of V in ethanol. TFE treatment of the 2-hr-old photolyzed solution gave a mixture containing only I, 50%; IV, 43%, and V, 6.7%. The observations that a photoproduct of I decays to V within 2 hr, and that the four products it yields on treatment with TFE and ethanol have elution times identical with those of the corresponding products from VI, leave little doubt that it is indeed VI. By correcting the results for the thermal decay and photolysis of VI, we estimate that I, which disappears with a quantum yield of 0.5, yields IV, 86%; V, 2%; and VI, 12%.

It is of some interest that the interconversion of benzvalenes I and VI, which involves a valence interchange between double bond and cyclopropane ring, is a transformation of a type envisaged[11] in the naming of this class of compounds. In the present case, such a transformation does occur upon photochemical excitation. That it does not occur thermally is obvious from the facts that VI decays to V, but not to I or IV, and that I on heating yields IV, but not V.

The results of the present study are summarized in the following diagram, in which the numbers represent quantum yields in isohexane solution at 2537 Å and 25°.

$$\begin{tikzcd}
\mathrm{VI} \arrow[r, shift left, "\sim 0.2"] \arrow[d, shift left, "\sim 0.6"] \arrow[dr, "\sim 0.2"'] \arrow[d, bend right=60, "t_{1/2} = 17\,\mathrm{min}"'] & \mathrm{I} \arrow[l, shift left, "0.06"] \arrow[d, shift right, "0.43"'] \arrow[dl, "0.01"] \\
\mathrm{V} \arrow[u, shift left, "0.12"] & \mathrm{IV} \arrow[u, shift right, "0.05"']
\end{tikzcd}$$

Acknowledgment. We are indebted to Miss Gail Norman for nmr analyses and to W. A. Mulac for assistance with the flash photolyses.

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[11] H. G. Viehe, *Angew. Chem.*, 77, 768 (1965); *Angew. Chem. Intern. Ed. Engl.*, 4, 746 (1965).

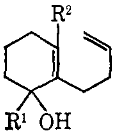
Allylic Cation Promoted Olefinic Cyclizations.[1] The Stereospecific Formation of a Tricyclic System and the Total Synthesis of *dl*-Fichtelite[2]

William S. Johnson, Norman P. Jensen, John Hooz, and Eric J. Leopold

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received April 30, 1968

Abstract: The cyclization of the trienol **3** has been studied. It was prepared as follows: the dienic bromide **5** was formed from the alcohol **11** which, in turn, was produced as suggested in the flowsheet, **7** → **8** → **9** → **10** → **11**. Alkylation of the keto ester **4** with the bromide **5** afforded the substance **6**, which upon hydrolysis and decarboxylation gave the trienone **13**. Treatment of this last substance with methyllithium afforded the trienol **3**. When the trienol **3** was shaken with formic acid, at room temperature, it was converted in high yield into a mixture of the carbinol **20** and the hydrocarbons **16**, **17**, **18**, and **19**. All of these substances were shown to belong to the same stereochemical series, having "natural" (*anti*, *trans*) configuration, by interconversion experiments and by their reductive transformation into the natural product, fichtelite (**21**).

In previous work from our laboratory it was shown that the butenylcyclohexenol **1** ($R^1 = R^2 = H$), on treatment with formic acid for a few minutes at room temperature, undergoes a highly stereoselective cyclization to give an excellent yield of the formate of the octalol **2** ($R^1 = R^2 = H$).[3] The process appears to proceed *via* an allylic cationic intermediate. It was also shown[4] that the homologous dienol **1** ($R^1 = H, R^2 = CH_3$) cyclized to give the formate of the methyloctalol **2** ($R^1 = CH_3, R^2 = H$) along with products derived from the addition of formic acid to the olefinic bond of this bicyclic substance; none of the product **2** ($R^1 = H, R^2 = CH_3$) containing an angular methyl group was formed. In connection with his ingenious synthesis of telekin and alantolactone, Marshall[5] had occasion to utilize the cyclization of the next higher homolog **1** ($R^1 = R^2 = CH_3$) which afforded the formate of the dimethyloctalol **2** ($R^1 = R^2 = CH_3$), containing an angular methyl group, in excellent yield. We have now extended our study to include an examination of the behavior of the trienol **3**.



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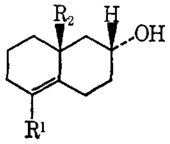

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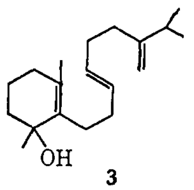

3

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[1] This represents paper XI of the series on olefinic cyclizations. Part X: W. S. Johnson, A. van der Gen, and J. J. Swoboda, *J. Amer. Chem. Soc.*, **89**, 170 (1967).

[2] For a preliminary account of this work, see W. S. Johnson, N. P. Jensen, and J. Hooz, *ibid.*, **88**, 3859 (1966).

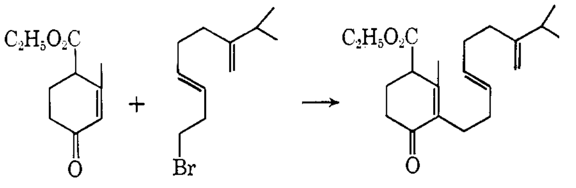
[3] W. S. Johnson, W. H. Lunn, and K. Fitzi, *ibid.*, **86**, 1972 (1964).

[4] W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *ibid.*, **87**, 5148 (1965).

[5] J. A. Marshall, N. Cohen, and A. R. Hochstettler, *ibid.*, **88**, 3408 (1966).

To our gratification we have found that this substance undergoes highly stereoselective ring closure to give tricyclic material in very high yield. An account of this study is given in the present paper.

Synthesis of the Trienol 3. In analogy to the preparation of the dienols **1** (R^1 = H, R^2 = CH_3)[4] and **1** (R^1 = R^2 = CH_3),[5] we envisaged using the well-known alkylation of the enolate anion of Hagemann's ester **4** with the bromo diene **5** to give the keto ester **6**, which on hydrolysis and decarboxylation followed by reaction with methyllithium[5] promised to give the trienol **3**.

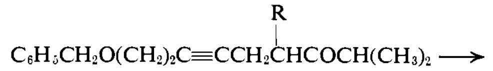


4 **5** **6**

The bromodiene **5** was prepared by the sequence depicted in the accompanying flowsheet. Commercially available 3-butyn-1-ol was converted, by reaction with sodium hydride followed by benzyl bromide, into the benzyl ether **7**. The acetylide, prepared by the action of ethylmagnesium bromide on the acetylenic ether **7**, was treated with formaldehyde to give the alcohol **8** (X = OH) which was transformed, by reaction with phosphorus tribromide, into the bromide **8** (X = Br). This bromide was used to alkylate the sodio derivative of ethyl isobutyrylacetate, giving the keto ester **9** (R = CO_2Et) which, on treatment with barium hydroxide, underwent hydrolysis and decarboxylation to afford the ketone **9** (R = H). An attempt to prepare this ketone by the copper bromide catalyzed addition of the aforementioned acetylide to isopropyl vinyl ketone was unsuccessful. The ketone **9** (R = H) was transformed, by treatment with methylenetriphenylphosphorane, into the enyne ether **10**. Treatment of this last substance with sodium in liquid ammonia effected stereoselective reduction of the acetylenic bond as well as hydrogenolysis of the benzyl ether to give the *trans*-dienol **11**. The conditions for this reduction step were critical. When excess metal was added to a solution of the substrate in ammonia, reduction of the acetylenic bond was always incomplete and, in addition, some spurious by-products were formed. When lithium was used instead of sodium, and tetrahydrofuran was employed as a cosolvent, very little reduction of the acetylenic bond occurred, and the major product was the enynol. Success was realized by carrying the reduction out in an "inverse" fashion, *i.e.*, an ethereal solution of the substrate was added to a solution of sodium in ammonia. In this way *trans*-dienol **11** of approximately 99% purity was readily obtained.

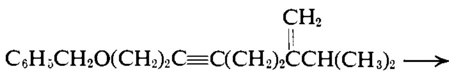
$C_6H_5CH_2O(CH_2)_2C{\equiv}CH \longrightarrow C_6H_5CH_2O(CH_2)_2C{\equiv}CCH_2X \longrightarrow$

7 **8**



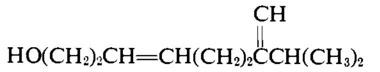
$$C_6H_5CH_2O(CH_2)_2C{\equiv}CCH_2\overset{\overset{\displaystyle R}{|}}{C}HCOCH(CH_3)_2 \longrightarrow$$

9



$$C_6H_5CH_2O(CH_2)_2C{\equiv}C(CH_2)_2\overset{\overset{\displaystyle CH_2}{\|}}{C}CH(CH_3)_2 \longrightarrow$$

10

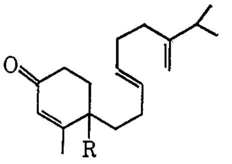


$$HO(CH_2)_2CH{=}CH(CH_2)_2\overset{\overset{\displaystyle CH}{\|}}{C}CH(CH_3)_2$$

11

Dienol **11** of excellent quality could be produced in approximately 40% over-all yield (in five steps) from the acetylenic alcohol **8** (X = OH) without purifying any of the intermediary products. This alcohol was readily transformed into the bromodiene **5** by converting it to the tosylate which, without purification, was treated with lithium bromide in acetone. In unpublished studies from our laboratory it has been noted that in the alkylation of keto esters with homoallylic tosylates (related to that described above) the yields were generally lower than with the bromides; hence, we did not examine the use of the tosylate in the present alkylation.

The alkylation of Hagemann's ester **4** with the bromodiene **5** under a variety of conditions always afforded the desired keto ester **6** contaminated with up to 15% of what we presume to be the isomeric product **12** (R = $CO_2C_2H_5$) of γ alkylation.[6] Alkaline hydrolysis and decarboxylation of this alkylation product afforded the desired trienone **13**, similarly contaminated with isomeric material **12** (R = H). This mixture could be rather inefficiently partially purified by column chromatography, and the nmr spectral properties (see Experimental Section) of the fractions enriched in the minor component were consistent with the structure **12** (R = H). In order to obtain pure trienone **13**, advantage was taken of the fact that the unwanted keto ester **12** (R = $CO_2C_2H_5$) is more resistant to saponification than the desired product **6** of α alkylation.[6] Thus when an excess of the enolate anion of Hagemann's ester **4** was treated with the bromodiene **5** in refluxing *t*-butyl alcohol, and the product submitted to controlled saponification conditions (see Experimental Section), it was possible to obtain 60–70% yields of trienone **13**, which was about 96% pure. A single chromatography gave a 48% yield of material that was 99.8% pure as determined by vapor phase chromatography analysis. Comparable results were obtained when the alkylation was carried out in refluxing toluene.[5]



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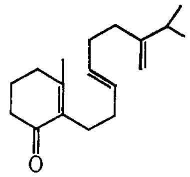

13

Treatment of the trienone **13** with methyllithium, as in the case of the preparation of the dienol **1** (R^1 = R^2 = CH_3),[5] afforded the trienol **3** (in 98% yield), the structure and configuration of which were unequivocally confirmed by infrared and nmr spectroscopy (see Experimental Section). As in the related system,[5] this trienol was exceedingly susceptible to dehydration. On dissolution in acetic acid at room temperature, the trienol was completely converted into a 3:2 (by vapor phase chromatography) mixture of hydrocarbons which are tentatively assigned the structures **14** and **15** on the basis of ultraviolet and infrared spectroscopic evidence (see Experimental Section).

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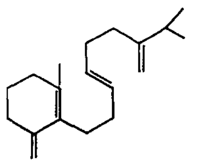
(6) *Cf.* D. Nasipuri, G. Sarkar, M. Guha, and R. Roy, *Tetrahedron Lett.*, 927 (1966).



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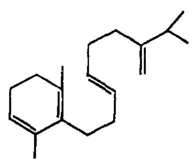
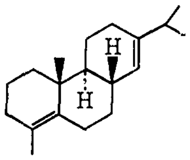


15

Cyclization Studies. When the trienol was added to anhydrous formic acid at room temperature, a heterogeneous mixture resulted, and the product contained a considerable amount of the tetraenes **14** and **15**, as shown by a combination of thin layer and vapor phase chromotographic analysis. These tetraenes, however, had completely disappeared after the heterogeneous reaction mixture was shaken for 11 min. The product, after saponification in order to cleave formate esters, was separable by chromatography into a hydrocarbon ($C_{19}H_{30}$) and alcoholic ($C_{19}H_{32}O$) fraction, isolated in 60 and 34% yields, respectively, after distillation.



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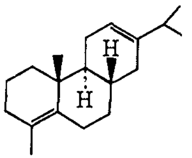

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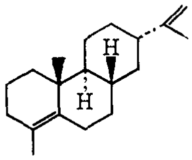

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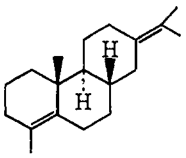
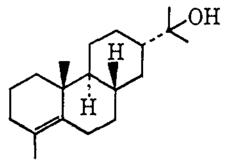


19

Vapor phase chromatographic analysis of the hydrocarbon mixture indicated the presence of four components A, B, C, and D (in order of increasing retention times) in the ratio of 23:45:2:30, respectively, as estimated by peak areas. These components were separated by preparative vapor phase chromatography; hydrocarbons A, B, and C were liquids at room temperature, and D was a crystalline solid, mp 63.5–64°. The following evidence demonstrated that the structures of these substances corresponded to formulas **16**, **17**, **18**, and **19**, respectively. The nmr spectra of each of these substances showed high-field three-proton singlet absorption for the angular methyl group at δ 0.93–0.96 ppm (relative to tetramethylsilane = 0), and three-proton singlet absorption at 1.57–1.59 for the vinyl methyl group at C-4 (steroid numbering). The spectra of hydrocarbons A and B were similar, showing typical six-proton doublet (J = 7 cps) absorption for the isopropyl group centered at 0.96 ppm and absorption for only one vinylic proton. The widths at half-height of the vinylic proton signals were 3 cps for A at 5.10 ppm and 7 cps for B at 5.33 ppm. These data are consistent with the structures **16** and **17**, respectively, the broader signal, in the case of B, being attributable to more extensive coupling of the C-12 vinylic proton with the *two* protons at C-11. The spectrum of hydrocarbon C showed typical absorption for $CH_2{=}C(CH_3)-$, namely a two-proton "singlet" at 4.59 and a three-proton triplet (J = 1 cps) at 1.67 ppm, and therefore corresponds to structure **18**. The terminal methylene structure was confirmed by the bands at 6.08 and 11.25 μ in the infrared spectrum. The nmr spectrum of hydrocarbon D showed no absorption for vinylic protons and nine-proton absorption in the 1.58–1.65-ppm region ($CH_3C{=}C$), corresponding to structure **19**.

Each of the four hydrocarbons, on shaking for 11 min with formic acid, was converted into mixtures of the four as shown by vapor phase chromatographic analysis. Evidently these reaction conditions were not sufficient to effect complete equilibration, because the ratios of the components were different for each of the products, the starting material being present in larger proportion, in each case, than found in the product of the cyclization. These interconversion experiments provided strong evidence that these substances differ only in the position of the double bond in ring C and that they all possess the same configuration at the ring junctures. It is assumed that extensive hydride shifts did not occur to any appreciable extent so as to involve the C-8 position, because in this event there should have been significant loss of the C-9 proton, giving a detectable amount of the thermodynamically preferred $\Delta^{8,9}$ isomer.[7]



20

The alcohol fraction from the cyclization experiment appeared to be essentially homogeneous on thin layer chromatography. The nmr spectrum showed no absorption for vinylic protons and six-proton singlet absorption at δ 1.07 ppm which is consistent with the tertiary dimethylcarbinol structure **20**. In accord with this formulation, dehydration with phosphorus oxychloride and pyridine gave, in 68% yield, a mixture of olefins consisting almost entirely of hydrocarbons C (**18**) and D (**19**), predominantly the former. This reaction, combined with cyclization conditions that favor formation of the alcohol (see below), provides a convenient source of hydrocarbon C which was obtained directly from the cyclization experiment (see above) in small amount, sufficient only for infrared identification. It is to be noted that the experiments performed on this hydrocarbon (see above and below) were carried out on material prepared by dehydration of the alcohol.

On shaking with formic acid, the alcohol was partially converted to the mixture of olefins A, B, C, and D. Therefore the alcohol clearly belongs to the same stereochemical series as the hydrocarbons. Since all these products seemingly are interconvertible in an equilibration process involving what appear to be conventional carbonium ion transformations, then the configuration of the group at C-13 in the hydrocarbon C and the alcohol should be mainly in the more stable α (equatorial) form as represented in formulas **18** and **20**.

Conclusive proof of the tricyclic nature and of the configurations of the reaction products described above was afforded by their conversion to the racemic form of

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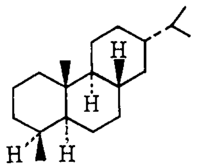
[7] *Cf. inter alia*, E. E. Royals, W. C. Bailey, and R. W. Kennedy, *J. Org. Chem.*, **23**, 151 (1958).

the natural product, fichtelite, which is known[8] to have the constitution shown in formula **21**.



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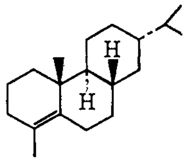


22

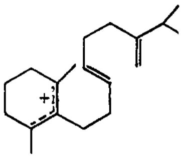
Each of the hydrocarbons A, B, C, and D, upon catalytic hydrogenation over platinum catalyst in ethanol, underwent selective reduction of the double bond in ring C to give the dihydro products A′, B′, C′, and D′, each of which contained significant amounts of the olefin **22** as shown by its nmr spectrum and its conversion to fichtelite. The only significant low-field absorption in the nmr spectra was a singlet at δ 1.57 ppm corresponding to the methyl group at C-4. The olefinic bond in ring A could be hydrogenated over platinum catalyst in acetic acid.[9] Thus each of the dihydro olefins A′, B′, C′, and D′ yielded mixtures of saturated hydrocarbons which, as estimated by vapor phase chromatography, contained 60, 30, 55, and 55% of *dl*-fichtelite, respectively. These fractions were isolated by preparative vapor phase chromatography and each was shown to have an infrared spectrum (liquid film) identical with that of natural fichtelite.[10] The other components of the saturated hydrocarbon mixtures were not examined; they presumably differ from fichtelite in the configuration at one or more of the centers, C-4, C-5, and C-13.

For an efficient preparation of *dl*-fichtelite, the crude mixture of hydrocarbons A, B, C, and D from the cyclization was exhaustively hydrogenated over platinum catalyst in acetic acid. The resulting mixture of saturated hydrocarbons was estimated by vapor phase chromatography to contain about 30% of *dl*-fichtelite. This fraction could be easily separated by preparative vapor phase chromatography. The infrared, mass, and nmr spectra were identical with the corresponding spectral properties of natural fichtelite.[10] The two substances also exhibited identical vapor phase chromatographic behavior.

The effect of the presence of water on the cyclization of the trienol **3** was examined. Since the trienol undergoes rapid dehydration, the actual cyclization of the resulting tetraene described above was performed in formic acid which was 18.6 m*M* with respect to water. When the concentration of substrate was adjusted so that the solution was 44 m*M* at the time of cyclization, the ratio of tricyclic hydrocarbons to alcohol was increased from about 1.7:1 to 2.4:1. On the other hand, when the relative amount of anhydrous formic acid to substrate was increased so that the cyclization medium was only 8 m*M* in water, this ratio decreased to about 0.6:1. Thus these more anhydrous conditions favored formation of tricyclic alcohol, and advantage was taken of this observation for the preparation of this material. In addition it was noted that somewhat higher proportions of the diene **18** were produced in the more anhydrous media. In order to test the cyclization under completely anhydrous conditions, the trienol **3** was dehydrated by the action of acetic acid (see above), and the tetraene mixture (**14** and **15**) was isolated and treated with anhydrous formic acid. Surprisingly the product consisted of a 4:1 mixture of tricyclic hydrocarbons and alcohol. The proportion of hydrocarbon **18**, however, was the highest obtained in a cyclization experiment, *i.e.*, it comprised about 8% of the hydrocarbon mixture.

The cyclization of the trienol **3** in homogeneous medium was also studied and is described in the following section.

Theoretical Considerations. The evidence at hand[11] is consistent with, but does not prove, the hypothesis that the formic acid promoted cyclization of alkenylcyclohexenols like **3** is initiated by the formation of a substituted hexenyl allylic cation, *i.e.*, **23** in the present case. The cation **23** then may be envisaged as cyclizing either by (a) a stepwise process involving the intermediacy of (solvated) cations **24** and **25**, or (b) a similar process involving the intermediacy of one or two bridged ions, or (c) a concerted process. It is not possible to decide unequivocally among these three possibilities. In any case the high yield and stereoselectivity of the formation of tricyclic material seemingly precludes the intermediacy of a bicyclic triene **26**.[12] Indeed had bicyclic material been formed, the reaction would have been expected, by analogy to the results of the cyclization of the substance **1** ($R^1 = R^2 = CH_3$), to stop at this stage with the formation of formate **27**. The mechanism of our cyclization therefore differs, at least in this respect, from that of the acid-catalyzed cyclization of desmethylfarnesic acid[13] which evidently proceeds *via* a monocyclic dienic intermediate.



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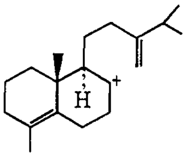

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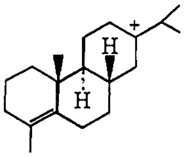

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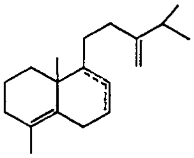

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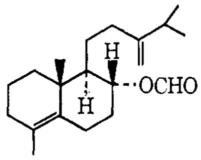

27

We were surprised as well as gratified to discover that the cyclization of the trienol **3** did not stop at all at the bicyclic stage (**27**). This finding was unexpected in view of the fact that the major product of formolysis of *trans*-5,9-decadienyl *p*-nitrobenzenesulfonate[14] and of its 9-methyl homolog[15] was that arising from mono-

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(8) A. W. Burgstahler and J. N. Marx, *Tetrahedron Lett.*, 3333 (1964).

(9) *Cf.* J.-F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Amer. Chem. Soc.*, 83, 3874 (1961).

(10) We are indebted to Professor R. E. Ireland for supplying us with this specimen of fichtelite which he obtained from Professor O. Jeger whom we also wish to thank.

(11) See W. S. Johnson and K. E. Harding, *J. Org. Chem.*, 32, 478 (1967), and references cited therein.

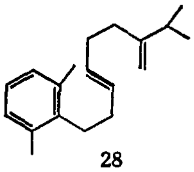
(12) Note that the formic acid promoted cyclization of 1-(Δ^3-butenyl)cyclohexanol proceeds in only 25% yield after 21 hr at 75° to give exclusively *cis*-2-decalols: W. S. Johnson and J. K. Crandall, *ibid.*, 30, 1785 (1965).

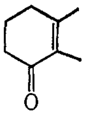
(13) A. Eschenmoser, D. Felix, M. Gut, J. Meier, and P. Stadler, *Ciba Found. Symp. Biosyn. Terpenes Sterols*, 217 (1959); W. S. Johnson, S. L. Gray, J. K. Crandall, and D. M. Bailey, *J. Amer. Chem. Soc.*, **86**, 1966 (1964).

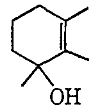
(14) W. S. Johnson, D. M. Bailey, R. Owyang, R. A. Bell, B. Jaques, and J. K. Crandall, *ibid.*, **86**, 1959 (1964).

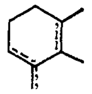
(15) W. S. Johnson, A. S. Katner, and G. S. Bayliss, unpublished observations.

rather than bicyclization. In these sulfonate ester solvolyses, the solvent evidently competes more successfully than the terminal olefinic bond for capture of the intermediary monocyclic cation. We do not have a satisfactory explanation of the failure of the solvent to interrupt the cyclization of the trienol **3** at the bicyclic stage. The insolubility of the substrate in the reaction medium is not responsible for this behavior as shown by cyclization experiments in homogeneous media (see below).


28


29


30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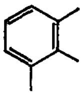
32

Treatment of the trienol **3** with a 1:1 mixture of anhydrous formic and acetic acids resulted in a homogeneous pink solution. After 11 min only about 11% of the tetraenes remained. The rest of the material appeared to consist mainly of the same tricyclic products produced in the cyclization experiments described above. There was no indication for the presence of an alcoholic product, *i.e.*, the product of hydrolysis of **27**, other than the tricyclic substance **20**. There was, however, evidence for an additional, new product having a vapor phase chromatography retention time close to, but different from, that of the diene **18**. It was found that as the formic acid concentration was lowered, more of this new product was formed at the expense of the known tricyclic materials. In acetic acid alone, after 6 days at room temperature, this new substance appeared to be the major product. Preliminary attempts to obtain this substance in a pure form failed, but the nmr and infrared spectra of the enriched material clearly showed that the dienic side chain of the substrate was completely intact, and that the molecule contained aromatic hydrogen atoms. We therefore suspected that the material contained the aromatized substance **28**. This surmise was strengthened by the known susceptibility of cyclohexadiene to aromatization,[16] and further by the results of a study of the behavior of the model substance, 1,2,3-trimethyl-Δ^2-cyclohexen-1-ol (**30**), mp 73–74°, which is readily accessible by the action of methyllithium on 2,3-dimethyl-Δ^2-cyclohexen-1-one (**29**).[17] The crystalline alcohol **30**, on treatment with acetic acid at room temperature for 11 min, was converted into an oily product which showed no absorption in the infrared spectrum for hydroxyl and exhibited a maximum at 240 mμ with a shoulder at 270 mμ in the ultraviolet spectrum. On vapor phase chromatography this oily product showed two low retention time (hydrocarbon) peaks, and it was therefore regarded as the mixture of dienes **31**, formed in close analogy to related examples (see above). As the treatment of the alcohol **30** with acetic acid was extended, the vapor phase chromatogram showed gradual disappearance of the diene peaks and emergence of a new longer retention time peak, in close parallel to the acetic acid experiment described above with the trienol **3**. After prolonged treatment the substance corresponding to the longer retention time peak was isolated by preparative vapor phase chromatography. This material was shown to be 1,2,3-trimethylbenzene by nmr and infrared spectroscopic comparison with authentic material. The rate of the aromatization reaction was capricious in our hands, perhaps due to traces of impurities (oxygen?). Thus in one experiment reaction was essentially complete after 5 days at room temperature while in another prolonged treatment involving heating at 100° was required.

Experimental Section[18]

4-Benzyloxy-1-butyne (7) was prepared by Edward K. W. Wat as follows. A solution of 56.0 g of 3-butyn-1-ol (Farchan Research Laboratories) in 50 ml of anhydrous tetrahydrofuran was added dropwise over a period of 1 hr to an ice-cooled, stirred suspension of 33.6 g of 53.5% sodium hydride–mineral oil dispersion (Metal Hydrides, Inc.) in 1 l. of tetrahydrofuran. After the addition was complete, the cooling bath was removed and stirring was continued at room temperature for 3 hr. The ice bath was replaced, and a solution of 134 g of benzyl bromide (Eastman Kodak White Label), bp 92.5–93.0° (21 mm), in 50 ml of tetrahydrofuran was added dropwise over a period of 1 hr, during which period a white precipitate began to form. The mixture was stirred under a nitrogen atmosphere at room temperature for 19 hr. A minimum amount of water was added to dissolve the precipitated salts. The organic layer was dried over anhydrous sodium sulfate and fractionally distilled through a 2-ft spinning-band column to give 105 g (87% yield) of colorless liquid: bp 78–79° (2.0 mm); $n^{25}\text{D}$ 1.5137; $\lambda_{\max}^{\text{film}}$ 3.0 (C≡CH), 4.7 (C≡C), 9.1 (C–O–C), 13.5 and 14.3 μ (C_6H_5). Vapor phase chromatography (Carbowax) indicated that the product was 100% pure.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46, H, 7.55. Found: C, 82.3; H, 7.5.

Material from another comparable run, bp 82–84° (2.7–3.0 mm), $n^{25}\text{D}$ 1.5131, was used in the next step.

5-Benzyloxy-2-pentyn-1-ol (8, X = OH). A solution of 32 g of the aforementioned 4-benzyloxy-1-butyne in 30 ml of anhydrous tetrahydrofuran was added over a 30-min period to the Grignard reagent prepared from 21.8 g of ethyl bromide and 5.28 g of magnesium turnings in 200 ml of anhydrous tetrahydrofuran. The mixture was heated at reflux with stirring for 2 hr and then cooled to *ca.* 25°. Formaldehyde, prepared by heating 7.2 g of paraformaldehyde (previously dried over phosphorus pentoxide at 80° and aspirator pressure for 48 hr) to 180–200°, was swept into the stirred acetylenic Grignard solution by means of a nitrogen stream;[19]

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(16) R. J. de Kock, N. G. Mimmaard, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **79**, 922 (1960).

(17) G. V. Kondrat'eva, G. A. Kogan, T. M. Fadeeva, and S. I. Zavyalov, *Izv. Akad. Nauk Ser. Khim.*, 1554 (1964).

(18) (a) The prefix *dl* has been omitted from the names of all racemic compounds described in this section. (b) Melting points were determined on a Kofler hot-stage microscope. (c) Nmr spectra were determined under the supervision of Dr. L. J. Durham on a Varian Associates A-60 nmr spectrometer. Carbon tetrachloride was employed as the solvent with tetramethylsilane as the internal reference. The chemical shifts are reported as δ values in parts per million relative to tetramethylsilane = 0. (d) Vapor phase chromatographic analyses were performed on an Aerograph Hy-Fi chromatograph, Model 600. The columns used were 7.5 × 0.125 in. packed either with neutral 5% SE-30 on Chromosorb W, referred to as the "SE-30" column, or with neutral 15% Carbowax 20M, referred to as the "Carbowax" column. Preparative vapor phase chromatography was performed on an Aerograph Autoprep Model A-700 apparatus employing a 20 ft × 0.25 in. 20% SE-30 column or a 20 ft × 0.375 in. 20% Carbowax 20M column. (e) Thin layer chromatography experiments were performed according to E. Stahl, "Dünnschicht-Chromatographie, Ein Laboratoriumshandbuch," Springer-Verlag, Berlin, 1962. Silica gel G (E. Merck AG) was employed as the absorbent and the solvent systems indicated below were used: benzene; benzene–ethyl acetate (2:1); benzene–ethyl acetate–acetic acid (17:2:1).

(19) H. Gilman and W. E. Catlin in "Organic Syntheses," Coll. Vol. I, 2nd ed, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p 188.

during this treatment gentle refluxing occurred spontaneously. The mixture was stirred for 20 min and heated at reflux for an additional 1 hr. The mixture was cooled, 35 ml of saturated ammonium chloride solution was added, and the solid salts remaining after decantation were washed with ether. The combined organic layers were dried over anhydrous sodium sulfate. The residue obtained on distillation of the solvent through a 6-in. Vigreux column at atmospheric pressure was fractionated through the same column to give, as the main fraction, 19.3 g of colorless liquid, bp 121° (4 μ), n^{24}D 1.5366. The nmr spectrum exhibited absorption for five protons as a singlet at δ 7.22 (aromatic protons), two protons as a singlet at 4.41 ($C_6H_5CH_2$–), two protons as a broad singlet at 4.08 (–CH_2OH), one proton at 3.82 (OH), two protons as a triplet centered at 3.47 (–OCH_2CH_2–), and two protons as a multiplet centered at 2.41 ppm (–$CH_2CH_2C{\equiv}C$–). An analytical specimen was obtained by evaporative distillation at 4 μ (pot temperature 120–135°).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.55; H, 7.3.

When this preparation was repeated on a 1-mol scale, a 68% yield of product, bp 114–122° (3–5 μ), $n^{23.5}$D 1.5362, was obtained. This material was used in the next step of the synthesis.

5-Benzyloxy-1-bromopent-2-yne (8, X = Br). A solution of 25.8 g of phosphorus tribromide in 20 ml of anhydrous ether was added over a 75-min period to a cooled and stirred solution of 45.2 g of the aforementioned acetylenic alcohol **8** (X = OH) in 125 ml of anhydrous ether. During the addition the temperature of the reaction mixture was not allowed to exceed 3°. The cooling bath was removed, and the mixture was stirred for an additional 5 hr at room temperature. The top layer was poured into ice–water, and the aqueous layer was extracted with ether. The combined organic layers were washed with water, 10% sodium bicarbonate solution, water, and saturated brine, and then were dried over anhydrous sodium sulfate. The residue obtained on removal of the solvent through a 24-in., Podbielniak-type column was distilled through a short Claisen head to give 49.7 g of colorless liquid, bp 102–104° (3 μ), n^{24}D 1.557. Combustion analysis of this material did not give satisfactory values. Thin layer chromatography (2:1 benzene–ethyl acetate) revealed a single spot, R_f 0.65. The nmr spectrum exhibited, in addition to absorption due to traces of impurity in the δ 3.8–4.2-ppm range, absorption for five protons as a singlet at 7.23 (aromatic protons), two protons as a singlet at 4.42 ($C_6H_5CH_2$–), two protons as a triplet centered at 3.78 (–CH_2Br), two protons as a triplet centered at 3.47 (–OCH_2CH_2–), two protons as a multiplet centered at 2.45 ppm (–$CH_2CH_2C{\equiv}C$–). When this reaction was repeated on an 0.8-mol scale, an 80% yield of material with n^{24}D 1.557 was obtained. This acetylenic bromide proved to be a severe skin irritant.

Ethyl isobutyroylacetate was prepared by an adaptation of a method for the preparation of 2-carbethoxycyclooctanone.[20] A 115.4-g portion of a 53% sodium hydride dispersion in oil was washed free of oil with anhydrous benzene and then covered with 1 l. of anhydrous benzene containing 212.4 g of diethyl carbonate. The mixture was stirred and heated at reflux while a solution of 77.4 g of methyl isopropyl ketone in 100 ml of anhydrous benzene was added over a period of about 6 hr. The mixture was heated at reflux for an additional 30 min and then cooled (ice bath), 180 ml of glacial acetic acid followed by 600 ml of water was added, and the aqueous phase was extracted with benzene. The combined organic layers were washed with water followed by saturated brine and were dried over anhydrous sodium sulfate. The solvent was removed by distillation through a 12-in. Vigreux column, and the residue was distilled through the same column to give 103.8 g of colorless liquid, bp 89–91° (14–15 mm), n^{23}D 1.4241 [lit.[21] bp 90–92° (15–16 mm), n^{25}D 1.4245]. The infrared spectrum was identical with that of a specimen obtained from the Aldrich Chemical Co.

2-Methyl-9-benzyloxynon-6-yn-3-one (9, R = H). A 27.8-g portion of a 53% sodium hydride dispersion in oil was washed free of oil with pentane and then covered with 600 ml of anhydrous tetrahydrofuran. The mixture was cooled (ice bath) and stirred while 97.9 g of ethyl isobutyroylacetate was added over a 2.25-hr period. The cooling bath was removed and a slow stream of nitrogen was passed through the mixture with stirring for an additional 2 hr. A solution of 156.8 g of the aforementioned acetylenic bromide, n^{24}D 1.557, in 140 ml of anhydrous tetrahydrofuran was added over a 90-min period, and the mixture was stirred for 14 hr at room temperature, followed by 2 hr at reflux. The mixture was cooled, diluted with water, and the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried over Drierite. The solvent was removed through a 6-in. Vigreux column, leaving 199.3 g of a crude orange liquid, $\lambda_{\max}^{\text{film}}$ 5.74 (ester C=O) and 5.84 μ (ketone C=O). This crude material was employed in the next step.

A portion of this material was distilled through a short-path column to give a sample of the keto ester **9** (R = CO_2Et) as a light yellow liquid, bp 159–160° (10 μ), the infrared spectrum of which was essentially identical with that of the crude product. The nmr spectrum of the distilled material showed absorption for five protons as a singlet at δ 7.23 (phenyl), two protons as a singlet at 4.45 ($C_6H_5CH_2$–), two protons as a quartet centered at 4.10 (–OCH_2CH_3), one proton as a triplet centered at 3.72 (O=C—CH—C=O), two protons as a triplet centered at 3.45 (–$CH_2OCH_2C_6H_5$), three protons as a triplet centered at 1.21 (–CH_2CH_3), and six protons as a doublet centered at 1.06 ppm (–$CH(CH_3)_2$). The absorption for the remaining five protons appeared as a multiplet at 3.18–2.11 ppm.

Decarbethoxylation of the keto ester was effected by an adaptation of a published procedure.[22] A mixture of 186 g of barium hydroxide octahydrate in 2.2 l. of water was added to a solution of 144 g of the aforementioned crude ethyl isobutyroylacetate in 600 ml of 95% ethanol, and the mixture was stirred and heated at reflux for 18 hr. The mixture was cooled, acidified with dilute hydrochloric acid, and extracted thoroughly with ether. The combined organic layers were washed in turn with sodium carbonate solution, water, and brine, and were then dried over anhydrous sodium sulfate. Removal of the solvent under reduced pressure left 96 g of residue which was 94% pure as estimated by vapor phase chromatography (SE-30, 195°). This material was satisfactory for the next step. Comparable material from another run was distilled through a short-path column to give a colorless liquid, bp 126–127° (7 μ), which was 95% pure as estimated by vapor phase chromatography. Attempts to prepare a 2,4-dinitrophenylhydrazone, a semicarbazone, or an oxime of this material failed.

An analytical sample was obtained by preparative vapor phase chromatography (SE-30, 225°), followed by short-path distillation at 12–13 μ (pot temperature 170–180°).

Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.7; H, 8.5.

The nmr spectrum showed absorption for five protons as a singlet at δ 7.24 (phenyl), two protons as a singlet at 4.49 ($C_6H_5CH_2$–), two protons as a triplet centered at 3.49 (–OCH_2CH_2–), seven protons as a multiplet at 2.8–2.0, and six protons as a doublet centered at 1.07 ppm (–$CH(CH_3)_2$). There was also small absorption at 1.29 ppm due to a trace of impurity.

2-Isopropyl-8-benzyloxyoct-5-yn-1-ene (10) was prepared by an adaptation of a general procedure.[23] A 32-g portion of a 53% sodium hydride dispersion in oil was washed with pentane to remove the oil. With the system under an atmosphere of nitrogen, 1500 ml of dimethyl sulfoxide was added and the mixture was stirred and maintained at 70–75° for about 80 min. The solution was cooled with an ice–water bath, and a solution of 284 g of triphenylmethylphosphonium bromide[24] in 350 ml of warm dimethyl sulfoxide was added with stirring. The cooling bath was removed, the mixture was stirred for an additional 30 min, and a solution of 87.3 g of the crude (*ca.* 94% pure) aforementioned ketone **10** in 100 ml of dimethyl sulfoxide was then added. The resulting mixture was stirred for an additional 4 hr, then diluted with water, and the aqueous phase was extracted thoroughly with pentane. The combined organic layers were washed successively with a 1:1 water–dimethyl sulfoxide solution, water, and brine, and were dried over anhydrous sodium sulfate. The residue obtained on removal of the solvent through a 24-in. Podbielniak-type column amounted to 81.4 g of liquid which showed a single peak on vapor phase chromatography (SE-30, 200°).

An analytical specimen was prepared by chromatography on Merck alumina. The fraction eluted with 85:15 pentane–benzene was evaporatively distilled at 10 μ (pot temperature 100–110°) to give a colorless liquid, $\lambda_{\max}^{\text{film}}$ 6.10 (–C=C–), 9.10 (C–O–C), and 11.22 μ

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[20] A. P. Krapcho, J. Diamanti, C. Cayen, and R. Bingham, unpublished procedure.

[21] E. H. Kroeker and S. M. McElvain, *J. Amer. Chem. Soc.*, **56**, 1171 (1934).

[22] M. Julia, S. Julia, and R. Guégan, *Bull. Soc. Chim. Fr.*, 1072 (1960).

[23] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[24] G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960).

($C=CH_2$). The nmr spectrum exhibited absorption for five protons as a singlet at δ 7.22 (phenyl), two protons as a doublet centered at 4.70 ($C=CH_2$), two protons as a singlet at 4.47 ($C_6H_5CH_2$–), two protons as a triplet centered at 3.48 (–OCH_2CH_2–), seven protons as a multiplet at 2.7–1.9, and six protons as a doublet centered at 1.02 ppm (–$CH(CH_3)_2$).

Anal. Calcd for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.0; H, 9.4.

The crude material (see above) was essentially identical by infrared spectroscopy with the analytical sample, and it was employed in the next step with further purification.

7-Isopropyl-*trans*-3,7-octadien-1-ol (11). A solution of 51.2 g of the aforementioned crude 2-isopropyl-8-benzyloxyoct-5-yn-1-ene in 400 ml of anhydrous ether was added over a 30-min period to a mixture of 30.6 g of sodium in about 3 l. of liquid ammonia (distilled from potassium metal). Care was taken to ensure that the solution was dropped directly into the ammonia solution and not on the walls of the flask. An additional 80 ml of ether was added, and the mixture was maintained at about −33° for 4 hr; then 85 g of ammonium chloride was gradually added. The ammonia was allowed to evaporate at room temperature, ether and water were added to the residue, and the organic phase was thoroughly washed with water and then dried over Drierite. The pale yellow residue remaining after removal of the solvent through a 24-in., Podbielniak-type column was chromatographed on 630 g of neutral alumina. The fractions eluted with pentane (6.2 g) were discarded. The fractions eluted with ether amounted to 22.3 g of colorless liquid, which appeared to be essentially homogeneous by thin layer chromatography and by vapor phase chromatographic analysis (Carbowax, 180°).

Evaporative distillation of a portion of the ether eluate at 7 μ (pot temperature 85–95°) gave a colorless liquid, $n^{25}\mathrm{D}$ 1.4658, $\lambda_{\max}^{\mathrm{film}}$ 3.0 (OH), 6.10 ($C=C$), 10.28 (*trans*-$CH=CH$), and 11.25 μ (–$C=CH_2$). The nmr spectrum showed absorption for two protons as a multiplet at δ 5.45 (–$CH=CH$–), two protons as a doublet (J = 5 cps) at 4.68 ($C=CH_2$), two protons as a triplet (J = 7 cps) at 3.52 (–CH_2OH), and six protons as a doublet (J = 7 cps) at 1.03 ppm (–$CH(CH_3)_2$).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.6; H, 11.9.

When potassium was employed in place of sodium, reduction was incomplete and there were produced, in addition to the desired dienol, at least three extraneous materials as detected by vapor phase chromatography on a Carbowax column at 181°. In another experiment a total of 0.618 g of sodium metal was added in portions over a 1-hr period to a mixture of 1.03 g of the substrate **10** in 30 ml of ether and 150 ml of ammonia. The blue color was allowed to discharge before each successive portion of sodium was added. The mixture was stirred for an additional 90 min at −33°; then solid ammonium chloride was added. Vapor phase chromatographic analysis (Carbowax, 180°) of an ethereal solution of the product, isolated as described above, revealed two major peaks with retention times 6.4 and 9.5 min, presumably corresponding, respectively, to the alcohol **11** and 7-isopropyloct-3-yn-7-en-1-ol (see below). In addition there were at least two other peaks with retention times of 7.0 and 7.5 min.

A reduction was carried out by adding a total of 0.12 g (17 mg-atoms) of lithium gradually to a mixture of 4 mmol of the substrate **10** in 10 ml of tetrahydrofuran and 40 ml of liquid ammonia. After the addition (about 1 hr) the heterogeneous mixture was stirred for an additional 5 hr at −33°; the product was then isolated as described above. Vapor phase chromatographic analysis (Carbowax, 181°) of the ethereal solution revealed two major peaks with retention times of 6.2 (6%) and 9.2 min (94%). The residue remaining after removal of the solvent was chromatographed on Merck neutral alumina (grade III). The major fraction (longer retention time product), eluted with 1:1 pentane–ether, was 99% pure by vapor phase chromatography. The nmr spectrum exhibited absorption for two protons as a doublet centered at δ 4.73 ($C=CH_2$), two protons as a triplet centered at 3.57 (–CH_2—O), one proton as a singlet (broad) at 2.75 (–OH) which could be exchanged on adding D_2O, seven protons as a multiplet at 2.5–1.9, and six protons as a doublet centered at 1.05 ppm (–$CH(CH_3)_2$) in agreement with the structure of **7-isopropyloct-3-yn-7-en-1-ol.**

Anal. Calcd for $C_{11}H_{26}O$: C, 78.51; H, 11.88. Found: C, 78.5; H, 11.8.

2-Isopropyl-8-bromo-*trans*-1,5-octadiene (5) was prepared by an adaptation of a published procedure.[25] An ice-cooled solution of 7.64 g of *p*-toluenesulfonyl chloride in 10 ml of pyridine was added to a solution of 1.68 g of the dienol **11** in 10 ml of pyridine cooled to 0°. The mixture was maintained at 5° for 21 hr, then poured into excess ice-cold dilute hydrochloric acid, and extracted with ether. The combined organic layers were washed with sodium carbonate solution and water, followed by brine, and were dried over Drierite. The residue obtained on removal of the solvent under reduced pressure possessed a strong odor of *p*-toluenesulfonyl chloride. It was taken up in 10 ml of pyridine and treated with water at 0°; the product was then reisolated as described above to give 2.70 g of pale yellow liquid. This material was essentially homogeneous by thin layer chromatography. The infrared spectrum (film) showed no absorption for OH and exhibited bands at 6.1 ($C=C$), 8.4, 8.5 (SO_3R), 10.3 (*trans*-$CH=CH$), and 11.2 μ ($C=CH_2$). When the tosylation was performed on a 50-mmol scale and processed exactly as described,[25] there was obtained a 94% yield of crude material which appeared by thin layer chromatography to be essentially homogeneous. This product was used in the next step without further purification.

A solution of 26.2 g of dry lithium bromide in 180 ml of acetone was added to 9.67 g of the aforementioned crude tosylate. The mixture was allowed to stand at room temperature in the dark for 48 hr; the acetone was then removed by distillation under reduced pressure. Water and ether were added to dissolve the residue. The organic layer was washed with water, followed by brine, and then was dried over Drierite. The residue obtained on removal of the solvent amounted to 6.73 g of pale yellow liquid which was homogeneous by thin layer chromatography. This material was used in the next step without further purification.

A portion of this material was chromatographed on Merck basic alumina (activity II). The fraction eluted with pentane was evaporatively distilled at 20 μ (90–100°) to give a colorless liquid, $\lambda_{\max}^{\mathrm{film}}$ 6.10 ($C=C$), 10.38 (*trans*-$CH=CH$), and 11.24 μ ($C=CH_2$). The nmr spectrum showed absorption for two protons as a multiplet at δ 5.6–5.3 ($CH=CH$), two protons as a doublet centered at 4.68 ($C=CH_2$), two protons as a multiplet at 3.29 (–CH_2Br), seven protons as a multiplet at 2.8–1.7, and six protons as a doublet centered at 1.03 ppm (–$CH(CH_3)_2$).

Anal. Calcd for $C_{11}H_{19}Br$: C, 57.15; H, 8.28; Br, 34.56. Found: C, 57.4; H, 8.4; Br, 34.6.

Alkylation of Hagemann's Ester with the Diolefinic Bromide 5. A. In Benzene–Dimethylformamide (Evidence for γ Alkylation). A solution of 1.82 g of Hagemann's ester[26] in 5 ml of dimethylformamide was added to a mixture of 0.486 g of a 53% sodium hydride–mineral oil dispersion (washed free of oil with benzene) in 30 ml of benzene and 5 ml of dimethylformamide. To the resulting orange solution was added 2.33 g of the bromide **5** in 5 ml of dimethylformamide, and the mixture was stirred at room temperature for a total of 57 hr and then heated at reflux for 44 hr. The mixture was diluted with water, and the aqueous phase was extracted with benzene. The combined organic layers were washed with water, followed by brine, and dried over Drierite. The yellow liquid remaining after removal of the solvent amounted to 2.81 g.

A solution of 0.58 g of 85% potassium hydroxide in 10 ml of 95% ethanol was added to 2.70 g of the aforementioned crude mixture, and the mixture was heated at reflux (nitrogen atmosphere) for 8 hr. The residue remaining after removal of the solvent under reduced pressure was diluted with water and extracted with ether. The combined organic layers were washed with water, followed by brine, and dried over Drierite. The infrared spectrum of the crude yellow liquid residue (0.93 g) indicated that decarbethoxylation was incomplete; therefore the saponification treatment was repeated just as described above to give 0.55 g of a pale yellow liquid. A portion of this material was evaporatively distilled at 12 μ (pot temperature 110–150°) to give a colorless liquid: $\lambda_{\max}^{\mathrm{EtOH}}$ 243 mμ; $\lambda_{\max}^{\mathrm{film}}$ 6.03 ($C=O$) with a shoulder at 6.16 ($C=C$), 10.25 (*trans*-$CH=CH$), 11.24 ($C=CH_2$), and 2.87 μ (O–H). Vapor phase chromatographic analysis (SE-30, 195°) showed the presence of volatile impurities followed by two major, incompletely resolved peaks, R_f 12.2 and 14.2 min, having relative peak areas of 85 and 15%, respectively. The lower retention time peak corresponded to the normal product **13** arising from α alkylation.

A portion of this material was chromatographed on Woelm neutral alumina (activity II). Material eluted with petroleum ether (bp 60–65°) was evaporatively distilled at 12 μ (pot temperature 110–135°). Vapor phase chromatographic analysis (SE-30, 197°) indicated that the composition of this fraction was about 9 and 91% of

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(25) E. J. Corey, H. J. Hess, and S. Proskow, *J. Amer. Chem. Soc.*, **85**, 3979 (1963).

(26) L. I. Smith and G. F. Rouault, *ibid.*, **65**, 631 (1943).

the aforementioned products of lower and higher retention times, respectively.

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.8; H, 10.6.

Further elution of the chromatographic column with 9:1 petroleum ether (bp 60–65°)–benzene gave a fraction which was shown by vapor phase chromatographic analysis to consist of the two alkylation products in a ratio of 55:45. The nmr spectrum of this mixture exhibited all of the absorption bands attributable to the pure product arising from α alkylation (see below), and in addition there was a broad singlet (or unresolved multiplet) centered at 5.71 ppm. Since the nmr spectrum of 3-methylcyclohexenone exhibits absorption for the α-vinylic proton as a quartet centered at 5.72, it appears likely that the material of higher retention time is the product **12** (R = H) derived from γ alkylation.

B. **In *t*-Butyl Alcohol (Isolation of Pure α-Alkylation Product).** A mixture of 911 mg of sodium hydride (54.7% dispersion in mineral oil) and 30 ml of anhydrous *t*-butyl alcohol was stirred for 15 min and then the system was degassed and filled with nitrogen. To this mixture was added a solution of 3.91 g of freshly distilled Hagemann's ester in 5 ml of *t*-butyl alcohol. The system was again degassed and filled with nitrogen. The clear pale orange solution was stirred for 15 min at room temperature; a solution of 2.31 g of the crude bromodiene **5** in 2 ml of *t*-butyl alcohol was then added. The system was again degassed and filled with nitrogen, and the mixture was then stirred for 23 hr at room temperature. The resultant cloudy orange mixture was heated at reflux for 2 hr, cooled to 15°, and the solvent evaporated at reduced pressure. Ether and water were added to the residue, the mixture was acidified with 10% hydrochloric acid, and the aqueous layer was extracted with ether. The combined ether extracts were washed with brine and dried over anhydrous magnesium sulfate. After removal of the solvent there remained 5.48 g of pale orange oil which was chromatographed on 130 g of Woelm neutral alumina (activity III). Initial elution with 150 ml of pentane gave 0.55 g of mineral oil mixed with starting bromide. Further elution with 250 ml of pentane, followed by 2:1 pentane–methylene chloride, gave 3.01 g of material which appeared to be mainly the keto ester **6**, $\lambda_{\max}^{\text{film}}$ 5.78 (ester C=O), 6.00 (conjugated C=O), 6.18 (C=C), and 11.3 μ ($C=CH_2$). Further elution of the column with 2:1 pentane–methylene chloride gave material which was identified as Hagemann's ester by its infrared spectrum.

To a mixture of the 3.01-g keto ester fraction and 820 mg of 85% potassium hydroxide under a nitrogen atmosphere was added 23 ml of 90% ethanol. The system was degassed and filled with nitrogen; then the clear pale orange solution was heated at reflux with stirring for 15 hr. The resultant yellow solution containing a white precipitate was cooled and then concentrated under reduced pressure. Ether and water were added to the residue, the mixture was acidified with 10% hydrochloric acid, and the aqueous layer was extracted with ether. The combined organic layers were washed with brine and dried over magnesium sulfate. Removal of the solvent left 2.45 g of yellow liquid. Vapor phase chromatographic analysis (SE-30, 175°) of this material exhibited a major peak (94% of total area) with a retention time of 20 min and two minor peaks representing 3% (17.5 min) and 1% (24.0 min) of the area. This product was chromatographed on 200 g of Woelm neutral alumina (activity II). Elution with 350 ml of 2:1 pentane–methylene chloride gave 1.24 g of colorless oil. Vapor phase chromatographic analysis indicated that the fractions were 99.8% pure. Evaporative distillation at 3 μ (pot temperature 100°) gave **2-(7-isopropyl-*trans*-octa-3,7-dienyl)-3-methylcyclohex-2-en-1-one (13)** as a colorless oil: $n^{25}\text{D}$ 1.5000; $\lambda_{\max}^{\text{film}}$ 6.00, 6.15 (-C=C-C=O), and 11.3 μ ($C=CH_2$); $\lambda_{\max}^{\text{EtOH}}$ 246 mμ (ε 11,900) and 311 (121). The nmr spectrum exhibited absorption for two protons as a triplet (*J* = 3 cps) centered at δ 5.37 (-CH=CH-), two protons as a doublet (*J* = 4 cps) centered at 4.67 ($C=CH_2$), three protons as a singlet at 1.90 ($C=C(CH_3)$-) and six protons as a doublet (*J* = 6.5 cps) centered at 1.04 ppm ($-CH(CH_3)_2$).

Anal. Calcd for $C_{18}H_{28}O$: C, 83.02; H, 10.84. Found: C, 82.8; H, 10.6.

The **2,4-dinitrophenylhydrazone** was obtained from 95% ethanol as red-orange crystals, mp 103.8–104.5° dec.

Anal. Calcd for $C_{25}H_{32}N_4O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.1; H, 7.4; N, 13.0.

1,3-Dimethyl-2-(7-isopropyl-*trans*-octa-3,7-dienyl)cyclohex-2-en-1-ol (3). To a solution of 1.24 g (4.77 mmol) of the pure trienone **13** in 35 ml of anhydrous ether (nitrogen atmosphere) was added 9.0 ml of a 1.67 *M* (5.08%) solution of methyllithium in ether. The mixture was stirred under nitrogen for 20 min and then poured onto 75 g of ice. Ether and water were added, and the aqueous layer was then saturated with sodium chloride and extracted with ether. The combined organic layers were dried first over anhydrous sodium sulfate and anhydrous potassium carbonate, then over anhydrous magnesium sulfate. The residue obtained on removal of the solvent amounted to 1.32 g of almost colorless oil, $\lambda_{\max}^{\text{film}}$ 6.11 μ (C=C), with a shoulder at 6.0 (C=O). This material was therefore retreated with methyllithium just as described above. Evaporative distillation of the product at 3 μ (pot temperature 100–120°) gave 1.29 g of colorless viscous product: $n^{25}\text{D}$ 1.4963; $\lambda_{\max}^{\text{film}}$ 2.96 (OH), 6.11 (C=C), and 11.3 μ ($C=CH_2$). The nmr spectrum exhibited absorption for two protons as a singlet ($\Delta\nu_{1/2}$ = 7 cps) at δ 5.42 (-CH=CH-), two protons as a doublet (*J* = 4 cps) centered at 4.67 ($C=CH_2$), three protons as a singlet at 1.61 ($C=CCH_3$), three protons as a singlet at 1.22 ($HOCCH_3$), and six protons as a doublet (*J* = 6.5 cps) centered at 1.04 ppm ($-CH(CH_3)_2$).

Anal. Calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.4; H, 11.5.

Cyclization Experiments. A. Treatment of the Trienol with Formic Acid. To 515 mg of 1,3-dimethyl-2-(7-isopropyl-*trans*-octa-3,7-dienyl)cyclohex-2-en-1-ol (**3**) was added with swirling 100 ml of anhydrous formic acid.[27] The addition required 50 sec. The flask was stoppered and shaken by hand for 11 min during which the initially formed yellowish precipitate disappeared and the heterogeneous mixture developed a pink tinge. The mixture was then poured slowly with cooling into a 30% sodium hydroxide solution containing 130 g of 97% sodium hydroxide. The addition required about 6 min in order to prevent the temperature of the mixture from rising above 25°. The solution was then stirred for 2.5 hr at room temperature (23°); it was then saturated with sodium chloride and extracted with ether. The combined organic layers were washed thoroughly with saturated brine and dried over anhydrous magnesium sulfate. The residue, obtained on evaporation of the solvent under reduced pressure, amounted to 574 mg of colorless oil. Chromatography on 30 g of neutral Woelm alumina (activity 2.5) gave on elution with pentane[28] 305.0 mg of colorless oil. Further elution with 4:1 pentane–methylene chloride containing 1% methanol gave 202 mg of colorless oil. Vapor phase chromatographic analysis of the pentane fraction (Carbowax, 175°) showed four peaks (A, B, C, and D) having relative peak areas of 23:45:2:30 at retention times of 21.3, 24.5, 26.8, and 30.0 min, respectively. In another run the ratio of these products was 27:45:5:23. This fraction was evaporatively distilled at 1 μ (pot temperature 110°) to give 287 mg (60% yield) of colorless oil.

Anal. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70. Found: C, 88.5; H, 11.5.

This material absorbed hydrogen for 2.08 double bonds (platinum oxide in acetic acid).[29] The pentane–methylene chloride fraction from the aforementioned chromatography appeared to be essentially homogeneous by thin layer chromatography, R_f 0.61 (2:1 benzene–ethyl acetate). Evaporative distillation at 1.5 μ (pot temperature 135°) afforded 176 mg (34% yield) of a colorless clear glass, $\lambda_{\max}^{\text{film}}$ 2.94 μ (OH), which partially decomposed on vapor phase chromatography. The nmr spectrum exhibited absorption for six protons as a singlet at 1.07 ($HOC(CH_3)_2$-), three protons as a singlet at 1.58 ($C=C-CH_3$), and three protons as a singlet at 0.94 ppm ($\geq CCH_3$). This product, therefore, is presumed to be **15-norabiet-4-en-18-ol (20)**.

Anal. Calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.09. Found: C, 82.3; H, 10.8.

In another cyclization experiment carried out exactly as described above except that the ratio of substrate to solvent was decreased from 1:200 to 1:500, there was obtained from 111 mg of the trienol **3** (treated with 50 ml of anhydrous formic acid), after chromatography and evaporative distillation, 34.6 mg (33% yield) of the hydrocarbon fraction and 56.8 mg (52% yield) of the alcohol fraction. The ratios of the components of the hydrocarbon fraction, estimated by vapor phase chromatography (see above) were 23% A, 46% B, 2% C, and 28% D.

A similar experiment with 1.20 g of substrate and 50 ml of formic acid gave 754 mg (67%) of chromatographed tricyclic hydrocarbon mixture (23% A, 45% B, 2% C, and 30% D), and 339 mg (28%) of tricyclic alcohol.

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[27] S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

[28] Air was removed from all solvents used in this chromatography by a process involving alternate evacuation and filling with nitrogen.

[29] The analysis was performed by E. Meier employing the microhydrogenation apparatus manufactured by H. Hoesli.

B. Dehydration of the Trienol and Cyclization of the Resulting Tetraene with Formic Acid. In another cyclization experiment, a solution of 95.8 mg of the trienol in 20 ml of anhydrous acetic acid was allowed to stand at room temperature for 11 min; then it was poured into 50 ml of cold (bath at −20°) 30% sodium hydroxide solution, and the mixture was extracted with ether. The combined organic layers were washed with saturated brine and dried over anhydrous magnesium sulfate. The residue, obtained on evaporation of the solvent under reduced pressure, was evaporatively distilled at 1.5 μ (pot temperature 85–95°) to give 78 mg of colorless oil. This product proved to be mainly a mixture of the tetraenes **14** and **15**. Vapor phase chromatographic analysis of such material on the Carbowax column at 168° indicated two components in a ratio of 2:3 with retention times of 21.5 and 24.5 min, respectively. There were no detectable signals for tricyclic products at longer retention times. The infrared spectrum showed, in particular, bands characteristic of the olefinic bonds, $\lambda_{\max}^{CCl_4}$ 6.10, 6.25 (conjugated $C{=}C$), and 11.25 μ ($C{=}CH_2$), and the ultraviolet spectrum exhibited conjugated dienic absorption, $\lambda_{\max}^{cyclohexane}$ 242 mμ (ϵ 8510) with a shoulder at 275 mμ.

A 77-mg specimen of the tetraene mixture was treated with 20 ml of anhydrous formic acid just as described above for the cyclization of the trienol. The chromatography gave 56 mg (78% yield) of the mixture of tricyclic hydrocarbons (29% A, 38% B, 8% C, and 25% D), and 16 mg (21% yield) of the tricyclic alcohol.

C. Treatment of the Trienol with 1:1 Formic and Acetic Acid (Homogeneous Reaction). A 9.8-mg sample of the trienol was dissolved in 2 ml of a 1:1 mixture of anhydrous formic and acetic acid. The pink homogeneous solution was allowed to stand for 11 min at room temperature. The total crude product, isolated as described above, amounted to 8.0 mg of an oil. Vapor phase chromatographic analysis (Carbowax, 165°) indicated the presence of a 40:60 mixture of the tetraene, amounting to 12% of the total peak area, at retention times of 22.2 and 25.5 min. The main products exhibited four peaks (88% of total area) in the ratio 21:38:14:27 at retention times of 31.0, 36.0, 39.4, and 44.5 min. The 39.4-min peak was poorly resolved and probably corresponded to a mixture of tricyclic hydrocarbon C and the uncyclized aromatized material **28** (see below). The 31.0-, 36.0-, and 44.5-min peaks corresponded to those of tricyclic hydrocarbons A, B, and D. Thin layer chromatography (2:1 benzene–ethyl acetate) showed two spots at R_f 0.78 and 0.49 corresponding to tricyclic hydrocarbons and tricyclic alcohols, respectively.

In an experiment carried out just as described above except that a 5% solution of formic acid in acetic acid was employed, 93% of the peak area of the vapor phase chromatogram corresponded to the tetraenes and 7% to the 39.4-min peak (see above).

D. Extended Treatment of Trienol with Acetic Acid (Formation of Aromatic Products). A solution of 52 mg of the trienol in 10 ml of anhydrous acetic acid was allowed to stand for 6 days at room temperature. Vapor phase chromatographic analysis (Carbowax, 175°) indicated that the initially formed short-retention time peaks, corresponding to the tetraenes, had disappeared, leaving a major peak with a retention time of 32 min. The product was isolated as in the cyclization experiments described above except that it was necessary to extract the aqueous phase with methylene chloride (as well as ether) in order to recover a total of 45 mg of material. This material was chromatographed on 4 g of Woelm neutral alumina (activity 2.5). Elution with pentane gave 23 mg of oil. Thin layer chromatography (2:1 benzene–ethyl acetate) showed two closely running spots at about R_f 0.64. The infrared spectrum (CCl_4 solution) showed, among other bands, absorption at 13.4 μ, probably due to aromatic C–H out-of-plane bending. The nmr spectrum exhibited the signals characteristic of the dienic side chain of the substrate. In addition there were strong singlets at δ 6.85 ppm (aromatic protons) and at 2.28 (benzylic protons) in the ratio of about 2:5 which is consistent with the signals expected for the hydrocarbon **28**. The mass spectrum of this material, after evaporative distillation at 1.5 μ (pot temperature 110°), showed a major (molecular ion) peak at 256 (calcd for $C_{19}H_{28}$, 256).

Separation and Identification of Components of Cyclized Hydrocarbon Fraction. The hydrocarbon fraction from a cyclization experiment like that described in detail above was submitted to preparative vapor phase chromatography (Carbowax, 200°). The following fractions were collected at the indicated retention times: A, 79 min; B, 88 min; D, 97 min. Fraction A, **15-norabieta-4,13-diene (16)**, crystallized in the collection tube at −78° but melted below room temperature. The nmr spectrum exhibited absorption for one proton as a singlet at δ 5.10 ($C{=}CH$) (width at half-height = 3 cps), three protons as a singlet at 1.58 ($C{=}CCH_3$), six protons as a doublet (J = 7 cps) centered at 0.96 ($-CH(CH_3)_2$) and three protons as a singlet at 0.94 ppm ($\geqslant CCH_3$). Fraction B, **15-norabieta-4,12-diene (17)**, also crystallized in the collection tube at −78° and melted below room temperature. The nmr spectrum exhibited absorption for one proton as a singlet at δ 5.33 (width at half-height = 7 cps) ($C{=}CH-$), three protons as a singlet at 1.59 ($C{=}CCH_3)_2$, six protons as a doublet (J = 7 cps) centered at 0.96 ($-CH(CH_3)_2$), and three protons as a singlet at 0.96 ppm ($\geqslant CCH_3$). Fraction C was isolated from another run only in sufficient quantity for determination of the infrared spectrum. The preparation of this material in quantity by dehydration of the alcohol **20** is described below. Fraction D, **15-norabieta-4,13(18)-diene (19)**, was crystalline at room temperature. Two recrystallizations from methanol gave, in 70% recovery, colorless crystals, mp 63.5–64°.

Anal. Calcd for $C_{19}H_{30}$: C, 88.30; H, 11.70. Found: C, 88.1; H, 11.6.

The nmr spectrum exhibited absorption for six protons as a singlet at 1.64 ($C{=}C(CH_3)_2$), three protons as a singlet at 1.57 ($C{=}CCH_3$), and three protons as a singlet at 0.93 ppm ($\geqslant CCH_3$). The mass spectra of substances A, B, and D exhibited molecular ion peaks at 258.

Dehydration of 15-Norabiet-4-en-18-ol with Phosphorus Oxychloride. A 0.34-g portion of Δ^4-15-norabieten-18-ol, separated by chromatography (see above), was mixed with 9 ml of anhydrous pyridine. The solution was cooled to −10°, 2.00 ml of phosphorus oxychloride was added with swirling, and the mixture was then allowed to warm to room temperature and to stand for 24 hr. It was poured slowly onto 70 g of ice, ether was added, and the mixture was acidified with concentrated hydrochloric acid. The organic layer was washed thoroughly with saturated brine, then with saturated sodium bicarbonate and again with brine, and was dried over anhydrous magnesium sulfate. The yellow oily residue (275 mg) obtained on evaporation of the solvent was chromatographed on 40 g of Woelm neutral alumina (activity III). Elution with pentane gave 215 mg of an oil. Vapor phase chromatographic analysis (see above) showed two major peaks in the ratio of 3:2 at retention times which were identical with those of substances C and D (see above). These two substances were separated by preparative vapor phase chromatography (Carbowax, 200°). Their infrared spectra were identical with those of hydrocarbons C and D, respectively, described above. The substance C, **15-norabieta-4,18-diene (18)**, obtained in the present experiment, was a colorless oil, $\lambda_{\max}^{film}$ 6.08 and 11.25 μ (terminal methylene). The nmr spectrum exhibited absorption for two protons as a "singlet" at δ 4.59 ($C{=}CH_2$), three protons as a triplet (J = 1 cps) centered at 1.67 ($CH_2{=}CCH_3-$), three protons as a singlet at 1.58 ($C{=}CCH_3$), and three protons as a singlet at 0.94 ppm ($\geqslant CCH_3$). The mass spectrum showed a molecular ion peak at 258.

Retreatment of Tricyclic Products with Formic Acid. Each of the dienes A–D (see above) was shaken with formic acid for 11 min, and the products were isolated as described above for the cyclization of the trienol **3**. The total unchromatographed products were submitted to vapor phase chromatographic analysis (see above). Only peaks with retention times corresponding to substances A–D were obtained. Thus from a 7-mg portion of diene A (**16**), which was 90% pure (contaminated with 10% of B), there was obtained, after treatment with 3 ml of formic acid, 7 mg of oil. Analysis indicated peaks corresponding to substances A, B, C, and D in the ratio 3:3:3:2. A 17-mg portion of B (90% pure with A as the major impurity) in 4.0 ml of formic acid gave 18 mg, ratio of components 1:3:1:1. An 8-mg portion of C (90% pure by vapor phase chromatography) in 2.5 ml of formic acid gave 7 mg of oil, 3:4:18:4. A 27-mg portion of D (85–90% pure with about 5% impurities of A and B) in 4.0 ml of formic acid gave 27 mg, 1:2:1:6. All the products from these experiments also contained some material which was more polar than the diene mixture A–D on thin layer chromatography and which had the same R_f value as the formate of the tricyclic alcohol **20**.

A 15.5-mg portion of the tricyclic alcohol **20** was treated with 3.0 ml of formic acid to give 14.3 mg of viscous oil which showed two spots on thin layer chromatography with R_f values corresponding to starting material and the hydrocarbons A–D. Vapor phase chromatographic analysis gave peaks corresponding to hydrocarbons A, B, C, and D, in the ratio of 2:3:3:2, respectively.

Hydrogenation. A. Of the Mixture of Tricyclic Hydrocarbons. A 117-mg portion of the chromatographed hydrocarbon fraction (A–D) from a cyclization experiment performed as described above was hydrogenated at room temperature and atmospheric pressure for 55 min in 15 ml of acetic acid in the presence of 75 mg of platinum oxide. Hydrogen uptake had ceased after 15 min. The residue, obtained on filtration and concentrated under reduced pressure, was dissolved in ether and washed with saturated sodium bicarbonate solution, and then dried over anhydrous magnesium sulfate. The oily residue obtained on evaporation of the solvent amounted to 121 mg. Vapor phase chromatographic analysis (SE-30, 168°) showed four peaks in the ratio of 1:4:9:6 at retention times of 13.8, 15.6, 18.2, and 20.3 min, respectively. Collection of the component exhibiting the peak at retention time of 20.3 by preparative vapor phase chromatography (SE-30, 215°) gave an oil, the liquid film infrared spectrum of which was identical with that (supercooled liquid film) of authentic fichtelite,[10] mp 44.8–45.1°, except for weak additional bands at 7.9 and 12.5 μ due to contamination with the SE-30 liquid phase from the gas chromatographic column. The mass spectrum, nmr spectrum, and vapor phase chromatographic behavior of this material were identical with the corresponding properties of authentic fichelite. This specimen of racemic fichtelite crystallized at −78°, but melted quickly when collected on the filter at room temperature.

B. Of the Dienes, A, B, C, and D. Dienes A (**16**), B (**17**), and D (**19**), obtained as described above, were hydrogenated on a 38- to 95-mg scale in 8–12 ml of absolute ethanol at room temperature and atmospheric pressure over 25–50 mg of platinum oxide catalyst. The reactions were slow, requiring times up to 16 hr (for diene D) or (in the case of A) retreatments with fresh catalyst, in order to effect absorption of 1 mol equiv of hydrogen. In the case of diene C the hydrogenation proceeded readily to the dihydro stage over 30% palladium on carbon in about 7 min. The dihydro products, A′, B′, C′, and D′, were isolated by filtration, evaporation of the solvent from the filtrate, and (except for the case of C′ which was simply treated with Norit) chromatography of the residue on Woelm neutral alumina (activity III) and elution with pentane. Except for product B′, which had undergone partial hydrogenation of the 4,5 double bond (apparently because of the presence of a trace of acetic acid), these products had very similar properties. The retention times of the major peak in the vapor phase chromatogram (SE-30, 163–165°) were the same; the infrared spectra were almost identical. The nmr spectra were also essentially identical, showing no vinylic proton absorption and three-proton singlet absorption at 1.57 ppm ($C{=}CCH_3$). The over-hydrogenated product, B′, showed absorption in this region for only 1.5 protons.

Each of the dihydro products, A′, B′, C′, and D′, were hydrogenated in 15 ml of acetic acid at room temperature and atmospheric pressure over 50 mg of platinum oxide. The products were isolated as described above in A. Vapor phase chromatographic analysis as described in A gave the four aforementioned peaks (in the order of increasing retention time) for the product from A′ in the area ratio of 0:1:3:6; from B′, 1:3:10:6; from C′, 0:3:6:11; and from D′, 0:3:6:11. In each case the component corresponding to the highest retention time peak, which was identical with that of authentic fichtelite, was separated by preparative vapor phase chromatography (Carbowax, 200°). The infrared spectra (liquid film) of each of these fractions were identical with each other as well as with the spectrum (supercooled liquid film) of an authentic specimen of fichtelite.

1,2,3-Trimethylcyclohex-2-en-1-ol (30). 2,3-Dimethylcyclohex-2-en-1-one was prepared according to the published procedure.[17] Our product had the following properties: bp 100–102° (25 mm) (lit.[17] bp 93–96° (20 mm)); $n^{21}\text{D}$ 1.4975 (lit.[17] $n^{21}\text{D}$ 1.4980); λ_{max}^{EtOH} 242 mμ (ε 14,460) (lit.[30] λ_{max}^{EtOH} 234 mμ (ε 13,200)). To a solution of 3.44 g of this unsaturated ketone in 220 ml of anhydrous ether was added slowly with stirring at room temperature an ethereal solution containing 0.14 mol of methyllithium (Foote Mineral Co.) in an atmosphere of nitrogen. After the addition was complete, the mixture was allowed to stir at room temperature for 20 min, and then it was slowly added to ice. The aqueous layer was extracted with ether, followed by methylene chloride; then the combined organic layers were washed with brine and dried over anhydrous magnesium sulfate. Removal of the solvent by distillation through a Widmer column gave a crystalline residue which upon recrystallization from pentane (Norit) gave 2.25 g of colorless crystals, mp 73–74°. The nmr spectrum exhibited absorption for three protons as a singlet at δ 1.18 (CH_3 at C-1), nine protons as a poorly resolved "doublet" at 1.59 and 1.63 (CH_3 at C-2 and C-3, C-4 and C-5 methylene), and three protons as a broad "singlet" at 1.88 ppm which was attenuated on addition of deuterium oxide exchange (C-6 methylene and OH).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.15; II, 11.5.

Dehydration of 1,2,3-Trimethylcyclohex-2-en-1-ol (30) to Give the Diene Mixture 31. A solution of 18 mg of 1,2,3-trimethylcyclohex-2-en-1-ol (**30**), mp 73–74°, in 3 ml of anhydrous acetic acid was allowed to stand at room temperature for 11 min; it was then poured into 7 ml of cold 30% sodium hydroxide solution and extracted with ether. The combined ether solutions were washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed by distillation through a Widmer column, leaving an oily residue, $\lambda_{max}^{CCl_4}$ 6.1, 6.2 (conjugated $C{=}C$) and 11.3 μ ($C{=}CH_2$); λ_{max}^{EtOH} 240 mμ with a shoulder at 270. Vapor phase chromatographic analysis (Carbowax, 100°) showed two peaks at retention time of 7 and 8 min in a ratio of about 40:37.

Behavior of 1,2,3-Trimethylcyclohex-2-en-1-ol (30) in Acetic Acid. A 468-mg portion of 1,2,3-trimethylcyclohex-2-en-1-ol (**30**) was added to 50 ml of deoxygenated (by alternately evacuating and filling with nitrogen) anhydrous acetic acid. The colorless solution was allowed to remain in the dark at room temperature for 5 days. Vapor phase chromatographic analysis of an aliquot (Carbowax, 125°) showed two peaks at the retention time of the dienes **31** and an additional single peak at longer retention time (4 min). A small amount (2 mol %) of water was added to the reaction mixture. After 1 additional day, vapor phase chromatographic analysis of an aliquot indicated a slight increase in the 4-min peak. The mixture was then heated on a steam bath for 12 hr. Vapor phase chromatographic analysis showed 25% dienes and 75% of the 4-min peak as well as some minor peaks at higher retention time. The orange solution was poured into cold (−10°) 30% sodium hydroxide solution and extracted with 1:1 pentane–methylene chloride. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, and the solvent was removed by distillation through a Widmer column. The residual dark oil was evaporatively distilled at 50 mm (pot temperature 130°) to yield 225 mg of colorless oil and 123 mg of residue. The distillate was submitted to preparative vapor phase chromatography, and the fraction corresponding to the 4-min peak was collected. The infrared spectrum of this material was identical with that of authentic 1,2,3-trimethyl benzene. The nmr spectra of the two materials were also identical, exhibiting absorption for three protons as a singlet at δ 6.85 (aromatic protons), six protons as a singlet at 2.24 (CH_3 at C-1 and C-3), and three protons as a singlet at 2.14 ppm (CH_3 at C-2). In another experiment a solution of 27.3 mg of 1,2,3-trimethylcyclohex-2-en-1-ol in 3 ml of acetic acid, after standing 5 days at room temperature, showed on vapor phase chromatographic analysis, only the peak for 1,2,3-trimethylbenzene.

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