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SODIUM PERBORATE - A CHEAP AND EFFECTIVE REAGENT FOR THE OXIDATION OF ANILINES AND SULPHIDES

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ABSTRACT Sodium perborate in acetic acid is an effective reagent for the oxidation of anilines to the corresponding nitroarenes; it is also highly effective for the oxidation of sulphides to either sulphoxides or sulphones.

Oxidation is a fundamental process in organic chemistry and the introduction of new reagents and the modification of existing ones is a continuous challenge. Reagents are now available for almost every conceivable type of oxidation, but in very many instances there are disadvantages associated with their use: high cost, difficulty in handling, lack of sensitivity, toxicity, instability, etc. Sodium perborate, the formula of which is almost invariably given as $NaBO_3.nH_2O$ (n = 1-4), is in fact the heterocycle 1,[1] and is a very cheap, large scale industrial chemical (over 500,000 tons per annum) which is used primarily as a source of "active oxygen" in detergents and as a mild antiseptic and a mouthwash. Surprisingly, there has been very little study of possible applications of this stable, crystalline and easily handled oxidant to organic synthesis. As far as we are aware it has only been used for the cleavage of α-diketones,[2] for the low yield epoxidation of a number of quinones,[3] for the oxidation of anilines to azo compounds,[4,5] and for the oxidation of alkenylboronic acids.[6] We now describe the preliminary results of an investigation of the oxidation of anilines and sulphides by sodium perborate.

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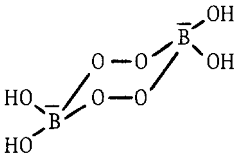


$2Na^+$ 0 - 6 H_2O

Anilines containing electron-withdrawing groups are smoothly oxidised to the corresponding nitroarenes in excellent yield on treatment with sodium perborate. The reaction is best carried out in glacial acetic acid and 50-55°C was found to be the optimum temperature. Completion of reaction is signalled by the separation of colourless crystalline sodium borate. Representative examples are listed in Table I, together with available comparative data for the three other reagents most commonly used for this transformation. Yields for the perborate oxidations are at least comparable to those obtained with the other reagents, and given the cheapness of the perborate, together with its non-toxic nature and ease of safe handling, it should be the reagent of choice for such oxidations.

TABLE I

Oxidation of Anilines to Nitroarenes

	Reagent and Yield, %			
$ArNH_2$	Sodium Perborate[a]	CH_3CO_3H[7]	CF_3CO_3H[8]	90% H_2O_2/CF_3COOH[8]
Ar=4-ClC_6H_4	92	62	87	
2,6-$Cl_2C_6H_3$	87			
2,4,6-$Cl_3C_6H_2$	82			
4-BrC_6H_4	88		90	85
2-$O_2NC_6H_4$	76		92	81
4-$O_2NC_6H_4$	85		94	86
2-NCC_6H_4	89			
4-NCC_6H_4	91		96	98
4-$CH_3COC_6H_4$	73			
4-$C_2H_5OOCC_6H_4$	84	66	99	

[a] Refers to pure, recrystallised or redistilled products

Anilines containing electron donating groups are also oxidised to nitroarenes under similar conditions, but overoxidation also occurs to a variable extent depending on the substrate and the products are always contaminated by tarry materials. The yields of pure nitroarenes are, therefore, moderate (45-80%) but this is of little consequence as these compounds are generally readily accessible by direct nitration methods. Interestingly, 2- and 4-aminopyridine are unaffected under the above conditions, but 3-aminopyridine was oxidised rapidly to a black tar, as were all anilines investigated which contained a phenolic OH group.

We next examined the use of sodium perborate for the oxidation of sulphides. Under identical conditions to those used for oxidation of anilines, or alternatively using 50% aqueous methanolic sodium hydroxide, and using an excess of perborate, sulphides were smoothly oxidised to the corresponding sulphones in excellent yield. When only a small excess of oxidant was employed in acetic acid solution, the sulphoxides were obtained in good yield; in each case a few percent of the sulphone was also present and was easily removed by chromatography. Representative data are given in Table II.

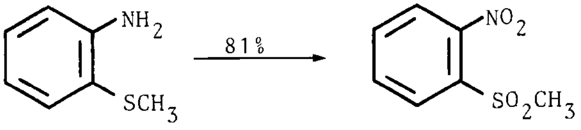
TABLE II

Oxidation of Sulphides to Sulphoxides and Sulphones

Sulphide R-S-R^1		Sulphoxide[a] Yield, %	Sulphone[a] Yield, %
n-C_4H_9	n-C_4H_9	93	99
t-C_4H_9	t-C_4H_9	72	97
C_6H_5	CH_3	70	94
4-$CH_3C_6H_4$	CH_3	75	91
4-ClC_6H_4	CH_3	85	98
C_6H_5	C_6H_5	71	98

[a] Refers to pure, recrystallised or redistilled products

Clearly sodium perborate is particularly effective for the sulphide → sulphone transformation. Moreover, oxidation of both an amino group and a sulphide can be readily accomplished; treatment of 2, for example, with an excess of oxidant in acetic acid gave 3 in 81% yield.



2 3

The above results clearly demonstrate that sodium perborate is indeed a highly effective reagent for the transformations studied. It also shows an attractive degree of selectivity with respect to other functional groups. Alcohols are unaffected, and olefins only very slowly oxidised, if at all, under the standard conditions employed. An additional but by no means unimportant aspect of the use of sodium perborate is that the byproducts are completely innocuous - thousands of tons are discharged into drainage systems every day - and hence there is no effluent problem in large scale applications

We are currently studying the use of sodium perborate in a variety of other oxidations and will report the results in due course.

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