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A CONVENIENT SYNTHESIS OF ARYL NITROSO COMPOUNDS

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Abstract: Aromatic C-nitroso compounds may be conveniently prepared by oxidation of hydroxylamines with PCC in THF.

Aryl C-nitroso compounds are useful intermediates for the synthesis of a variety of azo- and azoxy- derivatives, as well as being valuable end-products in themselves. Since comparatively few methods are available for their synthesis, new methods, such as that reported herein, are of considerable value.

Aryl C-nitroso compounds are usually prepared by reduction of a nitro compound to the hydroxylamine oxidation level and re-oxidation to the desired nitroso state, because it is not normally possible to stop the reduction of the nitro group at the nitroso oxidation level. A variety of methods are available for the preparation of hydroxylamines, but the most convenient, developed in these laboratories, involves catalytic transfer hydrogenation of the nitro group using a rhodium catalyst and hydrazine hydrate as the hydrogen donor.[1] Using this procedure a large range of aryl hydroxylamines are available in good yield. Tin (II) chloride also effectively reduces nitro to hydroxylamine, although this reagent must be used stoichiometrically.[2]

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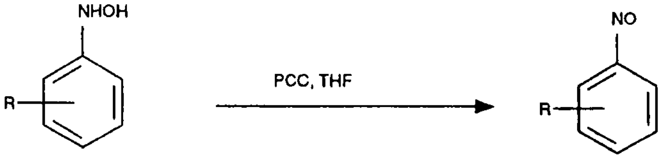


Scheme 1

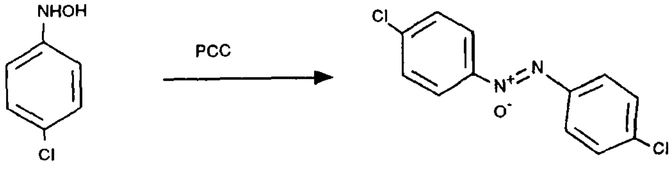
Only one reagent, $FeCl_3$, has been regularly used to oxidise hydroxylamines to nitroso.[3] This reagent, which is used under aqueous conditions, caused several problems in our work because some aryl nitroso compounds appeared to form hydrates which were difficult to dehydrate. In addition the compounds obtained by this method were fine powders which were generally difficult to filter. We therefore looked for an alternative method for selectively oxidising hydroxylamines to the nitroso oxidation state without over-oxidation. By analogy with the oxidation of primary alcohols to aldehydes, we considered the use of pyridinium chlorochromate (PCC),[4] a widely used oxidant which does not overoxidise alcohols to acids. We found that PCC in THF was a very effective, clean reagent for the preparation of aryl C-nitroso compounds on a laboratory scale.

A small selection of aryl hydroxylamines was oxidised by this method in good to excellent yield (Table 1). In addition, one aliphatic hydroxylamine has oxidised, although in this case the yield was only moderate. In the oxidation of 5-chlorophenylhydroxyamine (Scheme 2), a product arising from condensation of the product nitroso compound and the hydroylamine starting material was obtained. This type of condensation is well known.[5,6]

In conclusion, we have demonstrated a new method for the oxidation of the hydroxylamine group to the nitroso group that is simple to perform and gives

Table 1: Oxidation of Aryl Hydroxylamines with PCC

Entry	Product	Yield
1	4'-Ethoxy-4-nitrosobenzanilide	55
2	2'-Carboethoxy-4-nitrosobenzanilide	83
3	3'-Carboethoxy-4-nitrosobenzanilide	83
4	N-Cyclohexyl-4-nitrosobenzanilide	66
5	4-Nitrosobenzanilide	90
6	Nitrosocyclohexane	49



Scheme 2

good yields of readily isolable material. Furthermore the reagent used is well-known to be milder than other chromium oxidising agents. We believe this method has merit as a general synthesis of aryl and alkyl nitroso compounds.

Typical Experimental Procedure

4-Hydroxylaminobenzanilide (0.6 g, 2.6 mmol) was dissolved in THF (50ml) at room temperature and PCC (0.65 g, 3.0 mmol) was added. After 10 minutes t.l.c (1:1, hexane:ethylacetate) showed that the reaction was complete and the mixture was filtered through a dry pad of silica gel (flash grade) eluting with the same solvent mixture. The resulting solution was concentrated *in vacuo* to give the product (0.54 g, 90 %). M^+ 227 (M^++H); $C_{13}H_{16}N_2O_2$ requires C, 69.0; H, 4.5; N, 12.4; found C, 69.0; H, 4.6; N, 12.1%.

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