was dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo, leaving 31 mg of crude lactol which was dissolved in 10 mL of benzene under argon. Silver carbonate[19] (800 mg, 48% by weight) was added and the stirred reaction mixture was heated at reflux for 2.5 h. After being cooled to room temperature, the reaction mixture was filtered through a Celite pad. The filter pad was washed thoroughly with ether. Concentration under reduced pressure left 30 mg of crude product which was purified on 3 g of silica gel. Elution with hexane–ether (7:3) gave 20 mg (91%) of crystalline **23**: mp 152–153 °C; R_f 0.33 (ether–hexane, 2:1); IR ($CHCl_3$) 3450, 2963, 2918, 2837, 1722, 1685, 1655, 1443, 1390, 1378, 1367, 1341, 1315, 1290, 1275, 1188, 1130, 1032, 1002, 992, 910 cm^{-1}; ^1H NMR (220 MHz) ($CDCl_3$) δ 0.91 (d, 3 H, J = 6.5 Hz, C(4) methyl), 1.20 (s, 6 H), 1.89 (s, 3 H, C(13) methyl), 2.62 (s, 1 H, C(9) proton), 2.95 (dd, 1 H, J = 5.0, 16.0 Hz), 4.34 (br t, 1 H, J = 3 Hz, C(7) proton), 5.46 (br d, 1 H, J = 10 Hz, C(2) olefinic proton), 6.20 (s, 1 H, OH), 6.41 (d, 1 H, J = 10 Hz, C(1) olefinic proton). An analytical sample was prepared by recrystallization from hexane–ether; mp 152–153 °C. Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.82; H, 7.87.

12-(Acetyloxy)picrasa-1,12-diene-11,16-dione (24). To a solution of diosphenol **23** (140 mg, 0.424 mmol) in 3 mL of dry pyridine at room temperature was added 400 μL (4.24 mmol) of acetic anhydride. After 1.25 h, the reaction mixture was diluted with 150 mL of methylene chloride, washed with saturated copper sulfate solution (2 × 25 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue (160 mg) was chromatographed on 10 g of silica gel. Elution with hexane–ether (3:7) gave 141 mg (90%) of crystalline **24**: mp 160–161 °C; R_f 0.45 (ether); IR ($CHCl_3$) 3020, 2960, 2910, 2870, 2830, 1760, 1730, 1690, 1665, 1440, 1372, 1345, 1330, 1296, 1274, 1180, 1116, 1080, 1028, 1003, 990, 930, 915, 904, 883 cm^{-1}; ^1H NMR (220 MHz) ($CDCl_3$) δ 0.90 (d, 3 H, J = 6.5 Hz, C(4) methyl), 1.20 (s, 3 H), 1.30 (s, 3 H), 1.83 (s, 3 H, C(13) methyl), 2.25 (s, 3 H, acetyl methyl), 2.61 (s, 1 H, C(9) proton), 2.96 (dd, 1 H, J = 4.5, 17 Hz), 4.37 (t, 1 H, J = 2.5 Hz, C(7) proton), 5.43 (ddd, 1 H, J = 2.0, 5.0, 10.0 Hz, C(2) olefinic proton), 6.34 (d, 1 H, J = 10.0 Hz, C(1) olefinic proton). An analytical sample was prepared by recrystallization from methylene chloride–ether: mp 160–161 °C. Anal. Calcd for $C_{22}H_{28}O_5$: C, 70.95; H, 7.58. Found: C, 70.85; H, 7.80.

(1α,2α)-12-(Acetyloxy)-1,2-dihydroxypicras-12-ene-11,16-dione (25). To a stirred solution of olefin **24** (29 mg, 0.078 mmol) in 500 μL of dry pyridine at room temperature under argon was added 21.8 mg (0.086 mmol) of solid osmium tetraoxide. After 25 min the brown complex that had separated was decomposed by the addition of 500 μL of pyridine and a solution of 81 mg of sodium bisulfite in 800 μL of water. Stirring for 1 h at room temperature gave a light brown solution which was taken up in 50 mL of ethyl acetate. The organic layer was washed with saturated copper sulfate solution (2 × 25 mL), water (25 mL), and brine (25 mL). Concentration of the dried ($MgSO_4$) organic layer in vacuo left 50 mg of a residue which was chromatographed on 3 g of silica gel. Elution with hexane–ethyl acetate (3:7) afforded 31 mg (98%) of crystalline racemic monoacetate **25**: mp 207–209 °C; R_f 0.43 (ethyl acetate); IR ($CHCl_3$) 3500, 3000, 2960, 2930, 1755, 1725, 1690, 1665, 1447, 1400, 1376, 1350, 1300, 1280, 1182, 1120, 1032, 990, 952, 920, 820 cm^{-1}; ^1H NMR (220 MHz) ($CDCl_3$) δ 0.89 (d, 3 H, J = 6.5 Hz, C(4) methyl), 1.05 (s, 3 H), 1.30 (s, 3 H), 1.83 (s, 3 H, C(13) methyl), 2.24 (s, 3 H, acetyl methyl), 2.94 (dd, 1 H, J = 7.0, 18 Hz), 3.39 (s, 1 H, C(9) proton), 3.99 (m, 1 H, C(2) proton), 4.30 (br s, 1 H, C(7) proton), 4.49 (d, 1 H, J = 2.5 Hz, C(1) proton). An analytical sample was prepared by recrystallization from methylene chloride–ether mp 207–209 °C. Anal. Calcd for $C_{22}H_{30}O_7$: C, 65.01; H, 7.44. Found: C, 65.21; H, 7.48.

***dl*-Castelanolide (5).** To a stirred solution of monoacetate **25** (32 mg, 0.078 mmol) in 5 mL of anhydrous methanol was added 50 mg of anhydrous potassium carbonate. After 15 min, 50 mL of methylene chloride was added and the solution was washed with 3% hydrochloric acid (20 mL), saturated sodium bicarbonate solution (10 mL), water (10 mL), and brine (10 mL). After drying over anhydrous sodium sulfate, the organic layer was concentrated in vacuo and the residue was chromatographed on 1 g of silica gel. Elution with ethyl acetate afforded 26 mg (91%) of crystalline racemic castelanolide **5**; mp 135–137 °C; R_f 0.32 (hexane–ethyl acetate, 2:3); IR (KBr) 3500, 3400, 1935, 1860, 1730, 1685, 1655, 1445, 1390, 1235, 1125, 1040, 955, 918 cm^{-1}; NMR (220 MHz) (acetone-d_6) δ 0.89 (d, 3 H, J = 6.5 Hz, C(4) methyl), 1.10 (s, 3 H), 1.23 (s, 3 H), 1.85 (s, 3 H, C(13) methyl), 2.96 (dd, 1 H, J = 5, 18 Hz), 3.48 (s, 1 H, C(9) proton), 3.96 (m, 1 H, C(2) proton), 4.36 (br s, 1 H, C(7) proton), 4.52 (d, 1 H, J = 2.5 Hz, C(1) proton). An analytical sample was prepared by recrystallization from chloroform, mp 135–137 °C. Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.92; H, 7.74. Found: C, 65.87; H, 7.73.

Acknowledgment. This investigation was supported by a Public Health Service Research Grant (CA 28865) from the National Cancer Institute and, in part, by G. D. Searle and Co. We are grateful to Professor Giovanni Vidari for numerous discussions during the early stages of this work and Drs. J. C. Huffman and K. Folting for carrying out a single-crystal X-ray analysis of monoacetate **25**.

Out-of-Ring Claisen Rearrangements are Highly Stereoselective in Pyranoses: Routes to *gem*-Dialkylated Sugars[1]

Deen Bandhu Tulshian,[2] Raymond Tsang,[3,4] and Bert Fraser-Reid*

Chemistry Department, University of Maryland, College Park, Maryland 20742

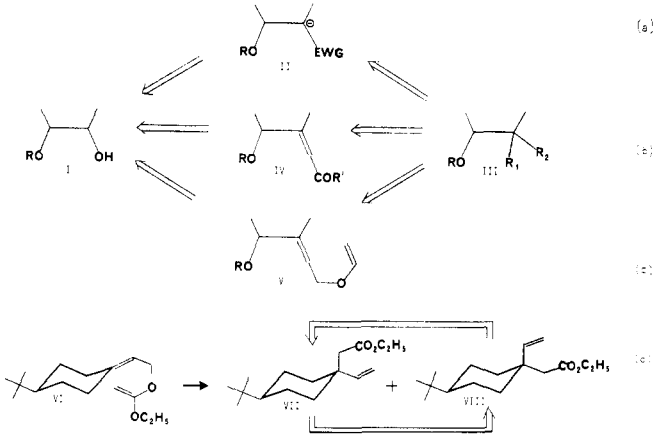
Received November 7, 1983

The Claisen rearrangement has been evaluated as a means for stereoselective creation of functionalized geminal substituents at C-2 and C-3 of hexopyrano systems. C-2 and C-3 keto sugars react with Wittig reagents to give α,β-unsaturated esters, one geometric isomer being obtained in each case. Reduction of the ester and trans vinylation with ethyl vinyl ether leads to allyl vinyl ethers which are thermolyzed in refluxing benzonitrile. The oxy-Cope rearrangement proceeds with complete stereoselectivity, the folding pattern being always from the β-face of the pyranose ring. Thus, the acetaldehyde moiety ends up axially oriented at C-2 and equatorially oriented at C-3. These stereochemical results are not affected by neighboring oxygen substituents nor by the presence or absence of an anomeric alkoxyl functionality.

In connection with a number of syntheses under way in our laboratory we need to be able to convert a secondary alcohol of a sugar residue into a functionalized *gem*-dialkyl center, e.g., I → III. Pathways involving α-alkylation of

0022-3263/84/1949-2347$01.50/0

Scheme I



an enolate ion, e.g., II [Scheme I, eq a], were ruled out by the threat of elimination of the β-oxygen substituent. Conjugate addition to a substrate such as IV [Scheme I, eq b] was a safe alternative; however, while the addition of dialkyl cuprates succeeded at C-4,[5] we have been unable to carry out comparable additions at C-2 and C-3 centers, for example, **5** and **13** (vide infra). The Claisen rearrangement of an allyl vinyl ether residue, for example, V [Scheme I, eq c], was appealing for several reasons. Firstly, the rearrangement product(s) would be III (R_1 = CH_2CHO, R_2 = $CH{=}CH_2$ or vice versa). In this connection the system VI shown in Scheme I, eq d, had been studied by House,[6] and it was found that the isomers VII and VIII were obtained in 48% and 52%, respectively. Reactions on carbohydrate rings frequently go with better stereoselectivities than on carbocyclic systems. Indeed, our recent study of the Claisen rearrangements at C-4,[5] confirm this trend. Nevertheless, it was of interest to see whether this would also hold for Claisen rearrangements at C-2 and C-3. In the event of poor stereoselectivity it was reassuring to note, that a sequence for converting the minor product into the major, for example, VII to VIII (or vice versa), could be readily devised.

In this manuscript we report that rearrangements at C-2 and C-3, as with the previous report study at C-4,[5] go with (virtually) exclusive stereoselectivities.

Results

Scheme II. Our general plan is illustrated in Scheme II. The readily available benzylidinated glucoside **1** was monosilylated and the isomeric products, **2** and **3**, were separated chromatographically. The former was processed to give the α,β-unsaturated ester **5** as the sole product of the Wittig olefination. In order to assign the geometry of the latter, the ester was reduced with lithium aluminum hydride, and the C-3 hydroxyl was liberated. When the resulting diol **7** was treated with dimethoxypropane, the acetonide **8** was isolated in 80% yield.

In order to effect the Claisen rearrangement, the allylic hydroxyl of **6** was vinylated by mercury-catalyzed exchange with ethyl vinyl ether. Heating of the resulting material **9a** in benzonitrile gave a single product in 85% yield. The gluco configuration **10** was assigned since upon desilylation a lactol (**11**) formed spontaneously. Such a ready lactolization would not have occurred with the C-2 epimer of **10**.

In a slight variation of the above procedure, the ether **9a** was desilylated first, and heating of the resulting alcohol **9b** led directly to **11** in 85% yield.

The C-3 alcohol **3** was processed along similar lines. The configuration of ester **13** was established by a standard sequence of reactions culminating with the acentonide **14**. The allyl vinyl ether **16** was heated and a single aldehyde was obtained in 95% yield. Assignment of gluco configuration **17a** to the latter was made by virtue of the fact that upon desilylation, the resulting aldehydo alcohol **17b** could not be induced to form a lactol.

The formation of **10** and **17** as the exclusive products from the Claisen rearrangements of **9** and **16**, respectively, was gratifying although unexpected, given the aforementioned study of House.[6] We wished to determine the effect of neighboring substituents on the stereochemical outcome and the results of a study on the corresponding 2- and 3-deoxy substrates are shown in Scheme III.

Scheme III. The well-known 3-deoxy sugar **18a**[7] was oxidized, and the resulting ketone **18b**[8] was processed in the usual way to give the vinyl ether **21**. All reactions proceeded smoothly with 73% overall yield. The thermal rearrangement also went in excellent yield and a single product was obtained. The configuration was assigned as **22** by correlation with the previously described material **10** as outlined in Scheme III. Thus, **10** was reduced, the resulting alcohol methylated, and the product was deoxygenated at C-3 by use of the Barton–McCombie procedure.[9] The product, **23**, was identical with material which was obtained from **22** by reduction followed by methylation.

The known 2-deoxy-3-uloside **24**[10] was converted into the vinyl ether **27** via the comparable intermediates **25** and **26**. Rearrangement of **27** gave a single aldehyde **28**. Attempts to correlate the structures of **28** and **17** by C-2 deoxygenation of the latter (comparable to the correlation of **10** and **22**, Scheme III) were unsuccessful because of the inability to obtain a C-2 xanthate ester. A more elaborate course, therefore, had to be devised.

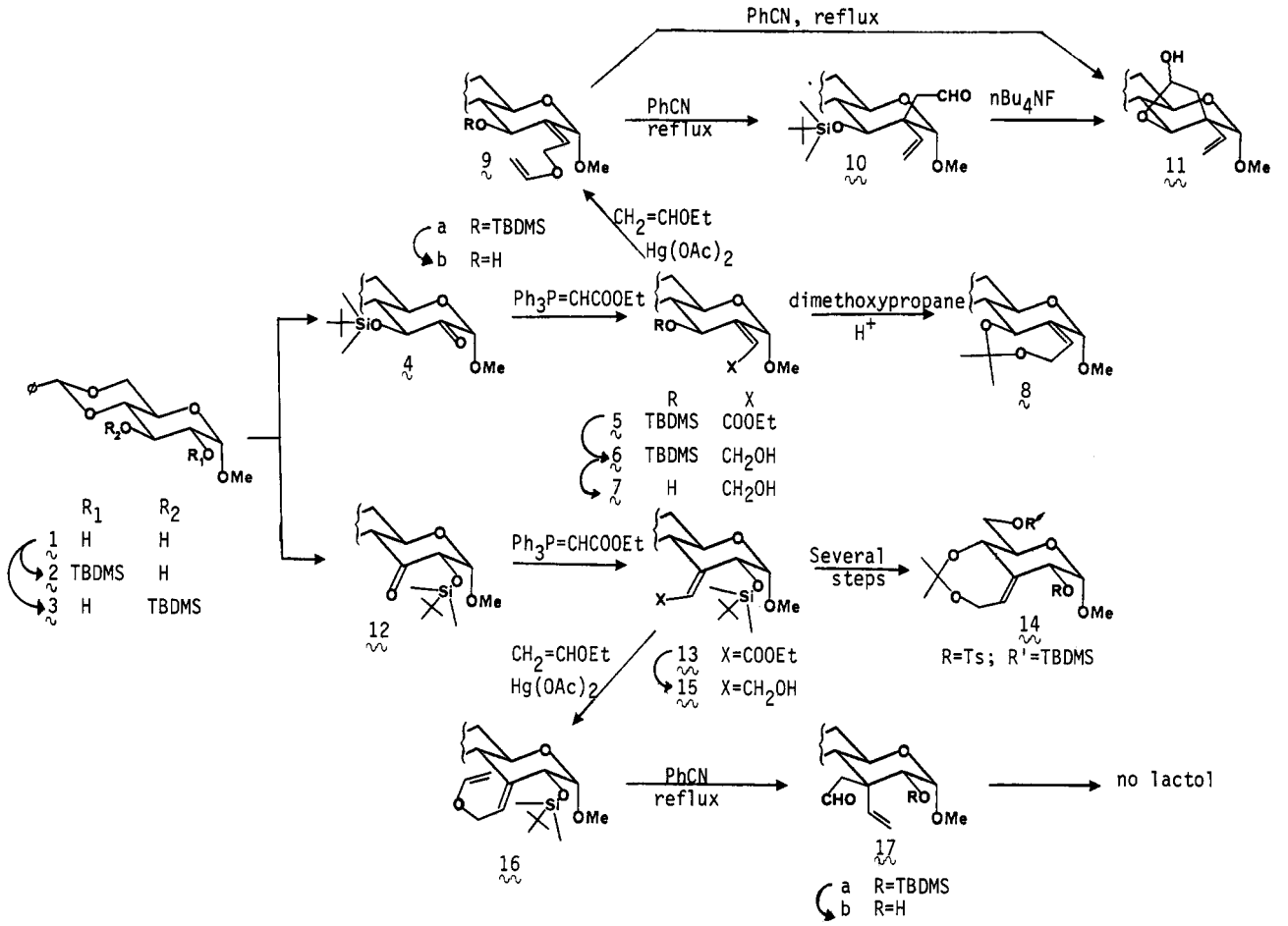
The aldehydo and vinyl groups of **28** were each reduced, and the silylated derivative, **30**, was subjected to the Hanessian–Hular reaction,[11] whereby the bromo benzoate **31** was formed. The C-4 benzoate of **31** was then processed to give the sulfonate **33**.

We then treated **33** with sodium benzoate in refluxing dimethylformamide in the expectation of displacing the C-4 sulfonate with inversion. The *tert*-butyldimethylsilyl group would then be replaced with a sulfonate, and the resulting product would be treated with base whereupon a tetrahydrofuran ring would form as indicated in **34**. In the event, treatment of **33** with sodium benzoate in refluxing dimethylformamide for 12 h led directly to **34** in 42% yield. The presence of the ester at C-6 (rather than at C-4) was readily apparent from the two-proton signal at 4.6 ppm assignable as H-6 and H-6′.

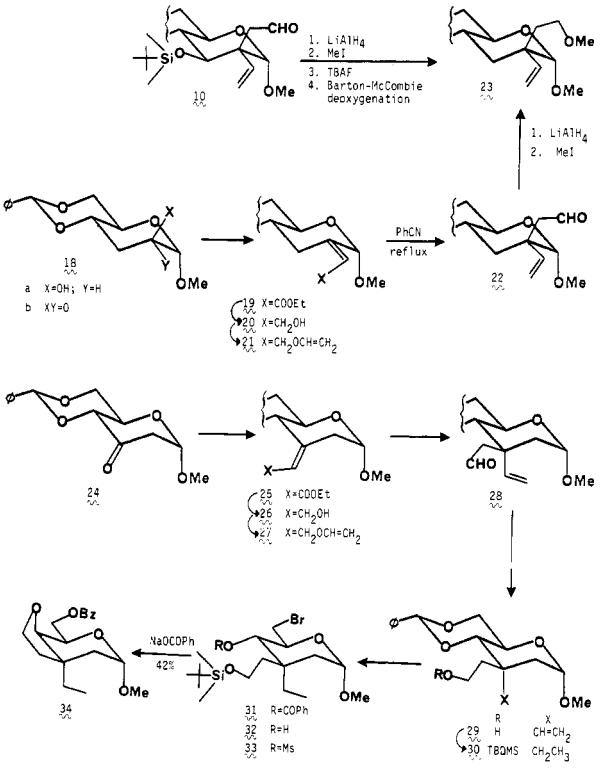
The stereoselectivities reported in Schemes II and III for the substrates **9**, **16**, **21**, and **27** could be influenced, conceivably, by the axially oriented glycosidic methoxyl. The corresponding 1-deoxy substrates were therefore

(1) For a preliminary account of this work see: B. Fraser-Reid, B.; Tsang, R.; Tulshian, D. B.; Sun, K.-M. *J. Org. Chem.* **1981**, *46*, 3764.
(2) Present address: Schering Corporation, 60 Orange St., Bloomfield, NJ 07003.
(3) Holder of a Graduate Fellowship in Chemistry from Merck, Sharp and Dohme (Rahway, NJ).
(4) Present address: Paul M. Gross, Chemical Laboratory, Duke University, Durham, NC 27706.
(5) Tulshian, D. B.; Fraser-Reid, B. *Tetrahedron*, in press.
(6) House, H. O.; Lubinkowski, J.; Good, J. *J. Org. Chem.* **1975**, *40*, 86.
(7) Prins, D. A. *J. Am. Chem. Soc.* **19487**, *70*, 3955.
(8) Rosenthal, A.; Catsoulacos, P. *Can. J. Chem.* **1968**, *46*, 2868.
(9) Barton, D. H. R.; McCombie, S. W. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1574.
(10) Horton, D.; Weckerle, W. *Carbohydr. Res.* **1975**, *44*, 227.
(11) Hanessian, S.; Plessas, N. R. *J. Org. Chem.* **1969**, *34*, 1035.

Scheme II



Scheme III



studied as outlined in Scheme IV.

Scheme IV. Commercially available 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide ("acetobromoglucose") **35** was debrominated by hydrogenolysis over Raney nickel, and the product **36** was processed to give the benzylidenated 1,5-anhydroglucitol **38**. This diol was treated with di-*n*-butyltin oxide according to the procedure of Anderson,[12] followed by *tert*-butyldimethylsilyl chloride, to give the isomers **39** and **40** in a 2:1 ratio. The corresponding ketones **41** and **42** were processed in the standard way. Ketone **41** led to aldehyde **47**, there being a trace (1% to 2%) of the C-2 epimer of **46** in the crude reaction product before chromatography. The configuration of **46** was assigned by virtue of the fact that desilylation caused immediate formation of the lactol **47**.

Ketone **42** upon the standard treatment afforded a single aldehyde **51** whose configuration was shown to be as in Scheme IV because the hydroxy aldehyde **52** could *not* be induced to form a lactol.

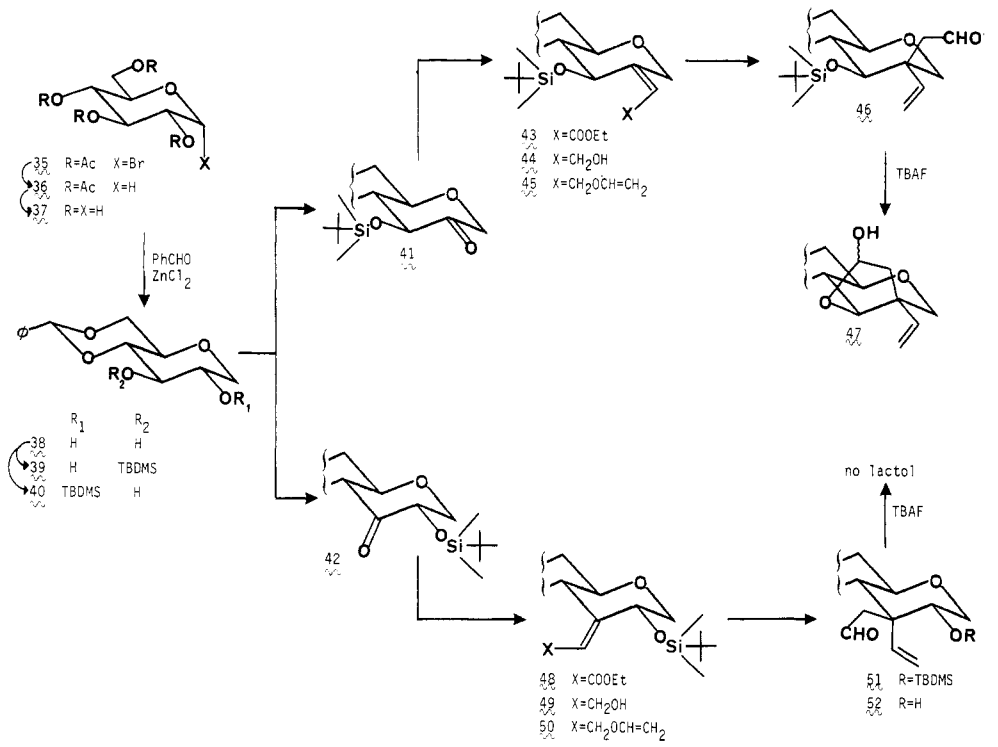
Discussion

The results in Schemes II, III, and IV show that oxy-Cope rearrangement on a hexopyranoside ring proceed with (Virtually) exclusive stereoselectivities. If we take into account our published work on the C-4 analogues,[5] the situation may be summarized as shown in Scheme V. Structure IX corresponds to both the C-2 and C-4 ketones, and structure XIV to the major or exclusive product(s) arising therefrom. The latter arises from the folding pattern XI and therefore implies that axial attack at these sites on the pyranose ring is favored over the equatorial alternative XII.

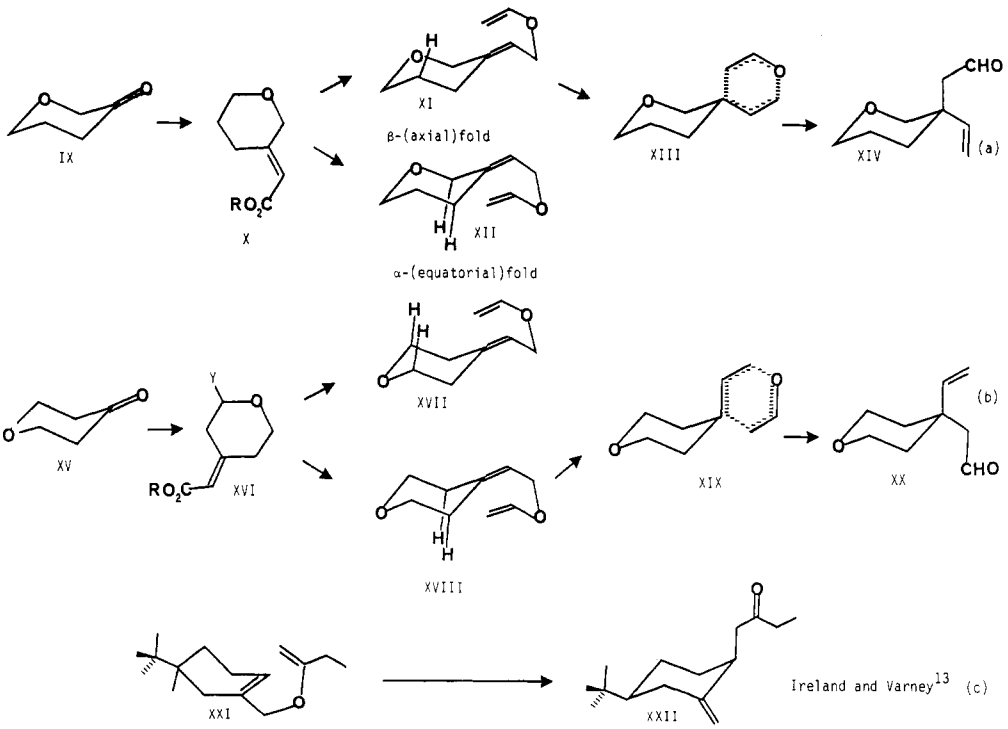
These results are strikingly at odds with those of House shown in Scheme I, eq d, according to which the prefer-

(12) (a) Nashed, M. A.; Anderson, L. *Tetrahedron Lett.* **1976**, 3505. (b) Manavu, R. M.; Szmant, H. H. *J. Org. Chem.* **1976**, *41*, 1832.

Scheme IV



Scheme V



ence, if any, should have been for the equatorial fold. In this connection, mention may be made of the results of Ireland and Varney shown in Scheme V, eq (c, in which the axial rearrangement product XXII was heavily favored. Ireland was able to rationalize this stereoselectivity on the basis of nonbonded interactions which destabilized the transition state from which the trans isomer corresponding to XXII would have arisen. An assessment of the folding patterns shown in Scheme V, eq a, indicates that XII would experience strong interactions between the vinyl group and axially oriented α and α' substituents, whereas XI would not be greatly affected by the lone axially oriented hydrogen on the β-carbon. Thus, the preferential formation of XIV could be explainable.

However, a consistent pattern does not emerge when similar considerations are applied to the 3-keto systems shown in Scheme V, eq b. Thus, XVIII should now be destabilized by the α and α' interactions. However, XVIII appears to be so highly favored that XX is the exclusive product from all the systems that we have studied. Thus, there has never been a trace of the 3-epi isomer arising

(13) Ireland, R. E.; Varney, M. D. *Ibid* **1983**, *48*, 1829.

through the folding pattern XVII.

Of particular importance in these considerations is the apparent irrelevance of the anomeric methoxyl as implied by the results in Scheme IV. Thus the axially oriented group seems to play no role either from the standpoint of steric hindrance or stereoelectronic control in these Claisen rearrangements.

The question of conformational rigidity of the pyranose system during the rearrangement might also be addressed. The trans-fused benzylidene ring prevents conformational mobility in the systems shown in Schemes II, III, and IV. However, with the C-4 ketone where no such benzylidene ring exists, the rearrangements were found to be equally stereoselective.[5]

Mention should also be made of the Wittig reactions which lead to one geometric isomer in each case such as X and XVI (Y = CH_2OR). Rationalizations for this stereochemical course are also not readily apparent.

A question arises concerning the effect of this geometric preference on the course of the rearrangement. However, models show that the geometry of the exocyclic double bond in the favored folding patterns, XI and XVIII, do not play any significant role. However, no experimental verification has been possible owing to the absence of the other geometric isomers corresponding to X to XVI. However, other routes to α,β-unsaturated esters are now being explored in the hope of obtaining such geometric isomers and to test their effect on the rearrangement.

In summary, the pattern that emerges is that the unsaturated appendages always fold from the β-face of the D-hexopyranose ring which results in axial attack occurring at C-2 and C-4, while equatorial attack occurs at C-3. A consistent rationalization to account for these results cannot be found by evaluation of nonbonded interactions. A number of other systems are currently being examined in the hope of shedding further light on the factors which govern these highly stereoselective processes.

Experimental Section

General Procedures. Melting points were determined in capillary tubes in a büchi Model 510 and are uncorrected. Elemental analyses were performed by Dr. F. Kasler, Department of Chemistry, University of Maryland. ^1H NMR spectra were determined in deuteriochloroform with internal tetramethylsilane as the standard, unless otherwise stated, on one of the following spectrometers: Varian T-60, Varian EM-360, Perkin-Elmer R-12B, Bruker WP-80, Varian XL-100, Varian XL-200, Bruker WM-250. Coupling constants were measured directly from the spectra or calculated from the peak listings. IR spectra were determined on either a Beckman IR-10 or a Perkin-Elmer 298 spectrometer. Neat samples were smeared on sodium chloride plates and solutions were placed in sodium chloride cells. Low-resolution MS were run on a Hitachi/Perkin-Elmer RMH-2 and HRMS were determined with a VG 7070F. Optical rotations were determined on a Perkin-Elmer 241 polarimeter. TLC was performed by using aluminum plates precoated with silica gel (HF-254, 0.2 mm thickness) containing a fluorescent indicator (E. Merck, CAT. 5539). The following solvent systems were used: (A) ethyl acetate–petroleum ether (30–60 °C) (10:90); (B) ethyl acetate–petroleum ether (30–60 °C) (20:80); (C) ethyl acetate–petroleum ether (30–60 °C) (33:67); (D) ethyl acetate–petroleum ether (30–60 °C) (50:50); (E) methanol–chloroform (10:90). The chromatograms were viewed under a UV light (254 nm), sprayed with concentrated sulfuric acid, and heated until charring occurred. PTLC was done by using glass plates (20 cm × 20 cm) coated with silica gel (PF-254, E. Merck) and the above-mentioned solvent systems. Column chromatography was carried out by using silica gel (E. Merck 70–230 mesh A.S.T.M. or 230–500 mesh A.S.T.M.).

Standard Procedure for Cleavage of *tert*-Butyldimethylsilyl Ethers. A solution of the silyl ether (1.0 g/100 mL) in dry tetrahydrofuran was stirred with 1 equiv of tetra-*n*-butylammonium fluoride until the cleavage was complete (TLC). The solvent was then evaporated and the residue was purified by column chromatography.

Standard Procedure for Oxidation of the Secondary Alcohols.[14] A solution of dimethyl sulfoxide (1.5 mmol) in dry methylene chloride (50 mL) was cooled to −78 °C under argon and to this was added trifluoroacetic anhydride (1.0 mmol) very slowly and the resulting reaction mixture was stirred at that temperature for 10 min. A solution of the sugar (1.0 mmol) in dry methylene chloride (5.0 mL) was then added slowly at −78 °C. After the addition, the reaction mixture was stirred for 0.5 h at −78 °C and dry triethylamine (2.0 mmol) was added slowly. The reaction mixture was then warmed up to room temperature, washed with water (2 × 20 mL), dried over sodium sulfate, and evaporated to give the desired keto sugar.

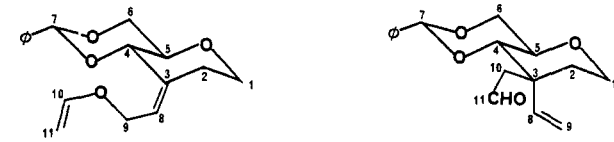
Standard Procedure for Reaction of Ketones with (Carboxymethylene)triphenylphosphorane. The keto sugar (1.0 mmol) and the Wittig reagent (1.5–3.0 mmol) were dissolved in dry acetonitrile (1.0 gm sugar/50 mL). The solution was refluxed and the course of the reaction was monitored by TLC. Upon completion, the solvent was evaporated and the residue was dissolved in a minimum amount of diethyl ether, filtered, and evaporated. The material was then chromatographed on a silica gel column. (The solvents for TLC and column chromatography will be specified).

Standard Procedure for Lithium Aluminium Hydride ($LiAlH_4$) Reduction of Esters. The ester to be reduced was dissolved in dry diethyl ether (1.0 gm of sugar/50 mL) and cooled to an appropriate temperature (the temperature will be specified). Lithium aluminium hydride (1.2 mmol/1.0 mmol of sugar) was added. The reaction was followed by TLC (solvent will be specified). After the reaction was complete, hydrated sodium sulfate was added until all lithium aluminium was destroyed. The reaction mixture was filtered on a pad of Celite with suction. Evaporation of the solvent yielded the desired product.

Standard Procedure for Ethyl Vinyl Ether Exchange Reaction with Alcohols.[15] A solution of the alcohol in ethyl vinyl ether (1.0 gm/200 mL) was stirred with a catalytic amount of mercuric trifluoroacetate until the reaction was complete. The solution was then washed with a saturated solution of sodium bicarbonate (3 × 50 mL) and water, dried over sodium sulfate, and evaporated to give the desired product.

Standard Procedure for the Claisen Rearrangement of Allyl Vinyl Ethers. A solution of the allyl vinyl ether in dry benzonitrile (1.0 gm/30 mL) was refluxed until the reaction was complete (TLC). The solvent was then evaporated under reduced pressure by using an oil pump to give the product.

The numbering pattern used for the ^1H NMR spectra is illustrated below.



Methyl 4,6-*O*-Benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (2) and Methyl 4,6-*O*-Benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-α-D-glucopyranoside (3). To a solution of the diol 1[16] (2.82 g, 10.0 mmol) in dry *N*,*N*-dimethylformamide (50 mL) were added imidazole (2.0 g, 30.0 mmol) and *tert*-butyldimethylsilyl chloride (1.81 g, 12.0 mmol). The mixture was stirred at room temperature for 4 h and was then diluted with diethyl ether (300 mL), washed several times with water, and dried. Evaporation of the solvent gave a 3:2 mixture of compounds 2 and 3 which was separated by column chromatography with solvent A. The crystalline compound 2 exhibited the following characteristics: mp 78–80 °C (recrystallized from ethyl acetate–petroleum ether); TLC R_f 0.58 (B); $[\alpha]_D$ +59.1° (*c* 1.1, $CHCl_3$); ^1H NMR (250 MHz) δ 0.10 and 0.12 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 3.38 (s, 3, OCH_3), 3.47 (t, $J_{3,4} \sim J_{4,5}$ = 10.0 Hz, H-4), 3.66 (dd, $J_{6,6'}$ = 10.0 Hz, $J_{5,6}$

(14) Hueng, S. L.; Omura, K.; Swern, D. *Ibid.* **1976**, *41*, 3329.
(15) Watanabe, W. H.; Conlon, L. E. *J. Am. Chem. Soc.* **1957**, *79*, 2828.
(16) Freudenberg, K.; Tolpffer, H.; Anderson, C. C. *Chem. Ber.* **1928**, *61*, 1750. Schmidt; O. T. *Methods Carbohydr. Chem.* **1962**, *1*, 349.

= 4.2 Hz, H-6) 3.74 (d, 1, H-6′), 3.80 (dd, 1, H-5), 3.95 (t, $J_{2,3}$ = 10 Hz, H-3), 4.25 (dd, $J_{1,2}$ = 5.0 Hz, H-2), 4.65 (d, 1, H-1). Anal. Calcd for $C_{20}H_{32}O_6Si$: C, 68.58 H; 8.13. Found: C, 66.39; H, 8.05. Compound **3**, a syrup, exhibited the following characteristics: TLC R_f 0.42 (B); ^1H NMR (80 MHz) δ 0.09 and 0.15 (s, 6, $(CH_3)_2Si$), 0.95 (s, 9, $(CH_3)_3CSi$), 3.40 (s, 3, OCH_3), 3.40–4.0 (m, 5, H-3, H-4, H-5, H-6, H-6′), 4.70 (d, 1, $J_{1,2}$ = 4.8 Hz, H-1). Anal. Calcd for $C_{20}H_{32}O_6Si$: C, 68.58; H, 8.13. Found: C, 66.42; H, 8.03.

Methyl 4,6-*O*-Benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-α-D-*arabino*-hexopryanosid-2-uloside (4). Compound **3** (2.0 g, 5.0 mmol) was oxidized to give **4** (1.75 g, 90%) as a syrup: TLC R_f 0.65 (D); ^1H NMR (60 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.90 (s, 9, $(CH_3)_3CSi$), 4.70 (d, 1, $J_{3,4}$ = 8.5 Hz, H-3), 5.45 (s, 1, H-7), 6.30 (s, 1, H-1), 7.3–7.5 (m, 5, C_6H_6). Anal. Calcd for $C_{20}H_{30}O_6Si$: C, 60.91; H, 7.61. Found: C, 60.86; H, 7.66.

Methyl 4,6-*O*-Benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-*C*-((*E*)-carbethoxymethylene)-α-D-*arabino*-hexopyranoside (5). The Wittig reaction on **4** (2.0 g, 5.0 mmol) gave **5** (2.1 g, 90%) as a syrup after column chromatography using solvent A: TLC R_f 0.58 (A); $[\alpha]^{20}_D$ −16.2° (*c* 0.6, $CHCl_3$); ^1H NMR (60 MHz) δ 0.08 (s, 6, $(CH_3)_2Si$), 0.87 (s, 9, $CH_3)_3CSi$), 1.25 (t, 3, *J* = 7.0 Hz, CH_2CH_3), 3.45 (s, 3, OCH_3), 3.50–4.40 (m, 6, H-4, H-5, H-6, H-6′, OCH_2CH_3), 4.73 (dd, 1, $J_{3,4}$ = 9.5 Hz, $J_{3,8}$ = 2.0 Hz, H-3), 5.45 (s, 1, H-7), 6.16 (d, 1, H-8), 6.35 (s, 1, H-1); Anal. Calcd for $C_{24}H_{36}O_7Si$: C, 62.06; H, 7.75. Found: C, 61.98; H, 7.78.

Methyl 4,6-*O*-Benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-*C*-((hydroxymethyl)methylene)-α-D-*arabino*-hexopyranoside (6). The ester **5** (1.5 g, 3.2 mmol) was reduced with $LiAlH_4$ (0.12 g, 3.2 mmol) at 0 °C in 0.5 h to give **6** (1.2 g, 90%) as a syrup: TLC R_f 0.55 (D); $[\alpha]^{20}_D$ −6.35° (*c* 0.63, $CHCl_3$); ^1H NMR (60 MHz) δ 0.05 (s, 6, $(CH_3)_2Si$), 0.87 (s, 9, $(CH_3)_3CSi$), 3.35 (s, 3, OCH_3), 3.40–4.50 (m, 6, H-4, H-5, H-6, H-6′, H-9, H-9′), 4.60 (bd, 1, $J_{3,4}$ = 10.0 Hz, H-3), 5.38 (s, 1, H-1), 5.45 (s, 1, H-7), 6.05 (dt, 2, $J_{8,9}$ = $J_{8,9'}$ = 7.0 Hz, $J_{3,8}$ = 2.0 Hz, H-9, H-9′).

Methyl 4,6-*O*-Benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-*C*-(((vinyloxy)methyl)methylene)-α-D-*arabino*-hexopyranoside (9a). Compound **6** (2.5 g, 5.9 mmol) was converted into **9a** in 90% yield: TLC R_f 0.78 (D); $[\alpha]^{20}_D$ −16.5° (*c* 0.83, $CHCl_3$); ^1H NMR (60 MHz) δ 0.05 (s, 6, $(CH_3)_2Si$), 0.86 (s, 9, $(CH_3)CSi$), 3.45 (s, 3, OCH_3), 3.50–4.50 (m, 8, H-4, H-5, H-6, H-6′, H-9, H-9′, H-11, H-11′), 4.60 (m, 1, H-3), 5.40 (s, 1, H-1), 6.05 (dt, 1, $J_{3,8}$ = 2.0 Hz, $J_{8,9}$–$J_{8,9'}$ = 6.0 Hz, H-8), 6.55 (dd, 1, $J_{10,11}$ = 7.5 Hz, $J_{10,11'}$ = 15.0 Hz, H-10). Anal. Calcd for $C_{24}H_{36}O_6Si$: C, 64.28; H, 8.03. Found: C, 64.24; H, 8.05.

The Acetonide of Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-((hydroxymethyl)methylene)-α-D-*arabino*-hexopyranoside (8). Compound **6** (0.5 g) was desilylated at room temperature in 3 h to give **7** (0.37 g, 90%) as a syrup: TLC R_f 0.10 (B); ^1H NMR (60 MHz) δ 3.35 (s, 3, OCH_3), 3.40–4.8 (m, 7, H-3, H-4, H-5, H-6, H-6′, H-9, H-9′) 5.30 (s, 1, H-1), 5.40 (s, 1, H-7), 6.0 (dt, 1, $J_{3,8}$ = 2.0 Hz, $J_{8,9}$ = $J_{8,9'}$ = 6.8 Hz, H-8), 7.3–7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{16}H_{20}O_6$: C, 62.34; H, 6.49. Found: C, 62.30; H, 6.42.

Compound **7** (0.03 g, 1.0 mmol) was stirred in dry benzene (20 mL) with dimethoxypropane (3.0 mmol) and a catalytic amount of *p*-toluenesulfonic acid for 4 h at room temperature. The reaction mixture was then washed with a saturated solution of sodium bicarbonate and dried over sodium sulfate, and evaporation gave **8** (0.27 g, 80%) as a syrup which exhibited the following characteristics: TLC R_f 0.60 (A); ^1H NMR (60 MHz) δ 1.38 (6, s, $(CH_3)_2$), 3.35 (s, 3, OCH_3), 5.30 (s, 1, H-1), 5.40 (s, 1, H-7), 6.0 (m, 1, H-8).

Methyl 4,6-*O*-Benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-*C*-(formylmethyl)-2-*C*-vinyl-α-D-glucopyranoside (10). Compound **9a** (2.0 g, 4.5 mmol) was rearranged to give **10** (1.70 g, 85%) as a syrup: TLC R_f 0.25 (A); $[\alpha]^{20}_D$ −20.0° (*c* 0.8, $CHCl_3$); IR (neat) 1720 (aldehyde) cm^{-1}; ^1H NMR (60 MHz) δ 0.05 (s, 6, $CH_3)_2Si$), 0.85 (s, 9, $(CH_3)_3CSi$), 2.5 (dd, 1, $J_{10,10}$ = 18.0 Hz, $J_{10,11}$ = 1.0 Hz, H-10), 3.0 (dd, 1, $J_{10',11}$ = 5.0 Hz, H-10′). 3.35 (s, 3, OCH_3), 3.8–4.3 (m, 4, H-4, H-5, H-6, H-6′), 4.40 (s, 1, H-1), 5.25 (d, 1, $J_{8,9'}$ = 18.0 Hz, H-9′), 5.40 (d, 1, $J_{8,9}$ = 11.0 Ha, H-9), 5.55 (s, 1, H-7), 6.1 (dd, 1, H-8), 9.88 (d, 1, H-11); HRMS calculated for $C_{24}H_{36}O_6Si$ (M + 1), 448.2359; found, 448.2315.

Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(((vinyloxy)methyl)methylene)-α-D-*arabino*-hexopyranoside (9b). Compound **9a** (0.2 g, 0.5 mmol) was desilylated in 3 h to give **9b** (0.13 g, 90%) as a syrup: TLC R_f 0.45 (D); ^1H NMR (60 MHz) δ 3.45 (s, 3, OCH_3), 3.50–4.55 (m, 9, H-3, H-4, H-5, H-6, H-6′, H-9, H-9′, H-11, H-11′), 5.40 (s, 1, H-1), 5.50 (s, 1, H-7), 6.15 (dt, 1, $J_{3,8}$ = 2.0 Hz, $J_{8,9}$ = $J_{8,9'}$ = 6.0 Hz, H-8), 6.50 (dd, 1, $J_{10,11}$ = 7.5 Hz, $J_{10,11'}$ = 15.0 Hz, H-10), 7.3–7.55 (m, 5, C_6H_5).

The Lactol of Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-(formylmethyl)-2-*C*-vinyl-α-D-glucopyranoside (11). (a) Compound **10** (0.49 g, 1.0 mmol) was desilylated to give the anomeric mixture **11** (0.3 g), as a syrup: TLC R_f 0.50 (D); ^1H NMR (60 MHz) δ 4.65 (s, 1, H-1), 4.90 (dd, 1, $J_{10,11}$ = 6.0 Hz, $J_{10',11}$ = 1.0 Hz, H-11), 5.68 (s, 1, H-1), 6.15 (dd, 1, $J_{8,9}$ = 11.0 Hz, $J_{8,9'}$ = 18.0 Hz, H-8).

(b) The allyl vinyl ether **9b** (0.1 g, 0.3 mmol) was rearranged in 2 h to give **11** (0.9 g, 90%) as a syrup. The product was a mixture of two anomers and displayed same characteristics as the material described in part a.

Methyl 4,6-*O*-Benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-α-D-*ribo*-hexopyranosid-3-uloside (12). Compound **2** (.01 g, 2.50 mmol) was oxidized to give **12** (0.77 g, 80%) as a syrup which exhibited the following characteristics: TLC R_f 0.55 (B); $[\alpha]^{20}_d$ +36.3° (*c* 1.4, $CHCl_3$); ^1H NMR (250 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 3.35 (s, 1, OCH_3), 3.80 (t, 1, $J_{6,6'}$ = 10.5, ~$J_{5,6}$ = 10.5, H-6), 3.95 (ddd, 1, $J_{5,6'}$ = 3.5 Hz, $J_{4,5}$ = 10.5 Hz, H-5), 4.15 (d, 1, H-4), 4.3 (dd, 1, H-6′), 4.4 (d, 1, $J_{1,2}$ = 3.0 Hz, H-1), 4.90 (d, 1, H-2). Anal. Calcd for $C_{20}H_{36}O_6Si$: C, 60.91; H, 7.61. Found: C, 60.72; H, 7.55.

Methyl 4,6-*O*-Benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-((*E*)-carbethoxymethylene)-α-D-*ribo*-hexopyranoside (13). The ketone **12** (1.0 g) was converted into ester **12** in 24 h (0.8 g, 76%). The product **12** was a syrup: TLC R_f 0.30 (B); ^1H NMR (80 MHz) δ 0.05 (s, 6, $(CH_3)_2Si$), 0.85 (s, 9, $(CH_3)_3CSi$), 3.3 (s, 3, OCH_3), 4.55 (d, 1, $J_{1,2}$ = 3.2 Hz, H-2) 6.0 (m, 1, H-8). Anal. Calcd for $C_{24}H_{30}O_7Si$: C, 62.06; H, 7.75. Found: C, 61.90; H, 7.66.

Methyl 4,6-*O*-Benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-((hydroxymethyl)methylene)-α-D-*ribo*-pyranoside (15). The ester **13** (1.5 g, 3.2 mmol) was reduced with a 1 molar solution of diisobutylaluminum hydride (10 mL) at 0 °C in toluene in 0.5 h. The reaction mixture was worked up by using a saturated solution of ammonium chloride, dried, and evaporated to give **15** (1.2 g, 90%) as a syrup which exhibited the following characteristics: TLC R_f 0.13 (A); $[\alpha]^{20}_D$ +28.40° (*c* 0.6, $CHCl_3$); ^1H NMR (250 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.90 (s, 9, $(CH_3)_3CSi$), 3.4 (s, 3, OCH_3), 3.70 (t, 1, H-6), 3.85 (ddd, 1, $J_{5,6'}$ = 10.5 Hz, $J_{4,5}$ = 10.5 Hz, $J_{5,6}$ = 5.0 Hz, H-5), 4.65 (dd, 1, $J_{4,8}$ = 1.2 Hz, H-4), 4.20 (dd, 1, $J_{1,2}$ = 4.0 Hz, $J_{2,8}$ = 1.2 Hz, H-2), 4.28 (dd, 1, H-6), 4.4 (ABq, 2, $J_{8,9}$ = 6.5 Hz, J_{AB} = 12.0 Hz, H-9, H-9′), 4.60 (d, 1, H-1), 5.45 (s, 1, H-7), 5.92 (t, t, 1, H-8). Anal. Calcd for $C_{22}H_{34}O_6Si$: C, 62.53; H, 8.11. Found: C, 62.41; H, 8.02.

Methyl 4,6-*O*-Benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-(((vinyloxy)methyl)methylene)-α-D-*ribo*-hexopyranoside (16). Compound **15** (1.0 g) was converted into the crystalline allyl vinyl ether **16** in 90% yield: mp 65–66 °C (sublimation); TLC R_f 0.50 (A), $[\alpha]^{20}_D$ +14.60° (*c* 1.0, $CHCl_3$); ^1H NMR (250 MHz) δ 0.10 (6, s, $(CH_3)_2Si$), 0.90 (9, s, $(CH_3)_3CSi$), 3.35 (s, 3, OCH_3), 4.70 (d, 1, $J_{1,2}$ = 4.15, H-1), 5.32 (d, 1, $J_{8,9}$ = 11.5 Hz, H-9), 5.40 (d, 1, $J_{8,9'}$ = 17.5 Hz, H-9′), 5.45 (s, 1, H-7), 6.40 (dd, 1, H-8). Anal. Calcd for $C_{24}H_{36}O_6Si$: C, 64.28; H, 8.03. Found: C, 64.21; H, 8.07.

Methyl 4,6-*O*-Benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-α-D-allopyranoside (17a). Compound **16** (0.2 g) was rearranged in 1.0 h to give **17a** (0.19 g, 95%) as a syrup: TLC R_f 0.65 (B); $[\alpha]^{20}_D$ +60.0° (*c* 1.2, $CHCl_3$); ^1H NMR (80 MHz) δ 0.12 (s, 6, $(CH_3)_2Si$), 0.95 (s, 9, $(CH_3)_3CSi$), 2.4 (dd, $J_{10,11}$ = 4.0 Hz, $J_{10,10'}$ = 15.0 Hz, H-10), 2.85 (dd, $J_{10,11}$ = 3.2 Hz, H-10′), 3.35 (s, 3, OCH_3), 3.40-4.50 (m, 5, H-2, H-4, H-5), H-6, H-6′), 4.62 (d, 1, $J_{1,2}$ = 3.3 Hz, H-1), 5.35 (d, 1, $J_{8,9}$ = 11.0 Hz, H-9), 5.40 (d, 1, $J_{8,9'}$ 17.0 Hz, H-9′), 5.48 (s, 1, H-7), 6.40 (dd, 1, H-8), 9.80 (dd, 1, H-11). Anal. Calcd for $C_{24}H_{36}O_6Si$: C, 64.25; H, 8.09. Found: C, 64.12; H, 7.98.

Methyl 4,6-*O*-Benzylidene-3-deoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-α-D-allopyranoside (17b). Compound **17a** (0.10 g) was desilylated in 2.0 h to produce alcohol **17b** as a syrup: TLC R_f 0.32 (D); $[\alpha]^{20}_D$ +44.5° (*c* 1.7, $CHCl_3$); ^1H NMR (80 MHz) δ 3.40 (s, 3, OCH_3), 5.30 (d, 1, $J_{8,9}$ = 11.0 Hz, H-9), 5.40 (d, 1, $J_{8,9'}$ = 17.0 Hz, H-9′), 5.5 (s, 1, H-7), 6.4 (dd, 1, H-8), 9.80 (dd, $J_{10,11}$ = 3.0 Hz, $J_{10',11}$ = 4.0 Hz, H-11); Anal. Calcd for $C_{18}H_{22}O_6$: C,

64-66; H, 6.63. Found: C, 64.54; H, 6.58.

Methyl 4,6-*O*-Benzylidene-2-*C*-((*E*)-carbethoxymethylene)-2,3-dideoxy-α-D-*erythro*-hexopyranoside (19). Methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*arabino*-hexopyranoside[17] **18a** (2.0 g, 8.0 mmol) was dissolved in dry methylene chloride (200 mL) and oxidation in the usual way gave **18b** (1.58 g, 80%) as a crystalline compound: mp 100–101 °C; TLC R_f 0.60 (D); $[\alpha]^{20}_D$ +92.0° (*c* 1.89, $CHCl_3$); ^1H NMR (60 MHz) δ 2.4–2.8 (m, 2, H-3, H-3′), 3.42 (s, 3, OCH_3), 3.7–4.5 (m, 4, H-4, H-5, H-6, H-6′), 5.55 (s, 1, H-7), 6.20 (s, 1, H-1), 7.4–7.5 (m, 5, C_6H_5). A portion of the ketone (1.5 g, 6.0 mmol) was converted into the syrupy ester **19** (1.80 g, 90%) in the usual way: mp 85–86 °C; TLC R_f 0.80 (D); $[\alpha]^{20}_D$ +26.8° (*c* 0.3, $CHCl_3$); ^1H NMR (60 MHz) δ 1.3 (t, 3, *J* = 6.0 Hz, CH_2CH_3), 2.4–2.8 (m, 2, H-3, H-3′), 3.45 (s, 3, OCH_3), 3.7–4.5 (m, 6, H-4, H-5, H-6, H-6′, OCH_3CH_3), 5.55 (s, 1, H-7), 6.25 (s, 1, H-1). Anal. Calcd for $C_{18}H_{22}O_6$: C, 62.79; H, 6.39. Found: C, 62.71; H, 6.32.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-((hydroxymethyl)methylene)-α-D-*erythro*-hexopyranoside (20). Compound **19** (2.0 g, 5.8 mmol) was reduced at 0 °C in 0.5 h to give **20** (1.5 g, 90%) as a syrup: mp 122–123 °C; TLC R_f 0.50 (D); $[\alpha]^{20}_D$ +57.3° (*c* 1.1, $CHCl_3$); ^1H NMR (60 MHz) δ 2.2–2.8 (m, 2, H-3, H-3′), 3.5 (s, 3, OCH_3), 3.7–43. (m, 6, H-4, H-5, H-6, H-6′, H-9, H-9′), 5.3 (s, 1, H-1), 5.5-5.7 (m, 2, H-7, H-8). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.75; H, 6.84. Found: C, 65.76; H, 6.81.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-(((vinyloxy)methyl)methylene)-α-D-*erythro*-hexopyranoside (21). Compound **20** (1.5 g, 5.1 mmol) was converted into the vinyl ether **21**, obtained as a syrup in 10 h: TLC R_f 0.75 (D); $[\alpha]^{20}_D$ +28.2° (*c* 1.9, $CHCl_3$); ^1H NMR (60 MHz) δ 2.3–2.8 (m, 2, H-3, H-3′), 3.45 (s, 3, OCH_3), 3.48–4.5 (m, 8, H-4, H-5, H-6, H-6′, H-9, H-9′, H-11, H-11′), 5.25 (s, 1, H-1), 5.5–5.7 (m, 2, H-7, H-8), 6.6 (dd, 1, $J_{9,10}$ = 7.5 Hz, $J_{9',10}$ = 15.0 Hz, H-10).

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-(formylmethyl)-2-*C*-vinyl-α-D-*ribo*-hexopyranoside (22). A portion of the vinyl ether **21** (1.0 g) was subjected to thermolysis for 2 h, and an oily product **22** (0.9 g) was obtained: TLC R_f 0.70 (D); $[\alpha]^{20}_D$ +36.0° (*c* 0.6, $CHCl_3$); ^1H NMR (60 MHz) δ 1.8–2.1 (m, 2, H-3, H-3′), 2.4 (dd, 1, $J_{10,10'}$ = 17.0 Hz, $J_{10,11}$ = 1.2 Hz, H-10), 2.7 (dd, 1, $J_{10',11}$ = 3.0 Hz, H-10′), 3.35 (s, 3, OCH_3), 3.7–4.2 (m, 4, H-4, H-5, H-6, H-6′), 4.4 (s, 1, H-1), 5.15 (d, 1, $J_{8,9'}$ = 18.0 Hz, H-9′), 5.40 (d, 1, $J_{8,9}$ = 11.0 Hz, H-9), 6.0 (dd, 1, H-8), 7.4–7.5 (m, 5, C_6H_5); HRMS calcd for $C_{18}H_{22}O_5$, 318.1466; found, 318.1462.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-(2-methoxyethyl)-2-*C*-vinyl-α-D-*ribo*-hexopyranoside (23). (a) Compound **22** (0.5 g, 1.5 mmol) was reduced with lithium aluminium (0.45 g, 90%) and the syrup obtained was dissolved in dry DMF (10 mL) and sodium hydride (0.05 g, 2.0 mmol) was added at 0 °C. After 0.5 h, methyl iodide (0.28 g, 2.0 mmol) was added and the reaction was stirred for another 0.5 h. A few drops of methanol were then added. The reaction mixture was poured into water and extracted with diethyl ether (50 mL), dried, and evaporated to give **23** (0.36 g, 85%) as a syrup: TLC R_f 0.65 (D); ^1H NMR (60 MHz) δ 1.45–2.0 (m, 4, H-3, H-3′, H-10, H-10′), 3.30 (s, 1, OCH_3), 3.35 (s, 3, OCH_3), 4.45 (s, 1, H-1). Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.26; H, 7.78. Found: C, 68.19; H, 7.73.

(b) Compound **10** (0.15 g) was reduced and methylated as described in part a, and the material was desilylated. The resulting alcohol (0.3 g, 0.9 mmol) was dissolved in dry diethyl ether (25 mL), was treated with oil free sodium hydride (0.003 g, 0.11 mmol), and was refluxed under argon for 1 h. Carbon disulfide (0.01 mL, 0.16 mmol) was then added and the solution was refluxed for an additional 3 h. This mixture was cooled and methyl iodide (0.01 mL, 0.16 mmol) was added and the resulting solution was refluxed for an additional 3 h. TLC showed a fast-moving product. Water was then added, and the solution was washed with 5% HCl, saturated sodium bicarbonate solution, and water and dried. Evaporation of the solvent gave a material which was dissolved in dry xylene (50 mL) and refluxed. A solution of tri-*n*-butyltin hydride (0.09 g, 0.35 mmol) was added slowly and the reaction mixture was refluxed for 10 h. Evaporation of the solvent and purification on a silica gel column gave a material which had the same ^1H NMR spectrum and R_f data reported for **23** in part a.

(17) Rosenthal, A.; Catsoulacos, P. *Can. J. Chem.* **1968**, *46*, 2868.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-((*Z*)-carbethoxymethylene)-α-D-*erythro*-hexopyranoside (25). The Wittig reaction was done on **24** (1.5 g, 6.0 mmol) in refluxing acetonitrile for 2 h to give **25** (1.75 g, ~87%) as a crystalline product: mp 125–128 °C (recrystallized from ethyl acetate/petroleum ether); TLC R_f 0.48 (C); $[\alpha]^{20}_D$ +51.0° (*c* 1.2, $CHCl_3$); ^1H NMR (200 MHz) δ 1.25 (t, 3, *J* = 6.7 Hz, CH_2CH_3), 3.32 (s, 3, OCH_3), 3.7–4.41 (m, 6, H-4, H-5, H-6, H-6′, OCH_2) 4.85 (d, 1, $J_{1,2}$ = 4.0, H-1), 5.6 (s, 1, H-7), 6.05 (s, 1, H-8). Anal. Calcd for $C_{18}H_{22}O_6$: C, 62.79; H, 6.39. Found: C, 62.73; H, 6.31.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-((*Z*)-(hydroxymethyl)methylene)-α-D-*erythro*-hexopyranoside (26). The ester **25** (1.0 g, 2.9 mmol) was reduced at 0 °C in 0.5 h to give **26** (0.75 g, 90%) as a crystalline product: mp 172–173 °C; TLC R_f 0.28 (D); $[\alpha]^{20}_D$ +170° (*c* 1.3, $CHCl_3$); ^1H NMR (200 MHz) δ 3.35 (s, 1, OCH_3), 3.80 (dd, 1, $J_{6,6}$ = 12.0 Hz, $J_{5,6}$ = 4.2 Hz, H-6), 3.88 (dd, 1, $J_{5,6'}$ = 10.2 Hz, H-6′), 4.0 (d, 1, H-4), 4.21 (dt, 1, $J_{4,5}$ = 10.2 Hz, H-5), 4.85 (d, 1, $J_{1,2}$ = 4.0 Hz), 5.6 (s, 1, H-7), 6.0 (bt, 1, $J_{8,9} \sim J_{8,9'} \simeq$ 6.6 Hz, H-8). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.75; H, 6.84. Found: C, 65.69; H, 6.78.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-α-D-*ribo*-hexopyranoside (28). Compound **26** (1.0 g) was converted into the vinyl ether **27**, and the material which proved to be unsatble was subjected to thermal rearrangement. The product **28** gave the following data: TLC R_f 0.32 (B); $[\alpha]_D$ +75.8° (*c* 1.8, $CHCl_3$); ^1H NMR (60.0 MHz) δ 1.8 (dd, 1, $J_{10,10'}$ = 14.5 Hz, $J_{10,11}$ = 3.5 Hz, H-10), 2.65 (dd, 1, $J_{10',11}$ = 3.5 Hz, H-10′), 3.3 (s, 3, OCH_3), 4.65 (d, 1, $J_{1,2}$ = 3.5 Hz, H-1), 5.25 (d, 1, $J_{8,9}$ = 11.0 Hz, H-9), 5.30 (d, 1, $J_{8,9'}$ = 18.0 Hz, H-9′), 5.5 (s, 1, H-7), 6.4 (dd, 1, H-8), 9.75 (t, 1, H-11). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.90; H, 6.97. Found: C, 67.82; H, 6.86.

Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-(2-hydroxyethyl)-3-*C*-vinyl-α-D-*ribo*-hexopyranoside (29). Compound **28** (0.25 g, 0.75 mmol) was reduced with lithium aluminium hydride to give **29** (0.22 g, 90%) as a syrup: TLC R_f 0.50 (D); $[\alpha]^{20}_D$ +66.6° (*c* 1.7, $CHCl_3$); ^1H NMR (60 MHz) δ 1.2 (m, 2, H-10, H-10′), 3.3 (s, 1, OCH_3), 5.20 (d, $J_{8,9}$ = 11.2 Hz, H-9), 5.28 (d, $J_{8,9'}$ = 17.5 Hz, H-9′), 5.5 (s, 1, H-7). Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.39; H, 7.42.

Methyl 4,6-*O*-Benzylidene-3-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-3-*C*-ethyl-α-D-*ribo*-hexopyranoside (30). Compound **29** (0.20 g) was hydrogenated in 95% ethanol (50 mL) at 16 psi using 5% palladium on carbon in 2 h. Filtration and evaporation of the solvent gave a syrup (0.17 g, 86%) which was dissolved in dry methylene chloride (10 mL) and stirred it at room temperature for 4 h with triethylamine (2 mL) and *tert*-butyldimethylsilyl chloride (0.09 g 0.6 mmol). The reaction was worked up by washing with water (2 × 20 mL), dried, and evaporated. After column chromatography, **30** was obtained as a syrup (0.21 g, 90%) which showed the following characteristics: TLC R_f 0.62 (D); $[\alpha]^{20}_D$ +78.0° (*c* 1.7, $CHCl_3$); ^1H NMR (80 MHz) δ 0.05 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 1.0–2.0 (m, 9, H-2, H-2′, CH_2-CH_3, CH_2CH_2OSi), 3.3 (s, 3, OCH_3), 3.4–4.4 (m, 6, H-4, H-5, H-6, H-6′, OCH_2Si) 4.55 (d, 1, $J_{1,2}$ = 3.8 Hz, H-1), 5.5 (s, 1, H-7). Anal. Calcd for $C_{24}H_{40}O_5Si$: C, 66.06; H, 9.18. Found: C, 65.92; H, 9.05.

Methyl 6-Bromo-3-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-3-*C*-ethyl-α-D-*ribo*-hexopyranoside (32). A solution of **30** (0.09 g, 0.2 mmol) in dry carbon tetrachloride (20 mL) was treated with *N*-bromosuccinimide (0.22 mmol) and few drops of dry pyridine under reflux. After 1.5 h the reaction mixture was filtered through a Celite bed, diluted with diethyl ether (30 mL), washed with water (4 × 10 mL), dried, and evaporated to give crude **31**, which was passed through a short silica gel column. Compound **31** exhibited the following characteristics: TLC R_f 0.60 (B); ^1H NMR (60.0 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), ~1.0–2.0 (m, 9, H-2, H-2′, CH_2CH_3, CH_2CH_2OSi), 3.35 (s, 3, OCH_3), 5.10 (d, 1, $J_{4,5}$ = 10.0 Hz, H-4), 7.2–7.5 and 7.9–8.1 (m, 5, C_6H_5COO). The material (0.08 g) was stirred overnight in dry methanol (10 mL) containing a catalytic amount of sodium methoxide. The solution was then evaporated, and the residue was dissolved in diethyl ether (30 mL), washed with water, dried, and evaporated to give **32** (0.056 g, 87.7%) as a syrup: TLC R_f 0.55 (B); ^1H NMR (60 MHz) 0.10 (6, S, $(CH_3)_2Si$), 0.85 (9, S, $(CH_3)_3CSi$), 1.0–2.0 (m, 9, H-2, H-2′, CH_2CH_3, CH_2CH_2OSi), 3.42 (s, 3, OCH_3), 3.5–4.0 (m, 5, H-5, H-6, H-6′,

OCH_2Si), 4.55 (d, 1, $J_{4,5}$ = 9.0 Hz, H-4), 4.80 (d, 1, $J_{1,2}$ = 3.5 Hz, H-1). Anal. Calcd for $C_{17}H_{35}O_4BrSi$: C, 49.66; H, 8.52. Found: C, 49.51; H, 8.46.

Methyl 6-*O*-Benzoyl-2,3-dideoxy-3-*C*-ethyl-α,D-*lyxo*-hexopyranosido[4,3-*b*]tetrahydrofuran (34). A solution of compound **32** (0.055 g, 0.138 mmol) in dry pyridine (10 mL) was stirred at room temperature for 0.5 h with methanesulfonyl chloride (0.1 mL). The resulting solution was poured on ice and diluted with diethyl ether (30 mL), washed with water, dried, evaporated, and passed through a short silica gel column to give **33** (0.038 g, 59%) as a syrup: TLC R_f 0.50 (B); ^{1}H NMR (60 MHz) δ 0.10 (6, s, $(CH_3)_2Si$), 0.85 (9, s, $(CH_3)_3CSi$), 1.0–2.0 (m, 9, H-2, H-2′, CH_2CH_3, CH_2CH_2OSi), 3.0 (s, 3, $CH_3C_6H_4SO_2$), 3.40 (s, 3, OCH_3), 3.45–4.00 (m, 5, H-5, H-6, H-6′, CH_2OSi), 4.7–4.8 (m, 2, H-1, H-4).

A portion of **33** (0.03 g, 0.06 mmol) in dry dimethylformamide (10 mL) was refluxed with excess of sodium benzoate for 12 h. The reaction mixture was then diluted with diethyl ether (50 mL), washed with water (4 × 10 mL), dried, and purified by using a short column (solvent B) to produce **34** as a clear oil (0.012 g, 42%) which exhibited the following characteristics: TLC R_f 0.45 (B); ^{1}H NMR (60.0 MHz) δ 1.6–2.0 (m, 9, H-2, H-2′, CH_2CH_3, CH_2CH_2O), 3.40 (s, 3, OCH_3), 4.6 (m, 2, H-6, H-6′), 4.70 (bs, 1, H-1), 7.3–7.6 and 7.9–8.1 (m, 5, CH_5COO). Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55. Found: C, 67.41; H, 7.48.

1,5-Anhydro-4,6-*O*-benzylidene-D-glucitol (38). To a solution of commercially available 2,3,4,5-tetra-*O*-acetyl-α-D-glucopyranosyl bromide "acetobromoglucose" **35** (40.0 g, 97.3 mmol) in dry ethyl acetate (120 mL) was added dry triethylamine (20 mL) and Raney nickel (10.0 g). The reaction mixture was hydrogenated for 2 h at 50 °C and 1000 psi. The solution was then filtered and evaporated and the residue was redissolved in methylene chloride, washed with water, dried, and evaporated to give **36** (26.5 g, 80%) as a syrup which exhibited the following characteristics: TLC R_f 0.4 (D); ^{1}H NMR (60 MHz) δ 2.05 and 2.1 (s, 12, 4 $OCOCH_3$), 3.1–3.3 (m, 2, H-1a, H-1e), 4.1–4.4 (m, 3, H-5, H-6, H-6′), 5.0–5.2 (m, 3, H-2, H-3, H-4). A portion of the material (5.0 g) was stirred in a mixture of methanol (100 mL), water (80 mL), and triethylamine (20 mL) for 10 h. The solution was then evaporated to give **37** as a syrup which was dried overnight on an oil pump. The residue was dissolved in benzaldehyde (6 mL) and shaken overnight with zinc chloride (3.0 g). The reaction mixture was poured on an ice–water mixture and washed with petroleum ether and water several times. The residue was recrystallized from methanol. Compound **38** exhibited the following characteristics: mp 152–153 °C; TLC R_f 0.3 (E); $[\alpha]^{20}_D$ −20.5° (*c* 1.2, $CHCl_3$); ^{1}H NMR (60 MHz) δ 3.3–4.8 (m, 8, H-1a, H-1e, H-2, H-3, H-4, H-5, H-6, H-6′), 5.5 (s, 1, H-7), 7.3–7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{13}H_{16}O_5$: C, 61.90; H, 6.34. Found: C, 61.83; H, 6.28.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-D-glucitol (40) and 1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-D-glucitol (39). Compound **38** (2.52 g, 10.0 mmol) was refluxed with di-*n*-butyltin oxide (3.0 g, 12.0 mmol) in toluene (100 mL) for 4 h.[12] The solvent was then evaporated and the residue was dissolved in dry DMF (50 mL). To this was added imidazole (0.82 g, 12.0 mmol) and *tert*-butyldimethylsilyl chloride (1.8 g, 12.0 mmol). The resulting solution was kept at 70 °C for 3 h, diluted with diethyl ether (300 mL), washed with water, dried, and evaporated to give **40** as 65% of the product. Compound **40** exhibited the following characteristics: mp 82–84 °C; TLC R_f 0.75 (D); $[\alpha]^{20}_D$ −12.6° (*c* 1.48, $CHCl_3$); ^{1}H NMR (60 MHz) δ 0.05 (s, 6, $(CH_3)_2Si$), 0.90 (s, 9, $(CH_3)_3CSi$), 3.1–4.2 (m, 8, H-1, H-1′, H-2, H-3, H-4, H-5, H-6, H-6′), 5.5 (s, 1, H-7), 7.3–7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{19}H_{30}O_5Si$: C, 62.29; H, 8.19. Found: C, 62.24; H, 8.16.

Compound **39** was a syrup and exhibited the following characteristics: TLC R_f 0.25 (A); $[\alpha]^{20}_D$ −24.1° (*c* 2.0, $CHCl_3$); ^{1}H NMR (80 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 3.3–4.4 (m, 8, H-1, H-1′, H-2, H-3, H-4, H-5, H-6, H-6′), 5.45 (s, 1, H-7), 7.3–7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{19}H_{30}O_5Si$: C, 62.29; H, 8.19. Found: C, 62.05; H, 8.10.

1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-D-*arabino*-2-ulohexitol (41). Compound **39** (1.0 g) was oxidized according to the genral procedure to give **41** (0.93 g, 93%) as a syrup: TLC R_f 0.32 (A); $[\alpha]^{20}_D$ −49.9° (*c* 2.7, $CHCl_3$); IR (neat) 1760 (ketone) cm^{-1}; ^{1}H NMR (250 MHz) δ 0.04 and 0.14 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 3.8 (t, 1, $J_{3,4}$ <<soc $J_{4,5}$ = 9.2 Hz, H-4), 4.05 (d, 1, $J_{1,1'}$ = 15.2 Hz, H-1), 4.22 (d, 1, H-1′), 4.35 (d, 1, H-3). Anal. Calcd for $C_{19}H_{28}O_5Si(H_2O)$: C, 62.63; H, 7.69. Found: C, 59.78; H, 7.92 (hydrated ketone).

1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-*C*-((*E*)-carbethoxymethylene)-2-deoxy-D-*arabino*-hexitol (43). Compound **41** (1.0 g) was converted into **43** using the general procedure (0.95 g, 80%). The crystalline product exhibited the following characteristics: mp 88–90 °C (recrystallized from ethyl acetate/petroleum ether); TLC R_f 0.44 (A); $[\alpha]^{20}_D$ −126.4° (*c* 2.65, $CHCl_3$); ^{1}H NMR (250 MHz) δ 0.03 and 0.08 (6, s, $(CH_3)_2Si$), 0.9 (9, s, $(CH_3)_3CSi$), 2.3 (3, t, *J* = 6.5, CH_3CH_2), 3.45 (1, t, $J_{5,6} \sim J_{6,6'}$ = 11.0 Hz, H-6), 3.53 (1, dt, $J_{5,6'}$ = 4.4 Hz, H-5), 3.68 (t, 1, $J_{3,4}$ = 11.0 Hz, H-4), 3.9 (d, 1, $J_{1,1}$ = 14.0 Hz, H-1), 4.2 (q, 2, OCH_2CH_3), 4.3 (dd, 1, H-6′), 4.38 (dd, 1, $J_{3,8}$ = 2.2 Hz), 5.5 (s, 1, H-7), 5.75 (d, 1, H-1′), 6.25 (d, 1, H-8). Anal. Calcd for $C_{23}H_{34}O_6Si$: C, 63.59, H, 7.83. Found: C, 63.56; H, 7.88.

1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-*C*-((hydroxymethyl)methylene)-2-deoxy-D-*arabino*-hexitol (44). To a cooled (0 °C) solution of **43** (1.5 g, 3.45 mmol) in dry toluene (50 mL) was added 1 M diisobutylaluminium hydride (10.5 mL). After 0.5 h the reaction was worked up by using a saturated solution of ammonium chloride to give **44** (1.19, 89%) as a syrup which exhibited the following characteristics: TLC R_f 0.1 (A); $[\alpha]^{20}_D$ −77.0° (*c* 2.1, $CHCl_3$); ^{1}H NMR (250 MHz) δ 3.8 (d, 1, $J_{1,1'}$ = 13.5 Hz, H-1), 4.25 (m, 2, H-9, H-9′), 4.72 (d, 1, H-1′), 5.5 (s, 1, H-7), 6.2 (dt, 1, $J_{3,8}$ = 2.2 Hz, $J_{8,9}$ = 7.2 Hz, H-8). Anal. Calcd for $C_{21}H_{32}O_5Si$: C, 66.04; H, 8.14. Found: C, 65.92; H, 8.20.

1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-*C*-(formylmethyl)-2-*C*-vinyl-D-glucitol (46). Compound **44** (0.25 g) was converted into the vinyl ether **45** by using the described general procedure. The syrup (0.23 g, 90%, R_f 0.35 (A)) was passed through a very short column of silica gel, and thermal rearrangement was carried out by using the standard procedure. The product was a mixture of two compounds (98:2), and after isolation by column chromatography the major component **46** exhibited the following characteristics: TLC R_f 0.30 (A); $[\alpha]^{20}_D$ −86.32° (*c* 1.3 $CHCl_3$); ^{1}H NMR (250 MHz) δ 2.23 (dd, 1, $J_{10,11}$ = 4.0 Hz, $J_{10,10'}$ = 15.2 Hz, H-10), 2.85 (dd, 1, H-10′), 3.43 (dt, $J_{5,6} \sim J_{4,5}$ = 10 Hz, $J_{5,6'}$ = 3.5 Hz, H-5), 3.55 (t, 1, H-6) 3.58 (dd, 1, $J_{1,1}$ = 12.0 Hz, $J_{1,8}$ = 1.6 Hz, H-1), 3.64 (t, 1, $J_{3,4}$ = 10.0 Hz, H-4), 3.75 (d, 1, H-3), 4.15 (d, 1, H-1′), 4.24 (dd, 1, H-6′), 5.35 (d, 1, $J_{8,9}$ = 17.5 Hz, H-9), 5.40 (d, $J_{8,9'}$ = 11.0 Hz, H-9′), 5.45 (s, 1, H-7), 6.18 (ddd, 1, H-8), 9.68 (dd, 1, H-11). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 66.04; H, 8.14. Found: C, 66.14; H, 8.05.

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-2-*C*-(formylmethyl)-2-*C*-vinyl-D-glucitol 2,3-Lactol (47). Compound **46** (0.10 g) was desilylated in 1.5 h to produce **47** (0.06 g, 88%) as a syrupy mixture of hemiacetals, the major component of which exhibited the following characteristics: TLC R_f 0.30 (B); ^{1}H NMR (80 MHz) δ 3.4–4.4 (m, 6, H-1, H-1′, H-4, H-5, H-6, H-6′), 5.22 (d, 1, $J_{10,11}$ = 5.0 Hz, H-11), 5.3 (d, 1, $J_{8,9}$ = 17.5 Hz, H-9), 5.35 (d, 1, $J_{8,9'}$ = 11.0 Hz, H-9′), 5.6 (s, 1, H-7), 5.95 (dd, 1, H-8).

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-D-*ribo*-3-ulohexitol (42). Compound **40** (1.0 g) was oxidized according to standard procedure to give **42** (0.9 g, 90%) as a syrup: TLC R_f 0.5 (B); IR (heat) 1750 (ketone) cm^{-1}; ^{1}H NMR (60 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 2.8–4.5 (m, 7, H-1, H-1′, H-2, H-4, H-5, H-6, H-6′), 5.5 (s, 1, H-7). Anal. Calcd for $C_{19}H_{28}O_5Si$: C, 62.63; H, 7.69. Found: C, 62.58; H, 7.72.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-((*E*)-carbethoxymethylene)-D-*ribo*-hexitol (48). Compound **42** (2.0 g) was converted into **48** by use of the general procedure (1.91 g, 80%): TLC R_f 0.4 (B); $[\alpha]^{20}_D$ −68.7° (*c* 0.6, $CHCl_3$); ^{1}H NMR (60 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 6.0 (m, 1, H-8), 7.4–7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{23}H_{34}O_6Si$: C, 63.59; H, 7.83. Found: C, 63.53; H, 7.79.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-((hydroxymethyl)methylene)-D-*ribo*-hexitol (49). The ester **48** (1.5 g, 3.45 mmol) was reduced with 1 M diisobutylaluminum hydride in toluene (10.5 mL) in

1 h (as described for 13 → 15) to give 49 (1.22 g, 90%) as a syrup: TLC R_f 0.18 (A); $[\alpha]^{20}_D$ -19.15° (c 1.5, $CHCl_3$); ^1H NMR (60 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 3.0-4.3 (m, 9, H-1, H-1′, H-2, H-8, H-9′, H-9, H-4, H-5, H-6, H-6′), 5.5 (s, 1, H-7), 5.9 (bt, 1, J = 6.0 Hz, H-8), 7.4-7.5 (m, 5, C_6H_5). Anal. Calcd for $C_{21}H_{32}O_5Si$: C, 64.29; H, 8.16. Found: C, 64.12; H, 8.28.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-(((vinyloxy)methyl)methylene)-D-*ribo*-hexitol (50). Alcohol 49 (0.3 g) was converted into the title compound 50 in the standard way: TLC R_f 0.64 (A); $[\alpha]^{20}_D$ -18.6° (c 0.9, $CHCl_3$); ^1H NMR (80 MHz) δ 0.1 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 5.5 (1, s, H-7), 5.75 (bt, 1, J = 6.2 Hz, H-8), 6.45 (dd, 1, $J_{10,11}$ = 7.0 Hz, $J_{10,11'}$ = 15.0 Hz, H-10). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 66.05; H, 8.14. Found: C, 66.21; H, 8.05.

1,5-Anhydro-4,6-*O*-benzylidene-2-*O*-(*tert*-butyldimethylsilyl)-3-deoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-D-allitol (51). Compound 50 (0.15 g) was rearranged in 1.0 h according to the standard procedure to afford 51 (0.13 g, 85%) as a syrup: TLC R_f 0.58 (A); $[\alpha]^{20}_D$ -35.20° (c 0.7, $CHCl_3$); ^1H NMR (80 MHz) δ 0.08 (s, 6, $(CH_3)_2Si$), 0.9 (s, 9, $(CH_3)_3CSi$), 2.4 (dd, 1, $J_{10,11}$ = 4.0 Hz, $J_{10,10'}$ = 17.0 Hz, H-10), 2.8 (dd, 1, $J_{10',11}$ = 2.0 Hz, H-10′), 3.35-3.8 (m, 6, H-1, H-1′, H-2, H-4, H-6, H-6′), 4.2 (m, 1, H-5), 5.30 (d, 1, H-9), 5.40 (s, 1, H-7), 5.45 (d, 1, H-9′), 6.25 ($J_{8,9}$ = 11.0 Hz, $J_{8,9'}$ = 17.5 Hz, H-8), 9.85 (dd, 1, H-11). Anal. Calcd for $C_{23}H_{34}O_5Si$: C, 66.04; H, 8.14. Found: C, 65.98; H, 8.20.

1,5-Anhydro-4,6-*O*-benzylidene-3-deoxy-3-*C*-(formylmethyl)-3-*C*-vinyl-D-allitol (52). Compound 51 (0.10 g) was desilylated in 1.5 h to give 52 (0.065 g, 90%) as a syrup: TLC R_f 0.32 (D); $[\alpha]^{20}_D$ -24.2° (c 1.2, $CHCl_3$); ^1H NMR (80 MHz) δ 2.2 (dd, 1, $J_{10,11}$ = 4.0 Hz, $J_{10,10'}$ = 17.5 Hz, H-10), 2.7 (dd, $J_{10',11}$ = 2.0 Hz, H-10′), 5.45 (s, 1, H-7), 6.25 (dd, 1, $J_{8,9}$ = 10.0 Hz, $J_{8,9'}$ = 16.0 Hz, H-8), 9.8 (dd, 1, H-11). Anal. Calcd for $C_{17}H_{20}O_5$: C, 67.13; H, 6.38. Found: C, 67.29; H, 6.42.

Acknowledgment. We are grateful to the National Institutes of Health (GM 32569), Merck, Sharp and Dohme, and Ciba Geigy for support of this work.

Registry No. 1, 3162-96-7; 2, 89872-82-2; 3, 89872-83-3; 4, 89920-65-0; 5, 78329-22-3; 6, 89889-10-1; 7, 89872-84-4; 8, 89872-85-5; 9a, 89872-86-6; 9b, 78329-23-4; 10, 78329-24-5; 11 (isomer 1), 89920-66-1; 11 (isomer 2), 89920-67-2; 12, 78329-10-9; 13, 78342-22-0; 14, 89873-09-6; 15, 89920-68-3; 16, 78342-23-1; 17a, 78329-14-3; 17b, 78329-16-5; 18a, 34266-73-4; 18b, 19272-50-5; 19, 89872-87-7; 20, 89872-88-8; 21, 89872-89-9; 22, 78342-34-4; 23, 78342-35-5; 24, 6752-49-4; 25, 89920-69-4; 26, 90024-28-5; 27, 78329-18-7; 28, 78342-30-0; 29, 89872-90-2; 30, 89872-91-3; 31, 89872-92-4; 32, 89872-93-5; 33, 89872-94-6; 34, 89872-95-7; 35, 572-09-8; 36, 13137-69-4; 37, 154-58-5; 38, 65190-39-8; 39, 89872-97-9; 40, 89872-96-8; 41, 89872-98-0; 42, 89873-03-0; 43, 89872-99-1; 44, 89889-00-9; 45, 89873-01-8; 46, 89873-00-7; 47 (isomer 1), 89873-02-9; 47 (isomer 2), 89920-70-7; 48, 89873-04-1; 49, 89873-05-2; 50, 89873-06-3; 51, 89873-07-4; 52, 89873-08-5; Ph_3P=CHCOOEt, 1099-45-2; CH_2=CHOEt, 109-92-2.

Photochemical Reactivity of α-Sulfonyloxy Enones: An Easy Method for Arylation of 1,2-Diketones

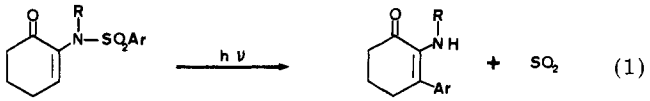
Alexandre Feigenbaum,* Jean-Pierre Pete, and Denise Scholler

Laboratoire de Photochimie,† U.E.R. Sciences, F. 51062 Reims Cedex, France

Received October 28, 1983

3-Aryl-1,2-cyclohexanediones 4 are prepared conveniently by photolysis of the corresponding 2-((arylsulfonyl)oxy)cyclohex-2-enones 1. The reaction was shown to occur from a triplet excited state. A biphotonic process involving the normal photo-Fries product 14 as an intermediate was ruled out by preparing and irradiating this compound. The difference of reactivity between 1 and 2-((arylsulfonyl)amido)cyclohexenones is discussed.

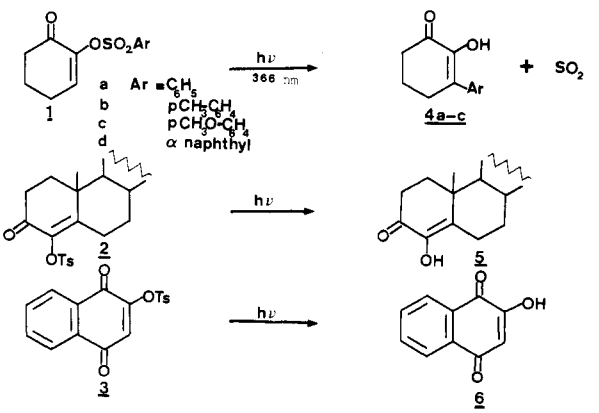
Photochemistry of conjugated enones depends strongly on the substitution.[1] With α-alkoxy or α-alkylamino groups the usually observed photocyclization products arise from the first singlet excited state of the enone. With α-*N*-(arylsulfonyl)amido substituents, a new photochemical reaction involving desulfonation and migration of the arene group to the β position was observed[2] (eq 1). In contrast



(1)

to the photocyclization this reaction was shown to occur from the lowest triplet state. If a similar process could be observed from α-(sulfonyloxy)cyclohexenones, 3-arylated 1,2-cyclohexanediones could be easily obtained from the unsubstituted diketone. Such α-aryl diones might be interesting intermediates in organic synthesis.[3] To check this idea, we prepared diketones 1-3 (Scheme I) and we report that desulfonation and migration of the aryl group

Scheme I



are indeed observed during the photolysis of 2-(arysulfonyl)oxy)-2-cyclohexenones and we discuss the scope

†Equipe de Recherche Associée au CNRS "Réarrangements thermiques et photochimiques" No. 688.

(1) Arnould, J. C.; Enger, A.; Feigenbaum, A.; Pete, J. P. *Tetrahedron* **1979**, *35*, 2501 and references cited therein.

(2) (a) Arnould, J. C.; Cossy, J.; Pete, J. P. *Tetrahedron* **1980**, *36*, 1585. (b) Cossy, J.; Pete, J. P. *Tetrahedron* **1981**, *37*, 2287.

0022-3263/84/1949-2355$01.50/0