Acetal Preparation. a) A mixture of 0.02 mole dialdehyde (Ia-d), 16.0 ml $HC(OEt)_3$, and 0.5 g NH_4NO_3 in 10 ml abs. ethanol was heated at reflux for 5-10 h. The reaction was monitored by gas—liquid chromatographic analysis. At the end of the reaction, the mixture was cooled and diluted with 50 ml ether. The organic layer was washed with aq. $NaHCO_3$ and water and dried over $MgSO_4$. After evaporation of the solvent, the residue was distilled. The yields and indices of the products are given in Table 1.

b) Trace amounts of $HClO_4$ at the tip of a capillary were added to a mixture of 0.05 mole dialdehyde (or 0.1 mole monoaldehyde), 25 ml $HC(OEt)_3$, and 5 ml abs. ethanol. In the case of volatile aldehydes, equimolar amounts of the aldehyde and ethyl orthoformate without solvent were used. The mixture was stirred for about 0.5 h. Care was taken that the temperature did not exceed 50-60°C. At the end of the reaction as indicated by gas—liquid chromatography, the reaction mixture was neutralized by ethanolic KOH and distilled. The yields and indices of the products are given in Table 2.

CONCLUSIONS

A convenient rapid method has been proposed for the acetalization of aldehydes by ethyl orthoformate in the presence of trace amounts of perchloric acid.

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REACTION OF PhLnI WITH AMINES AND AZOLES

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Several lanthanide derivatives with an Ln—N bond, in which the Ln ion is in a 3+ oxidation state, have been reported. It was of interest to elucidate the possibility of forming $RLnNR_2$ compounds since, having obtained such Ln^{2+} derivatives, such compounds may be used by analogy with magnesylamines in organic synthesis.

For this purpose, we studied the reactions of amines and azoles with PhLnI obtained in situ by the oxidative addition of iodobenzene to the metallic lanthanide in THF. The analogous reaction with HC acids was used previously for the synthesis of several organolanthanide compounds [2]

$$Ln + PhI \rightarrow PhLnI \xrightarrow{R^1R^2NH} R^1R^2NLnI$$

The reaction proceeds at about 20°C virtually quantitatively with imidazole (pK_a = 18.9), indole (pK_a = 21.3), pyrrole (pK_a = 23.3), and diphenylamine (pK_a = 25.0). In the case of aniline (pK_a = 30.7) and dipropylamine (reaction with CH_3YbI), a total of 10 and 20% unreacted amine remains in the reaction mixture after 1 h.

The formation of an amide is indicated by the disappearance of the νNH band in the IR spectrum at 3310-3360 cm^{-1}. In addition, the UV spectrum of the reaction mixture of PhYbI with diphenylamine shows a strong amine anion band at 330-340 nm. The reaction was carried out with Ph_3GeBr for the ytterbium derivatives of aniline and diphenylamine. Hydrolysis of the reaction mixture gave hexaphenyldigermanoxane, which is formed upon the reaction of water on $Ph_3Ge—NhPh$ compounds [3].

Hence, arylamines and azoles are metallated by the action of PhLnI much more readily than hydrocarbons with similar acidity. Thus, for example, triphenylmethane (pK_a = 31.1) and fluorene (pK_a = 22.8) do not react with PhYbI [2], in contrast to aniline and pyrrole.

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TABLE 1. Reaction of PhLnI with Aniline

Ln	Reaction time, h	Unreacted amine, %
Yb	1	10
	2	0
Sm	1	40
	20	20
Eu	1	60
	20	30

It is not excluded that the difference in protophilicity of PhLnI relative to CH and NH acids is a result of prior coordination of the lanthanide ion at the unshared electron pair of the nitrogen atom.

We should note that lanthanide-containing amides are stronger metallating reagents than PhLn. Thus, for example, a CH proton in fluorene is replaced by YbI by the action of Ph_2NYbI in situ in about 20% yield (as indicated by mass spectrometric analysis of deuterofluorene isolated from the reaction mixture after treatment with D_2O; in the absence of amine, 2.5% deuterofluorene was isolated from the analogous reaction).

The extent of amine metallation upon the action of PhLnI is significantly dependent on the nature of the lanthanide. In the case of the reaction with aniline and Ln = Yb, the reaction is complete in 2 h, but when Ln = Sm and Eu complete aniline consumption is not found even after 20 h (Table 1). In these experiments, we took an equimolar amount of aniline, taking account of the yield of PhLnI in the reaction of Ln with iodobenzene: 80% for Yb and Eu and 50% for Sm (the yield was evaluated relative to the amount of tetraphenyltin isolated after the reaction of PhLnI with Ph_3SnCl; this evaluation is in good accord with the data of other methods [4]). In our previous work [5], we also observed significantly higher reactivity of Yb derivatives relative to derivatives of Sm and Eu [5].

EXPERIMENTAL

All the operations were carried out in a dry argon atmosphere. The THF sample was purified by heating at reflux over Na/benzophenone and distillation immediately prior to the reaction.

The organic lanthanide derivatives PhLnI (Ln = Yb, Sm, and Eu) were synthesized according to our previous procedure [2] in THF with prior activation of the metal by the addition of 0.5-1 mole % CH_2I_2. The reaction was monitored by thin-layer chromatography.

The reaction of PhLnI with amines and azoles was carried out in THF at about 20°C. The metallation was monitored relative to the decrease in intensity of the νNH band at 3310-3360 cm^{-1}. The IR spectra were taken on a Specord spectrometer.

Reaction of PhLnI with amines and azoles. A solution of 4 mmoles amine or azole in 6 ml THF was added at −20°C to a solution of PhLnI (Ln = Yb, Sm, and Eu) obtained from 5 mmoles PhI and 5.5 mg-atoms Ln in 6 ml THF and stirred at about 20°C for 1 h for Ln = Yb and 20 h for Sm and Eu.

Reaction of PhRNYbI with Ph_3GeBr. A solution of 4 mmoles Ph_3GeBr in 5 ml THF was added to a solution of Ph(R)NYbI, where R = H and Ph, obtained from 5 mmoles PhI, 5.5 mg-atoms Yb, and 4 mmoles aniline or diphenylamine in 15 ml THF and stirred for 20 h at about 20°C. The mixture was decomposed by water acidified with HCl and extracted with two 20-ml portions of ether. The ethereal extracts were dried over Na_2SO_4. Removal of the solvent in vacuum and washing of the residue with hot hexane gave a 30% yield of hexaphenyldigermanoxane as white crystals with mp 182°C [6].

Reaction of PhLnI with Ph_3SnCl. A solution of 5 mmoles Ph_3SnCl in 5 ml THF was added at −20°C to a solution of PhLnI (Ln = Yb, Sm, and Eu) obtained from 5 mmoles PhI and 5.5 mg-atoms Ln in THF and stirred for 20 h at about 20°C. After decomposition of the mixture as described above, a sample of tetraphenyltin was obtained with mp 223°C [6]. The yield was 80% for Yb and Eu and 50% for Sm.

Reaction of Ph_2NYbI with Fluorene. A solution of 4 mmoles fluorene in 5 ml THF was added to a solution of Ph_2NYbI obtained from 5 mmoles PhI, 5.5 mg-atoms Yb, and 4 mmoles diphenylamine in 15 ml THF and stirred for 2.5 h at about 20°C. The mixture was decomposed with 3 ml D_2O acidified with CH_3CO_2D, extracted with ether, and dried over Na_2SO_4. Fluorene was isolated by thin-layer chromatography on a glass plate with Silpearl silica gel. The monodeuterofluorene content was 20%. Only 2.5% deuterofluorene was isolated in the parallel reaction of PhYbI with fluorene in the absence of amine.

CONCLUSIONS

1. The feasibility of the metallation of NH acids (pK_a = 18-31) by the action of PhLnI was demonstrated.

2. The reactivity for PhLnI decreases in the following order: Yb > Sm > Eu.

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ASYMMETRICAL SYNTHESIS OF LYSINE DERIVATIVES

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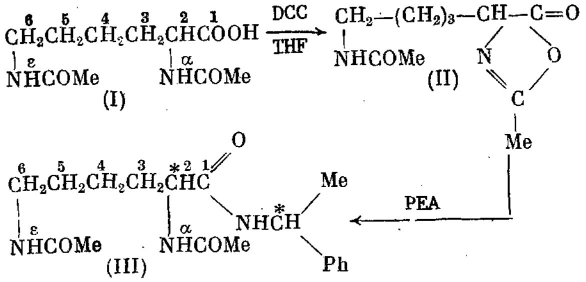
The development of reactions leading to the enrichment of lysine or its derivatives with the L isomer holds practical interest. Thus, we studied the stereoselective aminolysis of the azlactone of DL-diacetyllysine, which is an example of kinetic separation of stereochemically labile enantiomers.

DL-Diacetyllysine (I) was obtained in good yield by the hydrogenation of ethyl 5-cyano-2-oximinovalerate in acetic anhydride on a Raney nickel catalyst [1] with subsequent saponification of the ester group [2]. Starting with racemic (I), we developed a method for the synthesis of an optically pure diastereomer of an L-lysine derivative by the condensation of (I) to give azlactone (II) with the subsequent aminolysis of (II) by the action of chiral S-α-phenylethylamine (PEA). The last stage proceeds stereoselectively with the predominant formation of the SS-α-phenylethylamide of diacetyllysine (III):



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