1-Butoxy-2-heptafluoropropyl-1-methoxyethane (1) was obtained in an amount of 4.7 g (78 % yield), b.p. 70 °C (30 Torr), n_D^{20} 1.3443. ^{1}H NMR (C_6D_6), δ: 4.84 (t, 1 H, CH); 2.40 (m, 2 H, CH_2CF_2); 3.33 (s, 3 H, MeO); 3.56 (m, 2 H, CH_2O); 1.51 (m, 4 H, 2 CH_2); 0.92 (m, 3 H, Me).

1-Butoxy-1-isopropoxy-2-heptafluoropropylethane (2) was obtained in an amount of 3.5 g (53.3 % yield), b.p. 67 °C (5 Torr), n_D^{20} 1.3553. ^{1}H NMR (C_6D_6), δ: 4.90 (t, 1 H, OCHO); 2.44 (m, 2 H, CH_2CF_2); 3.61 (m, 2 H, CH_2O); 1.50 (m, 4 H, 2 CH_2); 1.01 (m, 9 H, 3 Me); 4.05 (m, 1 H, OCH).

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Synthesis of rare-earth monophthalocyanines containing fragments of sterically hindered phenols

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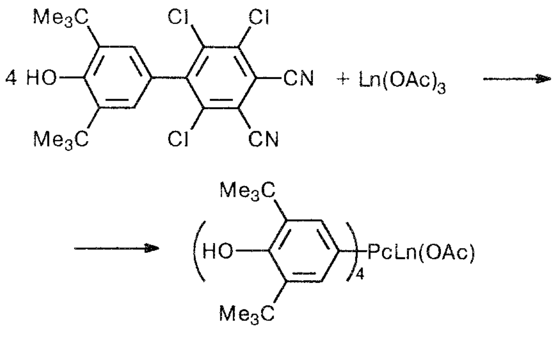
The monophthalocyanines of rare-earth elements (REE) are usually the side products of the synthesis of diphthalocyanines.[1] There have been several reports on the preparation of monophthalocyanines of REE in high yields.[2,3]

We have demonstrated that the introduction of a bulky substituent, 2,6-di-*tert*-butyl-4-hydroxyphenyl, into the molecule of the starting phthalonitrile makes it possible to direct the template synthesis toward the formation of the monophthalocyanine of REE as a major product.

By melting 3,5-di-*tert*-butyl-4-hydroxy-2',5',6'-trichloro-3',4'-dicyanodiphenyl[4] with the anhydrous acetates of Nd, Eu, and Lu (in a 4 : 1 molar ratio) at 290—300 °C for 1.5 h, the corresponding monophthalocyanines (**1a—c**) are formed in 83, 53, and 64 % yield, respectively. The data of the elemental analysis of the compounds obtained are in good agreement with the calculations.

The IR spectra (CCl_4) of compounds **1a—c**, ν/cm^{-1}: 3630—3645 (O—H); 2800—3100 (C—H); 1610—1660 (C=C). ^{1}H NMR spectrum (DMSO-d_6, δ) of Nd complex **1a**: 1.24 (s, 72 H, Bu^t); 4.86 (s, 4 H, OH); 6.84—7.04 (m, 8 H, Ph). The electron absorption spectra with the Q-bands at 673, 676, and 657 nm, respectively, point to the formation of the mononuclear complexes of REE.



1a—c

Ln = Nd(**a**), Eu(**b**), Lu(**c**)

Alterations in the reaction conditions (the molar ratio of the reagents, the temperature, or the reaction time) do not result in the formation of any products of diphthalocyanine type, their synthesis being apparently sterically hindered.

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Solid-phase synthesis of oxazolidines

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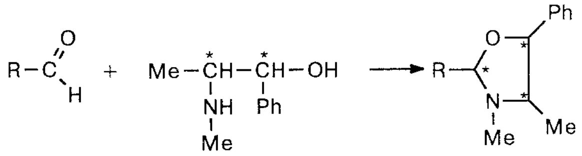
Oxazolidines are traditionally prepared by heating β-aminoalcohols with aldehydes in benzene (with the distillation of water) or in ethanol.[1,2] Earlier we have reported the synthesis of oxazolidines by heating the cymanthrenyl- and ferrocenylcarboxaldehydes (**1** and **2**, respectively) with the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