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SURFACTANT CONTROL OF THE ORTHO/PARA RATIO IN THE BROMINATION OF ANILINES.

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Summary: Products of the bromination reaction of a family of anilines have been examined both in homogeneous solution and in the presence of cethyltrimethylammonium bromide (CTAB). The presence of the surfactant induces a high regioselectivity that is opposite to that observed under homogeneous conditions: a high ortho/para ratio has been observed which increases with greater steric hindrance in the ortho position.

There have recently been many attempts to obtain product or regioselectivity control(1) by the use of micelles or similar submicroscopic aggregates, and limited success has generally been achieved.We report the unexpected behaviour observed in bromination of a series of anilines.

Electron releasing substituents in the phenyl group have an ortho/para orienting effect in electrophilic aromatic substitution(2), generally with a low o/p ratio. An increase in the bulk of the substituent on the amino group decreases the amount of the ortho isomer(2). We observed this behaviour in the bromination of a family of anilines under homogeneous conditions (Table) in $CHCl_3$, MeOH and H_2O. Surprisingly, an opposite trend was observed when the reaction was carried out in an aqueous solution of bromine and cethyltrimethylammonium bromide (CTAB), moreover an increase in the steric bulk of the ammino group increased the o/p ratio. Similar behaviour has been observed in the chlorination of phenol by alkyl hypochlorites(1e); however in that case, the increase in the o/p ratio was obtained with the chlorinating agent chemically bound to the surfactant.

A possible explanation for our results is that interaction between Br_3^- and the cationic head groups is so strong and specific that it localizes Br_3^- in a well defined position(3), very close to the ortho position of the aniline. This hypothesis could explain the high ortho:para ratio observed in the reaction carried out in an aqueous solution of CTAB but does not justify its increase with increasing bulk of the R substituent (Table). Replacing H with Me on the amino group changes the hydrophobic/hydrophilic balance of the aniline so that the part of the molecule that was hydrophilic becomes hydrophobic; consequently, the orientation of the aniline at the surface of the aggregate changes. This change can bring the ortho position of the aniline close to Br_3^-. This proximity effect induced by the aggregate overcomes steric

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hindrance due to substitution at the amino group and strongly favours bromination at the ortho position.

The hypothesis that the ammonium head group could be in some way responsible of the observed effect is rejected since in the bromination reaction carried out in an aqueous solution of tetrabuthylammonium bromide we obtained a low o/p ratio.

Table. Isomer* distribution in the bromination of anilines at 0° C, in various media

	aniline		N-methylaniline		N,N-dimethylaniline	
	%o	%p	%o	%p	%o	%p
$CHCl_3$	10	90	-	100	-	100
$CHCl_3$/TBAB	5	95	-	100	-	100
MeOH/LiBr	5	95	5	95	5	95
H_2O/LiBr	10	90	5	95	5	95
H_2O/TBAB	10	90	5	95	5	95
H_2O/CTAB	40	60	60	40	70	30

*Yields in monobrominated products were always higher than 90% with the exception of the reaction in H_2O/TBAB which gave 60%.

Experimental: all the reactions were carried out adding 0.50 mmoles of aniline to a 50 mL stirred solution 0.01 M in bromine and 0.05 M in bromide (if present) at 0° C. After a few minutes bromine colour disappeared; the reaction mixture was first washed with 0.10 M Na_2CO_3 solution, then concentrated and analyzed. For what concerns the reactions carried out in aqueous solution, they were first extracted with ether and the ether fraction neutralized. The reactions carried out in aqueous solutions of TBAB and CTAB were performed in presence of a yellow precipitate. Inverting the addition order, i.e. adding bromine to a solution of aniline, did not change products distribution.

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