Reactions of imides with samarium(II) iodide

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The tendency of a series of imides and lactams to react with samarium(II) iodide was investigated. Under the action of SmI_2 at ~20 °C, one of the carbonyl groups of *N*-phenylphthalimide was reduced to a CHOH or CH_2 group depending on the molar ratio of the reagents and the order of their introduction into the reaction mixture. Both CO groups of *N*-acetylcaprolactam are reduced with SmI_2 under similar conditions, whereas the CO group of ε-caprolactam is not reduced by SmI_2.

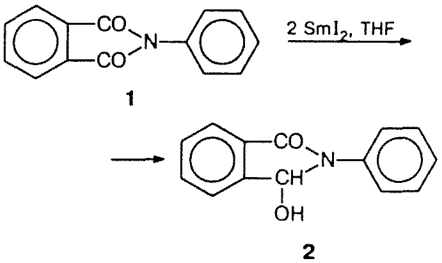
Key words: samarium(II) iodide; *N*-phenylphthalimide, *N*-acetylcaprolactam, ε-caprolactam, reduction; *N*-phenylphthalimidine, 3-hydroxy-2-phenylphthalimidine; NMR spectra; IR spectra.

Application of SmI_2 for reduction of organic compounds including phthalides and large lactone cycles[1,2] is based on its high redox potential. It is known, however, that carboxyl chlorides enter into the reaction of homocondensation under the action of SmI_2 to form benzils.[3] It was of interest to estimate the susceptibility towards SmI_2 of such carboxylic acid derivatives as imides, which serve as a basis for preparation of polyimides, which are important from the practical point of view. The present work deals with the reactions of cyclic imides and lactams with SmI_2.

Results and Discussion

The tendency of imides to the transformations under the action of SmI_2 was initially estimated by the example of a model reaction with imide **1**. When compound **1** was added to a mixture of SmI_2 with Sm (2 : 1) at ~20 °C, the color of the reaction mixture was quickly changed from blue-green to cherry-violet indicating a change in the valence state of samarium. The spectral data indicate that the changes in molecule **1** occur mainly at the imide cycle. The band at 1695 cm^{-1} appears in the IR spectrum instead of the bands at 1780, 1761 cm^{-1} (ν_sCO) and 1735, 1709 cm^{-1} (ν_{as}CO). An intensive band at 3389 cm^{-1} (νOH) and a weak band at 2907 cm^{-1} (νCH) are also observed.

The ^{1}H NMR spectrum of the compound obtained contains signals at δ 5.75 (CH) and 4.18 (OH). The signals at δ 143.72, 137.11, and 81.42 in the ^{13}C NMR spectrum of the product are assigned (using a DEPT technique)[7] to the aromatic C atoms and the carbon atom of the CH group of the partially reduced nitrogen-containing cycle. The spectral data and the melting point of the compound obtained (see Experimental) indicate the formation of 3-hydroxy-2-phenylphthalimidine (**2**) as a result of the reduction of imide **1**.



However, according to the ^{1}H NMR and IR spectral data, the imide fragment remains practically unchanged at a stoichiometric ratio of SmI_2 and **1**.

When the excess of SmI_2 increases (SmI_2 : **1** = 5 : 1), the more profound transformations of compound **1** occur. This is manifested in a significant change of its spectral parameters, *i.e.*, νCO band is observed at 1690 cm^{-1}, the bands at 1761 and 1780 cm^{-1} practically disappear, and the intensive bands at 2849 and 2920 cm^{-1} typical of valence vibrations of CH_2 groups appear. The signal at δ 5.25 corresponding to the CH_2 group is observed in the ^{1}H NMR spectrum of the compound obtained. The ^{13}C NMR spectrum of the product, along with the signal at δ 165.92 (CO) contains a signal at δ 49.79 that is assigned to the carbon atom of the CH_2 group using a DEPT technique. Based on these data and the determination of melting point, we made a conclusion about further reduction of the CHOH group under the action of SmI_2 with the formation of *N*-phenylphthalimidine.

It is interesting to note that imide **1** is not reduced if the reagents are mixed in the reverse order, *i.e.*, if a

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1236—1238, May, 1996.

1066-5285/96/4505-1176 $15.00

solution of SmI_2 is added to **1** in a 1 : 2 ratio.

Since we have found that one of the carbonyl groups of compound **1** is reduced with SmI_2, it was interesting to study the behavior of imides containing one of CO groups outside the cycle. The reaction of *N*-acetylcarprolactam (**3**) with SmI_2 was studied as a model.

No visual signs of the reaction were observed on the addition of a solution of compound **3** to a solution of SmI_2 and metal Sm in THF. However, the ^{13}C NMR spectral data (the disappearance of C=O signals at δ 171.13 and δ 176.31 and the appearance of a signal at δ 103.57 that is assigned to the carbon atom of the CH(OH)—N group) indicate that the reduction of the CO groups of the imide occurs. The comparison of the spectrum obtained with that of lactam **3** allows one to conclude that one of the CO groups is reduced to CH_2 and another one (in the acetyl fragment) to CHOH group.

For comparison, we have studied the action of SmI_2 on ε-caprolactam (**4**). From the comparison of the ^{13}C NMR spectrum of a mixture of SmI_2 with **4** in THF with that of individual **4** in THF it follows that the CO group of the lactam is not reduced under these conditions. However, taking into account that the signals in the ^{13}C NMR spectrum are somewhat shifted, the possibility of the formation of the ε-caprolactam—samarium complex cannot be ruled out.[8]

Thus, we have shown that imides are reduced with SmI_2 at ~20 °C. The capability of the imide fragment for the reduction depends mainly on its structure, molar ratio of reagents, and the order of their addition into the reaction mixture.

Experimental

IR spectra of the imides (in KBr) were recorded on an UR-20 spectrometer and a Bruker IFS-25 IR-FT spectrometer with resolution of 2 cm^{-1} (from 4000 to 400 cm^{-1}). ^1H and ^{13}C NMR spectra were obtained on a Bruker-WP-200-SY spectrometer (50.32 and 200.13 MHz, respectively) in DMF-d_7 and THF.

Diiodomethane purchased from Aldrich that contains 99 % of the main compound was washed with an aqueous solution of $Na_2S_3O_3$ and water, dried with calcined $MgSO_4$, and distilled *in vacuo* over copper chips. Metal samarium of an M-1 grade containing 99.9 % of the main compound was powdered immediately prior to the synthesis. Samarium(II) iodide was obtained[4] by the reaction of metal samarium with diiodomethane in abs. THF (the solvent was kept over KOH, refluxed for a prolonged period of time, distilled over NaH and collected directly into a reaction flask). *N*-Phenylphthalimide (**1**) was dried *in vacuo* at 100 °C for 7 h.

Reaction of SmI_2 with *N*-phenylphthalimide (1). Imide **1** was treated with samarium iodide at ~20 °C at a different ratio of the reagents.

A. A solution of **1** (1.00 g, 0.005 mol) in THF (20 mL) was added dropwise to a solution of SmI_2 (0.009 mol) for 10 min under dry argon. The mixture was stirred for 30 min, then 0.1 *N* HCl (10 mL) was added. The solvent was distilled off *in vacuo*, the precipitate formed was separated, washed repeatedly with 0.1 *N* HCl, water to neutral reaction, and ethanol, and dried for 8 h to give 0.67 g (67 %) of 3-hydroxy-2-phenylphthalimidine (**2**). Crystallization from ethanol with an activated carbon yielded 0.20 g of cream-colored crystals of **2**, m.p. 168—170 °C (literature data[5]: m.p. 170—172 °C).

B. A solution of **1** (1.53 g, 0.007 mol) in THF (60 mL) was added dropwise to a solution of SmI_2 (0.036 mol); the color of the reaction mixture changed from blue-green to cherry-violet. After 15 min the reaction mixture was treated with 0.1 *N* HCl (50 mL). The precipitate was separated, washed with HCl, water, and ethanol, and dried *in vacuo* at 70 °C to give 1.5 g (100 %) of *N*-phenylphthalimidine. Crystallization from ethanol with an activated carbon yielded 0.45 g (30 %) of the product, m.p. 158—164 °C (literature data[6]: m.p. 160 °C).

Reaction of SmI_2 with *N*-acetylcaprolactam (3). A solution of lactam **3** (0.71 mL, 0.05 mol) in THF was added dropwise to a solution of SmI_2 (0.1 mol) at ~20 °C for 7 min. The mixture was stirred for 1 h, then 0.1 *N* HCl (50 mL) was added to dissolve the Sm^{3+} salts. The reaction product was extracted with ether. The extract was washed with a 2.5 % solution of $NaHCO_3$, water, a 10 % solution of $Na_2S_2O_3$, and again with water, and dried with calcined $MgSO_4$. Ether and THF were distilled off, and the residue was analyzed by ^{13}C NMR spectroscopy.

Reaction of SmI_2 with ε-caprolactam (4). The reaction was carried out similarly to that described above (no change of color was observed). The precipitate of Sm^{3+} was filtered off. According to the ^{13}C NMR spectral data, the solution after the filtration contained initial lactam **4**. ^{13}C NMR (THF), δ: 182.31 (C=O); 42.01 (CH_2—N); 36.6 ($\underline{C}H_2$—CO); 29.21, 26.72, 21.12 (CH_2).

The ^{13}C NMR spectrum of ε-caprolactam (THF), δ: 178.43 (C=O); 42.63 (CH_2—N); 36.94 ($\underline{C}H_2C$=O); 30.72, 29.91, 23.43 (CH_2).

The authors are grateful to L. B. Danilevskaya for the samples of compounds **3** and **4**, and to N. N. Lapina for carrying out spectral studies.

This work was financially supported by the Russian Foundation for Basic Research (Grant 94-03-08082a).

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Received November 24, 1995;
in revised form January 17, 1996