Chemistry

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Abstract

Full Text

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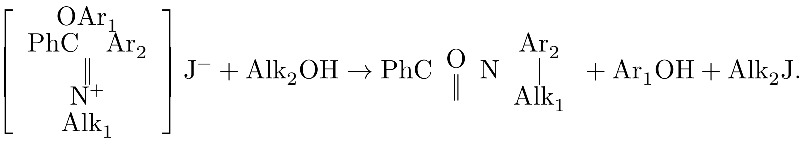
ON THE MECHANISM OF THE REARRANGEMENT OF IMIDO ESTERS

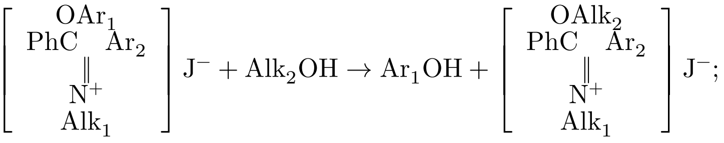
Ugi (^{1}) and Lander (^{2}) proposed that the rearrangement of imido esters into substituted amides in reaction with alkyl halides proceeds through a stage involving the formation of an intermediate addition product. Until now there has been no experimental evidence for such assumptions. The alkyl iodide salts of aryl benzimido esters (^{5}) that we obtained are the only known products of addition of alkyl halides to imido esters. However, upon decomposition of the iodide salts by heating, N-alkylbenzanilides—the products of rearrangement of imido esters—are not obtained. Success was achieved in studying the reaction of the iodide salts of imido esters with alcohols. It turned out that the reaction in boiling alcohol proceeds with formation of N-alkylbenzanilide, phenol, and an alkyl iodide according to the scheme:



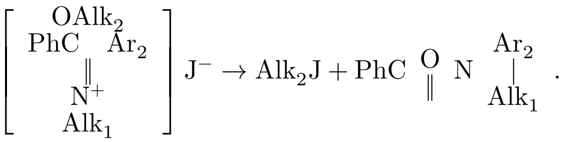
$$\left[\begin{array}{c}\mathrm{OAr}_1\\ \mathrm{PhC}\quad\mathrm{Ar}_2\\ \|\\ \mathrm{N}^+\\ \mathrm{Alk}_1\end{array}\right]\mathrm{J}^- + \mathrm{Alk}_2\mathrm{OH} \rightarrow \mathrm{PhC}\ \overset{\mathrm{O}}{\underset{\|}{}}\ \mathrm{N}\begin{array}{c}\mathrm{Ar}_2\\ |\\ \mathrm{Alk}_1\end{array} + \mathrm{Ar}_1\mathrm{OH} + \mathrm{Alk}_2\mathrm{J}. \qquad (1)$$

Thus, the conversion from an imido ester to an amide has been effected, and consequently the iodide salts are intermediate products in the rearrangement of imido esters.

We suppose that the first stage of reaction (1) is transesterification with liberation of phenol and formation of the unstable alkyl imido ester iodide salt (2), which rapidly undergoes spontaneous conversion into an amide, liberating alkyl iodide (3):



$$\left[\begin{array}{c}\mathrm{OAr}_1\\ \mathrm{PhC}\quad\mathrm{Ar}_2\\ \|\\ \mathrm{N}^+\\ \mathrm{Alk}_1\end{array}\right]\mathrm{J}^- + \mathrm{Alk}_2\mathrm{OH} \rightarrow \mathrm{Ar}_1\mathrm{OH} + \left[\begin{array}{c}\mathrm{OAlk}_2\\ \mathrm{PhC}\quad\mathrm{Ar}_2\\ \|\\ \mathrm{N}^+\\ \mathrm{Alk}_1\end{array}\right]\mathrm{J}^-; \qquad (2)$$



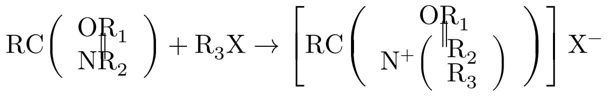
$$\left[\begin{matrix} & \mathrm{OAlk_2} & \\ \mathrm{PhC} & & \mathrm{Ar_2} \\ & \| & \\ & \mathrm{N^+} & \\ & \mathrm{Alk_1} & \end{matrix}\right]\mathrm{J^-} \rightarrow \mathrm{Alk_2J} + \mathrm{PhC}\begin{matrix}\mathrm{O}\\ \|\end{matrix}\ \mathrm{N}\begin{matrix}\mathrm{Ar_2}\\ | \\ \mathrm{Alk_1}\end{matrix}\ . \tag{3}$$

The course of the transesterification reaction (2) is confirmed by study of the reaction products of the iodomethylate of N-phenylbenzimidophenyl ether with ethyl mercaptan. In boiling mercaptan the reaction does not proceed, while at 100° the reaction proceeds in a complex manner, with resinification, and the reaction mixture does not contain

neither the products of transesterification—phenol or thiophenol—nor the product of rearrangement of the imido ester—the amide.

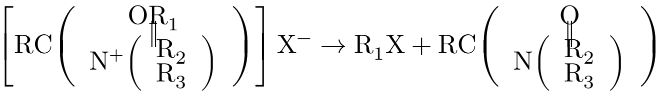
On the basis of the foregoing, it can apparently be considered proven that the rearrangement (and isomerization as a special case) of alkyl imido esters under the influence of alkyl halides proceeds in two stages, with formation of an unstable intermediate addition product, probably constructed analogously to the iodoalkylates of aryl imido esters according to the ionic type. The rearrangement is completed by migration of the radical R, in the form of a cation, from the oxygen of the ester group to the halide anion X.

The mechanism of the rearrangement in general form may be represented by the following scheme:



$$\mathrm{RC}\left(\begin{matrix}\mathrm{OR_1}\\ \| \\ \mathrm{NR_2}\end{matrix}\right) + \mathrm{R_3X} \rightarrow \left[\mathrm{RC}\left(\begin{matrix}\mathrm{OR_1}\\ \| \\ \mathrm{N^+}\left(\begin{matrix}\mathrm{R_2}\\ \mathrm{R_3}\end{matrix}\right)\end{matrix}\right)\right]\mathrm{X^-} \tag{4}$$

(1st stage)



$$\left[\mathrm{RC}\left(\begin{matrix}\mathrm{OR_1}\\ \| \\ \mathrm{N^+}\left(\begin{matrix}\mathrm{R_2}\\ \mathrm{R_3}\end{matrix}\right)\end{matrix}\right)\right]\mathrm{X^-} \rightarrow \mathrm{R_1X} + \mathrm{RC}\left(\begin{matrix}\mathrm{O}\\ \| \\ \mathrm{N}\left(\begin{matrix}\mathrm{R_2}\\ \mathrm{R_3}\end{matrix}\right)\end{matrix}\right) \tag{5}$$

(2nd stage)

The mechanism of the second stage of the rearrangement of imido esters, apparently, may be different and requires special study.

Experimental Part

Interaction of methyl iodide of *N*-phenylbenzimidophenyl ether with ethyl alcohol. 25 g of the methyl iodide and 40 ml of absolute ethyl alcohol were heated to maintain moderate boiling of the alcohol for 1.5 hours. From the homogeneous reaction mass, a colorless fraction with b.p. 72-80° was distilled off at normal pressure; from this fraction, on dilution with water, a heavy liquid with b.p. 72-73° and n_D^{20} 1.5171 was separated, which proved to be ethyl iodide.

The yield of ethyl iodide was 6.8 g (73% of theoretical). From the remaining part of the reaction mass, by distillation under vacuum, fractions with b.p. 75-78°/10 mm and 147-149°/1.5 mm were isolated. The fraction 75-78°/10 mm, at normal pressure, distilled at 179-182°, and crystallized completely with m.p. 41-42°. In its properties the substance is phenol. Yield of phenol: 5.1 g (89.5% of theory). The fraction 147-149°/1.5 mm crystallized completely after seeding with methylbenzanilide. The substance was recrystallized, and 9.5 g of methylbenzanilide with m.p. 60-61° was obtained (yield 75% of theory).

Found, %:	C 79.68; 79.62; H 6.00; 6.18; N 6.78; 6.86
$C_{14}H_{13}NO$. Calculated, %:	C 79.59; H 6.20; N 6.62

Literature data ([3,4]): m.p. 59°; b.p. 195°/12 mm.

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Note: Figure translations are in progress. See original paper for figures.

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