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ELECTROGENERATION OF N,O-DIAROYL-N-ARYLHYDROXYLAMINES AS PRECURSOR OF AROMATIC AMIDES.

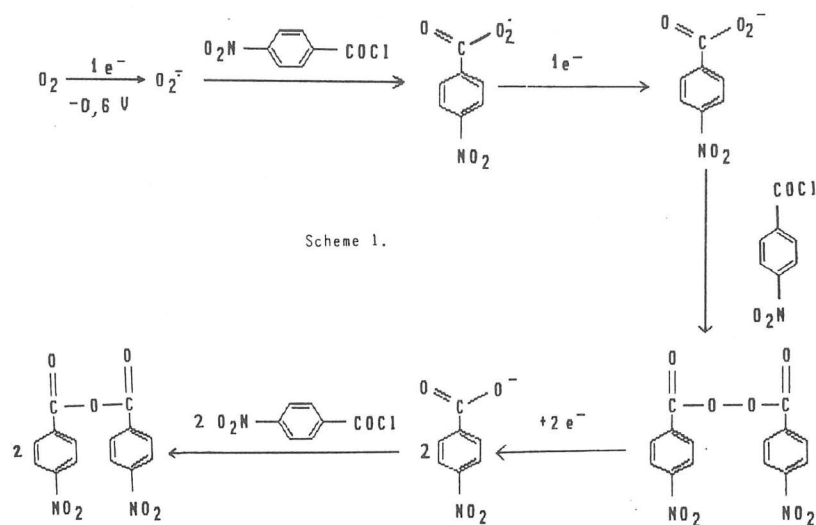
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In the present paper we show the cathodic reduction of aroyl chlorides with electron-withdrawing substituents (the nitro group) in ortho- and para- positions. Both compounds behave differently as expected by other aroyl chlorides<sup>(1-5)</sup> already studied by us.

Cyclic voltammetry of 4-nitrobenzoyl chloride shows a single irreversible reduction peak at -0.60 V vs SCE and for the 2-nitrobenzoyl chloride an irreversible peak at -1.2 V vs SCE (the delocalization would be prevented).

Preparative electrolysis in an aprotic medium (dry acetone - LiClO<sub>4</sub>), at controlled cathodic potential, were carried out in both cases.

When the reaction is run with the 4-nitrobenzoyl chloride in presence of oxygen, large amount of lithium 4-nitrobenzoate was formed. 4-Nitrobenzoyl peroxide was detected by TLC and the electricity consumption was 2 F mol<sup>-1</sup>.



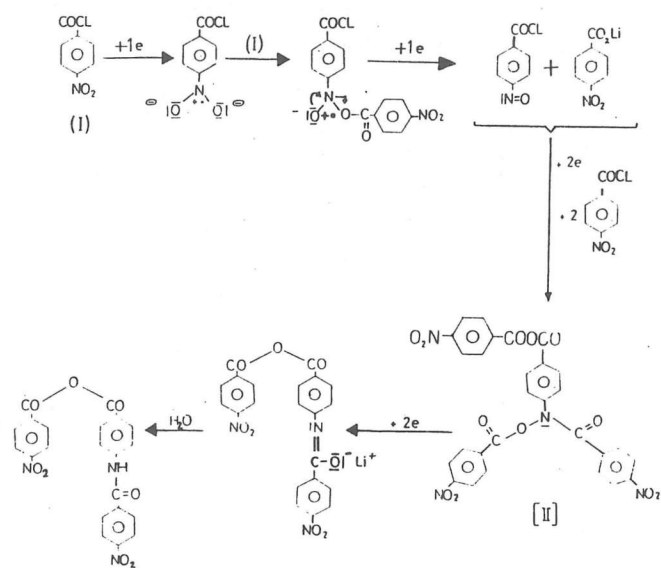
If the reaction is stopped when only 1 F mol<sup>-1</sup> is consumed 4-nitrobenzoic anhydride is formed. The process is summarized in scheme 1.

To prevent the formation of the above compounds the cathodic reduction of 4-nitrobenzoyl chloride is carried out under N<sub>2</sub> atmosphere. A flow of dry nitrogen was previously bubbled through the catholyte solution until total removal of oxygen.

The reduction consumed 1,5 F mol<sup>-1</sup> of electricity. The solvent was removed under reduced pressure and the crude washed with water. N-(4'-nitrobenzoyl)-4-aminobenzoic acid 4-nitrobenzoic acid anhydride was formed in 94% yield.

This product could be explained if we assume that some water was present in the reaction medium. To discard this possibility we have put a small amount of water in the reaction cell. The only product obtained was lithium p-nitrobenzoate. Under these conditions the -COCl group is hydrolysed and the carboxylic acids undergoes the cathodic reduction.

Our results are summarized in scheme 2.



Scheme 2.

Because the reduction potentials of intermediates are more positive than the reduction potential of the starting material it is not possible to isolate them. However, indirect experimental evidences to support this route can be pointed out. We synthesized N,O-dibenzoylphenyl-hydroxylamine<sup>(6)</sup> as a model compound of the intermediate structure (II). This compound was reduced at -0.70 vs SCE, the electrolysis consumed 2 F mol<sup>-1</sup> leading to benzanilide and lithium benzoate in nearly quantitative yield.

Analogous results were found when the 2-nitrobenzoyl chloride was electrolyzed.

When we carried out the cathodic reduction of nitrobenzene in presence of benzoyl chloride, N,O-Dibenzoyl-N-phenyl hydroxylamine, benzanilide and lithium benzoate were obtained.

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