minutes, then bromochloromethane (30 μL, 0.4 mmol) was added, and the mixture was heated to 60 °C for 4 h with stirring. On cooling, the suspension was diluted with 50 mL of Et_2O, washed twice with water, and dried over $MgSO_4$. Evaporation of the solvent and flash chromatography (15–20% ethyl acetate/hexane eluant) gave 42 mg (61%) of **3**, a white crystalline solid (R_f = 0.3 in 15% ethyl acetate/hexane eluant), which was recrystallized from CH_2Cl_2: mp 108–109 °C. ^1H NMR (300 MHz) in C_6D_6: δ 0.67 (d, 7.0 Hz, 3 H), 1.22 (m, 1 H), 1.88 (s, 3 H), 2.78 (dd, 13.5 and 9.6 Hz, 1 H), 2.96 (dd, 13.5 and 5.3 Hz, 1 H), 3.13 (dd, 11.5 and 2.5 Hz, 1 H), 3.45 (dd, 11.5 and 2.9 Hz, 1 H), 4.05 (m, 1 H), 4.39 (d, 11.1 Hz, 1 H), 5.48 (d, 11.1 Hz, 1 H), 6.75 (m, 2 H), 7.07 (m, 5 H), 7.71 (m, 2 H). ^{13}C NMR (75.42 Hz) in $CDCl_3$: δ 17.2 (CH_3), 21.3 (CH_3), 29.1 (CH), 37.7 (CH_2), 58.8 (CH), 67.9 (CH_2), 72.9 (CH_2), 126.4 (CH), 126.9 (CH), 128.4 (CH), 129.2 (CH), 129.3 (CH), 137.6 (C), 143.0 (C). Mass spectrum: calcd for $C_{26}H_{31}NO_3S$ 345.13985, found 345.14039.

Preparation of *syn*-Tetrahydro-1,3-oxazines 4. Tosyl amide **2** gave 41 mg (59%) of **4**, a colorless solid (R_f = 0.3 in 15% ethyl acetate/hexane eluant) when subjected to the sequence described above: mp 136–139 °C. ^1H NMR (300 MHz) in C_6D_6: δ 0.26 (d, 7.1 Hz, 3 H), 1.90 (s, 3 H), 2.03 (m, 1 H), 2.52 (m, 2 H), 3.08 (t, 11.6 Hz, 1 H), 3.38 (dd, 11.6 and 4.5 Hz, 1 H), 4.31 (m, 1 H), 4.4 (d, 11.8 Hz, 1 H), 5.59 (d, 11.8 Hz, 1 H), 6.72 (m, 2 H), 7.06–7.21 (m, 5 H), 7.62 (m, 2 H). ^{13}C NMR (75.42 Hz) in $CDCl_3$: δ 13.69 (CH_3), 21.26 (CH_3), 30.67 (CH_2), 31.70 (CH), 57.53 (CH), 68.39 (CH_2), 71.98 (CH_2), 126.08 (CH), 126.94 (CH), 128.1 (CH), 128.9 (CH), 129.10 (CH), 137.59 (C), 142.81 (C). $[\alpha]_D$ 68.5°, c = 0.0044 in $CHCl_3$. Mass spectrum: calcd for $C_{26}H_{31}NO_3S$ 345.13985, found 345.14039.

X-ray Diffraction Analyses. Crystals of **3** and **4** were mounted on glass fibers and fixed with epoxy cement. Data were collected on a Rigaku AFC5S single-crystal, automated diffractometer using Mo Kα radiation. Unit cell parameters based on 23 reflections for **3** and 21 reflections for **4** were obtained and after data reduction indicated the monoclinic and orthorhombic cells given in Table I, respectively. Symmetries expected for the monoclinic and orthorhombic cells were confirmed via intensity measurements of Laue symmetry equivalent reflections. Intensity statistics on the collected data indicated both cells to be eccentric as expected, given the known chiral nature of the starting materials. Structure determination for **3** and **4** followed the same procedures. Structure solution was accomplished by using SHELX86[4] followed by full-matrix least-squares refinements using TEXSAN (2.0).[5] All non-hydrogen atoms were refined anisotropically while hydrogen atoms were included in calculated positions but not refined (the placement of the hydrogen atoms on the methyl groups was based originally upon reasonable hydrogen locations found in the Fourier difference maps and subsequently idealized). For **4**, equivalent reflections were measured and were averaged in the final least-squares cycles. Data were corrected for LP and included terms for anomalous dispersion. No corrections were necessary for decay nor absorption [μ = 1.86 cm^{-1} (Mo Kα) for both determinations].

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Supplementary Material Available: ORTEP diagrams and tables of positional parameters and B(eq), crystallographic data collection and refinement parameters, and anisotropic thermal parameters for compounds **3** and **4** (14 pages). Ordering information is given on any current masthead page.

(4) Sheldrick, G. M. SHELX. SHELX86 Program for Crystal Structure Determination; 1986.

(5) Molecular Structure Corporation. TEXSAN (2.0), Program for Crystal Structure Determination and Refinement; The Woodlands, TX. Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, p 71 (scattering factors), p 148 (anamalous dispersion) (current distributor: Kluwer Academic Publishers, Dordrecht).

Bridging of the [2.2]Paracyclophane Nucleus by a Phenanthrene Unit[1]

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Polycyclic hydrocarbons consisting of aromatic subunits held in a rigid perpendicular arrangement are of interest not only for stereochemical and structural reasons but also as model compounds for the investigation of electronic interactions between orthogonal π-systems. Recently several "orthogonal cyclophanes" have been described that are formally composed out of biphenyl units whose benzene parts are held in strict orthogonality by molecular bridges.[2-5] For the synthesis of these novel aromatic systems, the intermediate generation and trapping of various [2.2]paracyclophynes[3,4,6] as well as the electrocyclic ring closure of 1,2,9,10-tetravinyl[2.2]paracyclophanedienes[5,7] have been particularly valuable.

We now introduce a new method for aromatic bridging of an already existing [2.2]paracyclophane unit that makes use of the throughly studied stilbene–phenanthrene photocyclization[8] and creates a novel bridge consisting of a condensed aromatic system.

Results and Discussion

Starting from 4,13-diformyl[2.2]paracyclophane (**3**), which is readily available in gram quantities by our paracyclophane synthesis from 1,2,4,5-hexatetraene (**1**) and propiolic aldehyde (**2**),[9,10] a double Grignard reaction with phenylmagnesium bromide in tetrahydrofuran is carried out first (Scheme I). The resulting diol **4**, formed in 95% yield, is stereochemically homogeneous as judged from its chromatographic behavior and spectroscopic data. Since the infrared spectrum of **4** is dominated by a very strong band at 3300 cm^{-1} and the OH groups appear as a broad peak at δ = 4.4 in the ^1H NMR spectrum we assume that strong intramolecular hydrogen bonding occurs and the diastereomer obtained has the structure shown in Scheme I. This would imply the (reasonable) assumption that the Grignard reagent has attacked **3** from the "outside" exclusively. Oxidation with pyridinium chlorochromate (PCC) in refluxing methylene chloride converts **4** into the diketone **5**, again in near quantitative yield (96%). Although the conformation of **5** was not explicitly determined, we believe that its carbonyl groups—rather than the phenyl substituents—point toward the ethano bridge. For a number of alkyl ketones this arrangement has been

(1) This is paper 32 of our cyclophane series; for paper 31, see: Hopf, H.; Witulski, B.; Ernst, L.; Jones, P. G. *Angew. Chem.* **1989**, *101*, 1290; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1279.

(2) Jacobsen, N.; Boekelheide, V. *Angew. Chem.* **1978**, *90*, 49; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 46.

(3) Hopf, H.; Psiorz, M. *Angew. Chem.* **1982**, *94*, 639; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 623.

(4) Chan, C. W.; Wong, H. N. C. *J .Am. Chem. Soc.* **1985**, *107*, 4790. Cf: Chan, C. W.; Wong, H. N. C. *J .Am. Chem. Soc.* **1988**, *110*, 462.

(5) Stöbbe, M.; Reiser, O.; Näder, R.; de Meijere, A. *Chem. Ber.* **1987**, *120*, 1667. Cf: Reiser, O.; Reichow, S.; de Meijere, A. *Angew. Chem.* **1987**, *99*, 1285; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1277.

(6) For a summary of some recent work on novel aromatic ring systems, see: Wong, H. N. C. *Acc. Chem. Res.* **1989**, *22*, 145.

(7) de Meijere, A.; Kaufmann, A.; Lackmann, R.; Militzer, H. C.; Reiser, O.; Schömenauer, S.; Weier, A. In *Organometallics in Organic Synthesis*, II; Erker, G., Werner, H., Eds.; Springer Verlag: Heidelberg, 1989; p 255. Cf: Reiser, O.; Weber, M.; de Meijere, A. *Angew. Chem.*, in press; *Angew. Chem., Int. Ed. Engl.*, in press.

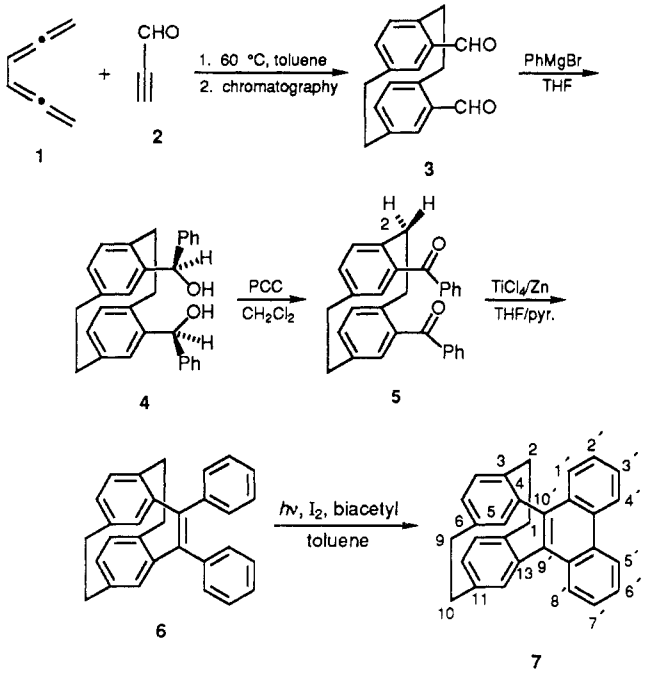
(8) Mallory, F. B.; Mallory, C. W. *Org. React.* **1984**, *30*, 1.

(9) Hopf, H.; Kleinschroth, J.; Böhm, I. *Org. Synth.* **1981**, *60*, 41.

(10) Hopf, H.; Raulfs, F.-W. *Israel J. Chem.* **1985**, *25*, 210. Cf: Broschinski, K. Ph.D. Dissertation, Braunschweig, 1984.

0022-3263/90/1955-1361$02.50/0

Scheme I



found to be the most stable one in solution by NMR spectroscopy.[11] In all these cases it has been noted that the hydrogen atom at C_2 directed toward the keto function experiences a downfield shift. Since this effect is also observed for **5** the conformation shown in Scheme I appears reasonable. With the preparation of this pseudogeminal derivative the series of all dibenzoyl[2.2]paracyclophanes is now complete, the other three diketones having been prepared by Iwamura in the course of his studies aimed at the preparation of low-dimensional organic ferromagnets.[12]

Although one would expect considerable steric hindrance in **5**, its McMurry coupling proceeds smoothly and provides the triply bridged phane **6** in nearly 80% yield. That the *cis*-stilbene bridge has indeed been formed may be inferred from the electronic spectrum of **6**, which shows absorption maxima (ethanol, λ_{max}, ϵ) at 206 (39 600), 227 (30 900), and 274 nm (8700). Whereas the first band is typical for the [2.2]paracyclophane unit, the last two maxima correspond to those of *cis*-stilbene itself: 224 (24 400) and 280 nm (10 500), respectively.[13] The final photocyclization step was carried out by irradiating **6** in toluene in the presence of iodine and biacetyl[14] with a high pressure mercury lamp. After chromatography and crystallization the desired 4,13-(9′,10′-phenanthreno)[2.2]paracyclophane (**7**) was isolated in 46% yield. The "composite" nature of this aromatic ring system is clearly demonstrated by its 400-MHz ^{1}H NMR spectrum, which in its aromatic part looks like a superimposition of the typical spectra for a 4,13-disubstituted [2.2]paracyclophane [δ = 6.57 (dd, J_1 = 1.8, J_2 = 7.9 Hz, H(7), H(16), 6.52 (d, J = 7.9 Hz, H(8), H(15), 6.46 (d, J = 1.8 Hz, H(5), H(12))] and a 9,10-disubstituted phenanthrene, respectively [δ = 8.85 (d, J = 8.4 Hz, H(4′), H(5′), 7.95 (dd, J_1 = 1.1, J_2 = 8.0 Hz, H(1′), H(8′), 7.72 (ps-t, J = 7.6 Hz, H(3′), H(6′), 7.57 (ps-t, J = 7.6 Hz, H(2′), H(7′))]. The ethano bridges of **7** absorb as complex, yet symmetrical multiplets at 3.07 (4 H) and 2.59 (4 H). Since the parent molecule [2.2]paracyclophane shows a signal at δ = 3.1 for its bridge protons, it is likely that the lower field multiplet of **7** is caused by H(9) and H(10), since these protons are further away from the penanthrene bridge than H(1) and H(2), respectively. Alternatively, the anisotropy of the condensed aromatic ring system could shift the four protons pointing toward it to higher field, while leaving the other four bridge protons practically uneffected. The mass spectrum of **7** is characterized by its comparatively small number of peaks. In particular, the peak at half molecular mass (m/z = 191) is very small (relative intensity 10%). Normally, in [2.2]paracyclophanes this is the base peak. Obviously, the third bridge inhibits the ready cleavage of the phane unit into two equal halves considerably. The complete spectral data of **7** as well as those of its precursor molecules may be found in the Experimental Section.

Since the phenylmagnesium bromide used in the first step of the synthesis reported here may in principle be replaced by other aromatic Grignard reagents, and the stilbene–phenanthrene photocyclization is one of the most general photochemical processes,[8] we believe that the above sequence could find wide application for the preparation of orthogonal phanes.

Experimental Section

General. IR spectra were recorded on a Perkin-Elmer 1420, UV spectra on a Beckman UV 5230 spectrometer. ^{1}H NMR spectra were obtained on a Varian T-60, a Bruker AM 300 and a Bruker WM 400 spectrometer with $(CH_3)_4Si$ as the internal standard. ^{13}C NMR spectra were recorded on a Bruker AM 300 or a Bruker WM 400 spectrometer with $CDCl_3$ as the solvent and the internal standard (δ 77.05). Mass spectra (electron impact ionization, 70 eV) were obtained on a MAT 8222 spectrometer. Melting points (Kofler hot stage) are uncorrected. THF was distilled from $LiAlH_4$ prior to use. All other reagents were analytical grade and were used without further purification.

4,13-Bis(phenylhydroxymethyl)[2.2]paracyclophane (4). A solution of phenylmagnesium bromide in THF was prepared from 72 mg (2.96 mmol) of magnesium and 465 mg (2.96 mmol) of freshly distilled bromobenzene in 2 mL of THF. Subsequently 185 mg (0.7 mmol) of dialdehyde **3** in 12 mL of THF was added at room temperature. After refluxing for 2 h, the reaction was terminated by careful addition of water at 0 °C. The precipitate was decomposed by the addition of 5 mL of 2 N HCl, and the aqueous phase was extracted several times with $CHCl_3$. The combined organic layers was neutralized with bicarbonate solution and dried over sodium sulfate. Solvent removal provided 280 mg of **4** (0.67 mmol, 95%) as slightly yellow crystals, shown to be homogenous by TLC (SiO_2, CH_2Cl_2, R_f = 0.105); mp >230 °C IR (KBr): $\bar{\nu}$ 3280 (vs, br), 1490 (m), 1455 (m), 1030 (m), 1020 (s), 765 (m), 735 (s), 700 cm^{-1} (vs). ^{1}H NMR (60 MHz): δ 7.2 (s, 10 H, C_6H_5), 6.5 (ps-s, 4 H, Ar H), 6.2 (ps-s, 2 H, Ar H), 4.4 (br m, 2 H, OH), 3.7–2.8 (m, 8 H, CH_2CH_2). MS (rel intensity): m/z = 402 ($M^+ - H_2O$, 50), 384 (10), 191 (100), 178 (70), 165 (40), 105 (40), 91 (80).

4,13-Dibenzoyl[2.2]paracyclophane (5). To a solution of 120 mg (0.29 mmol) of **4** in 70 mL of absolute CH_2Cl_2 was added 1.4 g (6.49 mmol) of pyridinium chlorochromate (PCC) in small portions. After refluxing for 3 h, the originally orange-colored reaction mixture had turned brown. The chromium salts were removed by filtering the reaction mixture through a short silica gel column. After solvent removal 116 mg of **5** (0.28 mmol, 96%) was obtained as a waxy solid. Further purification by column chromatography (silica gel, CH_2Cl_2) provides colorless, shiny plates, mp 220–222 °C. IR (KBr): $\bar{\nu}$ 1650 (s), 1640 (s), 1275 (s), 1270 (s), 970 (m), 835 (m), 700 cm^{-1} (s). ^{1}H NMR (60 MHz): δ 8.0–7.3 (m, 10 H, C_6H_5), 7.0–6.6 (m, 6 H, Ar H), 3.75–3.35 (m, 2 H,

(11) Laue, Th. Diploma Thesis, Braunschweig, 1988. Hopf, H.; Laue, Th.; Ernst, L. Unpublished work from these laboratories.

(12) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(13) Scott, A. I. *Ultraviolet Spectra of Natural Products*; Pergamon Press: Oxford, 1964: p 97.

(14) These conditions have been found to be particularly effective for the preparation of numberous [2.2]paracyclophanes containing condensed aromatic and heteroaromatic subunits: Hucker, J. Ph.D. Dissertation, Braunschweig, 1989. Cf: Hopf, H.; Mlynek, C.; El-Tamany, S.; Ernst, L. *J. Am. Chem. Soc.* **1985**, *107*, 6620.

CH_2CH_2, H atoms facing the carbonyl group, see main section), 3.3–2.7 (m, 6 H, CH_2CH_2). MS (rel intensity): m/z = 416 (M^+, 25), 208 (38), 207 (78), 149 (100), 57 (80).

4,13-(α,α′-Stilbeno)[2.2]paracyclophane (6). The McMurry coupling of **5** was carried out according to the Lenoir variant.[15] Dry THF (7 mL) was placed in a flame-dried 50-mL three-necked flask. Under nitrogen protection and magnetic stirring 520 mg (0.3 mL, 2.74 mmol) of $TiCl_4$ was added with a syringe at 0 °C. The ice bath was removed, and 366 mg (5.6 mmol) of zinc dust was added in small portions. The color of the reaction mixture changed from yellow through dark green to black-violet. When subsequently 0.18 mL of pyridine was added, the solution turned completely black. A solution of 0.52 g (1.25 mmol) of **5** in 27 mL of absolute THF was added within 20 min, and when the addition was complete the mixture was refluxed for 4 h. After cooling the room temperature, 60 mL of a dilute (10%) aqueous K_2CO_3 solution was added and the precipitate dissolved in 100 mL of CH_2Cl_2. After two more extractions of the aqueous phase, the combined organic layers were neutralized with bicarbonate solution and dried with magnesium sulfate. Solvent removal provided a slightly yellow solid, which was purified by chromatography on alumina (CCl_4): 0.379 mg of **6** (0.99 mmol, 79%). An analytically pure sample was obtained by recrystallization from ethanol/carbon tetrachloride: colorless plates, mp 199–199.5 °C. IR (KBr): $\tilde{\nu}$ 3045 (w), 2950 (w), 2930 (m), 2850 (w), 1600 (w), 1495 (m), 800 (m), 755 (m), 700 cm^{-1} (s). UV (ethanol): see main section. ^1H NMR (400 MHz): δ 7.43 (m, 4 H, C_6H_5), 7.25–7.17 (m, 6 H, C_6H_5), 6.56 (ps-s, 2 H, Ar H), 6.43–6.38 (m, 4 H, Ar H), 3.35–3.30 (m, 2 H, CH_2CH_2), 3.19–3.12 (m, 2 H, CH_2CH_2), 3.02–2.96 (m, 2 H, CH_2CH_2), 2.76–2.71 (m, 2 H, CH_2CH_2). MS (rel intensity): m/z = 384 (M^+, 1.7), 121 (25), 119 (96), 117 (100), 84 (18), 82 (24). Anal. Calcd for $C_{30}H_{24}$: 93.71 C, 6.29 H. Found: 93.50 C, 6.41 H.

4,13-(9′,10′-Phenanthreno)[2.2]paracyclophane (7). A solution of 225 mg (0.585 mmol) of **6** in 225 mL of absolute toluene was placed into an all-quartz photoreactor, and 16 mg (0.063 mmol) of iodine and 124 mg (1.44 mmol) of biacetyl were added. While dry nitrogen was passed through the reaction solution continuously, it was irradiated with a high-pressure mercury lamp (Hanau TQ 150). The progress of the cyclization was monitored by TLC (silica gel, CCl_4, R_f(**6**) = 0.2, R_f(**7**) = 0.28), and after 65 min the process was terminated. The toluene solution was washed with sodium bisulfite solution twice and three times with a saturated aqueous sodium chloride solution and dried over magnesium sulfate. After the solvent had been removed by rotatory evaporation, 273 mg of a yellow viscous oil was obtained. Column chromatography on silica gel (CCl_4) followed by preparative thick-layer chromatography (silica gel, CCl_4) provides 104 mg (0.27 mmol, 64%) of **7** as colorless, shiny plates. In a second fraction (47 mg) additional **7** contaminated with **6** was isolated. An analytically pure sample of **7** was obtained by high vacuum sublimation (10^{-3} Torr, 100 °C), mp 112–115 °C. IR (KBr): $\tilde{\nu}$ 3065–3000 (several maxima of medium intensity), 2930 (s), 2850 (m), 1485 (m), 1445 (m), 760 (vs), 750 (s), 730 cm^{-1} (vs). UV (ethanol): λ_{max} (ε) 306 (11 900), 293 (12 200), 280 (sh, 14 700), 270 (27 400), 257 (57 700), 254 (sh, 53 800), 224 (44 200), 211 (sh, 42 200), 208 nm (42 800). ^1H NMR (400 MHz): see main section. ^{13}C NMR (100.6 MHz): δ 142.95, 141.63, 141.54, 139.89, 139.68, 133.38, 131.28, 129.96, 129.81, 128.06, 126.73, 126.48, 122.77, 35.14, 33.61. MS (rel intensity): m/z = 382 (M^+, 100), 381 (26), 365 (16), 353 (20), 339 (16), 276 (10), 191 (10), 176 (16). Anal. Calcd for $C_{30}H_{22}$: 94.20 C, 5.80 H. Found: 94.35 C, 5.96 H.

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(15) Lenoir, D. *Synthesis* **1977**, 553.

Synthesis of All 2,3,4-Trimethoxy-5-hexenal (5,6-Dideoxy-2,3,4-tri-*O*-methylaldohex-5-enose) Isomers

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Among the numerous carbohydrate-derived synthons[1] various derivatives of 4,5-dideoxyaldopent-4-enoses and 5,6-dideoxyaldohex-5-enoses were recently used as starting materials for the synthesis of natural products, such as macrolides,[2] prostaglandins,[3] pheromones,[4] anthracyclinones,[5] deoxynojirimycin,[6] and pseudomonates.[7]

Inasmuch as members of this large and interesting group of "chirons"[1] were hitherto invariably prepared by zinc-induced reductions of appropriately structured ω-deoxyhaloaldosides,[8,9] we began a systematic study comprising the influences of the kind of halogen, ring size, functional group compatibility, activity and kind of reducing agent, solvent, and temperature on this type of transformation. In addition, because of the limited accessibility of a number of pentofuranoside and hexopyranoside configurations, alternative and complementory synthetic routes needed to be investigated. As a first result, this paper describes the efficient preparation of the eight stereoisomeric 5,6-dideoxy-2,3,4-tri-*O*-methylaldohex-5-enoses, four of which were obtained by conventional procedure[9] and were subsequently transformed into the remaining four configurations by interchanging the respective aldehyde and vinyl functions.

As depicted in Schemes I and II dealkoxyiodination of methyl-6-deoxy-6-iodo-2,3,4-tri-*O*-methyl-D-gluco- (**1a**), -D-manno- (**1b**), -D-galacto- (**1c**), and -D-allopyranosides (**1d**) by highly active zinc/silver–graphite in oxolane[9] yielded the 5,6-dideoxy-2,3,4-tri-*O*-methyl-D-*xylo*- (**2a**), -D-*lyxo*- (**2b**), -L-*arabino*- (**2c**), and -D-*ribo*-hex-5-enoses (**2d**). Each of these compounds was then treated with [(trimethylsilyl)methyl]magnesium chloride followed by dihydroxylation employing OsO_4 and acetonization. In the presence of catalytic amounts of $BF_3{\cdot}Et_2O$ the intermediates were subject to Peterson elimination[10] and to deacetonization on aqueous workup. Finally periodate fission of the resulting 6,7-dihydroxy-3,4,5-trimethoxy-1-heptenes **6** afforded the 5,6-dideoxy-2,3,4-tri-*O*-methyl-L-*xylo*- (**7a**), -D-*arabino*- (**7b**), -L-*lyxo*- (**7c**), and -L-*ribo*-hex-5-enoses (**7d**). As indicated in Scheme II, for the conventional synthesis of these compounds invariably 6-deoxy-6-iodohexopyranosides of uncommon configurations would have been needed.

The following observations are worth mentioning:

(1) For a review see: Hanessian, S. *Total Synthesis of Natural Products: The Chiron Approach*; Pergamon Press: Oxford, 1983.
(2) (a) Villalobos, A.; Danishefsky, S. *J. Org. Chem.* **1989**, *54*, 12. (b) Hanessian, S.; Ugolini, A., Therien, M. *J. Org. Chem.* **1983**, *48*, 4427.
(3) Ferrier, R. J.; Prasit, P. *J. Chem. Soc., Chem. Commun.* **1981**, 983. (b) Ferrier, R. J.; Furneaux, R. H.; Prasit, P.; Tyler, P. C.; Brown, K. L.; Gainsford, G. J.; Diehl, J. W. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1621.
(4) (a) Ferrier, R. J.; Prasit, P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1645. (b) Ferrier, R. J.; Schmidt, P.; Tyler, P. C. *J. Chem. Soc., Perkin Trans. 1* **1985**, 301.
(5) Florent, J. C.; Ughetto-Monfrin, J.; Monneret, C. *J. Org. Chem.* **1987**, *52*, 1051
(6) (a) Bernotas, R. C.; Ganem, B. *Tetrahedron Lett.* **1985**, 1123. (b) Bernotas, R. C.; Ganem, B. *Carbohydr. Res.* **1987**, *167*, 312. (c) Bernotas, R. C.; Pezzone, M. A.; Ganem, B. *Carbohydr. Res.* **1987**, *167*, 305
(7) Beau, J. M.; Abouraki, S.; Pougny, J. R.; Sinay, P. *J. Am. Chem. Soc.* **1983**, *105*, 621
(8) Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1979**, *62*, 1990.
(9) Fürstner, A.; Weidmann, H. *J. Org. Chem.* **1989**, *54*, 2307.
(10) For a review see: Ager, D. J. *Synthesis* **1984**, 384.

0022-3263/90/1955-1363$02.50/0