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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Registry No. **3**, 106819-11-8; **4**, 124511-93-9; **5**, 124618-53-7; **6**, 124511-94-0; **7**, 124511-95-1.

(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
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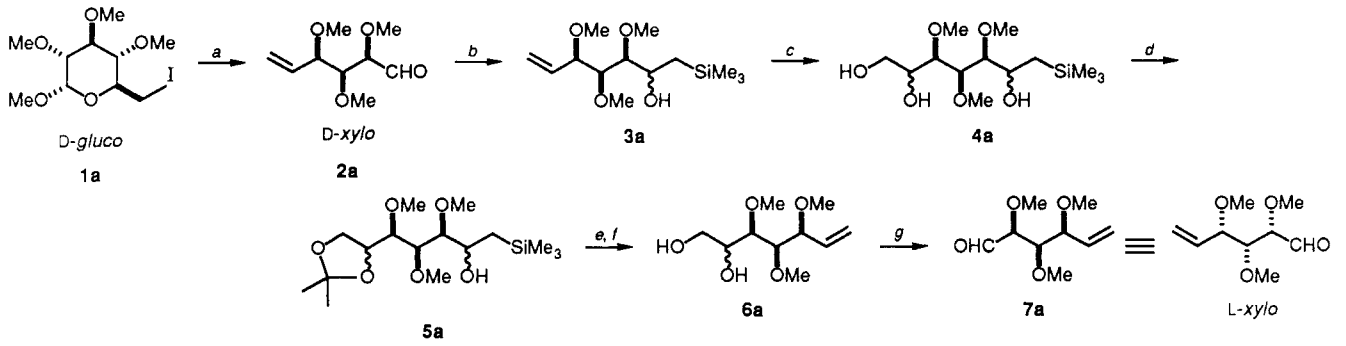
(9) Fürstner, A.; Weidmann, H. *J. Org. Chem.* **1989**, *54*, 2307.
(10) For a review see: Ager, D. J. *Synthesis* **1984**, 384.

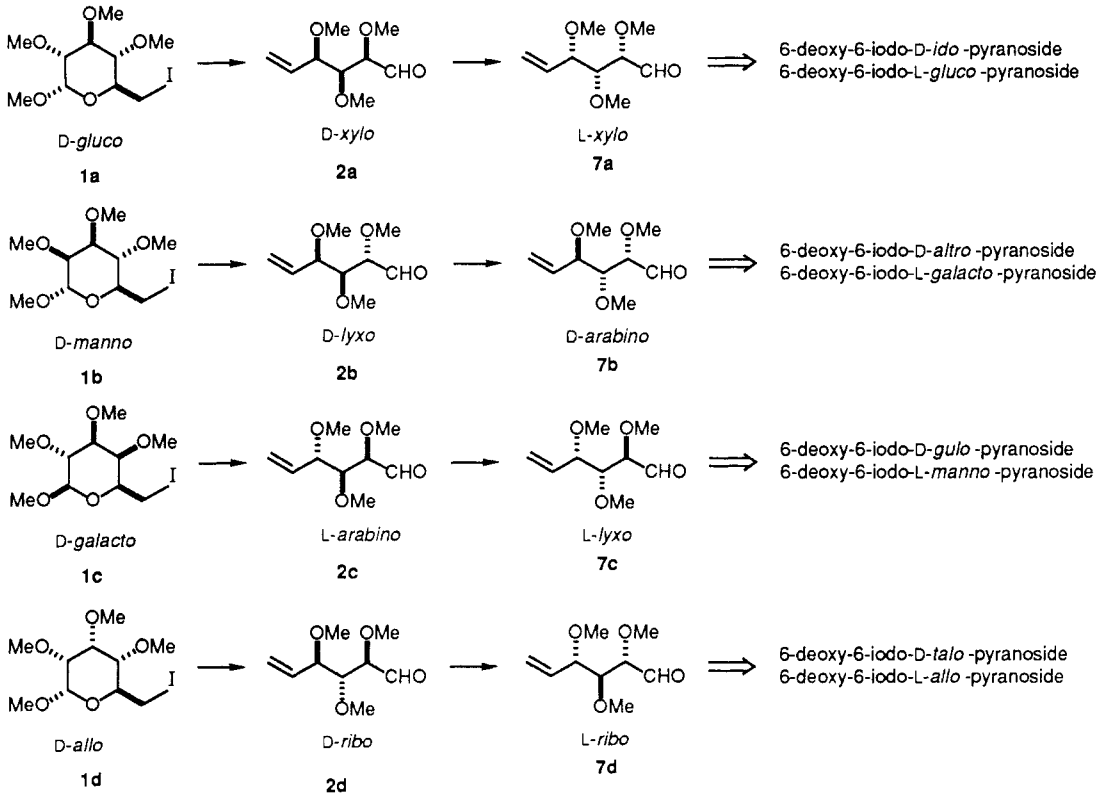
0022-3263/90/1955-1363$02.50/0

Scheme I



[a] Zn/Ag–graphite, THF, 10 min, 20 °C, 93%. [b] Me_3SiCH_2MgCl, THF, 60 min, 20 °C, 87%. [c] Catalyst OsO_4, *N*-methylmorpholine *N*-oxide monohydrate, acetone, 12 h, quantitative. [d] 2,2-Dimethoxypropane, *p*-TsOH, CH_2Cl_2, 15 min, 20 °C, 90%. [e] $BF_3{\cdot}Et_2O$, CH_2Cl_2, 10 min, 20 °C, quantitative. [f] H_2O, *p*-TsOH, 10 min, quantiative. [g] $NaIO_4$, H_2O/Et_2O, 15 min, 80%.

Scheme II



With the exception of the D-*lyxo*-configurated educt **2b** which in good agreement with previous observations[11] underwent both the Grignard and the cis hydroxylation reactions stereospecifically, the three remaining substrates reacted less selectively. Although there is generally no conclusive evidence whether either one or both of these reactions produce diastereomeric mixtures, a stereoselective cis-hydroxylation is the prerequisite for the formation of compound **8** under more forcing conditions (equimolar amount of $BF_3{\cdot}Et_2O$) from **4a** (Scheme III). The formation of the *O*-trityl derivative **9** proved the ring size of compound **8**.

In all cases described Lewis acid was found to be superior to base for Peterson eliminations.[10]

The intermediate isopropylidene derivatives **5** not only facilitated the identification of intermediates but also inhibited the formation of oxolane derivatives.

The final periodate fission was most favorably performed in the two-phase diethyl ether/water system.

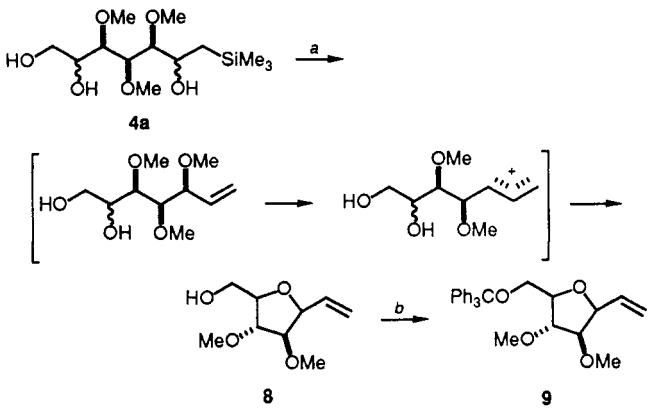
Investigations in this field of carbohydrate-derived unsaturated synthons are continued.

Experimental Section

General Procedures. NMR spectra were recorded with a Bruker MSL 300 instrument at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR), with $CDCl_3$ as solvent and tetramethylsilane as internal standard unless stated otherwise. Chemical shifts are given in ppm, coupling constants (*J*) in hertz. IR spectroscopy was performed with a Beckman IR 33 (film of the product on a NaCl plate). Optical rotations were measured with a Jasco DIP 370 polarimeter. Column chromatography was invariably performed on Merck silica gel (230–240 mesh) with mixtures of ethyl acetate/toluene in various proportions as eluant. Tetrahydrofuran (THF) was distilled over $LiAlH_4$ prior to use. [(Trimethylsilyl)methyl]magnesium chloride (1 M in diethyl ether) and OsO_4 were purchased from Aldrich. In all experiments graphite samples supplied by Lonza AG, Basel, Switzerland (HSAG 9), were em-

(11) (a) Redlich, H.; Thormählen, S. *Tetrahedron Lett.* **1985**, 3685. (b) Paulsen, H.; Schüller, M.; Nased, A.; Heitmann, A.; Redlich, H. *Tetrahedron Lett.* **1985**, 3689.

Scheme III



[a] BF_3·Et_3O, CH_2Cl_2, 3 h, 20 °C, 79%. [b] Ph_3CCl, pyridine, 30 °C, 6 h, 88%.

Table I. Yields and Physical Data of the Products

educt	product	yield, %	$[\alpha]^{20}_D$ (c, CH_2Cl_2), deg	IR, cm^{-1}
1a	**2a**[a]	93	+31.4 (1.7)	1730
2a	**7a**	61[b]	-31.4 (1.6)	
1b	**2b**	88	-22.8 (5.0)	1720
2c	**7c**	52[b]	+22.8 (4.0)	
1c	**2c**	95	+41.8 (4.4)	1730
2b	**7b**	50[b]	-41.6 (4.0)	
1d	**2d**	86	+35.4 (4.8)	1725
2d	**7d**	56[b]	-35.1 (1.3)	
4a	**8**	79	+24.6 (20)	1630[c]
8	**9**	88	+20.0 (2.5)	1625

[a] See ref 9. [b] Overall yield (steps *b–g* in Scheme I). [c] 3600–3150 cm^{-1} (br s).

ployed, but any other kind of graphite quality turned out to be equally suited.

Zinc/Silver–Graphite-Induced Fragmentations. General Procedure. A solution of each of the compounds **1a–d** (10 mmol) in THF (10 mL) was rapidly added to a suspension of Zn/Ag–graphite (15 mmol)[9] in THF (40 mL) with stirring under argon at ambient temperature. After 10 min the reaction mixture was filtered, the insolubles were repeatedly washed with THF (80 mL), the combined filtrates were evaporated under reduced pressure, and the residues were chromatographed, yielding **2a–d** in the yields indicated in Table I.

Reactions with [(Trimethylsilyl)methyl]magnesium Chloride. General Procedure. To each of the unpurified solutions of compounds **2a–d** in THF a solution of [(trimethylsilyl)methyl]magnesium chloride (1 M in diethyl ether, 13 mmol) was added by a syringe with stirring under argon at 20 °C. After 1 h water (30 mL) and diethyl ether (50 mL) were added, the organic phase was dried (Na_2SO_4) and evaporated, and the residues were subjected to column chromatography, affording pure **3a–d**.

Cis Hydroxylation Followed by Acetonization. General Procedure. Each of the compounds **3a–d** was dissolved in acetone (30 mL), OsO_4 (2 mg) and *N*-methylmorpholine *N*-oxide (10 mmol) were added, and the mixture kept for 12 h at ambient temperature. Then a saturated solution of $NaHSO_3$ (20 mL) was added, and the mixture repeatedly extracted with 20-mL portions of ethyl acetate. After evaporation of the dry solutions to each of the residues, a solution of 2,2-dimethoxypropane (3 mL) and a catalytic amount of *p*-toluenesulfonic acid in CH_2Cl_2 (30 mL) was added, and this was kept for 20 min at ambient temperature. After extraction with aqueous $NaHCO_3$ and water, the solutions were dried (Na_2SO_4) evaporated, and chromatographed, yielding products **5a–d**.

Peterson Elimination. General Procedure. Each of the solutions of the products **5a–d** described above (1.40 g, 4 mmol) in CH_2Cl_2 (30 mL) was treated with a catalytic amount of BF_3·Et_2O, causing immediate Peterson elimination. For workup the reaction mixture was extracted with an aqueous solution of *p*-toluenesulfonic acid (3%) and water, causing rapid deacetalization. Thus, pure **6a–d** is obtained after column chromatography.

Periodate Fission. General Procedure. Each of the compounds **6a–d** (0.66g, 3 mmol) was vigorously stirred in a two-phase mixture of diethyl ether (50 mL) and aqueous $NaIO_4$ (2.14 g, 10 mmol in 30 mL) for 30 min. For workup the organic phase was separated, dried (Na_2SO_4), evaporated, and chromatographed, affording pure **7a–d** in the yields given in Table I.

5,6-Dideoxy-2,3,4-tri-*O*-methyl-D (or L)-*xylo*-hex-5-enose (2a and 7a, respectively): ^1H NMR δ 9.73 (s, 1 H, CHO), 5.83 (dX part of an ABX, 1 H, H-5, J_{45} = 7.8, J_{56a} = 10.5, J_{56b} = 14.9), 5.34 (AB part of the ABX, 2 H, H-6a, H-6b), 3.81 (dd, 1 H, H-3, J_{23} = 4.4, J_{34} = 7.8), 3.74 (d, 1 H, H-2), 3.54 (dd, 1 H, H-4), 3.49, 3.43, 3.24 (s, 3 H each, OMe); ^{13}C NMR δ 201.12 (CHO), 134.81 (C-5), 119.07 (C-6), 84.38, 84.29, 81.83 (C-2, C-3, C-4), 60.37, 59.10, 56.54 (-OMe).

5,6-Dideoxy-2,3,4-tri-*O*-methyl-D (or L)-*lyxo*-hex-5-enose (2b and 7c, respectively): ^1H NMR δ 9.70 (d, 1 H, CHO, $J_{CHO,2}$ = 1.7), 5.81 (dX part of an ABX, 1 H, H-5, J_{45} = 8, J_{56a} = 13.6, J_{56b} = 8.4), 5.32 (AB part of the ABX, 2 H, H-6a, H-6b), 3.82 (dd, 1 H, H-2, $J_{CHO,2}$ = 1.7, J_{23} = 4.4), 3.76 (dd, 1 H, H-3, J_{34} = 7.9), 3.48 (dd, 1 H, H-4), 3.47, 3.46, 3.28 (s, 3 H each, OMe); ^{13}C NMR δ 201.88 (CHO), 135.07 (C-5), 119.91 (C-6), 85.74, 84.94, 82.73 (C-2, C-3, C-4), 60.52, 59.13, 57.02 (OMe);

5,6-Dideoxy-2,3,4-tri-*O*-methyl-L (or D)-*arabino*-hex-5-enose (2c and 7b, respectively): ^1H NMR δ 9.68 (d, 1 H, CHO, $J_{CHO,2}$ = 1.3), 5.67 (dX part of an ABX, 1 H, H-5, J_{45} = 7.9, J_{56a} = 10.2, J_{56b} = 6), 5.25 (AB part of the ABX, 2 H, H-6a, H-6b), 3.74 (dd, 1 H, H-2, $J_{CHO,2}$ = 1.3, J_{23} = 3.3), 3.64 (dd, 1 H, H-4, J_{34} = J_{45} = 7.9), 3.40 (dd, 1 H, H-3), 3.41, 3.34, 3.15 (s, 3 H each, OMe); ^{13}C NMR δ 203.10 (CHO), 135.44 (C-5), 119.76 (C-6), 86.18, 83.65, 81.20, (C-2, C-3, C-4), 60.41, 59.51, 59.19 (OMe).

5,6-Dideoxy-2,3,4-tri-*O*-methyl-D (or L)-*ribo*-hex-5-enose (2d and 7d, respectively): ^1H NMR δ 9.49 (d, 1 H, CHO, $J_{CHO,2}$ = 1), 5.65 (dX part of an ABX, 1 H, H-5, J_{45} = 7.6, J_{56a} = 13.6, J_{56b} = 7.5), 5.24 (AB part of the ABX, 2 H, H-6a, H-6b), 3.75 (dd, 1 H, H-2, $J_{CHO,2}$ = 1, J_{23} = 2.8), 3.66 (dd, 1 H, H-4, J_{34} = J_{45} = 7.6), 3.36 (dd, 1 H, H-3), 3.47, 3.35, 3.17 (s, 3 H each, OMe); ^{13}C NMR δ 201.06 (CHO), 135.44 (C-5), 119.01 (C-6), 85.42, 84.98, 80.65 (C-2, C-3, C-4), 59.33, 58.91, 56.53 (OMe).

5-(Hydroxymethyl)-3(*R*),4(*R*)-dimethoxy-2-vinyloxolane (8) and Trityl Ether (9). Treatment of compound **4a** (1.24g, 4 mmol) with an equimolar amount of BF_3·Et_2O (0.57g, 4 mmol) for 3 h at ambient temperature, extraction with water, and column chromatography of the residue afforded the title compound in 79% yield (0.595 g). Its reaction with triphenyl chloromethane (1.95 g, 7 mmol) in pyridine (20 mL) at 30 °C for 6 h gave compound **9** (1.52 g, 88%).

8: ^1H NMR δ 5.92 (ddd, 1 H, C*H*=CH_2, J = 17, 11.0, $J_{CH,H\text{-}2}$ = 6.7), 5.33 (dd, CH=C$H_a$$H_b$, J = 11.0, $J_{Ha,Hb}$ = 1.5), 5.19 (dd, 1 H, CH=C$H_a$$H_b$, J = 17), 4.38 (dd, 1 H, H-2, J_{23} = 6.0), 4.04 (dd, 1 H, H-5, J_{45} = 4, $J_{5,CH2OH}$ = 5.7), 3.65–3.76 (m, 3 H, H-3, H-4, C$H_a$$H_b$OH), 3.47 (dd, 1 H, C$H_a$$H_b$OH, $J_{Ha,Hb}$ = 9.2), 3.39, 3.40 (s, 3 H each, OMe), 2.89 (br s, 1 H, OH); ^{13}C NMR δ 136.59 (*C*HCH_2), 117.01 (CH*C*H_2), 89.80, 89.70, 86.13, 83.46, 82.92 (C-2, C-3, C-4, C-5, CH_2OH), 62.64, 57.71 (OMe).

9: ^1H NMR δ (benzene-d_6) 6.97–7.65 (m, 15 H, Ph), 6.00 (ddd, 1 H, C*H*=CH_2, J = 17.2, J = 10.7, $J_{CH,H\text{-}2}$ = 6.5), 5.33 (dd, 1 H, CH=C$H_a$$H_b$, J = 17.2, $J_{Ha,Hb}$ = 1.5), 5.03 (dd, 1 H, CH=C$H_a$$H_b$, J = 10.7), 4.59 (dd, 1 H, H-2, J_{23} = 6.1), 4.35 (ddd, 1 H, H-5, J_{45} = 3.7, J_{5,CH_aH_bOR} = J_{5,CH_aH_bOR} = 5.2), 3.90 (dd, 1 H, H-4, J_{34} = J_{45} = 3.7), 3.65 (dd, 1 H, H-3), 3.42 (dd, 2 H, CH_2OR, J = 5.2), 3.07, 3.03 (s, 3 H each, OMe); ^{13}C NMR δ (benzene-d_6) 145.09, 136.25 (*C*H=CH_2), 129.61, 128.92, 128.75, 128.51, 128.43, 128.11, 127.63 (Ph), 116.51 (CH=CH_2), 91.37, 87.97, 87.60, 84.09, 82.45 (C-2, C-3, C-4, C-5, CH_2OR), 65.38 (Ph_3C), 57.93, 57.72 (OMe).

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Registry No. 1a, 57467-10-4; **1b**, 124289-02-7; **1c**, 124289-03-8; **1d**, 124289-04-9; **2a**, 120333-17-7; **2b**, 124289-05-0; **2c**, 124289-06-1; **2d**, 124289-07-2; **3a** (isomer 1), 124377-55-5; **3a** (isomer 2), 124289-08-3; **3b** (isomer 1), 124376-13-2; **3b** (isomer 2), 124376-14-3; **3c** (isomer 1), 124376-15-4; **3c** (isomer 2), 124376-16-5; **3d** (isomer

1), 124376-17-6; **3d** (isomer 2), 124376-18-7; **4a** (isomer 1), 124289-18-5; **4a** (isomer 2), 124376-40-5; **4a** (isomer 3), 124376-41-6; **4a** (isomer 4), 124376-42-7; **5a** (isomer 1), 124289-09-4; **5a** (isomer 2), 124376-19-8; **5a** (isomer 3), 124376-20-1; **5a** (isomer 4), 124376-21-2; **5b** (isomer 1), 124376-22-3; **5b** (isomer 2), 124376-23-4; **5b** (isomer 3), 124376-24-5; **5b** (isomer 4), 124376-25-6; **5c** (isomer 1), 124376-26-7; **5c** (isomer 2), 124376-27-8; **5c** (isomer 3), 124376-28-9; **5c** (isomer 4), 124376-29-0; **5d** (isomer 1), 124376-30-3; **5d** (isomer 2), 124376-31-4; **5d** (isomer 3), 124376-32-5; **5d** (isomer 4), 124376-33-6; **6a** (isomer 1), 124289-10-7; **6a** (isomer 2), 124376-34-7; **6b** (isomer 1), 124376-35-8; **6b** (isomer 2), 124289-11-8; **6c** (isomer 1), 124376-36-9; **6c** (isomer 2), 124376-37-0; **6d** (isomer 1), 124376-38-1; **6d** (isomer 2), 124376-39-2; **7a**, 124289-12-9; **7b**, 124289-13-0; **7c**, 124289-14-1; **7d**, 124289-15-2; **8**, 124289-16-3; **9**, 124289-17-4; $(CH_3)_3SiCH_2MgCl$, 13170-43-9.

Supplementary Material Available: Complete set of NMR data for educts **1a–d** and the diastereomerically pure intermediates **3b**, **5b**, and **6b**, as well as a table with characteristic signals for **3a,c,d** and **5a,c,d** (diastereomeric mixtures) (4 pages). Ordering information is given on any current masthead page.

Unusual Diels–Alder Reactions of Eucarvone[1]

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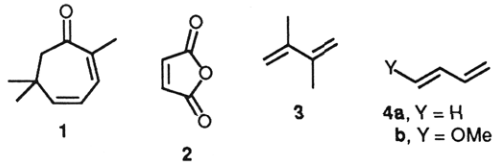
In continuation of a recent study of Diels–Alder reactions of conjugated, heteroannular dienones,[1b] an investigation of the cycloaddition behavior of a homoannular dienone, i.e., eucarvone (**1**), now has been undertaken.



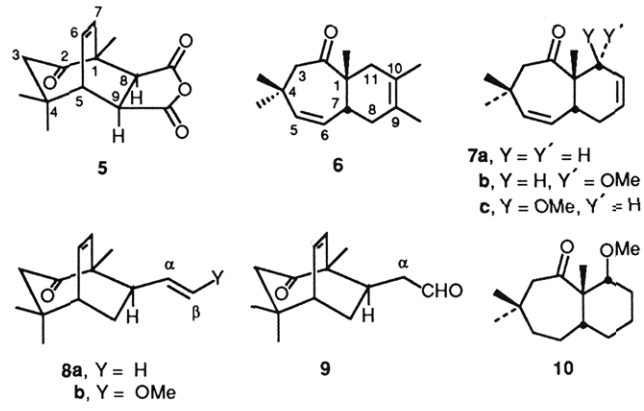
Whereas the Diels–Alder reactivity of 2,4-cyclohexadienones has been studied extensively,[3] little is known about the reaction characteristics of 2,4-cycloheptadienones. In an early study of the thermal interaction of 2,4-cycloheptadienone with the dienophile *N*-phenylmaleimide the dienone was shown to exhibit low dienic reactivity.[4] It was hoped that an investigation of the reactions of eucarvone (**1**) with maleic anhydride (**2**), 2,3-dimethyl-1,3-butadiene (**3**), 1,3-butadiene (**4a**), and (*E*)-1-methoxy-1,3-butadiene (**4b**) would shed more light on the Diels–Alder reaction behavior of dienones of the 2,4-cycloheptadienone type.

Diels–Alder Reaction Products. In accord with expectation, eucarvone (**1**) behaved as a diene in its conversion into adduct **5** (Chart I) in 48% yield on thermal treatment with maleic anhydride (**2**) and as a dienophile in its thermal and aluminum chloride catalyzed[5] cycloadditions with 2,3-dimethyl-1,3-butadiene (**3**), leading to adduct **6** in 50% (by GC analysis) and 87% yield, respectively. On the other hand, eucarvone (**1**) acted surprisingly as both dienophile and diene toward the butadienes **4**. This aluminum chloride induced reaction with 1,3-butadiene (**4a**) produced a 1.6:1 mixture of adducts **7a** and **8a** in 85% yield (by GC analysis). Thermal reaction with (*E*)-1-methoxy-1,3-butadiene (**4b**) afforded a 3.4:2:1 mixture of adducts **7b**, **8b**, and **7c** in 47% yield (by GC analysis), and $Yb(fod)_3$-promoted[6] reaction with diene **4b** gave a 3.3:1.2:1 mixture of the same products in 66% yield (by GC analysis).

Acid hydrolysis of enol ether **8b** furnished aldehyde **9** (97%), and hydrogenation of diene **7b** led nearly quantitatively to perhydrobenzosuberone **10**.

The structure assignment of compounds **5–10** was based on their NMR spectral analysis and the single-crystal X-ray crystallographic analysis of Diels–Alder adduct **7b**. Examination of hydrogen chemical shifts by COSY NMR experiments yielded hydrogen connectivities, which, in turn, determined the position of the vinyl side chains of compounds **8**. The H(5)–H(9)–H(8) coupling characteristics of bicycles **5** and **8** revealed these substances to possess endo stereochemistry. Thus, for example, ketones **5** and **8a** showed $J_{H(5)-H(9-exo)}$ and $J_{H(8)-H(9-exo)}$ values of <1

Chart I



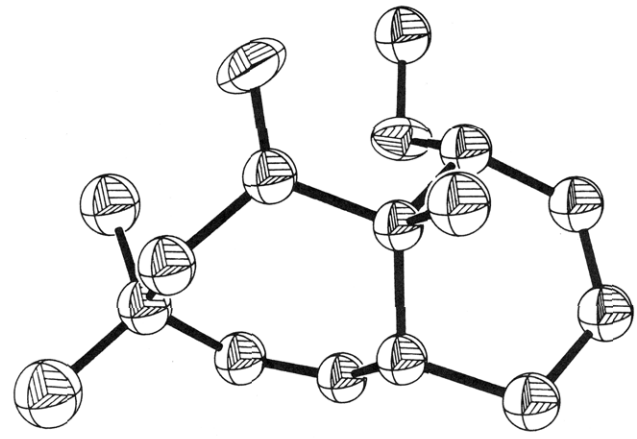


Figure 1. ORTEP drawing of structure **7b**.

(1) (a) Part 18 of the series: Diels–Alder Reactions of Cycloalkenones. (b) For part 17: see Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.*, in press.

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(5) (a) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Halls, T. D. J.; Wenkert, E. *J. Org. Chem.* **1982**, *47*, 5056. (b) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *Ibid.* **1983**, *48*, 2802.

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