hexanone (50 mmol) in THF (10 mL) was added dropwise and the mixture was stirred at room temperature for 2 h. Bromobenzene (25 mmol) in THF (10 mL) was then added and stirring was continued for 1 h. The mixture was poured into ice, extracted with diethyl ether, and dried over $MgSO_4$. After removal of the solvents under reduced pressure, the residual oil was chromatographed on HPLC preparative apparatus to yield **3d**.

3d: $C_{14}H_{18}O_3$; IR (film) 3660–3240 cm^{-1} (OH); UV (MeOH) λ nm (log ε) 274 (3.20), 267 (3.22), 260 (3.07), ^1H NMR (CCl_4) δ 0.76–2.36 (6 H, m, 3 × CH_2); 3.18–3.76 (8 H, m, with s at 3.32 and 3.49, 2 × OCH_3, benzylic H and OH, exchanged with D_2O), 7.00–7.56 (4 H, m, with br s at 7.24, Ar); ^{13}C NMR ($CDCl_3$) δ (aromatic carbons) 147.39, 144.73, 129.34, 127.52, 122.92, 122.13, (aliphatic carbons) 101.41 (>$C(OCH_3)_2$), 82.33 (ArCOH), 54.95 (ArCH), 51.37 and 49.01 (2 × OCH_3), 25.56, 22.41 and 17.81 (cyclic -CH_2).

3e: $C_{14}H_{16}O_3$; mp 94 °C (light petroleum); IR (CCl_4) 3640–3220 cm^{-1} (OH); UV (MeOH) λ nm (log ε) 273 (3.23), 266 (3.25), 260 (3.07); ^1H NMR (CCl_4) δ 0.93–2.31 (6 H, m, 3 × CH_2), 2.87 (1 H, br s, OH, exchanged with D_2O), 3.33–3.57 (1 H, pseudo t, benzylic H), 3.82–4.27 (4 H, m, >$\overline{COCH_2CH_2O}$); 6.96–7.39 (4 H, m with s at 7.16, Ar); ^{13}C NMR ($CDCl_3$) δ aromatic carbons 145.88, 144.97, 129.58, 127.77, 122.86, 122.62; aliphatic carbons 111.53 (>$\overline{COCH_2CH_2O}$); 80.82 (ArCOH), 65.79 and 65.55 (>$\overline{COCH_2CH_2O}$); 54.28 (ArCH), 28.35, 22.90 and 17.57 (cyclic CH_2).

3a: $C_{14}H_{18}O_3$; mp 72 °C (light petroleum); IR (KBr) 3600–3300 cm^{-1} (OH); UV (MeOH) λ nm (log ε) 272 (3.30), 266.5 (3.32), 260.5 (3.17), ^1H NMR (CCl_4) δ 0.78–1.98 (8 H, m, CH_2CH_3, with t at 1.07, J = 6.66 Hz, CH_2CH_3 and s at 1.30, CH_3), 2.97 (1 H, br s, OH, exchanged with D_2O), 3.20–4.04 (5 H, m, >$\overline{COCH_2CH_2O}$ and benzylic H), 7.06 (4 H, br s, Ar); ^{13}C NMR ($CDCl_3$) δ aromatic carbons, 148.24, 145.64, 129.40, 127.40, 122.49, 121.95; aliphatic carbons 111.05 (>$\overline{COCH_2CH_2O}$), 84.51 (ArCOH), 65.67 and 65.55 (>$\overline{COCH_2CH_2O}$), 52.83 (ArCH), 22.90, 20.36, 12.54 (CH_2, CH_3).

3b: $C_{14}H_{18}O_3$; mp 70 °C (pentane); IR (KBr) 3640–3300 cm^{-1} (OH); UV (MeOH) λ nm (log ε) 272.5 (3.23), 266 (3.24), 260 (3.09); ^1H NMR (CCl_4) δ 1.31 (3 H, s, CH_3), 1.41 (3 H, s, CH_3), 1.51 (3 H, s, CH_3), 2.96 (1 H, br s, OH, exchanged with D_2O), 3.27–4.02 (4 H, m, >$\overline{COCH_2CH_2O}$), 6.79–7.39 (4 H, m with br s at 7.07, Ar); ^{13}C NMR ($CDCl_3$) δ aromatic carbons 153.57, 144.73, 129.40, 127.34, 122.01, 119.83; aliphatic carbons 111.77 (>$\overline{COCH_2CH_2O}$), 86.33 (ArCOH), 65.91 and 64.22 (>$\overline{COCH_2CH_2O}$), 52.92 (ArCH), 25.44, 23.38 and 20.84 (CH_3).

Chemical properties of alcohols **3** are shown on one example, **3d** (Scheme II).

Reaction of 3d in Acidic Pentane. Through a solution of alcohol **3d** (500 mg, 2.14 mmol) in pentane (30 mL) was bubbled a slow stream of HCl. The reaction was instantaneous (monitored by TLC), and the mixture was poured into water and extracted with ether. The organic layer was then washed with a saturated solution of $NaHCO_3$, dried over $MgSO_4$, and evaporated under reduced pressure. A rapid filtration on column chromatography gave the keto ether **4b** (350 mg, 1.73 mmol; yield 81%): IR (film) 1715 cm^{-1} (C=O); UV (MeOH) λ nm (log ε) 295 (3.42), 249 (4.14); ^1H NMR (CCl_4) δ 0.97–2.47 (6 H, m, 3 × CH_2), 3.22 (3 H, s, OCH_3), 3.33–3.69 (1 H, m, benzylic H), 7.16–7.96 (4 H, m, Ar); CI mass spectrum (NH_3, pos), appropriate clusters at m/e 220 ($M + NH_4^+$), 203 ($M + H^+$).

Reaction of 3d in Acidic MeOH. The alcohol **3d** (500 mg, 2.14 mmol) was added to a mixture (50:50) of CH_3OH and dilute H_2SO_4 (30 mL). The reaction was instantaneous, and the mixture was worked up as above. After short chromatography, the keto alcohol **4a** was obtained (350 mg, 1.86 mmol; yield 87%): $C_{12}H_{12}O_2$; mp 84 °C (light petroleum); IR (film) 3660–3100 (OH), 1715 cm^{-1} (C=O); UV (MeOH) λ nm (log ε) 294 (3.39), 248 (4.14); ^1H NMR (CCl_4) δ 0.89–2.71 (6 H, m, 3 × CH_2), 3.31–3.62 (1 H, m, pseudo d, benzylic H), 4.24 (1 H, br s, OH, exchanged with D_2O), 6.98–7.78 (4 H, m, Ar).

Passage of 3d to 5. The acetate was prepared following a procedure described by Vorbrügger et al.[11] A mixture of alcohol **3d** (1.53 g, 6.5 mmol), acetic anhydride (760 mg, 7.5 mmol), and DMAP (1.125 g, 7.5 mmol) in CH_2Cl_2 (7 mL) was allowed to stand for 31 h at 25 °C. The solution was partitioned between ether and citric acid solution; the organic phase was washed with saturated $NaHCO_3$ solution, dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by chromatography: the ketal acetate was eluted (1.33 g, 4.82 mmol; yield 74%): IR (film) 1740 cm^{-1} (C=O); UV (MeOH) λ nm (log ε) 274 (3.27), 267.5 (3.29), 261.5 (3.13); ^1H NMR (CCl_4) δ 0.91–2.38 (9 H, m, 3 × CH_2, with s at 1.98, $OCOCH_3$), 3.18 and 3.31 (6 H, 2 s, 2 × OCH_3) 3.74–4.11 (1 H, m, benzylic H), 6.87–7.44 (4 H, m, Ar).

The ketal acetate (1.23 g, 4.46 mmol) in acetone (20 mL) and few drops of dilute HCl led to keto acetate **5** (930 mg, 4.04 mmol; yield 91%): $C_{14}H_{14}O_3$; IR (film) 1740–1715 cm^{-1} (C=O); UV (MeOH) λ nm (log ε) 275 (3.35), 268.5 (3.36), 263.5 (sh, 3.21); ^1H NMR (CCl_4) δ 1.04–2.56 (9 H, m, 3 × CH_2 with s at 2.04, $OCOCH_3$), 3.69–3.98 (1 H, m, benzylic H), 6.98–7.54 (4 H, m, Ar).

General Procedure for the Ring Opening of 3 (Scheme III). Typically, **3d** (1 mmol) in 10 mL of HMPA was added to a suspension of $NaNH_2$ (2 mmol) in 10 mL of HMPA at room temperature. After 15 min, the reaction was complete; classical workup and column chromatography yielded ketone **6d**.

6d: $C_{14}H_{18}O_3$; IR (film) 1715 cm^{-1} (C=O); UV (MeOH) λ nm (log ε) 244 (sh, 3.19); ^1H NMR (CCl_4) δ 1–2.13 (6 H, m, 3 × CH_2), 2.36–2.82 (2 H, m, benzylic CH_2), 3.16 (6 H, s, 2 × OCH_3), 6.86–7.36 (4 H, m, Ar).

6e: $C_{14}H_{16}O_3$; mp 78 °C (ethyl acetate–light petroleum); IR (KBr) 1720 cm^{-1} (C=O); UV (MeOH) λ nm (log ε) 245 (sh, 3.25); ^1H NMR (CCl_4) δ 1.41–2.11 (6 H, m, 3 × CH_2), 2.51–2.89 (2 H, m, benzylic CH_2), 4.00 (4 H, s, >$\overline{COCH_2CH_2O}$), 6.89–7.51 (4 H, m, Ar).

Acknowledgment. This work was partly supported by INSERM (Contract No. 81 3005). M.C.C. gratefully acknowledges the INSERM for financial support.

Registry No. **2a**, 61784-38-1; **2b**, 61784-40-5; **2c**, 66057-04-3; **2d**, 38461-13-1; **2e**, 4746-96-7; **2f**, 89874-31-7; **2g**, 89874-32-8; **2h**, 89874-33-9; **2i**, 89874-34-0; **3a**, 89874-22-6; **3b**, 89874-23-7; **3c**, 89874-24-8; **3d**, 89874-25-9; **3e**, 89874-26-0; **3f**, 89874-27-1; **3g**, 89874-28-2; **3h**, 89874-29-3; **3i**, 89874-30-6; **4a**, 89874-35-1; **4b**, 89874-36-2; **5**, 89874-38-4; **6d**, 88021-68-5; **6e**, 89874-39-5; **6f**, 89874-40-8; **6g**, 89874-41-9; **6h**, 89874-42-0; **6i**, 89874-43-1; PhBr, 108-86-1; $NaNH_2$, 7782-92-5; *t*-BuOH·Na, 865-48-5; benzyne, 462-80-6; 8b-acetoxy-1,1-dimethoxy-1,2,3,4,4a,8b-hexahydrobiphenylene, 89874-37-3; 2-(methylthio)cyclopentanone, 52190-35-9; 1,2-cyclohexanedione, 765-87-7; 1,2-cycloheptanedione, 3008-39-7; 1,2-cyclooctanedione, 3008-37-5; 1,2-cyclododecanedione, 3008-41-1.

(11) Höfle, G.; Steglich, W.; Vorbrüggen, H. *Synthesis* **1978**, 569.

Construction of the Hibaene Skeleton by way of an Abnormal Wolff Reaction

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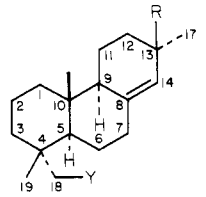
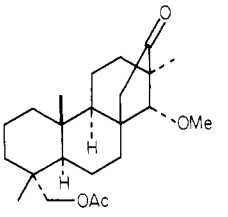
In connection with a diterpene synthesis problem, a pimaradiene with an acetic acid moiety in place of its vinyl group was needed as starting material. As a consequence it was decided to degrade the 13β-vinyl side chain to a carboxylic acid unit and to carry out a homologation by the standard Arndt–Eisert synthesis. As the following discussion illustrates, an unusual result was obtained.

0022-3263/84/1949-2052$01.50/0

Oxidation of pimarol acetate (**1a**)[1] with osmium tetroxide and subsequently with periodate yielded an aldehyde (**1c**), whose Jones oxidation gave carboxylic acid **1d**.





2

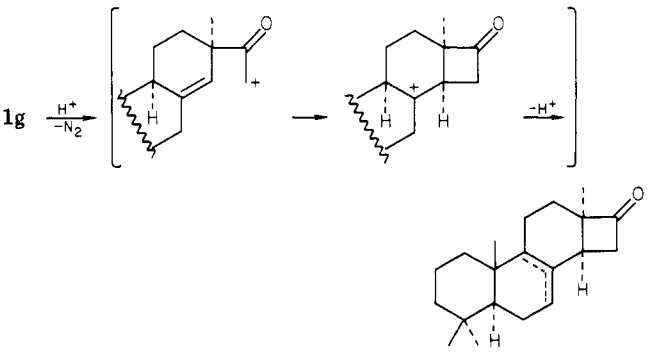
1a, R = $CH^{15}=CH_2^{16}$; Y = OAc
b, R = $CHOHCH_2OH$, Y = OAc
c, R = CHO; Y = OAc
d, R = CO_2H; Y = OAc
e, R = $COCHN_2$; Y = OAc
f, R = CH_2CO_2Me; Y = OAc
g, R = $COCHN_2$; Y = H

Treatment of the latter with oxalyl chloride and thereafter with diazomethane led to diazo ketone **1e**. Exposure of the diazo compound to silver oxide in methanol solution produced ester **1f** in 41% yield, accompanied by an isomer in 16% yield. Spectral analysis of the ester proved it to be a normal Wolff rearrangement product,[2] while the minor component of the reaction mixture required structure analysis.

The minor product proved to a keto ether acetate by its infrared and ^1H NMR spectra. The infrared spectrum showed a single carbonyl band at 1745 cm^{-1}, characteristic of the ester and a five-membered ring ketone. The ^1H NMR spectrum revealed methyl singlets at 0.86, 0.92, and 1.05 ppm, AB pairs of doublets for an α-ketomethylene and the acetoxymethylene[1] in the 1.5–2.7 and 3.5–3.9 ppm spectral regions, respectively, the acetate methyl signal at 2.07 ppm, an oxymethine singlet at 2.75 ppm,[4] and a methoxy singlet at 3.52 ppm. These facts and the following mechanistic interpretation of the double-bond involvement in the silver-mediated diazo ketone decomposition suggested structure **2** for the minor reaction product.

When a pimaradiene-derived diazo ketone (**1g**) had been decomposed with acid, the acylcarbonium ion had interacted with the nuclear double bond in a Markovnikov addition sense (despite the four-membered ring strain) and upon deprotonation had yielded cyclobutanone-containing tetracycles **3**.[6,7]

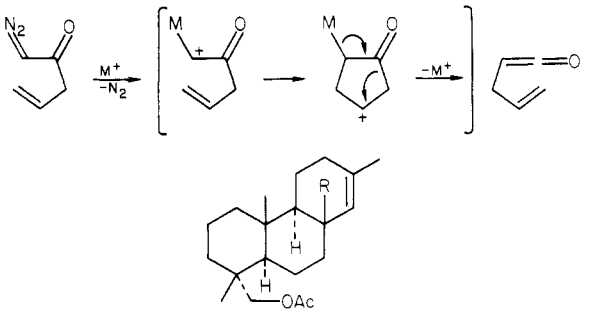
The more common mode of β,γ-unsaturated diazo ketone decomposition, especially under the influence of transition metals, involves the intermediacy of metallated, cationic cyclopentanones whose fragmentation leads to olefinic ketenes and on subsequent reaction with solvent



3

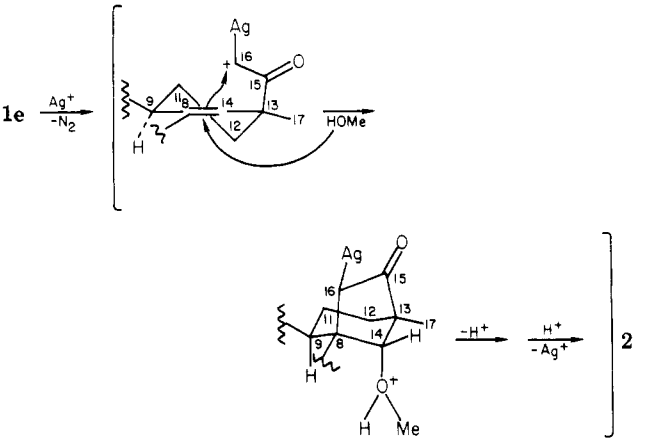
to γ,δ-unsaturated carboxylic acid derivatives.[3]

In the context of the decomposition of the present diazo ketone (**1e**), this reaction path would have been expected

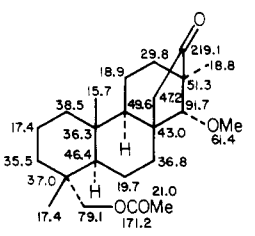


4a, $R^+ = CH=C=O$
b, $R = CH_2CO_2Me$

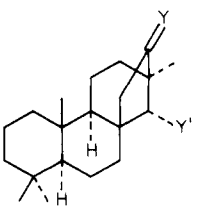
to furnish ketene **4a** and thence ester **4b**. However, the early intervention of the nucleophilic solvent avoids the necessity for cyclopentanone fragmentation and, instead, leads to a β-methoxycyclopentanone **2**.



The ^{13}C NMR spectral analysis of the minor Wolff reaction product proved its structure **2** unambiguously. Comparison of its carbon shifts, denoted on formula **5**, with those reported for hibane (**6a**), 14α-hibol (**6b**) and 15-hibone (**6c**)[8] permitted both shift and structure assignment.



5



6a, Y = H_2; Y' = H
b, Y = H_2; Y' = OH
c, Y = O; Y' = H

(1) Gaudemer, A.; Polonsky, J.; Wenkert, E. *Bull. Soc. Chim. Fr.* **1964**, 407.

(2) Whereas β,γ-unsaturated acyldiazomethanes have been shown to undergo abnormal Wolff rearrangement of the **1e** → **4b** type,[3] diazo ketone **1e** appeared to behave normally in the homologation process (i.e., the ^1H NMR data on the homoester being incompatible with alternate structure **4b**).

(3) (a) Smith, A. B., III. *J. Chem. Soc., Chem. Commun.* **1974**, 695. (b) Lokensgard, J. P.; O'Dea, J.; Hill, E. A. *J. Org. Chem.* **1974**, *39*, 3355. (c) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623. (d) Smith, A. B., III; Toder, B. H.; Branca, S. J. *Ibid.* **1976**, *98*, 7456. (e) Smith, A. B., III; Toder, B. H.; Branca, S. J.; Dieter, R. K. *Ibid.* **1981**, *103*, 1996.

(4) The oxymethine singlet of 14α-hibol is at 2.90[5a] or 2.88 ppm.[5b] (It also has been misplaced at 2.42 ppm.[5c])

(5) (a) Wenkert, E.; Kumazawa, Z. *J. Chem. Soc., Chem. Commun.* **1968**, 140. (b) Khac Manh, D. D.; Fêtizon, M.; Flament, J. P. *Tetrahedron* **1975**, *31*, 1897. (c) Edwards, O. E.; Rosich, R. S. *Can. J. Chem.* **1968**, *46*, 1113.

(6) Ceccherelli, P.; Tingoli, M.; Curini, M.; Pellicciari, R. *Tetrahedron Lett.* **1978**, 3869.

(7) Smith, A. B.; Dieter, R. K. *Tetrahedron* **1981**, *37*, 2407.

Experimental Section

Melting points were determined on a Reichert micro hotstage and are uncorrected. Infrared spectra of CCl_4 solutions were recorded on an Acculab 5 spectrophotometer, and ^1H NMR spectra of $CDCl_3$ solutions (Me_4Si, $\delta = 0$ ppm) were obtained on a Varian EM 390 spectrometer. The ^{13}C NMR spectra of $CDCl_3$ solutions were run on a Nicolet NT-200, wide-bore, broad-band spectrometer, operating with an Oxford magnet at 50.31 MHz in the Fourier transform mode. The carbon shifts on formula **5** are in ppm downfield from Me_4Si; $\delta(Me_4Si) = \delta(CDCl_3) + 76.9$ ppm.

18-Acetoxy-13β-devinyl-13β-carboxypimarene (1d). Osmium tetroxide, 1.00 g (4 mmol), was added slowly to a stirring solution of 1.32 g (4 mmol) of 18-acetoxypimaradiene (**1a**)[1] in 60 mL of dioxane, and the stirring was continued for 24 h. A stream of hydrogen sulfide gas was passed through the mixture for 1 h and the latter filtered through Celite. The filtrate was evaporated under vacuum and the resultant residue chromatographed on silica gel. Elution with 50:1 chloroform–methanol yielded 900 mg of amorphous diol **1b**: ^1H NMR δ 0.76, 0.86, 0.86 (s, 3 each, methyls), 2.04 (s, 3, COMe), 3.5–4.0 (m, 5, 2 OCH_2, OCH), 5.0–5.3 (m, 1, olefinic H).

A solution of 1.00 g of periodic acid dihydrate and 900 mg of diol **1b** in 50 mL of tetrahydrofuran was stirred for 1 h. Water, 10 mL, was added and the mixture extracted with chloroform. The extract was dried (Na_2SO_4) and evaporated, yielding 818 mg of liquid aldehyde **1c**: ^1H NMR δ 0.73, 0.86, 1.03 (s, 3 each, methyls), 2.08 (s, 3, COMe), 3.77 (q, 2, J = 13 Hz, OCH_2), 5.28 (br s, 1, olefinic H), 9.48 (s, 1, CHO).

A solution of 2.5 mmol of Jones reagent (prepared from a solution of 70 g of chromium trioxide in 500 mL of water and 61 mL of concentrated sulfuric acid) was added slowly to a stirring solution of 818 mg of aldehyde **1c** in 80 mL of acetone at room temperature. After 0.5 h the mixture was decomposed with 5% sodium bisulfite solution, diluted with 150 mL of water, and extracted exhaustively with chloroform. The extract was dried (Na_2SO_4) and evaporated. Chromatography of the residue on silica gel and elution with 25:1 chloroform–methanol gave 570 mg of solid whose crystallization from hexane afforded crystalline acid **1d**: mp 93–95 °C; ^1H NMR δ 0.75, 0.86, 0.90 (s, 3 each, methyls), 2.08 (s, 3, COMe), 3.71 (q, 2, J = 11 Hz, OCH_2), 5.35 (br s, 1, olefinic H).

Anal. Calcd for $C_{21}H_{32}O_4$: C, 72.38; H, 9.26. Found: C, 72.45; H, 9.40.

Methyl 18-Acetoxy-13β-devinylpimarene-13β-acetate (1f) and 14α-Methoxy-15-hibone (2). A solution of 570 mg of acid **1d** in 5 mL of oxalyl chloride was stirred at room temperature under nitrogen for 2 h, and then the excess reagent was removed by vacuum distillation. A solution of the residue in 30 mL of dry ether was added over a 1-h period to a stirring solution of 3 mmol of diazomethane in 30 mL of anhydrous ether, containing 1.8 mL of triethylamine, at 0 °C under nitrogen, and the stirring was continued at room temperature for 2 h. The mixture was filtered and the filtrate evaporated under vacuum, leaving 627 mg of semisolid diazo ketone **1e**: IR 2100 (C=N_2, s), 1725 (C=O, s), 1636 ($COCN_2$, s) cm^{-1}; ^1H NMR δ 0.77, 0.89, 1.15 (s, 3 each, methyls) 2.05 (s, 3, COMe), 3.75 (q, 2, J = 9 Hz, OCH_2), 5.28 (br s, 1, olefinic H), 5.46 (s, 1, CHN_2).

Silver oxide, 0.3 g, was added in portions to a stirring solution of 627 mg of diazo ketone **1e** in 30 mL of anhydrous methanol at 60 °C, and the stirring was continued at this temperature for 2 h. The mixture was filtered and the filtrate evaporated under vacuum. The organic residue, 485 mg, was chromatographed on silica gel. Elution with 50:1 benzene–ethyl acetate gave first 256 mg of amorphous ester **1f**: IR 1738 (C=O, s) cm^{-1}; ^1H NMR δ 0.80, 0.89, 1.04 (s, 3 each, methyls), 2.05 (s, 3, COMe), 2.61 (s, 2, $COCH_2$), 3.11 (s, 3, OMe), 3.74 (q, 2, J = 9 Hz, OCH_2), 5.21 (br s, 1, olefinic H).

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.62; H, 9.31.

Further elution led to 102 mg of solid, whose crystallization from methanol yielded crystalline keto ester **2**: mp 118–120 °C.

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.71; H, 9.25.

Acknowledgment. P.C. and M.C. acknowledge gratefully support for the work in Perugia by the Ministero Pubblica Istruzione. B.P. and E.W. are indebted to Banavara L. Mylari for the initial observation of the unusual reaction.

Registry No. **1a**, 1686-60-8; **1c**, 89710-39-4; **1d**, 89710-40-7; **1e**, 89710-41-8; **1f**, 89710-42-9; **2**, 89710-43-0.

(8) Duc, D. K. M.; Fétizon, M.; Lazare, S.; Grant, P. K.; Poisson, J.; Bernassau, J.-M.; Roque, N. F.; Wovkulish, P. M.; Wenkert, E. *Tetrahedron* **1981**, *37*, 2371. The C(18) shift of hibane (**6a**), recorded therein, should read "33.7 ppm".

Carbon–Carbon Bond Formation by the Reduction of Dienic Esters

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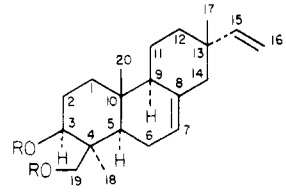
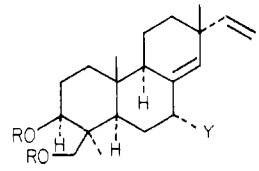
In an attempt of conversion of the isopimaradiene structure of the virescenols[1] into that of a sandaracopimaradiene system, i.e., moving the nuclear double bond from the Δ^7 to the $\Delta^{8(14)}$ position, an oxidation–reduction pathway was chosen. The reduction phase of the transformation took an unusual course, whose observation is the subject of the present report.

Photooxygenation of virescenol B diacetate (**1a**) has been shown to move the nuclear olefinic linkage to the $\Delta^{8(14)}$ location.[2] When on tosylation of the oxidation product

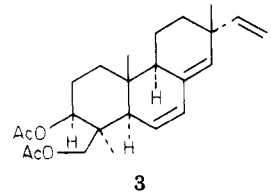


1a, R = Ac
b, R = H

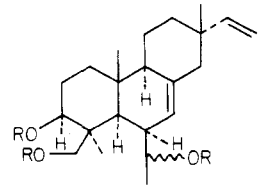


2a, R = Ac, Y = OH
b, R = Y = H

2a (for subsequent C-7 deoxygenation) the allylic alcohol underwent dehydration, the resultant diene **3** was exposed to reduction by lithium in ammonia. The reaction yielded three products, two of which were obtained in 42% yield in the form of a difficultly separable, ca. 2:1 mixture of virescenol B (**1b**) and its $\Delta^{8(14)}$ isomer **2b** and could be converted on acid treatment into a single isomer, the $\Delta^{8(9)}$ compound.[1] The major product, isolated in 47% yield, was a triol in which a hydroxyethyl group had been attached to the virescenol B skeleton. Structure **4a** could be as-



3



4a, R = H
b, R = Ac

(1) Polonsky, J.; Baskevitch, Z.; Cagnoli Bellavita, N.; Ceccherelli, P. *Bull. Soc. Chim. Fr.* **1970**, 1912.

(2) Ceccherelli, P.; Curini, M.; Tingoli, M.; Pellicciari, R. *Gazz. Chim. Ital.* **1978**, *108*, 129.

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