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Solid-phase synthesis of oxazolidines

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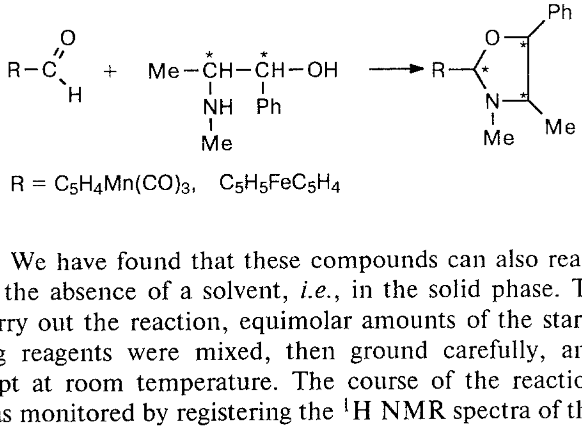
Oxazolidines are traditionally prepared by heating β-aminoalcohols with aldehydes in benzene (with the distillation of water) or in ethanol.[1,2] Earlier we have reported the synthesis of oxazolidines by heating the cymanthrenyl- and ferrocenylcarboxaldehydes (**1** and **2**, respectively) with the (−)-ephedrine or (+)-pseudoephedrine in ethanol.[3,4]



R = $C_5H_4Mn(CO)_3$, $C_5H_5FeC_5H_4$

We have found that these compounds can also react in the absence of a solvent, *i.e.*, in the solid phase. To carry out the reaction, equimolar amounts of the starting reagents were mixed, then ground carefully, and kept at room temperature. The course of the reaction was monitored by registering the ^{1}H NMR spectra of the benzene solutions of the probes of the reaction mixture. The monitoring showed that in all of the cases the corresponding spectroscopically pure oxazolidines were formed quantitatively in 1—3 days. The analysis of the spectra has also demonstrated that at 100 % conversion only one of the two possible diastereomers is mainly (88—100 %) formed. The absolute configurations of the major diastereomer formed either in solid phase or in alcohol solution turned out to be the same. Nevertheless, the reactions of **1** with the (−)-ephedrine in the liquid and in the solid phase differ substantially. The spectrum of a solution of the solid-phase reaction mixture after 5 h of the reaction (80 % conversion) indicates the major product to be the 2*R*,4*S*,5*R*-isomer of cymanthrenyloxazolidine (*RSR*/*SSR* = 3 : 1), the latter isomerizing into the 2*S*,4*S*,5*R*-isomer by further standing of the reaction mixture, so that the final *RSR*/*SSR* ratio becomes equal to 1 : 7. When the reaction is carried out in ethanol, the above-mentioned ratio is 1 : 4 at 80 % as well as at 100 % conversion.

The only real solid-phase process among all the oxazolidine syntheses described is that of the interaction of compound **2** with the (+)-pseudoephedrine. At every stage of it the reaction mixture makes a dry powder, whose color changes from dark-orange to light-yellow as the formation of the oxazolidine progresses. In the other cases the oxazolidine production is accompanied by the appearance of viscous syrupy oils, which crystallize only on long standing or by recrystallization from hydrocarbon solvents. The products obtained by carrying out the reaction in alcohol are also difficultly crystallizing oils.

The above-reported examples of the solid-phase synthesis of oxazolidines can possibly be more widely applied, since the corresponding oxazolidines are also formed by mixing the (−)-ephedrine with vanillin, the stereochemical course of the reaction, *i.e.*, the predominant formation of one of the diastereomers, being alike either in the solid phase or in ethanol.

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Enhanced electron-donating ability of allene derivatives containing organoelement substituents

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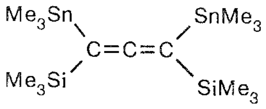
The formation of H-complexes of the type PhO—H...B—X_i between the phenol and the narrow range of the π-donors B—X_i, *i.e.*, the derivatives of benzene, ethylene, acetylene, *etc.* causes a shift of the frequency of the stretching vibration of the O—H bond, compared to that of the unassociated phenol, the shift value (Δν) being a quantitative factor of the change in the electron-donating ability (π-DA) of B—X_i under the influence of the substituents X_i attached to the π-donating center B.[1,2] Thus, when B = $H_2C{=}C$— or $Me_3CC{\equiv}C$—, the passage from X_i = Alk to X_i = $SnMe_3$ causes an increase in the Δν parameter from ~60 to ~70 cm^{-1} or from ~135 to 170 cm^{-1}, respectively.[2] The Δν value that we have measured for $Bu^t_3SnC{\equiv}CSnBu^t_3$ (200 cm^{-1}) could have been considered to be an indicator of the strongest influence of the substituents $MAlk_3$ (M = Si, Ge, or Sn) on the π-DA, but the influence of MMe_3 on the π-DA of the allene derivatives is even stronger. For $H_2C{=}C{=}CHX_i$, where X_i = Pr^n (**1**, Δν = 56 cm^{-1}), a moderate π-DA is observed, commensurable with that of $H_2C{=}CHAlk$. But with X_i = $SnMe_3$ (**2**), the Δν parameter increases dramatically to 165 cm^{-1}. The π-DA of allenes **3—5** is exclusively high, the Δν values amounting up to 310, 325, and 350 cm^{-1}, respectively.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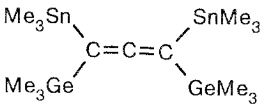
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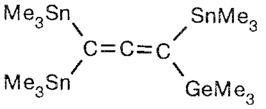
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The nonadditivity of the amplification of π-donating properties with the accumulation of the organoelement

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