5-Methyl-1,3-diphenylpyrido[1,2-a]benzimidazolium Perchlorate. A solution of 0.32 g (1 mmole) of IIIc and 0.5 ml of methyl iodide in 7 ml of alcohol was refluxed for 3 h, after which it was cooled, and the precipitated methiodide was removed by filtration and dissolved in the minimum amount of acetonitrile. The solution was treated with 1 ml of 57% $HClO_4$, and the precipitated perchlorate was removed by filtration and washed with acetonitrile to give 0.35 g (80%) of a product with mp 246-247°C.

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REACTION OF 3-INDOLYLPHENYLIODONIUM BETAINE WITH ELECTROPHILIC AGENTS

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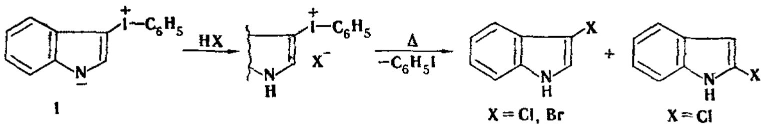
3-Indolylphenyliodonium chloride and bromide, respectively, were obtained by the action of hydrochloric and hydrobromic acids on 3-indolylphenyliodonium betaine. Pyrolysis of the chloride leads to a mixture of 2- and 3-chloroindoles, while pyrolysis of the bromide leads only to 3-bromoindole. 1-Benzyl-2-chloroindole is obtained in the reaction of the betaine with benzyl chloride. The betaine reacts with dimethyl sulfate to give an iodonium salt, the reaction of which with lithium chloride and ammonium chloride leads to 1-methyl-2-chloroindole.

Unstable 3-indolylphenyliodonium betaine (I) is formed by the action of phenyliodoso diacetate on indole in a solution of alcoholic alkali [1]. The dipolar betaine molecule is capable of reacting with both electrophilic and nucleophilic agents. In fact, protic acids with weakly nucleophilic anions react with the betaine to give indolyliodonium salts. This method has been used to obtain 3-indolylphenyliodonium tetrafluoroborate [1], tosylate [1, 2], and trifluoroacetate [2]. However, if the anion of the acid is sufficiently nucleophilic, further reaction between it and the iodonium salt is possible. In fact, haloindoles are formed by the action of hydrochloric and hydrobromic acids on 3-indolylphenyliodonium betaine. The intermediately formed iodonium salt can be isolated in this case. As we have already mentioned [3], bromide ion gives only 3-bromoindole, whereas a mixture of 2- and 3-chloroindoles is formed in the case of the chloride. The formation of 2-chloroindole is apparently associated with dissociation of the chloride of the iodonium salt and subsequent attack by the chloride ion on the α-carbon atom. Thus betaine I is initially protonated at the nitrogen atom, after which the phenyliodonium grouping undergoes nucleophilic substitution.



One might have expected that some other reagents would also be capable of acting similarly. In fact, 1-benzyl-2-chloroindole is formed when betaine I is heated with benzyl chlo-

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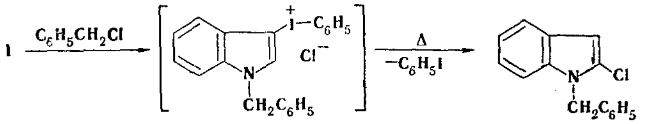
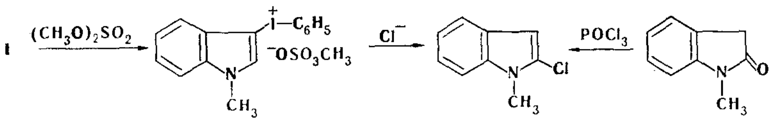
ride. The nitrogen atom of the betaine initially undergoes alkylation, after which the chloride ion replaces the phenyliodonium group nucleophilically. In this case, as in the case of 3-indolylphenyliodonium chloride, nucleophilic attack is directed primarily at the α-carbon atom. A chromatographic mass-spectral investigation of the reaction mixture makes it possible to detect a small amount of isomeric 1-benzylchloroindole.



If dimethyl sulfate is used as the alkylating agent, the resulting iodonium salt can be isolated owing to the low nucleophilicity of the methosulfate ion



It is interesting that, in contrast to other indolyliodonium salts [3], this salt reacts identically with lithium and ammonium chlorides to give 1-methyl-2-chloroindole. A chromatographic mass-spectral study of the reaction mixture makes it possible to detect the presence of a second isomer ($\sim$10%). If one takes into account the fact that 3-indolylphenyliodonium salts react with lithium chloride to give only 3-chloroindole, it may be noted that the presence of a methyl group attached to the nitrogen atom changes the direction of nucleophilic attack.

Thus the regiospecificity of nucleophilic substitution in 3-indolylphenyliodonium salts depends both on the degree of "hardness" of the nucleophile and the nature of the ambident electrophile of the salt.

EXPERIMENTAL

Preparation and Pyrolysis of 3-Indolylphenyliodonium Chloride. A 960-mg (3 mmole) sample of 3-Indolylphenyliodonium betaine [1] was added in portions to a cooled (to -15°C) solution of 3 ml of concentrated hydrochloric acid (36%) in 3 ml of absolute ethanol. The yellow betaine initially dissolved, afterwhich the white iodonium salt precipitated. After all of the betaine had been added, the reaction mixture was stirred for 30 min and diluted with 10 ml of ether that had been purified thoroughly to remove peroxides. The resulting precipitate was removed by filtration, washed with ether, and dried in a vacuum desiccator at 20°C to give 800 mg (75%) of 3-indolylphenyliodonium chloride with mp 82-83°C (dec.). Without further purification, 350 mg (1 mmole) of the salt was dissolved in 5 ml of dry DMSO, and the solution was heated at 100°C for 2 h. It was then diluted with water, and the aqueous solution was extracted with benzene. The extract was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed *in vacuo*, and the residue was chromatographed with a column filled with silica gel [elution with chloroform–carbon tetrachloride (1:2)]. The process was monitored by thin-layer chromatography (TLC) on Silufol (CCl_4). Workup gave 100 mg (70%) of 2-chloroindole with mp 72-73°C and 25 mg (15%) of 3-chloroindole with mp 89-91°C. According to the literature data, 2-chloroindole had mp 72-76°C [4], and 3-chloroindole had mp 91.5°C [5].

Preparation and Pyrolysis of 3-Indolylphenyliodonium Bromide. As in the preceding experiment, the reaction of 950 mg (3 mmole) of 3-indolylphenyliodonium betaine and 0.5 ml of concentrated hydrobromic acid (48%) gave 1 g (83%) of 3-indolylphenyliodonium bromide with mp 73-75°C (dec.), pyrolysis of which gave 315 mg (64%) of 3-bromoindole with mp 66-67°C (mp 67°C [5]).

1-Benzyl-2-chloroindole. A solution of 640 mg (2 mmole) of the betaine and 250 mg of benzyl chloride in 6 ml of dry DMSO was heated at 100°C for 2 h, after which it was cooled and diluted with water, and the aqueous mixture was extracted with benzene. The extract was dried with anhydrous magnesium sulfate, the solvent was removed *in vacuo*, and the residue was chromatographed with a column filled with silica gel (elution with carbon tetrachloride) to give 145 mg (30%) of 1-benzyl-2-chloroindole with mp 72-74°C (mp 73.5-75.5°C [4]).

(1-Methyl-3-indolyl)phenylidonium Methosulfate. A 1.89-g [1.55 ml (15 mmole)] sample of dimethyl sulfate was added dropwise at 20°C to a stirred suspension of 3.19 g (10 mmole) of 3-indolylphenyliodonium betaine in 10 ml of ethanol, and the mixture was stirred for 10 min. Ether (50 ml) was then added to the solution, and the resulting precipitate was removed by filtration to give 3.7 g (83%) of a product with mp 91-92°C (dec.). Reprecipitation from methanol by the addition of ether gave a product with mp 93-94°C (dec.). Found: C 42.8; H 3.7%. $C_{16}H_{16}INO_4S$. Calculated: C 43.2; H 3.6%.

1-Methyl-2-chloroindole. A) A solution of 0.9 g (2 mmole) of (1-methyl-3-indolyl)phenyliodonium methosulfate and 0.17 g (4 mmole) of lithium chloride in 8 ml of DMSO was heated at 100°C for 2 h, after which it was cooled and poured into water. The aqueous mixture was extracted with benzene, and the extract was washed several times with water and dried with anhydrous magnesium sulfate. It was then evaporated to a minimal volume and separated chromatographically with a column filled with silica gel [elution with ether—petroleum ether (1: 2)] to give 194 mg (60%) of 1-methyl-2-chloroindole with mp 63-64°C (mp 64-65°C [6]).

B) A mixture of 250 mg of 1-methyloxindole, 425 mg (0.2 ml) of phosphorus oxychloride, and 8 ml of chloroform was refluxed for 15 h, after which it was cooled and treated with 40 ml of a 5% solution of sodium hydrocarbonate. The organic layer was separated, and the aqueous layer was extracted with chloroform. The solvent was evaporated, and the residue was chromatographed with a column as in the preceding experiment to give 99 mg (35%) of 1-methyl-2-chloroindole with mp 62-63°C. The IR spectrum (mineral oil) was identical to the spectrum of a sample of the compound obtained in the preceding experiment.

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MASS-SPECTROMETRIC DETERMINATION OF THE TAUTOMERIC FORMS OF ALKYL(ARYL)BENZAZOLYLAZOKETOXIMES

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A mass-spectrometric study of a series of alkyl(aryl)benzazolylazoketoximes as compared with arylazoketoxime was made. The ratios of the tautomers (oxime ⇄ nitroso) in the gas phase at the moment of vaporization of the samples were determined. It is shown that the ratios of the tautomers are determined by both the basicity of the heterocycle and the character of the substituent attached to the methylidyne carbon atom.

The quantitative ratios of the tautomers and the relationship between the position of the tautomeric equilibrium and the aggregate state of the substances are of undoubted interest in the study of the tautomerism of organic compounds [1]. Mass spectrometry has been used with increasing frequency for the solution of these problems in recent years. The ratios of the tautomers in the composition of the molecular ions (M^+) are evaluated quantitatively by summation of the relative intensities of the characteristic fragment that correspond to a certain form of tautomer with their subsequent normalization [2].

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