99.5% purity as determined on a gas chromatograph. The benzene and tetrahydrofuran solvents were spectroscopically pure and were used without further purification. The chlorobenzene solvent was purified by double distillation. VPC analyses were done on 6 ft × 0.25 in. copper columns of 10% SE-30, 7% SE-30 and 3% Carbowax 20M, and 10% Carbowax 20M. The *N*-iodosuccinimide was determined to have 98.5–99.5% active iodine and was used as purchased. Irradiation of reaction mixtures was effected with a GE Projector Spot 150-W, 130-V tungsten lamp.

Oxidation of α-Hydroxy-α-methylbutyric Acid with NIS and Irradiation. A mixture of 0.0726 g (0.615 mmol) of α-hydroxy-α-methylbutyric acid, 0.2448 g (1.088 mmol) of NIS, and 5 mL of chlorobenzene was irradiated and stirred. Reaction times and percentage yields were as follows: 10 min (96%), 30 min (94%), 40 min (96%).

Oxidation of α-Hydroxy-α-methylbutyric Acid with NIS in the Dark at Ambient Temperatures. A mixture of 0.0752 g (0.637 mmol) of α-hydroxy-α-methylbutyric acid, 0.2532 g (1.125 mmol) of NIS, and 5 mL of chlorobenzene was stirred in the dark for 25 h. Reaction times and percentage yields were as follows: 1 h (34%), 3 h (71%), 6 h (88%), 7 h (99%), 24 h (104%), 25 h (103%).

Oxidation of Mandelic Acid with NIS and Irradiation. Determination of I_2 and CO_2 Percentages. Mandelic acid (6.506 g, 0.0428 mol) and 20 mL of diphenyl ether were placed in a 50-mL round-bottomed flask. NIS (6.2308 g, 0.0277 mol) was weighed in another flask. Both flasks were placed on a vacuum rack, and the system was evacuated. The chemicals were mixed, stirred, and irradiated for 20 min. Analyses gave a 99% yield of iodine and a 99% yield of carbon dioxide with a molecular weight of 43.8 g/mol. Mass spectrometer analysis of the carbon dioxide indicated a purity of 99.9%.

Iodine Determination. The iodine produced in the oxidation of α-hydroxy carboxylic acids with NIS was determined by adding reaction mixtures to 25 mL of a 1:1 mixture of acetic acid and water. Several drops of concentrated hydrochloric acid were added, and the iodine was titrated with a standardized solution of thiosulfate. The iodine was found in 85–99% yield, assuming that 1 mol of iodine is produced from 2 mol of NIS.

Succinimide Determination. Succinimide was recovered from the completed reactions by pouring the reaction mixtures into diethyl ether and extracting the ether solution with water. The combined water extracts were washed with fresh ether, and the water solution was evaporated. Succinimide was recovered in 80–98% yields.

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Registry No. 1, 90-64-2; 2, 516-12-1; α-hydroxy-α-methylbutyric acid, 3739-30-8; α-hydroxyisobutyric acid, 594-61-6; α-ethyl-α-hydroxybutyric acid, 3639-21-2; α-isopropylmandelic acid, 15879-60-4; benzilic acid, 76-93-7; phenyllactic acid, 156-05-8.

Synthesis of Benzhydryl Ethers by a C–C-Forming Reaction Using Benzhydryl 2-Chloroethyl Ether. A Method for Attaching a Protected 2-Hydroxyethyl Group to a Benzylic Carbon

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The established preparative route to an alcohol like $Ph_3CCH_2CH_2OH$, for example, involves a rather lengthy synthesis[1,2] (eq 1). The obvious organometallic route to

$$Ph_3COH \xrightarrow{CH_2(CO_2H)_2} Ph_3CCH_2CO_2H \rightarrow Ph_3CCH_2CH_2OH \quad (1)$$

triphenylpropanol, i.e., reaction of Ph_3CLi and ethylene oxide, fails to give the expected product. The reason is that the charge-delocalized organolithium reagents may exhibit reactivities toward ethylene oxide comparable to those of lithium alkoxides. Therefore, on addition of ethylene oxide to a reagent like Ph_3CLi, two competing reactions take place, namely, addition of the carbanion to the oxirane linkage and poly- or oligomerization of ethylene oxide by the catalytic action[3] of the alkoxide $Ph_3CCH_2CH_2OLi$. Perhaps, this is the reason that reactions of charge-delocalized organometallics with ethylene oxide have attracted the interest of polymer scientists.[4] One method[5] claims an ca. 50% yield of 3-(2-pyridyl)-propanol from 2-picolyllithium and ethylene oxide, which is not impressive.

Our need for a number of propanols with aryl substituents in the 3-position prompted us to search for a more convenient method of preparation. We chose to study the coupling between charged-delocalized organolithium reagents with benzhydryl 2-chloroethyl ether, 1. The reasons for choosing 1 are its ready availability[6] and the ease with which benzhydryl ethers can be cleaved or solvolyzed.[7] An additional reason was that benzhydryl ethers themselves constitute an interesting class of organic compounds from both synthetic[8] and mechanistic[9] standpoints.

Charge-delocalized organolithiums like tritylllithium, for example, react very readily with 1 and give the expected coupling product (eq 2). The yields, which ranged from

$$Ph_3CLi + ClCH_2CH_2OCHPh_2 \xrightarrow[90\%]{THF} Ph_3CCH_2CH_2OCHPh_2 \quad (2)$$

fair to excellent, are summarized, along with other relevant data, in Table I. Butyllithium does not couple with 1 in the presence of THF. This probably indicates that the charge-delocalized organolithiums behave as strong nucleophiles,[10] a contrasting feature to the simple alkyllithiums which, most probably, react by a SET mechanism.[11] Despite the simple structure of the benzhydryl ethers in Table I, all were previously unknown. This, perhaps, indicates the synthetic value of the present method. Noteworthy could be the ability of the method to

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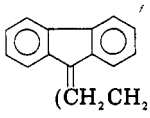
Table I. Benzhydryl Ethers Prepared by Coupling of Benzhydryl 2-Chloroethyl Ether with Various Benzylic Organolithium Reagents[a]

entry	reagent	product	% yield	mp or bp (mmHg), °C	NMR data[p]
1	$PhCH_2Li$	$Ph(CH_2)_3OCHPh_2$[b]	80.5	155-160 (0.05)	1.92, m, 2 H (CCH_2C); 2.72, dist t, 2 H (CH_2O); 3.44, dist t, 2 H ($PhCH_2$); 5.29, s, 1 H (PhCHO); 7.23, d, 15 H (3 Ph)
2	$2\text{-}PyCH_2Li$	$2\text{-}Py(CH_2)_3OCHPh_2$[c]	72	180-190 (0.2)	2.07, m, 2 H (CCH_2C); 2.91, dist t, 2 H (CH_2O); 3.48, dist t, 2 H ($PyCH_2$); 5.30, s, 1 H (PhCHO); 7.29, s-like m, 13 H (arom) 8.52, s-like d, 1 H (6-pyridyl)
3	$4\text{-}PyCH_2Li$	$4\text{-}Py(CH_2)_3OCHPh_2$[d]	52	liquid (high bp)	1.88, m, 2 H (CCH_2C); 2.66, dist t, 2 H (CH_2O); 3.40, dist t, 2 H ($PyCH_2$); 5.27, s, 1 H (PhCHO); 6.99, d, 7.27, s-like m, 12 H (arom); 8.42, br s, 2 H (2,6-pyridyl)
4	Ph_2CHLi	$Ph_2CH(CH_2)_2OCHPh_2$[e]	87	70-72 (MeOH)	2.34, q, 2 H (CCH_2C); 3.37, dist t, 2 H (CH_2O); 4.18, dist t, 1 H (PhCHC); 5.19, s, 1 H (PhCHO); 7.25, d-like, 20 H (4 Ph)
5	9-flLi[o]	 $(CH_2CH_2OCHPh_2)_2$	75	106.5-108 (hexane)	2.40, dist t, 4 H (CCH_2C); 2.86, dist t, 4 H (CH_2O); 4.89, s, 2 H (PhCHO); 7.11, 7.57, centers of m, 28 H (arom)
6	$2\text{-}Py(Ph)CHLi$	$2\text{-}Py(Ph)CH(CH_2)_2OCHPh_2$[g]	61	viscous liquid	2.50, m, 2 H (CCH_2C); 3.39, dist t, 2 H (CH_2O); 4.34, dist t, 1 H (PyCH); 5.21, s, 1 H (PhCHO); 7.29, s, 18 H (arom); 8.53, s-like d, 1 H (6-pyridyl)
7	$4\text{-}Py(Ph)CHLi$	$4\text{-}Py(Ph)CH(CH_2)_2OCHPh_2$[h]	77	66-67 (hexane)	2.35, dist q, 2 H (CCH_2C); 3.37, dist t, 2 H (CH_2O); 4.20, dist t, 1 H (PyCH); 5.21, s, 1 H (PhCHO); 7.25, d-like, 17 H (arom) 8.48, d-like, 2 H (2,6-pyridyl)
8	Ph_3CLi	$Ph_3C(CH_2)_2OCHPh_2$	90	130-131 (C_6H_6-MeOH)	3.15, m, 4 H (CH_2CH_2); 5.09, s, 1 H (PhCHO); 7.21, s-like d, 25 H (5 Ph)
9	$Ph(SPh)CHLi$	$Ph(SPh)CH(CH_2)_2OCHPh_2$[i]	100	viscous liquid	2.24, m, 2 H (CCH_2C); 3.45, m, 2 H (CH_2O); 4.44, t-like q, 1 H (PhCHS); 5.19, s, 1 H (PhCHO); 7.23, d-like, 20 H (4 Ph)
10	$Ph_2C(SPh)Li$	$Ph_2C(SPh)(CH_2)_2OCHPh_2$[j]	93	136-137.5 (C_6H_6-hexane)	2.55, dist t-like q, 2 H (CCH_2C); 3.53, dist t-like q, 2 H (CH_2O); 5.17, s, 1 H (PhCHO); 7.27, d-like, 25 H (5 Ph)
11	$Ph_2(CN)CLi$	$Ph_2C(CN)(CH_2)_2OCHPh_2$[k]	68	109-111 (C_6H_6-hexane)	2.77, dist t, 2 H (CCH_2C); 3.58, dist t, 2 H (CH_2O); 5.24, s, 1 H (PhCHO); 7.29, dist d-like, 20 H (4 Ph)
12	$(Ph_2CO)^{2-}Li_2^{2+}$	$Ph_2C(OH)(CH_2)_2OCHPh_2$[l]	60	97-98 (EtOH)	2.60, dist t, 2 H (CCH_2C); 3.55, dist t, 2 H (CH_2O); 4.75, s, 1 H (OH), 5.13, s, 1 H (PhCHO); 7.21, s, 20 H (5 Ph)
13	$PhCH(CO_2Li)Li$	$PhCH(CO_2H)(CH_2)_2OCHPh_2$[m]	86	118-120.5 (EtOH)	2.24, m, 2 H (CCH_2C); 3.39, m, 2 H (CH_2O); 3.87, dist t, 1 H (PhCHCO); 5.23, s, 1 H (PhCHO); 7.19, s, 15 H (3 Ph); 10.15, s, (acidic)
14	$Ph_2C(CO_2Li)Li$	$Ph_2C(CO_2H)(CH_2)_2OCHPh_2$[n]	52	129-131 (EtOH)	2.79, dist t, 2 H (CCH_2C); 3.28, dist t, 2 H (CH_2O); 5.14, s, 1 H (PhCHO); 7.24, d-like, 20 H (4 Ph); 10.20, s, 1 H (acidic)

[a] All benzhydryl ethers in the table gave satisfactory elemental analyses for C and H. The microanalyses were performed by the Microanalytical Laboratory of NHRF, Athens, Greece. [b] 1 added to an excess of $PhCH_2Li$ at −50 ± 20 °C, stirring for 0.5 h at room temperature. [c] Overnight at room temperature. [d] Overnight at room temperature. An unidentified crystalline product also formed. [e] 3 h at room temperature. [f] 1 added to 9-fluorenyllithium at 0-5 °C, 24 h at room temperature. [g] 18 h at 60 °C. [h] 18 h at 60 °C. Product purified by repeated precipitations, as an oil, from ether by adding hexane. [i] Overnight at room temperature. [j] 48 h at room temperature. [k] 48 h at 40-45 °C. [l] 3 h at room temperature. [m] 48 h at room temperature. Although spectral and other data have been reported for this compound, its synthesis is reported for the first time in this paper. Lit.[13] mp 100-102 °C. [n] 40 h at 45-50 °C. [o] Fluorenyl, fl. [p] Distorted doubletlike multiplet = "dist d-like m".

afford benzhydryl ethers containing an additional functional group such as OH, SPh, CO_2H (see entries 9–10, 12–14, Table I).

Most of the benzhydryl ethers reported here could be hydrolyzed to the respective alcohols by acid catalysis in aqueous dioxane (eq 3). Under the above-mentioned

$$RCH_2CH_2OCHPh_2 + H_2O \xrightarrow[100\%]{H^+} RCH_2CH_2OH + Ph_2CHOH \quad (3)$$

$$R = PhCH_2,\ Ph_2CH,\ Ph_3C,\ 4\text{-}PyCH_2,\ PhCH(CO_2H),\ 2\text{-}PyCH_2$$

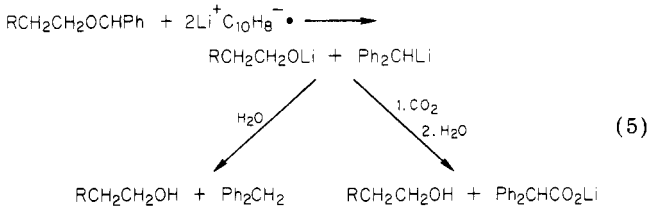
conditions the ether $Ph_2C(OH)CH_2CH_2OCHPh_2$, which contains the acid-labile functionality $Ph_2C(OH)$, underwent fragmentation.

Considerably more facile appeared to be the phenylthiolysis[12] of the Ph_2CHO group. In this reaction the benzhydryl group is transformed to the corresponding sulfide, according to eq 4. Again, the method is applicable to solvolysis of benzhydryl ethers without an acid-labile functional group.

$$RCH_2CH_2OCHPh_2 + PhSH \xrightarrow[100\%]{H^+} RCH_2CH_2OH + Ph_2CHSPh \quad (4)$$

R = as in eq 3, PhCH(SPh)

Lithium naphthalene radical anion, or lithium metal in THF under naphthalene catalysis,[13] was found to be a convenient method for cleaving benzhydryl ethers. In this case the benzhydryl group is converted to (diphenylmethyl)lithium. The latter can be transformed either to diphenylmethane on hydrolysis or to lithium diphenylacetate on carbonation. One then can choose between the two alternatives, guided by the convenience in the product isolation step (eq 5).



(5)

The benzhydryl ether $Ph_2C(OH)CH_2CH_2OCHPh_2$, which is not compatible with the reagents and the conditions of eq 3–5, was found to undergo a smooth catalytic hydrogenolysis (eq 6).

$$Ph_2C(OH)CH_2CH_2OCHPh_2 \xrightarrow{Pd/C,\ H_2} Ph_2C(OH)CH_2CH_2OH + Ph_2CH_2 \quad (6)$$

Experimental Section

Proton nuclear magnetic resonance spectra were recorded with a Varian FT-80 NMR spectrometer. Chemical shifts are reported in parts per million downfield from Me_4Si as follows: ppm, multiplicity, coupling constant, number of protons, and the segment to which the hydrogens are attached. The solvent used for the NMR spectra was $CDCl_3$.

Boiling points and melting points are reported uncorrected. The latter was obtained in open capillaries with a Büchi apparatus.

The various chemicals and solvents used were purchased from Merck or Fluka. THF was purified as described previously.[14] 1 was prepared according to the method in "Organic Syntheses".[6] $PhCH_2SPh$ was prepared from thiophenol and benzyl chloride in aqueous NaOH, and Ph_2CHSPh was prepared by a published procedure.[12] Benzyllithium,[15] PhCH(Li)SPh,[16] $Ph_2C(Li)SPh$,[13] and picolyllithium[17] were prepared according to published methods.

Reactions of air-sensitive reactants and/or products were carried out under an atmosphere of argon.

Exemplary Runs. Benzhydryl 3,3,3-Triphenylpropyl Ether. To a mixture of 12.2 g (50 mmol) of Ph_3CH and 50 mL of THF was added with cooling (dry ice and acetone bath) 40 mL (68 mmol) of 1.70 M BuLi in benzene. The reaction flask was surrounded with ice and the mixture was stirred at 0 °C for several hours and then at room temperature overnight. A solution of 12.5 g (50 mmol) of 1 in ca. 15 mL of THF was added to the trityllithium; and the reaction was allowed to proceed overnight. The reaction mixture was diluted with 50 mL of benzene and hydrolyzed. The organic layer was washed with water, dried over $MgSO_4$, and evaporated to constant weight, after removal of the drying agent. The product, after one recrystallization from benzene methanol, weighed 20.5 g, 90%, mp 127–130 °C. The pure ether had a melting point of 130–131 °C. See entry no. 8 in Table I for NMR data.

Hydrolysis of Benzhydryl 3-Phenylpropyl Ether. A 1.2-g sample of benzyhydryl 3-phenylpropyl ether was refluxed for 2 h with water (15 mL), dioxane (60 mL), and 70% perchloric acid (3 mL). The reaction mixture was diluted with water and extracted 3 times with 50-mL portions of benzene. The combined extracts were dried over $MgSO_4$ and evaporated to constant weight after removal of the drying agent. The product (1.3 g) was found by NMR analysis to be a mixture of Ph_2CHOH and 3-phenylpropanol: NMR δ 1.46 (br s, OH), 1.80 (m, CCH_2C), 2.63 (t-like q, CH_2O), 3.57 (dist t, $PhCH_2$), 5.75 (s, PhCHOH), 7.29 (d-like m, arom).

Phenylthiolysis of Benzhydryl 3,3-Diphenylpropyl Ether. Trifluoroacetic acid (2 mL) was added at once to a mixture of 1.9 g (5 mmol) of benzhydryl 3,3-diphenylpropyl ether and 1.0 mL of thiophenol. The resulting mixture within 1 min or less turned into a solid mass. Methylene chloride (10 mL) was added to the solid mixture and the resulting solution was stirred for 0.5 h at room temperature. More CH_2Cl_2 (50 mL) was added and the solution was washed with water, NaOH solution, water, and dried over $MgSO_4$. The drying agent was filtered off, and on evaporation to dryness, the filtrate left 2.6 g of a mixture of Ph_2CHSPh and 3,3-diphenylpropanol. A 1.5-g portion of this material was applied on a column of 50 g of neutral alumina. The sulfide was eluted twice with 100-mL portions of hexane–benzene (50:50, v/v): 0.80 g, mp 74 °C (lit.[18] 78 °C). Diphenylpropanol was eluted twice with 100-mL portions of $CHCl_3$–CH_3OH (90:10, v/v): 0.69 g, mp 20–22 °C (pentane); lit.[2] bp 185 °C (10 mmHg); NMR δ 2.20 (dist q, 2 H, CCH_2C), 2.52 (br s, 1 H, OH), 3.44 (dist t, 2 H, CH_2O), 4.04 (dist t, 1 H, PhCHC), 7.17 (s, 10 H, 2 Ph).

Cleavage of Benzhydryl 3,3,3-Triphenylpropyl Ether with Lithium in THF. A 2.3-g sample benzhydryl 3,3,3-triphenyl ether (ca. 5 mmol) was stirred under an atmosphere of argon with 0.140 g (20 mmol, 100% excess) of lithium chips and 10 mL of THF containing 43 mg of naphthalene. After 5 min the mixture turned yellow and then rapidly orange-red. Stirring was continued overnight. Anhydrous THF (10 mL) was added and the diluted reaction mixture was carbonated by siphoning it into a mixture of crushed dry ice and ether. Usual workup of the carbonation mixture afforded 1.05 g (100%) of Ph_2CHCO_2H, mp 125–137 °C [after one recrystallization from ethanol, mp 146–148 °C (lit.[19] mp 148 °C)]. From the neutral fraction of the carbonation mixture was isolated 1.2 g (83%) of crude 3,3,3-triphenylpropanol, mp 80–100 °C. Recrystallization from hexane improved the melting point to 105–108 °C (lit.[1b] mp 108.5–110 °C): NMR δ 1.37 (br s, 1 H, OH), 2.90 (dist t, B_2 part of an A_2B_2 system, 2 H, CCH_2C), 3.49 (dist t, A_2 part of the A_2B_2 system, 2 H, CH_2O), 7.24 (s, 15 H, 3 Ph).

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Registry No. 1, 32669-06-0; $PhCH_2Li$, 766-04-1; 2-$PyCH_2Li$, 1749-29-7; 4-$PyCH_2Li$, 26954-25-6; Ph_2CHLi, 881-42-5; 9-FlLi, 881-04-9; 2-Py(Ph)CHLi, 56501-99-6; 4-Py(Ph)CHLi, 81771-00-8; Ph_3CLi, 733-90-4; Ph(SPh)CHLi, 41979-02-6; $Ph_2C(SPh)Li$, 81771-01-9; $Ph_2(CN)CLi$, 66785-30-6; $(Ph_2CO)^{2-}Li_2^{2+}$, 34510-08-2; PhCH-$(CO_2Li)Li$, 56842-55-8; $Ph_2(CO_2Li)Li$, 60538-71-8; $Ph(CH_2)_3OCHPh_2$, 42113-39-3; 2-$Py(CH_2)_3OCHPh_2$, 81771-02-0; 4-$Py(CH_2)_3OCHPh_2$, 81771-03-1; $Ph_2CH(CH_2)_2OCHPh_2$, 81771-04-2; 9-Fl-$(CH_2CH_2OCHPh_2)_2$, 81771-05-3; 2-Py(Ph)$CH(CH_2)_2OCHPh_2$, 81771-06-4; 4-Py(Ph)$CH(CH_2)_2OCHPh_2$, 81771-07-5; Ph_3C-$(CH_2)_2OCHPh_2$, 81771-08-6; Ph(SPh)$CH(CH_2)_2OCHPh_2$, 68602-18-6; $Ph_2C(SPh)(CH_2)_2OCHPh_2$, 81771-09-7; $Ph_2C(CN)(CH_2)_2OCHPh_2$, 81771-10-0; $Ph_2C(OH)(CH_2)_2OCHPh_2$, 81771-11-1; $PhCH(CO_2H)$-$(CH_2)_2OCHPh_2$, 81771-12-2; $Ph_2C(CO_2H)(CH_2)_2OCHPh_2$, 81771-13-3; Ph_2CHOH, 91-01-0; 3-phenylpropanol, 122-97-4; 1,1′-[(phenylthio)methylene]bisbenzene, 21122-20-3; diphenylpropanol, 20017-67-8; diphenylacetic acid, 117-34-0; 3,3,3-triphenylpropanol, 15070-88-9.

Crystal Structure and Stereochemistry of Florigrandin[1]

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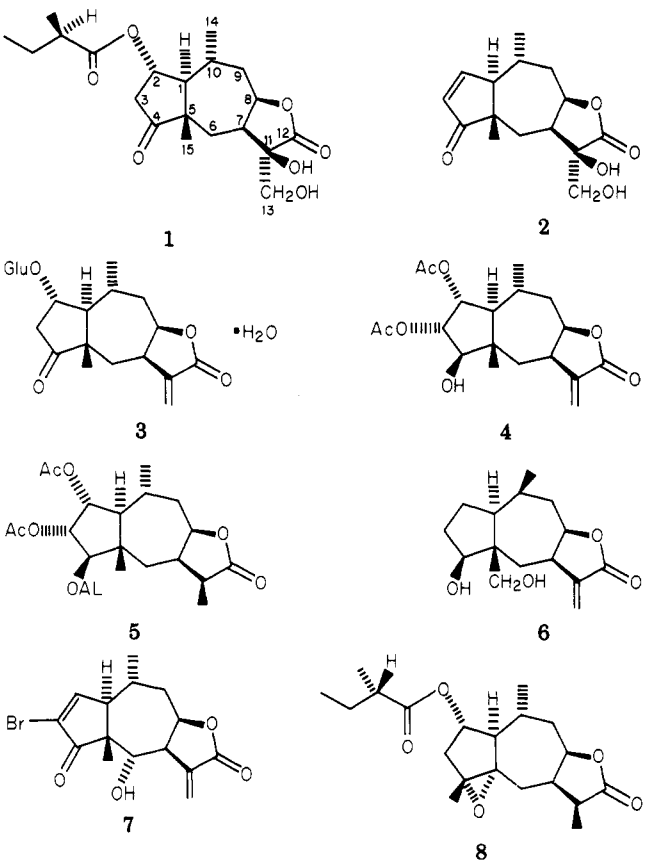
In a recent note[2] we discussed the problems associated with determining the C-11 stereochemistry of sesquiterpene lactones in which the α-methylene γ-lactone function is oxidized to an 11,13-diol. Two such compounds are the pseudoguaianolides florigrandin and hymenoflorin from *Hymenoxys grandiflora*.[3] The relative and absolute stereochemistry shown in formulas 1 and 2 for C-1, C-2 (for florigrandin), C-5, C-7, C-8, and C-10 has been established,[3] but attempts to use various chiroptical methods for solving the C-11 stereochemistry failed[3,4] and the configuration of the 2-methylbutyrate ester side chain of florigrandin remained unknown.

To settle these matters and to continue our study of the conformations of different types of sesquiterpene lactones, we undertook an X-ray analysis of florigrandin. Crystal data for florigrandin are listed in the Experimental Section. Figure 1a is a stereoscopic drawing of the molecule which shows that the C-11 hydroxyl group is β and that the earlier[3] stereochemical assignments for the other asymmetric centers were correct. Since β elimination of the five-carbon ester side chain results in conversion of florigrandin to hymenoflorin, the stereochemistry of the latter compound is thereby established as well. Figure 1a also represents the absolute configuration because of the negative Cotton effect due to the cyclopentenone chromophore of **2**. Hence the configuration of the 2-methylbutyrate ester side chain is *R*.



Tables I–IV listing final atomic and final anisotropic thermal parameters, bond lengths, and bond angles are available as supplementary material. Table V lists selected torsion angles. As is apparent from these and from Figure 1a and the framework model **1b**, the cycloheptane ring closely approximates a twist boat, whose C_2 axis passes through C-10 and the midpoint of the C-6,C-7 bond. Σ_2, the deviation of the ring from C_2 symmetry,[5] is only 11°. The two five-membered rings are attached to the cycloheptane ring in the C-5(e), C-1(e), and the C-7(e), C-8(e) positions, respectively. The cyclopentanone and the lactone rings are very slightly distorted envelopes with C-5 and C-7 as the respective flaps.

The conformation of the cycloheptane ring of florigrandin is very similar to the conformations found in the C-8 cis-lactonized pseudoguaianolides paucin monohydrate (**3**),[6] hymenograndin (**4**),[7] hymenolane (**5**),[8] and rudmollin (**6**)[9] but different from the conformation found in bromohelenalin (**7**), which approximates a twist chair.[10] Apparently the presence or absence of unsaturation in the cyclopentane ring is of some importance, whereas saturation of the α-methylene γ-lactone ring exercises little influence on the conformation of the seven-membered ring. For reasons that are not immediately apparent, the cyclopentanone ring of paucin monohydrate (**3**), which in all other respects very closely resembles florigrandin, is a half-chair rather than an envelope.[6] It is also noteworthy

(1) Work at the Florida State University was supported in part by a grant from the U.S. Public Health Service (CA-13121) through the National Cancer Institute.

(2) Herz, W.; Blount, J. F. *J. Org. Chem.* **1982**, *47*, 1594.

(3) Herz, W.; Aota, K.; Hall, A. L.; Srinivasan, A. *J. Org. Chem.* **1974**, *39*, 2013.

(4) However, the chemical shift of H-7 in hymenoflorin (2.74 ppm),[3] which indicates little or no deshielding by the C-11 hydroxyl, suggests that the latter is β orientated.

(5) McPhail, A. T.; Sim, G. A. *Tetrahedron* **1973**, *29*, 1751.

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