propane and **5**, as well as **2** and butyraldehyde, are formed at 90 °C (**5**/**2** = 10.5[19]), but propylene is not observed. This difference is consistent with an essentially irreversible formaldehyde elimination process compared with a reversible β-hydride elimination of an olefin, which ultimately leads to propane by irreversible C–H reductive elimination.

Further investigation of reactions of hydroxyacetyl complexes is now in progress.

Supplementary Material Available: Crystal structure analysis summary and tables of positional and thermal parameters of compound **3** (24 pages). Ordering information is given on any current masthead page.

(19) No attempt was made to remove the product aldehyde from the equilibrium mixture.

(20) **Note Added in Proof**: The octaethylporphyrin complex RhOEP($COCH_2OH$) was reported after submittal of this article for publication: Van Voorhees, S. L.; Wayland, B. B. *Organometallics* **1985**, *4*, 1887.

Synthesis of Crystalline (±)-Fecapentaene

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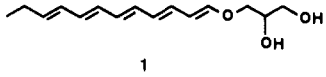
Since their discovery[1] and the structure elucidation[1,2] the fecapentaenes have gained worldwide scientific interest. These mutagenic glyceryl ether lipids can occur in trace amounts in the feces of people living in industrialized countries and are suspected to be a cause for colon cancer.[3]

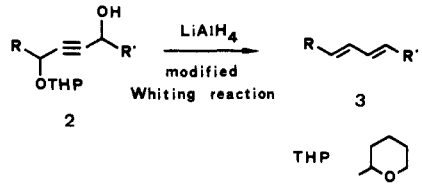
For the relevant carcinogenicity testing the mutagenic substances must be available in gram quantities, most desirably in pure form. Recently published syntheses[4] using Wittig and Horner–Wittig condensations to construct the polyene moiety lacked in stereochemical control and produced mixtures of cis–trans isomers which were extremely instable and difficult to handle.

We wish to communicate the first stereospecific route leading to the crystalline parent compound *all-trans*-fecapentaene-12 (**1**).



1

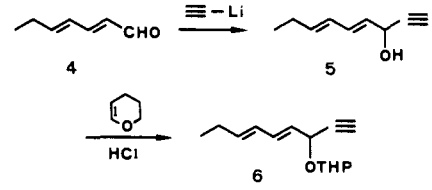
To avoid the difficulties encountered with the aforementioned nonselective preparations,[4] we chose an entirely different approach. In its key step, a modified[5] Whiting reaction[6] **2** → **3**, two of the



2 **3**

total five trans-oriented C=C double bonds in **1** are formed. This stereoselective reaction proceeds in one step starting with the precursor **2**, a derivative of an acetylenic diol.

According to a known method[7] lithium acetylide was added to *trans,trans*-hepta-2,4-dienal (**4**) to afford nona-4,6-dien-1-yn-3-ol (**5**) (bp 58–65 °C (0.01 mm), mp 8–10 °C, yield 67%), which in turn was transformed by 3,4-dihydro-2*H*-pyran together with a catalytic amount of hydrogen chloride to the tetrahydropyranyl derivative **6** (bp 108 °C (0.005 mm), yield 89%). Naturally, the

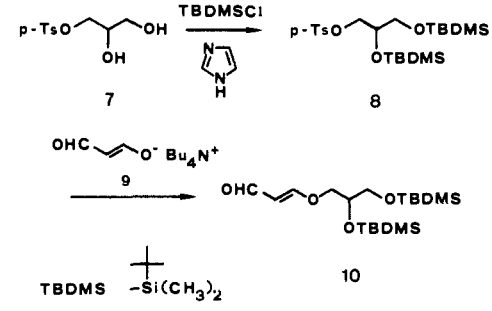


4 **5** **6**

trans-trans geometry of **4** was retained during these reactions. In the ^1H NMR spectrum of **6** no signals due to an isomer could be detected. Therefore **6** was most suitable to serve as the first building block in our synthesis.

To synthesize the other half of a precursor of the target molecule **1**, glyceryl *p*-toluenesulfonate (**7**) was protected[8] with *tert*-butyldimethylsilyl chloride and imidazol in dimethylformamide (room temperature, 6 h) to afford 2,3-bis(*tert*-butyldimethylsilyloxy)-propyl *p*-toluenesulfonate (**8**) in 91% yield after chromatography (silica gel, petroleum ether–ethyl acetate 98:2).

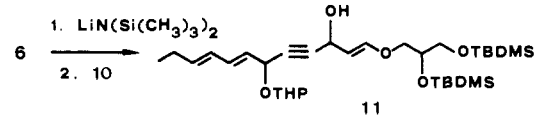
Up to now there existed no direct and convenient method[9] for the O-alkylation of malondialdehyde. We have found that the novel tetrabutylammonium salt **9** (mp 129–130 °C from glyme)—prepared in 67% yield from 1,1,3,3-tetraethoxypropane and 0.3 N aqueous hydrogen chloride (50 °C, 25 min) followed by addition of methanolic tetrabutylammonium hydroxide solution—easily reacted with the protected tosylate **8** (dry dimethylformamide, 1.5 equiv of **9**, concentrated solution, 50 °C, 22 h) to afford *trans*-3-[(2,3-bis[(*tert*-butyldimethylsilyl)oxy]-propyl)oxy]propenal (**10**) in 82% yield after chromatography



7 **8** **10**

(silica gel, petroleum ether–ethyl acetate 9:1 and 4:1). Its ^1H NMR spectrum in CCl_4 showing a clean doublet of the —O—CH= resonance at 7.3 ppm with a coupling constant of 12.5 Hz revealed that the (oxopropenyl)oxy moiety had been linked with the complete trans stereoselectivity desired in the production of the second building block **10**.

At this stage the two units **6** and **10** were combined. Adding the preformed lithium derivative of **6**—prepared with 1.1 equiv of lithium bis(trimethylsilyl)amide (fresh colorless solution in tetrahydrofuran, −78 → 0 °C)—to the aldehyde **10** (−78 → −30 °C) furnished the liquid key compound **11**[10] in 72% yield after



11

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(10) No attempts were made to separate the diastereomers or to determine their ratio.

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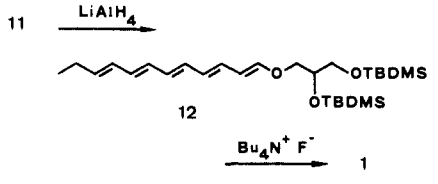
a low-temperature (−20 °C) chromatography on florisil (petroleum ether–ethyl acetate 9:1 and 2:1).

Containing the hydroxy and the tetrahydropyranyloxy function destined to serve as leaving groups properly positioned, **11** was converted by lithium aluminum hydride (5 molar equiv, room temperature, 2.5 h, argon atmosphere[11]) in dry tetrahydrofuran to the pale yellow liquid [(2,3-bis[(*tert*-butyldimethylsilyl)oxy]-propyl)oxy]dodeca-1,3,5,7,9-pentaene (**12**) in quantitative crude yield.[12]

As chromatography of the sensitive crude reaction product (**11** → **12**) was fairly inefficient, even at low temperature, it was conveniently used without purification in the final reaction step. With a technique previously employed[4,8] the protecting groups of **12** were removed by tetrabutylammonium fluoride (2.2 molar equiv, room temperature, 1.5 h, argon atmosphere[11]) in tetrahydrofuran–ether. From the resulting crude reaction product the hardly soluble,[13] analytically and isomerically pure *all-trans*-3-(dodeca-1,3,5,7,9-pentaenyloxy)propane-1,2-diol (**1**) crystallized



from hot butyl acetate as a pale yellow solid in 47% yield (based on **11**) and thus was easily separated from minor amounts of better soluble isomers and impurities.

With exclusion of air crystalline **1** was found to be stable at room temperature over a months period.[14] The following physical data of **1** are typical: mp 194–196 °C (sealed tube, argon atmosphere);[15] R_f 0.33 (ethyl acetate);[16] Mass spectrum, m/z 250 (M^+); UV (methylene chloride) λ_{max} 323 (ϵ 48 000), 338 (ϵ 74 000), 357 (ϵ 67 000) nm; IR (KBr) 3417, 3012, 2965, 2934, 2879, 1643, 1186, 1115, 1049, 1002 cm^{-1}; 500-MHz ^{1}H NMR (dimethyl sulfoxide-d_6) δ 6.77 (d, J = 12.5 Hz, 1 H, =CHO), 6.05–6.26 (m, 7 H, =CH), 5.73 (dt, $J_{10,11}$ = 7, $J_{9,10}$ = 15 Hz, 1 H, =C*H*CH$_2$CH$_3$), 5.63 (dd, $J_{1,2}$ = 12.5, $J_{2,3}$ = 11 Hz, 1 H, C*H*=CHO), 4.91 (d, J = 5 Hz, 1 H, CHO*H*), 4.65 (t, J = 5.5 Hz, 1 H, CH$_2$O*H*), 3.78–3.84 (m, 1 H, *H*CHOC), 3.62–3.69 (m, 2 H, HC*H*OC, C*H*OH),[17] 3.30–3.40 (m, 2 H, CH_2OH), 2.08 (dq, $J_{11,12}$ = 7.5, $J_{10,11}$ = 7 Hz, 2 H, CH_2CH$_3$), 0.96 (t, J = 7.5 Hz, 3 H, CH$_3$).

Acknowledgment. We take pleasure in acknowledging the generous support received from the German Research Society and the Funds of the Chemical Industry. Especially we would like to thank Professor Johann Sonnenbichler (Max Planck Institute of Biochemistry, Munich) for recording and discussion of the 500-MHz ^{1}H NMR spectrum.

Note Added in Proof. In the Ames bacterial assay **1** was found to be a very potent direct mutagen.[18]

(11) All transformations with polyene derivatives were carried out with strict exclusion of air. Before workup a trace of the radical inhibitor 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide was added to the reaction solution.

(12) A purity of approximately 75% was determined by ^{1}H NMR spectroscopy. In agreement with earlier investigations of the stereochemistry of the Whiting reaction (Demoule, E.; Enggist, P. *Helv. Chim. Acta* **1974**, *57*, 2087–2091), the remaining material is believed to contain the Δ3 and Δ5 cis isomers of **12**. This assignment is supported by additional doublets (J = 12 Hz) near the major doublet at 6.51 ppm in the NMR spectrum in $CDCl_3$ of the crude reaction product (**11** → **12**).

(13) *all-trans*-Polyenes are known to be much less soluble than their cis isomers: Bohlmann, F.; Mannhardt, H. *Chem. Ber.* **1956**, *89*, 1307–1315.

(14) Upon contact with air crystalline **1** deteriorates completely within 30 min at room temperature.

(15) Interestingly **1** retains its UV spectrum after melting and resolidification!

(16) Merck silica gel plate 60 F 254.

(17) The complexity of the glyceryl CH and CH$_2$ resonance signals suggests a hindered rotation of this part of the molecule.

(18) Göggelmann, W.; Maier, F. K.; Pfaendler, H. R. *Mutation Res.*, in press.

Molecular Hydrogen Complexes of the Transition Metals. 2. Evidence for a New Complex, Mo(CO)(dppe)$_2$(H$_2$), and for Solution Equilibrium between Dihydrogen and Dihydride Forms, M–η^2-H$_2$ ⇄ H–M–H, in W(CO)$_3$(PR$_3$)$_2$(H$_2$)

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Coordination of molecular hydrogen to transition metals is now firmly established, initially in the stable, structurally characterized complexes M(CO)$_3$(PR$_3$)$_2$(η^2-H$_2$)[1] (M = Mo, W; R = Cy, *i*-Pr), then in low-temperature stable Cr(CO)$_5$(H$_2$),[2] and recently in [IrH(H$_2$)(PPh$_3$)$_2$(C$_{13}$H$_8$N)]SbF$_6$,[3] [IrH$_2$(H$_2$)$_2$L$_2$]$^+$,[3] and [FeH(H$_2$)(dppe)$_2$]BF$_4$.[4] In order to better define the steric and electronic requirements for H$_2$ to bind in molecular fashion rather than being cleaved to hydride ligands, we report a new stable H$_2$ complex, Mo(CO)(dppe)$_2$(H$_2$) (dppe = diphenylphosphinoethane) (**1**). Also, NMR evidence is presented for a dynamic equilibrium between the H$_2$ complex W(CO)$_3$(P-*i*-Pr$_3$)$_2$(η^2-H$_2$), and an apparent *dihydride* complex, WH$_2$(CO)$_3$(P-*i*-Pr$_3$)$_2$, derived by oxidative addition of the H$_2$ ligand.

The formally 16-electron complex, Mo(CO)(dppe)$_2$, contains a weak, agostic interaction of a phenyl hydrogen with the metal and adds a sixth ligand such as N$_2$.[5] These features are similar to those of M(CO)$_3$(PR$_3$)$_2$,[6] the precursors to the first H$_2$ complexes, and suggest that Mo(CO)(dppe)$_2$ is likely to bind H$_2$ also. Addition of H$_2$ (1 atm) to deep brown Mo(CO)(dppe)$_2$ in benzene or toluene gives an orange solution from which well-formed solvated orange prisms of **1** slowly crystallize.[7] Solutions of **1** reversibly lose H$_2$ in a manner similar to M(CO)$_3$(PR$_3$)$_2$(H$_2$). **1** crystallized in two forms depending on solvent, and both have been examined by single-crystal X-ray methods.[8] Both structures show normal octahedral geometry for the complex with CO trans to the presumed η^2-H$_2$ ligand (Figure 1); i.e., the agostic hydrogen interaction present in the structure of Mo(CO)(dppe)$_2$ is no longer evident. The shortest distance between Mo and phenyl hydrogen (calculated on the basis of idealized hydrogen positions) in **1** is 3.4 Å compared to 2.98 Å for the parent Mo species. In both forms, the CO ligand is disordered across a crystallographic 2-fold axis and obscures the presumed H$_2$ ligand. Although the H$_2$ atom positions were not located, ^{1}H NMR (toluene-d_8, 25 °C, 300

(1) Part I of this series: Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.

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(6) (a) Kubas, G. J. *J. Chem. Soc., Chem. Commun.* **1980**, *61*. (b) Part 3 of this series: Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.*, in press.

(7) ν(CO) 1815 cm^{-1} (Nujol) for **1**·3C$_6$H$_6$. We find ν(CO) for Mo(CO)(dppe)$_2$ at 1723 cm^{-1} rather than at 1807 cm^{-1} as previously reported.[5a]

(8) (a) X-ray data for **1**·3C$_6$H$_6$: Space group: $P22_12_1$; cell constants: a = 12.114 (8) Å, b = 14.214 (5) Å, c = 17.491 (6) Å determined from 25 high-order reflections; Z = 4, D_x = 1.28 g/cm^3; crystal size 0.25 × 0.25 × 0.30 mm. Refinement included anisotropic temperature factors on all atoms heavier than hydrogen and converged to an unweighted R value of 0.070. No attempt was made to locate hydrogen atoms. Further details of data collection and the structural determination are presented as supplementary data. (b) X-ray data (−125 °C) for **1**·2C$_7$H$_8$: space group $P2/c$(*Pc*); cell constants, a = 12.125 (6) Å, b = 12.154 (8) Å, c = 19.133 (7) Å, β = 96.30 (3)°. *Xtl* size, 0.08 × 0.28 × 0.36 mm, Z = 2, D_x = 1.31 g/cm^3. Least squares refinements including anisotropic thermal parameters for all atoms heavier than carbon converged to an unweighted R value of 0.075.

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