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NITROBENZENE ALDEHYDE OXIDATIONS CATALYZED BY THE CONJUGATE BASES OF THIAZOLIUM IONS

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The increasing interest on thiazolium ion-catalyzed reactions[1], promts us to report our findings in this field.

Under the catalytic action of cyanide ion, nitrobenzaldehydes fail to afford benzoin[2] or benzoin-like[3] condensation products, giving rise, instead, to products of self oxido-reduction: nitro-, azo-, and azoxy- benzoic acids and esters. We find now a similar result when using the conjugate base of 3,4,5-trimethylthiazolium ion, I, as catalyst, in an attempted benzoin condensation of 4-nitrobenzaldehyde. These observations led us to study the feasibility of oxidizing aldehydes into acid derivatives by means of nitrobenzene, under the catalytic action of the conjugate bases of thiazolium ions. Some preliminary results are collected in the table.

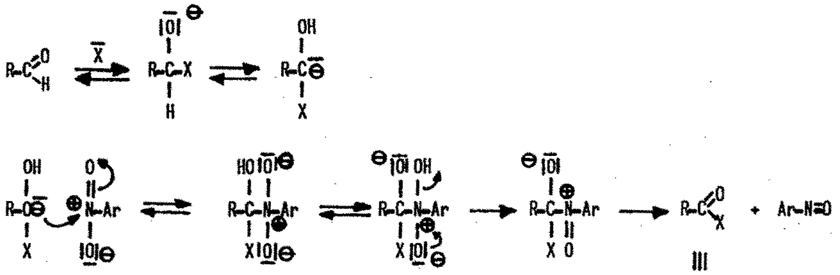
A typical ester preparation was as follows: a mixture of 5.79g of furfural, 7.43g of nitrobenzene, 1.54g of 3,4,5-trimethylthiazolium iodide, and 1.8 ml of triethylamine, in 50 ml of methanol was kept, under nitrogen, at 60º for 4 days. The mixture was treated with methylene chloride and water, and the organic layer was washed, dryed and evaporated. Distillation gave 79% yield of methyl 2-furoate together with excess of nitrobenzene. Column chromatography of the residue afforded 0.36g of azobenzene and 1.42g of azoxybenzene.

ALDEHYDE	CAT.	SOLVENT	OXIDATION PRODUCTS (%)	REDUCTION PRODUCTS
Benzaldehyde	IIa	CH_3OH	Methyl benzoate (59)	Azoxybenzene + aniline (traces)
Furfural	IIa	CH_3OH	Methyl 2-furoate (79)	Azoxybenzene + azobenzene
Furfural	IIb	CH_3OH	Methyl 2-furoate (65)	Azoxybenzene + azobenzene
Furfural	IIc	CH_3OH	Methyl 2-furoate (51)	Azoxybenzene + azobenzene
Furfural	IIa	Me_2CHOH	Isopropyl 2-furoate (23)	2-furoic acid anilide (traces)
4-Nitrobenzaldehyde[a]	IIa	DMF	4-Nitrobenzoic acid[b]	Not studied
4-Nitrobenzaldehyde[a]	IIa	CH_3OH	Methyl 4-nitrobenzoate (62)	Dimethyl azoxybenzoate + dimethyl azobenzoate
Benzaldehyde	IIa	ϕNH_2	N-(4-Aminobenzhydril)aniline (84)[c]	

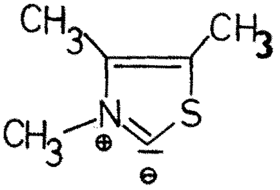
[a] No external nitrobenzene was used. [b] No yield is given because no attempt was made to purifie the product. [c] No Et_3N was added, and no oxido-reduction took place.

In a sense, the present nitrobenzene oxidations are similar to the cyanide catalized manganese dioxide oxidations of aldehydes and related groups[4,5].

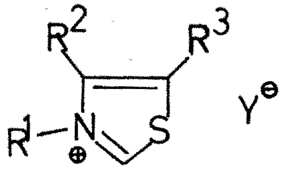
A reasonable mechanism, based on the analogy between a carbonyl and a nitro group, could be the one depicted in the scheme. The nitroso compound would be further reduced by an analogous mechanism, leading to the complex reduction mixtures, while the acyl derivative, III, would react with the pertinent nucleophile. In no case benzoins or furoin were detected[6].



$R\text{-}C(=O)X + MeOH \longrightarrow R\text{-}COOCH_3 + XH$; $\bar{X} = I$



I



IIa: $R^1 = R^2 = R^3 = CH_3$, $Y = I$
IIb: $R^1 = \phi CH_2$, $R^2 = CH_3$, $R^3 = H$, $Y = Cl$
IIc: $R^1 = CH_3$, $R^2 = R^3 = \phi$, $Y = I$

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