15% NMR yield of another $ZrCp_2$ derivative, which was indistinguishable from a species obtained by treating 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyl-1-zirconacyclopentadiene with PhLi. This contamination hampered attempts to obtain **7a** as a pure compound. Furthermore, its ^1H and ^{13}C NMR spectra were relatively uninformative.[12,13] Fourthly, treatment of $Cp_2Zr(C{\equiv}CTol\text{-}p)_2$ with 2 equiv of PhLi in the presence of PhC≡CPh produced, after protonolysis with 3 N HCl, a 62% GLC yield of (*Z*)-PhCH=CHTol-*p* without producing (*Z*)-stilbene (<0.2% if any). Tolan was recovered to the extent of 86%. The results clearly rule out dissociative mechanisms, such as that proceeding via reductive elimination to give free PhC≡CTol-*p* followed by complexation, and point to a nondissociative mechanism, such as 1,2-migration.

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Supplementary Material Available: IR and ^1H and ^{13}C NMR data for product enynes and alkenes (3 pages). Ordering information is given on any current masthead page.

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(11) Under comparable conditions, **8** reacted readily with alkynes, acetone, and benzaldehyde to give the expected five-membered zirconacycles, which were protonolyzed to give the corresponding dienes and allylic alcohols.[7,8,10]

(12) Attempts to obtain crystalline samples of **7a** for X-ray analysis have so far failed.

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Regioselective and Enantioselective Substitution of Allylic Sulfoximines with Organocopper Reagents. A Versatile Approach to Optically Active Isocarbacyclins

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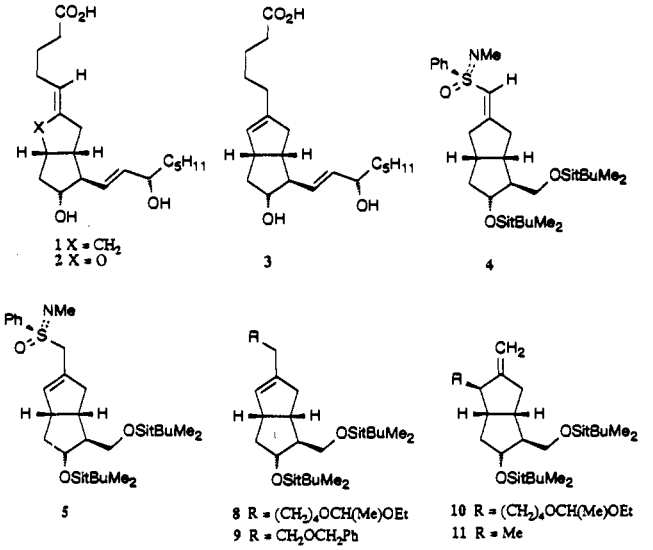
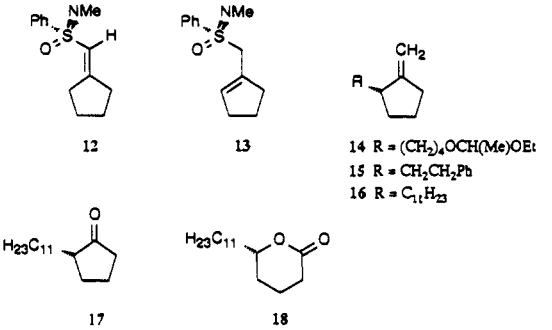
Carbacyclin (**1**)[1a] and isocarbacyclin (**3**),[1b] stable analogues of the unstable hemostase regulator prostacyclin (**2**),[1c] are the prototypes of a new generation of antithrombotic drugs. Modification mainly of their side chains has led to the attainment of highly potent derivatives[2] which show great promise for the treatment of obliterative peripheral artery disease.[3] Recently we described a stereoselective synthesis of carbacyclins via Ni-catalyzed cross-coupling reactions of the enantiomerically pure alkenyl sulfoximine **4**[4] with organozinc compounds.[5] We reasoned that **4** would likewise allow for a versatile synthesis of isocarbacyclins[6] provided it can be isomerized to the allylic sulfoximine **5** and this in turn made to allylate organocopper reagents such as, e.g., $LiCu[(CH_2)_4OCH(Me)OEt]_2$ (**6a**)[7a] or $Cu(CH_2)_4OCH(Me)OEt$ (**6b**),[7a] and $ClMgCu(CH_2OCH_2Ph)_2$ (**7a**) or $CuCH_2OCH_2Ph$ (**7b**),[7b] to give the precursors **8**[6b] and **9**,[6b,2e] respectively (Scheme I),[8] which were synthesized previously (with other protecting groups) by less direct routes.

Allylic sulfones gained synthetic importance since they allow the allylation of carbon electrophiles as well as nucleophiles via alkylation of their mono-[9] and dicarbanion[10,11f] salts and transition metal mediated substitution with organometallics or carbanion

Scheme I



Scheme II



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salts,[10c,11] respectively. Their principle limitation, however, stems from the achirality of the sulfonyl group which itself[13] does not impart asymmetric induction to either step. Allylic sulfoximines, on the other hand, which were up to now almost completely neglected,[12] are chiral analogues of allylic sulfones, and they could be used to circumvent this obstacle.[14]

Here we report on the regio- and enantioselective allylation of organocopper reagents with optically active allylic sulfoximines as exemplified in a new, versatile approach to isocarbacyclins (Scheme I) and a synthesis of exocyclic alkenes (Scheme II), respectively.

Regioselective isomerization of the alkenyl sulfoximine **4** was accomplished by treatment with LiOMe (3 equiv, THF/toluene/*n*-hexane, 5:4:1, 0 °C, 6 h) and subsequent aqueous workup to give the allylic sulfoximine **5**[15] in 97% yield. It contained, according to HPLC analysis, not more than 0.5% of the easily separable endocyclic isomer. The position of the CC double bond in **5** was assigned by ^{1}H NMR decoupling experiments.

We were gratified to find that reaction of **5** with 3 equiv of the homocuprate **6a**[7a,16a] (ether, Me_2S; −35 °C) proceeded highly selectively and delivered a 96% yield of the endocyclic alkene **8** with ≤0.5% of the γ-substitution product **10** (Scheme I).

Regioselective substitution in the γ-position,[17a] on the other hand, can be achieved by treatment of 4 equiv of the organocopper reagent **6b**[7a,16b] (THF, Me_2S; −30 °C, 3 h), to which at −78 °C an equimolar amount of BF_3·OEt_2 was added[17b] with a solution of 1 equiv of the allylic sulfoximine **5** in THF. The exocyclic alkene **10** could be isolated in 86% yield as a single diastereomer together with 2% of **8**. Without BF_3·OEt_2 no substitution of **5** with **6b** took place. Assignment of the configuration of **10** as depicted was made in analogy to that of the alkene **11**, which was synthesized in a similar manner in 68% yield as a single diastereomer from **5** and CuMe/BF_3·OEt_2 and whose configuration could be determined by ^{1}H NOE experiments.

Surprisingly, when the allylic sulfoximine **5** (THF, −78 °C) was combined with 4 equiv of the α-alkoxy organocopper reagent **7b**,[7b,16c] and then 1 equiv of BF_3·OEt_2 (THF; −78 °C) was added, substitution occurred not in the γ- but in the α-position and gave, with ≥98% regioselectivity in 89% yield, the endocyclic alkene **9**. An excess of BF_3·OEt_2 has to be avoided since an unwanted but interesting side product, the homologue of **9** with a (benzyloxy)propyl instead of a (benzyloxy)ethyl group, is formed in up to 20% yield (by using 4 equiv of BF_3·OEt_2). Substitution of **5** with the homocuprate **7a** is very slow but occurs selectively also in the α-position to yield **9**.

Conversion of the bicyclic alkenes **8** and **9** into the corresponding isocarbacyclin precursors having the complete upper side chains was carried out as described earlier by us[6b] and by others[2d,e] for closely related cases.

Next, asymmetric induction exerted by the sulfoximine group in γ-substitution was studied in the case of the allylic sulfoximine **13** with different organocopper reagents (Scheme II). Enantiomerically pure **13** was synthesized in 77% overall yield by isomerization (LiOMe, toluene/THF, 40 °C) of the alkenyl sulfoximine **12**, which was obtained from cyclopentanone and (*S*)-$LiCH_2S(O)(NMe)Ph$[18] as described for **4**.[4] We were pleased to note that the allylic sulfoximines **5** and **13** suffer at the S atom no epimerization and racemization, respectively, by heating, e.g., to reflux in toluene solution, and are stable.

Addition of the sulfoximine **13** to a THF/Me_2S/ether solution of 4 equiv of **6b** and 4 equiv of BF_3·OEt_2 at −100 °C and warming of the resulting mixture to −78 °C within 4 h gave, with ≥98% regioselectivity, the γ-substitution product **14** in 90% yield after workup. According to GC analysis of the trifluoroacetate of the parent alcohol on an octakis(2,3-di-O-pentyl-6-O-methyl)-γ-cyclodextrin capillary column,[19] **14** had an ee value of 71%. Similar treatment of **13** with $CuCH_2CH_2Ph$ in the presence of BF_3·OEt_2 gave in 87% yield a mixture of the alkene **15** and its endocyclic isomer in a ratio of 9:1 with an ee value of 78% for **15**.[20]

As a last example we synthesized, by reaction of **13** with Cu-$(CH_2)_{10}CH_3$ (4 equiv, THF, −100 °C → −78 °C, 12 h) in the presence of 4 equiv of BF_3·OEt_2, the alkene **16**[21a] with ≥99.5% regioselectivity in 95% yield. Ozonolysis of **16** (MeOH, CH_2Cl_2, −45 °C; Me_2S) cleanly afforded in 93% yield the ketone **17**,[22d,21b] which according to its chiroptical data had the *S* configuration and an ee value of 67%. Thus **16** has the *S* configuration. On the basis of this finding and by assuming the same sense of asymmetric induction for all three substitution reactions of **13**, the configuration of **14** and **15** was tentatively assigned as *R*. Baeyer–Villiger oxidation of **17** (*m*-ClC_6H_4COOOH, $CHCl_3$)[22d] gave in 86% yield hexadecanolide (**18**), whose chiroptical data indicated an ee value of 67% and the *S* configuration.[22]

Besides the alkenes **8**–**11**, and **14**–**16** in 90–95% yield, the sulfinamides (*R*)- and (*S*)-Me(H)NS(O)Ph,[12] respectively, were isolated whose chiroptical data and ^{1}H NMR spectra in the presence of Eu(tfc)$_3$ ($\Delta\Delta\delta$(NMe) = 0.67) indicated an ee value of ≥97%. Thus, substitution of **5** and **13** occurs with complete retention of configuration at the sulfur atom. We note that because of the known conversion of (*S*)-Me(H)NS(O)Ph into the sulfoximine (*S*)-$MeS(O)(NMe)Ph$[12,23] chirality is retained.

The above enantioselective substitutions of **13** with organocopper reagents are to the best of our knowledge the first examples for asymmetric induction by a chiral carbanion stabilizing nucleofuge in metal-assisted allylic substitutions.[24]

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Supplementary Material Available: Spectroscopic and analytical data for compounds **5** and **8-18** and experimental procedures for the preparation of compounds **8** and **16** (10 pages). Ordering information is given on any current masthead page.

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Example of Diffusion-Limited Behavior in the Reaction of a Geminate Radical Pair in Micelles[1]

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Triplet-derived. carbon-centered radical pairs in micelles undergo geminate processes in a few hundred nanoseconds.[4-8] In this time, the two radicals in a given micelle undergo several encounters. However, for reaction to take place between them, the radical pair must first cross from the triplet to the singlet state. That crossing can be slowed down further by applying a magnetic field that induces Zeeman splitting of the triplet sublevels. Earlier work has indicated that hyperfine couplings play an important role in controlling the decay of these radical pairs.[9]

The rate constant, k_{reacn}, for radical-pair reaction within a micelle is determined by diffusional processes and spin interactions. It can be expressed in terms of the rate constant for radical-radical encounters, k_e, and the probability, f, that a given encounter will have singlet character, eq 1.[10]

$$k_{reacn} = k_e f \qquad (1)$$

For a triplet-derived radical pair, the maximum value of f will be 0.25 if the radicals can separate over large distances so that the electron-exchange interaction, J, vanishes. However, this situation does not often arise in micelles where separation is limited by the phase boundary. Here, f will roughly depend upon J^{-1} and hence on r, the average separation between the radicals.[11] By contrast, k_e is proportional to r^{-n} ($2 \le n \le 3$). The intramicellar encounter time ($1/k_e$) can be expected to be of a magnitude comparable to those observed for excimer formation and energy transfer in related (but larger) micelles; these values are in the 50-100-ns range.[12,13]

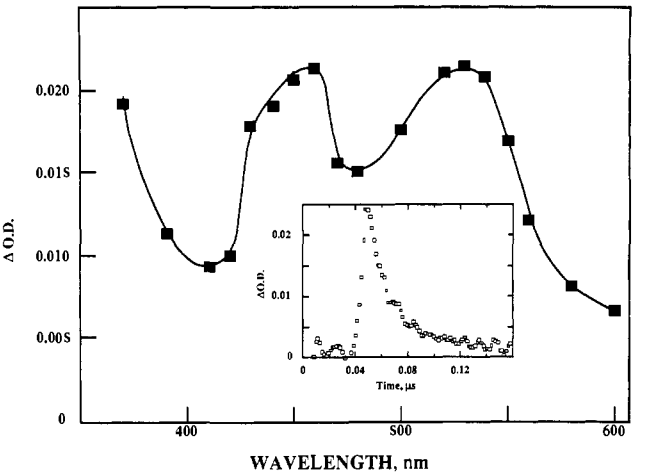

Figure 1. Transient absorption spectra following excitation of benzophenone (3 mM) in SDS micelles (0.2 M) in the presence of thiophenol (29 mM) ca. 6 ns after the laser pulse. The insert shows a decay trace recorded at 540 nm.

It has long been known that magnetic resonance properties such as differences in g values and/or hyperfine interactions control spin-state relaxation. To date, most of the experiments have focused upon the role of hyperfine interactions. We reasoned that in order to identify a system with very fast spin relaxation we should investigate radicals with broad or undetectable EPR lines. In this work, we have deliberately introduced a radical with a very anisotropic g tensor as partner in a triplet radical pair and show that this property can induce rapid loss of triplet character.

The system investigated involved the reaction of benzophenone triplet with thiophenol, reaction 2. Laser flash photolysis (337 or 308 nm) was used to monitor the triplet at 600 nm to avoid interference from $Ph_2C^{\bullet}OH$ (λ_{max} 540 nm) or $PhS^{\bullet}$ (λ_{max} 450 nm).[14] In benzene, $k_2 = (2.6 \pm 0.4) \times 10^8\ M^{-1}\ s^{-1}$, as determined from the effect of thiophenol on the rate of benzophenone triplet decay.

$$^3Ph_2CO^* + PhSH \rightarrow Ph_2C^{\bullet}OH + PhS^{\bullet} \qquad (2)$$

When benzophenone (0.003 M) was photolyzed in sodium dodecyl sulfate (SDS; 0.2 M) micelles, the ketone triplet decayed predominantly by hydrogen abstraction from the surfactant ($\tau \sim 300$ ns).[4] However, addition of thiophenol shortened the triplet lifetime (reaction 2) monitored at 600 nm, and at thiol concentrations $\ge$0.03 M (which leads to occupancies >7), it was below our detection limit (<5 ns). At this point, abstraction from the surfactant can be neglected. The transient spectrum corresponds to the thiyl (450 nm)[15] and ketyl (540 nm) radicals (Figure 1). The lifetimes for both transients were ca. 20 ns (see insert in Figure 1) and independent of further addition of thiol. There was no residual absorption following the decay, indicating that radical escape from the micelle was negligible and that decay took place

(1) Issued as NRCC-32322.
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