exo-5d, 90899-47-1; endo-5e, 90858-45-0; exo-5e, 90899-48-2; 6b, 84500-54-9; exo-6c, 90858-46-1; endo-6c, 90858-47-2; exo-6d, 90858-48-3; endo-6d, 90858-49-4; exo-6e, 90858-50-7; endo-6e, 90858-51-8; 7a, 84500-52-7; 7b, 84500-55-0; maleic anhydride, 108-31-6; dimethyl fumarate, 624-49-7; 2-chloroacrylnitrile, 920-37-6; acrylonitrile, 107-13-1; acetylenedicarboxylate, 44742-97-4; diethylchloroalane, 96-10-6; ammonium cerium(IV) nitrate, 16774-21-3.

Preparation of α- and β-Linked Disaccharides of 2,6-Dideoxy-D-*arabino*-hexose. Synthesis of Bamflalactone

Inge Lundt*

Department of Organic Chemistry, The Technical University of Denmark, DK-2800 Lyngby, Denmark

Joachim Thiem

Organisch-Chemisches Institut, Universität Münster, D-4400, Münster, Federal Republic of Germany

Archibald Prahst

Institut für Organische Chemie und Biochemie, Universität Hamburg, D-2000 Hamburg 13, Federal Republic of Germany

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1,4-α-Linked disaccharides of 2,6-dideoxy-D-*arabino*-hexose are prepared from the selectively protected 2,6-dideoxy sugars **3** or **4** and the 1,5-anhydrohex-1-enitol (**9**) by using the *N*-iodosuccinimide (NIS) method or from the deoxy sugar **6** and the acetylated 2,6-dibromo-2,6-dideoxy-α-D-mannopyranosyl bromide (**13**) in a glycosylation reaction. Dehalogenation leads to the tetradeoxy disaccharides **14**, **15**, and **17**. Deprotection of **17** gives the free α-linked disaccharide **19**. The β-linked disaccharide **27** is obtained by a glycosylation reaction involving **6** and the acetylated 2,6-dibromo-2,6-dideoxy-α-D-glucopyranosyl bromide (**26**). Dehalogenation affords the tetradeoxy disaccharide **29**, from which the free β-linked disaccharide (**31**) is obtained. Catalytic hydrogenolysis of **29** yields **30**, which is converted further into bamflalactone acetate (**28**).

Introduction

2-Deoxy saccharides are found as building units in many natural products having biological activities, for example, in antibiotics such as the orthosomycin group,[1] in anthracyclines,[2] and in cardiac glycosides.[3] Therefore, efforts have been made to develop methods for the synthesis of anomerically homogeneous glycosides of these sugars. In the case of 2-deoxy-α-glycopyranosides, efficient methods have been developed with glycals (1,5-anhydrohex-1-enitols) serving as starting materials. Alkoxyselenation[4] or reaction with alcohols in the presence of *N*-iodosuccinimide (NIS)[5] gave, as a result of anti addition to the double bond, α-glycosides with an axial substituent at C2 (SePh or I), subsequently removable to give α-glycosides of 2-deoxy sugars. Thus, this NIS method has been used extensively to assemble the α-linked sugar sequences in cardiac glycosides.[6] In these reactions, the high stereoselectivity is probably a result of a directing effect from the substituent at C2. That such an effect is operative, also in the case of a bromine atom positioned at C2, follows from our recent studies[7] of the glycosylation reaction between the two readily available[8] C2 epimeric 2,6-dibromo-2,6-dideoxy-D-manno- (**13**) and -D-glucopyranosyl bromides (**26**) and simple alcohols. From the manno isomer (**13**) only α-glycosides were obtained, while the gluco isomer (**26**) and other 2-bromo-2-deoxy sugars with a gluco configuration[7] gave the β-anomers as the main products. In other words 1,2-*trans*-glycosides were obtained in both cases. On hydrogenolysis these products were converted into simple α- or β-2-deoxyglycosides.[7]

In the present paper we describe the usefulness of the method for preparing 2'-deoxy-β-disaccharides including a 1,4-β-linked disaccharide of 2,6-dideoxy-D-*arabino*-hexose (**31**), which was further converted into the acetylated bamflalactone[9] (**28**), thus supporting the structure[8,10,11] of the terminal disaccharide unit in flambamycin.[1,9] We also prepared the corresponding α-anomer (**19**) both by a glycosylation reaction and by applying the NIS method.

Results and Discussion

When 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dideoxy-6-iodo-D-*arabino*-hex-1-enitol (**9**)[12] was allowed to react with methyl 3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (**3**) following the NIS procedure,[5] a high yield of the 1,4-α-linked disaccharide (**10**) was obtained. When the 3-*O*-*p*-nitrobenzoate (**4**) was employed, the disaccharide (**11**) was similarly formed. Alternatively, reaction of 3,4-di-*O*-acetyl-2,6-dibromo-2,6-dideoxy-α-D-mannopyranosyl bromide (**13**)[8] with benzyl 3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (**6**) yielded the 1,4-α-linked disaccharide (**12**). Since the equatorial hydroxy group at C-4

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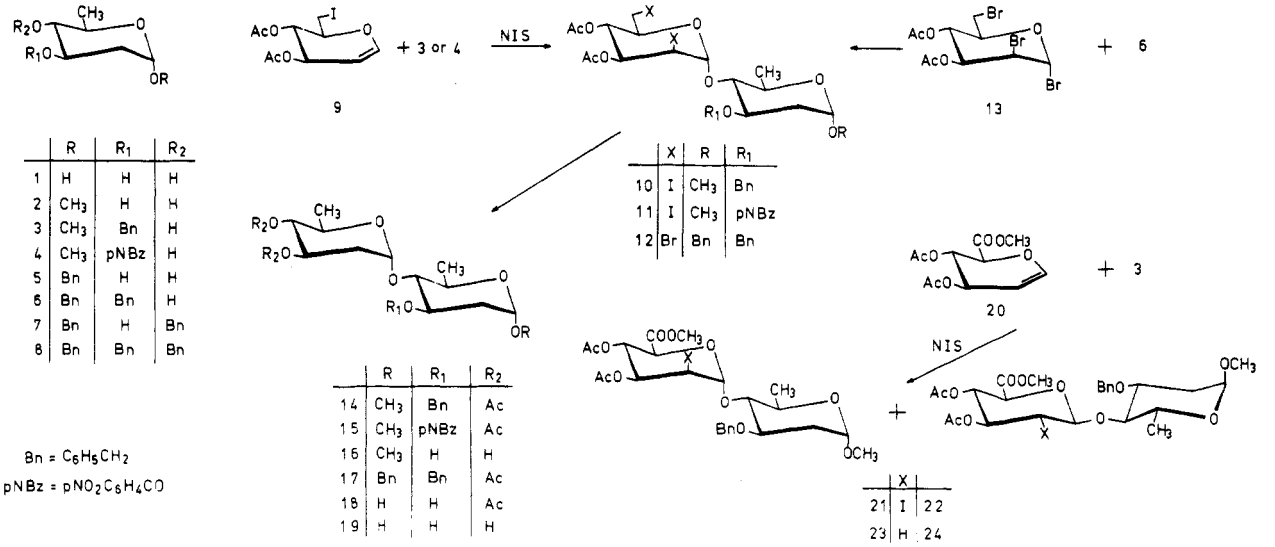
0022-3263/84/1949-3063$01.50/0

Scheme I



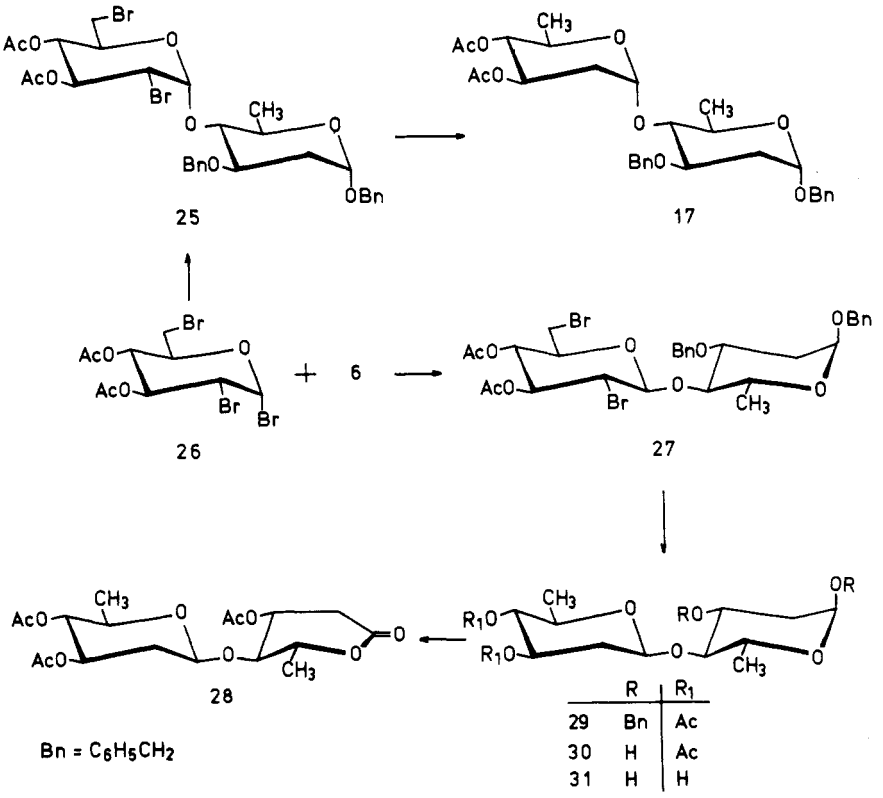
	R	R1	R2
1	H	H	H
2	CH_3	H	H
3	CH_3	Bn	H
4	CH_3	pNBz	H
5	Bn	H	H
6	Bn	Bn	H
7	Bn	H	Bn
8	Bn	Bn	Bn

	X	R	R1
10	I	CH_3	Bn
11	I	CH_3	pNBz
12	Br	Bn	Bn

	R	R1	R2
14	CH_3	Bn	Ac
15	CH_3	pNBz	Ac
16	CH_3	H	H
17	Bn	Bn	Ac
18	H	H	Ac
19	H	H	H

	X		
21	I	22	
23	H	24	

Scheme II



	R	R1
29	Bn	Ac
30	H	Ac
31	H	H

in hexopyranoses is rather unreactive,[13,14] the reactive promoter, silver trifluoromethanesulfonate (silver triflate), originally introduced by Hanessian and Banoub,[15] is utilized, resulting in a high yield of the α-linked disaccharide (**12**). The glycosides **14** and **15** were obtained from the iodo derivatives **10** and **11**, respectively, upon catalytic hydrogenolysis, whereas the bromine atoms were removed quantitatively from **12** by treatment with tributylstannane to give **17**. The two methods discussed above are comparable, both giving high yields of 1,4-α-linked disaccharides of 2,6-dideoxy-D-*arabino*-hexose. Debenzylation of **17**, upon catalytic hydrogenolysis, gave **18** which was fully deblocked to 2,6-dideoxy-4-*O*-(2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-D-*arabino*-hexopyranose (**19**).

Attempts to use the NIS method also for the synthesis of 2′-deoxy-β-glycosides were partly successful[10] with methyl 3,4-di-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitoluronate (methyl di-*O*-acetyl-D-glucuronal) (**20**)[16] as the starting material. This glycal (**20**) exists in an equilibrium between the $^4H_5$ D and the $^5H_4$ D half-chairs. The "normal" glycals, such as **9**, adopt the $^4H_5$ D conformation exclusively[10] and thus give only α-glycosides in these reactions. In fact, **20** formed α- and β-glycosides in about equal amounts.[10] We have now performed the reaction between **20** and the selectively protected dideoxy sugar **3** and did obtain a ca. 1:1 mixture of the anomeric

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disaccharides **21** and **22**. The total yield was low (ca. 20%), however, because of low reactivities of both the glycal (**20**) and **3** as discussed above. Hence, this method is not attractive for the synthesis of 1,4-β-linked disaccharides.

Returning to the glycosylation reactions, 3,4-di-*O*-acetyl-2,6-dibromo-2,6-dideoxy-α-D-glucopyranosyl bromide (**26**)[8] was reacted with **6** (Scheme II). In a polar solvent, with silver triflate as a promoter, the two fairly unreactive compounds gave a high total yield of disaccharides, from which the β-linked disaccharide (**27**) could be isolated in a yield of 57% by flash chromatography, together with a smaller quantity of the α-anomer **25** (16%). For comparison, the latter was dehalogenated to the tetradeoxy disaccharide (**17**) described above. Thus, the equatorial bromine at C-2 in **26** directs the aglycone preferentially into a trans position. The β:α ratio in this synthesis was 3.5:1; very recently it was shown,[17] that with the more reactive equatorial 3-hydroxy group of a protected sugar, the ratio increases to 6.5:1. This method thus seems attractive, and is, to our knowledge, the only one leading to β-linked disaccharides in which the 2′-group can be readily converted into a 2′-deoxy function.

The β-linked tetradeoxy disaccharide (**29**) was formed in a high yield as a crystalline compound upon treatment of **27** with tributylstannane, whereas catalytic hydrogenolysis of **27** did not proceed satisfactorily. Hydrogenolysis of **29** in ethanol–acetic acid gave the crystalline dihydroxy compound **30**. This derivative may be useful as a building block in reactions leading to larger saccharides. Finally, **30** was deacetylated to the free 2,6-dideoxy-4-*O*-(2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-D-*arabino*-hexopyranose 2,6-dideoxy-4-*O*-(2,6-dideoxy-β-β-D-*arabino*-hexopyranosyl)-D-*arabino*-hexopyranose (**31**).

When the free sugar **30** was oxidized with bromine in the presence of barium carbonate,[18] followed by acetylation, a crystalline compound was isolated. This was shown to be identical with the bamflalactonetriacetate,[9] isolated after degradation of flambamycin. Thus the terminal disaccharide of this antibiotic consists of two 2,6-dideoxy-D-*arabino*-hexopyranose units joined by a (1→4)-β-D-linkage.[8,10,11]

The assignment of the anomeric configurations of the disaccharides prepared above was based on ^1H and ^{13}C NMR data. Thus, the major product from the reaction of the gluco isomer **26**, namely **27**, was assigned as the β-anomer on the basis of the H1–H2 coupling constant (J_{12} = 8.6 Hz) while the minor product formed, **25**, was the corresponding α-anomer (J_{12} = 3.8 Hz). This conclusion was supported by the $^{13}C1$–$^1H1$ coupling constant.[21] Thus J_{C1H1} was found to be 163 Hz for **27** and 179 Hz for **25**. A value similar to the latter was found for **12** (J_{C1H1} = 175 Hz) indicating the α-configuration of this mannoside. Since J_{H1H2} are not indicative of the anomeric configuration in the mannose series (**10**, **11**, **12**) the α-configurations was further supported by analyzing the corresponding deoxy compounds (**14**, **15**, **17**). In the latter compounds the H1 protons have small coupling constants to both H2 protons, in agreement with the equatorially orientation of H1.

In the assignment of the structures **21** and **22** similar data were used in combination with $J_{2'3'}$, which for **22** was found to be 10.8 Hz in agreement with the gluco configuration; in **21** $J_{2'3'}$ was found to 3.9 Hz in accordance with the manno configuration in the nonreducing ring.

Finally ^1H and ^{13}C NMR data are given for bamflalactone acetate (**28**). Previously similar data were given for flambalactone.[9,23]

Experimental Section

General Procedures. ^1H NMR spectra were measured on Bruker HX-270 and WM 400 spectrometers and ^{13}C NMR spectra were obtained on a WH-90 instrument. For ^1H and ^{13}C NMR spectra measured in $CDCl_3$ solutions Me_4Si was used as internal reference, whereas for spectra measured in D_2O solution acetone (δ 2.22) was used for ^1H NMR spectra and 1,4 dioxane (δ 67.4) for ^{13}C NMR spectra. Optical rotations were measured on a Perkin Elmer 141 polarimeter.

Glycosylation reactions were all performed in a dry N_2 atmosphere. Column chromatography was made on silica gel (40–63 μm, Merck 9385) with the "flash technique".[19] Evaporations were performed in vacuo at 40 °C. Melting points are uncorrected. Microanalyses were performed by Novo Microanalytical Laboratory and by Analysenabteilung, Institut für Organische Chemie und Biochemie der Universität Hamburg.

Methyl 3-*O*-Benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (3). Methyl 2,6-dideoxy-α-D-*arabino*-hexopyranoside (**2**)[8] (103 mg, 0.63 mmol) together with tetrabutylammonium bromide (30 mg, 0.15 mmol) in dichloromethane (10 mL), 20% aqueous potassium hydroxide (5 mL), and benzyl bromide (100 mg, 0.61 mmol) was stirred vigorously at room temperature for 18 h. The organic layer was separated, washed with water, dried ($MgSO_4$), concentrated, and chromatographed (preparative TLC, ethyl acetate–hexane, 1:1) to give 52.9 mg (33%) of syrupy **3**: $[\alpha]^{20}_D$ +32 ° (*c* 0.23, CH_3OH); ^1H NMR (270 MHz, $CDCl_3$) δ 4.82 (dd, H-1), 1.66 (ddd, H-2a), 2.31 (ddd, H-2e), 3.70 (ddd, H-3), 3.27 (dd, H-4), 3.77 (m, H-5), 1.29 (d, H-6), 3.36 (s, OCH_3), 2.42 (s, 4-OH), 4.52 and 4.71 (AB pattern, J = 12.0 Hz, $PhCH_2$) 7.42 (m, 5 H, aryl H), J_{12a} = 3.6, J_{12e} = 1.0, J_{2a2e} = 12.6, J_{2a3} = 10.8, J_{2e3} = 5.2, J_{34} = 9.0, J_{45} = 9.3, and J_{56} = 6.9 Hz. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.91; H, 8.15.

Methyl 2,6-Dideoxy-3-*O*-(*p*-nitrobenzoyl)-α-D-*arabino*-hexopyranoside (4). Methyl 2,6-dideoxy-α-D-*arabino*-hexopyranoside (**2**)[8] (5.7 g, 35.2 mmol) in pyridine (60 mL) was cooled to 0 °C and *p*-nitrobenzoyl chloride (7.2 g, 38.8 mmol, 1.1 equiv) was added in the course of 15 min and the mixture was left over night at +5 °C. Dichloromethane (100 mL) was then added and washed successively with aqueous HCl, $NaHCO_3$, and water, dried ($MgSO_4$), and evaporated. This gave a product (9.4 g) which was crystallized from ethanol to give 5.1 g (46.6%) of **4**, mp 142–150 °C. Recrystallization from the same solvent gave the following: mp 157–158 °C; $[\alpha]^{20}_D$ +83.0° (*c* 0.5, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 4.80 (dd, H-1), 1.92 (ddd, H-2a), 2.33 (ddd, H-2e), 5.36 (ddd, H-3), 3.40 (t, H-4), 3.79 (m, H-5), 1.37 (d, H-6), 8.4–8.0 (m, aryl H), J_{12a} = 3.5, J_{12e} = 1.0, J_{2a2e} = 13.0, J_{2a3} = 11.5, J_{2e3} = 5.5, J_{34} = J_{45} = 9.0, and J_{56} = 6.0 Hz. These data were obtained after exchanging the OH group with D_2O. In the original spectrum the OH group absorbed at 2.1–2.4 δ. Anal. Calcd for $C_{14}H_{17}NO_7$: C, 54.02; H, 5.50; N, 4.50. Found: C, 53.94; H, 5.48; N, 4.47.

Benzyl 2,6-Dideoxy-α-D-*arabino*-hexopyranoside (5). 2,6-Dideoxy-D-*arabino*-hexose[8] (**1**) (19 g, 12.8 mmol) was acetylated in pyridine (50 mL) and acetic anhydride (100 mL) overnight at room temperature. After concentration in vacuo, ice was added and after 30 min the mixture was extracted with dichloromethane (100 mL), washed with aqueous HCl, $NaHCO_3$, and water, dried ($MgSO_4$), and concentrated. This gave a syrupy product (32.5 g, 90.5% consisting of an anomeric mixture of the tri-*O*-acetate (**1**, R = R_1 = R_2 = Ac) as seen from the ^1H and ^{13}C NMR spectra.

The product was dissolved in dichloromethane (200 mL) together with benzyl alcohol (100 mL) and BF_3–OEt_2 (30 mL) and left at room temperature for 2 h. Then more dichloromethane was added and the mixture was washed with water and saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated. A ^{13}C NMR spectrum showed the presence of the benzyl glycosides (**5**, R_1 =

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R_2 = Ac) in the ratio $\alpha:\beta \sim 9:1$. The mixture was deacetylated overnight in methanol containing sodium methoxide as a catalyst, neutralized with ion exchange resin (Amberlite IR 120, H^+), and concentrated. The excess of benzyl alcohol was removed at 70 °C (1 mmHg). The remaining syrup was dissolved in ethyl acetate, dried ($MgSO_4$), treated with activated carbon, filtered, and concentrated to give a syrup which crystallized when treated with ether. This gave the α-glycoside **5** (9.5 g, 33.7%), mp 106–108 °C. The mother liquor was subjected to column chromatography with ethyl acetate as eluent, to give a further amount of crystalline **5** (4 g, 14.2%) mp 105–107 °C. Recrystallization from ethyl acetate–pentane gave a product with mp 109–110 °C: $[\alpha]^{20}_D$ +127.9° (*c* 2.0, ethyl acetate); $[\alpha]^{20}_D$ +89.3° (*c* 0.3, H_2O) (lit.[20] mp 112 °C; $[\alpha]^{20}_D$ +88.9° (*c* 0.2, H_2O)); ^{13}C NMR ($CDCl_3$) δ 96.3 (C-1), 77.5, 68.7, 68.7, 67.7 (C-3, C-4, C-5, $PhCH_2$), 37.5 (C-2), 17.6 (C-6), 128.3, 127.7 (aryl C), J_{C1H1} = 165 Hz.[21]

A small amount of the β-anomer, benzyl 2,6-dideoxy-β-D-*arabino*-hexopyranoside, was isolated from the column: ^{13}C NMR ($CDCl_3$) δ 98.3 (C-1), 77.1, 71.2, 70.3, 68.8 (C-3, C-4, C-5, $PhCH_2$), 38.9 (C-2), 17.6 (C-6), 128.3, 127.8 (aryl C), J_{C1H1} = 155 Hz.[21]

Benzyl 3-*O*-Benzyl- and 4-*O*-Benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (6 and 7). The glycoside **5** (4.0 g, 16.8 mmol) in dichloromethane (200 mL) together with tetrabutylammonium bromide (1.6 g, 4.9 mmol), benzyl bromide (2.4 mL, 20.2 mmol), and 20% aqueous potassium hydroxyde (20 mL) was stirred vigorously for 5 days. Water was added and the mixture extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), and concentrated leaving a crude product (6.5 g), which was separated by chromatography (ethyl acetate–pentane, 1:3). The first product isolated was the dibenzylated glycoside **8** (2.0 g) contaminated with benzyl alcohol. The next compound obtained was the syrupy 3-*O*-benzylated glycoside **6** (1.55 g, 28%): $[\alpha]^{20}_D$ +61.8° (*c* 2.0, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 4.98 (bd, H-1), 1.65 (ddd, H-2a), 2.18 (ddd, H-2e), 3.83 (ddd, H-3), 3.26 (t, H-4), 3.77 (m, H-5), 1.29 (d, H-6), 4.68 and 4.66 (AB-pattern, J = 12.0 Hz, $PhCH_2$), 4.48 and 4.44 (AB pattern, J = 11.6 Hz, $PhCH_2$), 2.48 (s, 4-OH), 7.3 (m, aryl H), J_{12a} = 3.0, $J_{12e} \simeq 0.5$, J_{2e2a} = 12.9, J_{2a3} = 11.4, J_{2e3} = 5.0, $J_{34} = J_{45}$ = 9.0, J_{56} = 6.2 Hz; ^{13}C NMR ($CDCl_3$) δ 96.1 (C-1), 34.4 (C-2), 76.6, 75.7, 70.6, 68.3, 67.4 (C-3, C-4, C-5, 2 $PhCH_2$), 17.5 (C-6) and 138.0, 137.3, 128.0, 127.3 (aryl C). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.64; H, 7.41.

The next fraction isolation was the 4-*O*-benzyl ether (**7**) (2.56 g, 46%). The product crystallized from ether–pentane, mp 53–56 °C (lit.[22] 57–59 °C). The ^1H NMR data were in accordance with those reported[22] (the chemical shifts reported[22] for H-3 and H-5 must be interchanged). ^{13}C NMR δ 96.0 (C-1), 85.7, 74.5, 68.3, 68.3, 66.9 (C-3, C-4, C-5, 2$PhCH_2$), 37.6 (C-2), 17.8 (C-6) and 138–126 (aryl C). Finally, by eluting with ethyl acetate the starting material **5** (0.5 g, 12.5%) was recovered.

Methyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-2,6-diiodo-α-D-mannopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (10). A solution of **3** (212 mg, 0.84 mmol), **9**[12] (335 mg, 0.99 mmol), and *N*-iodosuccinimide (349 mg, 1.2 mmol) in dry acetonitrile (10 mL) was stirred at room temperature for 56 h. The mixture was concentrated, extracted with dichloromethane, and washed with saturated aqueous $Na_2S_2O_3$. The aqueous phase was reextracted with dichloromethane and the combined organic phases were dried ($MgSO_4$) and concentrated. The crude material was purified by chromatography (ethyl acetate–hexane 1:3) to give **10** (458 mg, 76%) as a colorless syrup: $[\alpha]^{20}_D$ +37.2° (*c* 0.35, CH_2Cl_2); ^1H NMR (270 MHz, $CDCl_3$) δ 4.81 (dd, H-1), 1.57 (ddd, H-2a), 2.27 (ddd, H-2e), 3.68 (ddd, H-3), 4.09 (dd, H-4), 3.73 (m, H-5), 1.29, (d, H-6), 5.52 (d, H-1′), 4.76 (dd, H-2′), 4.56 (dd, H-3′), 5.10 (dd, H-4′), 3.79 (m, H-5′), 3.21 (dd, H-6′a), 3.32 (dd, H-6′b), 4.52 and 4.71 (AB pattern, J = 11.8 Hz, $PhCH_2$), 3.36 (s, OCH_3), 1.93 and 2.02 (s, OAc), 7.4 (m, 5 H, aryl H), J_{12a} = 3.8, J_{12e} = 1.2, J_{2a2e} = 12.8, J_{2a3} = 11.2, J_{2e3} = 5.2, J_{34} = 9.4, J_{45} = 9.5, J_{56} = 5.8, $J_{1'2'}$ = 1.5, $J_{2'3'}$ = 4.4, $J_{3'4'}$ = 9.0, $J_{4'5'}$ = 9.7, $J_{5'6'a}$ = 2.5, $J_{5'6'b}$ = 7.5, $J_{6'a6'b}$ = 11.4. Anal. Calcd for $C_{24}H_{32}I_2O_9$: C, 40.13; H, 4.49; I, 35.33. Found: C, 40.21; H, 4.56; I, 35.02.

Methyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-2,6-diiodo-α-D-mannopyranosyl)-2,6-dideoxy-3-*O*-(*p*-nitrobenzoyl)-α-D-*arabino*-hexopyranoside (11). A solution of **4** (108 mg, 0.35 mmol) and **9**[12] (186.8 mg, 0.5 mmol) in dry acetonitrile (5 mL) was stirred at room temperature with *N*-iodosuccinimide (180 mg, 0.62 mmol) for 3 days. Workup as described for **10**, followed by chromatography (ethyl acetate–hexane, 1:1) gave **11** (247 mg, 72%) as a colorless syrup: $[\alpha]^{20}_D$ +67.3° (*c* 0.83, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 4.24 (dd, H-1), 1.77 (ddd, H-2a), 2.39 (ddd, H-2e), 5.49 (ddd, H-3), 3.70 (t, H-4), 3.85 (m, H-5), 1.38 (d, H-6), 5.53 (d, H-1′), 4.76 (dd, H-2′), 4.52 (dd, H-3′), 5.12 (t, H-4′), 3.88 (m, H-5′), 3.17 (dd, H-6′a), 3.28 (dd, H-6′b), 3.33 (s, OCH_3), 1.92 and 2.03 (s, OAc), 8.27 (m, 4 H, aryl H), J_{12a} = 4.2, J_{12e} = 1.5, J_{2a2e} = 12.6, J_{2a3} = 11.4, J_{2e3} = 5.4, J_{34} = 9.1, J_{45} = 9.2, J_{56} = 6.1, $J_{1'2'}$ = 1.4, $J_{2'3'}$ = 4.4, $J_{3'4'}$ = 9.4, $J_{4'5'}$ = 9.6, $J_{5'6'a}$ = 2.6, $J_{5'6'b}$ = 7.7, and $J_{6'a6'b}$ = 11.2 Hz. Anal. Calcd for $C_{24}H_{29}I_2NO_{12}$: C, 37.09; H, 3.76; I, 32.65; N, 1.80. Found: C, 37.14; H, 3.79; I, 32.21; N, 1.87.

Benzyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dibromo-2,6-dideoxy-α-D-mannopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (12). A solution of **6** (700 mg, 2.13 mmol) and collidine (0.6 mL, 4.5 mmol) in toluene (5 mL) was dried overnight (molecular sieve, 4 Å). Silver trifluoromethanesulfonate (silver triflate) (1.1 g, 4.3 mmol) was added and stirred for 1 h, and the mixture was then cooled to −30 °C. A solution of the mannosyl bromide (**13**) in nitromethane (5 mL), which had been dried (molecular sieve, 4 Å) overnight, was then added in the course of 1 h at −30 °C. Stirring was continued at −10 °C for 6 h, after which time the temperature was allowed to raise to room temperature overnight. The mixture was filtered and the filter washed thoroughly with dichloromethane. The combined filtrate was washed with aqueous solutions of $Na_2S_2O_3$, HCl, and $NaHCO_3$, dried ($MgSO_4$), and concentrated to give a residue (1.9 g) which by chromatography (ethyl acetate–pentane, 1:4) gave **12** (1.16 g, 78%) as a syrup: $[\alpha]^{20}_D$ +66.9° (*c* 2.5, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 4.92 (bd, H-1), 1.63 (ddd, H-2a), 2.35 (ddd, H-2e), 3.94 (ddd, H-3), 3.44 (m, H-4), 3.78 (ddd, H-5), 1.33 (d, H-6), 5.61 (d, H-1′), 4.36 (dd, H-2′), 5.16 (dd, H-3′), 5.27 (t, H-4′), 4.10 (ddd, H-5′), 3.42 (dd, H-6′a), 3.38 (dd, H-6′b), 4.64 and 4.43 (AB-pattern, J = 12.0 Hz, $PhCH_2$), 4.56 and 4.40 (AB pattern, J = 11.0 Hz, $PhCH_2$), 7.2–7.4 (m, aryl H), 2.04, (s, 2 OAc), J_{12a} = 3.5, J_{12e} = 1.2, J_{2e2a} = 13.0, J_{2a3} = 11.3, J_{2e3} = 5.0, J_{34} = 9.2, J_{45} = 9.5, J_{56} = 6.0, $J_{1'2'}$ = 1.8, $J_{2'3'}$ = 3.8, $J_{3'4'} = J_{4'5'}$ = 9.8, $J_{5'6'a}$ = 3.6, $J_{5'6'b}$ = 6.5, and $J_{6'a6'b}$ = 11.0 Hz; ^{13}C NMR ($CDCl_3$) δ 96.2 (C-1), 34.3 (C-2), 77.1 (C-3), 82.8 (C-4), 18.8 (C-6), 101.2 (C-1′), 49.7 (C-2′), 31.3 (C-6′), 70.9, 70.6, 68.9, 68.9, 68.7, 66.3 (C-3′, C-4′, C-5′, C-5, 2 $PhCH_2$), 137–127 (aryl C), 169.7 and 20.6 ($COCH_3$), J_{C1H1} = 166 Hz and $J_{C1'H1'}$ 175 Hz.[21] Anal. Calcd for $C_{30}H_{36}Br_2O_9$: C, 51.45; H, 5.18; Br, 22.82. Found: C, 51.18; H, 5.24; Br, 22.91.

Methyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (14). The disaccharide **10** (412 mg, 0.57 mmol) was dissolved in ethyl acetate (20 mL) and hydrogenolyzed with 10% palladium on carbon (45 mg) at room temperature for 20 h with addition of a drop of triethylamine after 2, 3, and 6 h. Filtration, followed by concentration and chromatographic purification (ethyl acetate-hexane, 1:3) gave **14** (137 mg, 52%) as a colorless syrup: $[\alpha]^{20}_D$ +65.5° (*c* 0.51, CH_2Cl_2); ^1H NMR (270 MHz, $CDCl_3$) δ 4.82 (dd, H-1), 1.66 (ddd, H-2a), 2.31 (ddd, H-2e), 3.70 (ddd, H-3), 4.07 (t, H-4), 3.78 (m, H-5), 1.27 (d, H-6), 5.21 (dd, H-1′), 1.61 (ddd, H-2′a), 2.05 (ddd, H-2′e), 5.49 (ddd,H-3′), 4.95 (dd, -H4′), 3.75 (m, H-5′), 1.19 (d, H-6′), 3.35 (s, OCH_3), 4.50 and 4.69 (AB pattern, J = 11.8 Hz, $PhCH_2$), 1.83 and 2.02 (each s, OAc), 7.41 (m, aryl H), J_{12a} = 3.8, J_{12e} = 1.1, J_{2a2e} = 12.7, J_{2a3} = 11.2, J_{2e3} = 5.3, $J_{34} = J_{45}$ = 9.4, J_{56} = 6.2, $J_{1'2'a}$ = 3.6, $J_{1'2'e}$ = 1.2, $J_{2'a2'e}$ = 12.8, $J_{2'a3'}$ = 11.6, $J_{2'e3'}$ = 5.3, $J_{3'4'}$ = 9.2, $J_{4'5'}$ = 9.6, and $J_{5'6'}$ = 6.5 Hz. Anal. Calcd for $C_{24}H_{34}O_9$: C, 61.79; H, 7.35. Found: C, 61.90; H, 7.37.

Methyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-2,6-dideoxy-3-*O*-(*p*-nitrobenzoyl)-α-D-*arabino*-hexopyranoside (15). The disaccharide **11** (185 mg, 0.24 mmol) dissolved in ethyl acetate (10 mL) was hydrogenolyzed with 10% palladium on carbon (30 mg) for 18 h at room temperature in the presence of a drop of triethylamine. After filtration the crude material was concentrated and purified by chromatography (ethyl acetate–hexane, 1:1) to give **15** (68.9 mg, 55%) as a colorless syrup: $[\alpha]^{20}_D$ +89.3° (*c* 0.69, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 4.25 (dd, H-1), 1.75 (ddd, H-2a), 2.38 (ddd, H-2e), 5.50 (ddd, H-3), 3.72 (t, H-4), 3.89 (m, H-5), 1.38 (d, H-6), 5.19 (dd, H-1′), 1.59 (ddd, H-2′a), 2.11 (ddd, H-2′e), 5.52 (ddd, H-3′), 4.91 (t, H-4′), 3.97 (m, H-5′), 1.17 (d, H-6′), 3.25 (s, OCH_3), 1.94 and 2.03 (s, OAc), 8.29 (m, aryl H), J_{12a} = 4.3, J_{12e} = 1.5, J_{2a2e} = 12.7, J_{2a3} = 11.2, J_{2e3} = 5.3, J_{34} = 9.2, J_{45} = 9.3, J_{56} = 6.1, $J_{1'2'a}$

= 3.4, $J_{1'2'e}$ = 1.3, $J_{2'a2'e}$ = 12.8, $J_{2'a3'}$ = 11.6, $J_{2'e3'}$ = 5.4, $J_{3'4'}$ = 9.4, $J_{4'5'}$ = 9.6, $J_{5'6'}$ = 6.5 Hz. Anal. Calcd for $C_{24}H_{31}NO_{12}$: C, 54.85; H, 5.95; N, 2.67. Found: C, 54.21; H, 6.02; N, 2.93.

Methyl 2,6-Dideoxy-4-*O*-(2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-α-D-*arabino*-hexopyranoside (16). A solution of **15** (62 mg, 0.12 mmol) in dry methanol (5 mL) was stirred with sodium carbonate (150 mg) for 2 h at room temperature, then filtered, concentrated, and purified via preparative TLC (ethyl acetate–methanol, 10:1) to give **16** (21.3 mg, 61%) as a colorless syrup: $[\alpha]^{20}_D$ +70.9° (*c* 0.63, CH_3OH). Anal. Calcd for $C_{13}H_{24}O_7$: C, 53.41; H, 8.28. Found: C, 53.29; H, 7.95.

Benzyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (17). The disaccharide **12** (543 mg, 0.77 mmol) was dissolved in dry toluene (10 mL) together with α,α′-azobis(isobutyronitrile) (65 mg, 0.4 mmol) in a N_2 atmosphere. Tributylstannane (0.66 mL, 2.48 mmol) was added and the mixture heated to 70 °C for 3 h. Evaporation of the solvent and chromatography (ethyl acetate–hexane, 1:3) of the residue gave **17** (390 mg, 93%) as a colorless syrup. An analytical sample was further purified by TLC (ether–pentane, 1:2): $[\alpha]^{20}_D$ +97.3° (*c* 1.0, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 4.92 (dd, H-1), 1.64 (ddd, H-2a), 2.30 (ddd, H-2e), 3.90 (ddd, H-3), 3.30 (t, H-4), 3.76 (m, H-5), 1.26 (d, H-6), 5.40 (dd, H-1′), 1.68 (ddd, H-2′a), 2.14 (ddd, H-2′e), 5.20 (ddd, H-3′), 4.67 (dd, H-4′), 3.94 (m, H-5′), 1.15 (d, H-6′), 4.65 and 4.30 (AB pattern, J = 12.0 Hz, $PhCH_2$), 4.57 and 4.44 (AB pattern, J = 11.5 Hz, $PhCH_2$), 2.02 and 1.98 (s, OAc), J_{12a} = 3.8, J_{12e} = 1.2, J_{2a2e} = 13.0, J_{2a3} = 11.2, J_{2e3} = 5.0, J_{34} = J_{45} = 9.0, J_{56} = 6.0, $J_{1'2'a}$ = 4.0, $J_{1'2'e}$ = 1.5, $J_{2'a2'e}$ = 13.0, $J_{2'a3'}$ = 11.8, $J_{2'e3'}$ = 5.2, $J_{3'4'}$ = 9.5, $J_{4'5'}$ = 10.0, and $J_{5'6'}$ = 6.0 Hz; ^{13}C NMR ($CDCl_3$) δ 96.3 (C-1), 98.1 (C-1′), 35.4 and 35.2 (C-2 and C-2′), 81.6 (C-4), 77.8 (C-4′), 74.8, 71.0, 69.0, 68.8, 66.6, 66.1 (C-3, C-5, C-3′, C-5′, 2 $PhCH_2$), 18.5 and 17.3 (C-6 and C-6′), 170.1, 170.4, 20.9 and 20.7 ($COCH_3$) and 138–127 (aryl C).

From 25 (See Below). The gluco isomer **25** (335 mg, 0.48 mmol) in dry toluene (6 mL) was treated with α,α′-azobis(isobutyronitrile) (40 mg, 0.25 mmol) and tributylstannane (0.41 mL, 1.5 mmol) as described above. Chromatography of the crude product gave **17** (233 mg, 90%). ^1H and ^{13}C NMR spectra were identical with those described above.

4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-2,6-dideoxy-D-*arabino*-hexopyranose (18). The benzylated disaccharide **17** (300 mg, 0.55 mmol) in ethanol (10 mL) and acetic acid (1 mL) was hydrogenolyzed for 2 days in the presence of 10% palladium on carbon (100 mg). Filtration and concentration left **18** (200 mg, 100%) as a homogeneous syrup (TLC, ethyl acetate): ^1H NMR (400 MHz, $CDCl_3$) α-anomer δ 5.79 (bd, H-1), 1.68 (ddd, H-2a), 2.13 (dd, H-2e), 4.15 (ddd, H-3), 3.16 (t, H-4), 3.9-4.1 (m, H-5), 1.29 (d, H-6), 5.88 (bd, H-1′), 1.78 (ddd, H-2′a), 2.34 (dd, H-2′e), 5.69 (ddd, H-3′), 4.76 (t, H-4′), 3.9–4.1 (m, H-5′), 1.17 (d, H-6′), 2.07 and 2.03 (s, OAc), J_{12a} = 3.6, J_{12e} = 1, J_{2a2e} = 13.0, J_{2a3} = 12.0, J_{2e3} = 5.6, J_{34} = J_{45} = 9.6, J_{56} = 6.0, $J_{1'2'a}$ = 3.6, $J_{1'2'e}$ = 1, $J_{2'a2'e}$ = 13.0, $J_{2'a3'}$ = 12.0, $J_{2'e3'}$ = 5.0, $J_{3'4'}$ = $J_{4'5'}$ = 9.6, and $J_{5'6'}$ = 6.0 Hz. Some of the β-anomer was also present (α:β ~ 2:1) and the following signals could be identified: δ 4.81 (dd, H-1), 1.59 (ddd, H-2a), 2.24 (ddd, H-2e), 3.77 (dd, H-3), 3.16 (t, H-4), 3.38 (m, H-5), 1.54 (d, H-6), J_{12a} = 9.0, J_{12e} = 1.0, J_{2a2e} = 12.5, J_{2a3} = 12.0, J_{2e3} = 5.6, J_{34} = J_{45} = 9.0, and J_{56} = 6.0 Hz. ^{13}C NMR δ 91.4 (C-1α), 93.5 (C-1β), 38.5 (C-2α), 41.2 (C-2β), 84.0 (C-4α), 82.9 (C-4β), 98.0 (C-1′), 74.4 (C-4′), 71.6, 70.7, 69.2, 68.6, 66.3 (C-3, C-5, C-3′, C-5′), 35.2 (C-2′), 18.2 and 17.2 (C-6 and C-6′), 20.8 and 20.6 (OAc).

2,6-Dideoxy-4-*O*-(2,6-dideoxy-α-D-*arabino*-hexopyranosyl)-D-*arabino*-hexopyranose (19). The acetate **18** (70 mg, 0.19 mmol) was dissolved in methanol (2 mL) and two drops of a 2 M solution of sodium methoxide in methanol was added. After 30 min at room temperature the mixture was neutralized with ion exchange resin (Amberlite IR 120, H^+). Filtration and concentration gave the free α-linked disaccharide **19** (45 mg, 85%): ^1H NMR (400 MHz, D_2O) α-anomer δ 5.29 (bd, H-1), 1.75 (ddd, H-2a), 2.10 (dd, H-2e), 4.00 (ddd, H-3), 3.24 (t, H-4), 3.92 (m, H-5), 1.28 (d, H-6), 5.41 (t, H-1′), 1.75 (ddd, H-2′a), 2.2–2.3 (m, H-2′e), 3.7–3.9 (m, H-3′), 3.13 (t, H-4′), 3.7–3.9 (m, H-5′), 1.27 (d, H-6′), J_{12a} = 3.0, J_{12e} ~ 0.5, J_{2a3} = 12.0, J_{2e3} = 5.0, J_{2a2e} = 13.0, J_{34} = J_{45} = 9.0, J_{56} = 6.0, $J_{1'2'a}$ = $J_{1'2'e}$ = 4.0, $J_{2'a2'e}$ = 13.0, $J_{5'6'}$ = 6.0 Hz. The β-anomer was also present (α:β ~ 1:1) and the following signals could be identified: δ 4.89 (dd, H-1), 1.54 (ddd, H-2a), 2.2-2.3 (m, H-2e), 3.7–3.9 (m, H-3), 3.20 (t, H-4), 3.47 (m, H-5), 1.30 (d, H-6), J_{12a} = 10.0, J_{12e} = 2.0, J_{2a2e} = 13.0, J_{2a3} = 12.5, J_{45} = 9.0, J_{56} = 6.0 Hz. ^{13}C NMR (D_2O) 91.9 (C-1α), 94.1 (C-1β), 41.3 (C-2α), 39.0 (C-2β), 83.2 (C-4α), 83.8 (C-4β), 18.6 and 17.4 (C-6, α and β), 99.5 (C-1′), 38.0 (C-2′), 77.4 (C-4′), 17.4 (C-6′), 71.9, 71.4, 69.4, 69.9, 68.5 (C-3, C-5, α and β, C-3′, C-5′).

Methyl 3-*O*-Benzyl-2,6-dideoxy-4-*O*-[methyl (3,4-di-*O*-acetyl-2-deoxy-2-iodo-α-D-manno- and -β-D-glucopyranosyl)uronate]-α-D-*arabino*-hexopyranoside (21 and 22). The hydroxy compound **3** (120 mg, 0.51 mmol) and the glucuronal **20**[16] (155 mg, 0.61 mmol) in dry acetonitrile (8 mL) was stirred at room temperature with powdered molecular sieves (3 Å). The solution was treated successively with *N*-iodosuccinimide (50 mg) every second day (all together 250 mg, 1.02 mmol). After 14 days the reaction was stopped, the mixture concentrated, dissolved in dichloromethane, and washed with aqueous $Na_2S_2O_3$. The washings were reextracted with dichloromethane and the combined organic layers dried ($MgSO_4$), concentrated, and purified by preparative TLC (ethyl acetate–hexane, 1:2) to give 61 mg (19%) of a colorless syrup of the isomers **21** and **22** (ratio 55:45), which could not be further separated. ^1H NMR (400 MHz, $CDCl_3$) **21**: δ 4.70 (dd, H-1), 1.70 (ddd, H-2a), 2.04 (ddd, H-2e), 3.62 (m, H-3), 1.25 (d, H-6), 5.25 (d, H-1′), 4.48 (dd, H-2′), 4.83 (dd, H-3′), 5.31 (t, H-4′), 4.41 (d, H-5′), 3.34 (s, OCH_3), 3.69 (s, $COOCH_3$), 4.48 and 4.70 (AB pattern, J = 12.0 Hz, $PhCH_2$), J_{12a} = 4.0, J_{12e} = 1.4, J_{2a2e} = 13.8, J_{2a3} = 3.8, J_{2e3} = 3.4, J_{56} = 6.1, $J_{1'2'}$ = 2.8, $J_{2'3'}$ = 3.9, $J_{3'4'}$ = 8.7, and $J_{4'5'}$ = 8.7 Hz. **22**: δ 4.75 (dd, H-1), 1.95 (m, H-2a), 2.20 (m, H-2e), 1.28 (d, H-6), 4.60 (d, H-1′), 4.01 (dd, H-2′), 3.38 (s, OCH_3), 3.70 (s, $COOCH_3$), 4.46 and 4.68 (AB pattern, J = 12.0 Hz, $PhCH_2$), J_{12a} = 4.0, J_{12e} = 1.6, J_{2a2e} = 14.2, J_{56} = 6.5, $J_{1'2'}$ = 8.9, $J_{2'3'}$ = 10.9 Hz. For **21** and **22**: 1.96–2.02 (4 OAc), 7.38–7.50 (m, aryl H).

Methyl 3-*O*-Benzyl-2,6-dideoxy-4-*O*-[methyl (3,4-di-*O*-acetyl-2-deoxy-α- and -β-D-*arabino*-hexopyranosyl)-uronate]-α-D-*arabino*-hexopyranoside (23 and 24). The disaccharide mixture **21** and **22** (56 mg, 0.088 mmol) dissolved in ethyl acetate (5 mL) was hydrogenolyzed for 26 h in the presence of 10% palladium on carbon (30 mg) and two drops of triethylamine. Filtration, concentration, and purification by preparative TLC (ethyl acetate–hexane, 1:3) gave a mixture of **23** and **24** (19.5 mg, 44%) as a syrup. ^1H NMR (400 MHz, $CDCl_3$) **23**: δ 4.72 (dd, H-1), 1.67 (m, H-2a and H-2′a), 2.40 (m, H-2e and H-2′e), 1.17 (d, H-6), 5.17 (dd, H-1′), 3.36 (s, OCH_3), 3.72 (s, $COOCH_3$), 4.25 and 4.56 (AB pattern, J = 12.0 Hz, $PhCH_2$), J_{12a} = 4.4, J_{12e} = 1.2, J_{56} = 6.3, $J_{1'2'a}$ = 3.4, and $J_{1'2'e}$ = 1.4. **24**: δ 4.76 (dd, H-1), 1.78 (m, H-2a), 2.16 (m, H-2e), 1.25 (d, H-6), 4.63 (dd, H-1′), 1.66 (m, H-2′a), 2.34 (m, H-2′e), 3.38 (s, OCH_3), 3.70 (s, $COOCH_3$), 4.34 and 4.62 (AB pattern, J = 11.8 Hz, $PhCH_2$), J_{12a} = 4.1, J_{12e} = 1.4, J_{56} = 6.2, $J_{1'2'a}$ = 9.5, and $J_{1'2'e}$ = 1.9 Hz. For **23** and **24**: 2.00–2.12 (4 OAc), 7.30–7.52 (m, aryl H).

Benzyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dibromo-2,6-dideoxy-β- and -α-D-glucopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (27 and 25). The hydroxy compound **6** (1.16 g, 3.54 mmol) in dry toluene (10 mL) together with collidine (1.0 mL, 7.56 mmol) was dried overnight (molecular sieve, 4 Å). The glycosyl bromide (**26**) (3.0 g, 6.62 mmol) in dichloromethane (8 mL) and nitromethane (6 mL) was dried overnight (molecular sieve, 4 Å). Silver triflate (1.70 g, 6.62 mmol) was then added to the toluene solution, and after stirring for 1 h at room temperature the mixture was cooled to −30 °C. At this temperature the solution containing the bromide was added in the course of 2 h. Stirring was continued at −20 to −10 °C for 6 h and then overnight, allowing the reaction to come to room temperature. At this time **6** was still present (TLC, ethyl acetate–pentane, 1:4). An additional amount of silver triflate (1.0 g, 3.96 mmol) was added together with collidine (0.55 mL, 4.16 mmol) and the mixture was cooled to −30 °C. At this temperature a dry solution of the bromide **26** (1.5 g, 3.3 mmol) in dichloromethane (4 mL) and nitromethane (4 mL) was added in the course of 1 h, and stirring was continued at −20 to −10 °C for 6 h and overnight allowing the temperature to raise to room temperature. The mixture was filtered, the filter washed thoroughly with dichloromethane, and the combined filtrate was washed with aqueous $Na_2S_2O_3$, HCl (4 N), and $NaHCO_3$, dried ($MgSO_4$), and concentrated to a syrup (~4 g). Chromatography (ethyl acetate–pentane, 1:3) gave as the first

fraction 3,4-di-*O*-acetyl-1,5-anhydro-2,6-dibromo-2,6-dideoxy-D-*arabino*-hex-1-enitol (1.0 g, 27% based on **26**) which crystallized, mp 61–62 °C. The compound was only characterized through its proton NMR spectrum: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, H-1), 5.45 (ddd, H-3), 5.39 (dd, H-4), 5.42 (m, H-5), 3.62 (dd, H-6a), 3.47 (dd, H-6b), 2.13 and 2.11 (s, OAc), J_{13} = 2.0, J_{34} = 3.8, J_{35} = 3.0, J_{45} = 4.6, J_{56a} = 6.4, J_{56b} = 6.7, and J_{6a6b} = 11.0 Hz.

The next compound isolated was the syrupy α-disaccharide **25** (401 mg, 16%). A sample was further purified by preparative TLC (ethyl acetate–pentane, 1:4): $[\alpha]^{20}_D$ +119.8° (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (bd, H-1), 1.68 (ddd, H-2a), 2.38 (dd, H-2e), 4.10 (ddd, H-3), 3.54 (t, H-4), 3.87 (m, H-5), 1.32 (d, H-6), 5.96 (d, H-1′), 3.90 (dd, H-2′), 5.40 (dd, H-3′), 4.86 (dd, H-4′), 4.18 (ddd, H-5′), 3.43 (dd, H-6′a), 3.32 (dd, H-6′b), 4.65 and 4.40 (AB pattern, J = 11.5 Hz, $PhCH_2$), 4.56 and 4.50 (AB pattern, J = 10.5 Hz, $PhCH_2$), 7.3–7.4 (m, aryl H), 2.06 and 2.04 (s, OAc), J_{12a} = 3.0, $J_{12e} \sim$ 0.1, J_{2a2e} = 13.0, J_{2a3} = 11.2, J_{2e3} = 5.0, J_{34} = J_{45} = 8.5, J_{56} = 6.0, $J_{1'2'}$ = 3.8, $J_{2'3'}$ = 11.0, $J_{3'4'}$ = 9.0, $J_{4'5'}$ = 10.0, $J_{5'6'a}$ = 2.2, $J_{5'6'b}$ = 6.3, and $J_{6'a6'b}$ = 11.0 Hz; ^{13}C NMR ($CDCl_3$) δ 96.1 (C-1), 34.8 (C-2), 79.3 and 77.7 (C-3 and C-4), 19.4 (C-6), 97.1 (C-1′), 47.5 (C-2′), 31.2 (C-6′), 71.8, 71.4, 70.2, 68.9, 68.9, 65.9 (C-5, C-3′, C-4′, C-5′, $2PhCH_2$), 169.4 and 20.5 ($COCH_3$), and signals in the region 138–127 (aryl C), J_{C1H1} = 167 Hz and $J_{C1'H1'}$ = 179 Hz. Anal. Calcd for $C_{30}H_{36}Br_2O_9$: C, 51.44; H, 5.18; Br, 22.82. Found: C, 51.43; H, 5.18; Br, 22.91.

Finally the β-disaccharide **27** was isolated as a syrup (1.40 g, 56.5%). A sample was further purified by preparative TLC (ethyl acetate–pentane, 1:4): $[\alpha]^{20}_D$ +90.4° (*c* 1.4, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.94 (m, H-1), 1.72 (bdd, H-2a), 2.34 (ddd, H-2e), 4.02 (ddd, H-3), 3.57 (t, H-4), 3.89 (m, H-5), 1.43 (d, H-6), 4.94 (d, H-1′), 3.79 (dd, H-2′), 5.23 (dd, H-3′), 4.90 (t, H-4′), 3.41 (ddd, H-5′), 3.21 (dd, H-6′a), 3.12 (dd, H-6′b), 4.70 and 4.67 (AB pattern, J = 12.0 Hz, $PhCH_2$), 4.65 and 4.43 (AB J_{C1H1} J = 12.3 Hz, $PhCH_2$), 7.4–7.5 (m, aryl H), 2.10 and 2.03 (s, OAc), J_{12a} = 3.8, J_{12e} = 1.0, J_{2a2e} = 13.0, J_{2a3} = 11.2, J_{2e3} = 5.0, J_{34} = 8.6, J_{45} = 9.2, J_{56} = 6.2, $J_{1'2'}$ 8.6, $J_{2'3'}$ = 10.6, $J_{3'4'}$ = 9.0, $J_{4'5'}$ = 9.8, $J_{5'6'a}$ = 3.0, $J_{5'6'b}$ = 5.0, $J_{6'a6'b}$ = 11.4 Hz; ^{13}C NMR ($CDCl_3$) δ 96.1 (C-1) 35.2 (C-2), 83.7 (C-4), 18.6 (C-6), 101.2 (C-1′), 50.7 (C-2′), 30.4 (C-6′), 75.0, 74.4, 72.3, 71.4, 66.7 (C-3, C-5, C-3′, C-4′, C-5′), 70.8 and 68.7 ($2PhCH_2$), 138–127 (aryl C), 169.6, 169.1 and 20.4 ($COCH_3$), J_{C1H1} = 166 Hz, $J_{C1'H1'}$ = 163 Hz. Anal. Found: C, 51.32; H, 5.16; Br, 22.97.

Benzyl 4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-3-*O*-benzyl-2,6-dideoxy-α-D-*arabino*-hexopyranoside (29). To the disaccharide **27** (1.32 g, 1.89 mmol) in dry toluene (35 mL) was added α,α'-azobis(isobutyronitrile) (155 mg, 0.95 mmol) and tributylstannane (1.5 mL, 5.67 mmol) in a N_2 atmosphere. The mixture was heated to 70 °C for 3 h and then concentrated. The tin compounds were removed on a short column (ether–pentane, 1:1) giving the tetradeoxy β-disaccharide **29** (760 mg, 74%) as a crystalline compound, mp 82–83.5 °C. Recrystallization from ethanol gave mp 83–84 °C: $[\alpha]^{20}_D$ +70.5° (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.94 (dd, H-1), 1.70 (m, H-2a), 2.30 (ddd, H-2e), 3.95 (ddd, H-3), 3.32 (t, H-4), 3.78 (dq, H-5), 1.28 (d, H-6), 4.81 (dd, H-1′), 1.69 (m, H-2′a), 2.35 (ddd, H-2′e), 4.90 (m, H-3′), 4.73 (t, H-4′), 3.33 (m, H-5′), 1.12 (d, H-6′), 4.75 and 4.43 (AB pattern, J = 12.0 Hz, $PhCH_2$), 4.61 and 4.65 (AB pattern, J = 11.7 Hz, $PhCH_2$), 7.4–7.2 (m, aryl H), 2.02 and 2.00 (each s, OAc), J_{12a} = 4.0, J_{12e} = 1.3, J_{2a2e} = 12.5, J_{2a3} = 11.0, J_{2e3} = 5.2, J_{34} = J_{45} = 9.5, J_{56} = 6.2, $J_{1'2'a}$ = 9.5, $J_{1'2'e}$ = 2.0, $J_{2'a2'e}$ = 12.0, $J_{2'a3'}$ = 11.8, $J_{2'e3'}$ = 5.0, $J_{3'4'}$ = 9.3, $J_{4'5'}$ = 9.5, and $J_{5'6'}$ = 6.2 Hz; ^{13}C NMR ($CDCl_3$) δ 96.3 (C-1), 99.7 (C-1′), 36.7 and 35.6 (C-2 and C-2′), 83.5 (C-4), 75.6, 74.0, 71.8, 70.6, 70.0, 68.7, 66.8 (C-3, C-5, C-3′, C-4′, C-5′, $2PhCH_2$), 18.1 and 17.5 (C-6 and C-6′), 170.1, 169.9 and 20.8 ($COCH_3$), 138-127 (aryl C). Anal. Calcd for $C_{30}H_{28}O_9$: C, 66.40; H, 7.06. Found: C, 66.27; H, 7.10.

4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-α-D-*arabino*-hexopyranose (30). The benzylated disaccharide **29** (417 mg, 0.77 mmol) in ethanol (10 mL) and acetic acid (1 mL) was hydrogenolyzed for 2 days in the presence of 10% palladium on carbon (200 mg). Filtration and concentration gave a syrup (280 mg, 100%) which crystallized by addition of ether. This gave **30** (222 mg, 80%), mp 135–137 °C. Recrystallization from ethyl acetate–pentane gave the following: mp 138–139 °C; $[\alpha]^{20}_D$ + 40.3° → +22.4° (1 week) (*c* 0.5, ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (bs, H-1), 1.61 (ddd, H-2a), 2.24 (dd, H-2e), 3.98 (m, H-3), 3.00 (t, H-4), 3.95 (m, H-5), 1.23 (d, H-6), 4.60 (bd, H-1′), 1.78 (ddd, H-2′a), 2.37 (ddd, H-2′e), 5.00 (ddd, H-3′), 4.79 (t, H-4′), 3.61 (m, H-5′), 1.28 (d, H-6′), 4.27 (s, OH), 2.07 and 2.04 (s, OAc), $J_{1,2a}$ = 2.4, $J_{12e} \sim$ 0, J_{2e2a} = 13.2, J_{2a3} = 12.0, J_{2e3} = 5.7, J_{34} = 9.6, J_{45} = 9.0, J_{56} = 6.5, $J_{1'2'a}$ = 9.6, $J_{1'2'e}$ = 2.0, $J_{2'a2'e}$ = 12.6, $J_{2'a3'}$ = 12.0, $J_{2'e3'}$ = 5.8, $J_{3'4'}$ = $J_{4'5'}$ = 9.6 and $J_{5'6'}$ = 6.0 Hz; ^{13}C NMR ($CDCl_3$) δ 91.6 (C-1α), 93.8 (C-1β), 36.8 (C-2α), 39.4 (C-2β), 89.3 (C-4α), 88.3 (C-4β), 100.3 (C-1′), 36.2 (C-2′), 73.3, 70.2, 70.2, 69.2, 66.3, 65.6 (C-3, C-5, C-3′, C-5′), 17.6 and 17.3 (C-6 and C-6′), 170.2, 169.8, 20.7 and 20.6 ($COCH_3$). Anal. Calcd for $C_{16}H_{26}O_9$: C, 53.03; H, 7.23. Found: C, 52.83; H, 7.26.

2,6-Dideoxy-4-*O*-(2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-D-*arabino*-hexopyranose (31). The diacetate **30** (164 mg, 0.45 mmol) in methanol (5 mL) was treated with a few drops of sodium methoxide in methanol (1 M) for 30 min. Neutralization with ion exchange resin (Amberlite IR 120, H^+) followed by filtration and concentration gave **31** (112 mg, 89%) as a crystalline compound, mp 113–116 °C. Recrystallization gave a product: mp 116–118 °C; $[\alpha]^{20}_D$ −4.0 → −1.3 (1 day) (*c* 0.4, H_2O). ^{1}H NMR (400 MHz, D_2O) α anomer: δ 5.30 (bd, H-1), 1.68 (ddd, H-2a), 2.28 (ddd, H-2e), 3.66 (m, H-3), 3.27 (t, H-4), 3.92 (ddd, H-5), 1.29 (d, H-6), 4.78 (m, H-1′), ca. 1.5 (m, H-2′a), 2.36 (m, H-2′e), 3.72 (ddd, H-3′), 3.09 (t, H-4′), 3.45 (m, H-5′), 1.31 (d, H-6′), J_{12a} = 3.5, J_{12e} = 2.0, J_{2a2e} = 13.0, J_{2a3} = 11.5, J_{2e3} = 5.0, J_{34} = 9.0, J_{45} = 9.5, J_{56} = 6.0, $J_{1'2'a}$ = 9.8, $J_{1'2'e}$ = 2.0, $J_{2'a3'}$ = 11.5, $J_{2'e3'}$ = 5.0, $J_{3'4'}$ = $J_{4'5'}$ = 9.0, $J_{5'6'}$ = 6.0 Hz. From the β-anomer the following signals could be identified: δ 4.91 (dd, H-1), ca. 1.5 (m, H-2a), 2.18 (ddd, H-2e), ca. 3.7 (m, H-3), 3.23 (t, H-4), 3.50 (m, H-5), 1.27 (d, H-6), J_{12a} = 9.8, J_{12e} = 1.8, J_{34} = J_{45} = 9.0, and J_{56} = 6.0 Hz; ^{13}C NMR (D_2O) δ 91.7 (C-1α), 94.0 (C-1β), 37.6 (C-2α), 39.8 (C-2β), 87.6 (C-4α), 87.0 (C-4β), 101.3 (C-1′), 39.3 (C-2′), 76.9 (C-4′), 76.9, 73.0, 70.9, 69.9, 67.5, 67.2 (C-3, C-5, C-3′, C-4′), 17.7 (C-6 and C-6′). Anal. Calcd for $C_{12}H_{22}O_7$: C, 51.79; H, 7.97. Found: C, 52.79; H, 8.33.

3-*O*-Acetyl-4-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-β-D-*arabino*-hexopyranosyl)-2,6-dideoxy-D-*arabino*-hexano-1,5-lactone (28). Bamflalactone Triacetate. The hydroxy compound **30** (50 mg, 0.14 mmol) in water (5 mL) was oxidized with a drop of bromine in the presence of $BaCO_3$ (500 mg, 2.5 mmol).[18] The mixture was stirred for 2 h at room temperature during which time gas evolution was observed and the bromine color fainted. Filtration and concentration left a product which was alcetylated in pyridine (1 mL) with acetic anhydride (1 mL) at 0 °C for 20 h. Workup in the usual way gave the δ-lactone **28** (44 mg, 80%) as a crystalline compound. The product was recrystallized from ether–pentane to give long needles: mp 131–133 °C; $[\alpha]^{20}_D$ +26.9 (*c* 0.5, $CHCl_3$) (lit.[9] mp 131 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (dd, H-2A), 2.70 (dd, H-2B), 5.50 (m, H-3), 3.63 (dd, H-4), 4.24 (m, H-5), 1.39 (d, H-6), 4.70 (dd, H-1′), 1.71 (ddd, H-2′a), 2.35 (ddd, H-2′e), 4.94 (ddd, H-3′), 4.74 (t, H-4′), 3.50 (m, H-5′), 1.20 (d, H-6′), 2.02, 2.05, and 2.06 (s, OAc), J_{2A2B} = 17.0, J_{2A3} = 4.8, J_{2B3} = 3.0, J_{34} = 1.8, J_{45} = 8.4, J_{56} = 6.0, $J_{1'2'a}$ = 10.2, $J_{1'2'e}$ = 1.8, $J_{2'a2'e}$ = 12.3, $J_{2'a3'}$ = 12.0, $J_{2'e3'}$ = 5.4, $J_{3'4'}$ = 9.6, $J_{4'5'}$ = 10.0, $J_{5'6'}$ = 6.0 Hz; ^{13}C NMR ($CDCl_3$) δ 170.2 (C-1) 100.2 (C-1′), 36.4 and 33.4 (C-2 and C-2′), 81.0 (C-4), 75.1, 73.5, 70.5, 70.2 (C-3, C-5, C-3′, C-4′, C-5′), 18.5 and 17.4 (C-6 and C-6′), 169.8, 169.3, 169.0, 20.8 ($COCH_3$).

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Registry No. **1**, 6988-55-2; **1** (R = R_1 = R_2 = Ac, α-isomer), 84129-81-7; **1** (R = R_1 = R_2 = Ac, β-isomer), 84129-82-8; **2**, 13322-79-7; **3**, 90762-83-7; **4**, 90762-84-8; **5**, 75810-07-0; **5** (β-isomer), 90762-85-9; **5** (R_1 = R_2 = Ac, α-isomer), 90762-86-0; **5** (R_1 = R_2 = Ac, β-isomer), 90762-87-1; **6**, 90762-88-2; **7**, 75124-38-8; **8**, 90762-89-3; **9**, 28413-99-2; **10**, 90762-90-6; **11**, 90762-91-7; **12**, 90762-92-8; **13**, 78138-28-0; **14**, 90762-93-9; **15**, 90762-94-0; **16**,

90762-95-1; **17**, 90762-96-2; **18** (α-isomer), 90762-97-3; **18** (β-isomer), 90762-98-4; **19** (α-isomer), 90762-99-5; **19** (β-isomer), 90763-00-1; **20**, 34296-99-6; **21**, 90763-01-2; **22**, 90763-02-3; **23**, 90763-03-4; **24**, 90763-04-5; **25**, 90763-05-6; **26**, 78138-31-5; **27**, 90763-06-7; **28**, 90763-07-8; **29**, 90763-08-9; **30**, 90763-09-0; **31** (α-isomer), 90763-10-3; **31** (β-isomer), 90790-04-8; 3,4-di-*o*-acetyl-1,5-anhydro-2,6-dibromo-2,6-dideoxy-D-*arabino*-hex-1-enitol, 90763-11-4.

Reactivity of Aryl Vinyl Di-π-methane Systems. Mechanistic and Exploratory Organic Photochemistry[1,2]

Howard E. Zimmerman* and Richard L. Swafford

Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706

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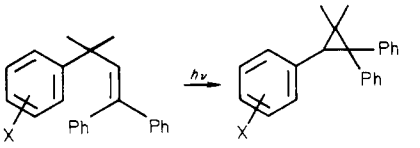
The di-π-methane rearrangement of a series of meta and para substituted arylvinylmethane reactants was investigated with the aim of determining the patterns of reactivity in systems in which initial excitation is localized in the aryl moiety. Thus the photochemistry of 3-methyl-3-phenyl-1-butene, 3-methyl-3-(*p*-cyanophenyl)-1-butene, 3-methyl-3-(*m*-cyanophenyl)-1-butene, 3-methyl-3-(*p*-methoxyphenyl)-1-butene, and 3-methyl-3-(*m*-methoxyphenyl)-1-butene was studied. The five systems rearranged photochemically to afford corresponding 1,1-dimethyl-2-arylcyclopropanes. The photochemistry of the cyclopropanes was also studied. Each of these opened to the corresponding 1,3-diradical, which then partitioned itself to isomeric 1-aryl-3-methylbutenes. The two processes observed were a 1,4-hydrogen transfer in the diradical and a 1,2-hydrogen shift. Di-π-methane quantum yields were determined. Also, biacetyl studies permitted determination of singlet vs. triplet reactivity. In the di-π-methane rearrangements it was determined that, on direct irradiation, the parent arylvinylmethane and the (cyanophenyl)vinylmethanes reacted only via the singlet excited states, while the anisyl di-π-methane reactants utilized both the singlet and the triplet for rearrangement. However, acetone sensitization was successful in generating the (cyanophenyl)vinylmethane triplets which then rearranged successfully. The main impediment to triplet di-π-methane rearrangement of the cyanoaryl reactants proved to be relatively inefficient intersystem crossing. In the case of the *m*-methoxyphenyl reactant it was possible to determine the triplet lifetime. Finally, singlet rates of decay and reaction were determined for the di-π-methane systems.

Introduction

Quite some years ago we noted that photochemical reactants having two π chromophores bonded to an sp^3 hybridized carbon undergo a general reaction; we termed this the di-π-methane rearrangement.[3] The initial example which precipitated our recognition of the reaction was the barrelene to semibullvalene conversion.[3d,e] Since that time, the reaction has proven itself to be one of the most general of photochemical reactions. Thus, we felt it was deserving of detailed further investigation.

One system of importance consisted of the aryl(diphenylvinyl)methanes **1** which afforded a series of vinylcyclopropanes **2**[3g,3l] by way of the first excited singlet states. Note eq 1. In these reactants the electronic excitation was

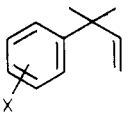


(1)

1 **2**

X = H, *p*-Br, *p*-MeO, *m*-MeO, *p*-CN

shown to be heavily localized in the diphenylvinyl chromophore. It seemed to be of particular interest to investigate the behavior of a related set of di-π-methane reactants in which the initial excitation is concentrated in the aromatic ring. Thus the arylvinylmethanes **3**–**5**, bearing meta and para cyano and methoxyl groups, were investigated.



3, X = H
4a, X = *p*-MeO
4b, X = *m*-MeO
5a, X = *p*-CN
5b, X = *m*-CN

Results

Synthesis of Photochemical Reactants and Potential Photoproducts. The previously unknown di-π-

(1) This is paper 140 of our photochemical series.
(2) For paper 139, see Zimmerman, H. E.; Wu, G.-S. *Can. J. Chem.* **1983**, *61*, 866–872.
(3) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (b) Zimmerman, H. E.; Mariano, P. S. *Ibid.* **1969**, *91*, 1718–1727. (c) Zimmerman, H. E.; Pagni, R. *Ibid.* **1968**, *90*, 6096–6108. (d) Zimmerman, H. E.; Grunewald, G. L. *Ibid.* **1966**, *88*, 183–184. (e) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *Ibid.* **1969**, *91*, 3316–3323. (f) Zimmerman, H. E.; Welter, T. R. *Ibid.* **1978**, *100*, 4131–4145. (g) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *Ibid.* **1978**, *100*, 4146–4162. (h) Zimmerman, H. E.; Blinn, J. R. *Tetrahedron* **1981**, *19*, 3237–3243. (i) Zimmerman, H. E.; Wu, G-S. *Can. J. Chem.* **1983**, *61*, 866–871. (j) For a general review see: Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. Also see ref 3k. (k) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3. (l) A series of styryl para substituted arylmethanes was studied by Hixson.[4]
(4) Hixson, S. S. *J. Am. Chem. Soc.* **1972**, *94*, 2507–2508.

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