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Abstract

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ON THE INTERACTION OF IMIDOETHERS WITH ALKYL HALIDES

In 1899, Wheeler and Johnson established that imidoethers, upon interaction with alkyl halides at temperatures of 100-150°, are converted into amides of carboxylic acids substituted at nitrogen (^{1}). The rearrangement reaction is represented in general form by the following scheme:

$$\mathrm{RC(OR') = NH + R'Hal \rightarrow RC(=O)NHR' + R'Hal.}$$

If the radicals of the halide and of the ether group are identical, the amide obtained is an isomer of the starting imidoether. In the case where these radicals are different, the formation is possible of amides containing at nitrogen either the radical of the ether group or that of the corresponding alkyl halide. Alkyl esters of aliphatic and aromatic imido acids, substituted and unsubstituted at nitrogen, enter into the rearrangement reaction ($^{1-3}$).

The present work is the first part of an investigation in the field of imidoethers, undertaken by us for the purpose of further studying the interaction of imidoethers with alkyl halides. The reactions of a series of imidoethers with ethyl iodide, benzyl iodide, benzyl bromide, and triphenylmethyl bromide have been studied.

Table 1

Imidoethers of composition $C_6H_5C(OR) = NC_6H_5$

R	M.p., °C	B.p., °C/mm	d_4^{20}	n_D^{20}	Gross formula	MR_D, found	MR_D, calc.	N %, found	N %, calc.	Yield, %
iso-C_3H_7	43-44	162-163°/10	–	–	$C_{16}H_{17}NO$	–	–	6.07; 6.19	5.85	72
n-C_4H_9	–	179-181°/10	1.0289	1.5468	$C_{17}H_{19}NO$	78.06	77.82	5.68; 5.75	5.52	43
iso-C_4H_9	–	174.5-175°/10	1.0278	1.5450	$C_{17}H_{19}NO$	77.92	77.82	5.59; 5.78	5.52	37

R	M.p., °C	B.p., °C/mm	d_4^{20}	n_D^{20}	Gross formula	MR_D, found	MR_D, calc.	N %, found	N %, calc.	Yield, %
iso-C_5H_{11}	–	149–150°/0.6	1.0134	1.5395	$C_{18}H_{21}NO$	82.71	82.44	5.67; 5.72	5.23	45

Four higher alkyl N-phenylbenzimidoethers not described in the literature have been synthesized, and their behavior toward alkyl halides has been investigated. Table 1 gives the characteristics of the newly synthesized imidoethers. The constants of imidoethers described earlier are not given. All imidoethers used in the work were synthesized by the known method (^{4}), by reaction between N-phenylbenzimidochloride, obtained according to (^{5}), and the corresponding sodium alcoholate in an alcohol–ether medium.

Table 2

Imido ester	Alkyl halide	Ratio of reactants, g-mol.	Reaction temp., °C	Reaction duration, h	Main reaction product: compound	Yield, %
$C_6H_5C(OC_2H_5)=NC_6H_5$	C_2H_5J	1 : 1	155	10	$C_6H_5C(=O)N(C_6H_5)(C_2H_5)$	98
$C_6H_5C(OC_2H_5)=NC_6H_5$	$C_6H_5CH_2Cl$	1 : 1	100155	37	$C_6H_5C(=O)N(C_6H_5)(CH_2C_6H_5)$	90
$C_6H_5C(OC_2H_5)=NC_6H_5$	$C_6H_5CH_2Br$	1 : 1	155210	81.5	$C_6H_5C(=O)N(C_6H_5)(CH_2C_6H_5)$	98
$C_6H_5C(OC_2H_5)=NC_6H_5$	$(C_6H_5)_3CBr$	1 : 1	140–180	–	Resin	
$C_6H_5C(OCH_2C_6H_5)=NC_6H_5$	$C_6H_5CH_2J$	1 : 1	155	8	$C_6H_5C(=O)N(C_6H_5)(CH_2C_6H_5)$	96
$C_6H_5C(OCH_3)=NC_6H_5$	$C_6H_5CH_2Cl$	1 : 1	155	8	1) $C_6H_5C(=O)N(C_6H_5)(CH_2C_6H_5)$2) $C_6H_5C(=O)N(C_6H_5)(CH_3)$	4635
$C_6H_5C(OC_3H_7\text{-iso})=NC_6H_5$	iso-C_3H_7J	1 : 1	155	17	$C_6H_5C(=O)NHC_6H_5$	40
$C_6H_5C(OC_3H_7\text{-iso})=NC_6H_5$	CH_3J	1 : 1.2	100–155	14	$C_6H_5C(=O)N(C_6H_5)(CH_3)$	61
$C_6H_5C(OC_4H_9\text{-n})=NC_6H_5$	n-C_4H_9J	1 : 2	155–212	17.5	$C_6H_5C(=O)NHC_6H_5$	35
$C_6H_5C(OC_4H_9\text{-n})=NC_6H_5$	CH_3J	1 : 1.3	100–155	16	$C_6H_5C(=O)N(C_6H_5)(CH_3)$	37
$C_6H_5C(OC_4H_9\text{-iso})=NC_6H_5$	iso-C_4H_9J	1 : 1	155–210	19.5	$C_6H_5C(=O)NHC_6H_5$	23
$C_6H_5C(OC_4H_9\text{-iso})=NC_6H_5$	CH_3J	1 : 1	100–155	19	$C_6H_5C(=O)N(C_6H_5)(CH_3)$	46
$C_6H_5C(OC_5H_{11}\text{-iso})=NC_6H_5$	CH_3J	1 : 1	155	10	$C_6H_5C(=O)N(C_6H_5)(CH_3)$	31

The reaction of the imido ester with the alkyl halide was carried out in a sealed glass tube. The conditions of all the reactions performed and the yields of the principal products are given in Table 2. The percentage yield of the principal product is at the same time the percentage conversion of the imido ester; from the reaction mixture, in each case, the corresponding amount of imido ester that had not succeeded in reacting was recovered. Separation of the amides and imido esters was carried out by vacuum distillation or was based on their different solubilities.

N-Phenylbenzimidoethyl ether was quantitatively isomerized into *N*-ethylbenzanilide on heating with ethyl iodide for 10 h at 155°. This is in good agreement with the data of Lander (^{3}), who isomerized the same imido ester almost completely with ethyl iodide in 13 h at 150—160° at a reactant ratio (in g-mol.) of $1:0.5$. In the reaction with iodide and

with benzyl bromide, rearrangement occurs with formation of N-benzylbenzanilide. The absence of N-ethylbenzanilide among the reaction products makes it possible to conclude that, under the corresponding conditions, the benzyl radical is a considerably more active reagent than ethyl in the reaction with imido ethers. With triphenylmethyl bromide the imido ether does not enter into the rearrangement reaction. Up to 140° no change in the reagents occurs, and above this temperature the reaction product proved to be a water- and alcohol-insoluble resin, from which individual compounds could not be isolated.

N-Phenylbenzimidobenzyl ether is isomerized quantitatively by benzyl iodide. On interaction of N-phenylbenzimidomethyl ether with benzyl iodide, two amides are formed: N-benzylbenzanilide and N-methylbenzanilide, the former being isolated in larger amount than the latter. Apparently, benzyl iodide is a more active reagent in this reaction than methyl iodide.

Higher (beginning with isopropyl) N-phenylbenzimido ethers are not isomerized by the corresponding alkyl iodides; benzanilide and the corresponding olefin are formed. The reaction apparently proceeds according to one of the schemes:

$$\begin{aligned} &\text{a)}\quad \text{iso-}C_3H_7J \rightarrow C_3H_6 + HJ,\\ &\text{b)}\quad C_6H_5C(OC_3H_7\text{-iso}){=}NC_6H_5 + HJ \rightarrow C_6H_5C(=O)NHC_6H_5 + \text{iso-}C_3H_7J; \end{aligned} \qquad \text{(I)}$$

$$C_6H_5C(OC_4H_9\text{-iso}){=}NC_6H_5 \xrightarrow{t>200^\circ} C_4H_8 + C_6H_5C(=O)NHC_6H_5 \qquad \text{(II)}$$

The decomposition of sec-butyl N-phenylbenzimido ether according to scheme (II) was shown in an attempt at its thermal isomerization (^{6}). The reaction with methyl iodide proceeds with formation of N-methylbenzanilide, i.e., rearrangement takes place.

On the basis of our experiments and literature data ($^{1-3}$), the corresponding halogen derivatives may be arranged in the following series of decreasing activity in rearrangement reactions of imido ethers:

$$C_6H_5CH_2J > CH_3J > C_6H_5CH_2Br > C_2H_5J > C_3H_7J > C_2H_5Br.$$

Higher alkyl iodides apparently do not enter into the rearrangement reaction.

Experimental Part

1. N-Phenylbenzimidochloride. 50 g of benzanilide and 52 g of phosphorus pentachloride were placed in a distillation flask with a side arm, protected from atmospheric moisture, and stirred. The flask was heated on a water bath, whereupon a vigorous reaction began with evolution of hydrogen chloride and liquefaction of the reaction mass. After completion of the reaction, phosphorus oxychloride was distilled off under vacuum. The residue was dissolved in 100 ml of dry ether and, after filtration, was used for the synthesis of the imido ether.

2. N-Phenylbenzimidoisopropyl ether.
a) Into a 500-ml round-bottomed three-necked flask, equipped with a stirrer, a tube for introducing hydrogen into the mass, and a reflux condenser protected from atmospheric moisture, were placed 200 ml of absolute isopropyl alcohol and 6 g of sodium. To the cooled crystalline mass of sodium isopropylate was added dropwise an ethereal solution of the imidochloride obtained from 50 g of benzanilide. A white turbidity of the sodium chloride being formed appeared at once. After completion of the reaction, the yellowish-orange solution was separated from the sodium chloride and distilled. After two distillations, 43.6 g of imido ether were obtained, b.p. 162—163° at 10 mm, yield 72% based on benzanilide. After distillation the product completely crystallized, m.p. 43—44°.

Found, %:	C 80.49; 80.27;	H 7.17; 7.43;	N 6.07; 6.19
$C_{16}H_{17}ON$. Calculated, %:	C 80.30;	H 7.16;	N 5.85

b) The reaction was carried out under the conditions of the preceding experiment, but the reaction mixture was treated with water, part of the ether was distilled off, and the residue was poured into cold water. The oil that separated soon crystallized. The product was recrystallized three times from dilute alcohol. The yield was 53%. M.p. 43-44°. The crystals had the appearance of yellowish needles, with a faint odor.

Analogously to experiment a), the following N-phenylbenzimidate esters were synthesized: methyl, ethyl, benzyl, *n*-butyl, isobutyl, and isoamyl. All the esters are syrupy liquids, greenish-yellow in color, with a faint odor. They are soluble in alcohol, ether, ethyl acetate, fatty and aromatic hydrocarbons, and alkyl halides. They are insoluble in water. With dilute mineral acid they are hydrolyzed with cleavage of the C=N bond and formation of alkyl benzoates and aniline.

3. **Reaction of N-phenylbenzimidic ethyl ester with benzyl iodide.** Into a glass tube were sealed 8 g of imido ester and 7.8 g of benzyl iodide (molar ratio 1:1). The tube was heated for 3 hours at 100° and for 7 hours at 155°. The reaction mixture was transferred to a distillation flask, and ethyl iodide was distilled off at atmospheric pressure. From the residue, at a pressure of 10 mm and a bath temperature up to 180–200°,

nothing distilled. The mass poured into a dish crystallized when triturated with ether. After two recrystallizations from alcohol, white prisms of N-benzylbenzanilide were obtained. Weight 9.0 g (90%). M.p. 105-106°.

Found, %: N 4.97; 5.09
$C_{20}H_{17}NO$. Calculated, %: N 4.88.

Literature data (7): m.p. 105°.

Thus, seven alkyl N-phenylbenzimidate esters have been synthesized and their interaction with alkyl halides studied. It has been established that higher alkyl imido esters are not isomerized by the corresponding alkyl iodides, but enter into a rearrangement reaction with methyl iodide.

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