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RADICAL ADDITION OF PROTONATED N-CHLOROAMINES TO OLEFINS.

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Recently R.S.Neale[1] has reported that the protonated N-chloroamines add in good yields to certain substituted olefins, particularly vinyl chloroderivatives, whereas with unsubstituted olefins the reaction occurs in low yields or doesn't at all. The reasons adduced for this behaviour are the competing electrophilic chlorination and the assumption that the Cl-group may enhance the radical addition. The former reason is correct and it has been formulated also by us[2], the latter is in contrast with our previous results concerning the influence of substituents upon the radical addition of unprotonated N-chloroamines to olefins[2,3] and upon the homolytic aromatic amination of halobenzenes by protonated N-chloroamines[4]. In these cases the polar features of the amino radical prevail over the resonance stabilization of the intermediate alkyl radical,

$$R_2N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{\bullet}{C}}-X \longleftrightarrow R_2N-\overset{|}{\underset{|}{C}}-\overset{|}{C}=X\bullet$$

so that chlorobenzene is about tenfold less reactive than benzene and acrylonitrile and acrylates undergo no reaction with amino radicals. For the same reason chloroolefins also should react less than the corresponding unsubstituted olefins with unprotonated and protonated amino radicals so that the radical addition in the last case should be possible if only the ionic reaction could be avoided.

To avoid the ionic reaction we have used the same expedient already utilized for aminating with protonated N-chloroamines aromatic substrata strongly activated towards electrophilic chlorination, as anisole, acetanilide (in these cases 50-60% yields of amination are obtained[5]). That is, the N-chloroamine, dissolved in concentrated sulphuric acid, is dropped into a mixture of 65% sulphuric acid, ferrous sulphate (one mole for mole of N-chloroamine) and olefin. In this way, owing to the relatively high concentration of ferrous sulphate, the reduction of the protonated N-chloroamine,

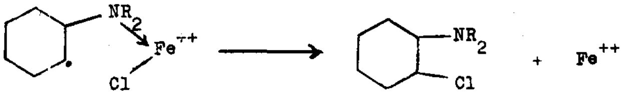
$$R_2\overset{+}{N}HCl \quad + \quad Fe^{++} \longrightarrow R_2\overset{+}{N}\underset{\bullet}{H} \quad + \quad FeCl^{++}$$

prevails over the electrophilic chlorination of the olefin.

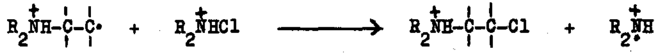
Actually under these conditions N-chloropiperidine adds to olefins, which are highly reactive towards electrophilic chlorination, as cyclohexene, styrene, cis 2-pentene and 1-hexene. We have not investigated the optimum conditions, which probably also depend upon solubility of the particular olefin and upon influence of the olefin on the solubility of the ferrous sulphate; moreover an alternative route, already described by us[2], is available for the radical addition of unprotonated N-chloroamines to these olefins. However the yields obtained with cyclohexene (54%) and styrene (58%) in these conditions clearly indicate that the radical addition of protonated N-chloroamines is not restricted to particularly substituted olefins, but it is also general with unsubstituted olefins.

With styrene the reaction product is the same already obtained with unprotonated N-chloroamine[2], C_6H_5-CHCl-CH_2-NC_5H_{10}; the orientation of the addition clearly indicates the radical character.

With cyclohexene both cis and trans isomers are obtained, but the cis stereoselectivity, observed with unprotonated N-chloropiperidine, is lost. This result corroborates our previous hypothesis[6] that the cis stereoselectivity may be correlated with a coordination of the unprotonated amino group with the ferric salt, which is mainly responsible for chlorine atom transfer:



In sulphuric acid a chlorine transfer from ferric salt is less probable; the transfer would occur by a radical chain,



$$R_2\overset{+}{N}H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \quad + \quad R_2\overset{+}{N}HCl \longrightarrow R_2\overset{+}{N}H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl \quad + \quad R_2\overset{+}{\underset{\cdot}{N}}H$$

the ferrous salt operating as initiator of chains, which would be relatively short owing to frequent termination by the same ferrous salt:

$$R_2\overset{+}{\underset{\cdot}{N}}H \quad + \quad Fe^{++} \quad + \quad H^{+} \longrightarrow R_2\overset{+}{N}H_2 \quad + \quad Fe^{+++}$$

Furthermore we have found, by a competitive experiment, that 1-chlorocyclohexene is <u>less reactive</u> than cyclohexene towards the radical addition of protonated N-chloroamines. From equimolecolar amounts of cyclohexene and chlorocyclohexene, N-2-chlorocyclohexylpiperidine and N-2,2-dichlorocyclohexylpiperidine are obtained in 4/1 ratio. This result shows the greater reactivity of the cyclohexene, even though it does not give the exact measure of the relative rates owing the lack of homogeneity of the solution.

A competitive experiment in homogeneous solution, as previously[2] described with unprotonated N-chloroamines, always starting from equimolecolar amounts of cyclohexene and chlorocyclohexene, has given more than 95% of N-2-chlorocyclohexylpiperidine.

These results confirm that also with vinyl chlorides the polar features of the protonated or unprotonated amino radicals (in the last case the amino radical can be considered coordinated with the ferric salt) prevail over the resonance stabilization of the incipient alkyl radical and that the contribution of polar forms to the transition state must determine the reactivity.

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