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NUCLEOPHILIC CHARACTER OF ALKYL RADICALS—II

SELECTIVE ALKYLATION OF PYRIDINE, QUINOLINE AND ACRIDINE BY HYDROPEROXIDES AND OXAZIRANES

F. MINISCI
Istituto di Chimica Organica dell'Università, Via M. D'Azeglio 85, 43100 Parma

R. GALLI, V. MALATESTA and T. CARONNA
Istituto di Chimica del Politecnico, Piazza L. Da Vinci 32, 20133 Milano

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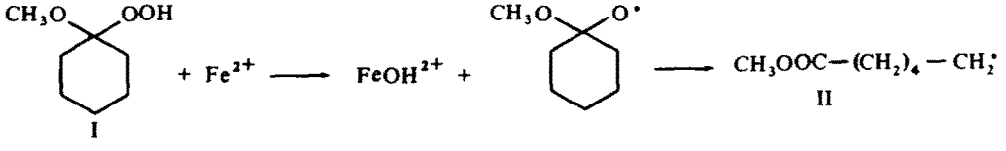
Abstract—Homolytic alkylation of pyridine, quinoline and acridine by redox systems is a selective process as regards orientation and reactivity. The synthetic aspects and the mechanism of the reduction of oxaziranes and homolytic substitution are discussed.

A PRELIMINARY communication[1] showed the possibility of achieving new syntheses by taking advantage of the nucleophilic character of alkyl radicals. Quantitative data has been published[2] concerning the affinity of alkyl radicals for conjugated olefins, which clearly confirm this nucleophilic character. Now we report the results obtained in the alkylation of pyridine, quinoline and acridine by redox systems formed by hydroperoxides or oxaziranes and ferrous salts.

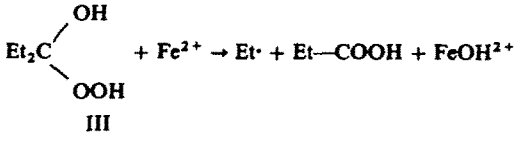
Radical sources

(A) *Hydroperoxides.* (1) 1-Methoxycyclohexylhydroperoxide (I)[3] with ferrous salt gives rise to the 5-(methoxycarbonyl)-pentyl radical (II):



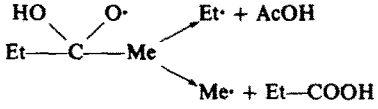
I II

(2) The peroxide obtained from diethylketone and hydrogen peroxide can be formulated as III and produces ethyl radicals with a ferrous salt:



III

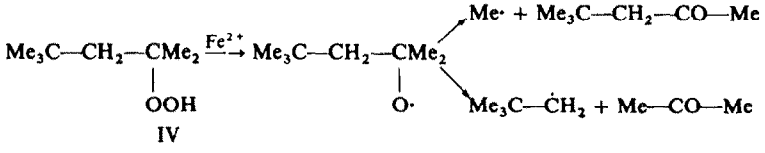
(3) In the analogous peroxide obtained from methyl-ethyl-ketone, the β-scission of the alkoxy radical, formed initially, is not selective, but leads mainly to ethyl radicals and, to a minor extent, to Me radicals:



(4) t-Butylhydroperoxide gives rise to Me radicals:

$$(Me)_3COOH + Fe^{2+} \rightarrow Me—CO—Me + Me\cdot + FeOH^{2+}$$

(5) 2,4,4-Trimethyl-2-hydroperoxypentane (IV) is obtained by adding hydrogen peroxide to diisobutylene.[4] In this case there are also two possibilities of β-scission, giving rise to either a neopentyl or a Me radical:

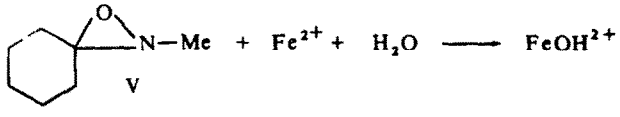


IV

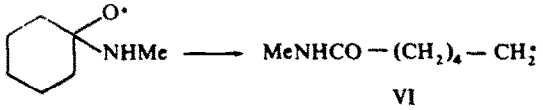
A quantitative investigation of this reaction was not undertaken, but a qualitative study did not reveal a possible rearrangement of the neopentyl radical:

$$Me_3C—\dot{C}H_2 \rightarrow Me_2\dot{C}—CH_2—Me$$

(B) *Oxaziranes.* 2-Methyl-3,3-pentamethyleneoxazirane (V)[5] yields alkyl radical VI by the suggested sequence:[6]

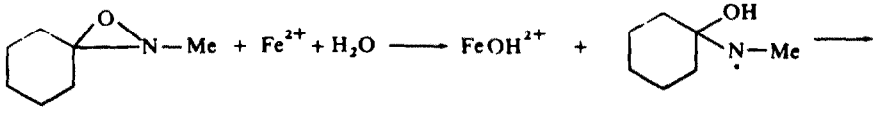


V



VI

We have suggested[7] an alternative mechanism involving formation of an amino radical, which subsequently undergoes β-scission:



Our hypothesis was based on (a) the structural analogy with hydroxylamines, which give amino radicals on reduction with metal salts:

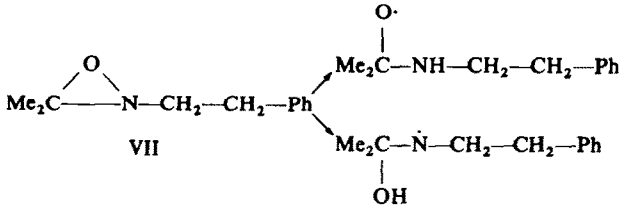
$$R_2N{-}OH + Ti^{3+} \rightarrow R_2N\cdot + TiOH^{3+}$$

(b) considerations concerning an electron transfer on the N—O bond, and (c) the behaviour of the oxaziranes with cuprous salts.[8]

Since in the case of the oxazirane V each of the two mechanisms leads to the same alkyl radical intermediate VI, the reaction product cannot be used to discriminate between them. Thus, ε-derivatives of caproic acid N-methylamide are formed by a redox transfer process in the presence of halogen or pseudohalogen ions,[7] in a way similar to the behaviour of the alkyl radicals from peroxides:[9]

$$MeNHCO{-}(CH_2){-}CH_2\cdot + FeX^{2+} \rightarrow MeNHCO{-}(CH_2)_5{-}X + Fe^{2+}\quad X = Cl, Br, N_3, SCN \text{ etc}$$

To verify our hypothesis we used 2-phenethyl-3,3-dimethyloxazirane (VII), for which two redox processes are possible:

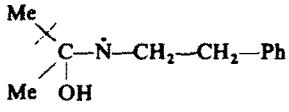


VII

The alkoxy radical may give rise to a Me radical by β-scission:

$$Me_2C(O\cdot){-}NH{-}CH_2{-}CH_2{-}Ph \rightarrow Me\cdot + Me{-}CO{-}NH{-}CH_2{-}CH_2{-}Ph$$

whereas the amino radical may give two different alkyl radicals, a Me or a benzyl radical:



The higher stability of the benzyl over the Me radical favoured the formation of the former in the case of an intermediate amino radical and therefore suggested the possibility of distinguishing between the two mechanisms. Actually the reaction of the oxazirane VII with ferrous sulphate in the presence of ferric chloride led to benzyl chloride, formed by a redox transfer process on the benzyl radical, thus supporting our hypothesis:

$$Ph{-}CH\cdot_2 + FeCl^{2+} \rightarrow Ph{-}CH_2{-}Cl + Fe^{2+}$$

RESULTS AND DISCUSSION

The reactions were carried out in aqueous solution with protonated heteroaromatic bases, except in the case of the peroxide I, for which MeOH was used, since it is

insoluble in water. MeOH was also used to investigate non-basic aromatic substrates insoluble in water, such as benzene, chlorobenzene and naphthalene. In the absence of heteroaromatic substrates the alkyl radicals react in various ways, mainly by dimerization and, to a lesser extent, by oxidation and reduction. Thus, the peroxide I and the oxazirane V lead respectively to the methyl ester[10] and the N-methylamide[6] of 1,12-dodecandioic acid in good yields. In contrast, in the presence of protonated heteroaromatic bases, no dimerization of the radical but alkylation of the heteroaromatic ring takes place. The results obtained with the peroxide I and the oxazirane V are summarized in Table 1; Tables 2 and 3 show the data concerning Me and Et radicals.

With quinoline the reaction leads exclusively to substitution products with both hydroperoxides and oxazirane. Only the isomers substituted at positions 2 and 4 are obtained and that substituted at the 2-position always prevails over that at the 4-position. When an excess of radical source is used, 2,4-disubstituted derivatives are formed.

With the peroxide of methylethylketone the ethyl- to methyl-quinolines ratio is about 5:1, indicating that the formation of Et radicals prevails over that of Me radicals in accordance with their relative stabilities. However, this ratio cannot be regarded as a quantitative measure of β-scission of the intermediate alkoxy radical, since the alkylation yield, in this case, is about 40%. Actually, the peroxide is reduced mainly to the starting ketone, without undergoing radical scission:

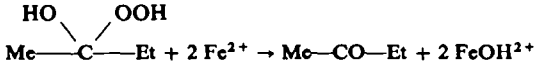


TABLE 1. ALKYLATION BY PEROXIDE I AND OXAZIRANE V

Heterocyclic Base	Radical	Isomers %	Total yield[a] %
Quinoline	VI	2- : 53·1 4- : 46·9	80
	II	2- : 53·8 4- : 46·2	60
Acridine	VI	9-	76
	II	9-	67
Pyridine	VI	2- + 4- + dimer VIII	79
	II	2- : 34 4- : 66	not determined

VI = $-(CH_2)_5CONHMe$; II = $-(CH_2)_5COOMe$

[a] Yield calculated on the radical source

TABLE 2. METHYLATION AND ETHYLATION OF QUINOLINE

Peroxide	Quinoline/ peroxide ratio	Quinoline %	Methyl-quinolines %		2,4-Dimethyl-quinolines %	Ethyl-quinolines %	
			2	4		2	4
t-Butylhydroperoxide	1 : 3	23·7	32·4	29·3	14·6		
Diethylketone peroxide	2 : 1	83·4				9·6	6·9
Methylethylketone peroxide	1 : 1	59·5	4·5	3·8		17·0	15·1

TABLE 3. METHYLATION AND ETHYLATION OF PYRIDINE

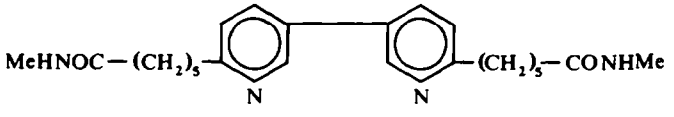
Peroxide	Pyridine: peroxide ratio	Pyridine %	Methylpyridines %		Ethylpyridines %	
			2	4	2	4
t-Butylhydroperoxide	1 : 1	86·9	3·8	9·3		
Diethylketone peroxide	2 : 1	80·1			5·0	14·9
Methylethylketone peroxide	1 : 1·5	49·8	1·7	5·4	9·4	33·8

and, furthermore, not all the radicals react only with quinoline, so that the ethyl- to methyl-quinoline ratio may lose its quantitative significance owing to the differing reactivity of the two radicals.

The products of the reaction between the peroxide IV and quinoline were not quantitatively analyzed but only qualitatively investigated, in order to verify a possible rearrangement of the neopentyl radical: the NMR spectrum of the basic reaction product shows only singlets for the Me and methylene groups, but no signal of the Et group, thus excluding the rearrangement of the neopentyl radical during the alkylation.

The alkylation reaction in the case of acridine is selective with both peroxides and oxazirane, and leads to exclusive substitution at the position 9.

With pyridine and peroxides only substitution at positions 2 and 4 takes place, whereas with the oxazirane V these isomers are accompanied by the dimer VIII:



VIII

The 4-substituted isomer is always prevalent over that substituted at the 2-position. This behaviour is in contrast with the data for alkylation of pyridine by acyl peroxides and electrolysis of carboxylic salts[11] (the analytical methods were not accurate in these cases), for benzylation by dibenzylmercury[12] and homolytic arylation:[13] in all these cases a large prevalence of the 2-substituted isomer was reported.

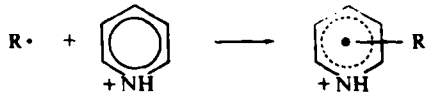
Two aspects emphasize the importance of the nucleophilic character of the alkyl radicals in these reactions: orientation and reactivity. Orientation in the positions 2 and 4 has been reported[11] in the alkylation of pyridine with acylperoxides. It was however observed[14] that the absence of the 3-substituted isomer in these reactions is probably a result of the method of analysis (isolation by distillation) during which a small portion of this isomer may have been lost, since there is evidence that in general the isomer distribution obtained in homolytic methylation is similar to that obtained in phenylation. Actually our results indicate that the position 3 is not attacked either in pyridine or in quinoline (with quinoline no position of the benzene ring is attacked): certainly the analytical conditions used are able to reveal concentrations of 3-methylpyridine and quinoline lower than 0·5%, as shown by careful GLC analyses with authentic samples. The selectivity of attack at positions 2 and 4 is therefore complete, at least with the redox systems used.

As regards the 2-substituted:4-substituted isomer ratios, which in our case are noticeably different from the results previously reported with different radical sources, we think that the different experimental conditions, some sort of complexing between the alkyl radicals and the metal salts and, in some cases, the formation of dimers may play an important role. This high selectivity in the orientation is also accompanied by a remarkable selectivity in the reactivity towards different aromatic substrates. In fact, under the experimental conditions used with heteroaromatic bases, benzene, chlorobenzene and naphthalene do not react, but the reaction takes place as in the absence of such substrates, *i.e.* dimerization of the alkyl radicals takes place.

This behaviour may be connected with the nucleophilic character of the alkyl radicals, *i.e.* with the contribution of polar forms to the transition state:

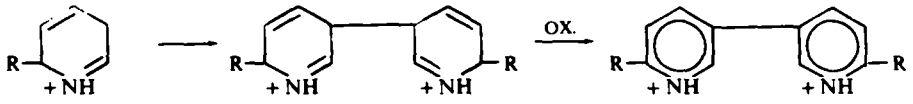
This contribution of polar forms would be favoured by solvents such as water or methanol which can solvate and stabilize the alkyl cations, and probably also by some sort of complexation of the alkyl radical with the metal salt. The protonation of the aromatic base increases the nucleophilic reactivity.

The mechanism of the substitution is not completely clear: the first step is characterized by addition of the alkyl radical to the heteroaromatic ring, as generally accepted in homolytic aromatic substitution:[15]



IX

In this respect the formation of the dimer VIII is indicative: it arises from dimerization of the intermediate radical IX and subsequent oxidation:



We have obtained analogous dimers with pyrazine and isoquinoline,[1] but not with quinoline or acridine: it seems that they can be formed only when the position *para* to the radical attack is free (with exclusion of the heteroatom).

For the rearomatization of the intermediate radical IX several possibilities may be considered: oxidation or reduction (followed by oxidation of the dihydroderivative) by metal salts, oxidation by the radical source, abstraction of an H atom by intermediate radicals. It may also be that a single mechanism is not responsible for the rearomatization process in all cases.

We hope to obtain more information about these mechanistic details from the study of the reaction with quaternary salts of heteroaromatic bases.

EXPERIMENTAL

Reaction of 2-methyl-3, 3-pentamethylene-oxazirane (V) *with quinoline*

To a soln of quinoline (19·2 g) in 20% H_2SO_4 (100 ml), 2-methyl-3,3-pentamethylene-oxazirane (9·5 g) and a soln of $FeSO_4 \cdot 7H_2O$ (21 g) in water (50 ml) were simultaneously added dropwise with stirring over a period of 30 min, temperature: 20°–38°. After completion of the addition, the soln was extracted with $CHCl_3$, then basified with 10% NaOH and the basic product extracted with $CHCl_3$. In the first extract only a small amount of cyclohexanone was present. The basic extract, after removal of the solvent and excess quinoline, gave 15 g product (80% yield). TLC (EtOAc-MeOH 9 : 1) revealed two components. The qualitative separation and the identification of the compounds were accomplished as follows:

Isomer in position 4: The mixture gave a picrate from MeOH, m.p. 183°. (Found: C, 54·3; H, 4·8; N, 14·4. $C_{22}H_{23}N_5O_8$ requires: C, 54·4; H, 4·7; N, 14·4%) MS of the picrate is identical with the spectrum of the free base, obtained from the picrate with alcoholic NaOH. The spectrum shows the molecular ion M (256) and significant ions at 226 (M—$NHCH_3$), 198 (226–CO), 184, 170, 156, 143, 128 corresponding to a gradual fragmentation of the aliphatic chain; the IR spectrum of the free base shows typical bands of the —CO—NH— group at 1650 cm^{-1} and 3250 cm^{-1}; NMR spectrum ($CDCl_3$) shows that it is the 4-substituted isomer: in fact for 6 aromatic protons, 10 aliphatic protons are present and a Me—NH— group (d at 2·75 δ); the aromatic pattern shows the protons in position 2 at 8·71 δ (d) and in position 3 at 7·15 δ (d) and 4 protons of the benzene ring at 7·4–8·2 δ (m).

Isomer in position 2: The mixture of the two isomers was chromatographed on silica gel (EtOAc-MeOH 9:1). At first the pure 2-substituted isomer was separated, m.p. 70° (Found: C, 75·1; H, 7·9; N, 10·7. $C_{16}H_{20}N_2O$ requires: C, 75·0; H, 7·8; N, 10·9%); picrate, m.p. 153° (Found: C, 54·2; H, 4·6; N, 14·6. $C_{22}H_{23}N_5O_8$ requires: C, 54·4; H, 4·7; N, 14·4%). The MS is practically identical with the spectrum of the 4-substituted isomer; IR spectrum shows typical bands of the CO—NH— group at 1650 cm^{-1} and 3250 cm^{-1}; NMR spectrum reveals the substituted position: the ratios of aromatic, CH_2,NH,Me protons (6:10:1:3) indicate a monosubstituted quinoline; the absence of signals at $\delta > 8{\cdot}2$ indicates that the position 2 is substituted. The quantitative analysis of the mixture was accomplished by transforming the amides into methyl esters. A soln of 6·5 g of the mixture of isomers in 20 ml conc HCl was refluxed for 8 h, then evaporated to dryness, 50 ml MeOH added and 2 ml conc. H_2SO_4. The soln was refluxed for 6 h, diluted with water, basified with Na_2CO_3 and extracted with ether. After removal of the solvent, the residue was distilled to yield 5·3 g of product b.p. 180°–185°/1·5 mm. It was analyzed by GLC (C. Erba Fractovap GV, flame ionization detector, 2 m × 3 mm i.d. Pyrex column with 1% Silicon SE-30 on Gas-Chrom P, at 180°; He at 40 ml/min flow rate). Only two compounds were present: the 2-substituted isomer (53·1%) and the 4-substituted isomer (46·9%). The pure isomers for comparison were prepared with the same procedure starting from the pure amides qualitatively isolated as previously described.

Reaction of 1-methoxycyclohexyl hydroperoxide (I) *with quinoline*

34% H_2O_2 (7·5 ml) was added to cyclohexanone (14·8 g) while the temp was kept below 40° by intermittent cooling. The mixture was then dissolved in MeOH (100 ml) which contained conc H_2SO_4 (14 ml). The soln obtained was added to a soln of quinoline (38 g) and conc H_2SO_4 (8·4 ml) in MeOH (200 ml); finely powdered $FeSO_4 \cdot 7H_2O$ (21 g) was added over a period of 40 min with stirring and N_2 flushing at 20–30°. The soln was extracted with ether to remove non basic products and then basified with 10% NaOH at 0°. The basic products were extracted with ether: after removal of the solvent and excess quinoline,

the residue (11·5 g, 60% yield) was directly analyzed by GLC. The analysis, carried out as described for the reaction with V, showed only two compounds: the 2-substituted isomer (53·8%) and the 4-substituted isomer (46·2%).

Reaction of 2-methyl-3,3-pentamethylene-oxazirane (V) *and 1-methoxycyclohexyl hydroperoxide* (I) *with acridine*

To a soln of acridine (4·5 g) and H_2SO_4 (2 ml) in water (200 ml), V (3 g) and a soln of $FeSO_4 \cdot 7H_2O$ (7·5 g) in water (50 ml) were simultaneously added dropwise with stirring over a period of 1·5 hr (acridine sulphate is partially soluble), temp: 20–30°. After completion of the addition, the soln was stirred for an additional 30 min and extracted with $CHCl_3$, then basified with 10% NaOH and the basic product extracted with $CHCl_3$. The basic extract, after removal of the solvent, gave 5·5 g product crystallized from EtOAc, m.p. 168° (Found: C, 78·6; H, 7·2; N, 9·1. $C_{20}H_{22}N_2O$ requires: C, 78·4; H, 7·2; N, 9·1%); MS shows molecular ion M (306) and significant ions at 276 (M–$NHCH_3$), 248 (276 —CO), 234, 220, 206, 193, 180 corresponding to fragmentation of the aliphatic chain; IR bands at 1560 and 3250 cm^{-1} (—CO—NH—); NMR: ratio of aromatic, CH_2, NH and Me protons = 8:10:1:3; the absence of signals at $\delta > 8{\cdot}2$ indicates that position 9 is substituted. The reaction with I was carried out under the conditions described for quinoline, yielding 67% of the product substituted in position 9. It was identified as free acid, m.p. 167°, by comparison with an authentic sample obtained by hydrolysis of the amide from the oxazirane V.

Reaction of 2-methyl-3,3-pentamethylene-oxazirane (V) *and 1-methoxycyclohexyl hydroperoxide* (I) *with pyridine*

To a soln of pyridine (16 g) in 20% aq H_2SO_4 (100 ml) V (6·4 g) and a soln of $FeSO_4 \cdot 7H_2O$ (14 g) in water (50 ml) were simultaneously added dropwise with stirring over a period of 20 min, temp: 15–35°. The soln was stirred for an additional 15 min at room temp and extracted with $CHCl_3$ to remove non-basic products, then basified the 10% NaOH. The basic products were extracted with $CHCl_3$; after removal of the solvent and excess pyridine, 8·2 g product (79% yield) was obtained; TLC (EtOAc-MeOH 8:2) revealed 3 comps. The qualitative identification of these comps was accomplished as follows:

Compound VIII: The mixture was crystallized from EtOAc-MeOH (9:1) to give VIII, m.p. 185°. (Found: C, 70·4; H, 8·2; N, 13·5. $C_{24}H_{34}N_4O_2$ requires: C, 70·2; H, 8·3; N, 13·6%); IR bands at 1650 and 3250 cm^{-1}; MS: molecular ion M (410); significant ions at 380(M—$NHCH_3$), 352 (380 —CO), 338, 324, 310, 297, 266, 251, 238, 223, 209, 187 and 183 corresponding to a gradual fragmentation of the aliphatic chains; NMR spectrum ($CDCl_3$) shows a doublet at 2·76 δ (—CH_3—NH—) and 3 aromatic protons for 5 CH_2 groups. The aromatic protons centered at 8·60 δ (position 2), 7·65 δ (position 4) and 7·15 δ (position 5) confirm the structure VIII.

Isomer in position 4: The EtOAc-MeOH soln, after crystallization of VIII, was evaporated to dryness. The product was extracted with warm EtOAc and TLC of the residue showed the presence of VIII and the 4-substituted isomer. This last compound was isolated, as a viscous liquid, by chromatography on silica gel (EtOAc-MeOH 8:2). (Found: C, 70·1; H, 8·5; N, 13·7. $C_{18}H_{18}N_2O$ requires: C, 70·0; H, 8·7; N, 13·6%); IR bands at 1650 and 3250 cm^{-1} (—CO—NH—); MS: molecular ion M (206), significant ions at 176 (M—$NHCH_3$), 148 (176 —CO), 134, 120, 106, 93 (fragmentation of the aliphatic chain); NMR: doublet at 2·75 δ (CH_3—NH—) and 4 aromatic protons for 5 CH_2 groups; 2 aromatic protons are centered at 8·50 δ (α-protons) and 2 at 7·10 δ (β-protons) indicating substitution in position 4.

Isomer in position 2: The products soluble in EtOAc were transformed into methyl esters by the procedur described in the reaction with quinoline and analyzed by GLC (conditions used for the reaction with quinoline, at 140°). Only 2 compds were present: the 2-substituted isomer (28·3%) and the 4-substituted (71·7%); these compounds were identical to those obtained in the reaction of pyridine and I. This last reaction was carried out under the conditions described for quinoline but only partial decomposition of the peroxide took place. GLC showed 34% of the 2-substituted isomer and 66% of the 4-substituted isomer. The two isomers were isolated by preparative GLC and characterized as 2-substituted the isomer with lower retention time and as 4-substituted the other. NMR spectra show for one Me group (s at 3·65 δ, —OMe) 5 CH_2 groups and 4 aromatic protons. The spectra are practically identical for both isomers as regards aliphatic protons, but they are quite different in the aromatic protons: the 4-substituted isomer shows a pattern very similar to the spectrum of the corresponding N-methylamide, above separated, i.e. two pairs of protons centered at 7·10 δ (β-protons) and 8·50 δ (α-protons); the 2-substituted isomer has a more complex spectrum, in which, however, the appearance of a multiplet centered at 7·60 δ (γ-protons) and the attenuation of the signals centered at 8·60 δ (α-protons) agree with the assigned structure.

Alkylation of pyridine and quinoline by t-butyl hydroperoxide and the peroxides of methyl ethyl ketone and diethyl ketone

t-Butyl hydroperoxide was a commercial product. The peroxides of diethyl and methyl ethyl ketone were prepared as previously described.[17]

General procedure. To a soln of heteroaromatic base (0·1 M) and H_2SO_4 (0·1 M) in water (50 ml) equimolecular amounts of hydroperoxide and $FeSO_4$ aq were simultaneously added dropwise with stirring and cooling (15–20°) over a period of 30 min. After completion of the addition, the soln was extracted with ether to remove non basic products, then basified to separate the basic products, which were then directly analyzed by GLC (Aerograph A-600 B with flame ionization detector, aluminium column, 2 m × $\frac{1}{8}$" packed with 7% Silicon DC-550 + 3% Carbowax 20 M on Chromosorb P alkalized (5% KOH), 60/80 mesh, N_2 at 30 ml/min flow rates; column temp 80° for pyridines and 150° for quinolines). The results are shown in Tables 2 and 3.

Quinoline and 2,4,4-trimethyl-2-hydroperoxy-pentane. The reaction was carried out according to the above general procedure. The products were not analyzed by GLC; NMR spectrum shows only singlets at 0·85 δ (Me—) and 2·82 δ (—CH_2—Ar) indicating the attack of the neopentyl radical without rearrangement.

Reaction of 2-phenethyl-3,3-dimethyl-oxazirane (VII) *with iron salts and chlorine ion.*

The oxazirane was prepared according to the procedure of Krimm[18] from 2-phenethylamine, acetone and perbenzoic acid, and 2-phenethyl-3,3-dimethyl-oxazirane (16 g) was added, dropwise with stirring and under N_2, to a soln of $FeSO_4 \cdot 7H_2O$ (25 g) and $FeCl_3$ (25 g), temp: 20–30°. The mixture was then acidified and extracted with ether. After removal of the solvent, 3·8 g benzyl chloride was distilled off; the product was identified by comparison with an authentic sample (GLC, IR, MS).

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