The Formaldehyde-Levopimaric Acid Adduct Revisited†

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As a model for studying the addition of heteroatomic dienophiles to levopimaric acid, we selected the formaldehyde–levopimaric acid adduct **1a**, originally synthesized by Parkin and Hedrick.[1] However, it soon became apparent that, in our hands, the chemical behavior of 1 and its derivatives often varied considerably from that reported in the literature. Due to the importance of **1a** as a basis for studying other heteroatomic cycloadducts of levopimaric acid, we here report a detailed analysis of products resulting from hydrolysis and reduction.

Results and Discussion

Hydrolysis. Acid hydrolysis of the formaldehyde adduct was reported by Parkin and Hedrick[1] to give 12α-(hydroxymethyl)abietic acid (**2a**) in 83% yield. In our hands, reproduction of the reported reaction conditions, however, afforded the two hydrolysis products **2a** and **3**, with the production of a third product **4**[2] at elevated temperatures (Scheme I).

In addition, the ratio of neoabietic **3** and abietic **2a** isomers was observed to change dramatically with reaction conditions (Table I). (a) Repetition of the literature procedure,[1] which uses a small solvent volume, resulted in precipitation of 12α-(hydroxymethyl)neoabietic acid (**3**) from the reaction mixture to give an overall yield of 26%, while the thermodynamically more stable isomer **2a** was produced in 74% yield, as determined by ^{1}H NMR integration. (b) Extended reaction times—under otherwise identical conditions—afforded a marked increase in the yield of **3** (44%) relative to the abietic isomer **2a** (15%). However, (c) at more dilute concentrations a higher percentage of **2a** was produced at the expense of its neoabietic isomer. And finally, (d) acid hydrolysis of the formaldehyde adduct—as well as **3**—at higher temperatures (65–80 °C) afforded a third hydrolysis product, 12-methyldehydroabietic acid (**4**).

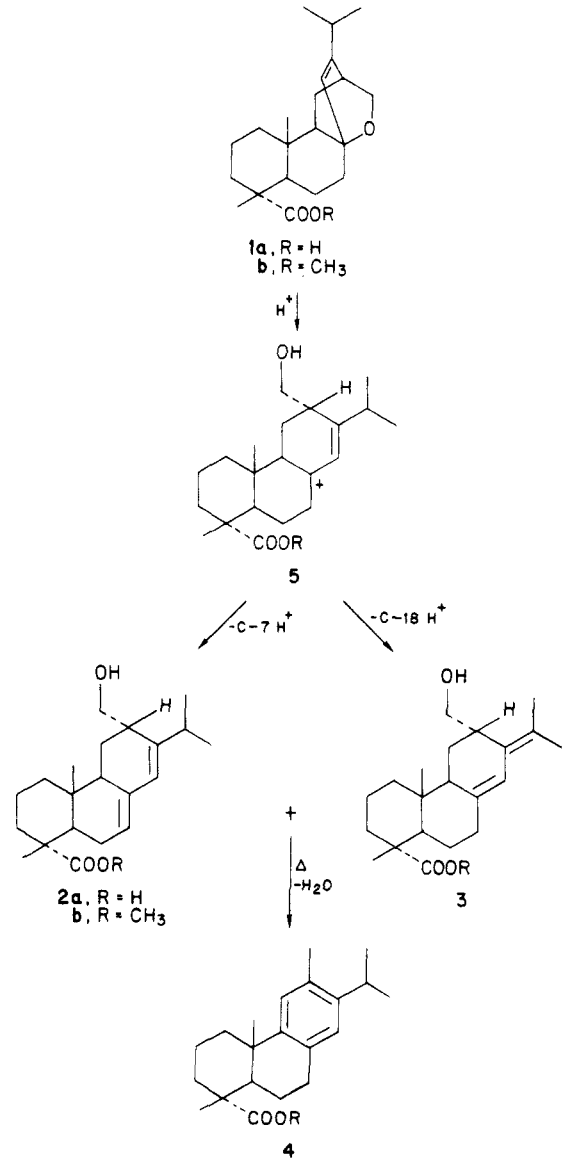
The production of **2a** and **3** at room temperature can be visualized as occurring through a common intermediate (**5**) (Scheme I). Isolation of the neoabietic derivative, however, can only be attributed to its precipitation from the reaction mixture, since only trace amounts of **3** are observed with more dilute reaction conditions. Thus, increasing the solubility of any 12α-(hydroxymethyl)neoabietic acid (**3**) produced in the reaction increased the yield of **2a**. The third product (**4**) is presumably formed by dehydration of **2a** or one of its isomers, followed by aromatization.[3]

In addition to the formaldehyde adduct's sensitivity to acidic conditions, Parkin and Hedrick[1] also reported *opening of the ether linkage at 130 °C to again yield* **2a**. This thermal instability is further exemplified by the adduct's behavior toward various methods of esterification. While gentle treatment of pure **1a** with diazomethane in ether at 0 °C gives the corresponding methyl ester **1b** as a viscous oil in essentially quantitative yield,[4] we found that heating the adduct with methyl iodide in aqueous acetone in the presence of sodium carbonate for 0.5 h affords instead an almost quantitative yield of methyl 12α-(hydroxymethyl)abieta-7,13-dien-18-ate (**2b**).

Reduction. We also investigated diborane reductions of **1a**. Diborane can reduce not only the carboxyl function—as do other hydride reducing agents—but can also add to the carbon–carbon double bond. Two borane reduction products, **6** and **7**, were isolated from the reduction of **1a** with 1 M borane–THF complex in THF (Scheme II).

Support for the structural assignments for the borane reduction products **6** and **7** comes from ^{1}H NMR spec-

Scheme I. Acid Hydrolysis of 1a



† Dedicated to the memory of Dr. Robert L. Settine (deceased May, 1985).

(1) Parkin, B. A., Jr.; Hedrick, G. W. *J. Org. Chem.* **1965**, *30*, 2356.
(2) Black, D. K.; Hedrick, G. W. *J. Org. Chem.* **1967**, *32*, 3758.
(3) Herz, W.; Baburao, V. *J. Org. Chem.* **1971**, *36*, 3271.
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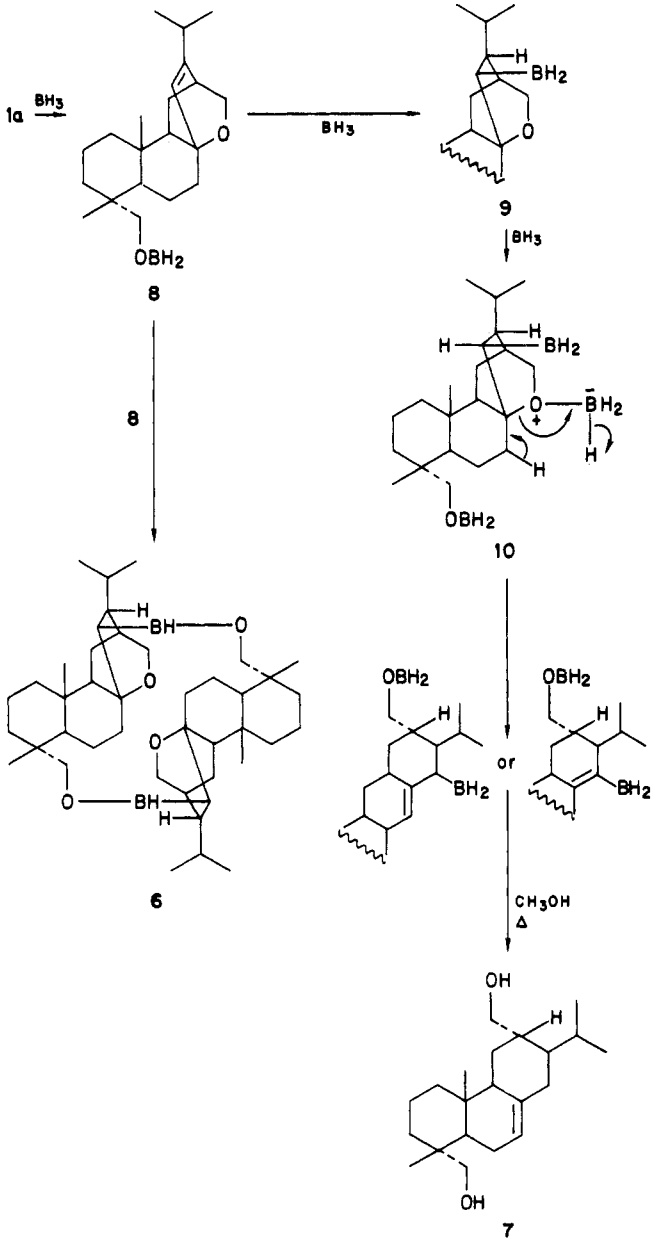
Table I. Acid Hydrolysis of the Formaldehyde Adduct at Room Temperature

reactn time	solvent vol: 1 g adduct	%3	%2a
21 h	2 mL of EtOH	26[a]	74[a]
		11[b]	
17 days	2 mL of EtOH	44[b]	15[b]
17.5 h	3–4 mL of EtOH	18[a]	82[a]
			59[b]
17.5 h	170 mL of EtOH	18[a]	82[a]
18 h	350 mL of EtOH	5[b]	53[b]
17 h	350 mL of MeOH	tr	79[b]

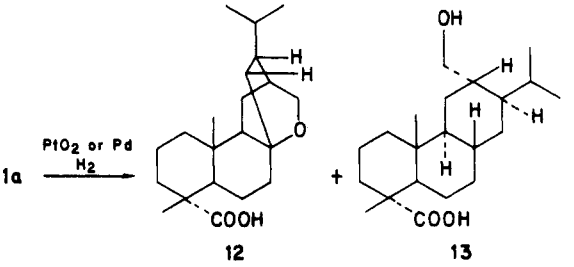
[a] Percentage determined solely by ^{1}H NMR integration and assumes 100% yield. [b] Represents an isolated yield. [c] Ratio of solvent vol. to 1 g of adduct

Scheme II. Diborane Reduction of 1a



troscopy, elemental analyses, infrared spectroscopy, and comparison to similar or authentic samples. The ^{1}H NMR spectrum of the organoborane **6**, which exhibits no absorption in the olefinic region, displays an AB quartet at δ 4.07 and 3.93, which is indicative of an intact oxymethylene bridge. The C-4 methylene appears as another AB quartet at δ 3.52 and 3.24. Addition of diborane to the

Scheme III. Catalytic Hydrogenation and Hydrogenolysis of 1a



carbon–carbon double bond of **1a** from the direction of the oxymethylene bridge is evidenced by the restricted rotation and the shielding of the nonequivalent isopropyl methyls by the C-10 methyl group. The ^{1}H NMR signal from these C-15 methyls takes the form of two doublets appearing at δ 0.92 and 0.76. The C-10 methyl is reciprocally shielded by the isopropyl group and resonates at δ 0.73. Elemental analysis and the infrared spectrum of **6**, which confirm the absence of both a BH_2 group (2640–2350 cm^{-1})[5] and a hydroxyl group, suggest the proposed dimeric structure.

Steric hindrance by the C-10 methyl group forces the borane reduction to proceed from the direction of the oxymethylene bridge by an anti-Markovnikov addition to the carbon–carbon double bond. At initially low borane concentrations, production of **6** can be viewed as occurring by an initial reduction of the carboxyl group of two adduct molecules, followed by an intermolecular reduction of both carbon–carbon double bonds by one of the remaining hydrides of each of the resulting alkoxyboranes **8** (Scheme II).

On the other hand, the other borane reduction product, 12α-(hydroxymethyl)-7-abieten-18-ol (**7**) (Scheme II) displays an olefinic proton (C-7) in the form of a multiplet at δ 5.36 in its ^{1}H NMR spectrum. The C-12 and C-4 methylenes, respectively, appear as a doublet at δ 3.55 and as an AB quartet at δ 3.31 and 3.01. Formation of **7** can be visualized as occurring via an ether cleavage of an intermediate organoborane **9** (Scheme II). This cleavage presumably involves a nucleophilic attack of the ethereal oxygen lone pair of **9** on the electron-deficient boron of the now excess borane reagent to form an intermediate complex **10**, which facilitates ring opening at the ether linkage. Opening of the ring can transpire by a trans elimination involving either the methine at C-7 or that at C-14. Facile cleavage of the resulting intermediate allyl or vinyl boranes, respectively, under methanolic reflux, followed by isomerization to the thermodynamically more stable olefin, conceivably affords the observed **7**. A similar ether cleavage was previously proposed by Stibr, Hermanek, Plesek, and Stuchlik[6] to explain the mixture of products, including propene, obtained upon treatment of isopropyl ether with diborane at 80 °C. In addition, an authentic sample of product **7** was obtained in 46% yield from the hydrogenation of 12α-(hydroxymethyl)abieta-7,13-dien-18-ol (**11**)[1] over 10% palladium on carbon.[2,3,7]

Catalytic hydrogenation of **1a** over a platinum oxide catalyst afforded in low yield a reduction product **12**[1] as well as a second reduction product **13** (Scheme III). Derivative **12** was first prepared by Parkin and Hedrick,[1] who disclosed little information concerning either the

(5) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Methuen & Co., Ltd: London, by Barnes & Noble: New York, 1968; p 118.
(6) Stibr, B.; Hermanek, S.; Plesek, J.; Stuchlik, J. *Collect. Czech. Chem. Commun.* **1968**, *33*, 976.
(7) Black, D. K.; Hedrick, G. W. *Amer. Chem. Soc., Div. Org Coatings Plast. Chem., Reprints* **1967**, *27*, 369.

details of its ^1H NMR spectrum or the identity of any other reduction products present in the reaction mixture. However, close examination of the ^1H NMR spectrum of this reduced adduct **12** shows a number of similarities to the spectrum displayed by its structurally similar C-14 alkoxyboryl derivative **6**. The ^1H NMR spectrum of **12** in a mixture of deuterated solvents (Me_2SO, $CDCl_3$, and D_2O) clearly depicts the nonequivalence of the two ethereal methines. These ethereal protons appear at δ 3.56 and 3.30 as an AB quartet that has been split further by the C-12 methine. The upfield contribution (δ 3.30), derived from the endo ethereal proton, is thus the result of coupling of this endo proton with both the exo proton and with the C-12 methine, with which it makes an acute angle (J = 6 Hz). The exo proton, however, which makes an angle with the C-12 methine that more nearly approaches 90°, shows a secondary coupling of only 3 Hz and appears downfield at δ 3.56. In addition, the C-10 methyl group, which no longer experiences a shielding effect from a carbon–carbon double bond, displays a downfield shift to δ 1.07, relative to the corresponding resonance for the formaldehyde adduct (δ 0.50). The proximity of this C-10 methyl group to the isopropyl group in **12** is responsible for the hindered rotation of the isopropyl group, as evidenced by the appearance of the C-15 methyls as two doublets at δ 0.90 and 0.76.

Competing with catalytic hydrogenation of the hindered carbon–carbon double bond of **1a**—especially with a platinum oxide catalyst—is the alternate allylic hydrogenolysis of the ethereal oxygen bond at C-8 (Scheme III). Hydrogenation of the carbon–carbon double bond of the resulting intermediate 12α-(hydroxymethyl)-8βH-abiet-13-en-18-oic acid from the less hindered α-face of the molecule subsequently affords the observed hydrogenolysis product, 12α-(hydroxymethyl)-8βH,13βH-abietan-18-oic acid (**13**) as the major reduction product. The ^1H NMR spectrum of product **13** clearly supports the proposed structural assignment. Opening of the ether linkage of the adduct is evidenced by the appearance of the signal arising from the magnetically similar C-12 methylene protons as a doublet at δ 3.53. Furthermore, absence of any absorption in the olefinic region of the spectrum indicates a complete loss of the intermediate 13(14)-carbon–carbon double bond. Elimination of the possibility of the existence of a tetrasubstituted olefin, however, is conclusively provided by elemental analysis and by the mutually contrasting physical data for the proposed tetrahydro derivative **13** and the previously prepared 12α-(hydroxymethyl)-8(9)-abieten-18-oic acid, as reported by Black and Hedrick.[2] The stereochemistry at C-8 has been assigned on the basis that both platinum and palladium catalysts have been shown to promote inversion of the configuration at the reactive site of hydrogenolysis.[8] Thus, the stereochemistry at C-8 is presumably opposite to that obtained by Hedrick, Sugathan, and Rohde[9] upon high pressure hydrogenation of **2a** at 200 °C by Parkin et al.[10] from a similar reduction of **2a** to the corresponding diol and by Herz et al.[11] from a low pressure hydrogenation of 12α-hydroxyabieta-7,13-dien-18-oic acid. Furthermore, reduction of the formaldehyde adduct over 10% palladium on carbon showed a marked preference for the hydrogenation product **12** (31%) at the expense of the corresponding hydrogenolysis product **13**, which was observed in very low yield (~3%).

(8) Rylander, P. N. *Catalytic Hydrogenation over Platinum Metals*; Academic Press: New York and London, 1967; p 289.
(9) Hedrick, G. W.; Sugathan, K. K.; Rohde, W. A. *J. Chem. Eng. Data* **1971**, *16*, 299.
(10) Parkin, B. A., Jr.; Summers, H. B.; Settine, R. L.; Hedrick, G. W. *Ind. Eng. Chem., Prod. Res. Develop.* **1966**, *5*, 257.
(11) Herz, W.; Wahlborg, H. S.; Lloyd, W. D.; Schuller, W. H.; Hedrick, G. W. *J. Org. Chem.* **1965**, *30*, 3190.

Experimental Section

Melting points, which are uncorrected, were determined in an Electrothermal melting point apparatus. ^1H NMR data are reported in δ (ppm) downfield from the internal standard Me_4Si.

Acid Hydrolysis of the Formaldehyde–Levopimaric Acid Adduct (1a) at Room Temperature. 1. Adduct **1a** (23.4 g, 0.07 mol) was slurried in EtOH (52 mL) at room temperature. HCl (6 N, 4 mL) was added and the adduct slowly dissolved. After 24 h, the mixture became turbid and began to precipitate a white solid. After a total of 17 days reaction time, the precipitate was filtered and washed with EtOH to give 10.38 g (44%) of **3** that was recrystallized from MeOH–H_2O as colorless prisms: mp 203–211 °C; IR (KBr) 3350 cm^{-1} (OH), 1690 (C=O), 1640 and 1630 (C=C), 1460 (CH_2), 1380 (CH_3), and 1255 and 1020 (C—O); ^1H NMR ($CDCl_3$, δ) 6.07 (s, H, C-14), 3.42 (d, 2 H, C-12 methylene, $J_{C\text{-}12\ methine,\ C\text{-}12\ methylene}$ = 7.5 Hz), 1.78 (s, 6 H, C-15 methyls), 1.23 (s, 3 H, C-4 methyl), and 0.79 (s, 3 H, C-10 methyl). Anal. Found: C, 75.86, H, 9.74. Calcd for $C_{21}H_{32}O_3$: C, 75.86, H, 9.70.

The filtrate was warmed and diluted with H_2O to yield a viscous oil that became a semisolid upon washing with H_2O. The crude gum was crystallized from CH_3CN–H_2O with seeding to give **2a** (3.54 g, 15%): mp 162–168 °C (lit.[1] mp 166.5–168 °C).

2. The formaldehyde adduct **1a** (1.0 g, 3 mmol) in a solution of HCl (6 N, 3 drops) and EtOH (95%, 2.0 mL) was stirred for 21 h at room temperature. Compound **3** had precipitated (0.11 g, 11%) and was collected by filtration. The filtrate was diluted with H_2O until precipitation was complete. ^1H NMR analysis of the crude precipitate from the filtrate showed it to consist of a mixture of **3** and **2a** in the ratio of 1:5, respectively.

Acid Hydrolysis of 1a in Boiling Methanol. Adduct **1a** (5.1 g, 15.4 mmol) was heated under reflux in a solution of concentrated HCl (3 drops) and MeOH (50 mL) for 21.5 h. The reaction mixture was then concentrated under vacuum, washed with H_2O, and filtered to give a slightly yellow gum consisting of a mixture of **3** (21%), **4** (3%), and **2a** (76%), according to the ^1H NMR integration.

Dehydration of 2a with Phosphoric Acid. Compound **2a** (0.51 g, 1.5 mmol) was heated under reflux in a solution of H_3PO_4 (85%, 20 mL), EtOH (20 mL), and H_2O (2–4 drops) for 1.75 h. The reaction mixture was then concentrated by distillation of the solvent, diluted with H_2O, and extracted with $CHCl_3$. The extracts were washed with H_2O, dried over anhydrous $CaCl_2$, and evaporated to give **4** as a brown gum in low yield. Recrystallization of the crude product from MeOH–H_2O afforded **4** as colorless needles: mp 172.0–173.3 °C; IR (KBr pellet), 3290 cm^{-1} (OH), 3050 (aromatic CH), 1700 (C=O), 1385 (isopropyl CH_3); ^1H NMR ($CDCl_3$, δ) 6.90 and 6.81 (2 s, 2 H, C-11 and C-14 methines), 2.25 (s, 3 H, C-12 methyl), 1.30 (s, 3 H, C-4 methyl), 1.20 (s, 3 H, C-10 methyl), and 1.21 and 1.14 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 3 Hz); mass spectrum, m/e (rel intensity) 314 (33), 299 (100), 253 (81), 155 (42), 143 (22), and 131 (23). (Cf. ref 2 and 3 for methyl ester.)

Acid Isomerization of 3 at Room Temperature. Acid **3** (0.13 g, 0.38 mmol) was dissolved in EtOH (25 mL). HCl (6 N, 6 drops) was added, the flask was corked, and the mixture was allowed to stir at room temperature for 12 days. H_2O was then added until precipitation was complete. The precipitate was filtered and washed with H_2O. The crude product (0.04 g, 33%) was recrystallized from CH_3CN–H_2O with seeding to give **2a** as almost colorless prisms: mp 162–168 °C (lit.[1] mp 166.5–168 °C).

Acid Isomerization of 3 in Boiling Ethanol. Derivative **3** (0.3 g, 0.9 mmol) was partially dissolved in EtOH (50 mL). Six drops of both concentrated HCl and H_2O were added and the colorless mixture was heated under reflux for 2 days. The light yellow solution was concentrated under reduced pressure and diluted with H_2O until precipitation was complete. The crude, pale yellow solid consisted of a mixture of unreacted **3** (20%), **2a** (40%), and **4** (39%), as determined by integration of the ^1H NMR spectrum.

Reaction of 1a wtih Methyl Iodide and Sodium Carbonate. The adduct **1a** (0.53 g, 1.58 mmol) was dissolved in a solution of

acetone (25 mL) and H_2O (20 drops). Na_2CO_3 (1.2 g, 11.3 mmol) and MeI (12 mL, 193 mmol) were added and the mixture was heated under reflux. The initially yellow solution quickly became colorless. After 15 min, additional MeI (5 mL, 80 mmol) was added, and again the color disappeared in 1 to 2 min. After a total reaction time of 30 min, heating was discontinued and the mixture was twice extracted with $CHCl_3$. The organic layer was washed with H_2O, dried over anhydrous $CaCl_2$, and evaporated to give a yellow gum. The methyl ester **2b** was obtained in essentially quantitative yield with only a trace of contamination by the unopened ester **1b**.[1] The methyl ester **2b** gives the following spectral data: IR (KBr pellet), 3430 cm^{-1} (OH), 1735 (C=O), 1650 and 1630 (C=C), 1455 (CH_2), and 1375 (CH_3); ^1H NMR ($CDCl_3$, δ) 5.81 (s, H, C-14), 5.35 (br m, H, C-7), 3.60 (s, 3 H, C-15 methyl), 1.27 (s, 3 H, C-4 methyl), 1.07 and 1.00 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 1 Hz), and 0.83 (s, 3 H, C-10 methyl).

Diborane Reduction of the Adduct 1a. Through a flame-dried, three-necked flask, equipped with a gas inlet tube, a gas outlet tube with a bubbler, and a rubber septum, was passed a stream of nitrogen that had been dried by passage through both H_2SO_4 and NaOH traps. Dry THF (5 mL) was added to the flask, followed by the adduct **1a** (1.14 g, 3.4 mmol), which partially dissolved. After the mixture was cooled in an ice bath, a 1 M solution of borane–THF complex (15 mL, 15 mmol) was added dropwise during 10 min through the septum with the aid of a syringe. The initially turbid reaction mixture cleared and effervesced during the addition of the first 5 mL of borane complex. When the addition was complete, the flask was stoppered and the clear solution was stirred at room temperature for 2 h, after which time it became slightly turbid and was cooled in an ice bath. An excess of MeOH, which caused the mixture to again effervesce, was added dropwise. The mixture was then stirred at room temperature for an hour, followed by heating under reflux for an hour and stirring overnight at room temperature. The solvents were then removed under reduced pressure. Methanol was repeatedly added to the residue and removed by vacuum distillation to give a white gum. The ^1H NMR spectrum of the crude product mixture indicated a 1:2 ratio of **6**, as the dimeric organoborane, and 12α-(hydroxymethyl)-7-abieten-18-ol (**7**). The crude mixture was recrystallized from ethyl acetate to give colorless prisms of **6** (0.24 g, 22%): mp 328–330 °C; IR (KBr) 1725 cm^{-1} (BH), 1473–1265 cm^{-1} (BC), 1455 (CH_2), 1380 (CH_3), and 1065–1023 (CO); ^1H NMR of the monomeric unit ($CDCl_3$, δ) 4.07 and 3.93 (AB q with further unresolved splitting, 2 H, ether methylene), 3.52 and 3.24 (AB q, 2 H, C-4 methylene), 0.92 and 0.76 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6 Hz), 0.89 (s, 3 H, C-4 methyl), and 0.73 (s, 3 H, C-10 methyl). Anal. Found: C, 76.57; H, 10.79. Calcd for $(C_{21}H_{35}O_2B)_2$: C, 76.36; H, 10.68.

Crude **7** from the filtrate was recrystallized from CH_3CN as colorless crystals: mp 166.8–170.1 °C (mmp 166.5–170 °C with authentic **7**).

Catalytic Hydrogenation of 11 over Palladium. 12α-(Hydroxymethyl)abieta-7,13-dien-18-ol (**11**) (1.49 g, 4.7 mmol), from the $LiAlH_4$ reduction of **1a** or **2a**, was dissolved in MeOH (200 mL). Palladium on carbon (10%, 0.08 g) was added and the reaction mixture was treated with hydrogen at 35–40 psi for 16 h at room temperature. The catalyst was removed by filtration and the reaction mixture was evaporated under reduced pressure to give a colorless gum. The crude **7** was recrystallized from CH_3CN as colorless crystals (0.69 g, 46%): mp 169–169.1 °C; IR (KBr pellet) 3290 and 3190 cm^{-1} (OH), 1653 (C=C), 1450 (CH_2), 1380 (CH_3), and 1150 and 1055–1000 (CO); ^1H NMR ($CDCl_3$, Me_2SO-d_6, D_2O, δ) 5.36 (m, H, C-7), 3.35 (d, 2 H, C-12 methylene, $J_{C\text{-}12\ methine,\ C\text{-}12\ methylene}$ = 6.9 Hz), 3.31 and 3.01 (AB q, 2 H, C-4 methylene), 0.91 (d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6 Hz), and 0.74 (2 s, 6 H, C-4 and C-10 methyls). Anal. Found: C, 78.91; H, 11.51. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. (Cf. ref 2 for hydrogenation of **2a**.)

Catalytic Hydrogenation of 1a. 1. Adduct **1a** (4.00 g, 12.1 mmol) was slurried in EtOH (100 mL). Platinum oxide (0.10 g) was added and the mixture was hydrogenated at 40–45 psi of hydrogen for 16 h at room temperature. The mixture was then filtered and evaporated to give a colorless gum. The crude product was crystallized from 95% EtOH to give a mixture (0.94 g) of 12α-(hydroxymethyl)-8βH,13βH-abietan-18-oic acid (**13**) and the reduced adduct **12**.

Product **12** was repeatedly recrystallized as colorless cubes (0.20 g, 5%) from 95% EtOH: mp 241–242.5 °C (lit.[1] mp 240.9–243.8 °C); IR (KBr pellet) 3450 cm^{-1} (OH), 1675 (C=O), 1450 (CH_2), 1375 (CH_3), and 1246, 1160, and 1003 (CO); ^1H NMR ($CDCl_3$, Me_2SO-d_6, D_2O, δ) 3.56 and 3.30 (AB q, 2 H, exo ethereal methine, $J_{C\text{-}12\ methine,\ exo}$ = 3 Hz, and endo ethereal methine, $J_{C\text{-}12\ methine,\ endo}$ = 6 Hz), 1.17 (s, 3 H, C-4 methyl), 1.07 (s, 3 H, C-10 methyl), and 0.90 and 0.76 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6 Hz).

Concentration or dilution of the filtrate with H_2O gave **13** as colorless crystals (1.76 g, 43%). The crude product **13** was repeatedly recrystallized from 95% EtOH and also from CH_3CN: mp 213–214 °C; IR (KBr pellet) 3470 cm^{-1} (OH), 2960–2820 (CH), 1685 (C=O), 1450 (CH_2), 1375 and 1355 (CH_3), and 1250 and 1165 (CO); ^1H NMR ($CDCl_3$, Me_2SO-d_6, δ), 4.17 (br peak, 2 H, OH), 3.53 (m, 2 H, C-12 methylene), 1.14 (s, 3 H, C-4 methyl), 0.93 (d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6 Hz), and 0.84 (s, 3 H, C-10 methyl). Anal. Found: C, 74.86; H, 10.79. Calcd for $C_{21}H_{36}O_3$: C, 74.95; H, 10.78. (Cf. ref 10.)

2. The formaldehyde adduct **1a** (1.00 g, 3 mmol) and palladium on carbon (10%, 0.21 g) were slurried in EtOH (50 mL). The mixture was hydrogenated at 45 psi for 16.25 h at room temperature. The catalyst was removed by filtration and the resulting colorless solution was concentrated to about 5 mL under a stream of nitrogen. The white precipitate (0.35 g) of **12** was collected by filtration and was washed with EtOH. Dilution of the filtrate with H_2O caused the further precipitation of a white solid (0.57 g), which was recrystallized from CH_3CN as colorless feathers of **12** (0.19 g). The combined crude product (0.54 g, 53%) of **12** was recrystallized from 95% EtOH as colorless prisms (0.31 g, 31%): mp 238.5–242.5 °C. The mother liquor from the precipitation of **12** was concentrated to give a mixture (0.06 g) of 12α-(hydroxymethyl)-7-abieten-18-oic acid[2] and presumably **13**, according to the ^1H NMR spectrum in the ratio of 1:1. (Cf. ref 2, 7, 10, and 11.)