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Allylic Alkylation versus Michael Induced Ring Closure: Chelated Enolates as Versatile Nucleophiles

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Abstract: Allylic carbonates **8** bearing an electron-withdrawing ester functionality can act as substrates for palladium-catalyzed allylic alkylations or as Michael acceptors with the option to undergo subsequent ring closure. Chelated amino acid ester enolates **1′** are versatile nucleophiles for both reactions giving high yields and selectivites.

Domino reactions have become a very powerful synthetic tool in organic synthesis, not only because the production of waste and the consumption of solvents can be reduced, but also because several bonds can be formed in one sequence and without the isolation of intermediates.[1] Especially if cyclizations are involved in this sequence, very often ring closure proceeds in a highly stereoselective fashion. This makes the domino reactions highly attractive for natural product synthesis and related applications.[2] The Michael induced ring closing reactions (MIRC)[3] play a dominant role in this field of chemistry and many synthetic applications are described in the literature so far.[1,2] Toward the synthesis of natural and unnatural amino acids, e.g., the lithium enolates of O'Donnell's phenylimino glycin esters can be used,[4] as illustrated with several syntheses of cyclopropyl glycines.[5] An interesting sequence giving rise to cyclohexyl amino acid derivatives was reported by Moreno-Manas et al., based on a double Michael addition and subsequent Dieckman condensation.[6] But other nucleophiles such as the enolates of Schöllkopf's bislactim ethers,[7] sarcosinates,[8] or *N*,*N*-dibenzylglycinates[9] also can be used.

Transition metal-catalyzed reactions also play an important role in organic synthesis.[10] Palladium, which can be used for cyclizations, cross-coupling reactions, and allylic substitutions, holds a predominant position among these transition metals.[11] Especially the palladium-catalyzed allylic alkylation has developed into one of the standard reactions in organic synthesis, not the least because asymmetric variations of this reaction are possible.[12]

With respect to the reaction mechanism, palladium-catalyzed allylic alkylations proceed via π-allyl palladium complexes, and the configuration of the substitution products depends on the geometry of these π-allyl intermediates.[13] Thus, the oxidative addition of palladium(0) to (*E*)-allyl-acetates **A** and -carbonates leads to allyl complexes with syn/syn configuration,[14] which can react with nucleophiles at both allylic positions (a and b) to provide the corresponding (*E*)-substituted products **B** and **C** (Scheme 1). Anti/syn complexes are generated by the attack of palladium on (*Z*)-substrates **D**. Reactions with nucleophiles would provide (*E*)-substitution product **C** or (*Z*)-product **E** if $\pi-\sigma-\pi$ isomerization did not occur.[15] This isomerization causes a fast interconversion of the π-allyl complexes, normally preferring the syn/syn complex. Therefore, the major problems of palladium-catalyzed reactions are the selective conversions of (*Z*)-allyl substrates with retention of the olefin geometry[16,17] and the regioselectivitiy of the nucleophilic attack on substrates bearing two similar substituents (R and R′) at the allylic termini. Both problems can only be solved if one could run the reaction at temperatures where isomerization reactions do not yet take place,[18] and if the two different allylic positions in the anti/syn complex show different reactivity.

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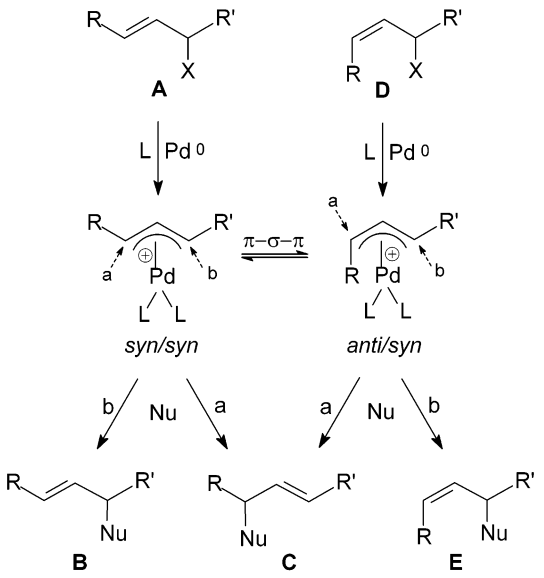
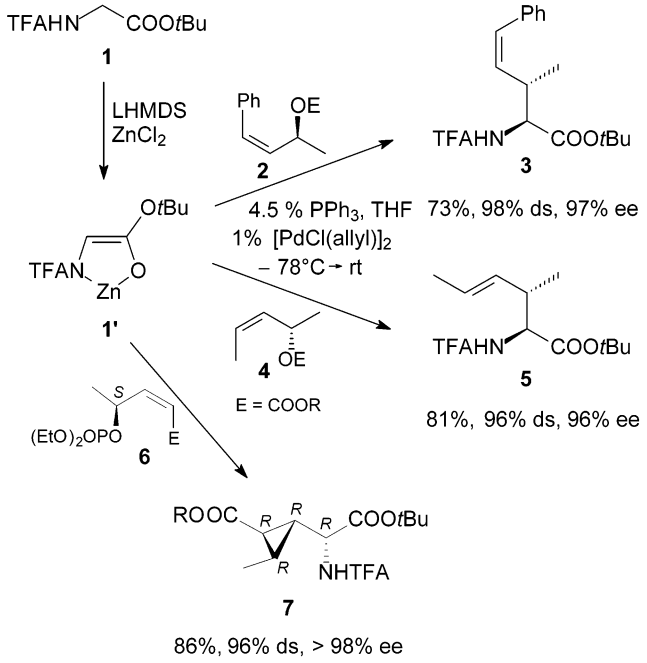
SCHEME 1. Formation and Reaction of π-Allyl Complexes

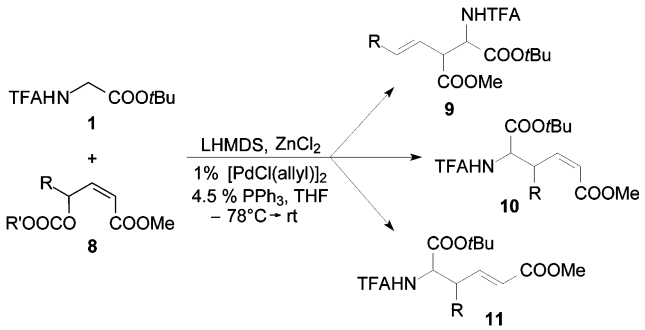


SCHEME 2. Reactions of Chelated Enolates 1′



Our group has been involved for several years in the synthesis of unnatural and nonproteinogenic amino acids, in which γ,δ-unsaturated amino acids play a major role. Chelated amino acid ester enolates, such as **1′** (Scheme 2), were found to give especially good results in various types of enolate reactions[19] including palladium-catalyzed allylic alkylations.[20] Since these reactions already proceed at −78 °C, chelated enolates are especially suited to fulfill the precondition mentioned above. When chelated enolate **1′**, obtained from the corresponding amino acid ester **1**, was treated with optically active allyl carbonate **2** the unsaturated amino acid **3** was obtained as a single regioisomer, with excellent diastereoselectivity and chirality transfer (Scheme 2). Obviously, the isomerization can be suppressed completely under the reaction conditions used, and the regioselectivity is controlled by the conjugation effect. On the other hand, if the optically pure dimethylated substrate **4** was used, the (*E*)-product was obtained exclusively. The nearly perfect chirality transfer also clearly indicates that no isomerization occurred here (which would result in racemic product via the symmetrical syn/syn complex), and that the anti position (attack a) is the more reactive one.[21] This higher reactivity of the anti position can also be used for regioselective allylations of substrates bearing different substituents.[22]

SCHEME 3. Allylic Alkylation of Glycine Enolates with Allylic Substrates 8



Very recently we also reported on a highly stereoselective synthesis of substituted cyclopropylglycines based on a Michael addition of **1** toward (*Z*)-configured acceptor **6**. Four stereogenic centers are formed simultaneously with perfect chirality transfer from the stereogenic center in **6**.[23]

Originally we wanted to use **6** as a substrate for palladium-catalyzed allylic alkylations, but obviously the MIRC reaction was faster than the allylic alkylation, which was quite surprising with respect to the mild conditions of the palladium-catalyzed allylation. With this background we investigated the reaction of (*Z*)-α,β-unsaturated esters **8**. We were interested to see which effect is stronger: (a) the higher reactivity of the anti position, which should provide the aspartate derivative **9**, (b) the conjugation effect of the carbonyl group, which should direct the nucleophilic attack to the "syn position", giving rise to a (*Z*)-configured substitution product **10**, or (c) the $\pi-\sigma-\pi$ isomerization, which might give rise to a (*E*)-product with a conjugated double bond **11**. Indeed, in the reaction of **8a** with **1′** in the presence of [PdCl(allyl)]$_2$ all three products were obtained, albeit in a very moderate yield of 38%. Obviously also with this substrate the higher reactivity of the anti position dominates the regiochemical outcome of the reaction, and **9** is obtained as the major product with excellent selectivity (97% ds).

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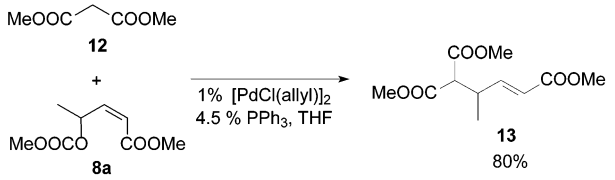
TABLE 1. Product Distribution of Allylations with Sustrates 8

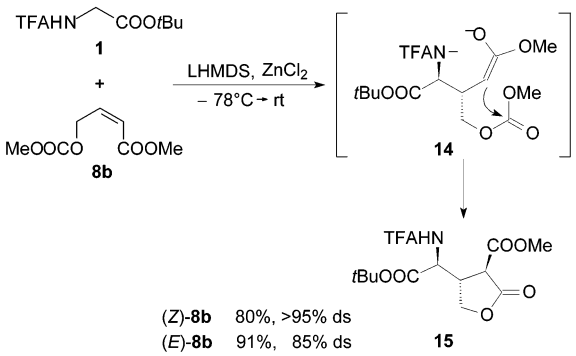
substrate	R	R′	yield [%]	product ratio **9**:**10**:**11**
8a	Me	Me	38	80:10:10
8b	H	Me		
8c	Me	*t*Bu	72	86:3:11

SCHEME 4. Allylic Alkylation of Malonates with Allylic Substrate 8a



But to some extend the conjugation effect of the carbonyl group cannot be neglected as illustrated with the formation of **10**. The thermodynamically more stable product **11** probably is formed after $\pi-\sigma-\pi$ isomerization.[24] But an overall ratio of only 10% isomerization product clearly indicates that the isomerization is mainly suppressed. To make sure that these effects discussed are responsible for the product distribution and that the mixture obtained is mainly kinetically and not thermodynamically controlled, we investigated the reaction of the same substrate with the "standard nucleophile" for allylic alkylations. With dimethylmalonate **12** at room temperature only the expected thermodynamical product **13** was obtained. In this reaction no additional base was required, and under these neutral conditions the yield was much better. The lower yield obtained with the chelated enolate **1′** was quite surprising, because in general these nucleophiles react under much milder conditions in comparison to malonates and therefore with better selectivity and (often) better yields. With respect to the complete consumption of the substrate, some side reactions must be responsible for this deficit. We assumed that deprotonation of the π-allyl complex by the base required for enolate formation might be the reason. The dienoic acid ester obtained could undergo polymerization resulting in a "loss" of product. Such eliminations were not observed previously in allylic alkylations of chelated enolates, but the ester functionality in the substrate should favor such an elimination. Therefore we also subjected substrate **8b**, which should form a monosubstituted π-allyl complex (R = H) unable to eliminate, to our reaction conditions. Surprisingly none of the products **9b**−**11b** was obtained but the malonate derivative **15**. Obviously with substrate **8b** Michael addition of the chelated enolate is much faster than the allylic alkylation and the enolate **14** formed as an intermediate undergoes rapid cyclization giving rise to **15**.[25] Three stereogenic centers were formed by this process in a highly diastereoselective fashion. The yield of **15** could be increased to 80% if the reaction was carried out under the same reaction conditions but in the absence of Pd^0. Our group

SCHEME 5. Michael Induced Ring Closure (MIRC) of Substrate 8b



has been investigating Michael additions of chelated enolates **1′** for quite some time, and we observed that Michael products are only obtained if intermediates such as **14** can undergo subsequent reactions such as in this case. Otherwise the Michael addition is a reversible process, with an equilibrium mainly on the side of the starting materials. This probably results from the greater stability of the chelated enolate **1′** (five-membered ring) in comparison to enolates such as **14**, which should form a seven-membered ring if chelation occurs. Therefore, if the cyclization can be suppressed in substrates **8**, one might expect a higher yield in the palladium-catalyzed allylic alkylation. And indeed, if the methyl carbonate **8a** was replaced by the *tert*-butyl carbonate **8c**, the yield could be increased to 72%. **9a** again was the major isomer, which was formed in a highly diastereoselective fashion (98% ds). The reaction was complete after only 2.5 h at −78 °C, which indicates that *tert*-butyl carbonates are more reactive than other alkyl carbonates. The excellent diastereoselectivities (97−98% ds) observed in the formation of **9a** are typical and in very good agreement with the selectivities obtained with other (*Z*)-configured substrates.

The relative configuration of allylation product was always found to be anti as determined by X-ray structure analyses and GC investigations.[26] Therefore we assume that the anti isomer is also formed preferentially in this reaction.

Such excellent diastereoselectivities are not only observed in allylic alkylations of (*Z*)-configured substrates such as **8**, but also in their corresponding Michael reactions. Unfortunately the diastereomeric ratio of **15** could not be determined by GC, but no second set of signals was observed by NMR (>95% ds). After cleavage of the *tert*-butyl ester of **15** crystals are obtained suitable for X-ray structure analysis, which confirmed the relative configuration shown. The 2,3-anti, 3,4-anti product was formed exclusively, what is in good agreement with previous observations. For comparison, the corresponding (*E*)-**4b** was also subjected to the Michael addition, and in this case a second diastereomer (2,3-syn, 3,4-anti) could be obtained in 15% (85% ds) yield.

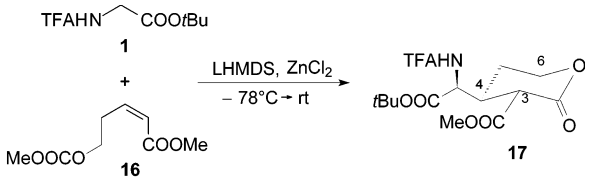
To prove the generality of this MIRC reaction, we also investigated the reaction of several other protected

(24) The configuration of the olefin geometry was determined via the ^{1}H NMR couplings ($J_{(E)}$ = 15.5 (**9**), 15.8 Hz (**11**), $J_{(Z)}$ = 11.4 Hz (**10**)) of the vinylic protons.

(25) The primary Michael adduct could be isolated and characterized if the reaction was quenched after 30 min at −78 °C. A 1:1 mixture of protonated enolate **14** and MIRC product **15** was obtained.

(26) See ref 21c. The corresponding syn-configured products for comparison can be obtained via chelate Claisen rerarrangement: Kazmaier, U. *Liebigs Ann.* **1997**, 285−295 and references therein.

SCHEME 6. Synthesis of Larger Rings via MIRC



glycine esters. Changing the ester had no influence on the selectivity (always >95% ds) but on the yield. While with the methyl ester the yield dropped to 35%, the corresponding benzyl ester gave excellent results (88%). Changing the *N*-protecting group had a stronger influence. The Z-group is suitable as well (63%, >95% ds) but with Tos and BOC, both yield and selectivity were worse (22−26%, 80% ds).

To see if the MIRC is also suitable for the synthesis of larger rings, we subjected a homologated carbonate **16** to our reaction conditions. Six-membered-ring product **17** was obtained in comparable yield as **15**, albeit the diastereoselectivity was a little lower (93% ds). The diastereomeric ratio was determined by NMR. In both diastereomers a NOE was observed between the H at C-4 and the axial one at C-6, which confirms the equatorial orientation of the amino acid substituent. We found two different couplings for 3-H/4-H. A coupling constant of $J = 8.8$ Hz for the major isomer can be explained by an equatorial orientation of the substituent, while the smaller value of $J = 7.1$ Hz for the minor isomer results from an axial/equatorial coupling of these hydrogens. In summary we have shown that chelated enolates react with excellent selectivities not only in palladium-catalyzed allylic alkylations but also in Michael additions. Best results in both cases are obtained with (*Z*)-configured substrates.

Experimental Section

Palladium-Catalyzed Allylic Alkylations with Substrate 8c. Preparation of the chelated enoalte 1′: In a Schlenk flash HMDS (200 mg, 2.48 mmol) was dissolved in THF (1.5 mL) under argon. The solution was cooled to −78 °C before 1.6 M BuLi (0.70 mL, 1.13 mmol) was added. The solution was stirred for 20 min at −40 °C and a further 15 min after removing the cooling bath. In a second Schlenk flash *tert*-butyl trifluoroacetyl glycinate (102 mg, 0.45 mmol) was dissolved in THF (3 mL) and cooled to −78 °C, before the solution of LHMDS was added. After 15 min a solution of fresh dried $ZnCl_2$ (68 mg, 0.5 mmol) in THF (1 mL) was added, and the mixture was allowed to stir for 30 min at −78 °C.

Allylic alkylation: A solution of allyl palladium chloride dimer (10 mg, 0.025 mmol) and triphenylphosphine (30 mg, 0.11 mmol) in THF (5 mL) was prepared, and 0.6 mL of this solution was added to the solution of chelated enolate **1′** at −78 °C, subsequently followed by a solution of **8c** (128 mg, 0.60 mmol) in THF (0.5 mL). After 2.5 h at this temperature all starting material was consumed (for **8a** the reaction was warmed to room temperature for completion) and the reaction was quenched by addition of 1 N $KHSO_4$ (5 mL). After flash chromatography (silica, hexanes/EtOAc 88/12) the isomeric products **9**−**11** were obtained in an overall yield of 72% (135 mg, 0.43 mmol). **9** was obtained as the major product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 9H), 1.69 (dd, $J = 6.3$, 1.1 Hz, 1H), 3.47 (dd, $J = 9.4$, 5.3 Hz, 1H), 3.70 (s, 3H), 4.78 (dd, $J = 8.3$, 5.3 Hz, 1H), 5.50 (ddq, $J = 15.4$, 9.4, 1.5 Hz, 1H), 5.67 (dq, $J = 15.4$, 6.4 Hz, 1H), 6.94 (d, $J = 7.4$ Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.9, 27.9, 51.5, 52.4, 54.6, 84.0, 115.6 (q, $J = 288$ Hz), 123.0, 132.6, 156.7 (q, $J = 38$ Hz), 167.6, 171.2. **10** was obtained only in traces, selected signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (d, $J = 6.6$ Hz, 3H), 1.46 (s, 9H), 3.74 (s, 3H), 3.80 (m, 1H), 4.19 (dd, $J = J = 5.3$ Hz, 1H), 5.90 (d, $J = 11.7$ Hz, 1H), 5.95 (dd, $J = 11.4$, 9.8 Hz, 1H), 7.72 (d, $J = 6.6$ Hz).^{13}C NMR (75 MHz, $CDCl_3$) δ 16.9, 27.9, 35.4, 51.8, 57.5, 83.2, 121.5, 148.3, 167.3, 168.6, 168.7. **11** was obtained as a minor product, selected signals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, $J = 7.0$ Hz, 3H), 1.46 (s, 9H), 3.01 (m, 1H), 3.73 (s, 3H), 4.58 (dd, $J = 7.7$, 4.1 Hz, 1H), 5.87 (dd, $J = 15.8$, 1.3 Hz, 1H), 6.75−6.90 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ 14.6, 38.8, 83.5, 122.6, 147.0, 172.0. GC (Chira-Si-L-Val, isothermic, 120 °C): $t_{R(9)} = 43.36$ min, $t_{R(9)} = 44.93$ min, $t_{R(11)} = 46.91$ min, $t_{R(10)} = 70.11$ min, $t_{R(10)} = 74.75$ min. HMRS (CI) calcd for $C_{14}H_{21}NF_3O_5$ ($[M + H]^+$) 340.1372, found 340.1372.

3-[*tert*-Butyloxycarbonyl(trifluoroacetylamino)methyl]-2-methoxycarbonylbutyrolactone (15). The chelated enolate **1′** was prepared as described above. To the solution of this enolate was added a solution of (*Z*)-**8b** (89 mg, 0.51 mmol) in THF (0.5 mL). The mixture was stirred overnight while warming to room temperature. Ether was added (10 mL) and the reaction was quenched by addition of 1 N $KHSO_4$ (10 mL). The layers were separated, and the aqueous layer was extracted twice with CH_2Cl_2. After evaporation of the solvent and flash chromatography (hexanes/EtOAc 75/25) **15** was obtained (123 mg, 0.41 mmol, 80%) as a colorless solid, mp 92−94 °C. The anti diastereoselectivity was determined by NMR to be >95% ds. A minor cis diastereomer could be obtained in the reaction of (*E*)-**8b**. ^{1}H NMR (500 MHz, $CDCl_3$) δ =1.47 (s, 9H), 3.47 (m, 1H), 3.62 (d, $J = 8.8$ Hz, 1H), 3.78 (s, 3H), 4.21 (dd, $J = 9.8$, 8.2 Hz, 1H), 4.53 (dd, $J = 9.8$, 8.2 Hz, 1H), 4.62 (dd, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 7.9$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 42.1, 49.2, 53.4, 53.9, 68.6, 85.6, 115.4 (q, $J = 287$ Hz), 157.4 (q, $J = 38$ Hz), 167.0, 167.6, 170.0. Selected signals of the syn diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 7.29 (d, $J = 7.3$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.2, 48.3, 53.2, 53.5, 67.6, 85.6, 167.1, 170.0. Anal. Calcd for $C_{14}H_{18}F_3NO_7$ (369.29): C 45.53 H 4.91. Found: C 45.59 H 5.24.

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Supporting Information Available: Preparation and analytical/spectroscopic data of all substrates and products as well as X-ray data of deprotected **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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