distorted toward a neopentylidyne ligand.[4,6]

Reduction of a mixture of $Ta(CH_2CMe_3)Cl_4$ and $Ta(CD_2CMe_3)Cl_4$ in the presence of PMe_3 gave a significant amount of $Ta(CDCMe_3)(H)(PMe_3)_3Cl_2$ (by 250-MHz ^1H NMR). Since we showed that a mixture of $Ta(CHCMe_3)(H)(PMe_3)_3Cl_2$ and $Ta(CDCMe_3)(D)(PMe_3)_3Cl_2$ yielded no $Ta(CDCMe_3)(H)(PMe_3)_3Cl_2$, this "α-elimination" reaction may not be a relatively simple intramolecular version.

The reduction of $Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)Cl_3$ in the presence of PMe_3 gave another neopentylidene hydride complex, **2** (eq 2), as the only NMR observable product. It is extremely soluble

$$Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)Cl_3 + 2Na/Hg + 2PMe_3 \rightarrow \underset{\mathbf{2}}{Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(H)(PMe_3)Cl} \quad (2)$$

in pentane but can be isolated in 30% yield from concentrated solutions at −30 °C. The IR and NMR data for **2** are in complete accord with its formulation.[9] The neopentylidene ligand is, again, one of the distorted variety with $J_{CH_\alpha} = 72$ Hz and $\nu_{CH_\alpha} = 2525$ cm^{-1}, and $\nu_{TaH} = 1730$ cm^{-1}.

Since the neopentlyidene ligands in **1** and **2** are distorted, we were interested in knowing whether the hydride would behave as a leaving group and abstract H_α. Heating **1a** with excess PMe_3 led only to intractable oils, but **2** gave **3**[10] (eq 3) in good yield.

$$\underset{\mathbf{2}}{Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(H)(PMe_3)Cl} \xrightarrow[60\ °C]{PMe_3} \underset{\mathbf{3}}{Ta(\eta^5\text{-}C_5Me_5)(CCMe_3)(PMe_3)_2Cl} \quad (3)$$

The preparation of an alkylidyne–hydride complex from an alkylidene complex was similarly successful. $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)Br_2$[11] in the presence of 2 equiv of PMe_3 gives $Ta(\eta^5\text{-}C_5Me_5)(CCMe_3)(PMe_3)_2(H)$ (**4**) in 80% yield on reduction with 2 equiv of sodium amalgam. A more convenient synthesis (but one which is probably more complex mechanistically) employs $Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2Cl_2$ (eq 4). (**2** was first prepared by

$$Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2Cl_2 + 2PMe_3 + 2Na/Hg \rightarrow \underset{\mathbf{4}}{Ta(\eta^5\text{-}C_5Me_5)(CCMe_3)(PMe_3)_2(H)} \quad (4)$$

treating **3** with LiC_2H_5;[12] it is believed to be a trans tetragonal pyramidal molecule analogous to **3** and $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$.[13]) A related compound (**5**) can be prepared employing dmpe instead of PMe_3 (eq 5). Its ^1H, ^{13}C, and ^{31}P NMR

$$Ta(\eta^5\text{-}C_5Me_5)(CH_2CMe_3)_2Cl_2 + Me_2PCH_2CH_2PMe_2 + 2Na/Hg \rightarrow \underset{\mathbf{5}}{Ta(\eta^5\text{-}C_5Me_5)(CCMe_3)(dmpe)(H)} \quad (5)$$

spectra suggest that both ends of the dmpe ligand are coordinated to Ta and that they are equivalent.[14] We believe the geometry to be pseudo-tetrahedral with the hydride ligand capping the PPC_α face.

In light of the above findings, it is interesting to note that reduction of $Ta(CHCMe_3)(PMe_3)_2Cl_3$ in the presence of PMe_3 under argon does *not* give an alkylidyne–hydride complex, but **6** (eq 6), the only "d^2" alkylidene complex which does not contain

$$Ta(CHCMe_3)(PMe_3)_2Cl_3 \xrightarrow[3PMe_3]{2Na/Hg} \underset{\mathbf{6}}{Ta(CHCMe_3)(PMe_3)_4Cl} \quad (6)$$

an olefin ligand.[15] NMR data suggest that **6** contains one of the most distorted alkylidene ligands so far. We found the α-proton signal at δ −7.4, the α-carbon signal at 209 ppm with $J_{CH_\alpha} = 69$ Hz, and the CH_α stretch at 2200 cm^{-1}.[16] The α-proton signal is a quintet ($^3J_{HP} = 5.9$ Hz) at 25 °C, and we have not yet been able to obtain a low-temperature-limiting NMR spectrum characteristic of a less symmetric molecule. There, we believe some low-energy intramolecular process is equilibrating all PMe_3 ligands.

These results demonstrate how potentially complex the chemistry of alkyl and alkylidene complexes of early transition metals in "intermediate" oxidation states can be, and that under the right circumstances we can expect to observe or isolate alkylidene–hydride or alkylidyne–hydride complexes of other early transition metals such as Mo, W, or Re.[17] However, it is not yet clear that they can be formed by an *intramolecular* α-elimination reaction.

Acknowledgment. We thank the National Science Foundation for support (CHE79-05307).

(9) IR (cm^{-1}, Nujol): 2525 (ν_{CH_α}), 1730 (ν_{MH}). ^1H NMR (ppm from Me_4Si, toluene-d_8, 250 MHz, −30 °C): 7.53 (d, 1, $J_{HP} = 73.6$ Hz, $J_{HH_\alpha} = 1.8$ Hz, Ta–H), 2.44 (d, 1, $J_{HH_\alpha} = 1.83$ Hz, $CHCMe_3$), 2.09 (s, 15, C_5Me_5), 1.18 (d, 9, $J_{HP} = 7.3$ Hz, PMe_3), 1.11 (s, 9, $CHCMe_3$). ^{13}C NMR (ppm, toluene-d_8, 67.89 MHz, −30 °C, gated ^1H decoupled): 232.4 (dd, $J_{CP} = 6.5$ Hz, $J_{CH} = 72$ Hz, $CHCMe_3$), 112.1 (s, C_5Me_5), 47.4 (s, $CHCMe_3$), 33.4 (q, $J_{CH} \approx 122$ Hz, $CHCMe_3$), 18.41 (qd, $J_{CP} = 25.6$ Hz, $J_{CH} \approx 125$ Hz, PMe_3), 13.0 (q, $J_{CH} = 130$ Hz, C_5Me_5). ^{31}P NMR (ppm from H_3PO_4, C_6D_6, 36.4 MHz, 30 °C): −14.9 ($J_{PH} = 71$ Hz).

(10) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962–5964.

(11) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210–3222.

(12) Wood, C. D. Ph.D. Thesis, MIT, 1979; unpublished results.

(13) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171–176.

(14) In the $^{13}C\{^1H\}$ NMR spectrum, $CCMe_3$ is found at 306.4 ppm (t, $J_{CP} = 8.9$ Hz). The hydride signal was not found in the ^1H NMR spectrum, but coupling to it could be observed in the ^1H-coupled ^{31}P NMR spectrum [28.5 ppm (d, $J_{PH} = 62$ Hz)].

(15) (a) Examples are $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(C_2H_4)(PMe_3)$[15b] and $Ta(CHCMe_3)(C_2H_4)(PMe_3)_2Et$.[15c] (b) Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.*, in press. (c) Fellmann, J. D., unpublished results.

(16) ^1H NMR (ppm, 250 MHz, toluene-d_8): −7.4 (quintet, 1, $^3J_{HP} = 5.9$ Hz, $CHCMe_3$), 1.10 (s, 9, $CHCMe_3$), 1.5 (t, 36, $J_{HP} = 2.4$ Hz, PMe_3). ^{13}C NMR (ppm, 22.93 MHz, toluene-d_8): 25.29 (quartet of quintets, $J_{CH} = 127$ Hz, $J_{CP} = 3.9$ Hz, PMe_3), 34.65 (q, $J_{CH} = 127$ Hz, $CHCMe_3$), 47.57 (s, $CHCMe_3$), 208.8 (dt, $J_{CP} = 7.8$ Hz, $J_{CH} = 69$ Hz, $CHCMe_3$).

(17) Alkylidyne hydride complexes of Mo and W are already known. M. Green reported *trans*-$Mo(\eta^5\text{-}C_5H_5)[P(OMe)_3]_2(H)(CCH_2CMe_3)$.[18a] We have found that the $W(dmpe)_2(C_5H_{10})$ complex mentioned previously[18b] is *trans*-$W(dmpe)_2(CCMe_3)(H)$.[18c]

(18) (a) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795–5796. (b) Clark, D. N.; Schrock, R. R. *Ibid.* **1978**, *100*, 6774–6776. (c) Clark, D. N., to be published.

(19) Camille and Henry Dreyfus Teacher-Scholar, 1978.

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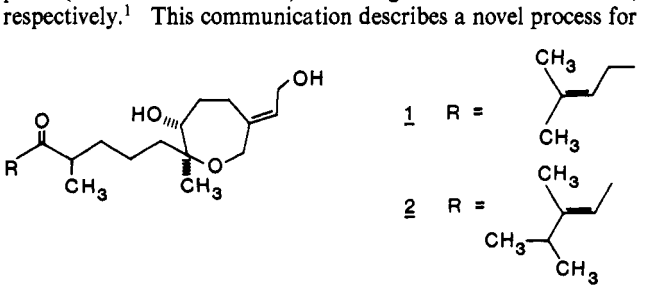
Total Synthesis of (±)-Zoapatanol

Sir:

Zoapatanol and montanol, two novel and biologically active oxepane diterpenoids, were isolated from the leaves of the zoapatle plant (*Montanoa tomentosa*) and assigned structures **1** and **2**, respectively.[1] This communication describes a novel process for

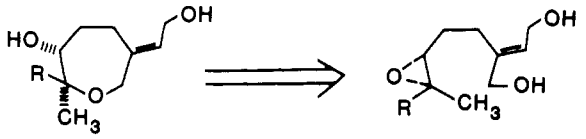


(1) Levine, S. D.; Adams, R. E.; Chen, R.; Cotter, M. L.; Hirsch, A. F.; Kane, V. V.; Kanojia, R. M.; Shaw, C.; Wachter, M. P.; Chin, E.; Huettemann, R.; Ostrowski, P.; Mateos, J. L.; Noriega, L.; Guzmân, A.; Mijarez, A.; Tovar, L. *J. Am. Chem. Soc.* **1979**, *101*, 3404–3405.

0002-7863/80/1502-6609$01.00/0

the construction of an oxepane ring and its application in the total synthesis of (±)-zoapatanol (**1**).[2]

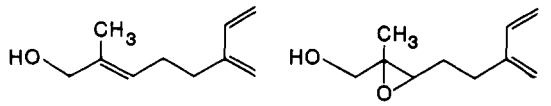
From a retrosynthetic perspective, it appeared that compound **3** would be a suitable intermediate for the synthesis of **1**. It not only allows the introduction of the 2-hydroxyethylidene group at



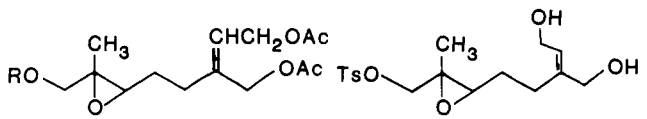
3

an early stage but also presents the possibility of allowing the formation of the 2,3-substituted oxepane ring in a stereospecific fashion.[3]

The readily available 2-methyl-6-methylene-(*E*)-2,7-octadien-1-ol (**4**)[4] upon treatment with *m*-chloroperoxybenzoic acid (1 equiv) in methylene chloride at 0 °C for 2 h afforded the epoxy



4 **5**

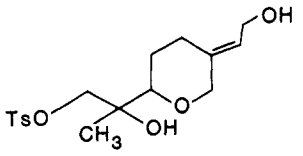


6 R = H
7 R = Ts

8

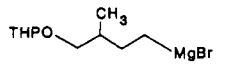
alcohol **5** (85%). Reaction of **5** with bromine (1 equiv) in methylene chloride at 0 °C for 30 min gave the crude dibromide which was treated with potassium acetate (10 equiv) in acetone at reflux for 20 h to form a mixture of diacetate derivatives **6** (25% from **5**, the ratio of *E*/*Z* was ~4:1 by ^{1}H NMR). Treatment of **6** with *p*-toluenesulfonyl chloride (1.1 equiv) and triethylamine (1.1 equiv) at 25 °C for 16 h afforded the corresponding tosylate mixture **7** (80%). Basic hydrolysis (CH_3OH–H_2O–K_2CO_3) of **7** at 25 °C gave pure diol **8** (70%) after workup with magnesium sulfate.[5]

Cyclization of **8** with trifluoroacetic acid (0.1 equiv) in methylene chloride at 0 °C afforded the crystalline pyran derivative **9** (75%, mp 102–105 °C, decomposed) without any trace of an oxepane derivative. This may be due to the electron-withdrawing properties of the tosyl group.[6]

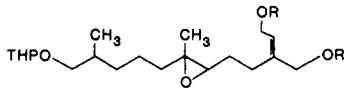


9

Reaction of **8** with Grignard reagent **10**[7] (3.3 equiv) in the presence of a catalytic amount of dilithio tetrachlorocuprate[9] (Li_2CuCl_4) in tetrahydrofuran for 4 h (−20 to 0 °C) gave a



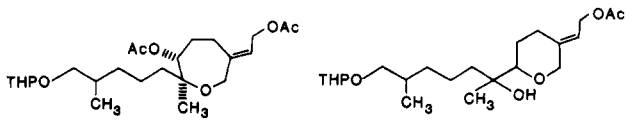
10



11 R = Ac
12 R = H

complex mixture which was treated directly with an excess of acetic anhydride. The desired epoxide (**11**)[10] was obtained in 35% yield after column chromatography on silica gel. Basic hydrolysis of **11** (CH_3OH–H_2O–K_2CO_3) at 25 °C gave the key intermediate **12** (90%).

Cyclization of **12** with trifluoroacetic acid (0.1 equiv) in methylene chloride at 0 °C for 30 min followed by treatment with pyridine and acetic anhydride afforded the desired oxepane **13**[10] (30%) and the pyran derivative **14** (17%) after column chroma-



13 **14**

tography on silica gel.[11] Completion of the synthesis now required transformation of the terminal tetrahydropyran-2-yloxy group of **13** to the desired side chain. This was accomplished by oxidation of **13** with Jones reagent (20 equiv) in acetone–water at 25 °C for 3 h to produce the acid (81%) which was treated with an excess amount of 3-methyl-2-butenyllithium[12] in ether–tetrahydrofuran (2:1) at 0 °C for 1 h to give (±)-zoapatanol (**1**, 30%) after column chromatography on silica gel. The infrared (neat), ^{1}H NMR (60 MHz, $CDCl_3$), and GC–mass spectral data of synthetic **1** were identical with those of the natural product.[13]

(2) The effort described in this paper was initially disclosed in U.S. Patent 4182717, 1980.

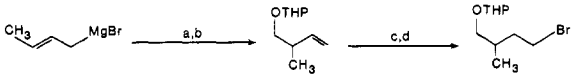
(3) The stereospecific formation of a tetrahydrofuran ring from an appropriate epoxy alcohol has recently been published: Fukuyama, T.; Vranesic, B.; Negri, D. P.; Kishi, Y. *Tetrahedron Lett.* **1978**, 2741–2744.

(4) Büchi, G.; Wüest, H. *Helv. Chim. Acta* **1967**, *50*, 2440–2445.

(5) We have observed that the use of magnesium sulfate as a drying reagent very effectively (>95%) removed the corresponding *Z* isomer.

(6) The corresponding bromide and mesylate also gave the corresponding pyran derivatives exclusively.

(7) Grignard reagent **10** was prepared from the corresponding bromide and magnesium in tetrahydrofuran at room temperature under argon. The bromide, in turn, was prepared in 33% overall yield according to the following scheme.



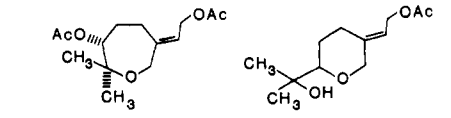
a) HCHO; b) ,TsOH; c) B_2H_6, THF; d) Br_2, $NaOCH_3$

(8) Brown, H. C.; Clinton, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 6660–6661.

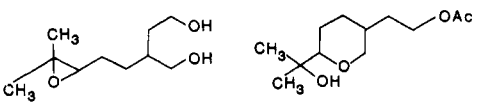
(9) Tamura, M.; Kochi, J. *Synthesis* **1971**, 303–305.

(10) **11**: ^{1}H NMR δ 0.92 (d, *J* = 7 Hz, 3 H), 1.22 (s, 3 H), 2.01 (s, 3 H), 2.04 (s, 3 H), 2.69 (t, *J* = 6 Hz, 1 H), 4.62 (m, 5 H), 5.60 (br t, *J* = 7 Hz, 1 H). **13**: ^{1}H NMR δ 0.93 (d, *J* = 7 Hz, 3 H), 1.18 (s, 3 H), 2.03 (s, 6 H), 4.10 (br s, 2 H), 4.61 (m, 4 H), 5.38 (br t, *J* = 7 Hz, 1 H). Satisfactory infrared, proton magnetic resonance ($CDCl_3$), and mass spectral data were obtained for each synthetic intermediate by using purified and chromatographically homogeneous samples.

(11) The unsaturated model compound **3** (R = CH_3) also gave only two products (i and ii) while the saturated epoxy diol iii afforded pyran iv exclusively under the same conditions.



i ii



iii iv

(12) Birch, A. J.; Corrie, J. E. T.; Subba Rao, G. S. R. *Aust. J. Chem.* **1970**, *23*, 1811–1817.

(13) The stereochemistry of the methyl group α to the ketone has not been determined in the natural product. We assume it possesses the *R* configuration, based on the X-ray crystallographic determination of a derivative of **1**.[1] The synthetic material is a mixture of *R* and *S* at that center, giving a pair of diastereomers.

Acknowledgment. We thank Dr. M. L. Cotter, J. Grodsky, R. Naldi, and W. Farley for the ^1H NMR and IR data and C. Shaw for the mass spectral data. We also thank R. Mallory and E. Deegan for the preparation of several intermediates in large quantities and Professor J. A. Marshall for helpful discussions. We thank Professor K. C. Nicolaou of the University of Pennsylvania for informing us of his successful synthesis of (±)-zoapatanol prior to publication.

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Total Synthesis of (±)-Zoapatanol

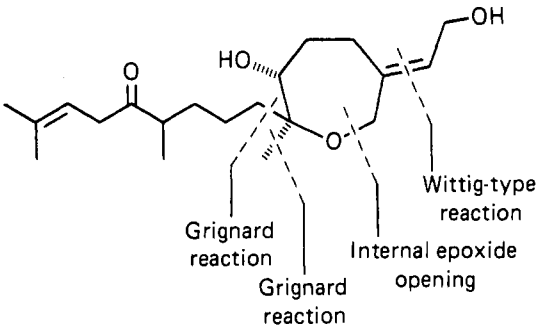
Sir:

In 1979, Levine and his associates[1] reported the isolation and structural elucidation of zoapatanol, one of two novel, oxepane-containing diterpenoids with potent contragestational activity. These biologically active molecules were extracted from the leaves of zoapatle (*Montanoa tomentosa*), a Mexican plant which Mexican women have been using for centuries to prepare "tea", to induce menses and labor, and to terminate early pregnancy. Due to the potential of this new class of compounds for use in human contraception and the novelty of their unique molecular structures, we recently initiated a program directed toward their synthesis. In this communication, we report an efficient and stereocontrolled total synthesis of zoapatanol (Scheme I).

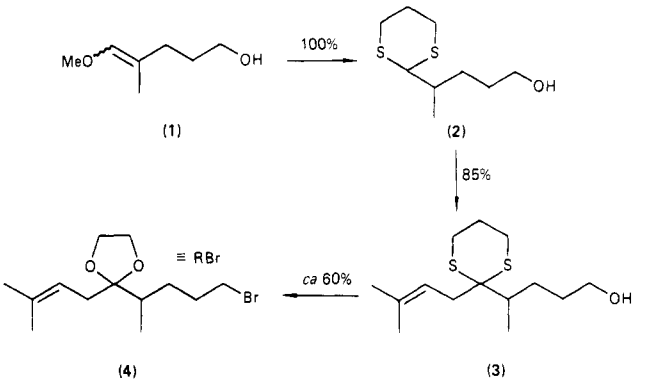
Our synthetic planning was based on the strategic bond analysis of the molecule outlined in Scheme I. Due to the sensitivity of the natural product toward intramolecular-type reactions,[1] our synthesis was designed with the appropriate protections of the three reactive groups and the provision of their liberation under mild conditions at the final stages of the synthesis. Furthermore, our strategy was designed to address the selectivity required to construct (i) the oxepane ring, (ii) the geometrical isomerism of the allylic system, and (iii) the stereochemistry of the two asymmetric centers on the ring system. Since the methyl group adjacent to the carbonyl group in zoapatanol is not defined stereochemically,[1] we were not concerned with its stereochemistry in our initial work.

The long side chain of zoapatanol (as the bromide **4**) was synthesized as illustrated in Scheme II. 5-Hydroxy-2-pentanone on reaction with excess (methoxymethyl)triphenylphosphorane furnished the methoxy enol ether **1**[2] (mixture of geometrical isomers, 75% yield) which was directly converted to the dithiane

Scheme I. Strategic Bond Analysis of Zoapatanol



Scheme II. Synthesis of the Side Chain of Zoapatanol



derivative **2** under standard conditions [$HS(CH_2)_3SH$, HCl gas, $CHCl_3$, 0–25 °C] in quantitative yield. Alkylation of **2** as its dianion (2.2 equiv of *n*-BuLi–THF, −78 → −15 °C) with 1-bromo-3-methyl-2-butene (1.1 equiv, −78 → −15 °C) proceeded smoothly to afford **3** in 85% yield. The conversion of **3** to the required bromide **4** was accomplished in ca. 60% overall yield by the following sequence of reactions: (1) acetylation [1.5 equiv of Ac_2O, 2 equiv of pyridine, 0.05 equiv of 4-(dimethylamino)-pyridine (DMAP), CH_2Cl_2, 0 °C], (2) removal of the dithiane group (2.2 equiv of $HgCl_2$, 2.2 equiv of $CaCO_3$, MeCN–H_2O, reflux), (3) ethylene ketal formation ($HOCH_2CH_2OH$, TsOH, benzene, reflux), (4) deprotection of the hydroxyl group (LAH, ether, 0 °C), and (5) bromide formation (1.3 equiv of CBr_4, 1.35 equiv of PPh_3, CH_2Cl_2, −40 → 0 °C).

Having secured a pathway to the side chain of zoapatanol, we turned our attention to the construction of the natural product itself according to Scheme III. Reaction (−78 → 25 °C, 6 h) of glycidol tetrahydropyranyl (THP) ether **5** (1 equiv) with the dilithio reagent derived from 2-methyl-2-propen-1-ol[4] (1.5 equiv), *n*-BuLi (3 equiv in hexane), and TMEDA[5] (3 equiv) (−78 → 25 °C, 12 h) afforded the diol **6** in 80% yield. Sequential protection of the primary (1.1 equiv of Ph_2-*t*-BuSiCl, 1.5 equiv of Et_3N, 0.04 equiv of DMAP, CH_2Cl_2, 25 °C, 88%)[6] and secondary (3 equiv of $PhCH_2OCH_2Cl$, 6 equiv of *i*-Pr_2EtN, CH_2Cl_2, 25 °C, 85%) alcohols proceeded with high selectivity and efficiency to furnish the triol derivative **7**, in which the three hydroxy groups are distinguished by protection and can be generated individually as they are needed in the synthesis. Thus, mild acid (AcOH–THF–H_2O, 3:2:2, 45 °C, 6 h) treatment of **7** removed only the tetrahydropyranyl ether, leading, after oxidation (9 equiv of SO_3·pyridine complex, 20 equiv of Et_3N, Me_2SO, 25 °C),[7] to the aldehyde **8** (95% overall yield from **7**). Incorporation of the long side chain of zoapatanol was accomplished at this point by coupling the Grignard reagent (RMgBr) derived from bromide **4** (1 equiv) (Mg, THF, 25 °C) with the aldehyde **8** at −78 °C to give a secondary alcohol (mixture of four diastereoisomers, 80% yield)

(1) Levine, S. D.; Adams, R. E.; Chen, R.; Cotter, M. L.; Hirsch, A. F.; Kane, V. V.; Kanojia, R. M.; Shaw, C.; Wachter, M. P.; Chin, E.; Huettemann, R.; Ostrowski, P.; Mateos, J. L.; Noriega, L.; Guzmán, A.; Mijarez, A.; Tovar, L. *J. Am. Chem. Soc.* **1979**, *101*, 3402.

(2) All new compounds exhibited satisfactory infrared, proton magnetic resonance, and mass spectroscopic data. Yields refer to isolated chromatographically homogeneous materials.

(3) ^1H NMR spectral data (250 MHz, $CDCl_3$) **11**: τ 2.63 (m, 5 H, benzenoid), 4.82 (br t, J = 7.5 Hz, 1 H, olefinic CH), 4.94, 5.12 (br s, 1 H each, olefinic CH_2), 5.05, 5.22 (d, J = 7 Hz, 1 H each, OCH_2O), 5.26, 5.37 (d, J = 12 Hz, 1 H each, benzylic), 5.92, 5.95 (s, 1 H each, CH_2OH), 6.06 (m, 4 H, OCH_2CH_2O), 6.65 (dd, J = 8, 3 Hz, 1 H, CHO), 6.79, 6.82 (s, 0.5 H each, OH), 7.67 (d, J = 7.5 Hz, 2 H, $Me_2C{=}CHCH_2$), 8.29, 8.37 (s, 3 H each, vinyl CH_3), 8.86, 8.89 (s, 1.5 H each, *tert*-CH_3), 9.07, 9.09 (d, J = 7 Hz, 1.5 H each), 7.60–9.00 (m, 12 H, CH, CH_2, OH). **14**: τ 2.66 (m, 5 H, benzenoid), 4.84 (br t, J = 7 Hz, 1 H, olefinic), 5.15, 5.24 (d, J = 7 Hz, 1 H each, OCH_2O), 5.38 (s, 2 H, benzylic), 5.84, 6.02 (d, J = 18 Hz, 1 H each, $OCH_2C{=}O$), 6.07 (m, 4 H, OCH_2CH_2O), 6.34 (dd, J = 8, 3 Hz, 1 H, CHO), 7.36 (m, 2 H, $CH_2C{=}O$), 7.66 (d, J = 7 Hz, allylic), 8.29, 8.38 (s, 3 H each, vinyl CH_3), 8.81 (s, 3 H, *tert*-CH_3), 9.05 (d, J = 7 Hz, 3 H, *sec*-CH_3), 7.82–9.00 (m, 9 H, CH, CH_2). **17**: τ 4.53 (t, J = 7 Hz, 1 H, $=CHCH_2OH$), 4.69 (t, J = 7 Hz, 1 H, $(CH_3)_2C{=}CH$), 5.80 (d, J = 7 Hz, 2 H, CH_2OH), 5.87 (s, 2 H, $OCH_2C{=}$), 6.45 (dd, J = 8, 4 Hz, 1 H, CHOH), 6.84 (d, J = 7 Hz, 2 H, $=CHCH_2$), 7.33–7.85 (m, 3 H, $O{=}CCH$, $CH_2CH_2C{=}$), 8.23, 8.35 (s, 3 H each, vinyl CH_3), 8.83, 8.84 (s, 1.5 H each, *tert*-CH_3), 9.01 (d, J = 7 Hz, 3 H, *sec*-CH_3), 8.10–9.00 (m, 10 H, CH, CH_2, OH).

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