tone-d_6) δ 1.0 (d, 3 H, CH_3), 1.4–1.9 (br m, 3 H, $CHCH_2COOH$), 2.3 (s, 3 H, Ar CH_3), 2.9 (m, 2 H, SCH_2), 7.3 ($A_2'X'_2$, 4 H, Ar H), 8.3 (s, 1 H, COOH). Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.26; H, 7.19. Found: C, 64.23; H, 7.18.

4-[3,4-(Methylenedioxy)phenyl]butanoic Acid. The organoborane (10 mmol) was carbonylated and oxidized as shown in the general procedure to yield 1.76 g (84%); mp 69–72 °C; ^{13}C NMR (acetone-d_6) δ 175.3; MS, m/e 209 (calcd 209); ^1H NMR (acetone-d_6) δ 2.0 (m, 2 H, $ArCH_2CH_2$), 2.2–2.8 (m, 4 H, $ArCH_2$, CH_2COOH), 5.9 (s, 2 H, OCH_2O), 6.6 (s, 3 H, Ar H), 9.3 (s, 1 H, COOH). Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.46; H, 5.81. Found: C, 63.42; H, 5.99.

Decanol. Decanal (5 mmol) prepared and purified as outlined in the general procedure was reduced with BH_3·THF to yield 0.71 g (90%); 3,5-dinitrobenzoate derivative mp 57.5–58.5 °C (lit.[22] 57.7 °C); ^{13}C NMR (CCl_4) δ 60.1; ^1H NMR (CCl_4) δ 0.9 (br t , 3 H, CH_3), 1.3 (br s, 14 H, aliphatic CH_2), 2.4 (s, 1 H, OH), 3.5 (t, 2 H, CH_2OH).

Cyclohexanemethanol. Cyclohexanecarboxaldehyde (5 mmol) was reeduced with BH_3·THF as described in the general procedure to yield 0.5 g (88%); 3,5-dinitrobenzoate derivative mp 91–92 °C (lit.[23] 94 °C); ^{13}C NMR ($CDCl_3$) δ 54.9; ^1H NMR ($CDCl_3$) δ 1.0–2.0 (br m, 11 H, CH_2, CH), 3.2 (s, 1 H, OH), 3.4 (d, 2 H, CH_2OH).

1,12-Dodecanediol. 12-Hydroxydodecanal (5 mmol) was reduced with BH_3·THF as described in the general procedure to yield 0.94 g (93%); mp 80–81 °C (lit.[24] 80.5–81 °C); 3,5-dinitrobenzoate derivative mp 89–90 °C; ^{13}C NMR (CCl_4) δ 60.3; ^1H NMR (CCl_4) δ 1.3 (br, 20 H, aliphatic CH_2), 3.6 (t, 2 H, CH_2OH).

4-(*p*-Tolylthio)-3-methylbutanol. 4-(*p*-Tolylthio)-3-methylbutanal (5 mmol) was reduced with BH_3·THF as described in the general procedure to yield 0.94 g (90%); 3,5-dinitrobenzoate derivative mp 81.5–82.5 °C; ^{13}C NMR (CCl_4) δ 59.8; ^1H NMR (acetone-d_6) δ 1.0 (d, 3 H, CH_3), 1.3–2.0 (m, 3 H, CH_2CHCH_3), 2.3 (s, 3 H, Ar CH_3), 2.6 (s, 1 H, OH), 2.8 (m, 2 H, SCH_2), 3.6 (t, 2 H, CH_2OH), 7.2 ($A_2'X_2'$, 4 H, Ar H). Anal. Calcd for $C_{19}H_{20}O_6SN_2$: C, 56.43; H, 4.98; N, 6.93. Found: C, 56.26; H, 5.02; N, 6.82.

4-[3,4-(Methylenedioxy)phenyl]butanol. 4-[3,4-(methylenedioxy)phenyl]butanal (5 mmol) was reduced with BH_3·THF as described in the general procedure to yield 0.95 g (98%); 3,5-dinitrobenzoate derivative mp 82–83 °C; ^{13}C NMR (CCl_4) δ 61.7; ^1H NMR ($CDCl_3$) δ 1.5 (m, 4 H, $ArCH_2CH_2CH_2$), 2.4 (m, 2 H, $ArCH_2$), 3.4 (t, 2 H, CH_2OH), 5.8 (s, 2 H, OCH_2O), 6.6 (s, 3 H, Ar H). Anal. Calcd for $C_{18}H_{16}O_8N_2$: C, 55.67; H, 4.15; N, 7.21. Found: C, 55.57; H, 4.02; N, 7.16.

Acknowledgment. We thank the Department of Energy (DE-AS05-90EV10363) for support of this research.

Registry No. 1-Nonene, 124-11-8; cyclohexene, 110-83-8; safrole, 94-59-7; 3-(*p*-tolylthio)-2-methylpropene, 54844-24-5; 10-undecen-1-ol, 112-43-6; decanal-^{13}C, 87803-55-2; cyclohexanecarboxaldehyde-^{13}C, 87803-56-3; 4-[3,4-(methylenedioxy)phenyl]butanal-^{13}C, 87803-57-4; 4-(*p*-tolylthio)-3-methylbutanal-^{13}C, 87803-58-5; 12-hydroxydodecanal-^{13}C, 87803-59-6; decanoic-^{13}C acid, 84600-66-8; cyclohexanecarboxylic-^{13}C acid, 50530-16-0; 4-[3,4-(methylenedioxy)phenyl]carboxylic-^{13}C acid, 84600-67-9; 4-(*p*-tolylthio)-3-methylbutanoic-^{13}C acid, 84600-68-0; 12-hydroxydecanoic-^{13}C acid, 84600-69-1; 1-decanol-^{13}C, 87803-60-9; cyclohexanemethanol-^{13}C, 65305-14-8; 4-[3,4-(methylenedioxy)phenyl]-1-butanol-^{13}C, 87803-61-0; 4-(*p*-tolylthio)-3-methyl-1-butanol-^{13}C, 87803-62-1; 1,12-dodecanediol-^{13}C, 87803-63-2; decanal-^{13}C 2,4-dinitrophenylhydrazone, 87803-64-3; cyclohexanecarboxaldehyde-^{13}C 2,4-dinitrophenylhydrazone, 87803-65-4; 12-hydroxydodecanal-^{13}C 2,4-dinitrophenylhydrazone, 87803-66-5; 4-(*p*-tolylthio)-3-methylbutanal-^{13}C 2,4-dinitrophenylhydrazone, 87803-67-6; 4-[3,4-(methylenedioxy)phenyl]-butanal-^{13}C 2,4-dinitrophenylhydrazone, 87803-68-7; 1-decanol-^{13}C 3,5-dinitrobenzoate, 87803-69-8; cyclohexanemethanol-^{13}C 3,5-dinitrobenzoate, 87803-70-1; 1,12-dodecanediol-^{13}C 3,5-dinitrobenzoate, 87803-71-2; 4-(*p*-tolylthio)-3-methylbutanal-^{13}C 3,5-dinitrobenzoate, 87803-72-3; 4-[3,4-(methylenedioxy)phenyl]butanol-^{13}C 3,5-dinitrobenzoate, 87803-73-4; 9-BBN, 280-64-8.

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Convenient and Stereospecific Synthesis of Deoxy Sugars. Reductive Displacement of Trifluoromethanesulfonates

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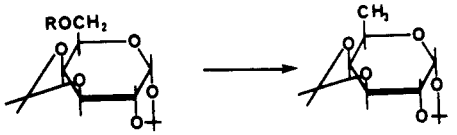
Received July 27, 1983

The replacement of sugar hydroxyls by hydrogen, the preparation of deoxy sugars, is important in natural products chemistry where deoxy sugars are frequently encountered as constituents of these materials. Most of the preparative methods that have been introduced recently involve photolysis[2-4] or other free-radical reactions.[5] Although these latter reactions can be quite stereoselective, they tend not to be stereospecific,[6] and further, they sometimes[5] give poor yields when primary hydroxyls are converted to methyl groups. Deoxygenation via S_N2 reaction by hydride reagents, which would not be subject to the above disadvantages, has seen little use in sugar chemistry because, ordinarily, the inconvenient reagent lithium aluminum hydride is required for the displacements which are limited to the overall conversion of primary hydroxyls to methyl groups; ordinarily activated secondary sugar hydroxyls are too unreactive to be displaced by lithium aluminum hydride but rather suffer O–S cleavage.[7] The introduction into sugar chemistry of the triflate leaving group by Maradufu and Perlin[8] and elaborated by Hall and Miller[9] has provided a leaving group that permits many displacement reactions to be carried out smoothly at secondary sugar carbons,[10,11] and we describe below the reaction of sugar triflates,both primary and secondary, with sodium borohydride which, in many cases, can be carried out under very mild conditions and which can be used, by employing sodium borodeuteride, to stereospecifically introduce deuterium into sugars.

The reaction of the triflate **2**[12] of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (1) gave, with excess sodium borohydride in acetonitrile at room temperature, an excellent yield of the 6-deoxy sugar **3**. By contrast, the



1 R=H
2 R=SO_2CF_3

3

tri-*n*-butylstannane reduction of 6-*O*-(imidazolylthio-

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(12) Curiously, this compound is noted as an intermediate in ref 10, and Hall's manuscript[9] is cited as the first preparation of **2**. However, in ref 9 the attempt to prepare **2**, using pyridine as the acid acceptor, yielded the pyridinium triflate salt derived from 1 in 90% yield. The ^1H NMR spectrum recorded for **2** in ref 10 does not accord with the spectrum we observed for that compound.

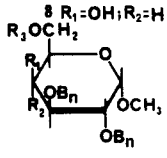
0022-3263/84/1949-0176$01.50/0

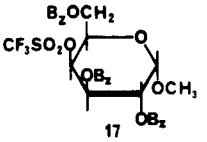
carbonyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose gave 31% of **3** and 57% of **1**.[5]

When the allose triflate **5**[9] was treated under the above conditions, an excellent yield of the 3-deoxy sugar **6** was

4 R_1=OSO_2CF_3; R_2=H
5 R_1=H; R_2=OSO_2CF_3
6 R_1=R_2=H
7 R_1=D; R_2=H
8 R_1=OH; R_2=H

9





10 R_1=H; R_2=OH; R_3=B_n
11 R_1=H; R_2=OSO_2CF_3; R_3=B_n
12 R_1=R_2=H; R_3=B_n
13 R_1=D; R_2=H; R_3=B_n
14 R_1=H; R_2=OH; R_3=B_z
15 R_1=H; R_2=OSO_2CF_3; R_3=B_z
16 R_1=R_2=H; R_3=B_z

obtained. Further, when sodium borodeuteride was used as the displacing agent, a quantitative yield of product was obtained whose ^1H spectrum was in excellent agreement with that presented by Patroni and Stick[6] for the substitution of the exo hydrogen by deuterium; i.e., the product was that of the S_N2 reaction, **7**. Only traces of **6** were present. The proton-decoupled ^{13}C spectrum showed C-3 as a triplet as expected.

The reduction of the glucose triflate **4**[9] pointed up some of the limitations of the process. Compound **4** is much less reactive toward displacement reactions than **5** and is known to be prone to the elimination of triflic acid. Indeed, upon reaction with sodium borohydride, the minor product (15% yield) was **6** accompanied by 23% of the elimination product **9** and 42% of the product of attack at sulfur, compound **8**. This latter type of cleavage is the usual reaction when secondary sugar mesylates and tosylates are reduced with lithium aluminum hydride.[7,13]

The tri-*O*-benzyl sugar **10**[14] was converted to its triflate **11** and subjected to the standard reaction conditions. Again, a quantitative yield of the 4-deoxy sugar **12** was obtained whose ^1H spectrum showed two well-separated one-proton multiplets upfield from the methoxyl singlet. The large couplings of the more upfield multiplet clearly identified it as the axial hydrogen. When the reduction of **11** was repeated with sodium borodeuteride, a good yield of the S_N2 product **13** was obtained. The ^1H and ^{13}C spectra showed the high degree of conversion to **13**; only traces of **12** could be noted in the spectra.

An attempt to apply the reduction to the triflate of a benzoate-blocked sugar, **17**,[15] was not successful. A large number of products were formed according to TLC, probably as a result of elimination and/or deacylation. Attempts to carry out displacements on this triflate with weak nucleophiles (e.g., CN^-) have given similar results.[16] However, the reaction can tolerate *O*-benzoates since the reduction of the triflate **15** of the 6-*O*-benzoyl sugar **14**,[17] where *O*-benzyl groups appear at C-2 and C-3, gave the 4-deoxy sugar **16**. The ^1H spectrum showed almost the identical pattern for the protons at C-4 that was seen in the spectrum of **12**, and the retention of the *O*-benzoyl group was clear.

Aside from the obvious limitations of the reduction that were seen with **4** and **17**, the low rate of the reaction under the conditions used is a disadvantage. Undoubtedly, a higher temperature could be used with most of the compounds without complicating the reduction, and possibly more advantageous solvents could be employed. We effected the reduction in DMF, but solvent removal was troublesome with the oils that were encountered in this work. It is also possible that sodium cyanoborohydride might be a better reducing agent for these triflates than sodium borohydride since that reagent has been used to reduce tosylates under mild conditions.[18]

Experimental Section

General Methods. Melting points were determined with a Meltemp apparatus (Laboratory Devices, Cambridge, MA) and are uncorrected. NMR spectra were recorded with Varian EM-360A (^1H), EM-390 (^1H), and CFT-20 (^{13}C) spectrometers, for solutions in $CDCl_3$ with Me_4Si as an internal standard unless otherwise noted. Chemical shifts are reported in δ units. Optical rotations of 1% solutions in chloroform were measured with a Perkin-Elmer Model 141 automatic polarimeter at the sodium D line (literature citations also refer to the D line). Flash chromatography[19] was performed with Woelm 32-63 silica gel. Thin-layer chromatography (TLC) separations were performed by using Brinkman Polygram SiL G/UV_{254} plates, sometimes employing a short bed/continuous development chamber (Regis, Morton Grove, IL). Spots were detected with UV light or with a 20% aqueous sulfuric acid spray, followed by carbonization. The solvent system used was ethyl acetate/hexane (5/95 to 60/40 v/v) unless otherwise noted. The general workup procedure for most products isolated after acylation was to pour the reaction mixture into ice-cold saturated sodium bicarbonate solution, extract into chloroform or dichloromethane (10–15 mL/g), wash with cold 3 N aqueous hydrochloric acid (often omitted in the triflate preparation), cold saturated sodium bicarbonate, and cold water, and dry over anhydrous magnesium sulfate followed by evaporation in vacuo, generally below 40 °C. Elemental analyses were obtained from Micro-Analysis, Inc. (Wilmington, DE).

1,2:3,4-Di-*O*-isopropylidene-6-*O*-triflyl-α-D-galactopyranose (2). The general procedure of Hall and Miller[9] was employed except that 2,6-dimethylpyridine, rather than pyridine, was used as the acid acceptor. A mixture of 2.72 g (10.45 mol) of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**1**) and 1.85 mL (15.88 mmol) of dry 2,6-dimethylpyridine in 40 mL of dry dichloromethane was treated with 2.50 mL (14.86 mmol) of triflic anhydride. A conventional workup gave 3.40 g (83%) of product, recrystallization of which from hexane gave colorless crystals: mp 48.5–50 °C; $[\alpha]^{27}$ −49.9°; ^1H NMR 5.49 (d, 1 H, J = 4.5, H_1), 4.67–4.53 (2 d, H_3 and H_6), 4.42–4.03 (m, 3 H, H_2, H_4, and H_6), 1.51, 1.42, 1.33 (3 s, 12 H, Ip).

6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (3). A mixture of 2.63 g (6.70 mmol) of **2**, 0.688 g (18.19 mmol) of powdered sodium borohydride, and 30 mL of dry acetonitrile was stirred at room temperature for 48 h when TLC (10/90 v/v, continuous development) showed that no triflate was present. The solvent was evaporated, the residue was dissolved in 50 mL of water, and the solution was extracted with two 30-mL portions of dichloromethane. The extracts were dried and evaporated to leave 1.50 g (92%) of a syrup that was chromatographically homogeneous. The syrup was chromatographed on 90 g of silica gel with ethyl acetate/hexane (10/90 v/v) for elution to give 1.01 g (68% recovery) of product: mp 33–34 °C; $[\alpha]^{23}$ −50.0° [lit.[3] mp 33–35 °C, $[\alpha]^{19}$ −53.6° (*c* 1.2, $CHCl_3$)]; ^1H NMR spectrum consistent with the literature.[3]

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3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose (6). A mixture of 0.67 g (17.7 mmol) of powdered sodium borohydride, 2.30 g (5.86 mmol) of the allose triflate **5**,[9] and 30 mL of dry acetonitrile was stirred at room temperature for 95 h when TLC showed the disappearance of **5**. A workup as for **3** yielded 1.24 g (87%) of a chromatographically homogeneous syrup. Chromatography of this material over 90 g of silica gel with ethyl acetate/hexane (15/85 v/v) for elution gave a 90% recovery of material that crystallized upon refrigeration and had $[\alpha]^{25}$ −5.60° [lit.[3] $[\alpha]^{21}$ −6.3° (*c* 1.9, $CHCl_3$)] and ^1H and ^{13}C spectra that agreed with the recorded[3,6] descriptions.

3-Deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-[3-^{2}H]glucofuranose (7). The above experiment was repeated with 1.51 g (3.85 mmol) of **5**,[9] 0.50 g (11.9 mmol) of sodium borodeuteride, and 30 mL of dry acetonitrile, and a quantitative yield of a chromatographically homogeneous product was obtained. The material was purified by flash chromatography[19] over 30 g of silica gel to give an 84% yield of material that was used for the NMR studies. In the ^1H spectrum, H_{3endo} appeared as a singlet at 2.17, and H_{3exo} appeared as a trace signal. In the decoupled ^{13}C spectrum, C_3 appeared as a triplet centered at δ 35.86.

Reaction of 1,2:5,6-Di-*O*-isopropylidene-3-*O*-triflyl-α-D-glucofuranose (4) with Sodium Borohydride. A mixture of 2.50 g (6.37 mmol) of **4**,[9] 0.72 g (19.03 mmol) of sodium borohydride, and 45 mL of acetonitrile was heated at 60 for 9 days when TLC [ethyl acetate–hexane (5/95 v/v)] showed only a trace of **4**. The solvent was evaporated and the residue partitioned between water (150 mL) and dichloromethane (125 mL). The organic solution was dried and evaporated to give 1.47 g of a yellow solid whose TLC showed several spots. Flash chromatography[19] of a portion (0.62 g) of the residue on about 50 g of silica gel with ethyl acetate/hexane (40/60 v/v) for elution gave, after separation of a small amount of **4**, partial separation of the three major reaction products **6**, **8**, and **9**. Rechromatography of fractions that contained more than one component eventually gave 0.15 g (23%) of **9** [mp 48.5–49.5 °C (lit.[20] mp 50–52 °C)], 0.10 g (15%) of **6**, and 0.30 g (42%) of **8** (mp 105.5–106.5 °C, undepressed on mixture with authentic **8**), listed in the order of elution. All three materials had ^1H NMR spectra that duplicated those of authentic samples.

Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-triflyl-α-D-glucopyranoside (11). The standard processing[9] of a mixture of 0.50 g (1.08 mmol) of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**10**),[14] 0.15 mL (1.86 mmol) of pyridine, 0.26 mL (1.55 mmol) of triflic anhydride, and 20 mL of dry dichloromethane yielded 0.60 g (93%) of a yellow oil that, after being recrystallized from 95% ethanol, had a melting point of 80 °C. Anal. Calcd for $C_{29}H_{31}F_3O_8S$: C, 58.38; H, 5.24. Found: C, 58.60; H, 5.46.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-α-D-*xylo*-hexopyranoside (12). A slurry of 2.0 g (3.35 mmol) of the triflate **11**, 0.80 g (21.2 mmol) of powdered sodium borohydride, and 160 mL of acetonitrile was stirred at room temperature for 72 h when TLC [ethyl acetate–hexane (5/95 v/v), continuous development] showed the disappearance of the starting material **11**. A workup as for **3** yielded 1.50 g (100%) of a colorless oil. A portion (0.50 g) of the residue was subjected to flash chromatography[19] over about 50 g of silica gel using ethyl acetate/hexane (15/85 v/v) for elution. The collected fractions that showed a single spot upon TLC were evaporated to give 0.50 g of colorless oil: $[\alpha]^{26}$ +27.4°; ^1H NMR 7.26 (s, 15, Ar), 4.85–4.09 (m, 7, H_1 and $ArCH_2$), 4.07–3.63 (m, 2 H, H_3 and H_5), 3.57–3.17 (m, 6 H, H_2, H_6 and CH_3), 2.15–1.89 (m, 1 H, H_{4eq}), 1.65–1.13 (m, 1 H, H_{4ax}); ^{13}C NMR 99.07 (C_1), 66.75 (C_6), 55.14 (CH_3), 33.96 (C_4), plus signals for aromatic carbons, for the benzyl carbons, and for C_2 and C_3 which showed some overlapping with the benzyl resonances. Anal. Calcd for $C_{28}H_{32}O_5$: C, 74.98; H, 7.19. Found: C, 75.23; H, 7.15. Compound **12** was unstable and became yellow on storage at room temperature.

Methyl 2,3,6-Tri-*O*-benzyl-4-deoxy-α-D-[4-^{2}H]galactopyranoside (13). The above reaction conditions were repeated by using 1.70 g (2.85 mmol) of **11**, 0.98 g (23.3 mmol) of sodium borodeuteride, and 140 mL of acetonitrile stirred at room temperature for 48 h to give 1.35 g (105%) of a chromatographically homogeneous oil. Flash chromatography[19] of 0.5 g of the residue, using the above procedure, yielded 0.4 g of an oil whose ^1H spectra (as compared to that of **12**) showed the disappearance of the H_{4ax} signal, the simplification of the H_{4eq} signal to an approximate doublet, and some simplification of the H_3,H_5 multiplet. The only change in the ^{13}C spectrum was the conversion of the δ 33.96 signal to a low-intensity symmetrical triplet.

Methyl 6-*O*-Benzoyl-2,3-di-*O*-benzyl-4-*O*-triflyl-α-D-glucopyranoside (15). Triflation of 1.50 g (3.13 mmol) of methyl 6-*O*-benzoyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (**14**)[17] by the conventional method gave 1.8 g of residue that crystallized on standing. Recrystallization from hot petroleum ether (60–80 °C) gave 1.05 g of white solid, mp 85–90 °C dec. The material was unstable, and the melting point varied with the temperature of insertion and the rate of heating. A second recrystallization from hot hexane gave material with the following: mp 90–91 °C (insertion at 85 °C and heating rate 2 °C/min); ^1H NMR 8.02 (d of d, 2 H, H_2 and H_6 of benzoyl), 7.52–7.14 (m, 13 H, Ar), 5.08–4.00 (m, 10 H, benzyl CH_2, H_1, H_3, H_4, H_5, H_6), 3.62 (d of d, 1 H, H_2), 3.37 (s, 3 H, OCH_3).

Methyl 6-*O*-Benzoyl-2,3-di-*O*-benzyl-4-deoxy-α-D-*xylo*-hexopyranoside (16). Reaction of 0.40 g (0.66 mmol) of **15** with 0.20 g (5.3 mmol) of sodium borohydride in 40 mL of acetonitrile for 18 h resulted in an apparent consumption of the triflate **15** according to TLC [ethyl acetate–hexane (5/95 v/v)]. A conventional workup gave 0.23 g of residue which was subjected to flash chromatography[19] over about 50 g of silica gel with ethyl acetate–hexane (15/85 v/v) for elution. A single material (0.075 g) as a colorless oil was collected from the earlier fractions, and later fractions yielded 0.10 g of unchanged **15**, demonstrating that the reaction had not gone to completion. For the oil: ^1H NMR 8.02 (d of d, 2 H, H_2 and H_6 of benzoyl), 7.54–7.12 (m, 13 H, Ar), 4.96–4.59 (m, 5 H, benzyl CH_2, H_1), 4.48–3.79 (m, 4 H, H_3, H_5, H_6), 3.46 (d of d, 1 H, H_2), 3.36 (s, 3 H, OCH_3), 2.26–1.99 (m, 1 H, H_{4eq}), 1.83–1.24 (m, 1 H, H_{4ax}); mass spectrum, *m/e* 463.2123 (M^+) (calcd. for $C_{28}H_{30}O_6$, 463.2121).

Acknowledgment. We are grateful to Dr. L. A. Reed, III, who first prepared the triflate **11**, obtained 270-MHz NMR spectra for **6** and **7** and made arrangements for the high-resolution mass spectrum of **16**. We are also grateful to Professor E. Abushanab, who obtained the ^{13}C spectra and advised us on their interpretation, to D. F. Sears, who obtained many of the ^1H spectra, and to Dr. H. A. Scoble, who measured the mass spectrum of **16**.

Registry No. 1, 4064-06-6; 2, 71001-09-7; 3, 4026-27-1; 4, 55951-93-4; 5, 55951-90-1; 6, 4613-62-1; 7, 70005-84-4; 8, 582-52-5; 9, 2774-28-9; 10, 19488-48-3; 11, 87871-03-2; 12, 87871-04-3; 13, 87871-05-4; 14, 66781-85-9; 15, 87871-06-5; 16, 87871-07-6; 17, 79580-70-4.

(20) Tewson, T. J.; Welch, M. J. *J. Org. Chem.* **1978**, *43*, 1090.

Structures of the Germacranolides Isoaristolactone and Pyroaristolactone

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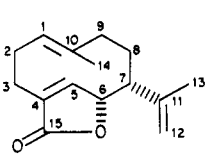
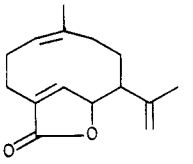
Received May 31, 1983

In 1964 the germacranolide aristolactone was assigned structure **1** (relative stereochemistry of the substituents at C-6 and C-7 was left undefined), and structure **2** was



1, aristolactone



2

suggested for isoaristolactone, which was obtained from

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