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HOMOLYTIC AMINATION OF AROMATIC COMPOUNDS BY REDOX SYSTEMS. REACTIVITY AND ORIENTATION.

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RECENTLY we[1] have obtained the amination of olefins and aromatics by three different redox systems. Most of the results agree with the formation of amino radicals in the redox systems:

$$NH_2OSO_3H + Fe^{++} \longrightarrow \cdot\overset{+}{N}H_3 + Fe^{+++} + SO_4^{--}$$

$$NH_2OH.HCl + Fe^{++} \longrightarrow \cdot NH_2 + Fe^{+++} + Cl^-$$

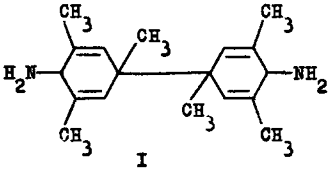
$$R_2NCl + Fe^{++} \longrightarrow R_2N\cdot + FeCl^{++}$$

Here we report some data on reactivity and orientation in the amination of aromatic compounds by these redox systems.

Hydroxylamine-O-sulfonic acid. The reactions were carried out at room temperature (18-20°C) by adding a methanolic solution of $FeCl_2$ to the methanolic solution of the aromatic substratum and the NH_2OSO_3H. Aromatic amines are the sole basic product of the reaction and were analyzed by gas-liquid chromatography and I.R. spectra. Yields are in the range of 10-40%. The relative rates were calculated from the amounts of aromatic amines in competitive reactions[2].

Both reactivity and orientation point to an electrophilic character of the attacking species (electrophilic radical) (tables 1 and 2).

Hydroxylamine. The NH_2OH/Ti^{+++} redox system, which allows to work at room temperature, leads to exclusive aromatic substitution only with compounds activated by strong electron-releasing groups, as anisole[3]. Less activated aromatics lead to diaminodicyclohexadienyls: in the case of mesitylene the compound I was actually isolated[4].



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Therefore we used $NH_2OH.HCl$ and $FeCl_2$ in boiling methanol,as in the case of amino-chlorination of olefinic bonds[5].Yields are rather low (5-15%),NH_2OH being reduced by ferrous salt and also oxidised by ferric salt,but the aromatic amines are the sole basic product of the reaction.

Reactivity and orientation(tables 1 and 2) are considerably different from those obtained with NH_2OSO_3H.The attacking species shows a lower electrophilic character;toluene has higher reactivity compared with anisole,which however is always charaterised by a complete selectivity in ortho-para positions.

N-chlorodialkylamines.The use of N-chlorodialkylamines makes the comparison with the former redox systems less significant owing to the high sensitivity of these reactions to steric influence,which is shown by dramatic changes in ortho-para ratio in the amination of anisole by hydroxylamine and N-oxypiperidine[1].The possibility of N-chloroamines to act as electrophilic and radical agent of chlorination does not allow an extensive and correct application of the competitive method and requires different reaction conditions for various aromatic substrata.

With benzene,toluene and meta-xylene the reaction was carried out at room temperature (20-30°) in 15-30 minutes by adding solid $FeSO_4.7H_2O$ to a solution of the aromatic compound and the N-chloroamine in acetic and sulfuric acid (ratio 1:3) (yields 60-80%).

Naphtalene and solid N-chlorodimethylamine sulphate were dissolved in CF_3COOH and solid $FeSO_4.7H_2O$ added at 20-30°C.

In the case of anisole in acidic medium a good solvent of $FeSO_4$ was required in order that the reaction between ferrous salt and N-chloroamine could compete with the electrophilic chlorination of the anisole; therefore a solution of N-chloroamine in conc. H_2SO_4 was added to a methanolic solution of anisole and $FeSO_4$ at 20-35°C. Under these conditions toluene and benzene react only in traces and this fact indicates an electrophilic character of the attacking species, which is pointed out also by competitive reactions (table 2).

The high amount of meta isomer in the case of toluene and meta-xylene can be related with a steric hindrance in the ortho positions and with the radical character of the attacking species.

The simultaneous formation of benzyl chlorides observed in the amination of toluene and meta-xylene is significant with regard to the radical character of the reaction and shows a competition between the attack on the ring and the methyl group by amino radical ion:

$$C_6H_5\text{-}CH_3 + R_2\dot{N}H^+ \longrightarrow C_6H_5\text{-}CH_2^{\bullet} + R_2NH_2^+$$

$$C_6H_5\text{-}CH_2^{\bullet} + FeCl^{++} \longrightarrow C_6H_5\text{-}CH_2\text{-}Cl + Fe^{++}$$

$$C_6H_5\text{-}CH_2^{\bullet} + R_2NHCl^+ \longrightarrow C_6H_5\text{-}CH_2\text{-}Cl + R_2\dot{N}H^+$$

The formation of amino radicals by the redox system,

$$R_2NHCl^+ + Fe^{++} \longrightarrow R_2\dot{N}H^+ + Fe^{+++} + Cl^-$$

would indicate that this process should not occur through an electron transfer, but by a chlorine transfer, as already indicated for unprotonated N-chloroamines[6]:

$$R_2NHCl^+ + Fe^{++} \longrightarrow R_2NH^+ \text{-}\text{-}\text{-} Cl \text{-}\text{-}\text{-} Fe^{++} \longrightarrow R_2\dot{N}H^+ + FeCl^{++}$$

The same isomer distribution was recently[7] observed in the thermic and photochemical amination of toluene by protonated N-chloroamines, in which probably the same amino radicals are involved in a radical chain addition of the protonated N-chloroamines followed by HCl elimination.

The protonation of the N-chloropiperidine determines in the case of anisole only a slightly higher ortho-para ratio in comparison with that of unprotonated N-chloropiperidine[1].

Table 1. Orientation.

Toluene

	ortho%	meta%	para%
NH_2OSO_3H	37	21,5	41,5
NH_2OH	41,2	19,5	39,3
$(CH_3)_2NCl$	9	53	38

Anisole

	ortho%	meta%	para%
NH_2OSO_3H	34	-	66
NH_2OH	52	-	48
$C_5H_{10}NCl$	9,3	-	90,7

Meta-xylene

	2,6-dimethylamino%	2,4-dimethylamino%	3,5-dimethylamino%
NH_2OSO_3H	10,8	78,3	10,9
NH_2OH	21,6	68,2	10,2
$(CH_3)_2NCl$	0,5	28	71,5

Naphtalene

	alpha	beta
NH_2OSO_3H	76,8	23,2
NH_2OH	40,4	59,6
$(CH_3)_2NCl$	97	3

Para-methylanisole

	2-amino-4-methylanisole%	3-amino-4-methylanisole%
NH_2OSO_3H	88,5	11,5
NH_2OH	51,9	48,1

Table 2. REACTIVITY IN COMPETITIVE REACTIONS.

		NH_2OSO_3H	NH_2OH	$(CH_3)_2NCl$
toluene benzene	K_t/K_b	3,1	2,4	4,6
anisole benzene	K_a/K_b	7,9	1,7	—
anisole toluene	K_a/K_t	2,6	0,7	—
mesitylene toluene	K_m/K_t	3,0	1,4	—
metaxylene benzene	K_m/K_b	—	—	5,5

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