reduced under these conditions. The mixture was heated at 45 °C for 16 h. The remaining Zn–Cu was removed by centrifugation and the supernatant liquid was added to water (100 ml) containing hydrochloric acid (0.5 ml). The water was extracted with pentane (4 × 2 ml), and the pentane was washed with 5% sodium bicarbonate solution and saturated sodium chloride solution. After drying with magnesium sulfate the product (0.285 g, 42%) was isolated by preparative GC (10 ft × 0.25 in. 5% OV-101 at 45 °C): $[\alpha]_D$ <0.04 (c 13.75, ethanol); mass spectrum (70 eV) m/e (rel intensity) 116 (5), 115 (51, M^+), 114 (3), 86 (58), 85 (66), 43 (100).

Acknowledgments. This research was supported through grants from the National Science Foundation (CHE-7517816) and the Dreyfus Foundation through a Teacher–Scholar Fellowship.

Registry No.—Zn, 7440-66-6; Cu, 7440-50-8.

Supplementary Material Available. The Raman spectra and a table of normalized Raman intensities for the three isomeric 1,4-dideuteriobutadienes as well as ^{13}C NMR parameters for the deuterated products (3 pages). Ordering information is given on any current masthead page.

References and Notes

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(8) Conventional mass spectrometry is not particularly useful for detecting small amounts of nondeuterated (for example m − 1) material in the presence of large m^+ ions. Thus only a few cases (Table I, entries 5 and 18) allow a comparison of ^{13}C NMR and MS methods. In these cases the agreement was within a few percent.
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Novel C_{19} Trienes from Abietic Acid in Fluorosulfonic Acid[1a,b]

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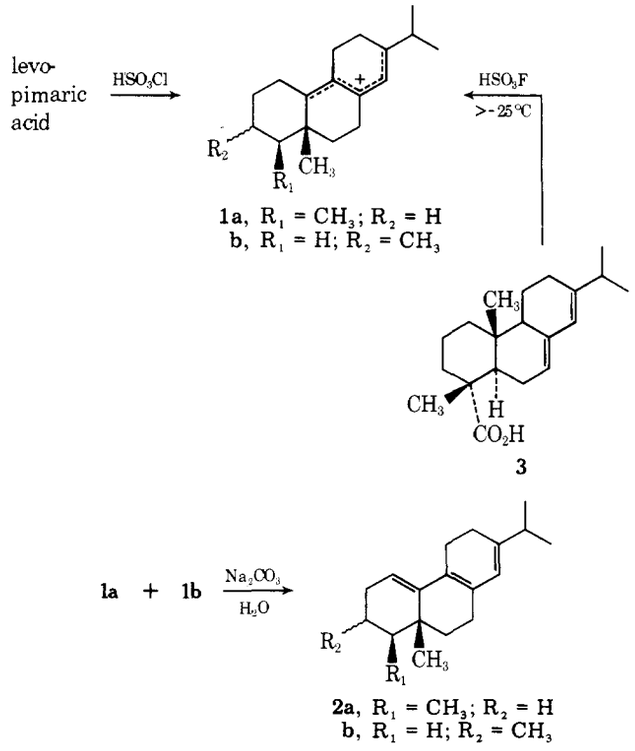
Abietic acid can be recovered from fluorosulfonic acid below −40 °C. At higher temperatures an irreversible rearrangement takes place (Scheme III) to give stable carbocations **1a** and **1b**. Quenching the cations in aqueous sodium carbonate afforded a 1:2 mixture of trienes **2a** and **2b** whose structures were established by their spectroscopic properties, the degradation shown in Scheme I, and the independent synthesis of key degradation products shown in Scheme II.

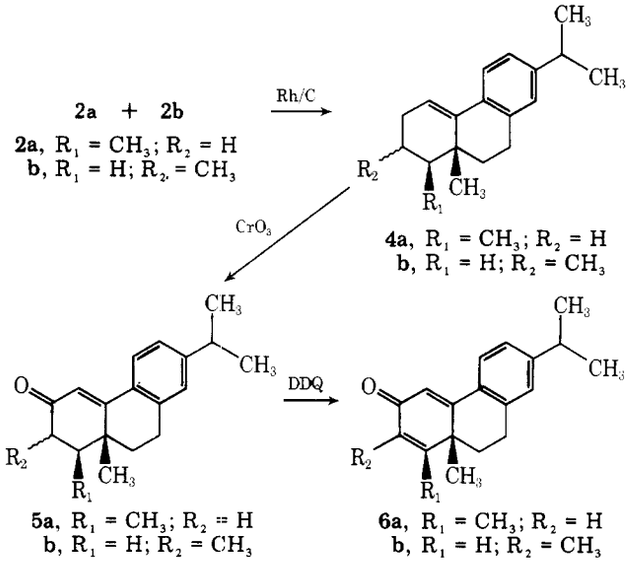
The reaction of levopimaric acid in the carbocation-stabilizing solvent chlorosulfonic acid to give cations **1a** and **1b**, and, after quenching, trienes **2a** and **2b**, has been reported by Mehta and Kapoor.[2] These authors referred to our independent investigation of the reaction of abietic acid (**3**) in fluorosulfonic acid above −25 °C to give the same cations and trienes. Although our report of our work was delayed in the refereeing and rewriting process, we would like to describe some aspects of it now, since a detailed account has not yet appeared, the structural conclusions of Mehta and Kapoor depend to some extent on comparison with our compounds, and some interesting and perhaps generally useful synthetic work was done in the course of our investigation.



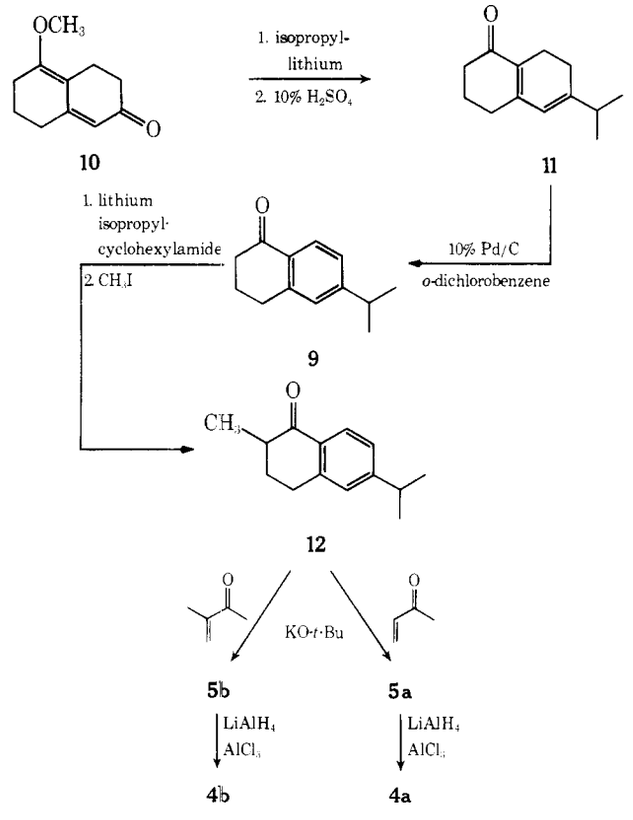
The preparation and spectroscopic properties of the cations and trienes have already been described and interpreted in the literature,[2] and our very similar results are described in detail in the Experimental Section. Therefore, we will confine our discussion primarily to the structure determination of trienes **2a** and **2b**,[3] outlined in Scheme I, and the synthesis of the degradation products, the styrenes, **4a** and **4b**, and the enones, **5a** and **5b**, outlined in Scheme II.

Structure Determination. Our degradative scheme differs somewhat from that of Mehta and Kapoor in that we were able to separate the trienes **2a** and **2b** by chromatography on a silver nitrate–alumina column[4] and obtain styrenes **4a** and **4b**, respectively, from them by rhodium on carbon dehydrogenation.[5] The other workers obtained a mixture of styrene **4a** and a further dehydrogenation product of **4b** on palladium–carbon dehydrogenation of the triene mixture. The position of the tertiary methyl group (R_1 or R_2) in "ring A" of the styrenes was established in our work by oxidation of **4a** and **4b** to the enones **5a** and **5b**, respectively, and dehydrogenation of these to their respective dienones **6a** and **6b**. The α hydrogen (R_2) on the dienone **6a** appeared at higher field

Scheme I. Degradation of Trienes 1a and 1b

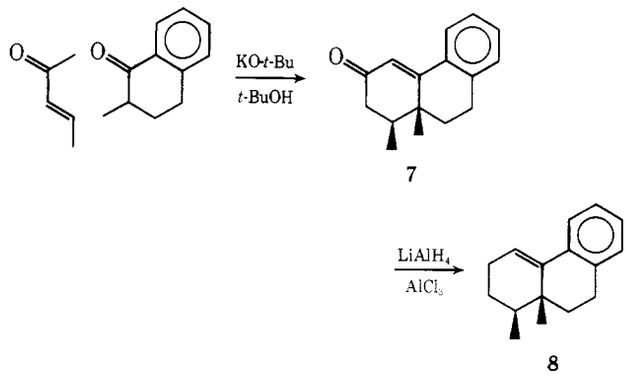


Scheme II. Synthesis of Some Degradation Products from Trienes 1a and 1b



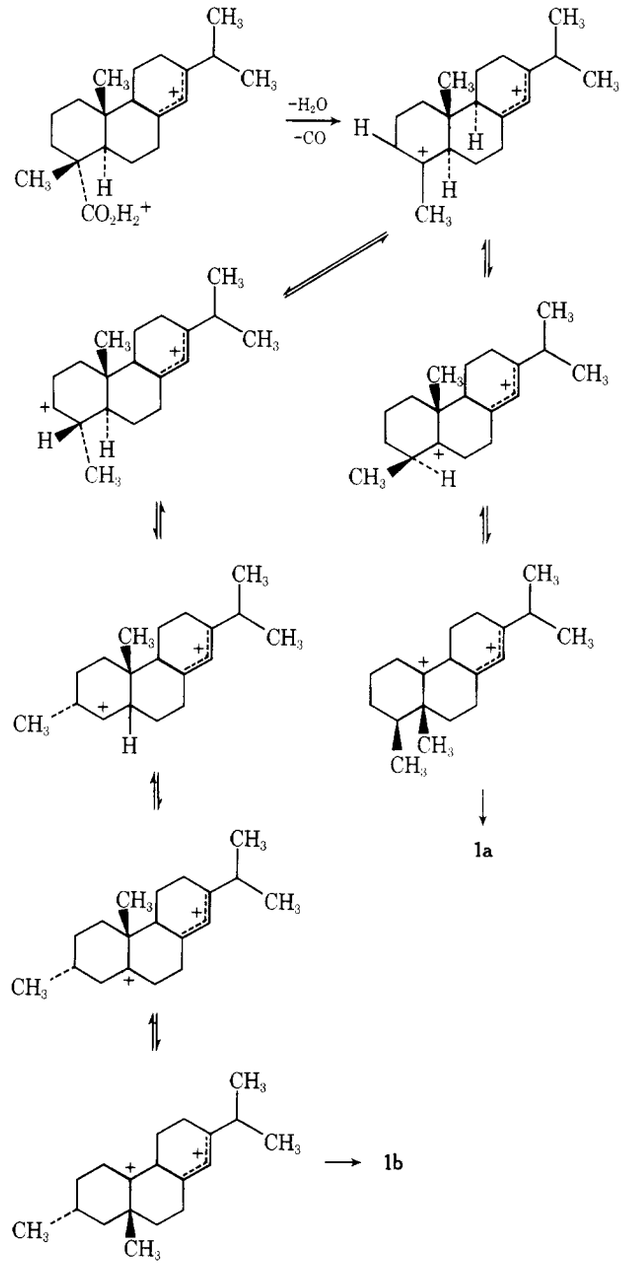
in the ^{1}H NMR (δ 6.04) than the β hydrogen (R_1) of **6b** (δ 6.48), while the β-methyl (R_1) of **6a** appeared at lower field (δ 2.03) than the α-methyl (R_2) of **6b** (δ 1.86), consistent with our structural assignment.[6] The remaining spectroscopic properties of all the degradation products (IR, UV, MS) were consistent with the assigned structures, as were the combustion analyses, and all were optically active.[8] Although the structures appeared to be reasonably well secured, we chose to obtain further evidence by independent synthesis of some key degradation products.

Syntheses. The syntheses of **4a**, **4b**, **5a**, and **5b** in Scheme II are patterned after the Whitlock syntheses of some related compounds, **7** and **8**, lacking the isopropyl group.[7]



Although the tetralone **9** required for our synthesis had been reported,[10] we found it convenient to prepare this compound by the alternate route in Scheme II, which makes use of enol ether **10** reported by Patterson and Reusch,[11] and Nazarov and Zavyalov.[12] The syntheses require no comment, although it might be noted that the reconversion of **5a** and **5b** to **4a** and **4b** by Cava's method[13] provides reassurance that no deep-

Scheme III



seated structural reorganization took place in the reverse degradative transformation.

Mechanism. We agree with Mehta and Kapoor on the essential features of a plausible mechanism for the transformation of abietic acid to cations **1a** and **1b**, diagrammed in more detail in Scheme III. Separation of the isomeric trienes **2a** and **2b** has enabled us to demonstrate that cations **1a** and **1b** can be re-formed from their respective trienes in fluorosulfonic acid and are not interconverted at room temperature. We therefore suggest that the last step in the formation of each of these cations in Scheme III, which generates the dienylic cation from a dication, is irreversible, while all previous steps are reversible. It is possible that the wandering methyl group at C_2 in cation **1b** may have made still further excursions to C_3 and C_4 and we just did not isolate the resultant products from our mixture. However, the absence of any NMR peaks in the spectrum of the cation mixture from abietic acid not also present in the spectra of the individual cations prepared from their trienes, and the absence of significant peaks in the GC of the triene mixture other than those of the trienes **2a** and **2b**, limit the amount of such further rearrangement to no more than 10%. Such restriction of the freedom of the methyl group probably simply reflects the availability of the rapid, irreversible formation of **1b**, which drains the cations away before they have time to experiment further. Note that the mechanism predicts a cis disposition of the 1,10 methyl groups in **1a**, as observed, and a trans disposition of the 2,10 methyls in **1b** as is most probably the case based on the synthesis of **5b**.

Experimental Section

General. All melting points were taken on a Thomas-Hoover apparatus. Infrared spectra were recorded as neat films on a Perkin-Elmer 237B spectrophotometer, and ultraviolet spectra in methanol solutions on a Unicam SP800 spectrophotometer. Nuclear magnetic resonance spectra were taken on Varian T-60 and Varian HA-100 spectrometers. Tetramethylammonium tetrafluoroborate (τ 6.87[14]) was used as an internal standard for all carbocation spectra, and tetramethylsilane was used as an internal standard for all other spectra. A Hitachi RM-U6 spectrometer was used to obtain all mass spectra.

Purification of Abietic Acid. Abietic acid was prepared from N-grade wood rosin (Hercules Powder Co.) by Sanderson and Weldy's modification of the *Organic Syntheses* procedure.[15,16] Thus, the N-grade wood rosin was refluxed in glacial acetic acid for 3 h, and the resultant mixture of resin acids, "Steele's acids", was recrystallized from ethyl acetate. Isolation of the major component, abietic acid, was achieved by the preparation and subsequent acetone recrystallizations (five) of the di-*n*-amylamine salt. The free acid was then generated by treating a cold ethanolic solution of the amine salt with acetic acid. Addition of water precipitated the abietic acid which was recrystallized from acetone–water to give colorless crystals (mp 171–174 °C) in 10–15% yield.

Quenching of the Abietic Acid −40 °C Cation. Regeneration of Abietic Acid. A solution of abietic acid in fluorosulfonic acid which had been warmed to −40 °C was quenched in aqueous sodium carbonate. The solution was acidified with dilute hydrochloric acid and extracted with ether to give abietic acid in approximately 80% recovery.

Rearrangement of Abietic Acid in Fluorosulfonic Acid. Isolation of *cis*-1,10a-Dimethyl-7-isopropyl-1,2,3,5,6,9,10,10a-octahydrophenanthrene (2a) and 2,10a-Dimethyl-7-isopropyl-1,2,3,5,6,9,10,10a-octahydrophenanthrene (2b). Using the procedure described previously a solution of 10.0 g (0.033 mol) of abietic acid in 80 ml of fluorosulfonic acid was prepared and warmed to 25 °C for 2 h. As the solution was warmed from −78 °C it turned from a bright yellow to a deep burgundy and gas evolution was noticed. It was again cooled to −78 °C and quenched in 1400 ml of aqueous sodium carbonate containing 200 ml of hexane. The hexane layer was removed, and the aqueous phase extracted twice with 200 ml of hexane. Removal of the solvent gave 7.7 g (91%) of a yellow oil.

A portion of this oil, 1.60 g, was adsorbed on a 28 × 2.2 cm column of 20% silver nitrate impregnated alumina. Elution with 200 ml of hexane gave 100 mg of a colorless oil which was a complex hydrocarbon mixture (NMR) and was not investigated further. Elution with 400 ml of 1:4 benzene–hexane gave 850 mg (53%) of a yellow oil which contained **2a** and **2b** as the major products in a ratio of approximately 1:2 (GLC). Preparative GLC (230 °C, 5 ft × 0.38 in. column of 20% Carbowax 20M on Anakrom 40–100 mesh) afforded two major fractions.

Fraction 1 contained **2b** with a 10% impurity of **4b** (NMR). These were separated by column chromatography. Thus, 73 mg of fraction 1 was adsorbed on a 15 × 1.0 cm column of 20% silver nitrate impregnated alumina. The column was eluted with 30 ml of 2% ether–hexane, then 5% ether–hexane until UV analysis indicated that all of **4b** had been removed. Elution with 50 ml of 1:4 benzene–hexane gave 45 mg of **2b** as a light yellow oil: IR (neat film) 1648 cm^{-1}; UV λ_{max} (MeOH) 298 nm (ϵ 22 100); NMR δ (CCl_4) 5.47 (1 H, m), 5.43 (1 H, s), 1.04 (6 H, d, J = 7 Hz), 0.98 (3 H, s), 0.96 (3 H, d, $J_{apparent}$ = 7 Hz); MS *m/e* (rel intensity) 256 (M^+, 100), 241 (56), 214 (20), 213 (58).

Fraction 2 contained **2a** and 30% **4b** (NMR). Column chromatography of 41 mg by the procedure described for **2b** gave 20 mg of **2a** as a light yellow oil: IR (neat film) 1648 cm^{-1}; UV λ_{max} (MeOH) 300 nm (ϵ 23 100); NMR δ (CCl_4) 5.52 (1 H, t, J = 4 Hz), 5.43 (1 H, s), 1.04 (6 H, d, J = 7 Hz), 0.98 (3 H, d, $J_{apparent}$ = 6 Hz), 0.93 (3 H, s); MS *m/e* (rel intensity) 256 (M^+, 100), 241 (51), 214 (13), 213 (53).

Cations of *cis*-1,10a-Dimethyl-7-isopropyl-1,2,3,5,6,9,-10,10a-octahydrophenanthrene (2a) and 2,10a-Dimethyl-7-isopropyl-1,2,3,5,6;9,10,10a-octahydrophenanthrene (2b) in Fluorosulfonic Acid. Solutions of **2a** and **2b** in fluorosulfonic acid were prepared at −78 °C and their NMR spectra recorded at −30 and 25 °C. The spectra did not change with temperature. **2a:** NMR δ (FSO_3H) 6.93 (1 H, s), 1.31 (6 H, d, J = 7 Hz), 1.26 (3 H, s), 1.05 (3 H, d, $J_{apparent}$ = 5 Hz). **2b:** NMR δ (FSO_3H) 6.93 (1 H, s), 1.40 (3 H, s), 1.31 (6 H, d, J = 7 Hz), 1.00 (3 H, d, J = 6 Hz).

Dehydrogenation of the Abietic Acid–Fluorosulfonic Acid Rearrangement Product. Isolation of *cis*-1,10a-Dimethyl-7-isopropyl-1,2,3,9,10,10a-hexahydrophenanthrene (4a) and 2,10a-Dimethyl-7-isopropyl-1,2,3,9,10,10a-hexahydrophenanthrene (4b). The crude rearrangement product, 4.82 g (0.019 mol), was dissolved in 100 ml of *o*-xylene, and to it was added 2.0 g of 5% rhodium on carbon. The mixture was heated with stirring and 20 ml of xylene was distilled to remove traces of water. The distilling head was replaced with a condenser equipped with a nitrogen inlet, and the mixture was heated at reflux for 15 h after which time it was cooled to room temperature and the catalyst removed by filtration. The solvent was removed under vacuum leaving 4.67 g of a dark yellow oil.

Most of the above product, 4.39 g, was adsorbed on a 400 g (45 × 3 cm) column of 20% silver nitrate impregnated alumina. Elution with 500 ml of hexane gave 1.10 g (25%) of a colorless oil containing ii and iii (footnote 5) as the major products (GLC, NMR) in a ratio of 3.4:4.8. Elution with 1:4 benzene–hexane (500 ml) gave 2.07 g (47%) of a light yellow oil. Analysis by GLC showed two major components in a ratio of 3.5:2.8.

Preparative GLC (230 °C, 5 ft × 0.38 in. column of 20% Carbowax 20M on Anakrom 40–100 mesh) afforded **4b** as the first component: mp 76–77 °C; $[\alpha]^{25}D$ −68°; IR (neat film) 1635 cm^{-1}; UV λ_{max} (MeOH) 256 nm (ϵ 16 700); NMR δ (CCl_4) 7.27 (1 H, d, J = 8 Hz), 6.84 (1 H, br d, J = 8 Hz), 0.99 (3 H, s), 0.98 (3 H, d, $J_{apparent}$ = 6 Hz); MS *m/e* (rel intensity) 254 (M^+, 100), 249 (99), 211 (92), 169 (32), 141 (31).

Anal. Calcd: C, 89.70; H, 10.30. Found: C, 89.73; H, 10.30.

The second component was **4a**: bp 125–130 °C (0.4 mm); $[\alpha]^{25}D$ −91°; IR (neat film) 1635 cm^{-1}; UV λ_{max} (MeOH) 256 nm (ϵ 17 400); NMR δ (CCl_4) 7.27 (1 H, d, J = 8 Hz), 6.84 (1 H, br d, J = 8 Hz), 6.79 (1 H, br s), 6.01 (1 H, t, J = 4 Hz), 1.20 (6 H, d, J = 7 Hz), 0.94 (3 H, d, $J_{apparent}$ = 6 Hz), 0.84 (3 H, s); MS *m/e* (rel intensity) 254 (M^+, 100) 249 (92 211 (68), 169 (37), 141 (50).),

Anal. Calcd: C, 89.70; H, 10.30. Found: C, 89.56; H, 10.26.

Individual Dehydrogenations of 2a and 2b. When **2b** (44 mg) was dehydrogenated under the above conditions there was obtained 39 mg of a yellow oil containing **4b** (NMR, GLC) as the major component. Similarly 18 mg of **2a** gave 14 mg containing **4a**.

Oxidation of 4a and 4b. Preparation of *cis*-1,10a-Dimethyl-7-isopropyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (5a) and 2,10a-Dimethyl-7-isopropyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (5b). In a flask equipped with a mechanical stirrer and a nitrogen inlet were placed 30.0 g (0.38 mol) of pyridine and 250 ml of methylene chloride. To this was added with stirring 19.0 g (0.10 mol) of chromium trioxide (dried over phosphorus pentoxide under vacuum) in small portions over a 20-min period. The solution was stirred for an additional 15 min, and to it was added 3.18 g (0.012 mol) of the 2.8:3.5 mixture of **4a** and **4b**. After 1.5 h the methylene chloride

solution was decanted, and the flask washed twice with 100 ml of ether. The combined solutions were washed with three 100-ml portions of 5% sodium hydroxide, 5% hydrochloric acid, and 10% sodium carbonate, respectively. After drying over sodium sulfate the solvent was removed to give 2.31 g of a dark red oil.

The product was adsorbed on a 45 × 3 cm column of silica gel, and the column eluted with 500 ml portions of 1:9, 1:4, 3.3:6.7, and 2:3 ether–hexane, respectively, with 25-ml fractions being collected. Fractions 39–43 were combined to give 193 mg (~10%) of **5b** (80% pure by NMR and GLC). An analytical sample was obtained by preparative TLC on silica gel eluted with 1:1 ether–hexane as a light yellow oil which was evaporatedly distilled at 100 °C (0.4 mm): $[\alpha]^{25}D$ −277°; IR 1660 and 1585 cm^{-1}; UV λ_{max} (MeOH) 304 nm (ϵ 26 200); NMR δ (CCl_4) 7.57 (1 H, d, J = 8 Hz), 7.01 (1 H, br d, J = 8 Hz), 6.95 (1 H, br s), 6.28 (1 H, s), 1.24 (6 H, d, J = 7 Hz), 1.21 (3 H, s), 1.12 (3 H, d, J = 6 Hz); MS m/e (rel intensity) 268 (M^+, 10), 226 (100), 184 (57), 169 (39), 155 (39), 141 (43).

Anal. Calcd: C, 85.02; H, 9.01. Found: C, 84.97; H, 8.94.

Fractions 55–63 gave 360 mg (30%) of **5a** (90% pure by NMR and GLC). An analytical sample was obtained by preparative TLC on silica gel eluted with 3:1 ether–hexane as a light yellow oil which was evaporatedly distilled at 100 °C (0.4 mm): $[\alpha]^{25}D$ −263°; IR 1660 and 1585 cm^{-1}; UV λ_{max} (MeOH) 306 nm (ϵ 21 100); NMR δ (CCl_4) 7.59 (1 H, d, J = 8 Hz), 7.01 (1 H, br d, J = 8 Hz), 6.95 (1 H, br s), 6.34 (1 H, s), 1.24 (6 H, d, J = 7 Hz), 1.04 (3 H, d, J = 6.5 Hz), 1.02 (3 H, s); MS m/e (rel intensity) 268 (M^+, 67), 226 (100), 184 (55), 169 (34), 155 (38), 141 (41). The 2,4-dinitrophenylhydrazone had mp 265 °C dec.

Anal (2,4-DNP). Calcd: C, 66.94; H, 6.29; N, 12.49. Found: C, 66.62; H, 6.35; N, 12.40.

Individual Oxidations of 4a and 4b. Oxidation of **4b** (88 mg) with chromium trioxide–pyridine complex under the above conditions provided 10 mg of **5b**. Similarly 52 mg of **4a** gave 14 mg of **5a**.

Dehydrogenation of 5b. Preparation of 2,10a-Dimethyl-7-isopropyl-9,10-dihydro-3(10a*H*)-phenanthrone (6b).[7] A solution of 70 mg (0.26 mmol) of **5b** and 70 mg (0.27 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 15 ml of dry dioxane was cooled to 10 °C, and hydrogen chloride was bubbled through it for 5 s. The solution was stirred at room temperature for 2 h after which time an additional 40 mg (0.17 mmol) of DDQ was added and the reaction heated at reflux for 1 h. After it had been cooled to room temperature the reaction mixture was poured on to a 10 × 1 cm column of activity II alumina, and the column eluted with 75 ml of ether. The solvent was removed to give 60 mg of a light orange oil which was purified by preparative TLC on alumina eluted with 2:1 ether–hexane to give 35 mg (50%) of **6b**. The light yellow oil was evaporatively distilled at 90 °C (0.3 mm): $[\alpha]^{25}D$ −101°; IR (neat film) 1660, 1625, and 1600 cm^{-1}; UV λ_{max} (MeOH) 315 nm (ϵ 12 500); NMR δ (CCl_4) 7.53 (1 H, d, J = 8 Hz), 7.04 (1 H, br d, J = 8 Hz), 6.96 (1 H, br s), 6.48 (1 H, q, J = 1.5 Hz), 1.18 (3 H, s); MS m/e (rel intensity) 266 (M^+, 100), 251 (84), 238 (68), 223 (81).

Dehydrogenation of 5a. Preparation of 1,10a-Dimethyl-7-isopropyl-9,10-dihydro-3(10a*H*)-phenanthrone (6a). Following the same procedure as described for **5b**, 70 mg of **5a** gave, after preparative TLC on alumina eluted with 3:1 ether–hexane, 30 mg (43%) of **6a** as a light yellow oil which was evaporatively distilled at 90 °C (0.3 mm): $[\alpha]^{25}D$ −119°; IR 1660, 1625, and 1600 cm^{-1}; UV λ_{max} (MeOH) 315 nm (ϵ 13 700); NMR δ (CCl_4) 7.53 (1 H, d, J = 8 Hz), 7.04 (1 H, br d, J = 8 Hz), 6.96 (1 H, br s), 6.43 (1 H, d, J = 1.7 Hz), 6.04 (1 H, m), 2.03 (3 H, d, J = 1.5 Hz), 1.24 (6 H, d, J = 7 Hz), 1.25 (3 H, s); MS m/e (rel intensity) 266 (M^+, 70), 251 (32), 238 (84), 223 (100).

6-Isopropyl-3,4,7,8-tetrahydro-1(2*H*)-naphthalenone (11). To 50 ml of ether which had been cooled to −78 °C under a nitrogen atmosphere was added 17.5 ml (0.035 mol) of 2 M isopropyllithium in pentane (ROC/RIC Chemical Corp.). A solution of 5.34 g (0.03 mol) of enol ether **10**[11,12] in 50 ml of ether was then added dropwise over a 15-min period. The mixture was stirred at −78 °C for 1 h, and 100 ml of 10% sulfuric acid was added. After stirring for 15 min the ether layer was removed, and the aqueous phase was extracted with 100 ml of ether. The ether solutions were combined, and washed twice with 100 ml portions of water, 5% sodium bicarbonate, and saturated potassium chloride solution. The solvent was removed, and the product was evaporatively distilled at 50 °C (0.3 mm) to give 2.91 g of a nearly colorless oil.

The product was adsorbed on silica gel (45 × 3 cm column), the column was eluted with 1:4 ether–hexane, and 20-ml fractions were collected. Fractions 31–50 were combined to give 1.83 g (32%) of **11** of approximately 90% purity (NMR). An analytical sample was obtained from preparative TLC on alumina eluted with 3:1 ether–hexane as a colorless oil: IR 1660 and 1580 cm^{-1}; UV λ_{max} (MeOH) 315 nm (ϵ 11 300); NMR δ (CCl_4) 5.68 (1 H, br s), 1.08 (6 H, d, J = 7 Hz); MS m/e (rel intensity) 190 (M^+, 17), 148 (36), 147 (100), 91 (57). The 2,4-dinitrophenylhydrazone had mp 208–209 °C.

Anal (2,4-DNP). Calcd: C, 61.61; H, 5.97; N, 15.13. Found: C, 61.48; H, 6.05; N, 15.16.

6-Isopropyl-3,4-dihydro-1(2*H*)-naphthalenone (9). In a 250-ml three-neck flask equipped with a nitrogen inlet, condenser, and distilling head were placed 3.0 g of 10% palladium on carbon and 100 ml of *o*-dichlorobenzene (ODCB). The mixture was heated to reflux, and 20 ml of ODCB distilled to remove traces of water. A solution of 1.7 g (8.9 mmol) of **11** in 50 ml of ODCB was added dropwise over a 1-h period. After the addition was complete the solution was heated for an additional 30 min, cooled to room temperature, and the catalyst removed by filtration. The solvent was removed under vacuum leaving a yellow oil which was evaporatively distilled at 45 °C (0.3 mm) to give 1.20 g (72%) of **9** of greater than 90% purity (GLC). A pure sample was obtained from preparative GLC (220 °C, 6 ft × 0.25 in. column of 20% SE-30 on Chromosorb W): IR 1680 and 1605 cm^{-1}; UV λ_{max} (MeOH) 259 nm (ϵ 16 200); NMR δ (CCl_4) 7.93 (1 H, d, J = 8 Hz), 7.14 (1 H, br d, J = 8 Hz), 7.03 (1 H, br s), 1.29 (6 H, d, J = 7 Hz); MS m/e (rel intensity) 188 (M^+, 74), 173 (100), 160 (81), 145 (44). The 2,4-dinitrophenylhydrazone had mp 195–196 °C (lit. mp 196.0–196.3 °C).[10]

6-Isopropyl-2-methyl-3,4-dihydro-1(2*H*)-naphthalenone (12).[18] To 1.7 ml (2.8 mmol) of 1.67 M *n*-butyllithium in hexane was added, under a nitrogen atmosphere, 0.48 ml (2.8 mmol) of isopropylcyclohexylamine. The contents were stirred for 10 min with most of the hexane being removed with a stream of nitrogen. The flask was cooled to 0 °C, and 4 ml of tetrahydrofuran was added. A solution of 480 mg (2.6 mmol) of **9** in 3 ml of tetrahydrofuran was added dropwise over a 1-min period, and the solution was stirred for 5 min. Methyl iodide (1.7 g, 12.2 mmol) was then added rapidly. The ice bath was removed, and the reaction mixture was stirred for 1 h at room temperature. After this time 15 ml of 10% hydrochloric acid was added, and the product was extracted with two 25-ml portions of hexane. The hexane extract was washed with water and 10% sodium carbonate, and dried over sodium sulfate. The solvent was removed, and the product was chromatographed on a 25 × 1.5 cm column of activity II alumina. The column was eluted with 1:9 ether–hexane, and 15-ml fractions were collected. Fractions 5–8 were combined to give 400 mg (78%) of **12**: mp 41–42 °C (from hexane, low temperature); IR 1680 and 1605 cm^{-1}; UV λ_{max} (MeOH) 257 nm (ϵ 18 700); NMR δ (CCl_4) 7.93 (1 H, d, J = 8 Hz), 7.03 (1 H, br s), 1.29 (6 H, d, J = 7 Hz), 1.23 (3 H, d, J = 7 Hz); MS m/e (rel intensity) 202 (M^+, 44), 188 (20), 173 (22), 160 (100).

Anal. Calcd: C, 83.12; H, 8.97. Found: C, 83.10; H, 8.90.

Fractions 10–16 gave 70 mg of the starting tetralone.

***cis*-1,10a-Dimethyl-7-isopropyl-1,9,10,10a-tetrahydro-3-(2*H*)-phenanthrone (5a) from *trans*-3-Penten-2-one and 6-Isopropyl-2-methyl-3,4-dihydro-1(2*H*)-naphthalenone (12).** A solution of potassium *tert*-butoxide in *tert*-butyl alcohol was prepared by adding 30 mg (0.77 mmol) of potassium metal to 2 ml of *tert*-butyl alcohol (distilled from calcium hydride). To this was added 100 mg (0.50 mmol) of **12** in 1 ml of *tert*-butyl alcohol. After stirring for 15 min the solution was cooled with an ice bath until the solvent began to freeze, and 63 mg (0.75 mmol) of *trans*-3-penten-2-one[19] in 1 ml of *tert*-butyl alcohol was added. The reaction mixture was stirred for 20 h, after which water was added, and the product was extracted with two 20-ml portions of ether. Preparative TLC on silica gel eluted with 2:1 ether–hexane followed by molecular distillation [trace impurities at 50 °C (0.3 mm), and **5a** at 100 °C (0.3 mm)] gave 48 mg (36%) of **5a** whose spectral properties were identical with those obtained for material isolated from the oxidation of **4a**.

2,10a-Dimethyl-7-isopropyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (5b) from 3-Methyl-3-buten-2-one and 6-Isopropyl-2-methyl-3,4-dihydro-1(2*H*)-naphthalenone (12). To a solution of 0.77 mmol of potassium *tert*-butoxide in 2 ml of *tert*-butyl alcohol was added 100 mg (0.50 mmol) of **12** in 1 ml of *tert*-butyl alcohol. After stirring for 15 min the solution was cooled with an ice bath until the solvent began to freeze, and 100 mg (1.2 mmol) of 3-methyl-3-buten-2-one (distilled from Pfaltz and Bauer material) in 1 ml of *tert*-butyl alcohol was added. After stirring for 20 h water was added, and the mixture was extracted with two 20-ml portions of ether. Preparative TLC on silica gel eluted with 1:1 ether–hexane followed by molecular distillation at 100 °C (0.3 mm) gave 55 mg (41%) of **5b** whose spectral properties were identical with those obtained for the oxidation product of **4b**.

2,10a-Dimethyl-7-isopropyl-1,2,3,9,10,10a-hexahydrophenanthrene (4b) from Reduction of 5b.[13] To a solution of 40 mg (0.15 mmol) of **5b** in 5 ml of ether was added 40 mg (0.30 mmol) of aluminum chloride followed after 1 min by 11 mg (0.30 mmol) of lithium aluminum hydride. The solution was stirred for 2 h, several drops of

water were added, and stirring was continued for 15 min. One gm of potassium sodium tartrate was then added, and the reaction mixture was filtered. The solid residue was washed several times with ether. The ether was removed, and the product was adsorbed on a 7 × 0.5 cm column of activity II alumina. Elution with hexane (20 ml) gave 28 mg (75%) of **4b** whose spectral properties were identical with those of the derivative obtained from the abietic acid rearrangement.

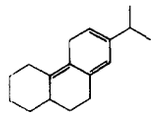
***cis*-1,10a-Dimethyl-7-isopropyl-1,2,3,9,10,10a-hexahydrophenanthrene (4a) from Reduction of 5a.** Following a procedure which was identical with that described for **4b**, 40 mg of **5a** gave 26 mg (69%) of **4a** whose spectral properties were identical with those for the derivative obtained from the abietic acid rearrangement.

Acknowledgment. We thank the Hercules Powder Co. for a generous sample of N-grade Rosin.

Registry No.—**2a**, 60606-84-0; **2b**, 60606-85-1; **3**, 514-10-3; **4a**, 49815-77-2; **4b**, 60606-86-2; **5a**, 60606-87-3; **5a** 2,4-DNP, 60606-88-4; **5b**, 60606-89-5; **6a**, 60606-90-8; **6b**, 60606-91-9; **9**, 60606-92-0; **10**, 51238-73-4; **11**, 60606-93-1; **11** 2,4-DNP, 60619-77-4; **12**, 60606-94-2; *trans*-3-penten-2-one, 3102-33-8; 3-methyl-3-buten-2-one, 814-78-8.

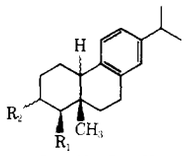
References and Notes

(1) (a) Supported by the National Science Foundation under Grants GP-10734 and GP-27994. (b) Abstracted in part from the Ph.D. Thesis of R. A. Mader, Michigan State University, 1972. (c) Dow Chemical Co. Summer Fellow, 1972.
(2) G. Mehta and S. K. Kapoor, *Tetrahedron Lett.*, 2385 (1973).
(3) The alternate arrangement of double bonds (i) considered by Mehta and



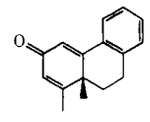
i

Kapoor[2] for trienes **1a** and **1b** is also compatible with all the data available to us.
(4) Like Mehta and Kapoor,[2] we observed decomposition of the trienes on attempted chromatography on $AgNO_3$–SiO_2.
(5) We also obtained the aromatic hydrocarbons ii and iii obtained by Mehta



ii, $R_1 = CH_3$; $R_2 = H$
iii, $R_1 = H$; $R_2 = CH_3$

and Kapoor, also isolated by catalytic hydrogenation of styrenes **4a** and **4b**.
(6) The ^1H NMR of **6a** is very similar to that of the model compound iv.[7]



iv

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(8) The optical activity of these products is not a trivial observation, since racemization has been observed in tetrahydroabietic acid in sulfuric acid, possibly by an "unzipping" mechanism.[9]
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Fluorine-19 Nuclear Magnetic Resonance. Electric Field Shifts of Bicyclic Fluorides

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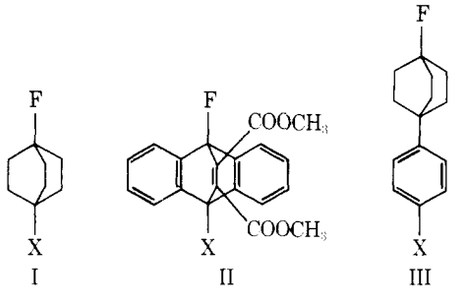
A number of 1-fluoro-4-para-substituted phenylbicyclo[2.2.2]octanes have been synthesized and their ^{19}F NMR spectra recorded. Significant *upfield* substituent chemical shifts (SCS) are observed for strong electron-withdrawing dipolar and charged substituents in a situation where substituent-induced structural effects cannot be invoked. The results strongly suggest that the previous interpretation of "anomalous" ^{19}F SCS for 4-substituted bicyclo-[2.2.2]octyl-1-fluorides in terms of structural effects alone requires reappraisal. Further, the results impinge importantly on the factors determining ^{19}F chemical shifts in general.

Substituent-induced *upfield* shifts have been detected by Anderson and Stock[1] for a limited number of 1-fluoro-4-substituted bicyclo[2.2.2]octanes (I, X = F and $COOC_2H_5$).



I II III

A consideration of several factors by these workers led to the conclusion that these substituent chemical shifts (SCS)[2] are anomalous and probably a consequence of substituent-induced structural deformation of the flexible bicyclooctyl skeletal framework rather than a manifestation of dipolar electrostatic-field effects: (1) upfield SCS are not in accord with preconceptions regarding the electron-withdrawing influence of dipolar substituents on chemical shifts; (2) ^{19}F chemical shifts of various unsubstituted bicyclic fluorides are structurally dependent; (3) the fact that substituents do measurably alter the structure of the more rigid bicyclo[2.2.1]-heptyl system; and (4) the observation that ^{19}F substituent chemical shifts (SCS) for the more rigid dibenzobicyclo[2.2.2]-octyl derivatives, in particular, adducts of 10-substituted 9-