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Solid-phase synthesis of oxazolidines

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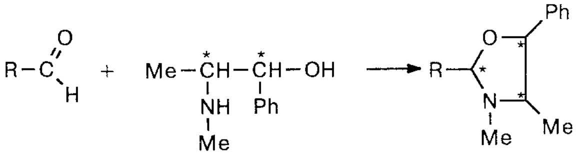
Oxazolidines are traditionally prepared by heating β-aminoalcohols with aldehydes in benzene (with the distillation of water) or in ethanol.[1,2] Earlier we have reported the synthesis of oxazolidines by heating the cymanthrenyl- and ferrocenylcarboxaldehydes (**1** and **2**, respectively) with the (−)-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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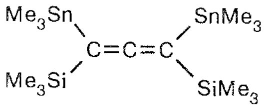
The formation of H-complexes of the type PhO−H...B−X_i between the phenol and the narrow range of the π-donors B−X_i, *i.e.*, the derivatives of benzene, ethylene, acetylene, *etc.* causes a shift of the frequency of the stretching vibration of the O−H bond, compared to that of the unassociated phenol, the shift value ($\Delta\nu$) 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 $\Delta\nu$ parameter from ~60 to ~70 cm^{-1} or from ~135 to 170 cm^{-1}, respectively.[2] The $\Delta\nu$ 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**, $\Delta\nu$ = 56 cm^{-1}), a moderate π-DA is observed, commensurable with that of $H_2C{=}CHAlk$. But with X_i = $SnMe_3$ (**2**), the $\Delta\nu$ parameter increases dramatically to 165 cm^{-1}. The π-DA of allenes **3**—**5** is exclusively high, the $\Delta\nu$ values amounting up to 310, 325, and 350 cm^{-1}, respectively.



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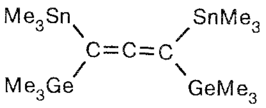

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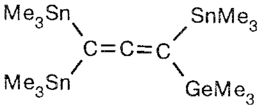

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The nonadditivity of the amplification of π-donating properties with the accumulation of the organoelement

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substituents in the allene molecule and their greater value, as compared, for instance, with the analogous properties of the ethers, are unexpected. The large Δν values for the H-complexes of allenes **3—5** are accompanied by the small values of the equilibrium constants of their formation (~1 L mol^{-1}, according to the approximate estimations). Thus, although having a high π-DA, the donating centers of compounds **3—5** are heavily blocked by the bulky MMe_3 substituents. The enhancement of the π-DA of the compounds $B-X_i$ in passing from X_i = Alk to X_i = MMe_3 is caused by an increase in the σ,π-conjugation. According to the literature data,[3] the σ,π-conjugation is the strongest of the three electron effects in the organotin compounds (the other two are the inductive effect and the d,π-conjugation). The extent of the σ,π-conjugation depends on the energy as well as on the spatial interposition of the interacting σ(M—C)- and π-orbitals.[3] Apparently, already in compound **2**, as compared to the other compounds $B-X_i$, the stereoelectron conditions are provided, which are the most favorable for the σ,π-conjugation of the three Sn—C σ-bonds with the cumulated double bonds. Therefore, the π-DA is dramatically increased in going from allene derivative **1** to **2**. The further enhancement of the σ,π-conjugation and π-DA follows the order **2** < **3** < **4** < **5**. This is in agreement with the increase in the capacity of $MAlk_3$ for the σ,π-conjugation in the order Si < Ge < Sn (see Refs. 2, 3). Judging from the Δν values of compounds **2—5**, the influence of the substituents MMe_3 on the π-DA of compounds **3—5** is weaker than on the π-DA of compound **2**. This might be due to the possible worsening of the steric conditions for the σ,π-conjugation in the sterically overcrowded allenes **3—5** in comparison to those in **2**, as well as to the presence of the counter-conjugation between the substituents in the MMe_3 moiety that reduces their electron-donating properies.

The compounds studied have been prepared according to the known procedures.[4,5]

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