

**NUCLEOPHILIC CHARACTER OF ALKYL RADICALS:
NEW SYNTHESSES BY ALKYL RADICALS GENERATED IN REDOX PROCESSES**

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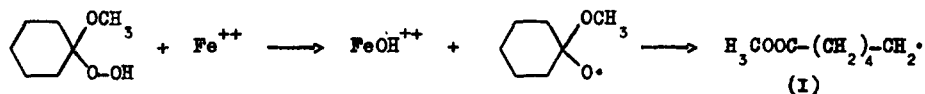
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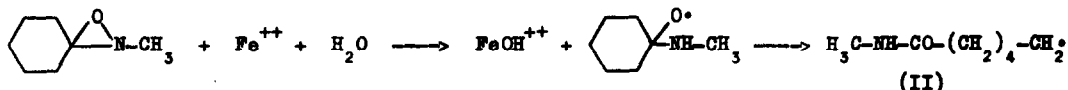
NEW syntheses, whose occurrence is strictly connected with the nucleophilic character of the alkyl radicals, are performed by means of radicals generated in redox processes.

Two redox processes are used:

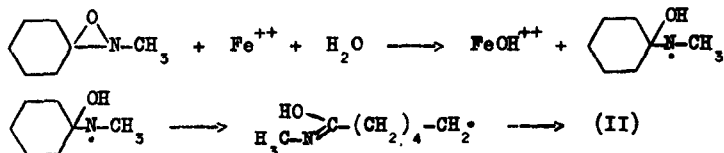
A) Cyclohexanone peroxide and ferrous sulfate:



B) 2-methyl-3,3-pentamethylenecrazirane and ferrous sulfate; in this case the formation of the alkyl radical was explained by an analogous sequence¹:



while our results, which will be discussed elsewhere, indicate a somewhat different pathway:



1) Alkylation of protonated heteroaromatic bases.

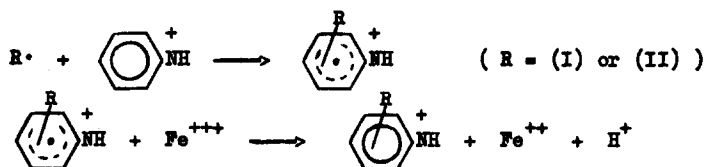
A number of heteroaromatics is alkylated with both redox systems in acidic solution (Table). In the most studied cases (Pyridine and Quinoline) 70-80% yield, based on the radical source, is obtained: g.l.c. only shows the isomers 2 and 4 (Pyridine: 2= 34%; 4= 66%; Quinoline: 2= 47%; 4= 53%). The synthetic interest is connected with the easy availability of the radical sources² and the simple experimental conditions: the reaction is immediate in

water or methanol at room temperature.

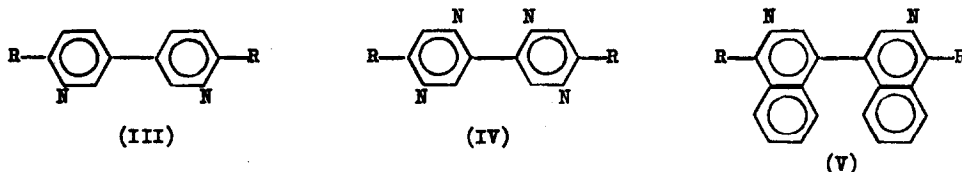
TABLE

Substratum	Positions of attack	
	(I)	(II)
pyridine	2,4	2,4
quinoline	2,4	2,4
acridine	9	9
pyrazine	—	2
isoquinoline	—	1
2-aminopyrimidine	—	4
benzothiasole	—	2

The reaction mechanism involves a redox chain :



With pyridine, pyrazine and isoquinoline the dimers (III), (IV) and (V), arising from dimerization of the intermediate radical and subsequent oxidation, are isolated as by-products :



The nucleophilic character, as driving force for this new type of radical alkylation, is clearly indicated by the isomer distribution and by the fact that aromatics such as benzene, chlorobenzene and naphthalene do not react under the same experimental conditions in homogeneous medium.

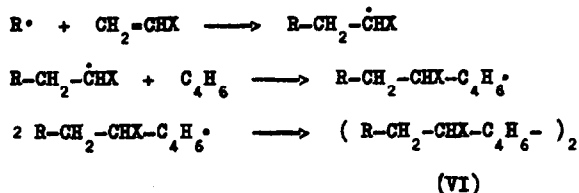
2) Syntheses of polyfunctional long-chain compounds by alternating free radical additions to conjugated olefins.

Addition of the radical (I) to conjugated olefins in the presence of metal salts redox systems was studied by us³ and by Kochi and Rust⁴, who reported that the reactivity of the radical (I) is higher with butadiene and styrene than with olefins conjugated with electron-withdrawing groups, such as acrylonitrile or methyl acrylate, owing to the electrophilic character of the radical. Our results indicated an opposite sequence according to a nucleo-

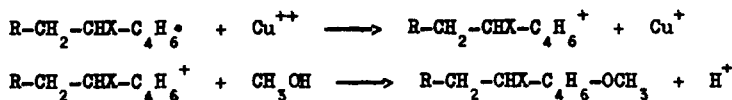
philic character of (I).

Two new syntheses of general character show that our conclusions were correct:

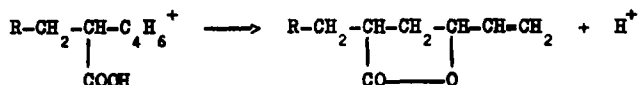
a) The radicals (I) and (II), generated in the simultaneous presence of butadiene and an olefin conjugated with an electron-withdrawing group ($X = \text{CN}, \text{COOH}, \text{COOCH}_3, \text{COCH}_3$) give rise mainly to (VI) :



b) Catalytic amount of cupric sulfate in methanol oxidizes quantitatively the allylic radicals :



When X is carboxyl group an intramolecular reaction of the allylic cation takes place:



Analogously (VII) and (VIII) are obtained with α -methyl-styrene instead of butadiene :

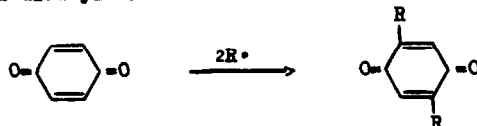


70-80% yield, based on the radical source, is obtained in the most favourable cases.

Since the resonance energies of α -cyano, carboxy and keto alkyl radicals cannot be as high as that of allylic or benzylic radicals, the observed sequence of reactivity and the consequent synthetic possibilities are clearly determined by the nucleophilic character of (I) and (II).

3) Alkylation of benzoquinone.

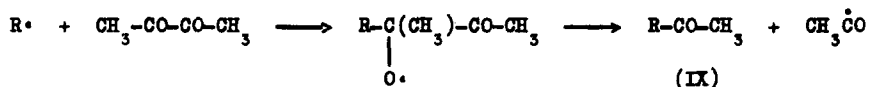
With benzoquinone a dialkyl derivative is obtained :



The presence of butadiene does not notably alter the reaction course : this indicates a much higher reactivity of the alkyl radicals towards benzoquinone, according to their nucleophilic character.

4) Reaction with biacetyl.

Both (I) and (II) with biacetyl give rise to (IX) :



This addition to carbonyl carbon, recently observed also in thermal and photochemical processes⁵, is, in our opinion, determined by the nucleophilic character of the alkyl radicals.

Work in progress shows that also acyclic sources of alkyl radicals can be used for these syntheses: for instance, ethylation is performed by the redox system methyl-ethyl-ketone peroxide/ ferrous sulfate.

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