distillation gave 2-CO_2CH_3 as a colorless oil (2.9 g, 17.5 mmol, 50%): bp 62–64 °C (4.5–5.0 mm); IR (neat) 3075 (cyclopropyl CH), 1738 (C=O), 1272 (asymmetric C—O), 1088 (symmetric C—O) cm^{-1}; NMR (CCl_4) δ 3.57 (s, 3, CH_3O), 0.4–2.7 (m, 11). No exo ester 1-CO_2CH_3 was found to be present. An analytical sample was collected by GC (QF-1, 132 °C). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.82; H, 8.37.

***endo*-Tricyclo[3.2.1.0^{2,4}]octyl-1-carbinyl Tosylate (2-CH_2OTs).** Alcohol 2-CH_2OH was made by lithium aluminum hydride reduction of ester 2-CO_2CH_3. Vacuum distillation gave a 79% yield of a colorless oil: bp 82–94 °C (2.0 mm); IR (neat) 3330 (OH), 3070 (cyclopropyl CH), 1013 (C–O) cm^{-1}. The crude alcohol was treated with tosyl chloride and pyridine and tosylate 2-CH_2OTs was formed in 82% yield after one recrystallization from petroleum ether (bp 30–60 °C). Seven recrystallizations gave a pure sample: mp 81.5–83 °C; NMR ($CDCl_3$) δ 7.2–8.0 (AA'XX', 4, Ar H), 4.17 (s, 2, CH_2O), 2.43 (s, 3, CH_3), 2.2–2.3 (m, 1, bridgehead), 0.6–2.1 (m, 10). Anal. Calcd for $C_{16}H_{20}SO_3$: C, 65.72; H, 6.89. Found: C, 65.62; H, 6.91.

***endo*-Tricyclo[3.2.1.0^{2,4}]octane-1-carboxylic Acid (2-COOH).** Ester 2-CO_2CH_3 was saponified with 10% sodium hydroxide under reflux for 3 h to give a 68% yield of acid 2-COOH. Purification can be accomplished by chromatography on silica gel with chloroform as eluant or by recrystallization from petroleum ether (bp 30–60 °C). Three recrystallizations gave a pure sample: mp 98–98.5 °C; IR (KBr) 2500–3600 (OH), 1687 (C=O), 1294 (C—O) cm^{-1}; NMR ($CDCl_3$) δ 12.1 (s, 1, COOH), 0.6–2.5 (m, 11). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.91; H, 7.96.

pK_a Studies. The pK_a of acids 1-COOH, 2-COOH, and 9-COOH was taken by dissolving 0.30 mmol in 50% ethanol (50 mL, 1:1 absolute ethanol–distilled water, v/v) and titrating with 0.05 N aqueous sodium hydroxide at ambient temperature while the pH was measured vs. increments of base added. The pK_a was obtained from the pH at the half-neutralization point. Results are given in Table I.

Kinetic Studies. Standard procedures were followed for the acetolysis studies. Standardized 0.05 M sodium acetate in glacial acetic acid containing 0.3% acetic anhydride was the solvent, with a tosylate concentration of 0.025 M. Aliquots (2 mL) were sealed in ampules and heated to the reaction temperature. The excess sodium acetate was back titrated in the ampule with standard 0.014 *p*-toluenesulfonic acid in acetic acid, using bromophenol blue indicator (yellow to colorless end point). The first-order plots were linear to at least 75% completion. Infinity titers were at least 94%. All correlation coefficients were at least 0.992. Results are given in Tables II and III.

Acetolysis Products. All three tosylates were studied by dissolution in acetic acid with 2 equiv of anhydrous sodium acetate and refluxing for a number of half-lives. Water was added and the products were extracted with ether. The combined ether layers were washed with 10% sodium bicarbonate, water, and brine. The resulting solution was dried with anhydrous magnesium sulfate and filtered, and the filtrate was rotary evaporated. Only one major product of each tosylate was found, as shown in Table IV.

For the products of *exo*-tosylate 1-CH_2OTs gas chromatography (SE-30, 157 °C, and QF-1, 124 and 151 °C) showed two acetates with ratios varying from 99.0:1.0 to 95.4:4.6. The mixture was vacuum distilled, bp 66–67 °C (1.0 mm), and a pure sample was obtained by GC. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.37; H, 8.83. NMR analysis of the major product indicated that a tertiary acetate was apparent. Comparison of its spectrum with that of known acetate **11**[19] conclusively eliminated this structure: IR (neat) 3085 (cyclopropyl CH), 1747 (C=O), 1258 (asymmetric C—O), 1058 (symmetric C—O) cm^{-1}; NMR (CCl_4) δ 1.83 (s, 3, CH_3CO_2), 1.3–2.6 (m, 9), 0.1–1.0 (m, 4, cyclopropyl).

Acetate **13** was eliminated as a possible structure by saponifying the acetate products and comparing the spectra with those of the alcohol corresponding to **13**.[19] The IR and NMR were different: NMR (CCl_4) δ 3.63 (s, 1, OH), 2.2–2.5 (m, 1, bridgehead), 0.9–2.0 (m, 8), 0–0.9 (m, 4, cyclopropyl). Thus the major product was unequivocally established as acetate **10**, formed by cyclopropano ring expansion.

For the products of *endo*-tosylate 2-CH_2OTs, gas chromatography (QF-1 at 154, 121, and 100 °C) showed only one major acetate product, 99.1:0.9. The IR and NMR spectra matched those of acetate **11**.[19]

For the products of norbornyl tosylate 9-CH_2OTs, gas chromatography (QF-1, 151 °C) showed only one major acetate with a percentage varying from 97.7-98.3. The IR and NMR showed that the major acetate was **12**, as shown previously by Wilt[14a] in this solvolysis.

Acknowledgment. This research was supported in part by the University of Wisconsin—Eau Claire Faculty Research Fund.

Registry No. 1 (CO_2CH_3), 75420-99-4; 1 (CH_2OH), 75421-00-0; 1 (CH_2OTs), 75421-01-1; 1 (COOH), 75421-02-2; 2 (CO_2CH_3), 75494-56-3; 2 (CH_2OH), 75444-02-9; 2 (CH_2OTs), 75444-03-0; 2 (COOH), 75444-04-1; 6, 15023-46-8; 7, 35730-27-9; 8, 75421-03-3; 9 (COOH), 18720-30-4; 9 (CH_2OTs), 13866-80-3; 10, 75421-04-4; 11, 75421-05-5; 12, 56714-23-9; 20, 75421-06-6; cyclopropene, 2781-85-3.

Structure Proof by Synthesis of Unusual Secodehydroabietanes from Tall Oil[1]

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Received August 21, 1980

A noncrystalline substance to which Conner and Rowe have assigned the unusual secodehydroabietanolide formula **1** (9,10-secoabieta-8,11,13-trien-18,10-olide) is a minor component of the neutral fraction of distilled tall oil. It also occurs in the bark of jack pine and western pine.[2,3] As identification of the very limited sample was based only on spectroscopic evidence and on biogenetic arguments, an unambiguous synthesis of optically active material was needed to provide conclusive evidence for the proposed structure. This has now been accomplished. We have also shown, by synthesis, that the structure of a second secodehydroabietane, presumed to be **12**, from the acid fraction of tall oil and from thermal rearrangement of methyl levopimarate must be revised to **11** and have confirmed the structure of a third secodehydroabietane from the thermal rearrangement as **10**.

The successful approach to the synthesis of **1** was initiated with a Diels–Alder–retro-Diels–Alder condensation of levopimaric acid (**2a**) with ethyl propiolate, giving **3b**.[5] The yield was improved to 90% from the reported[5] 35% by raising the temperature to 160 °C. After hydrolysis to **3a**, decarboxylation was effected in 53% yield by heating with Cu powder in quinoline giving **4a**. The purity of the basic solvent was crucial in raising the yield to this figure; under somewhat different conditions (Cu_2O, triply distilled quinoline) **4a** was accompanied by appreciable quantities of lactone **5**.

Ester **4b** was prepared from **4a** in 99% yield by treatment of the sodium salt with MeI in HMPA. Although **4b** could be converted to **6b** in two stages by osmylation–

(1) Supported in part by a grant from the Forest Service, U.S. Department of Agriculture.
(2) Conner, A. H.; Rowe, J. W. *Phytochemistry* **1977**, *16*, 1777.
(3) Conner, A. H.; Rowe, J. W. *J. Am. Oil Chem. Soc.* **1975**, 334.
(4) Zinkel, D. F.; Rowe, J. W.; Zank, L. C.; Gaddie, D. W.; Ruckel, E. R. *J. Am. Oil Chem. Soc.* **1969**, *46*, 633.
(5) Herz, W.; Blackstone, R. C.; Nair, N. G. *J. Org. Chem.* **1966**, *31*, 1800.
(6) Bacha, J. D.; Kochi, J. K. *Tetrahedron* **1968**, *24*, 2215.

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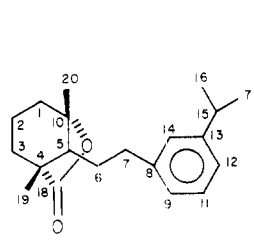

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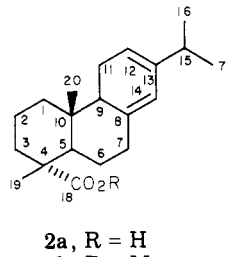

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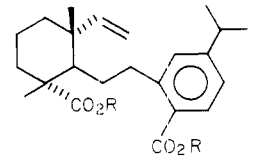
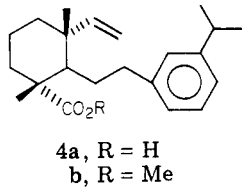
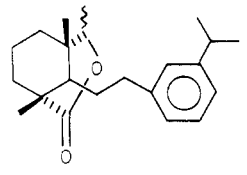
b, R = Me



3a, R = H
b, R = Et



4a, R = H
b, R = Me



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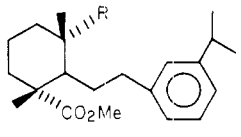
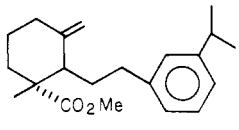
oxidation to **6a** (66%) and subsequent oxidation, a cheaper, more convenient, higher yield (86%) one-pot process to **6b** utilized $KMnO_4$–$NaIO_4$ oxidation of **4b**. Unexpectedly, oxidative decarboxylation of **6b** (PB-$(OAc)_4$–$Cu(OAc)_2$–pyridine–benzene) then gave a 30% yield of **1**, which had properties identical in all respects (TLC, GLC, IR, NMR) with those of the sample originally isolated from tall oil. A 57:36:7 mixture of **7**, **8**, and **9** was also formed in 48% yield.



6a, R = CHO
b, R = CO_2H



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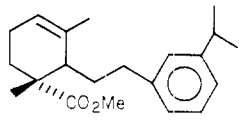

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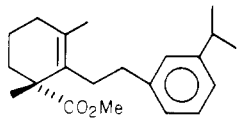
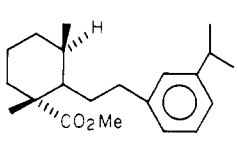


9

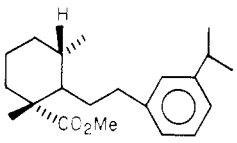
The availability of **6a** and the olefin mixture **7**–**9** made it of interest to attempt to verify the structure of two noncrystalline secodehydroabietanoates to which structures **10** and **12** have been assigned. The supposed **10** and **12** were identified among the products of the base-catalyzed thermal rearrangement of methyl levopimarate (**2b**);[7] **12** was also isolated from the acid fraction of distilled tall oil after conversion to the methyl esters.[3]

Although decarbonylation of **6a** to **10** with tris(triphenylphosphine)rhodium chloride was unsuccessful, catalytic reduction of the mixture of **7**, **8**, and **9** led to formation, by hydrogenation of **7** only, of a mixture of **10** and **11**. The components could not be separated by high-performance LC but were easily distinguishable by NMR spectrometry at 270 MHz. Comparison of the NMR data of **10** and **11** with those reported by the Madison[3] and Olustee[7] workers indicated that our **10** was identical with

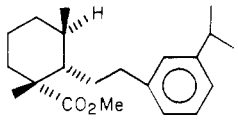
(7) Takeda, H.; Schuller, W. H.; Lawrence, R. V. *J. Org. Chem.* **1968**, *33*, 3718; **1969**, *34*, 1459.



10



11



12

their **10** but that their presumed **12** was actually **11**. This was confirmed by GLC analysis which permits separation of **10** and **11** and by direct comparison of the synthetic material with GLC retention values of authentic samples.

Experimental Section

Condensation of Levopimaric Acid and Ethyl Propiolate. A mixture of 10 g of **2a** and 5.5 mL of ethyl propiolate was sealed under vacuum, kept at 150–160 °C for 15 h, cooled, taken up in ether, and extracted with 0.2 N KOH. Acidification of the basic extract with 5 N HCl and reextraction with ether furnished 12 g of **3b** (90.5%)[5] which gave a single spot on TLC: IR 3400–2500 (OH), 1725 (ester), 1700 (acid), 1635, 1420 and 920 (terminal vinyl), 1610, 850, and 800 cm^{-1} (1,2,4-trisubstituted benzene); NMR (270 MHz, $CDCl_3$) 7.70 (d, J = 8 Hz, H-11), 7.07 (dd, J =7, 2 Hz, H-12), 7.02 (br, H-14), 5.78 (dd, J = 18, 10 Hz, H-21), 4.90 (dd, 2 H, J = 18, 10 Hz, H-22), 4.33 (q, 2 H, J = 7 Hz, OCH_2CH_3), 1.37 (t, J = 7 Hz, OCH_2CH_3), 1.30 (C-4 methyl), 1.25 (d, J = 7 Hz, isopropyl methyls), 1.03 ppm (C-10 methyl).

Hydrolysis and Decarboxylation of 3b. A solution of 11.25 g of **3b** in 10% methanolic KOH was refluxed in a nitrogen atmosphere for 8 h, concentrated at reduced pressure, and diluted with water. Acidification furnished 10 g (96%) of **3a** as an amorphous powder, mp 111–115 °C, whose NMR spectrum was superimposable on that of **3b** except for the absence of the signals of the ester group. Decarboxylation was effected by heating 5.6 g of **3a** with 50 mL of quinoline (purified by distilling doubly distilled quinoline first over KOH and then over anhydrous barium oxide) and 11.2 g of Cu powder at 220–230 °C for 7 h. The mixture was cooled, concentrated in vacuo, taken up in ether, filtered, washed with 2 N HCl and water, dried, and evaporated. The crude product was chromatographed over silicic acid; ether–hexane (1:9) eluted 2.63 g of **4a** (53%) as a gum: $[\alpha]^{25}$ –31° (c 0.13, $CHCl_3$); IR 3400–2500 (OH), 1685 (acid), 1630, 1410 and 920 (terminal vinyl), 1600, 840, 800, and 175 cm^{-1} (1,3-disubstituted benzene); NMR (270 MHz, $CDCl_3$) 7.13, 6.97, and 6.91 (4 aromatic protons), 5.74 (dd, J = 18, 10 Hz, H-21), 4.96 (dd, 2 H, J = 18, 10 Hz, H-22), 2.84 (sept, J = 7 Hz, H-15), 2.52 (t, 2 H, J = 8 Hz, H-7), 1.29 (C-4 methyl), 1.23 (d, J = 7 Hz, isopropyl methyls), 1.03 ppm (C-10 methyl); mass spectrum, m/e 328 (M^+), 185, 146, 133, 131, 117, 95, 91, 81, 67, 55.

Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.81. Found: C, 79.98; H, 9.89.

A solution of 0.94 g of **4a** in mL of HMPA was stirred with 5 mL of 25% aqueous NaOH for 1 h at room temperature and then mixed with 2 mL of methyl iodide. Stirring was continued overnight, and the solution was acidified with 1 N HCl and extracted with ether. The usual workup furnished 0.97 g (99%) of **4b** as a gum: $[\alpha]^{25}_D$ –12.2° (c 0.109, $CHCl_3$); IR 1725, 1630, 1600, 1415, 920 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.18, 7.03, 6.93 (four aromatic protons) 5.74 (dd, J = 18 Hz, H-21), 4.96 (dd, J = 18, 10 Hz, H-22), 3.67 (OMe), 2.86 (sept, J = 7 Hz, H-15), 1.27, 1.25 (d), 1.25 (d), and 1.03 ppm (methyls); mass spectrum, m/e 342 (M^+), 283, 282, 213, 185, 160, 159, 149, 147, 146, 145, 137, 134, 133, 131, 121, 117, 105, 95, 93, 91, 81, 79, 69, 67, 55.

Anal. Calcd for $C_{23}H_{34}O_2$: C, 80.65; H, 10.01. Found: C, 80.81; H, 10.02.

When the decarboxylation of 5 g of **3a** was carried out in 50 mL of triply distilled quinoline (BaO) with 1.5 g of Cu_2O at 240 °C for 5 h in a nitrogen atmosphere, chromatography of the crude product over silica gel furnished first 1.56 g (35%) of **4a** and then

Table I

	GLC-glass capillary column, R_{pim}	
	SE-30 (170 °C)	DBS (190 °C)
10 (this work)	0.862	0.903
11 (this work)	0.801	0.813
10[7]	0.862	0.903
11[7]	0.799	0.811
11[4]	0.800	0.809

1.12 g (25%) of lactone **5**: $[\alpha]^{25}_D$ −21.9° (*c* 0.19, $CHCl_3$); IR 1725 (δ-lactone) cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.23, 7.70, 7.00 (4 aromatic protons), 4.19 (q, *J* = 7 Hz, H-21), 2.86 (sept, *J* = 7 Hz, H-15), 2.60 (t, 2 H, *J* = 8 Hz, H-7), 1.32 (d, C-9 methyl), 1.25 (C-4 methyl), 1.23 (d, isopropyl methyls), 0.84 ppm (C-10 methyl); mass spectrum, *m/e* 328 (M^+).

Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.82. Found: C, 80.09; H, 9.86.

Preparation of 6a. A solution of 2 g of **4a** in 60 mL of THF and 20 mL of H_2O was stirred with 90 mg of OsO_4 for 10 min (N_2 atmosphere). After addition of 10 g of sodium metaperiodate the mixture was stirred for 24 h, filtered, and extracted with ether. The washed and dried ether extract was evaporated and the residue chromatographed over silica gel; 10% ether–hexane eluted 1.32 g (66%) of **6a** as a gum: IR 1730–1720 (double strength), 1605 cm^{-1}; NMR 9.12 (H-21), 7.18, 7.05, and 6.92 (four aromatic protons), 3.67 (OMe), 2.87 (sept, *J* = 7 Hz, H-15), 1.27, 1.23 (d), 1.23 (d), and 1.13 ppm (methyls); mass spectrum, *m/e* 344 (M^+), 255, 187, 146, 133, 131, 123, 117, 109, 105, 101, 91, 81, 55. Because the substance underwent autooxidation to **6b** (vide infra) it was not analyzed. Decarbonylation of **6a** with tris(triphenylphosphine)rhodium(I) chloride could not be achieved in benzene solution at 80 °C or in benzonitrile at 180 °C.

Preparation of 6b. To a solution of 0.1 g of $KMnO_4$ and 10 g of $NaIO_4$ in 400 mL of H_2O and enough 3% aqueous K_2CO_3 to maintain the pH at 6 was added 1.83 g of **4a** in 300 mL of *tert*-butyl alcohol. The mixture was stirred at room temperature for 3 days, acidified with 1 N HCl, and extracted with $CHCl_3$. After being washed, dried, and evaporated, the $CHCl_3$ extract was chromatographed over silica gel. $CHCl_3$ eluted 1.66 g (86%) of **6b** as a gum: $[\alpha]^{25}_D$ 13.8° (*c* 0.087, $CHCl_3$); IR 3500–2500, 1730, 1695, 1605 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.16, 7.02, and 6.93 (four aromatic protons), 3.67 (OMe), 2.84 (sept, *J* = 7 Hz, H-15); mass spectrum, *m/e* 360 (M^+) 328, 147, 146, 134, 133, 131, 123, 121, 117, 109, 105, 96, 93, 92, 91, 81, 79, 67, 55. The elemental analysis remained somewhat unsatisfactory.

Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 72.29; H, 8.94.

Oxidative Decarboxylation of 6b. A. A solution of 1 g of **6b** in 50 mL of benzene (distilled over CaH_2 and $Pb(OAc)_4$) and 10 mL of pyridine (distilled over KOH and $Pb(OAc)_4$) was stirred for 20 min with 60 mg of $Cu(OAc)_2 \cdot H_2O$ in an argon atmosphere free of oxygen. $Pb(OAc)_4$ (3 g) was added and stirring was continued for 1 h. The mixture was then transferred to a quartz tube; a slow stream of oxygen-free dry argon gas was passed through the solution for 45 min after which the mixture was photolyzed in a Rayonet photochemical reactor for 6 h while a slow stream of argon was bubbled through. The mixture was diluted with 20 mL of ethylene glycol and then H_2O and extracted with ether. The washed and dried ether extract was evaporated and chromatographed over silica gel; 3% ether–hexane eluted 0.42 g (48%) of a 57:36:7 mixture of **7**, **8**, and **9** (NMR analysis) as a viscous oil: IR 1730, 1645, 1605 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.21 and 7.04 (aromatic protons), 5.27 (m, H-1 of **9**), 4.89 and 4.72 (H-20 of **8**), 3.64, 3.62, and 3.60 (OMe of **9**, **8**, and **7**, respectively), 2.85 (sept, *J* = 7 Hz, H-15), 1.73 and 170 (C-10 methyl of **9** and **8**, respectively), 1.23 (d, *J* = 7 Hz, isopropyl methyls of all three compounds), 1.19, 1.17, and 1.04 ppm (C-4 methyl of **9**, **8**, and **7**, respectively); mass spectrum, *m/e* 314, 255, 181, 147, 146, 133, 131, 121, 109, 91.

Anal. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62; mol wt 314.2245. Found: C, 79.60; H, 9.69; mol wt (mass spectrum) 314.2279.

Further elution with 5% ether–hexane furnished 0.25 g (30%) of **1** as a gum: $[\alpha]^{25}_D$ 9.5° (*c* 0.11, $CHCl_3$); IR 1770, 1603 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.24 and 7.05 (4 aromatic protons), 2.89 (sept, *J* = 7 Hz, H-15), 2.65 (m, benzylic hydrogens), 1.38 (C-10 methyl), 1.24 (d, *J* = 7 Hz, isopropyl methyls), 1.16 ppm (C-4 methyl); mass spectrum, *m/e* 300 (M^+), 256, 146, 133, 131, 123, 122, 121, 117, 111, 110, 109, 91, 81, 67. In a second experiment, 1.12 g of **7** furnished 0.42 g (47%) of the mixture of **7**, **8**, and **9** and 0.27 g (29%) of **10**. The synthetic material was identical in all respects (NMR, TLC, GLC, IR) with an authentic sample supplied by Drs. J. W. Rowe and A. H. Conner.

Preparation of 10 and 11. Hydrogenation of 0.3 g of the mixture of **7**, **8**, and **9** in 25 mL of EtOAc over 30 mg of PtO_2 at 50 psi and room temperature for 24 h, filtration, evaporation, and high-performance LC (4 ft × $^3/_8$ in. Porasil B, 1% ether–heptane) gave 0.14 g of a mixture of **10** and **11** as a gum which exhibited two peaks on GLC (Apiezon M): IR 1730, 1603, 1587, 1487 cm^{-1}; NMR (270 MHz, $CDCl_3$) 7.19 and 7.00 (aromatic protons), 3.67 and 3.65 (OMe of **10** and **11**, respectively), 2.85 (sept, *J* = 7 Hz, H-15), 2.60 (t) and 2.59 (t) (*J* = 9 Hz, benzylic protons of **11** and **10**, respectively), 1.25 (d) and 1.23 (d) (*J* = 7 Hz, isopropyl methyls of **10** and **11**), 1.15 and 1.13 (C-4 methyls of **10** and **11**), 1.01 (d) and 0.91 (d) (*J* = 7 Hz, C-10 methyls of **11** and **10**); mass spectrum, *m/e* 316, 284, 192, 187, 147, 134, 133, 131, 123, 117, 109, 105, 101, 95, 92, 91, 81, 69, 67, 55. Further elution with the same solvent system furnished 0.09 g of a 2:1 mixture of **8** and **9** (NMR analysis). Further hydrogenation of 70 mg of this mixture (PtO_2, H_2 at 50 psi, 24 h), followed by high-performance LC, resulted in formation of 4 mg of a mixture of **10** and **11** and recovery of 65 mg of a mixture of **8** and **9** in which the proportion of **8** had decreased slightly. Evidently reduction of **8** under these conditions proceeds only very slowly and reduction of **9** not at all. This eliminates the possibility that hydrogenation of **7** might actually have given rise to a mixture of **10** and **12** by prior isomerization to **9** and subsequent reduction.

A direct GLC comparison of the synthetic mixture of **10** and **11** with samples of the methyl secodehydroabietates derived from tall oil[4] and thermal isomerization of methyl pimarate[7] was carried out by Dr. Duane Zinkel at the Forest Products Laboratory, Madison, WI. The results shown in Table I established their identity.

Acknowledgment. We are indebted to Dr. Duane Zinkel for carrying out the GLC comparison of **10** and **11** with authentic material.

Registry No. **1**, 57119-17-2; **2a**, 79-54-9; **3a**, 6512-55-6; **3b**, 75399-78-9; **4a**, 75399-79-0; **4b**, 75399-80-3; **5**, 75399-81-4; **6a**, 75399-82-5; **6b**, 75399-83-6; **7**, 75399-84-7; **8**, 75399-85-8; **9**, 75399-86-9; **10**, 75443-46-8; **11**, 19556-81-1; ethyl propiolate, 623-47-2.

Specific Dealkylation of 3-Benzyladenines in the Presence of 9-Benzyladenines

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The decomposition of onium ions, e.g., oxonium, sulfonium, and ammonium ions, constitutes an important class of carbenium ion generating reactions[1] (Scheme I). Ammonium salts derived from *N*-heterocycles have been employed as sources of carbenes,[2] nitrenes,[3] and oxenium ions,[4] but we are unaware of the formation of carbenium ions from these starting materials.[19]

We now report a specific dealkylation of 3-benzyladenines that proceeds via benzyl carbenium ion formation and the successful application of this reaction to the quantitative removal of the 3-isomer from adenine al-

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