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Diastereoselective [3+2] Cycloaddition of Allyltrialkylsilanes to Intermediate *N*-Acyliminoesters Obtained from Methyl 4-Methoxy-2-Imidazolidinone- and 2-Oxazolidinone-4-carboxylates

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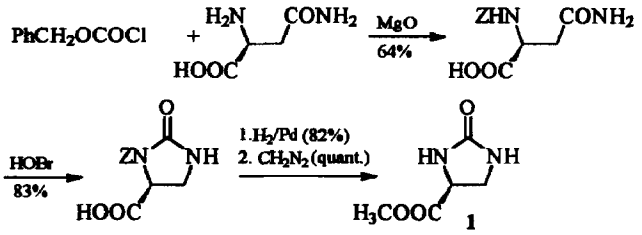
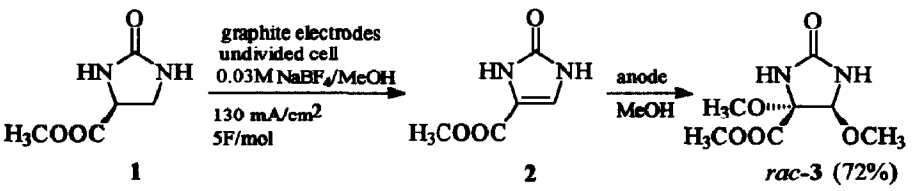
Abstract: The amidoalkylation reaction of methyl 4-methoxy-2-imidazolidinone-4-carboxylates or methyl 4-methoxy-2-oxazolidinone-4-carboxylates using allylsilanes as nucleophiles in the presence of $TiCl_4$ affords three carbon ring annulation products **5** and **9** via a [3+2] cycloaddition. Besides that,the simple methoxy group substitution product is formed. The ring annulation occurs with practically total diastereoselectivity so that all substituents are located on the ß-side of the bicyclic product.

In our studies on the application of electrochemically generated chiral amidoalkylation reagents, we have shown that α-methoxylated cyclic derivatives of α-amino acids containing a *N*-acyl function can easily be generated electrochemically. The methoxy group exchange by carbon nucleophiles under catalysis of a proton or a Lewis acid usually takes place with high diastereoselectivity leading to products of high enantomeric purity. Thus, ß-amino alcohols and non-proteinogenic α-amino acids can be obtained[1].

Starting from Z-(L)-asparagine, methyl 2-imidazolidinone 4-carboxylate (**1**) can easily be obtained in 68% yield over three steps using an improved literature procedure[2] with the Hofmann rearrangement as key step (Scheme 1) followed by esterification with diazomethane and hydrogenolytic deprotection. Unexpectedly, direct electrochemical oxidation in methanol using an undivided cell under galvanostatic conditions (130 mA/cm^2) at graphite electrodes after consumption of 5 F/mol leads to the dimethoxylated product **3**. The methyl 2-imidazolinone-4-carboxylate (**2**) is formed as intermediate followed by anodic dimethoxylation of the double bond (Scheme 2).



Scheme 1: Formation of compound **1**



Scheme 2: Anodic oxidation of **1** in methanol

The final product, methyl 4,5-dimethoxy-2-imidazolidinone-4-carboxylate (**3**) is formed in 72% material yield with practically total *trans*-diastereoselectivity for the methoxy groups, however in racemic form. After consumption of 2.9 F/mol, the intermediate product **2** can be isolated in 17% yield together with 58% of **3**.The expected monomethoxylated product methyl 5-methoxy-2-imidazolidinone-4-carboxylate could not be isolated. Because of the vicinal carboxylic ester function, methanol is eliminated under the electrolysis conditions to afford the enamido ester **2**. Because of its lower oxidation potentential of 1.5 V vs. $Ag/AgNO_3$ as compared with **1** (>2 V vs. $Ag/AgNO_3$), **2** is directly further oxidized to give **3**. The practically total *trans*-diastereoselectivity of the dimethoxylation (proved by ^1H NMR NOE experiments) indicates a stepwise introduction of the two methoxy groups. The first methoxy function in 5-position surprisingly effectively controls the introduction of the second in 4-position.

Methoxy group exchange by allyl trimethylsilane in the presence of $TiCl_4$ did not only result in the expected formation of the *trans*-diallyl compound **4** but, to our surprise, also afforded the ring annulation product **5a** (Scheme 2)[3]. All three susbtituents are located on the ß-side of the bicyclic compound as has been established by X-ray crystallographic determination of the relative configuration (Figure 1).

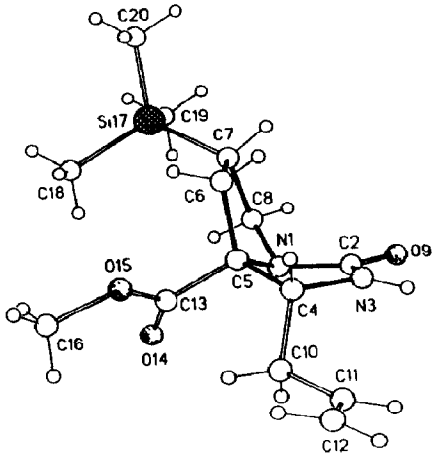
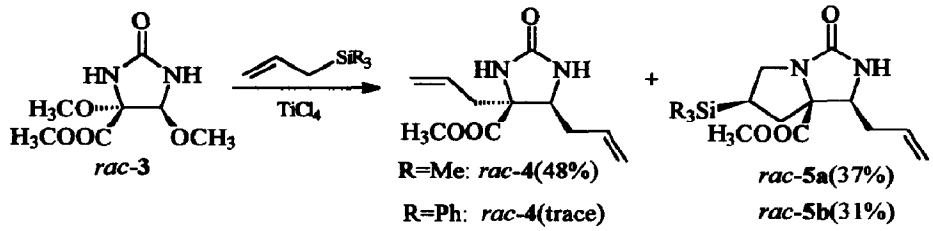
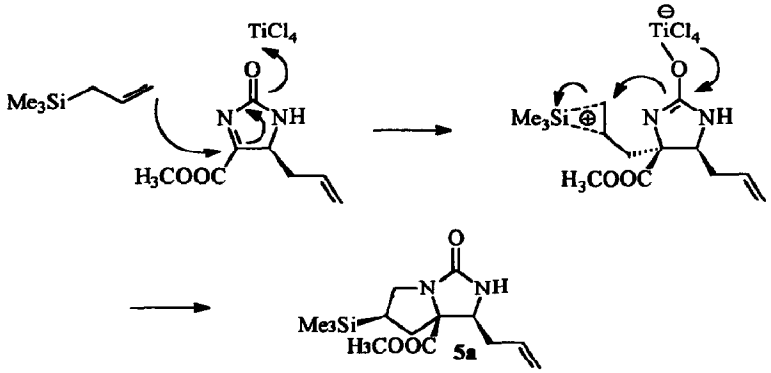


Figure 1: X-ray crystollographic structure of compound **5a**[5]



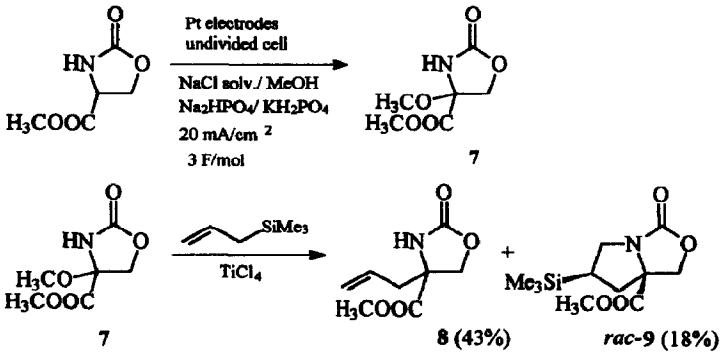
Scheme 3: Methoxy group exchange in *rac*-**3** by allyl trialkylsilanes

This hetero-ring annulation of allylsilanes is, to our knowledge, unprecedented. It is, however, strongly related to the sila-cyclopentane annulation by [3+2] cycloaddition of propargylsilanes[4a] and allylsilanes to enones reported by *Knölker* and others[4]. However, in *Knölker's* work, the annulation to 1-acetyl-2-methylcyclo-alkenes results in total or at least predominant *endo*-selectivity[4f] with regard to the trialkylsilyl group. Contrary to these observations, we find total *exo*-selectivity such that the trialkylsilyl group stays on the convex side of the bicyclic hemisphere (Fig. 1). Another striking feature of our reaction is the fact, that of both methoxy groups in compound **3** only the one in α-position to the carboxymethyl group is replaced under ring annulation while the other one simply undergoes a Sakurai-type reaction. The reason for this behaviour can only be assumed. While in the former case the reaction might take place via the intermediate *N*-acyl-iminoester, in the latter case the *N*-acyl-iminium ion might be the intermediate. As it has been demonstrated that the methoxy group exchange is more difficult in α-position to a carboxymethyl group, it is assumed that the first allylation takes place in the 5-position via the intermediate *N*-acyliminium ion. This is followed by the attack of the nucleophile onto the subsequently formed *N*-acyl-iminoester resulting in a non-classical pentavalent silicium cation[4f], which then cyclizes under 1,2-silyl shift (Scheme 4).Using allyl triphenylsilane, the reaction with **3** afforded the ring annulation product **5b** in 31% yield.



Scheme 4: Formation of compound **5a** via the non classical silicium cation

A similar reaction starting from the serine derivative 7, which can easily be obtained in quantitative yield by indirect electrochemical oxidation in methanol solution in the presence of NaCl as redox catalyst, afforded besides the methoxy substitution product **8** the ring annulation product **9** in 18% yield (Scheme 5).



Scheme 5: Formation of 7 by anodic oxidation in methanol followed by methoxy group exchange by allyl trialkylsilane

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[5] X-ray crystallographic structure determination of **5a**: space group P2(1)/c (Nr. 14), a = 6.474 (1), b = 13.978 (1), c = 18.791 (2) A, β = 97.64 (1)°, V = 1685.5 (3) A^3, Z = 4, R = 0.049 (for 185 parameters and 2229 observed reflections with F>4σ (F). More details on the crystal structure analysis are available from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-58415, the names of the authors, and the literature citations.

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