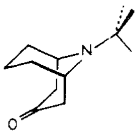
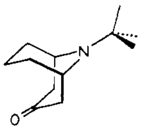
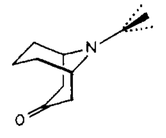
basis of an equilibrium of N-planar conformations **7c**, **7d** (and **7e**) with **7c** predominating over **7d**. Carbons 2 and 4 would be deshielded by the δ effect in **7c** and carbons 6 and 8 would be deshielded in **7d**. An attempt to resolve the question by low temperature ^{1}H NMR was unsuccessful. While some changes were evident, the spectra were not sharp enough to permit any rigorous conclusions.[16]



7c



7d



7e

(16) C. Hackett Bushweller, private communication.

(17) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 57.

(18) D. M. Grant and V. B. Cheney, *J. Am. Chem. Soc.*, **89**, 5315, 5319 (1967).

(19) It should be pointed out that the methyl groups do not experience shifts corresponding in magnitude to those of the carbons 2(4) or 6(8) and the bridgehead carbons. Such a lack of reciprocity of shifts for sterically interacting carbons is not uncommon.[20] In addition, the opposite directions of the γ and δ steric effects would tend to counteract one another in the case of the methyl groups. The shifts of the methyl groups observed as more methyl groups are added are typical of β substituent effects.[17]

(20) (a) D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 6612 (1967); (b) *ibid.*, **94**, 5318 (1972); (c) E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magn. Reson.*, **5**, 277 (1973).

(21) (a) J. Hansson, *Svensk. Kem. Tidskr.*, **67**, 256 (1955); (b) P. Geneste, I. Hugon, Cl. Reminiac, G. Lamaty, and J. P. Roque, *Bull. Soc. Chim. Fr.*, 845 (1976).

(22) (a) R. C. Cookson, J. Henstock, and J. Hudec, *J. Am. Chem. Soc.*, **88**, 1060 (1966); (b) J. Hudec, *Chem. Commun.*, 829 (1970); (c) A. W. J. D. Dekkers, J. W. Verhoeven, and W. N. Speckamp, *Tetrahedron*, **29**, 1691 (1973); (d) C. Worrell, J. W. Verhoeven, and W. N. Speckamp, *ibid.*, **30**, 3525 (1974); (e) A. M. Halpern and A. L. Lyons, *J. Am. Chem. Soc.*, **98**, 3242 (1976); (f) T. Sasaki, S. Eguchi, T. Kiriyama, and Y. Sakito, *J. Org. Chem.*, **38**, 1648 (1973); (g) W. A. Ayer, B. Altenkirk, R. H. Burnell, and M. Moinas, *Can. J. Chem.*, **47**, 449 (1969).

(23) J. Kuthan and J. Palecek, *Collect. Czech. Chem. Commun.*, **28**, 2260 (1963).

(24) G. Thomson, *J. Chem. Soc.*, 1113 (1946).

Terpenes and Related Systems. 16.[1] Fate of Representative Bicyclic Sesquiterpenes in Strong Acid Medium. A General Rearrangement of Hydroazulene Sesquiterpenenes to Decalin Types

Goverdhan Mehta* and Brij Pal Singh

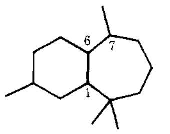
Department of Chemistry, Indian Institute of Technology, Kanpur-208016, U.P., India

Received August 23, 1976

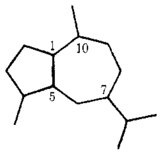
Rearrangement of several naturally occurring bicyclic sesquiterpenes of himachalane (**1**), guaiane (**2**), cadalane (**3**), and eudesmane (**4**) types has been studied in strong acid medium under stable carbocation conditions. The structures of the carbocations (**8** and **40**) formed from α- and β-himachalenes (**5** and **6**) and from selinenes (**38**), respectively, have been deduced from ^{1}H NMR spectral data. Quenching of these cationic solutions provides convenient preparation of conjugated dienes **9**, **10**, and **28**. A novel and general rearrangement of guaiane-type hydroazulenic sesquiterpenes to (+)-10-epizonarene (**22**), a naturally occurring heteroannular diene of the cadalane family, has been discovered. (−)-γ-Murrolene (**33**) has been found to rearrange stereospecifically to another heteroannular diene, (−)-zonarene (**34**), of cadalane type. Probable mechanisms for the rearrangements encountered in the present study are discussed.

Acid-catalyzed rearrangements of polyisoprenoids have been extensively investigated by organic chemists since the dawn of this century.[2] This high level of interest has been sustained by the unraveling of numerous unique rearrangements that are synthetically useful and mechanistically fascinating.[3] Furthermore, the recognition[4a–d] that cationic cyclizations play a key role in the biogenesis of isoprenoids has provided the impetus to mimic[4e,f] many of these rearrangements in the laboratory by generating appropriate carbonium ions. Isoprenoids in particular, as they contain tertiary carbon centers and double bonds, are highly amenable to deep-seated structural changes on creation of an electron-deficient site.[2–4] Over the years, a variety of media have been employed to study the acid-catalyzed rearrangements of terpenoid substrates. The recent advent of carbonium ion stabilizing solvents,[5–7] e.g., H_2SO_4, FSO_3H, etc., has opened new possibilities for deflecting the normal course of terpene rearrangements, under stable carbonium ion conditions.[5,6]

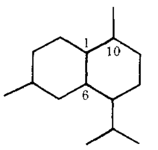
The dichotomy in the behavior of carbonium ions under varying acidity of the medium has been demonstrated in many cases. Perhaps the earliest example[8] in the field of isoprenoids is the conversion of camphor to β-camphorsulfonic acid in sulfuric acid and camphor-π-sulfonic acid in fuming sulfuric acid. Recently, Deno[9] and Sorenson[10] have extensively studied the rearrangements of monoterpenes camphene, fenchol, and borneol in sulfuric acid and fluorosulfonic acid and shown that stable cyclohexenyl cations are formed in this medium, in direct contrast[2,11,12] to their behavior in weakly acidic media. A similar dependence of the mode of rearrangement on the acidity of the reaction medium has been demonstrated by us[13,15,17,18] in the rearrangements of sesquiterpene hydrocarbons humulene[13,14] and longifolene[15,16] as well as abietic-type[17–19] diterpene resin acids. This ability of polyisoprenoids to undergo novel molecular rearrangements[9,10,13,15,17–20] in strong acid medium, under the conditions salubrious to the formation of stable carbocations, has encouraged us to in-



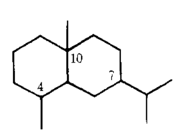
1



2



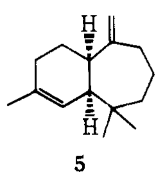
3

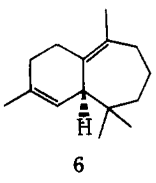


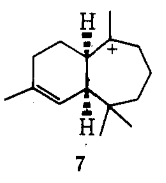
4

vestigate the rearrangement of representative bicyclic sesquiterpenes in strong acid medium. Consequently, the fate of several naturally occurring bicyclic sesquiterpene hydrocarbons[21] belonging to himachalane (1), guaiane (2), cadalane (3), and eudesmane (4) types in concentrated H_2SO_4 has been studied. The highlight of these studies is the discovery[22] of a facile and general rearrangement (2 → 3) of perhydroazulenes to decalinic ring systems. These results are discussed here.

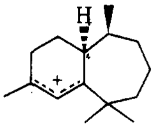
The Cation from Himachalenes and Its Quenching Products. α- and β-himachalenes (5, 6)[23] are the major sesquiterpene hydrocarbons of *Cedrus deodar* Loud, and are

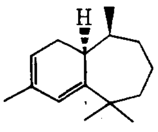

5

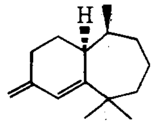

6


7

widely distributed in nature. Their acid-catalyzed rearrangements are of considerable interest as the cation 7 derived from 5 and 6 has been implicated[4c,d] in the biogenesis of several tri- and tetracyclic sesquiterpenes. However, no report concerning the cationic cyclization or acid rearrangement of 5 and 6 has appeared in the literature. When a solution of either α- or β-himachalene (5 or 6) in methylene chloride was rapidly dispersed in concentrated H_2SO_4 (97–99%) at 0–5 °C, a clear orange solution [λ_{max} (H_2SO_4) 340 nm] was obtained. This solution exhibited a reasonably clean ^1H NMR spectrum with a singlet at δ 7.6 corresponding to a central hydrogen of a cyclohexenyl cation, a broad singlet at δ 2.87 due to a methyl attached to the termini of an allylic cation, a pair of singlets at δ 1.45 and 1.63 due to the geminal dimethyl, and a doublet at δ 0.97 (J = 7 Hz) due to the tertiary methyl group. These data are consistent with the reasonable structure 8 for the cation, mechanistically accessible from either 5 or 6 via a couple of 1, 2- or a 1,3-hydride shift.

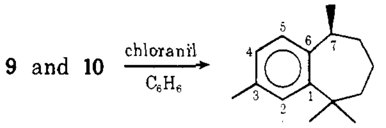

8


9


10

Further confirmation of the carbon skeleton of the cation 8 came from the quenching products obtained by careful destruction of the cation in aqueous sodium carbonate at 0 °C. A 90% yield of a light yellow oil containing more than 66% of a 4.5:1.5:1 mixture of 9, 10, and 11 was obtained. The mixture could be conveniently separated by column chromatography over $AgNO_3$ impregnated silica gel. The structures of dienes 9 and 10 were easily deduced from their spectral characteristics. The major component 9 was a homoannular diene [λ_{max} (MeOH) 274 nm] and exhibited in its ^1H NMR spectrum two dienylic hydrogens (δ 5.73, 1 H, s, and 5.17, 1 H, m), along with a vinylic methyl (δ 1.67, 3 H; s), a nonequivalent geminal dimethyl group (δ 1.05 and 1.15, 3 H, s), and a tertiary methyl group (δ 0.90, d, J = 7 Hz). The minor diene 10 was heteroannular [λ_{max} (MeOH) 249 nm] and its IR spectrum revealed the presence of a terminal methylene group (3120, 1630, and 885 cm^{-1}) and trisubstituted olefinic linkage (860 cm^{-1}). The ^1H NMR spectrum displayed an olefinic proton singlet at δ 6.1 and a terminal methylene doublet at δ 4.60 and 4.68 along with methyl singlets at δ 1.01 (3 H, s), 1.18 (3 H, s), and 0.81 (3 H, d, J = 7 Hz). The third component was readily identified as *ar*-himachalene 11 by comparison of its spectral data with those of an authentic[24,25] specimen.

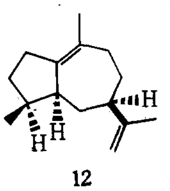
Both the dienes 9 and 10 were smoothly aromatized by chloranil in refluxing benzene to (+)-*ar*-himachalene (11).[24]

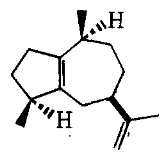


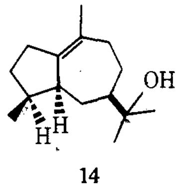
11

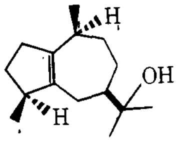
This conversion establishes the *S* configuration of the chiral center at C_7 in 9 and 10 as the $[\alpha]_D$ +3.8° of 11 prepared from these dienes is comparable to the $[\alpha]_D$ +5.90° of (+)-*ar*-himachalene (11) prepared[24] from (+)-*ar*-turmerone, a compound of well-established absolute stereochemistry. The ring junction hydrogen at C_6 in dienes 9 and 10 is tentatively assigned α-H stereochemistry from mechanistic considerations. The conformation[26] of α- and β-himachalenes (5 and 6) would be expected to favor protonation from the α face to give the common cation 7, which can undergo either a series of 1,2-hydride shifts or a direct 1,3-hydride shift leading to cation 8 with the assigned C_6 stereochemistry. It remains to be seen whether the dienes 9 and 10 prepared in this work will be found to occur in nature. However, it may be noted that conjugated dienes with disposition of double bonds as in 9 and 10 have been known in the cadinane and bisabolane[27] framework for long time.

The Cation from Guaiane-Type Sesquiterpenes and Its Quenching Product. Among the guaiane family of sesquiterpene, α-bulnesene (12), α-guaiene (13), α-bulnesol (14), and guaiol (15) are commonly encountered[21] in nature and 14 and 15 are considered biogenetically important.[4c,d] Acid-catalyzed reactions of 12–15 have been extensively studied[28] using a variety of acid catalysts and shown to lead to the formation of an equilibrium mixture of various guaiene isomers (16–20) and guaioxide (21), depending on the reaction conditions, without any skeletal rearrangement (Scheme I).

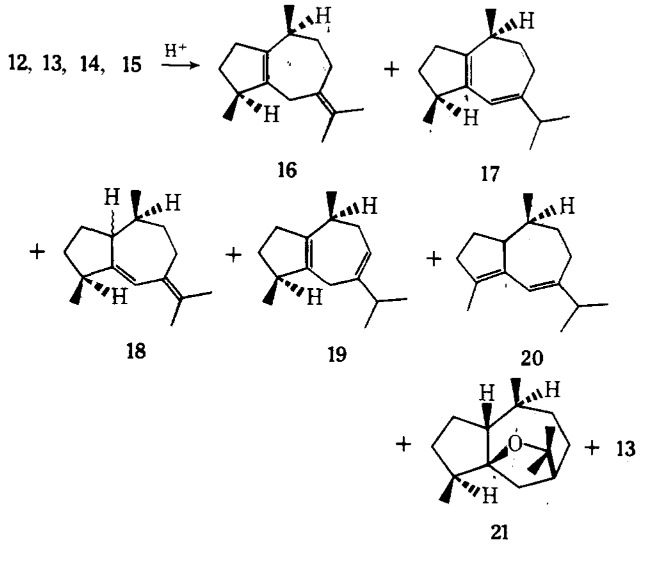

12


13


14


15

Scheme I



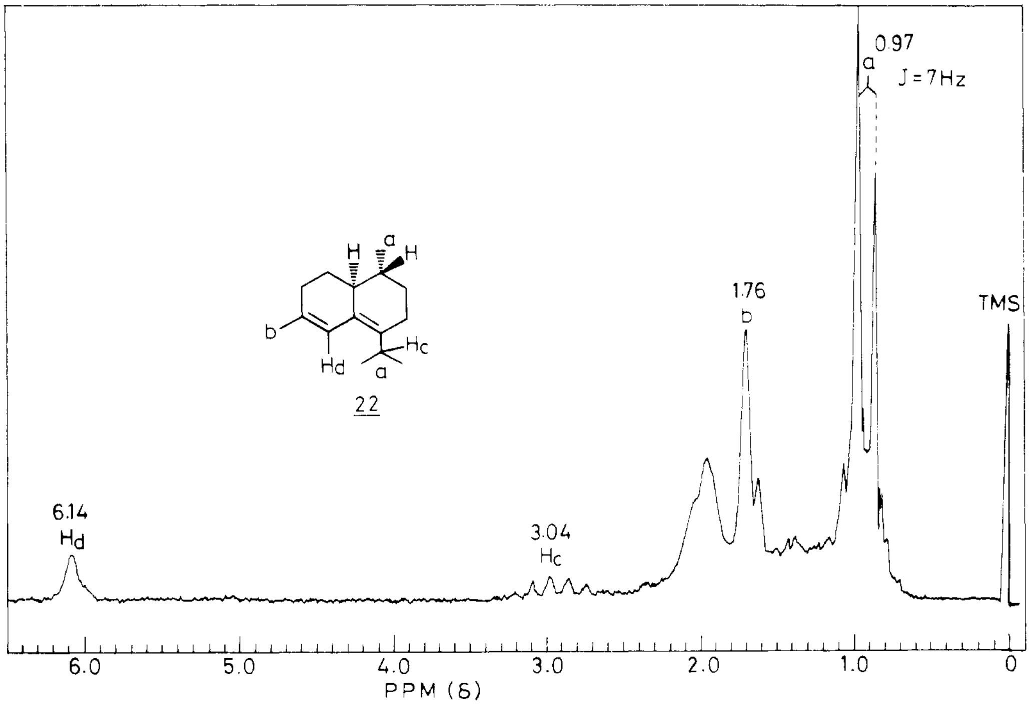
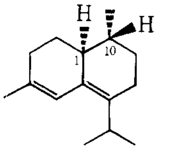


Figure 1. ^{1}H NMR spectrum of (+)-10-epizonarene (22).

When a solution of either guaiol (15), α-bulnesene (12), or α-guaiene (13) in concentrated H_2SO_4 (97–99%) was prepared at 0–5 °C, a clear orange-brown solution [λ_{max} (H_2SO_4) 330 nm] was obtained. The ^{1}H NMR spectrum of this solution, although indicative of the formation of an enylic cation, was not sufficiently clean to make any definite structural assignment. Quenching of the sulfuric acid solution in iced aqueous sodium carbonate led to the recovery of 80–95% organic material. Analysis by GLC and $AgNO_3$-silica gel TLC indicated the presence of a major component which was readily separated and obtained pure in 30–40% isolated yield. Several minor products were present but could not be obtained pure and characterized owing to extensive and rapid polymerization. The major product was indicated to be a heteroannular diene [λ_{max} (MeOH) 249 nm], whose structure was more clearly defined by its ^{1}H NMR spectrum (Figure 1, an isopropyl group, a tertiary methyl group, a vinylic methyl, and an olefinic proton). These gross structural features at first sight pointed to the structure of iso-α-gurjunene (20),[28f,29] but a comparison with an authentic sample showed that they were indeed not identical. Perusal of literature data for several sesquiterpene heteroannular dienes and mechanistic considerations then led to the characterization of this diene as (+)-10β*H*-murrola-4,6-diene[30,31] (*ent*-10-epizonarene, 22). A direct spectral comparison[34] established the identity of 22 with the naturally occurring 10-epizonarene. Furthermore, the optical rotation (Table I) of 22 obtained from various precursors delineates its absolute stereochemistry.[31] However, the optical activity of 22 obtained from different precursors varies significantly and appears to be considerably racemized compared to the natural product.



22

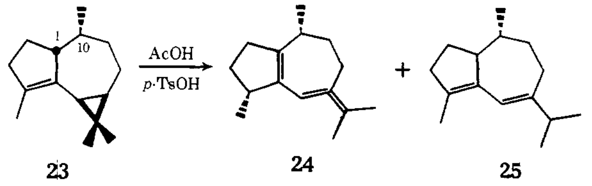
Table I. Rearrangement of Guaiane-Type Sesquiterpenes to (+)-10-Epizonarene (22) in Concentrated H_2SO_4 at 0–5 °C

Starting olefin	Yield[a] of 10-epizonarene, %	$[\alpha]^{21}_D$ ($CHCl_3$)	Ref
α-Bulnesene 12 $[\alpha]_D$ ±0°	30–35	+24	Present work
α-Guaiene 13 $[\alpha]_D$ −22.4°	30	+4	Present work
Guaiol 15 $[\alpha]_D$ −32°	25	+80	Present work
α-Gurjunene 23 $[\alpha]_D$ −180°	50	+125	Present work
Chamaecyparis nooktkatensis		+175	31

[a] Isolated yield from several experiments.

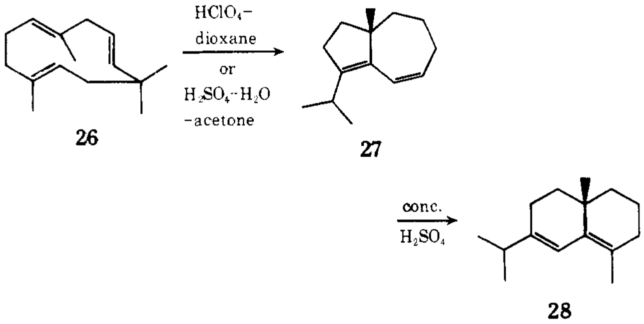
The generality of the rearrangement of guaiane sesquiterpenes to (+)-10-epizonarene was further demonstrated by the smooth rearrangement of (−)-α-gurjunene 23 to 22 in concentrated sulfuric acid in 50% yield (Table I). This result again contrasts[28f,35] with the behavior of α-gurjunene 23 in less acidic nucleophilic medium, when a mixture of isogurjunene A (*ent*-γ-guaiene, 24) and iso-α-gurjunene B (25) is obtained (Scheme II). Similarly, bicyclohumulene (27), an acid rearrangement product[14] of the monocyclic sesquiterpene humulene (26), further rearranged to a new heteroannular diene in concentrated sulfuric acid medium. This diene [UV λ_{max} (MeOH) 241, 249, and 256 nm; ^{1}H NMR isopropyl group (δ 1.06, 6 H, d, $J = 7$ Hz), quaternary methyl group (δ 0.92, 3 H, s), vinylic methyl group (δ 1.67, 3 H, br s), and olefinic proton

Scheme II



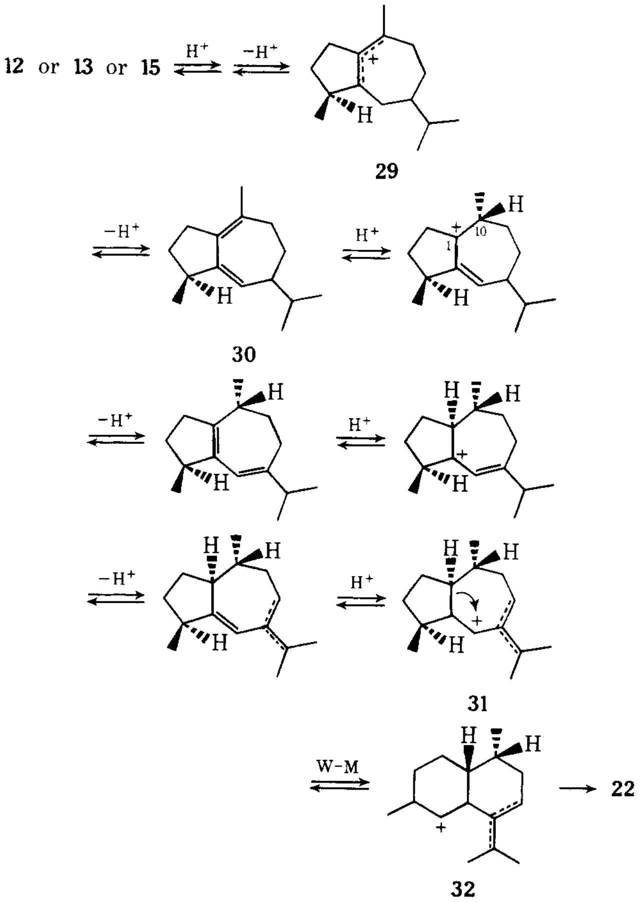
(δ 6.17, 1 H, s)], as expected, turned out to be identical[36] with δ-selinene (**28**) (Scheme III). The identity of **28** was further established through a direct spectral comparison.

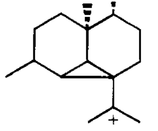
Scheme III



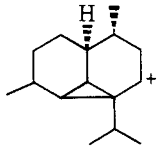
Although the course of rearrangement of perhydroazulenes (**12, 13, 15, 23,** and **27**) to the decalin system (**22** and **28**) is for the most part mechanistically unexceptional, there are a few stereochemical features that elicit interpretive comment. Firstly, the exclusive formation of *ent*-10-epizonarene (**22**) from α-guaiene (**13**) and guaiol (**15**) indicated that the C_{10} methyl group had epimerized (from β to α) during the rearrangement process. Secondly, C_1 and C_{10} centers are stereoselectively protonated from the β face and α face, respectively, to generate the relative stereochemistry of C_1 and C_{10} present in **22**. We would like to visualise this rearrangement as proceeding through a common intermediate (e.g., carbonium ion **29** and diene **30**) derivable from **12, 13,** and **15** though a protonation–deprotonation sequence (Scheme IV). An examination of a Drieding model of either **29** or **30** revealed only marginal steric preference for the observed protonation (at C_1 and C_{10}) and therefore much racemization could be anticipated in this step. This is borne out by the low optical purity of (+)-10-epizonarene (**22**) obtained in this rearrangement (Table I). Finally, in case of (−)-α-gurjunene (**23**) the C_1 stereochemistry is reversed from β- to α-H but the C_{10} stereochemistry is retained and the product obtained has high chiral retention (Table I). The ease of rearrangement of **31** to **32** is somewhat unexpected as it involves an uphill climb from a conjugated, substituted allyl cation **31** to an unconjugated secondary cation **32**. However, it is reasonable to speculate that the activation energy for the rearrangement may be lowered through contribution from structures such as **32a** and **32b**.

Scheme IV





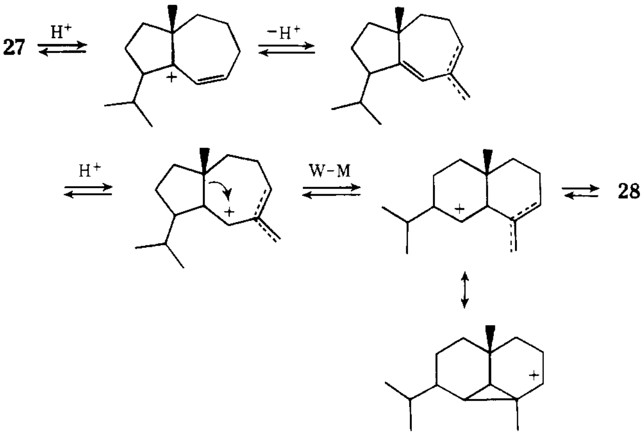
32a



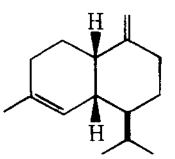
32b

The interesting rearrangement of bicyclohumulene[14] (**27**) to δ-selinene (**28**), constituting a fascinating overall humulene (**26**) → δ-selinene (**28**) conversion,[13] is analogous to the guaiane → cadalane type transformation. A plausible mechanism is depicted in Scheme V.

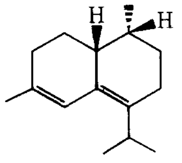
Scheme V



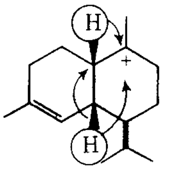
The Cation from Cadinane Types and Its Quenching Product. Acid-catalyzed rearrangement of several cadinanic sesquiterpenes has been studied[31,37] previously. These studies have essentially resulted in isomerization of double bonds, disproportionation, and aromatization to calamenenes. Presently, we have looked into the behavior of (−)-γ-murrolene (**33**) in strong acid medium. Extraction of **32** into concentrated H_2SO_4 (96–98%) from a methylene chloride solution at 0–5 °C furnished an orange-colored solution having intense UV absorption [λ_{max})h$_2$SO$_4$) 340 nm]. Quenching of the acid solution into iced aqueous sodium carbonate furnished an oily product (85%) consisting of a major component which was separated by AgNO$_3$–silica gel column chromatography in 40% yield. The spectral characteristics [UV λ_{max} (MeOH) 249 nm; ^{1}H NMR (Figure 2) δ 0.72 (3 H, d, J = 7 Hz, tertiary methyl), 0.90 (6 H, d, J = 6.5 Hz, isopropyl methyls), 1.71 (3 H, br s, vinylic methyl), 6.08 (1 H, br s, olefinic proton)] indicated its



33



34



35

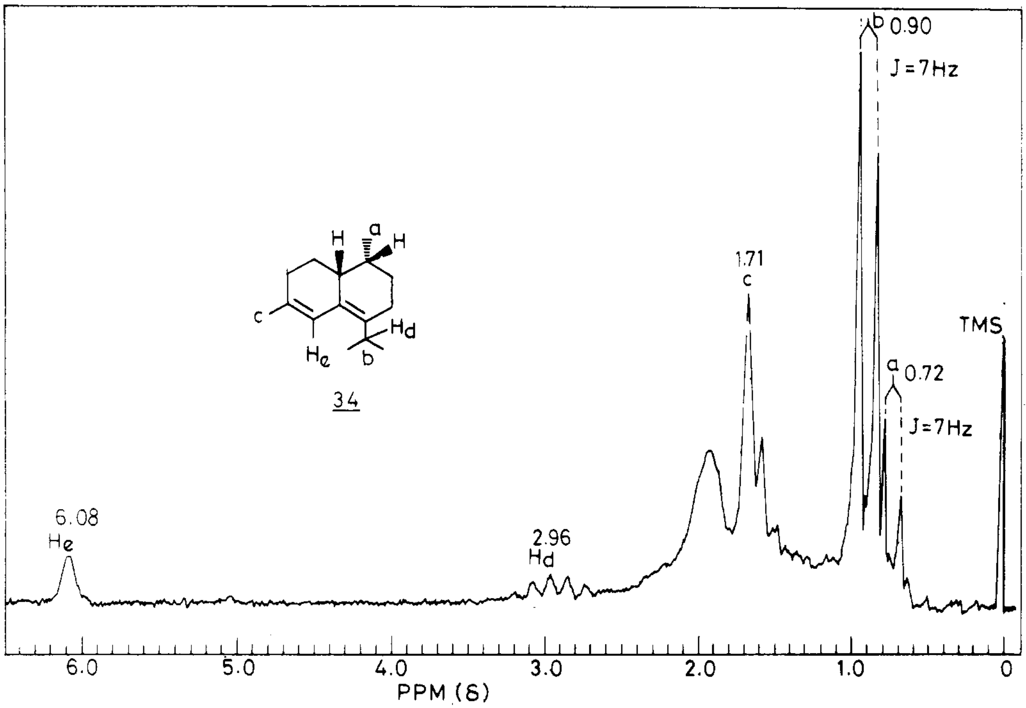
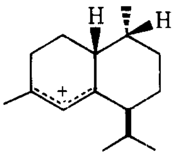
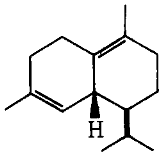


Figure 2. ^{1}H NMR spectrum of (−)-zonarene (34).

structure as (−)-10β*H*-murrola-4,6-diene (zonarene, 34) and a direct spectral comparison with the natural product[31,32,34] unambiguously established its formulation. The stereospecific transformation of (−)-γ-murrolene (33) to (−)-zonarene (34) can be accounted for in terms of either 1,2-hydride shifts (1, 10 and 6, 1) or a direct 1,3-hydride shift (6, 10) in the initially formed cation 35 and eventuating in the formation of stable cyclohexenyl cation 36. The stereospecificity of the 33 → 34 rearrangement is particularly noteworthy in view of the recently reported[31] isomerization of (+)-δ-cadinene (37) to (+)-10-epizonarene (22) of low optical purity.

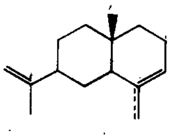


36

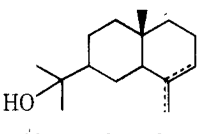


37

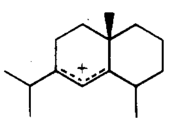
The Cation 40 from Eudesmane (Selinane) Types and Its Quenching Product. The α- and β-selinenes (38) as well as α- and β-eudesmols (39) are known to isomerize to δ-selinene (28) with acidic reagents.[38] Extraction of 38 and 39 from methylene chloride solutions into sulfuric acid at 0–5 °C effected facile isomerization to the cyclohexenyl cation 40 whose structure was evident from its ^{1}H NMR spectrum (δ 7.53, s, central proton of an enylic cation, 1.48 d, J = 7 Hz, isopropyl methyls, 1.53, s, quaternary methyl, and 1.53, d, J = 6.5 Hz, tertiary methyl group) and intense UV absorption [λ_{max} (H_2SO_4) 340 nm]. Destruction of the cation 40 in iced aqueous sodium carbonate led to near-quantitative recovery of a single diene identified as δ-selinene (28) by spectral comparison.[36] The formation of 40 is simply accommodated by either 1,2-hydride shifts or a protonation–deprotonation sequence leading to a stable enylic cation.



38, α-endocyclic
β-exocyclic



39, α-endocyclic
β-exocyclic



40

Conclusions

It has been demonstrated that a variety of bicyclic sesquiterpene hydrocarbons form stable enylic cations in strong acid medium whose structures can be examined by ^{1}H NMR spectroscopy. There is a marked propensity for the formation of stable 1,3-dialkylated cyclohexenyl carbonium ions of the type 8, 36, and 40 and the rearrangement of perhydroazulenic dienes to the decalinic system is the outcome of this favorable stability change. The guaiane → cadalane rearrangement observed here establishes the first direct correlation between the two most abundantly distributed sesquiterpene carbon skeletons and may be of some biogenetic significance. Quenching of the stable carbonium ion solutions with base provides a preparatively useful method for the synthesis of conjugated sesquiterpene dienes, many of which occur widely in nature.

Experimental Section[39]

Starting Materials. Samples of natural products, procured from various sources, were purified via column chromatography followed by distillation or crystallization and adequately characterized through spectral methods. Sulfuric acid (AR grade, BDH, 98%) was used for the preparation of carbonium ion solutions.

Preparation and Quenching of Stable Carbocations in Sulfuric Acid. General Procedure. In the preparative experiments the carbocations were prepared by adding 10% solutions of the natural products in methylene chloride dropwise to a well-stirred solution of sulfuric acid (98%) which had been cooled in an ice bath (0–5 °C). The resultant carbocation solutions were usually 10% with respect to the organic cation. Aliquots from this solution were withdrawn and used for UV and ^{1}H NMR determinations. After stirring for about 30 min at 0–5 °C the cation solution was added dropwise to a vigorously stirred mixture of petroleum ether and aqueous sodium carbonate containing crushed ice. The general apparatus used for these operations was a slight modification of that described earlier.[15] The petroleum ether extract and washings from the quenching solution were dried and evaporated to dryness on a rotary evaporator. The residual oils were analyzed by TLC on 15% silver nitrate impregnated silica gel plates and GLC on a 10-ft Carbowax 20% on Chromosorb P column at 145 °C.

The Cation 8 from Himachalenes 5 and 6. Preparation of

Dienes 9 and 10. Following the above general procedure, a CH_2Cl_2 solution (15 ml) of α-himachalene **5** or β-himachalene[42] **6** (3 g, 15 mmol) in sulfuric acid (30 ml) afforded the cation **8** as an orange solution: UV λ_{max} (H_2SO_4) 340 nm; ^1H NMR (H_2SO_4) δ 0.98 ($\mathbf{CH_3}CH$, 3 H, d, J = 7 Hz), 1.45 ($>CCH_3$, 3 H, s), 1.63 ($>CCH_3$, 3 H, s), 2.86 ($CH_3C{=}C^+{=}C<$, 3 H, s), 7.6 ($>C{=}CH^+{=}C<$, 1 H, s). Quenching of the cation in iced aqueous sodium carbonate (75 g in 500 ml of water), extraction with petroleum ether, washing, and drying furnished 2.7 g (90%) of a yellow oil. Distillation at 100–110 °C (2 mm) yielded 2.0 g (66%) of a colorless oil and left behind a viscous polymeric residue. GLC analysis coupled with TLC ($AgNO_3$–SiO_2) resolved the distilled oil into three main components. Efficient separation was achieved by column chromatography on a $AgNO_3$–silica gel column (80 g, 60 × 2 cm). The first of these (64% by GLC), **9** [bp 90–100 °C (1 mm) n^{30}D 1.5170] showed the following spectral properties: UV λ_{max} (MeOH) 274 nm (ε 5200); IR 1670, 1601, 860, and 782 cm^{-1} (trisubstituted olefin); ^1H NMR (CCl_4) δ 0.90 ($\mathbf{CH_3}CH$, 3 H, d, J = 7 Hz), 1.05 and 1.15 ($\mathbf{CH_3}C\mathbf{CH_3}$, 3 H, s), 1.67 ($CH_3C{=}C<$, 3 H, s), 5.17 ($HC{=}C<$ 1 H, m), 5.73 ($HC{=}C<$, 1 H, s). Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.18; H, 11.77. The second component (21% by GLC), **10** [bp 95–100 °C (2 mm), n^{30}D 1.5145], showed the following spectroscopic properties: UV λ_{max} (MeOH) 248 nm (ε 18 400); IR 3120, 1630, 885 (exocyclic methylene), 1595, 860 cm^{-1} (trisubstituted olefin); ^1H NMR (CCl_4) δ 0.81 (CH_3CH, 3 H, d, J = 7 Hz), 1.0 ($>CCH_3$, 3 H, s), 1.09 ($>CCH_3$, 3 H, s), 4.60 and 4.68 ($H_2C{=}C<$, 2 H, d), 6.1 ($HC{=}C<$, 1 H, s). Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 89.06; H, 11.40. The last component (14% by GLC), **11** [bp 110–115 °C (2 mm), n^{30}D 1.5285, $[\alpha]_D$ +3.8°, c 2.3] exhibited IR 3010, 1620, 1580, 1450, 810 cm^{-1} (aromatic); ^1H NMR (CCl_4) δ 1.26 ($\mathbf{CH_3}CH$, 3 H, d, J = 7 Hz), 1.30 ($>CCH_3$, 3 H, s), 1.38 ($>CCH_3$, 3 H, s), 2.26 ($Ar\mathbf{CH_3}$, 3 H, s), 6.98 (Ar, 3 H, m). The IR and ^1H NMR spectra of **11** were superimposable with those of an authentic specimen.[24,25] The literature[24] records $[\alpha]_D$ +2.92° (c 1.7) for the naturally occurring material and $[\alpha]_D$ +5.90° (c 1.04) for the (+)-*ar*-himachalene **11** obtained from (+)-*ar*-tumerone. Anal. Calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.90; H, 10.60.

Aromatization of Dienes 9 and 10 with Chloranil. A mixture of dienes **9** and **10** (1.5 g) and 3 g of chloranil in dry benzene (60 ml) was refluxed for 6 h under a nitrogen blanket. The precipitate was filtered and washed with 10 ml of benzene. The solvent was stripped off on a rotary evaporator and the residual oil dissolved in aqueous acetone (25 ml). Powdered potassium permanganate was added pinch by pinch to destroy any olefinic impurity. When no more of the oxidant was being consumed, the reaction mixture was diluted with water (30 ml), extracted with petroleum ether, washed, and dried. Filtration through a silica gel (20 g) column yielded (0.8 g, 55%) pure **11** identical in all respects with an authentic sample.[24,25]

Rearrangement of Guaiol (15), α-Guaiene (13), and α-Bulnesene (12) in Sulfuric Acid. Preparation of (+)-10-Epizonarene (22). Following the general procedure, guaiol[43] (**15,** 2 g, 9 mmol) in CH_2Cl_2 (15 ml) was dispersed in sulfuric acid (20 ml) to furnish an orange-brown solution, UV λ_{max} (H_2SO_4) 330 nm. This solution did not exhibit any well-defined signals in the ^1H NMR spectrum. Quenching of the sulfuric acid solution in iced aqueous sodium carbonate (50 g in 500 ml of water), extraction with petroleum ether (50 ml × 3), washing, and drying furnished 1.4 g (70%) of a colorless oil. GLC analysis in conjunction with $AgNO_3$–silica gel TLC revealed the presence of one major component (~50%) together with several minor products which rapidly became viscous on standing or on passage through a $AgNO_3$–silica gel column. The major product **22** was, however, eluted from a $AgNO_3$–silica gel column (50 g, 40 × 2 cm) with petroleum ether–benzene (9:1) and obtained pure in 20–25% yield. The diene **22** (bp 100–105 °C (2 mm), n^{31}D 1.5145, $[\alpha]_D$ +80°, c 2.8) exhibited the following spectral characteristics: UV λ_{max} (MeOH) 249 nm (ε 15 600); IR 1645, 1610, 861 cm^{-1} (trisubstituted olefin); ^1H NMR (CCl_4) δ 0.97 ($\mathbf{CH_3}CH\mathbf{CH_3}$ and CH_3CH, 9 H, d, J = 7 Hz), 1.76 ($CH_3C{=}C<$, 3 H, br s), 3.04 ($CH_3\mathbf{CH}CH_3$, 1 H, septet, J = 7 Hz), 6.14 ($HC{=}C<$, 1 H, s) and led to its identification[31,34] as (+)-10-epizonarene. The IR and ^1H NMR spectrum of **22** was indistinguishable from that of the natural product.[31,34] Anal. Calcd for $C_{15}H_{24}$: C, 88.16; H, 11.84. Found: C, 88.41; H, 11.40. Similarly, preparation of the cation solution from α-guaiene[44] (**13,** 1.5 g, 7.3 mmol) in sulfuric acid (15 ml) followed by quenching and usual workup led to the isolation of yellow, oil material (1.4 g, 93%). Distillation at 100–110 °C (2 mm) furnished 0.95 g (63%) of a colorless oil and a dark brown resinous material remained in the distillation bulb. GLC and TLC ($AgNO_3$–silica gel) indicated the presence of one major product (50%), **22,** which was isolated by column chromatography on $AgNO_3$–silica gel and resulted in the isolation (30%) of pure (+)-10-epizonarene **22,** $[\alpha]_D$ +4.00°. In an identical fashion α-bulnesene[44] (**12,** 0.8 g, 3.9 mmol) was dispersed in sulfuric acid (10 ml) and after usual quenching and workup furnished a colorless oil (0.75 g, 95%). Column chromatography on a $AgNO_3$–silica gel column yielded pure **22,** $[\alpha]_D$ +24.2° (c 1.97), in 30–35% yield.

Rearrangement of α-Gurjunene[45] (23) in Sulfuric Acid. Formation of (+)-10-Epizonarene (22). α-Gurjunene (**23,** 1.5 g, 7.3 mmol) in methylene chloride (15 ml) was dispersed in sulfuric acid (15 ml) as described above. Quenching the sulfuric acid solution in iced aqueous sodium carbonate (40 g in 300 ml of water), extraction with petroleum ether, and usual workup yielded 1.4 g (93%) of a yellow oil. Distillation at 100–110 °C (2 mm) gave 1 g (66%) of a colorless oil. GLC and TLC indicated the presence of one major compound **22,** which was isolated (50% yield) by column chromatography on a $AgNO_3$–silica gel column (20 g, 40 × 1.4 cm) and elution with petroleum ether–benzene mixture (9:1). The spectral (IR, ^1H NMR) characteristics of **22,** $[\alpha]_D$ +125° (c 2.9), were identical with those of (+)-10-epizonarene.

Rearrangement of Bicyclohumulene (27) in Sulfuric Acid to δ-Selinene (28). Bicyclohumulene[46] (**27**) was prepared from humulene[47] (**26**) according to the procedure of Dauben et al. A methylene chloride (10 ml) solution of **27** (0.3 g, 1.5 mmol) was added to sulfuric acid (4 ml) as described earlier. Quenching the solution in iced aqueous sodium carbonate (15 g in 100 ml of water) and usual workup led to the isolation of 0.2 g (65%) of a labile mixture of dienes as a colorless oil. Column chromatography on a $AgNO_3$–silica gel column (20 g, 40 × 1.4 cm) and elution with petroleum ether–benzene mixture (9:1) led to the isolation of pure δ-selinene (**28**) in 20–25% yield. The diene **28** was characterized through its spectral characteristics [UV λ_{max} (MeOH) 249 nm (ε16 500); IR 1620, 872 cm^{-1} (trisubstituted olefin); ^1H NMR (CCl_4) δ 0.92 ($>CCH_3$, 3 H, s), 1.06 ($\mathbf{CH_3}CH\mathbf{CH_3}$, 6 H, d, J = 7 Hz), 1.67 ($CH_3C{=}C<$, 3 H, s), 6.17 ($HC{=}C<$, 1 H, s)] and direct comparison with the reported spectra.[36]

Rearrangement of (−)-γ-Murrolene (33) in Sulfuric Acid to (−)-Zonarene (34). (−)-γ-Murrolene[48] (**33,** 0.5 g, 2.5 mmol) in methylene chloride (5 ml) was rapidly dispersed in sulfuric acid (5 ml) as described in the general procedure. Quenching in iced sodium carbonate (15 g in 100 ml of water), extraction with petroleum ether (25 ml × 2), and workup as described above furnished 0.42 g (85%) of an oily product. This product was charged on a $AgNO_3$–silica gel column (20 g, 30 × 1.4 cm) and elution with petroleum ether–benzene mixture (9:1) yielded 0.2 g (40%) of pure diene **34.** The diene **34** [bp 90–100 °C (2 mm), $[\alpha]_D$ −89° (c 1.2)] was identified as (−)-zonarene on the basis of the spectral data [UV λ_{max} (MeOH) 249 mm (ε 18 000); IR 1645, 1610, 864, 840 cm^{-1} (trisubstituted olefin); ^1H NMR (CCl_4) δ 0.72 ($\mathbf{CH_3}CH$, 3 H, d, J = 7 Hz), 0.90 ($\mathbf{CH_3}CH\mathbf{CH_3}$, 6 H, d, J = 7 Hz), 1.71 ($CH_3C{=}C<$, 3 H, s), 2.96 ($CH_3\mathbf{CH}CH_3$, 1 H, septet, J = 7 Hz), 6.08 ($HC{=}C<$, 1 H, s)] and direct spectral comparison with the natural product.[31–34]

The Cation 40 from Selinenes (38) and Eudesmols (39). Preparation of δ-Selinene (28). A mixture of α- and β-selinene (**38,** 3 g, 15 mmol) in methylene chloride (25 ml) was dispersed in sulfuric acid (30 ml) to give an orange-brown solution of cation **40,** UV λ_{max} (H_2SO_4) 340 nm; ^1H NMR (H_2SO_4) δ 1.48 ($\mathbf{CH_3}CH\mathbf{CH_3}$, 6 H, d, J = 7 Hz), 1.53 ($>CCH_3$, 3 H, s), 1.53 ($\mathbf{CH_3}CH$, 3 H, d, J = 7 Hz), and 7.53 ($>C{=}C^+{=}C<$). Quenching the cation **40** in aqueous sodium carbonate (80 g in 500 ml of water), extraction with petroleum ether (50 ml × 3), washing, drying, and removal of solvent furnished 2.8 g (93%) of a pale yellow oil. Column chromatography on a $AgNO_3$–silica gel column (80 g, 50 × 2 cm) and elution with petroleum ether–benzene (9:1) furnished 1.6 g of pure δ-selinene (**28**) in 53% yield. In an identical experiment, a mixture of α- and β-eudesmols (**39,** 1 g) furnished 0.48 g (50%) of δ-selinene (**28**), which was identified by spectral comparison with an authentic sample.[36]

Acknowledgment. The authors would like to express their sincere thanks to Professor G. B. Singh (BHU, India) and Dr. S. Raghu (Michigan State University) for the ^1H NMR spectral data reported in this paper.

Registry No.—**5,** 3853-83-6; **6,** 1461-03-6; **8,** 60909-18-4; **9,** 60909-27-5; **10,** 60909-28-6; **11,** 19419-67-1; **12,** 3691-11-0; **13,** 3691-12-1; **15,** 489-86-1; **22,** 41702-63-0; **23,** 489-40-7; **27,** 60909-26-4; **28,** 28624-23-9; **33,** 24268-39-1; **34,** 41929-05-9; α-**38,** 473-13-2; β-**38,** 17066-67-0; β-**39,** 473-16-5; β-**39,** 473-15-4; **40,** 60909-17-3.

References and Notes

(1) Part 15: G. Mehta, S. K. Kapoor, and B. G. B. Gupta, *Indian J. Chem.*, in press.

(2) For a comprehensive account of earlier work, see J. L. Simonsen, "The

Terpenes", Vol. I–V, Cambridge University Press, Cambridge, U.K., 1947–1957.

(3) (a) J. King and P. de Mayo in "Molecular Rearrangements", Vol. 2, P. de Mayo, Ed., Interscience, New York, N.Y., 1964; (b) A. A. Newman, Ed., "Chemistry of Terpenes and Terpenoids", Academic Press, New York, N.Y., 1972; (c) G. Ourisson, *Proc. Chem. Soc., London,* 294 (1964); (d) T. S. Santhanakrishnan, *J. Sci. Ind. Res.*, **12,** 631 (1965); (e) D. V. Banthorpe and D. Whittaker, *Chem. Rev.*, **66,** 643 (1966); (f) D. V. Banthorpe and D. Whittaker, *Q. Rev., Chem. Soc.*, **20,** 373 (1966); (g) W. G. Dauben, *J. Agric. Food Chem.*, **22,** 156 (1974).

(4) (a) L. Ruzicka, A. Eschenmoser, and H. Heusser, *Experientia*, **9,** 357 (1953); (b) L. Ruzicka, *Proc. Chem. Soc., London,* 341 (1959); (c) J. B. Hendrickson, *Tetrahedron,* **7,** 83 (1959); (d) W. Parker, J. S. Roberts, and R. Ramage, *Q. Rev., Chem. Soc.*, **21,** 331 (1967); (e) W. S. Johnson, *Acc. Chem. Res.*, **1,** 1 (1968); (f) E. E. Van Tammelen, *ibid.*, **1,** 111 (1968).

(5) (a) G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, N.Y., 1973, and references cited therein; (b) D. Bethel and V. Gold, "Carbonium Ions, an Introduction", Academic Press, New York, N.Y., 1967; (c) G. A. Olah and P. von R. Schleyer, "Carbonium Ions", Vol. 1–4, Wiley-Interscience, New York, N.Y., 1968–1972.

(6) D. G. Farnum, *J. Am. Chem. Soc.*, **86,** 934 (1964).

(7) R. J. Gillespie and T. E. Peel, *Adv. Phys. Org. Chem.* **9,** 1 (1971).

(8) M. A. Reychler, *Bull. Soc. Chim. Fr.* **3,** 19, 120 (1898); F. S. Kipping and W. J. Pope, *J. Chem. Soc.*, **63,** 548 (1893); P. Lipp and H. Knapp, *Ber.*, **73B,** 915 (1940).

(9) N. C. Deno, *Chem. Eng. News,* **42,** 88 (1964); N. C. Deno and J. J. Houser, *J. Am. Chem. Soc.*, **86,** 1741 (1964).

(10) E. Huang, K. Ranganayakulu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **94,** 1779 (1972).

(11) S. Coffey, Ed., "Rodd's Chemistry of Carbon Compounds", Vol. II, Elsevier, Amsterdam, 1969, p 243. Also, M. F. Ansell, Ed., supplement to "Rodds Chemistry of Carbon Compounds", S. Coffey, Ed., Elsevier, Amsterdam, 1974, pp 53–93.

(12) W. Huckel and D. Volkmann, *Justus Liebigs Ann. Chem.*, **31,** 664 (1963).

(13) G. Mehta and B. P. Singh, *Tetrahedron Lett.*, 3961 (1975).

(14) Several groups have recently reported the rearrangements of humulene employing various acid reagents. A. Nickon, T. Iwadare, F. J. McGuire, J. R. Mahajan, S. A. Narang, and B. Umezawa, *J. Am. Chem. Soc.*, **92,** 1688 (1970); Y. Naha and Y. Hirose, *Chem. Lett.*, **133,** 727 (1973); D. Baines, J. Forrester, and W. Parker, *J. Chem. Soc., Perkin Trans. 1,* 1598 (1974); W. G. Dauben, J. P. Hubbell, and N. D. Vietmeyer, *J. Org. Chem.* **40,** 479 (1975).

(15) D. G. Farnum and G. Mehta, *Chem. Commun.*, 1643 (1968); D. G. Farnum, R. A. Mader, and G. Mehta, *J. Am. Chem. Soc.*, **95,** 8692 (1973).

(16) For earlier reports on the rearrangement of longifolene, see J. R. Prahlad, U. R. Nayak, T. Santhanakrishnan, and S. Dev, *Tetrahedron Lett.*, 417 (1964); S. C. Bisarya, U. R. Nayak, and S. Dev, *ibid.*, 2323 (1969); G. Mehta, *Chem. Ind.* (*London*), 1264 (1970).

(17) G. Mehta, N. M. Pattnaik, and S. K. Kapoor, *Tetrahedron Lett.*, 4947 (1972).

(18) G. Mehta and S. K. Kapoor, *Tetrahedron Lett.*, 2385 (1973).

(19) B. E. Cross, M. R. Firth, and R. E. Markwell, *J. Chem. Soc., Chem. Commun.*, 930 (1974).

(20) D. V. Banthorpe, P. A. Boullier, and W. D. Fordham, *J. Chem. Soc., Perkin Trans. 1,* 1637 (1974).

(21) For a recent review on sesquiterpenes, see G. Rucker, *Angew. Chem., Int. Ed. Engl.*, **2,** 793 (1973).

(22) This observation has been reported in the form of a preliminary communication: G. Mehta and B. P. Singh, *Tetrahedron Lett.*, 1585 (1975).

(23) J. B-Son. Bradenberg and H. Erdtman, *Acta Chem. Scand.*, **15,** 685 (1961); T. C. Joseph and S. Dev, *Tetrahedron*, **24,** 3809 (1968).

(24) R. C. Pandey and S. Dev, *Tetrahedron*, **24,** 3829 (1968).

(25) G. Mehta and S. K. Kapoor, *J. Org. Chem.*, **39,** 2618 (1974).

(26) T. C. Joseph and S. Dev, *Tetrahedron,* **24,** 3841 (1968).

(27) T. K. Devon and A. I. Scott, "Handbook of Naturally Occurring Compounds", Vol. II, "Terpenes", Academic Press, New York, N.Y., 1972.

(28) (a) R. B. Bates and R. C. Slagel, *Chem. Ind.* (*London*), 1715)1962); (b) K. Takeda, H. Minato, and J. Nosaka, *Tetrahedron,* **13,** 308 (1961); (c) R. B. Bates and R. C. Slagel, *J. Am. Chem. Soc.*, **84,** 1307 (1962); (d) M. V. Kadival, M. S. R. Nair, and S. C. Bhattacharya, *Tetrahedron,* **23,** 1241 (1967); (e) P. Ledoux, B. P. Vaterlaus, and G. Chiurdoglu, *Bull. Soc. Chim. Belg.*, **75,** 551 (1966); (f) C. Ehret and G. Ourisson, *Tetrahedron,* **25,** 1785 (1969); (g) H. Ishii, T. Tozyo, and M. Nakamura, *ibid.*, **27,** 4263 (1971).

(29) We would like to thank Professor G. Ourisson (Strasbourg, France) for kindly supplying us with the IR and ^{1}H NMR spectra of iso-α-gurjunene B (**20**).

(30) Recently, two heteroannular dienes of cadalane skeleton, (−)-zonarene (**33**) and 10-epizonarene (**22**), in both its enantiomeric forms have been shown to occur widely in several essential oils[31] and brown seeweed[32] *Dictyopteris zonariodes.* Both **22** and **33** have also been obtained in racemic form as the minor products of cyclization[33] of farnesol with boron trifluoride etherate. Andersen et al.[31] have elucidated the absolute configuration of zonarenes from the CD data by the application of transoid diene chirality rule.

(31) N. H. Andersen, D. D. Syrdal, B. M. Lawrence, S. J. Terhune, and J. W. Hogg, *Phytochemistry,* **12,** 827 (1973).

(32) W. Fenical, J. J. Sims, R. M. Wing, and P. C. Radlick, *Phytochemistry,* **11,** 1161 (1972).

(33) Y. Ohta and Y. Hirose, *Chem. Lett.*, 263 (1972).

(34) We would like to thank Professors N. H. Andersen and W. Fenical for the IR and ^{1}H NMR spectra of zonarenes.

(35) W. Treibs and D. Merckel, *Justus Liebigs Ann. Chem.*, **617,** 129 (1958).

(36) M. L. Maheshwari, T. C. Jain, R. B. Bates, and S. C. Bhattacharya, *Tetrahedron,* **19,** 1079 (1963); B. S. Tyagi, B. B. Ghatge, and S. C. Bhattacharya, *ibid.*, **19,** 1189 (1963).

(37) N. H. Andersen, D. D. Syrdal, and C. Graham, *Tetrahedron Lett.*, 903 (1972).

(38) L. Westfelt, *Acta Chem. Scand.*, **20,** 2852 (1966); A. Zabza, M. Ramanauk, and V. Herout, *Collect. Czech. Commun.*, **31,** 3373 (1966); Y. Ohta and Y. Hirose, *Tetrahedron Lett.*, 1601 (1969).

(39) Boiling points are uncorrected and refer to bath temperature in those cases where short-path bulb-to-bulb distillations were carried out. The petroleum ether corresponds to the fraction of bp 60–80 °C. All solvent extracts were dried over anhydrous sodium sulfate. Silver nitrate impregnated silica gel (15%) for TLC and column chromatography was prepared according to the procedure of Gupta and Dev.[40] GLC analysis were carried out on a CIC (India) Model AC1-TC gas chromatograph. Specific rotations were measured in chloroform on a JASCO DIP automatic polarimeter. The ultraviolet spectra were recorded on a Beckman DU spectrophotometer in sulfuric acid (cations) or methanol (dienes). Infrared spectra were recorded on a Perkin-Elmer Model 137B spectrophotometer as neat liquids. ^{1}H NMR spectra were taken on a Varian A-60D spectrometer. Tetramethylammonium tetrafluoroborate[41] (δ 3.13) was used as an internal standard for all carbonium ion spectra, and tetramethylsilane (δ 0.0) was used as an internal standard for all other spectra. Microanalyses were performed by Mr. A. H. Siddiqui in the microanalytical laboratory of our department.

(40) A. S. Gupta and S. Dev, *J. Chromatogr.*, **12,** 189 (1963).

(41) D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Am. Chem. Soc.*, **86,** 673 (1964).

(42) α- and β-himachalene (**5** and **6**) were isolated from the essential oil of *Cedrus deodar* Loud. by fractional distillation and column chromatography. We would like to thank Dr. K. L. Handa (RRL, Jammu) for a generous gift of the essential oil.

(43) (−)-Guaiol (**15,** $[\alpha]_D$ −32°) was kindly supplied by Dr. W. Bruhn (Dragoco, Holzmindent) and Professor S. C. Bhattacharya (IIT, Bombay).

(44) (−)-α-Guaiene (**13**) and α-bulnesene (**12,** $[\alpha]_D$ 0) were isolated from commercial patchouli oil supplied by Fritzsche Brothers, Inc., New York, N.Y.

(45) (−)-α-Gurjunene (**23,** $[\alpha]_D$ −180°) was kindly provided by Professor G. Ourisson.

(46) We would like to thank Professor W. Parker (Sterling, U.K.) for the spectra of bicyclohumulene (**27**).

(47) Humulene (**26**) was isolated from wild ginger oil, kindly supplied by Drs. S. Dev and B. A. Nagasampagi.

(48) (−)-γ-Murrolene (**33,** $[\alpha]_D$ −3°) was kindly provided by Professor V. Herout (Prague, Czechoslovakia).