL-8-ISOPROPYLBICYCLO (5.3.0)DEC-7-ENE (**16**).—The following data was obtained for compound **16**: bp 50–51°/0.07 mm; ν film 1440, 1365, 1080, 1035, 1000, 980 cm^{-1}; ^1H nmr ($CDCl_3$) 0.93 (3H, d, J=6 Hz), 0.97 (3 H, s), 0.97 (3 H, d, J=6 Hz), 0.98 (3 H, d, J=6 Hz); 13C nmr ($CDCl_3$) 140.9, 139.7 and 13 higher field signals; *m/e* 206 (M^+, 10), 191 (42), 163 (100), 135 (9), 121 (24), 107 (18), 95 (20), 93 (15), 91 (15), 81 (15), 79 (12), 77 (11%); Calc. for $C_{15}H_{26}$: C, 87.37; H, 12.63; Found: C, 87.34; H, 12.63.

1β, 4β-DIMETHYL-8β-ISOPROPYLBICYCLO (5.3.0)DEC-6-ENE (**17**).—The following data was obtained for compound **17**: bp 54–55°/0.05 mm; ν film 1461, 1377, 1111, 1161, 1183, 1050, 967, 889, 861, 844 cm^{-1}; ^1H nmr ($CDCl_3$) 0.75 (3 H, d, J=6 Hz), 0.86 (3 H, d, J=6 Hz), 0.93 (3 H, d, J=6 Hz), 0.98 (3 H, s), 5.40 (1 H, m); ^{13}C nmr ($CDCl_3$) 153.9, 118.0 and 13 higher field signals; *m/e* 206 (M^-, 8), 191 (21), 163 (100), 149 (10), 135 (6), 121 (18), 107 (38), 95 (37), 93 (20), 91 (22), 81 (33), 79 (19), 77 (14%); Calc. for $C_{15}H_{26}$: C, 87.37; H, 12.63; Found: C, 87.33; H, 12.65.

EQUILIBRATIONS OF DEHYDRODIHYDROCAROTOLS **15**, **16** AND **17** WITH 90% FORMIC ACID.—Approximately 10 mg of each of the isomers **15**, **16** and **17** were separately added to 0.5 ml of 90% formic acid, and the magnetically stirred solutions were periodically analyzed by glc (4′ x ¼″, 3% SE-30 column at 130°). There was no change in **15** or **16** after 20 hr and after 30 days. However, after one hour the glc of **17** showed its conversion to **16** in 15% yield.

In another experiment a solution of 98 mg of **17** in 5 ml of 90% formic acid was stirred at rt for 19 hr after which water (5 ml) was added, and the solution was then extracted with ether. After washing with $KHCO_3$ until basic, then with water until neutral, drying over $MgSO_4$, evaporation and removal of solvent *in vacuo*, there remained 80 mg of a colorless oil the glc of which indicated 73% **16**, 7% unidentified and 20% unchanged **17**. Chromatography of this oil on silica gel impregnated with silver nitrate (25%) gave 16, identical in all respects with that previously reported.

REACTION OF DIHYDROCAROTOL (**14**) WITH 90% FORMIC ACID.—A solution prepared by the addition of 100 mg of dihydrocarotol (**14**) to 5 ml of 90% formic acid was stirred at rt. Glc analysis (4′ SE-30 column) after 20 min showed no starting material and three products. After an additional 40 min of stirring, the solution was worked up as described above to give 82 mg of a pale yellow oil. Glc analyses at 132° on three columns (4′ 3% SE-30; 6′ 10% XE-60; 6′ 20% XF-1150) showed 25% **15**, 70% **16** and 5% **17**.

HYDROGENATION OF DAUCENE (**6**). ISOLATION OF **15**, **16**.—Daucene (175 mg, **6**) and 10 mg of 83.5% PtO_2 were added to 5 ml of ethyl acetate and the solution was stirred in a hydrogen atmosphere at 23° and 740 mm. Hydrogen uptake (25 cc) ceased after 3 hr; filtration through Celite 545 and removal of the solvent *in vacuo* gave 156 mg of a pale yellow oil. Glc analysis on three columns (see above) showed a 1:1 mixture of **15** and **16**. This oil remained unchanged when dissolved in ethyl acetate (5 ml) and subjected to 3 atm of hydrogen pressure in the presence of 10 mg of 83.4% PtO_2 for 23 hr.

When 220 mg of daucene was hydrogenated at 3 atm hydrogen pressure in ethanol (4 ml) containing 2 drops of conc. HCl in the presence of 15 mg of 10% Pd on C at rt for 24 hr, 215 mg of a colorless oil was obtained. Glc analysis showed 33% **16**, 53% **15** and 14% daucane (**18**).

HYDROGENATION OF CAROTOL. FORMATION OF DAUCANE (**18**).—Carotol (520 mg) in glacial acetic acid (5 ml) was stirred at 22° under hydrogen at atmospheric pressure in the presence of

104 mg of 10% Pd on carbon. After six days hydrogen uptake ceased; the solution when worked up in the usual manner gave 465 mg of a colorless oil with properties analogous to those previously reported (22) for daucane. The following data was obtained: bp 44–45°/0.02 mm; ν film 1455, 1380, 1370, 1160, 1080, 1020, 960, 940 cm^{-1}; ^1H nmr ($CDCl_3$) 0.75–100 (9 H, overlapping doublets), 0.93 (3 H, s); *m/e* 208 (37), 193 (54), 165 (85), 138 (42), 137 (38), 124 (66), 123 (90), 109 (96), 97 (42), 96 (60), 95 (100), 83 (63), 82 (72), 81 (83%).

REACTION OF **16** WITH *M*-CHLOROPERBENZOIC ACID. FORMATION OF **22**.—A solution of 85% *m*-chloroperbenzoic (640 mg) in 20 ml of methylene chloride was added dropwise to a solution of 500 mg of **16** in 20 ml of methylene chloride at 0°. After 0.5 hr, no peracid could be detected with starch-iodide paper. After an additional 15 min of stirring, the solution was allowed to warm to rt, washed with saturated $KHCO_3$ until basic, with water until neutral, dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* gave 497 mg of a colorless oil, and glc (6′ x ¼″ 10% XE–60 column) of which showed two peaks in a ratio of 2:1. Column choromatography on silica gel, acid-washed, neutral and basic alumina failed to resolve the mixture. The following data was obtained for the oil: ν film 1450, 1380, 1015, 980, 960, 940, 920, 890 cm^{-1}; ^1H nmr ($CDCl_3$) 0.93 (3 H, d, $J=6$), 1.00 (3 H, d, $J=6$), 1.03 (3 H, d, $J=6$), 1.07 (3 H, s); ^{13}C nmr ($CDCl_3$) 27 observable lines, two of which (76.2 and 74.7) could be assigned to ether carbons; *m/e* 222 (13), 161 (14), 136 (36), 123 (18), 121 (20), 119 (11), 109 (16), 107 (20), 95 (44), 94 (11), 93 (15), 82 (12), 81 (31), 79 (12), 43 (100%); exact mass Calc. for $C_{15}H_{24}O$: 222.198; found: 222.196±0.004.

REACTION OF **15** WITH *M*-CHLOROPERBENZOIC ACID. FORMATION OF **23**.—Epoxidation of **15** (400 mg), as described above, gave 256 mg of a colorless oil which was shown by glc to be a 1:1 mixture of products. With exactly the same ratio of *m*-chloroperbenzoic acid to olefin and identical conditions, the starch-iodide test indicated the disappearance of peracid only after 3 hr for the reaction with **15**, whereas with **16** a negative test was obtained after only 0.5 hr! Product **23** showed the following properties: ν film 1450, 1380, 1362, 1010, 985, 960, 940, 920, 885, 860, 855 cm^{-1}; ^1H nmr ($CDCl_3$) 5 sharp signals with several shoulders from 0.85–1.20 (12 H); ^{13}C nmr ($CDCl_3$) 25 observable lines, two of which (75.2, 74.4) could be assigned to ether carbons; *m/e* 222 (20), 136 (75), 121 (29), 107 (35), 95 (36), 81 (38), 71 (52), 55 (38), 43 (100%); exact mass Calc. for $C_{15}H_{24}O$: 222.198; found: 222.196±0.004.

REACTIONS OF **22** AND **23** WITH FORMIC ACID AND STANNIC CHLORIDE.—A solution of **22** (156 mg) in 6 ml of 90% formic acid containing 1 ml of dioxane and 0.1 ml water was stirred at rt. Glc analysis (4′ x ¼″ 3% SE–30 column) indicated that the composition of the solution remained constant after 3 min. After an additional 2 hr, water was added and the mixture was extracted with ether. The combined ether extracts were washed with saturated $KHCO_3$ solution until basic, then with water until neutral and, finally, dried over $MgSO_4$ and filtered. Removal of the solvent *in vacuo* gave 118 mg of a yellow oil, the glc analysis (same column as above) of which indicated three major products (45, 30 and 10%) and four minor products.

Stannic chloride (0.2 ml) was added to a chilled solution (ice bath) of **22** (100 mg) in 10 ml anhydrous benzene. After the solution was warmed to rt and stirred for 2 hr, 5 g of ice water was added, and the solution was then extracted with benzene. After washing with water, drying over $MgSO_4$, filtration and removal of the solvent *in vacuo*, a viscous yellow oil (112 mg) was obtained. Glc analysis (6′ x ¼″ 10% XE–60 column) showed two major products comprising about 85% and 12 minor products. Glc indicated no starting material remaining after 10 min of reaction time.

Similar treatment of **23** (244 mg) with formic acid to that described above gave complete reaction after 10 min. The solution was worked up after 15 hr, as described above, to give 220 mg of a yellow oil, glc analysis of which (3% SE–30 column above) indicated six major components.

Treatment of 10 mg of **23** with stannic chloride, as described above, resulted in the disappearance of the starting material after 2 min; the product composition appeared invariant after 12 min. Workup, as described above, after 48 hr gave a product which on glc analysis (10% XE–60 column above) showed at least 12 volatile products, three of which comprised about 70% of the mixture.

PREPARATION OF "CAROTOL-ETHER" (**8**).—2,5-Dimethyl-2-(4-methyl-3-pentenyl)-4-cycloheptenone (**9**) was prepared as previously described and showed ir, ^1H nmr and mass spectra similar to those previously reported (12); ^{13}C nmr ($CDCl_3$) 215.9 (C=O), 136.8, 131.5, 124.3, 121.6 (olefinic carbons). The cycloheptenone **9** was converted into "carotol-ether" (**8**) as described by Demole *et al.* (12) and showed identical ir, ^1H nmr and mass spectra to those reported (12); ^{13}C nmr ($CDCl_3$) 134.0, 119.9 (olefinic carbons), 86.7, 78.0 (ether carbons).

PREPARATION OF 2,5-DIMETHYL-2-(4-METHYL-3-PENTENYL)-4-CYCLOHEPTENOL (**24**).—A solution prepared by the addition of 1.02 g of cycloheptenone **9** and 1.74 g of $LiAlH_4$ to 40 ml of anhydrous ether was stirred at rt for 3 hr. After the usual workup, 1.03 g of a yellow oilish product was obtained. Chromatography of this product on silica gel and elution with 1:1 benzene-hexane gave 0.70 g of pure alcohol **24** (glc on 3% SE–30 column). The compound exhibited the following

data: bp 60–61°/0.05 mm; ν film 3400, 1015 cm^{-1}; ^1H nmr ($CDCl_3$) 0.85 (3 H, s), 0.97 (3 H, s), 1.63 (3 H, s), 1.72 (3 H, d, $J=1$); 1.75 (3 H, d, $J=0.5$), 3.53 (1 H, bm), 5.32 (2 H, bm); ^{13}C nmr ($CDCl_3$) 140.1 (s), 130.9 (s), 125.4 (d), 122.4 (d), 81.2 (d); the ^{13}C spectrum indicates the presence of two isomers by the doubling of many lines and those listed for the major isomer; *m/e* 222 (13), 204 (11), 161 (9), 135 (16), 123 (11), 122 (38), 121 (23), 119 (36), 109 (56), 107 (45), 95 (34), 94 (24), 93 (72), 82 (69), 81 (42), 78 (33), 69 (71), 67 (38), 55 (46), 41 (100%), Calc: for $C_{15}H_{26}O$: C, 81.02; H, 11.78; Found: C, 80.84; H, 11.80.

Several attempts to prepare the tosylate of **24** using *p*-toluenesulfonyl chloride and pyridine failed.

REACTION OF CYCLOHEPTENENOL **24** WITH FORMIC ACID.—After a solution prepared by the addition of 50 mg of **24** and several drops of 90% formic acid in 5 ml of acetone was refluxed for 19 hrs, glc analysis (4′ x ¼″ 3% SE-30 column) indicated no reaction. Addition of water, basification to pH 10, extraction with ether and the usual workup gave unchanged **24**.

A solution prepared by addition of 60 mg of **24** to 5 ml of 90% formic acid was refluxed for 1.5 hr and then worked up as described above gave 20 mg of a yellow oil which, on glc analysis (same column as above), showed 26% of unreacted **24**, 38% of a product of lower retention time, 26% of a product of higher retention time and 10% of a product of even higher retention time.

When a solution of 99 mg of **24** in 4 ml of 90% formic acid was stirred at rt for 3 hr, a blue color developed after 0.5 hr which became more intense with time. The color disappeared when the solution was added to water. The usual workup gave 85 mg of a yellow oil which, by glc analysis (same column as above), showed 15 distinct peaks.

PREPARATION OF DIHYDROCAROTOL ETHER (**25**).—A stirred solution of 483 mg of "carotol-ether" in 6 ml of acetic acid containing 39 mg of 83.4% PtO_2 was hydrogenated at 740 mm and 23°. The usual workup gave 267 mg of a yellow oil, the glc analysis (6′ x ¼″ 10% XE-60 column) of which indicated a 86:14 ratio of epimers. Chromatography on silica gel gave a "dihydrocarotol-ether" with identical ^1H nmr and mass spectra to that previously reported (12); ^{13}C nmr ($CDCl_3$) 86.9, 77.5 (ether C's) and 13 other lines; *m/e* 222 (M^+, 14), 194 (30), 164 (82), 149 (75), 121 (84), 107 (75), 95 (85), 81 (75), 69 (100%).

REACTION OF "CAROTOL-ETHER (**8**) WITH $LiAlH_4/AlCl_3$.—A solution of 1.37 g aluminum chloride in 4 ml of anhydrous ether was added to a suspension of 0.19 g of lithium aluminum hydride in 4 ml of anhydrous ether cooled in an ice bath. A solution of 1.12 g of "carotol-ether" (**8**) in 5 ml of anhydrous ether was slowly added to the above refluxing solution. After 2 hr of refluxing, the usual work-up gave 1.04 g of yellow oil the glc analysis (4′ x ¼″ 3% SE-30 column) of which showed a complex mixture of at least 7 components with no major product.

REACTION OF "CAROTOL-ETHER" (**8**) WITH FORMIC ACID.—A solution of "carotol-ether" (103 mg) in 90% formic acid (4 ml) was stirred at rt for 3 hr after which time glc analysis (same column as above) showed 63% "carotol-ether" remaining and three additional volatile products. The solution was then heated at 50° with stirring for 3 hr, then cooled to rt, 5 ml of water was then added and the solution was extracted with ether. The ether extracts were washed with saturated $KHCO_3$ until basic and with water until neutral, dried over $MgSO_4$ and filtered. When the solvent was removed *in vacuo*, 84 mg of a yellow oil was obtained. Glc analysis (same column as above) showed "carotol-ether" (21%), one more volatile product (47%) and five less volatile products.

When this reaction was repeated with 11 mg of "carotol-ether" in 1 ml of 90% formic acid at rt, after three days glc analysis showed the same mixture as obtained under the above conditions (50°, 3hr) and the composition remained invariant up to 30 days.

REACTION OF "DIHYDROCAROTOL-ETHER" (**25**) WITH STANNIC CHLORIDE AND FORMIC ACID.—A solution of stannic chloride (83 mg) in 2 ml of anhydrous benzene was added dropwise to a chilled solution of "dihydrocarotol-ether" (71 mg) in anhydrous ether. After being stirred for 1 hr, the solution was then made basic with saturated K_2CO_3 and extracted with benzene. The latter extracts were washed with water, dried, filtered and evaporated to give 51 mg of a yellow oil. Glc analysis (6′ x ¼″ 10% XE-60 column) showed 15% "dihydrocarotol-ether", three more volatile products and one less volatile product.

A solution of "dihydrocarotol-ether" (11 mg) in 1 ml of 90% formic acid was stirred at rt for thirty days. Glc analysis (4′ x ¼″ 3% SE-30 column) indicated greater than 90% "dihydrocarotol-ether" remaining after this time.

PREPARATION OF CAROTOL ACETATE (**26**).—Carotol acetate was prepared as previously described (14) and showed ir and ^1H nmr spectra identical to those previously reported; bp 80–81° (0.06 mm); ^{13}C nmr ($CDCl_3$) 169.5 (C=O), 136.0, 121.2 (olefinic C's), 97.4 (C–O) and nine other lines; *m/e* 204 (M^+-$C_2H_4O_2$, 35), 161 (100), 136 (49), 121 (42), 119 (36), 107 (25), 105 (54), 94 (53), 93 (35), 91 (26), 81 (45%). In order to prevent rearrangement, it was necessary to distill the carotol acetate from K_2CO_3 in an apparatus previously rinsed with 1N NaOH then water.

REARRANGEMENT OF CAROTOL ACETATE (**26**) ON SILICA GEL.—Carotol acetate (5.19 g) dissolved in hexane was passed through a silica gel (300 g) column and the column was eluted with hexane to give 4.83 g of a colorless oil. Stripping of the column with benzene failed to give any products detectable by glc. Glc analysis (4′ x ¼″ 3% SE-30 column at 130°) showed the following products: R_t=2.7 min (54%), R_t=3.4 min (7%), R_t=3.6 min (19%), R_t=3.9 min (15%), R_t=5.5 min (5%). A sample of component R_t=2.7 min was isolated by preparative glc (6′ x ¼″ 3% SE-30 column, 101°) and showed an ^{1}H nmr spectrum and glc retention time identical to that of an authentic sample of daucene (**6**). A sample of component R_t=3.6 min was collected by preparative glc (same conditions as above) and shown by ^{1}H nmr and glc retention time to be acoradiene **7**. In a similar manner, component R_t=3.9 was isolated and identified as acoradiene **11**.

One gram of the original product mixture was chromatographed on silica gel impregnated with silver nitrate (25%). The first fraction eluted with petroleum ether gave 113 mg of a 3:2 mixture of components R_t=3.4 min and R_t=5.5 min respectively. Preparative gas chromatography, as described above, gave each component in >98% purity with the properties indicated below.

R_t=3.4 Min, Compound **27**.—ν film 815, 710 cm^{-1}; $\lambda_{max\ 253}^{CHCl_3}$ mm (ϵ=3470), $\lambda_{max\ 275}^{hexane}$ (2090); ^{1}H nmr ($CDCl_3$) 0.83 (3 H, d, J=6), 0.92 (3 H, d, J=6), 0.85 (3 H, s) 1.63 (3 H, m), 5.23 (1 H, d, J=10), 5.32 (1 H, m), 5.67 (1 H, d, J=10); *m/e* 204 (14), 161 (17), 119 (100), 105 (72%); exact mass Calc. for $C_{15}H_{24}$: 204.188; found: 204.187±0.004.

R_t=5.5 Min. Compound **28**.—ν (CCl_4) 1445, 1370, 1130, 1125, 1100, 1060, 1015, 980 cm^{-1}; ^{1}H nmr ($CDCl_3$) 0.70 (3 H, s), 1.57 (3 H, s), 1.72 (6 H, s), 5.40 (1 H, m); *m/e* 202 (M^+, 11), 173 (7), 159 (100), 157 (14%).

REACTION OF CAROTOL ACETATE (**26**) WITH FORMIC ACID.—Carotol acetate (6.2 mg) was stirred in 90% formic acid at rt. Glc analysis after one minute showed two components and no starting material. After an additional 30 min, glc analysis (4′ x ¼″ 3% SE-30 column) showed no further change and the solution was worked up. One ml of ether was added to the solution, which was then washed with saturated $KHCO_3$ until basic, then with water until neutral, dried and filtered. Glc analysis, alone and on admixture with authentic samples, showed that the mixture was comprised of 83% daucene (**6**) and 17% acoradiene **7** on the three columns: 4′ x ¼″ 3% SE-30; 6′ x ¼″ 10% XE-60; 6′ x ¼″ 20% XF-1150.

DIHYDROCAROTOL ACETATE (**29**).—Carotol acetate (2.00 g) in 20 ml of ethyl acetate was stirred in the presence of 50 mg of 83.4% PtO_2 under a hydrogen atmosphere at rt and 740 mm pressure and after 2 hr the theoretical quantity of hydrogen was absorbed. The usual workup followed by distillation from K_2CO_3 in an apparatus previously washed with 1N NaOH gave 1.94 g of dihydrocarotol acetate. It gave the following data: bp 79.0–79.5/0.05 mm; ν film 1730, 1250, 1015 cm^{-1}; ^{1}H nmr ($CDCl_3$) complexity of methyl region indicates a mixture of isomers, 1.95 (3 H, s); ^{13}C ($CDCl_3$) 169.2, 98.2, one intense set of peaks and a second weak set of peaks; *m/e* 206 (M^+–$C_2H_4O_2$, 10), 191 (16), 163 (100), 121 (13), 107 (37), 95 (34), 81 (42), 60 (20), 55 (20); exact mass Calc. for $C_{15}H_{30}O_2$–$C_2H_4O_2$: 206.204; found: 206.204±0.004.

When an attempt was made to prepare dihydrocarotol acetate by addition of acetyl chloride to dihydrocarotol in *N,N*-dimethylaniline at 50°, the exact conditions used in the preparation of carotol acetate (14), there was obtained a colorless oil containing at least six volatile products with the desired acetate comprising approximately 30% of the mixture.

REACTION OF DIHYDROCAROTOL ACETATE (**29**) WITH FORMIC ACID.—A solution of dihydrocarotol acetate (6.3 mg) in 0.4 ml of 90% formic acid was stirred at rt. Glc analysis (4′ x ¼″ 3% SE-30 column) after one minute showed three peaks, none of which corresponded to the starting material. After an additional 30 min, the composition of the mixture was invariant and the solution was worked up in the usual manner. Glc analysis alone and on admixture with authentic samples showed the mixture to contain: **15** (16%), **16** (81%) and **17** (3%) on the three glc columns mentioned above for the analysis of the reaction of carotol acetate with formic acid.

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LITERATURE CITED

1. T. K. Devon and A. T. Scott, "Handbook of Natural Products—Volume II", Academic Press, New York, N. Y., 1972.
2. M. C. Sriraman, B. A. Nagasampagi, R. C. Randy and S. Dev, *Tetrahedron*, **29**, 985 (1973).
3. C. A. Williams and J. B. Harborne, *Phytochemistry*, **11**, 1981 (1972).
4. Y. Tsuda, M. Kaneda, A. Tada, K. Nitta, Y. Yamamoto and Y. Iitaka, *J. C. S. Chem. Comm.*, 160 (1978).
5. K. Rajendran, S. K. Paknikar, G. K. Trivedi and S. C. Bhattacharyya, *Ind. J. Chem.*, **16B**, 4 (1978).
6. A. G. Gonzalez, B. M. Fraga, M. G. Hernandez, J. G. Luis, R. Estevez, J. L. Baez and M. Rivers, *Phytochemistry*, **16**, 265 (1977).

7. A. I. Saidkhodzhoev and G. K. Nikonov, *Khim. Prir. Soedin*, 105 (1976); *C. A.*, **85**, 59567 Y.
8. A. Sh. Kadyrov, A. T. Saidkhodzhoev and G. K. Nikonov, *Khim. Prir. Soedin*, 102 (1976); *C. A.*, **85**, 59565 W.
9. M. Souček, *Coll. Czech. Chem. Comm.*, **27**, 2929 (1962).
10. P. Naegli and R. Kaiser, *Tetrahedron Lett.*, 2013 (1972).
11. M. Yamaski, *Chem. Comm.*, 606 (1972).
12. E. Demole, P. Enggist and Mlle. C. Borer, *Helv. Chim. Acta*, **54**, 1845 (1971).
13. R. Kaiser and P. Naegeli, *Tetrahedron Lett.*, 2009 (1972).
14. J. Levisalles and H. Rudler, *Bull. Soc. Chim. France*, 2059 (1967).
15. ibid, 299 (1968).
16. M. Allard, J. Levisalles and H. Rudler, ibid, 303 (1968).
17. H. deBroissia, J. Levisalles and H. Rudler, ibid, 4314 (1972).
18. R. B. Bates, C. D. Green and T. C. Sneath, *Tetrahedron Lett.*, 3461 (1969).
19. V. Sykora, L. Novotny, M. Holub, V. Herout and F. Sorm, *Coll. Czech. Chem. Comm.*, **26**, 788 (1961).
20. James H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959).
21. F. Sorm and L. Cirbanek, *Coll. Czech. Chem. Comm.*, **13**, 49 (1948); ibid., 420 (1948).
22. G. Chuirdoglu and M. Descamps, *Tetrahedron*, **8**, 271 (1960).
23. G. J. Matthews and A. Hassner, in "Organic Reactions in Steroid Chemistry, Vol. II", edited by J. Fried and J. A. Edwards, Van Nostrand Reinhold Co., New York, 1972, pp. 2–19.