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Abstract

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ON SOME NEW DERIVATIVES OF IMIDO ESTERS

Alkyl imido esters react with alkyl halides with formation of rearrangement products—amides of carboxylic acids ([1–3]). We have for the first time studied the interaction of aryl imido esters with alkyl halides. It was found that the reaction with methyl iodide at 100° and with ethyl iodide at 130° proceeds only in one direction, with formation of addition products. The reaction with the benzimido esters substituted at nitrogen, which we used in the present work, is represented by the scheme:

$$C_6H_5C\begin{matrix}OAr'\\ \\ NAr''\end{matrix} + AlkJ \longrightarrow \left[C_6H_5C\begin{matrix}OAr'\\ \\ N\begin{matrix}Ar''\\ Alk\end{matrix}\end{matrix}\right]^+ J^-. \qquad (1)$$

The addition products presented in Table 1 are new derivatives of imido esters, unknown up to the present time. They may be called iodalkylates of imido esters. We assign to the iodalkylates the structure of a salt built according to the ionic type.

The reaction apparently begins with electrophilic attack at the nitrogen atom, with formation of an imonium ion, which with the iodide anion forms salt (I). Further electron shifts in the molecule are possible, with formation of structures (II) or (III):

$$C_6H_5C\begin{matrix}OAr'\\ \\ \ddot{N}Ar''\end{matrix} \cdots R{-}J \longrightarrow \left[C_6H_5C\begin{matrix}OAr'\\ \\ N\begin{matrix}Ar''\\ R\end{matrix}\end{matrix}\right] J \rightleftarrows \qquad (2)$$

$$\rightleftarrows \left[C_6H_5\overset{+}{C}\begin{matrix}OAr'\\ \\ N\begin{matrix}Ar''\\ R\end{matrix}\end{matrix}\right] J \rightleftarrows \left[C_6H_5C\begin{matrix}OAr'\\ \\ N\begin{matrix}Ar''\\ R\end{matrix}\end{matrix}\right]^+ J^-$$

(Ionic state of iodine in the addition products, as well as the bond of the alkyl *R* (2) with the nitrogen atom, is confirmed by the hydrolysis reaction. Already at ordinary temperature, when an iodalkylate is placed in water, an acid reaction to litmus is observed. With slight heating, hydrolysis proceeds with formation of aryl benzoates and alkylarylamines (3):

$$\left[C_6H_5C \begin{matrix} OAr' \\ \\ N\begin{matrix} Ar'' \\ Alk \end{matrix} \end{matrix} \right]^+ J^- + H_2O \longrightarrow C_6H_5C \begin{matrix} OAr' \\ \\ O \end{matrix} + \left[\begin{matrix} Ar'' \\ \\ Alk \end{matrix} NH_2 \right] J. \qquad (3)$$

This reaction may be proposed as one of the methods for obtaining alkylarylamines.

At temperatures of 200–220° the decomposition of the iodoalkylates was carried out with elimination of alkyl halide (4), i.e., according to the decomposition scheme for substituted ammonium salts:

$$\left[\begin{matrix} OAr' \\ C_6H_5C \\ \| \\ N\begin{matrix} Ar'' \\ Alk \end{matrix} \end{matrix} \right]^+ J^- \longrightarrow C_6H_5C \begin{matrix} OAr' \\ \| \\ NAr'' \end{matrix} + AlkJ. \qquad (4)$$

Experiments on the synthesis of products of addition of alkyl halides to *o*-nitrophenyl, *p*- and *o*-chlorophenyl N-phenylbenzimido ethers, as well as to phenyl N-*p*-chlorophenylbenzimido ether, did not give positive results.

Apparently, electron-withdrawing substituents, owing to the manifestation of the inductive effect and the conjugation effect, strongly withdraw the free electron pair of the nitrogen atom, suppressing the basic properties of the molecule. Confirmation of this point of view is also provided by the report[4] that N-phenylbenzimido-*o*-nitrophenyl ether does not form salts with sulfuric acid. All addition products, in the absence of moisture (better in a vacuum), remain unchanged for a long time.

The N-*p*-ethoxyphenylbenzimidophenyl ether and N-β-naphthylbenzimidophenyl ether used in this work were synthesized for the first time.

Table 1

Addition products of alkyl halides to imido ethers
(the yield of the products in all experiments is close to theoretical)

Formula of compound $[C_6H_5C(OR_1)=N(R_2)R_3]^+ J^-$	M.p. (decomp.), °C	Crystal form	Empirical formula	J, % found	J, % calculated
$R_1 = C_6H_5$; $R_2 = C_6H_5$; $R_3 = CH_3$	160	Light-yellow needles	$C_{20}H_{18}NOJ$	30.52	30.55
$R_1 = C_6H_5$; $R_2 = C_6H_5$; $R_3 = C_2H_5$	169	Same	$C_{21}H_{20}NOJ$	29.78	29.56
$R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$-*o*; $R_3 = CH_3$	139-140	Same	$C_{21}H_{20}NOJ$	29.63	29.56
$R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$-*o*; $R_3 = C_2H_5$	131-132	Same	$C_{22}H_{22}NOJ$	28.74	28.62
$R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$-*p*; $R_3 = CH_3$	184	Same	$C_{21}H_{20}NOJ$	29.70	29.56
$R_1 = C_6H_5$; $R_2 = C_6H_4CH_3$-*p*; $R_3 = C_2H_5$	171-172	Same	$C_{22}H_{22}NOJ$	28.62	28.62
$R_1 = C_6H_5$; $R_2 = C_{10}H_7$-β; $R_3 = CH_3$	126-127	Light-yellow prisms	$C_{24}H_{20}NOJ$	27.11	27.27
$R_1 = C_6H_5$; $R_2 = C_{10}H_7$-β; $R_3 = C_2H_5$	116-118	Same	$C_{25}H_{22}NOJ$	26.42	26.47
$R_1 = C_6H_5$; $R_2 = C_6H_4OCH_3$-*p*; $R_3 = CH_3$	175-176	Same	$C_{21}H_{20}NO_2J$	28.53	28.52
$R_1 = C_6H_5$; $R_2 = C_6H_4OCH_3$-*p*; $R_3 = C_2H_5$	148-150	Same	$C_{22}H_{22}NO_2J$	27.60	27.63

Formula of compound $[C_6H_5C(OR_1)=N(R_2)R_3]^+ J^-$	M.p. (decomp.), °C	Crystal form	Empirical formula	J, % found	J, % calculated
$R_1 = C_6H_5$; $R_2 = C_6H_4OC_2H_5$-*p*; $R_3 = CH_3$	179-180	Same	$C_{22}H_{22}NO_2J$	27.42	27.63
$R_1 = C_6H_4CH_3$-*o*; $R_2 = C_6H_5$; $R_3 = CH_3$	181	Light-yellow needles	$C_{21}H_{20}NOJ$	29.93	29.56
$R_1 = C_6H_4CH_3$-*o*; $R_2 = C_6H_5$; $R_3 = C_2H_5$	163-164	Same	$C_{22}H_{22}NOJ$	29.00	28.62
$R_1 = C_6H_4CH_3$-*m*; $R_2 = C_6H_5$; $R_3 = CH_3$	189-190	Same	$C_{21}H_{20}NOJ$	29.41	29.56
$R_1 = C_6H_4CH_3$-*m*; $R_2 = C_6H_5$; $R_3 = C_2H_5$	180-181	Same	$C_{22}H_{22}NOJ$	28.58	28.62
$R_1 = C_6H_4CH_3$-*p*; $R_2 = C_6H_5$; $R_3 = CH_3$	191	Same	$C_{21}H_{20}NOJ$	29.65	29.56
$R_1 = C_6H_4CH_3$-*p*; $R_2 = C_6H_5$; $R_3 = C_2H_5$	169-171	Same	$C_{22}H_{22}NOJ$	28.35	28.62
$R_1 = C_{10}H_7$-α; $R_2 = C_6H_5$; $R_3 = CH_3$	136-137	Same	$C_{24}H_{20}NOJ$	27.01	27.27
$R_1 = C_{10}H_7$-α; $R_2 = C_6H_5$; $R_3 = C_2H_5$	132	Same	$C_{25}H_{22}NOJ$	26.81	26.47
$R_1 = C_{10}H_7$-β; $R_2 = C_6H_5$; $R_3 = CH_3$	192-193	Same	$C_{24}H_{20}NOJ$	27.13	27.27

Formula of compound $[C_6H_5C(OR_1)=N(R_2)R_3]^+J^-$	M.p. (decomp.), °C	Crystal form	Empirical formula	J, % found	J, % calculated
$R_1 = C_{10}H_7$-β; $R_2 = C_6H_5$; $R_3 = C_2H_5$	171	Same	$C_{25}H_{22}NOJ$	26.41	26.47
$R_1 = C_6H_4CH_3$-p; $R_2 = C_6H_4CH_3$-p; $R_3 = CH_3$	174-175	Same	$C_{22}H_{22}NOJ$	28.58	28.62
$R_1 = C_6H_4CH_3$-p; $R_2 = C_6H_4CH_3$-p; $R_3 = C_2H_5$	141	Light-yellow prisms	$C_{23}H_{24}NOJ$	27.47	27.74

Experimental Part

N-*p*-Ethoxyphenylbenzimidophenyl ether.
a) On the basis of (5,6), N-*p*-ethoxyphenylbenzimidochloride was prepared from 50 g of *p*-phenetidine and 43 g of phosphorus pentachloride by heating on a water bath. After distillation of phosphorus oxychloride, the reaction product was dissolved in 400 ml of dry ether and used for the synthesis of the imido ether. b) In a flask equipped with a stirrer, sodium phenolate was prepared from 19.6 g of phenol and 4.8 g of sodium in 250 ml of anhydrous alcohol. The imidochloride obtained in a) was added dropwise to the phenolate. The reaction mixture was filtered, and the precipitate on the filter was washed with water to remove sodium chloride. After two recrystallizations from ethyl alcohol, 47 g (72%) of the imido ether was obtained as white plates, m.p. 112-113°.

Found, %: 4.51; 4.47
$C_{21}H_{19}NO$. Calculated, %: 4.41

N-β-Naphthylbenzimidophenyl ether was obtained analogously to that described above. Light-yellow prismatic crystals (from alcohol) of the imido ether were obtained, m.p. 101-102°, in 68% yield.

Found, %: 4.37; 4.41
$C_{23}H_{17}NO$. Calculated, %: 4.33

Iodomethylate of N-phenylbenzimidophenyl ether.
Into a glass tube were sealed 20 g of N-phenylbenzimidophenyl ether and 20 g of methyl iodide. The tube was kept at 100° for 8 h, then opened, the contents were transferred to a dish, and the volatile material was removed in vacuo. The yellow powder was recrystallized from a chloroform-ether mixture. Obtained:

30 g (99%) of the iodomethylate of N-phenylbenzimidophenyl ether, m.p. 160° (decomp.).

Found, %: C 57.98; 57.77; H 4.40; 4.42; N 3.51; 3.57; I 30.52; 30.61
$C_{20}H_{18}NOI$. Calculated, %: C 57.84; H 4.36; N 3.37; I 30.55

Iodoethylate of N-phenylbenzimidophenyl ether was obtained analogously to that described above from the imido ether and ethyl iodide; the reaction was carried out for 10 h at 130°. Yield 97%, m.p. 169° (decomp.).

Found, %: C 58.58; 58.73; H 4.92; 4.67; N 3.41; 3.31; I = 29.78; 29.81
$C_{21}H_{20}NOI$. Calculated, %: C 58.75; H 4.68; N 3.26; I 29.56

Thus, we have synthesized a series of previously unknown derivatives of imido ethers–products of the addition of alkyl iodides–and have studied some of their properties.

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