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CHEMISTRY OF THE AMINO RADICAL IONS.
A NEW CHAIN PROCESS OF THE PROTONATED N-CHLORAMINES.

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Summary: α -*Deprotonation of amino radical cation occurs competitively with intramolecular hydrogen abstraction or aromatic amination depending on the acidity of the medium.*

Amino radical cations, $R_2\overset{+\bullet}{N}H$, are very interesting species involved in chemical[1] and biological processes[2].

Protonated N-haloamines are important sources of these radicals, which give rise to several chain processes of high synthetic value (intra-[3] and intermolecular[1b] processes concerning alkane halogenation, aromatic[1c] and olefin amination[1a]). The great synthetic interest is often due to the exceptional selectivity caused by polar effects.

However most of theese chain processes do not occur when the same species, $R_2\overset{+\bullet}{N}H$, are generated from different sources (i. e. chemical or elettrochemical oxidation of amines[4], photolysis of N-nitrosoamines[5]).

The main difference is constituted by the strong acidic medium used with N-chloramines.

Now we report a new radical chain of protonated N-chloramines, which well explains this behaviour.

Recently[6] we have shown how the dicyclohexyl-N-chloramine in sulphuric acid provides for the most selective method of benzylic chlorination of alkylbenzenes.

The reaction yields are however very sensitive to the concentration of sulfuric acid; thus we have investigated the reaction in the absence of alkylbenzenes at different concentrations of sulphuric acid.

The reaction, initiated by Fe(II) salt (eq. 1) at room temperature, leads to 4-chlorodicyclohexylamine (2) and the imine (3).

The results, at different concentrations of H_2SO_4, are reported in Table 1.

Table 1 - Reaction products of dicyclohexyl-N-chloramine

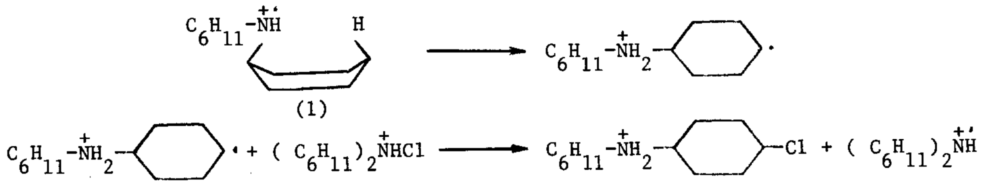
H_2SO_4 %	(2) mole %	(3) mole %	(2):(3)
96	97	3	32.3
92.5	93.4	6.6	14.2
90	91.9	8.1	11.3
80	82.4	17.6	4.7
75	60.0	40.0	1.5
CF_3COOH	22.5	77.5	0.3
CH_3COOH	trace	99.9	0.01

Two competitive processes (Schemes 1 and 2), involving the same amino radical cation intermediate (1), explain, in our opinion the results:

(eq. 1)

$$(C_6H_{11})_2\overset{+}{N}HCl + Fe^{2+} \longrightarrow (C_6H_{11})_2\overset{+\cdot}{N}H + Fe^{3+} + Cl^-$$

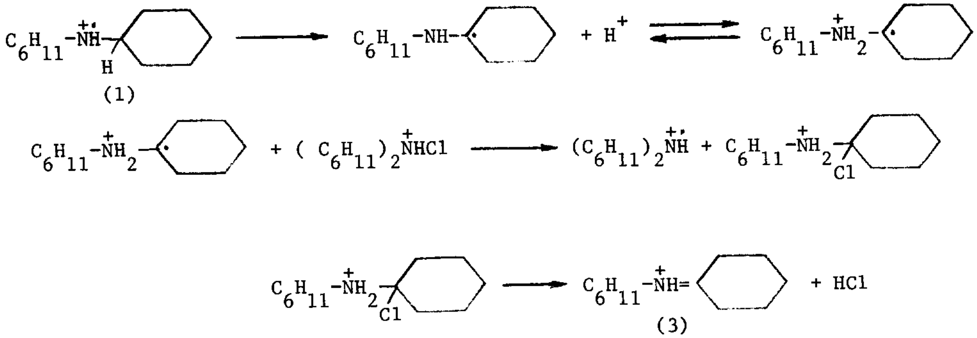
(1)



(1)

(2)

Scheme 1



(1)

(3)

Scheme 2

The chain of the Scheme 1 reproduces the well-known Hoffmann- Löffler reaction[3], with the peculiarity that the intramolecular hydrogen abstraction is slower compared with the acyclic dialkylamines because the cycloexyl group must be forced to the boat conformation.

Thus not only the intermolecular hydrogen abstraction from benzylic C-H bonds are quite selective, competitive processes[6], but also the chain of Scheme 2 competes with the intramolecular hydrogen abstraction.

The loss of a proton by (1) is strongly affected by the medium acidity and that is reflected by the increasing importance of the chain of Scheme 2 with the decreasing acidity.

In less acidic medium , CF_3COOH solution, compound (3) is obtained predominantly.

In a still less acidic medium, CH_3COOH solution, only the chain of the Scheme 2 occurs and (2) is not formed in significant amount.

The chain of Scheme 2 appears to be general for N-chloramine.

Thus methylbenzyl-N-chloramine very selectively reacts in concentrated H_2SO_4 in the presence of Fe(II) salt with benzene by a free-radical chain mechanism[1c] to give the amination product (4):

$$\mathrm{Ph{-}H + CH_3\overset{+}{N}HClCH_2Ph \longrightarrow \underset{(4)}{Ph{-}\overset{+}{N}H(CH_3)CH_2Ph} + HCl}$$

However decreasing the concentration of H_2SO_4, the competitive formation of the imine (5) $PhCH{=}\overset{+}{N}HCH_3$, becames always more important to the detriment of (4) and at 70% H_2SO_4 only traces of (4) are formed.

Table 2 - Reaction products of methylbenzyl-N-chloramine with benzene in H_2SO_4

H_2SO_4 %	(4) mole %	(5) mole %	(4):(5)
96	98.4	1.6	61.5
90	98.2	1.8	54.6
85	95.9	4.1	23.4
80	84.9	15.1	5.6
70	trace	99.9	<0.01

In all cases in the absence of Fe(II) salt under the same conditions no appreciable reaction takes place.

The imines (3) and (5) can be isolated as sulphates, but they undergo easy hydrolysis to carbonyl compounds (respectively cyclohexanone and benzaldehyde) and alkylamines (cyclohexylamine and methylamine).

These results allow, thus, to razionalize the acidity effect on the reactivity of protonated alkylamino radicals.

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