Tetrahedron Letters No. 6, pp. 357-360, 1963. Pergamon Press Ltd.
Printed in Great Britain.

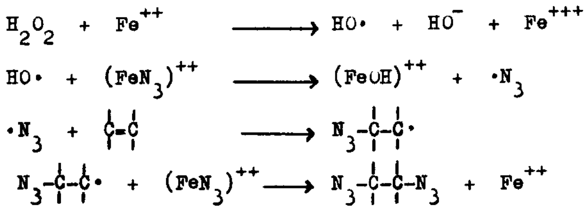
REACTIVITY OF HYDROXY AND ALKOXY RADICALS IN PRESENCE OF OLEFINS AND OXIDATION-REDUCTION SYSTEMS.

INTRODUCTION OF AZIDO, CHLORO AND ACYLOXY GROUPS IN ALLYLIC POSITION AND AZIDO-CHLORINATION OF OLEFINS

Francesco Minisci and Remo Galli
Istituto di chimica Generale del Politecnico Milano.

(Received 4 December 1962)

IN a previous letter[1] we pointed out how it is possible to add two azido groups to the olefinic double bond, according to a process which was outlined by us as follows:



$$H_2O_2 + Fe^{++} \longrightarrow HO\cdot + HO^- + Fe^{+++} \qquad (a)$$

$$HO\cdot + (FeN_3)^{++} \longrightarrow (FeOH)^{++} + \cdot N_3 \qquad (b)$$

$$\cdot N_3 + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \longrightarrow N_3-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot \qquad (c)$$

$$N_3-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + (FeN_3)^{++} \longrightarrow N_3-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-N_3 + Fe^{++} \qquad (d)$$

The last step (d) may be correlated with previous reactions of organic peroxides discovered by us[2], in which carbon free radicals, arising from peroxide decomposition, would react according to the scheme:

$$\text{Peroxide} + Me^+ \longrightarrow R\cdot + Me^{++}$$

$$R\cdot + (MeX)^+ \longrightarrow RX + Me^+$$

$Me^+ = Cu^+$ or Fe^{++}; $R\cdot$ = carbon free radical.

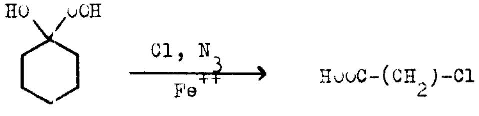
$X = Cl, Br, J, N_3, SCN, CN, S_2O_3Na, R'OCS_2$.

---

[1] F.Minisci and R.Galli, Tetrahedron Letters No.12, 533 (1962).

[2] F.Minisci,Ital.Pat. 580,012 (May 17, 1957);Communication to VIIIth National Congress of Chemistry,Torino,May 27, 1958: Gazz.Chim.Ital. **89** 626 (1959);La Chimica e l'Industria, **44**, 740 (1962).

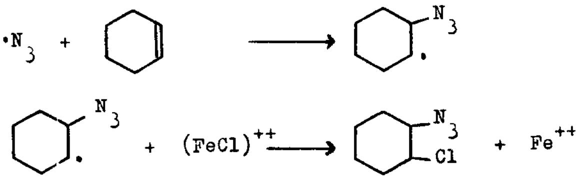
We have now examined the competitive reactivity in the formation of azido- and chlor-derivatives. Thus in the decomposition of cyclohexanone peroxide, simply indicated with the structure I , with ferrous salt in the presence of both chlorine and azido ions, we obtained mostly ε-chlorcaproic acid:


I

This result suggested that, if the addition of two azido groups occurs via the sequence outlined by us in (c) and (d), in carrying out the reaction in the presence of ferric chloride, we should obtain the azido-chlorination of the olefin. This actually occurred: thus, for instance, in the hydrogen peroxide decomposition with ferrous sulphate in the presence of sodium azide, ferric chlorine and cyclohexene, 1-chlor-2-azido-cyclohexane was obtained. The interactions resulting in the formation of this compound should, therefore, be the following:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + \cdot OH + OH^-$$

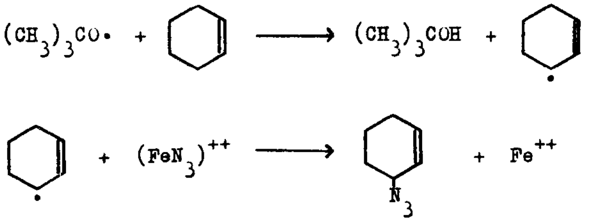
$$\cdot OH + (FeN_3)^{++} \longrightarrow (FeOH)^{++} + \cdot N_3$$



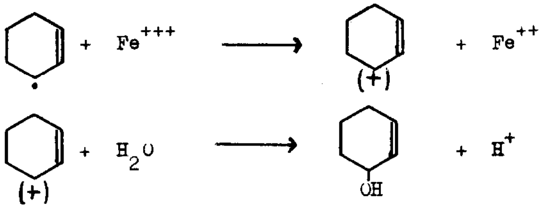
So this result, besides being a <u>new type of addition to olefins</u>, sheds new light on the addition mechanism of two azido groups to olefins and, in some respects, may be included in the general group of reactions, which also includes Sandmeyer's reaction of diazonium salts, which we have fully discussed previously[2].

The reaction occurs in a different way when t-butylhydroperoxide is used instead of hydrogen peroxide. In this case the prevalent reaction of the t-butyloxy radical, besides its further reduction to t-butylalcohol by the ferrous salt, results in a hydrogen atom abstraction, yielding an allylic radical and consequently azidocyclohexene:

$$(CH_3)_3COOH + Fe^{++} \longrightarrow (CH_3)_3CO\cdot + OH^- + Fe^{+++}$$



Similarly the corresponding chlorcyclohexene was obtained in presence of ferric chloride. Among the side products, cyclohexenol is formed. The latter can arise from hydrolysis of the allylic derivative or from the oxidation of the allylic radical by the oxidant ion, since the reaction is carried out in alcoholic-aqueous solution:



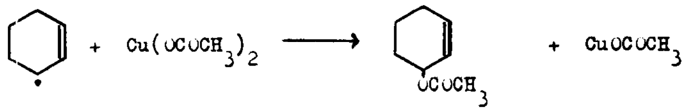
While allylic halogenation is exemplified, for instance, in the use of N-bromosuccinimide[3a] and t-butylhypochlorites[3b], and as a secondary process in radical additions of halogen derivatives to olefins[4], we believe that the direct introduction of an azido group in the allylic position was unknown until now.

[3a] C.Walling, Free Radicals in Solution p.132. John Wiley, New York (1957)

[b] ibid. p.386.

[4] E.S.Huyser, J.Org.Chem. 26 3261 (1961).

Further research is in progress in order to establish whether a rearrangement of the allylic system occurs in these reactions and whether there is some analogy with the copper salt-catalysed reaction between peresters and olefins, discovered by Kharasch and coworkers[5]. In this regard some reactions, studied by us, in the presence of copper acetate, are significant. The t-butylhydroperoxide decomposition with ferrous sulphate in the presence of cyclohexene and cupric acetate in aqueous-alcoholic solution at low temperatures(÷ 0°) led to the acetyloxycyclohexene togheter with the corresponding alcohol. This leads us to think that allylic radical oxidation in presence of cupric acetate is responsible for the ester formation, as already suggested by some Authors in the case of Kharasch reaction:[6]



Whereas in the case of the Kharasch's reaction the alkoxy radical and the acetyloxy group would arise from the same perester molecule, in our case the alkoxy radical arises from the action of the ferrous salt on the hydroperoxide and the acetyloxy group from the copper acetate. In comparison with the chlor- and azido-derivatives, the acetyloxy compound formation is more affected by polar solvents. This behavior can be attributed to a lower efficiency of copper acetate in blocking allylic radicals: consequently the free radical oxidation to carbonium ion is increased. Alternatively the above behavior could also be attributed to the fact that the formation of the acetyloxy derivative occurs through the oxidation of the radical to a carbonium ion, at least in polar solvents: this, in our opinion, does not occur in the case of chlor- and azido-derivatives.

Acknowledgement. We wish to thank Professor A.Quilico for his continued and active interest in this work and for helpful discussions.

---

[5] M.S.Kharasch and G.Sosnovsky, J.Am.Chem.Soc. 80 756 (1958).

[6] J.K.Kochi, J.Am.Chem.Soc. 83 3162 (1961); A.L.J.Beckwith and G.W.Evans Proc.Chem.Soc. 63 (1962).