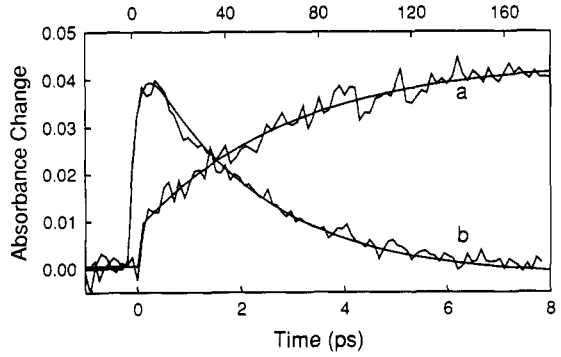

Figure 3. (a) Rise of the carotenoid radical cation species in **1** after excitation measured as an absorbance change centered at 960 nm (0.1-ps increments, lower axis). Regression analysis yields a time constant of 2.9 ps. (b) Rise and decay of the carotenoid radical cation signal (2-ps increments, upper axis). The decay time constant is 51 ps.

quenching. The electronics interaction required for electron transfer is provided by the amide linkage.[6] The necessary driving force is furnished by the high electron affinity of the fluorinated porphyrin. Cyclic voltammetric measurements locate the CS-state energy ca. 420 meV below that of the porphyrin excited singlet state (Figure 1). The absorption spectrum of **1** is essentially a linear combination of those of models **2** (5-(4-carbomethoxyphenyl)-10,15,20-tris(pentafluorophenyl)porphyrin) and **3** (7-apo-7'-(4-benzamidophenyl)-β-carotene), indicating that interchromophore interaction is weak. ^{1}H-NMR conformational studies[17] show that the carotenoid extends out, away from the porphyrin.

The fluorescence of **1** derives from the porphyrin component and is indistinguishable from that of **2** except in quantum yield. The fluorescence excitation spectrum demonstrates that excitation of the carotenoid in **1** results in 17% efficient singlet energy transfer to the porphyrin. From fluorescence decay measurements of **1** and **2**, the rate constants k_1 for quenching of the porphyrin first excited singlet state were found to be 1.3×10^7, 2.1×10^9, and 1.8×10^{10} s^{-1} in *n*-hexane, toluene, and butyronitrile, respectively (the fluorescence lifetimes of **2** were 8.3, 9.7, and 11.0 ns in these solvents). Because CS-state energy decreases with solvent dielectric constant and theory[18] predicts a corresponding electron-transfer rate increase,[19] these results are indicative of electron transfer. In low dielectric solvents the porphyrin triplet yield is significant and rapid triplet energy transfer to populate the carotenoid triplet is observed.

Transient absorption spectra of **1**, **2**, and **3** in butyronitrile taken after laser excitation are presented in Figure 2. All three compounds show the expected excited-singlet-state features, including prominent porphyrin stimulated emission at ca. 710 nm for **1** and **2**. The spectrum of dyad **1** is dominated by a transient absorption at 975 nm. This band rises with a time constant of 2.9 ps (Figure 3a), decays with a lifetime of 51 ps (Figure 3b), and is characteristic of the carotenoid radical cation ($\lambda_{max} \sim 960$ nm in dichloromethane, ~1025 nm in benzene, $\epsilon \sim 2 \times 10^5$ M^{-1} cm^{-1}).[20]

The direct observation of $C^{\bullet+}$–$P^{\bullet-}$ by the characteristic absorption of the carotenoid radical cation confirms electron-transfer quenching in **1**. The kinetic behavior of the $C^{\bullet+}$–$P^{\bullet-}$ transient appears unusual in that its decay time of 51 ps correlates with the 54-ps lifetime of the porphyrin singlet precursor while its rise time is much faster (ca. 3 ps). However, this behavior is expected if $k_3 \ll k_1$ and $k_2 \gg k_1$ (Figure 1). Moreover, there is a special signature for $k_2 > k_1$. Although the yield of $C^{\bullet+}$–$P^{\bullet-}$ is essentially 1 (quenching is >99%), the maximum concentration of the CS species is reduced from that of the initial C–^{1}P by k_1/k_2. We calculate from ϵ of $C^{\bullet+}$–$P^{\bullet-}$ and the fraction of C–P excited to C–^{1}P that the observed absorbance change is indeed reduced by ca. 20-fold from that expected for $k_1 \gg k_2$. Therefore, the quenching of C–^{1}P is assigned to electron transfer yielding $C^{\bullet+}$–$P^{\bullet-}$ with a formation time of just over 50 ps ($k_1 \sim 1.8 \times 10^{10}$ s^{-1}) and a lifetime of ca. 3 ps ($k_2 \sim 3.3 \times 10^{11}$ s^{-1}).

The transient species characteristic of energy-transfer quenching in **1** were not observed. Moreover, since energy transfer in these systems is not expected to be strongly solvent dependent, the negligible quenching observed in *n*-hexane sets an upper limit for the energy-transfer process. In other types of carotenoid interactions with cyclic tetrapyrroles energy transfer or other quenching mechanisms could occur.[13-16]

In conclusion, the observation of porphyrin fluorescence quenching by electron transfer from a carotenoid provides a mechanism for similar energy-dissipating electron-transfer quenching in vivo[5] and warns that because of the kinetics it could be very difficult to detect the transient species in pigment-bearing proteins. A rapid charge recombination process would be advantageous because it would preclude deleterious reactions of the radical ions in the photosynthetic membranes. Through energy dissipation, carotenoids could play a role in controlling photosynthetic energy flow.

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Selective Reduction of Steroid 3- and 17-Ketones Using $LiAlH_4$ Activated Template Polymers

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Extensive work, particularly by Wulff and his associates, has shown that molecular cavities with regularly spaced functional groups may be created with the molecular imprinting technique.[1] It has also been shown by Mosbach and his co-workers that shape selective cavities may be prepared by a similar technique.[2] Both techniques have been used for chromatographic separation of enantiomers and other types of molecular recognition.[3] For some

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Table I. Reduction of Steroid Ketones by Template Polymers in Tetrahydrofuran

entry	keto steroid	polymer[a]	swelling (%)	3β-OH (%)	3α-OH (%)	17β-OH (%)	17α-OH (%)	conv[f] (%)
1	**1**	**4c**	120[b]			70	30	35
2	**1**	**4c**	200[c]	15		80	5	70
3	**2**	**4c**	120[b]	60	40			7
4	**2**	**5c**	125[b]	28	72			40
5	**2**	**5c**	200[c]	74	26			80
6	**2**	**5c**	gel[d]	85	15			100
7	**1**	**5c**	125[b]	25	70	5		40
8	**1**	no template[e]	150[c]	89	11			42
9	**2**	no template[e]	150[c]	90	10			78

[a] In all entries, 0.2 mmol/g polymer of **1** or **2** was used, except for entry 8 where 0.4 mmol/g polymer was used. The ratio of obtained isomers was determined by NMR. All polymers were prepared with 5 mol % of **4c** or **5c**/g polymer. [b] No solvent in polymer preparation. [c] Toluene 10 mL was used as solvent in polymer preparation. [d] Polymer prepared as bulk polymer, cf. refs 1e, 3e, and 3k. [e] Methyl acrylate instead of steroid **4c** or **5c** was used as comonomer to obtain a corresponding functional group. [f] Determined by NMR, by comparing the 18-Me or 19-Me singlet of product and starting material.

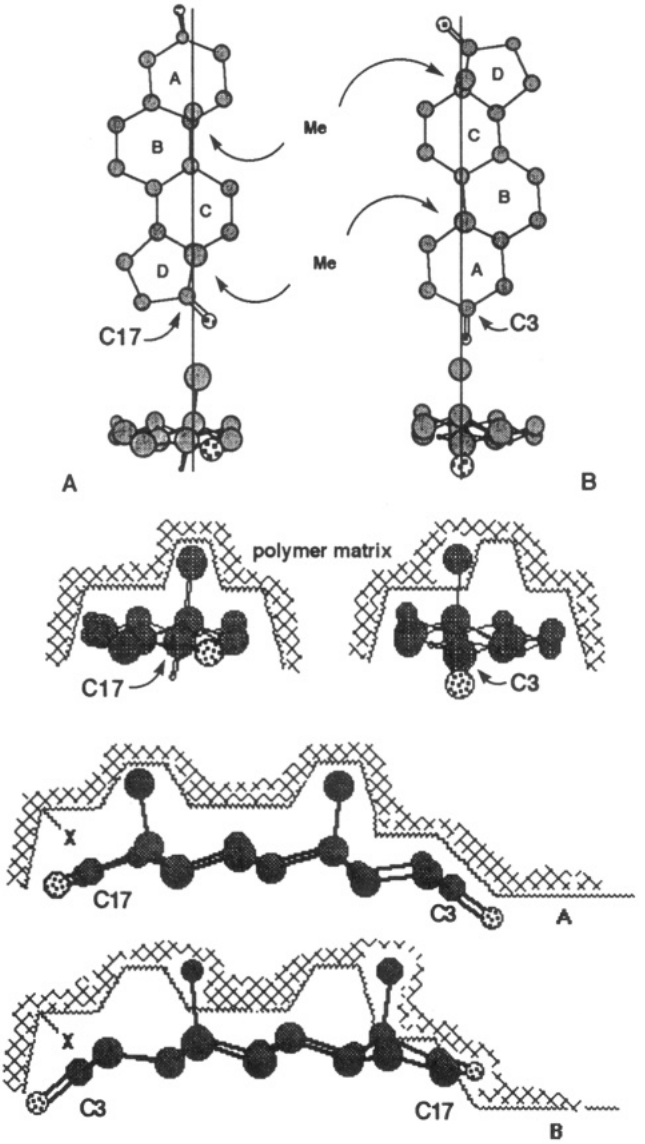
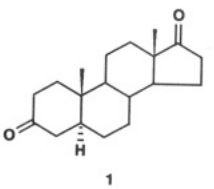


Figure 1. (Top) Match (A) and mismatch (B) of **1** in a cavity which origins from **4c**. (Bottom) Side view of **1** showing match (A) and mismatch (B) in a cavity (from **4c**). The reagent X reacts from the desired side of the substrate molecule **1** when this fits properly into the cavity.

time we have been interested in selective functionalization of steroids. Although synthetic applications of the molecular imprinting technique have proven limited and only moderately successful, the method seemed attractive for large hydrophobic molecules such as steroids, which might be expected to interact strongly with the polymer. As a model reaction, it was decided to study whether regio- and stereochemistry of hydride reduction of the steroidal ketones **1** and **2** could be controlled by shape selective molecular cavities. Figure 1 illustrates the match and



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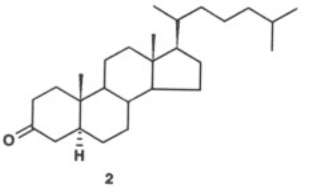


2

mismatch of substrate **1** in a cavity which originates from the imprint molecule **4c**. The reagent, which is located in a specific position of the cavity, reacts regio- and stereospecifically with a matching molecule, Figure 1a. When matching, the reagent can react from the β-side of the substrate to give the desired α-isomer.

The results, which are presented in Table I, show that already a somewhat unsophisticated approach gives remarkably good results.

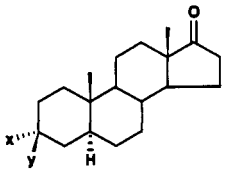
Two different imprint molecules were used, **4c** and **5c**.[4] The purpose with **4c** was to create molecular cavities with the shape of **1** and containing a hydride function spatially close to the 17-carbonyl. This was done by copolymerizing the monomer **4c** with technical grade divinylbenzene.[5] After extraction with hot water and THF/$CHCl_3$, the imprint molecule was removed by treatment with $LiAlH_4$/THF.[6] By repeating this procedure several times, 50–60% of the imprint molecules could be removed from the polymers of low swellability (120%) and 70–80% from polymers with high swellability (200%).[7] The rest of the imprint molecules are trapped within the polymer framework and inaccessible to chemical reactions. The attachment of hydride to the now available hydroxy groups in the empty molecular cavities was then accomplished by treatment with $LiAlH_4$ in THF, followed by removal of unreacted $LiAlH_4$. The beads were then suspended in THF at room temperature, and an excess of the diketone **1** was added. Analysis of the reduced product showed complete preference for reduction at the 17-position (entry 1, Table I). This

(4) Prepared by adding 1.75 equiv of acryloyl chloride to a stirred solution of 1 equiv of the corresponding sterol and 2.2 equiv of Et_3N in $CHCl_3$ at 25 °C. When the sterol was consumed, normally after 5–15 min (TLC), ice/water was added and the mixture was stirred for 30 min. The inorganic phase was extracted with $CHCl_3$, and the combined organic phases were washed twice with water, dried ($MgSO_4$), and evaporated to give more than 90% of pure (NMR) product as a white powder.

(5) Technical grade DVB, obtained from Aldrich, is a mixture of 55% divinylbenzene and 45% ethylstyrene. Azaisobutyronitrile (AIBN) was used as initiator in a suspension polymerization process. The polymer obtained was macroporous with beads of diameter 0.05–0.1 mm; cf. Hodge, P.; Sherrington, D. C., Eds. *Polymer-supported Reactions in Organic Synthesis*; John Wiley & Sons Ltd.: New York, 1980; pp 469–475.

(6) When NaOH/MeOH or MeONa/MeOH was used instead of $LiAlH_4$, the ester group of the template was unaffected.

(7) When toluene or $CHCl_3$ was used as cosolvent in the polymerization process, swelling up to 200% of the prepared polymer was observed.



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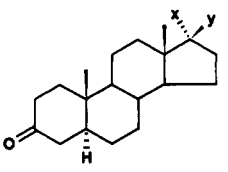


4

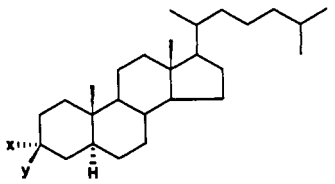
3a (3 α): x = OH, y = H

3b (3 β): x = H, y = OH

4a (17 α): x = OH, y = H

4b (17 β): x = H, y = OH

4c: x = H, y = CH_2=CH-CO_2-



5

5a (3 α): x = OH, y = H

5b (3 β): x = H, y = OH

5c: x = H, y = CH_2=CH-CO_2-

is in complete contrast to reduction in solution, which gives ca. 99% preference for reduction at the 3-position.[8] In contrast, when polymer beads imprinted with **5c** were used, essentially complete reduction of the 3-position was obtained, (entry 7, Table I). These latter beads were also used with their "true" substrate cholestan-3-one, **2**. The cholestanol obtained in this way was predominantly the less readily available 3α-OH isomer **5a** (3α-OH/3β-OH = 72/28, entry 4, Table I). Again this is in sharp contrast to the result from hydride reduction in homogeneous solution, which gives a ratio 3α-OH/3β-OH = 10/90.

In order to ascertain that nonspecific surface effects from the polymer are not the origin of these results, a hydroxylated polymer without molecular imprints was prepared by copolymerizing methyl acrylate and divinylbenzene. This polymer was activated in the same way as the imprinted polymers and then reacted with **1** and **2**. The results (entries 8 and 9, Table I) were essentially the same as those for reaction in homogeneous solution.

It is interesting to note that some stereocontrol is evident also in the reduction of the 17-keto group of **1** because the 17α-OH/17β-OH ratio is higher in the reduction with template polymer (30/70) than without (4/96). The result is, however, much less spectacular than that for the reduction of **2**, probably due to the interference from the 18-methyl group.

The polymer quality is important to the results, and early experiments with very swellable polymers, which are often advantageous because of fairly free diffusion of solvents and reactants, were less successful. Examples are entry 2, Table I, which shows about 15% reduction at the 3-position of **1**, and entry 5, which gave only 26% of the 3α-OH isomer **5a**. Also, bulk polymers, which have been frequently used in the earlier studies, are less satisfactory, and the result from one experiment with compound **2** (entry 6, Table I) shows only marginally better selectivity for the 3α-OH isomer than reduction in homogeneous solution. Although the studies described here are still at an early stage, they appear promising and very clearly show that selective functionalization is possible on the basis of molecular shape and stereochemical information transferred from the imprint molecules to the polymer matrix together with the attractive interactions between the partial charges present on the ketones and the reactive center.

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Zirconacyclobutanes from Thermal Rearrangement of Permethylzirconocene Bis(allyl) and Related Complexes. An Unprecedented Synthesis of β-Substituted Metallacyclobutanes

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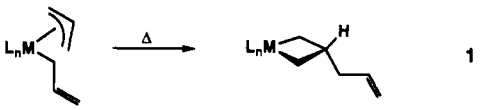
The investigation of metallacyclobutane complexes has been a compelling focus in organotransition metal chemistry for two decades.[2] Metallacyclobutanes are known throughout the transition series and have been prepared by numerous methods,[2] including cyclopropane oxidative addition,[3] cyclometalation,[4] coupling of alkenes with metal alkylidenes or alkylidene precursors,[2a] addition of 1,3-dimagnesiopropanes and related dianions,[5] the rearrangement of a σ-cyclopropyl hydride complex,[6] and nucleophilic addition to the central carbon of η^3-allyl complexes.[7] Here we report an unprecedented entry into the metallacyclobutane structural class via an unusual thermal rearrangement of zirconium bis(allyl) and related complexes (eq 1).



1

Permethylzirconocene bis(allyl) complex **2** was obtained from the addition of allylmagnesium chloride to dichloride **1**[8] (Scheme

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