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NEW SYNTHESES BY AMINO RADICALS AND OXYGEN.
CONVERSION OF OLEFINS INTO α-AMINOKETONES.

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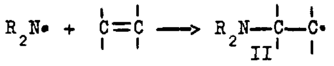
WE have pointed out recently[1] how the amino radicals,produced by the redox system N-chloroamine/ferrous or cuprous salt,

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

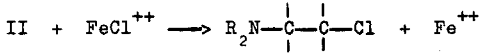
easily add to olefinic bonds,except when these are conjugated with strong electron withdrawing groups[2].

Now we describe a new synthesis of α-aminoketones from olefins,which affords a meaningful evidence for the radical mechanisms we have suggested for these reactions[1,2]. Our criterion is to interfere in a radical process, which takes place in several steps,by means of a competitive process,that is able to modify one of these steps.In the radical addition of N-chloroamines to olefins in presence of the oxidation-reduction systems Fe^{+++}/Fe^{++} or Cu^{++}/Cu^{+},we outlined three steps,as regards the main process[1,2]: the first one (a) is the oxidation-reduction process,which gives rise to the amino radical; in the second one (b) the radical attacks the olefin

(b) 

$$R_2N\cdot + \ce{>C=C<} \longrightarrow \underset{II}{R_2N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot}$$

and finally the oxidation of the alkyl radical takes place by ligand transfer, according to (c)

(c) 

$$II + FeCl^{++} \longrightarrow R_2N-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Cl + Fe^{++}$$

To verify this sequence we introduced a radical agent,the oxygen,which is unreactive towards the amino radicals and therefore does not interfere with steps (a) and (b),whereas is very reactive towards alkyl radicals,

TABLE 1

OLEFIN	N-CHLOROAMINE	α-AMINOKETONE	YIELD% (°)
Styrene	Dibutylamine	b.p. 123°/ 1mmHg	76
Styrene	Piperidine	b.p. 134°/ 0,9mmHg picrate m.p. 153°	61
Styrene	Morpholine	m.p. 52° picrate m.p. 158°	41,5
Trans-stilbene	Dibutylamine	m.p. 50° picrate m.p. 122°	21,7
Trans-stilbene	Piperidine	m.p. 86° picrate m.p. 144°	73
Trans-stilbene	Morpholine	m.p. 78° picrate m.p. 174°	43
Isosafrole	Piperidine	b.p. 178°/0,8mmHg picrate m.p. 194°	43
2-vinylpyridine	Dibutylamine		traces
2-vinylpyridine	Piperidine		traces

(°) Yield based on N-chloroamine.

especially the benzylic ones, with which it yields peroxy radicals

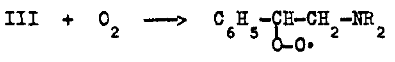
$$R\cdot + O_2 \longrightarrow R{-}O{-}O\cdot$$

When II is a secondary benzylic radical, the oxygen succeeds in beating entirely the competition of the interaction (c), so that only negligible amount of chloroderivative is obtained and the peroxy radical formed is reduced almost completely to ketone, as shown in Table 1.

For this process we suggest the following reaction sequence:

$$C_6H_5{-}CH{=}CH_2 + R_2N\cdot \longrightarrow C_6H_5{-}\underset{\bullet}{CH}{-}CH_2{-}NR_2$$

III



$$III + O_2 \longrightarrow C_6H_5{-}\underset{O{-}O\cdot}{CH}{-}CH_2{-}NR_2$$

IV

$$IV + Fe^{++} \longrightarrow C_6H_5{-}CO{-}CH_2{-}NR_2 + FeOH^{++}$$

The orientation in the attack on unsymmetric olefins was shown by IR analysis (a conjugated carbonyl was always present) and furthermore in the case of styrene by comparison with products obtained from phenacyle bromide and amines.

The yields are always high if based on the olefin but vary notably if based on the N-chloroamines. In our opinion polar and steric factors affect the reactivity of amino radicals in these reactions. Thus, N-chloropiperidine and N-chloromorpholine, nearly equivalent from the steric viewpoint, give rise to different yields owing to the different polar character of the corresponding amino radicals: because of its greater electrophilic character the morpholino radical is more sensitive than the piperidine-radical to the competitive reduction reaction :

$$R_2N\cdot + Fe^{++} + H_2O \longrightarrow R_2NH + FeOH^{++}$$

The very poor yields obtained with the 2-vinylpyridine (only traces revealed by IR analysis) confirm the influence of the electrophilic character of the amino radicals in their interaction with olefins, as we have pointed out recently[2]: the electron withdrawing effect of the pyridine nucleus on the olefinic bond would lower the contribution of polar forms to the transition state

$$R_2N\cdot \ + \ \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \longrightarrow R_2N_{(-)} \ (+) \ \overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$

The poor yield of N-chlorodibutylamine with stilbene in comparison with styrene is to be attributed,in our opinion,to steric hindrance.

When II is a radical arising from unconjugated olefins,the reaction shows lower selectivity: on the one hand the oxygen fails to beat completely the competition of the interaction (c),at least in our reaction conditions(oxygen at atmospheric pressure and temperature about 0°C) so that some aminochloroderivative is formed(15-20%);on the other hand the aminoketone,which is always the main reaction product,is accompanied by a smaller amount of the corresponding alcohol.That is the reduction of the peroxy radical yields some alcohol in addition to ketone.
Thus,cyclohexene and 1-butene,in the reaction with N-chloropiperidine and oxygen in presence of ferrous sulphate,give rise to α-aminoketones which are separated from the side-products(aminochloroderivatives and aminoalcohols)as picrates of respectives m.p. 140and 126°.

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