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NITROLYSIS (NITRATIVE CLEAVAGE) OF (INDOLYL-3) PHENYLIODONIUM SALTS

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Reactions of (Indolyl-3) phenyliodonium salts with sodium nitrite have been investigated. Effect of trifluoroacetate and tosylate as counterion was also studied. The mechanism of the reactions is discussed.

INTRODUCTION

Beringer and his colleagues (1953) have provided examples of reactions of diaryliodonium salts with simple inorganic anions which appear to involve only an S$_N$Ar (Nucleophilic Aromatic Substitution) reaction. For example, the reaction of diphenyliodonium bromide with sodium nitrite in aqueous solution gave nitrobenzene in 66% yield, while the reaction of phenyl-o-nitrophenyliodonium bromide with the same reagent afforded o-dinitrobenzene in 84% yield. No benzene was reported to have been formed. In the like manner, the reaction of unsymmetrically substituted diaryliodonium salts with nitrite ion in aqueous acetate gave, in a nucleophilic nitrolysis reaction, a mixture of corresponding nitroarenes (Olah *et. al.*, 1978). Similarly, Lubinkowski *et al.* (1978) reported that diphenyliodonium tetrafluoroborates with sodium nitrite in aqueous dioxane gave nitrobenzene in 72-76 % yield and a similar reaction with phenyl-p-totyl-iodonium tetrafluoroborate yielded a mixture of nitrobenzene and p-nitrobenzene in a ratio of 2.3:1. On the other hand, aromatic hydrocarbon formation was a major competing reaction when potassium cyanide was used as the inorganic salt thus suggesting a radical chain reaction.

In order to gain some insight into the factors determining whether the reaction of diaryliodonium salt (having indolyl as a ligand) with potassium nitrite will proceed mainly by an S$_N$Ar reaction or (presumably) by a radical chain reaction, we decided to investigate in some depth the reactions of (Indolyl-3) phenyliodonium salt with potassium nitrite.

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MATERIALS AND METHODS

Melting points were taken in capillary tubes. In this connection it was found that the iodonium salts decomposed near their meltiing points, which depended strongly on the duration of heating. Therefore after an approximate melting point had been taken, a new sample was introduced at about 10 °C below this point, and then the temperature was slowly raised. These melting points are not highly precise.

(Indolyl-3) phenyliodonium trifluoroacetate: Material of melting point 127-128 °C, wasprepared by th method of Chughtai *et al.* (1981).

(Indolyl-3) phenyliodonium tosylate: This salt, melting point 95-96 °C was obtained according to the procedure described by Chughtai *et al.* (1981).

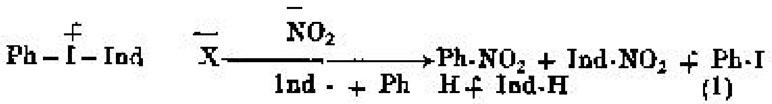
Reaction of (Indolyl-3) Phenyliodonium trifluoroacetate with potassium nitrite: The mixture of 0.595 g (0.007 mol) of potassium nitrite and 2.165 g (0.005 mol) of (Indolyl-3) phenyliodonium trifluoroacetate in 15 ml of dry DMSO was heated at 60 °C for two hours. At the end of reaction, the reaction mixture was poured into cold water, extracted twice with ether and the extract was dried over anhydrous magnesium sulphate. The reaction mixture was evaporated to its minimum volume which was then analyzed by chromatomass-spectrometry. The results are given in Table 1.

(Indolyl-3) phenliodonium tosylate and potassium nitrite: Using 2.455 g (0 005 mol) of (Indolyl-3) phenyliodonium tosylate, the reaction and analyses were performed as with (Indolyl-3) phenyliodonium trifluoroacetate. The results are shown in Table 1.

RESULTS AND DISCUSSION

To carry out the nitrolysis, indolyliodonium salts were heated with potassium nitrite in DMSO at 60 °C for 2.0 hours. The reaction was repeated in an inert atmosphere, one equivalent of 1,1-diphenylethylene was also added to the reaction mixture to see the effect on a competing free radical reaction.

It is clear from the data presented in Table 1 that nitrolysis of iodonium salts under investigation gave a number of products. Chromatographic separation of the reaction mixture and careful chromatomass-spectrometric analyses showed that the reaction of (Indolyl-3) phenyliodonium salts with ambident nitrite ion gave all possible products of this reaction (eq. 1).



$$\mathrm{Ph}-\overset{+}{\mathrm{I}}-\mathrm{Ind}\quad \overset{-}{\mathrm{X}}\xrightarrow[\mathrm{Ind}\cdot\ +\ \mathrm{Ph}\quad \mathrm{H}+\ \mathrm{Ind{\cdot}H}]{\overset{-}{\mathrm{NO_2}}}\mathrm{Ph{\cdot}NO_2}+\mathrm{Ind{\cdot}NO_2}+\mathrm{Ph{\cdot}I}\qquad (1)$$

$$(\mathrm{X}=\mathrm{CF_3COO}\ ,\ \mathrm{OTs}\ )$$

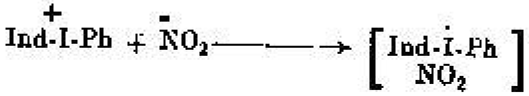
Table 1. *Total yields in the reactions of (Indolyl-3) phenyliodonium salts with potassium nitrite in DMSO at 60 °C for 2.0 hours*

Counteranion of iodonium salt	Special conditions	Nitro indol (%)	Iodo indol (%)	Nitro benzene (%)	Iodo benzene (%)	Indo (%)	Benzene (%)	Biphenyl (%)
CF_3COO^-	Air	25	23	22	24	17	16	Trace
	Argon	26	24	24	28	16	15	Trace
	Argon, DPE[a]	28	26	25	27	14	13	Trace
OTs^-	Air	24	25	26	25	16	14	Trace
	Argon	24	26	25	26	14	15	Trace
	Argon, DPE[a]	25	24	26	23	13	12	Trace

a = 1.0 equiv. of 1,1-diphenylethylene (DPE) present, of which 100% was recovered unchanged.

The orientation obtained in the reaction of nucleophiles with indolyliodonium salts is quite unexpected. It has recently been demonstrated that an aromatic nucleophilic mechanism is operating in the reaction of indolyliodonium salts and alkali metal halides (Chughtai *et al.*, 1981). However, formation of a number of products, especially aromatic hydrocarbons as a major competing reaction, clearly preclude a mechanism involving an aromatic nucleophilic displacement reaction. On the other hand, addition of 1,1-diphenylethylene as an inhibitor of a radical reaction to the reaction mixture, give similar products in nearly identical amounts. This perhaps suggests a typical radical chain reaction which leads to the parent hydrocarbons.

These results appear to be in better agreement with the suggestion of Beringer and Falk (1964) that two different reaction paths are available for formation of the arylated nucleophiles. With some nucleophiles and iodonium salts, the Normal nucleophilic Aromatic Substitution reaction occurs. In other cases which appear to be applicable to the reaction of indolyl-phenyliodonium salts with nitirite ion, the reaction proceeds (initiated by electron-transfer from $\bar{N}O_2$ to iodonium cation) via radical pairs in a solvent cage. This radical pair, under reaction conditions is dissociated into free radicals giving a number of products (eq. II). Such type of mechanism has also been supported by Gronowitz and Holm (1977).



$$\overset{+}{\text{Ind-I-Ph}} + \overset{-}{N}O_2 \longrightarrow \left[\begin{matrix}\text{Ind-}\dot{\text{I}}\text{-Ph}\\ NO_2\end{matrix}\right] \quad \text{Ind-I-Ph}\dot{N}O_2 \quad \text{(II)}$$

It was also observed that oxygen of the air did not influence the reactions of the (Indolyl-3) phenyliodonium salts with potassium nitrite. Similar results have been reported for the reactions of diaryliodonium salts with sodium alkoxides (Lubinkowski *et al.* 1975).

Substitution of trifluoroacetate for tosylate as counterion did not affect the product distribution in the nitration of (Indolyl-3) phenyliodonium salts. These results suggest that the counterion has no particular effect on the reactions.

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