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NEW SYNTHESES BY AMINO RADICALS FROM N-CHLOROAMINES IN THE PRESENCE OF OLEFINS AND OXIDATION-REDUCTION SYSTEMS.

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N-chloroamines, in some respects, are analogous to organic peroxides. This analogy has been demonstrated by substituting N-chloroamines in some of the known reactions with peroxides — based upon interaction at low temperatures.[1]

(a) $R_2N\text{-}Cl + M^+ \longrightarrow R_2N^\cdot + MCl^+$; $M^+ = Cu^+$ or Fe^{++}

similar to that of organic peroxides:

(b) $ROOR' + M^+ \longrightarrow RO^\cdot + MOR'$

We have found that in the presence of butadiene and the oxidation-reduction systems, Fe^{+++}/Fe^{++} and Cu^{++}/Cu^+, the following main reactions take place:

(c) $R_2N^\cdot + M^+ + H_2O \longrightarrow R_2NH + MOH^+$

(d) $R_2N^\cdot + C_4H_6 \longrightarrow R_2N\text{-}C_4H_6^\cdot$

(e) $2\ R_2N\text{-}C_4H_6^\cdot \longrightarrow R_2N\text{-}(C_4H_6)_2\text{-}NR_2$

(f) $R_2N\text{-}C_4H_6^\cdot + MCl^+ \longrightarrow R_2N\text{-}C_4H_6\text{-}Cl + M^+$

On the other hand it is well known [2a,b] that the alkoxy radicals, formed in (b), can give rise to reactions analogous to (c), (d), (e) and (f), which as shown take place with the amino radicals.

According to reaction conditions and the oxidation-reduction system used, it is possible to direct the course of these reaction: excess of reducing salt favours the reduction of the amino radical according to (c) and diminishes the attack on the olefin. In order to promote reaction with the olefin, the reducing salt should be added to the mixture of the other reagents. The nature and concentration of the metal ions are also important. Excess of ferrous sulphate favours production of the dimer of the allylic radical according to

(d) and (e). Some aminochlorobutene is always formed in this reaction because as the concentration of $FeCl^{++}$ increases during the reaction, partial oxidation of the allylic radical by a transfer process takes place.[2b] As has been pointed out, it is possible to reduce the yield of the dimer or even to eliminate it entirely by oxidation of the allylic radical with ferric or cupric salts.

Moreover we have discovered that the radical addition reaction of N-chloroamines in presence of oxidation-reduction systems is general and even occurs in non-conjugated olefins such as cyclohexene and 1-hexene. The yield, calculated for the N-chloroamines, is lower in these cases (30-40%) than in the case of butadiene (70-80%), owing to the greater importance of the reaction (c), while the yields calculated for the olefin are always high.

It is of interest to emphasize the difference between the diacylamino radicals, arising from N-bromoimides, which cause abstraction of allylic hydrogens, and the dialkylamino radicals, which add to the ethylenic bonds. In our opinion the dialkylamino radical ions $R_2\overset{+}{\underset{\cdot}{N}}H$ should cause abstraction of allylic hydrogens instead of addition to olefins. The reactions, carried out in acid medium with copper and iron salts present, so far have proved unsuccessful, because halogenation reactions dominate. The presence of such dialkylamino radical ions have been invoked in the case of the Hoffmann-Loeffler reaction of N-chloroamines[3] and quite recently in the case of radical chain addition of N-chloroamines to butadiene[4] catalysed by strong acids. Actually the latter reaction seems to be limited to butadiene and probably to analogous dienes, since as pointed out, with other olefins the halogenation of the olefin occurs.

The experimental details of these processes will be published in Italian journals.

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