Tetrahedron Vol 32, pp 2741 to 2745 Pergamon Press 1976 Printed in Great Britain

NUCLEOPHILIC CHARACTER OF ALKYL RADICALS—XII[1]

MECHANISM AND NEW SYNTHESES IN THE OXIDATION OF ALCOHOLS BY PEROXYDISULPHATE

TULLIO CARONNA,* ATTILIO CITTERIO, LORIS GROSSI, FRANCESCO MINISCI and KEIICHIRO OGAWA
Istituto di Chimica del Politecnico, Milano, Italy

(*Received in the UK* 13 *April* 1976; *Accepted for publication* 27 *April* 1976)

Abstract—The debated mechanism of the oxidation of alcohols by peroxydisulphate was investigated by trapping the nucleophilic carbon-centered free-radical intermediates by protonated quinoline. The oxidation of t-butanol, 1-hexanol, 2,3-dimethyl-2-butanol and ethylene glycol in the presence of silver salt takes place via alkoxy radical intermediates arising from the interaction $R\text{-}OH + Ag^{2+} \rightarrow R\text{-}O^{\cdot} + Ag^{+} + H^{+}$; it gives rise to new interesting selective synthetic processes. In the absence of silver salt the hydrogen abstraction from C–H bonds is the main reaction.

The widespread assumption of hydrogen abstraction by $SO_4^{\cdot -}$, as the primary step in oxidation of alcohols by peroxydisulphate ion[2] (eqn 1), has been recently reconsidered

$$SO_4^{\cdot -} + CH_3OH \rightarrow HSO_4^{-} + {\cdot}CH_2OH. \qquad (1)$$

On the ground of spin trapping experiments, an alternative mechanism, involving an electron-transfer oxidation (Scheme 1), has been suggested.[3]

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$$
$$SO_4^{\cdot -} + CH_3OH \rightarrow SO_4^{2-} + CH_3\text{—}\overset{\cdot}{\underset{+}{O}}\text{—}H$$
$$CH_3\text{—}\overset{\cdot}{\underset{+}{O}}\text{—}H \rightarrow CH_3\text{—}O\cdot + H^{+}$$
$$CH_3O\cdot + CH_3OH \rightarrow CH_3OH + {\cdot}CH_2OH$$

Scheme 1.

The results obtained in the oxidation of 2-phenylethanol and related compounds (Scheme 2) supports this mechanism.[4]

$$Ph\text{—}CH_2\text{—}CH_2\text{—}OH + SO_4^{\cdot -} \rightarrow$$
$$Ph\text{—}CH_2\text{—}CH_2\text{—}\overset{\cdot}{\underset{+}{O}}\text{—}H + SO_4^{2-}$$
$$Ph\text{—}CH_2\text{—}CH_2\text{—}\overset{\cdot}{\underset{+}{O}}\text{—}H \rightarrow Ph\text{—}CH_2\text{—}CH_2\text{—}O\cdot + H^{+}$$
$$Ph\text{—}CH_2\text{—}CH_2\text{—}O\cdot \rightarrow Ph\text{—}CH_2\cdot + CH_2 = O$$
$$2Ph\text{—}CH_2\cdot \rightarrow Ph\text{—}CH_2\text{—}CH_2\text{—}Ph$$

Scheme 2.

It was also suggested that with primary and secondary alcohols the initially-formed alkoxy radical rapidly interconverts to its thermodynamically more stable isomer $R_2\dot{C}\text{–}OH$, thus explaining the difficulty in establishing alkoxy radicals as intermediates in alcohol oxidation processes.[4]

The recognition that the peroxydisulphate ion oxidises alcohols by an electron-transfer route promises considerable application of this reagent; however it has been observed that the spin-trapping evidence is not unambiguous[5] and a different mechanism[6] has also been suggested for the reaction of Scheme 2. In order to elucidate these aspects and, at the same time, to look for new synthetic routes we have investigated the problem from a different approach.

Our previous studies concerning homolytic aromatic substitution[7] have led to three interesting developments, due to the great reactivity of nucleophilic carbon-centered free-radicals towards protonated heteroaromatic bases:

(i) A variety of new types of homolytic substitutions, the synthetic interest of which is related to the high positional and substrate selectivity.[7]

(ii) The most sensitive models for investigating the relative nucleophilicities of carbon free-radicals.[8]

(iii) Diagnostic criteria for revealing free-radicals present in a reaction, based on the high trapping effectiveness of protonated heteroaromatic bases.[9]

These criteria are very effective because for several carbon free-radicals ($R^{\cdot}$) and protonated hetero-aromatic bases (ArH_2^{+}) the rates of addition (eqn 2) are very high[10] ($k_a \geq 10^5\ M^{-1}\,sec^{-1}$), almost as in the "spin trapping" technique

$$R^{\cdot} + ArH_2^{+} \xrightarrow{k_a} R\text{—}ArH_2^{+\cdot} \rightarrow R\text{—}Ar. \qquad (2)$$

Moreover these criteria have the advantage, compared with the "spin trapping" technique, to allow the simple isolation, identification and quantitative evaluation of the products of attack (R–Ar).

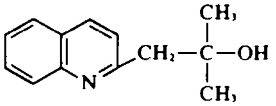
Thus we[11] have already shown that the oxidation of methanol by peroxydisulphate leads to the selective hydroxymethylation of the 2-methylquinoline (only the isomer 4 is formed) in high yields (86%). This result, however, cannot establish if the $\cdot CH_2OH$ radical arises according to eqn (1) or Scheme 1 because the alkoxy radicals do not react with protonated heteroaromatic bases.

We have now investigated the peroxydisulphate oxidation of four different alcohols, t-butanol, 1-hexanol, 2,3-dimethyl-2-butanol and ethyleneglycol; in all these cases the intermediate formation of alkoxy radicals should be unambiguous.

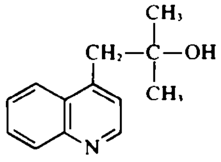
RESULTS

t-Butanol. The oxidation has been carried out with four different oxidizing agents in the presence of protonated quinoline.

(i) *Peroxydisulphate and silver salt.* The main products of the reaction are 2-methylquinoline (**1**) and 4-methylquinoline (**2**). 2,4-Dimethylquinoline (**3**) and the alcohols **4** and **5** are formed in small amount



4



5

(ii) *Peroxydisulphate without silver salt.* No trace of methylquinolines is formed (the GLC conditions can clearly reveal the presence of 0.1% of methylquinolines). Only the alcohols **4** and **5** are formed in low yields.

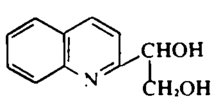
(iii) *Peroxydisulphate and ferrous sulphate.* No methylquinoline is formed, but only the alcohols **4** and **5** in low yields.

(iv) *Hydrogen peroxide and ferrous sulphate.* Also in this case only the alcohols **4** and **5** are formed. The yields are always low because the inductive effect of the O atom reduces the nucleophilic character of the β-hydroxyalkyl radical ($\cdot CH_2{-}C(CH_3)_2{-}OH$).

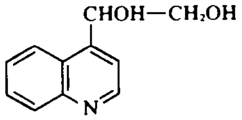
2,3 - *Dimethyl* - 2 - *butanol.* The oxidation with peroxydisulphate and silver salt in the presence of protonated quinoline gives 2-isopropylquinoline (**6**), 4-isopropylquinoline (**7**) and 2,4-diisopropylquinoline (**8**). Only traces of 2-methyl (**1**) and 4-methylquinoline (**2**) are formed. The reaction is therefore interesting from a synthetic point of view because alcohols of the general structure $R{-}C(CH_3)_2{-}OH$ are easily available from acetone and RMgX, the experimental conditions are very simple and the yields based on quinoline are very high.

In the absence of silver salt under the same experimental conditions no trace of methyl- or isopropyl-quinolines are formed.

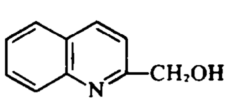
Ethyleneglycol. The oxidation with peroxydisulphate in the presence of protonated quinoline leads to the glycols **9** and **10**, with no formation of the hydroxymethyl derivatives **11** and **12**



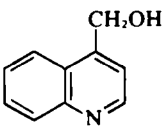
9



10



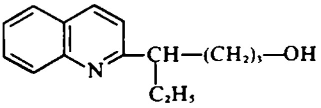
11



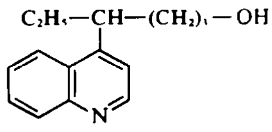
12

In the presence of silver salt **11** and **12** are the main products of the reaction.

1-*Hexanol.* With peroxydisulphate and silver salt the isomers **13** and **14** are the only products of the reaction of quinoline



13



14

The reaction is quite clean and the yields are good; the process appears to be of considerable synthetic interest for δ-hydroxyalkylation of protonated heteroaromatic bases and in general for the selective intramolecular attack of alcohols with a C–H bond in δ-position (for example tetrahydrofurane derivatives can be easily obtained).[10]

In the absence of silver salt the reaction is unselective; at least six isomers of **13** and **14** in comparable amounts are revealed in GLC indicating a rather random hydrogen abstraction from 1-hexanol.

DISCUSSION

The results clearly indicate that alkoxy radicals are formed in all cases in the oxidation of the alcohols with peroxydisulphate and silver salt and the new reaction may have interesting synthetic features.

We explain these results on the ground of the basic interaction of eqn (3)

$$R{-}O{-}H + Ag^{2+} \rightarrow R{-}O^{\cdot} + H^{+} + Ag^{+} \qquad (3)$$

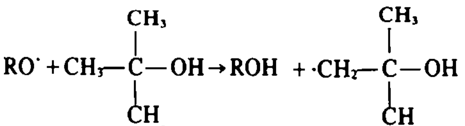
Ag^{2+} is formed according to the redox process of eqn (4), so that a catalytic amount of silver salt is effective

$$\begin{aligned} S_2O_8^{2-} + Ag^{+} &\rightarrow SO_4^{2-} + SO_4^{-\cdot} + Ag^{2+} \\ SO_4^{-\cdot} + Ag^{+} &\rightarrow SO_4^{2-} + Ag^{2+}. \end{aligned} \qquad (4)$$

Thus with t-BuOH the homolytic methylation of quinoline results from the β-scission of the t-butoxy radical (eqn 5)

$$(CH_3)_3C{-}O\cdot \rightarrow CH_3{-}CO{-}CH_3 + \cdot CH_3. \qquad (5)$$

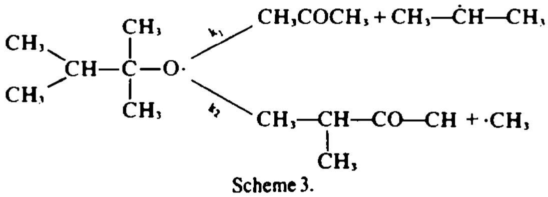
The compounds **4** and **5** obtained with $S_2O_8^{2-}$ alone and with the redox systems $S_2O_8^{2-}/Fe^{2+}$ and H_2O_2/Fe^{2+} arise by hydrogen abstraction from t-BuOH (eqn 6). The abstracting species (R–O·) with H_2O_2 is ·OH, while with $S_2O_8^{2-}$ can be either $SO_4^{-}\cdot$ or ·OH formed according to the well known eqn (7).



$$RO^{\cdot} + CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH \rightarrow ROH + \cdot CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}{-}OH \qquad (6)$$

$$SO_4^{-\cdot} + H_2O \rightarrow HSO_4^{-} + \cdot OH. \qquad (7)$$

With 2,3 - dimethyl - 2 - butanol and $S_2O_8^{2-}/Ag^{+}$ the β-scission mainly occurs with formation of the isopropyl radical (Scheme 3), but small amounts of Me radical are also formed



Scheme 3.

Since the value of the ratio k_1/k_2 is in the range[12] of 2000–3500, the formation of detectable amounts of 2- and 4-methylquinolines once again emphasizes the high trapping effectiveness of protonated heteroaromatic bases towards nucleophilic alkyl radicals.

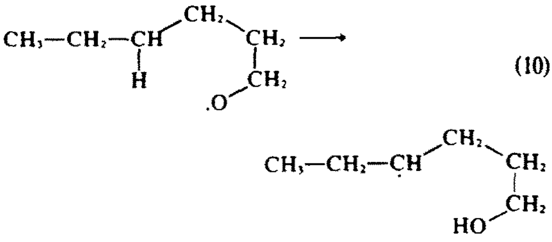
None of the products expected from Scheme 3 was observed in the absence of silver salt. The formation of the hydroxymethylquinolines **11** and **12** in the oxidation of ethyleneglycol with $S_2O_8^{2-}/Ag^+$ also agrees with the intermediate formation of an alkoxy radical (eqn 8)

$$CH_2OH—CH_2O^{\cdot} \rightarrow {\cdot}CH_2OH + CH_2 = O. \qquad (8)$$

In contrast a hydrogen abstraction (eqn 9) occurs in the absence of silver salt and gives the glycols **9** and **10**; also in this case the abstracting species (RO˙) can be $SO_4^{\cdot -}$ or ·OH

$$R—O^{\cdot} + CH_2OH—CH_2OH \rightarrow R—OH + \dot{C}HOH—CH_2OH. \qquad (9)$$

The behaviour of 1-hexanol and the selective formation of the compounds **13** and **14** can be explained only by an intramolecular hydrogen abstraction (eqn 10) by the corresponding alkoxy radical



(10)

The random hydrogen abstraction (also the attack in the positions 1, 3 and 5 of 1-hexanol is revealed by NMR and mass spectra) indicates an intermolecular process in the absence of silver salt, as in the previous cases.

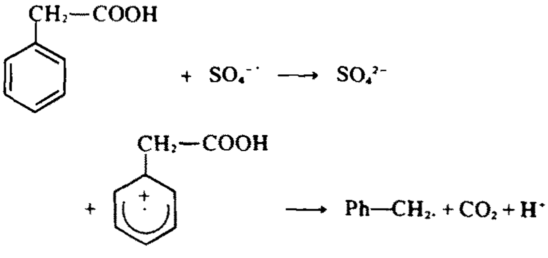
No evidence was therefore obtained as regards an electron-transfer oxidation of alcohols by peroxydisulphate; it appears that this process either does not occur or it is quite a minor aspect of the reaction.

How can these results be reconciled with the evidence of Ledwith *et al.*[3,4] supporting the mechanism of Schemes 1 and 2?

We think that the chemical evidence shown in the mechanism of the Scheme 2 is not conclusive. Norman,[6] on the ground of analogous results obtained in the oxidation of phenylacetic acid, has already suggested a different mechanism involving the addition of the radical $SO_4^{\cdot -}$ to the aromatic ring, according to the Scheme 4.

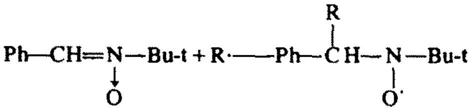
We, however, on the ground of the results obtained in the oxidation of γ-phenylbutyric acid by peroxydisulphate,[13] suggest a different mechanism (Scheme 5).

This mechanism, in our opinion, is more reasonable than that of Scheme 2 because the ionization potentials of the alkyl benzenes are somewhat lower than those of the alcohols. In an analogous way the oxidation of phenylacetic acid could be explained (eqn 11)



Spin-trapping experiments

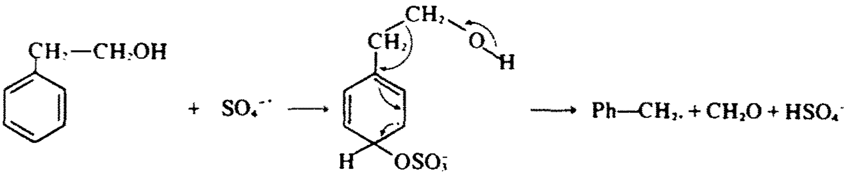
Since the main evidence concerning the mechanism of Scheme 1 comes from spin-trapping experiments,[2] we have also used the spin-trapping technique for investigating the oxidation of methanol, ethyleneglycol and t-butanol by peroxydisulphate in the presence or absence of silver salt. The benzylidene nitrone **15** has been used as scavenger



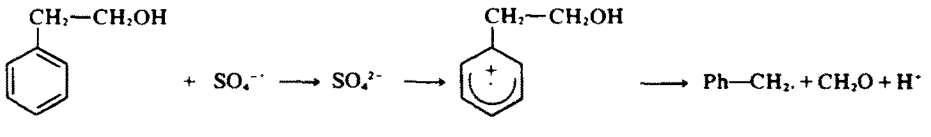
$$\underset{\mathbf{15}}{Ph—CH{=}\underset{\substack{\downarrow\\O}}{N}—Bu\text{-}t} + R\cdot — \underset{\mathbf{16}}{Ph—\overset{\substack{R\\|}}{C}H—\underset{\substack{|\\O^{\cdot}}}{N}—Bu\text{-}t}$$

15 **16**

The results with methanol are given in the Table 1. Oxidation of methanol in the presence of **15** was studied in greater detail. Eight different conditions were investigated in the presence and absence of silver salt, at low and high concentration of nitrone and with two different ratios of methanol: water (9:1 and 1:2). These conditions reproduce the range of conditions used by Ledwith *et al.*;[2] we however were not able to reproduce their results. We observed only small differences between the splitting constants determined in the two different solvents, which, in our opinion, can be ascribed to the solvent effect on the splitting constant of nitroxide radicals.[14] In each solvent



Scheme 4.



Scheme 5.

Table 1. Splitting constants of nitroxide (**16**) obtained in the oxidation of methanol by $K_2S_2O_8$ at 60°C

Ratio $\frac{\text{methanol}}{\text{water}}$	[Nitrone] (M)	$[K_2S_2O_8]$ (M)	$[Ag^+]$	a_N (G)	a_H (G)
9:1	0.01	0.01	—	14.84	3.16
9:1	0.01	0.01	Ag^+	14.80	3.13
9:1	0.3	0.01	—	14.80	3.12
9:1	0.3	0.01	Ag^+	14.78	3.05
1:2	0.01	0.01	—	15.25	3.43
1:2	0.01	0.01	Ag^+	15.10	3.25
1:2	0.3	0.01	—	15.17	3.38
1:2	0.3	0.01	Ag^+	15.12	3.30

no significant difference of the splitting constants has been determined under the different conditions used. Moreover our values of the splitting constants are intermediate between those reported by Ledwith *et al.*[2] for **16** when R is CH_3O ($a_N = 14.35$–$14.50G$; $a_{\beta_H} = 2.86$–$2.98G$) and CH_2OH ($a_N = 15.31$–$15.41G$; $a_{\beta_H} = 3.73$–$3.76G$).

We think that all the splitting constants reported in the Table correspond to the nitroxide **16**, in which R is CH_2OH. This radical, originated under the same conditions, is in fact very effectively trapped by protonated heteroaromatic bases.[11] Moreover we believe that there is some analogy between nitrones and protonated heteroaromatic bases: both compounds are characterized by the strongly electron-deficient $-CH{=}\overset{+}{N}\!\!<$ group, so that polar effects should play an important role in both cases. The protonated bases are in fact extremely sensitive to the polar nature of the attacking radical; no attack takes place with the electrophilic alkoxy radicals, whereas, very high rate constants ($k = 10^6$–$10^7\ M^{-1}\ sec^{-1}$) characterize the addition of nucleophilic alkyl radicals to protonated heteroaromatic bases.[10] We should expect analogous effects for the radical addition to the nitrone; that is, $\cdot CH_2OH$ should be much more reactive than $CH_3O\cdot$ towards the nitrone **15**. Thus the value of $k > 6 \times 10^7\ M^{-1}\ sec^{-1}$ evaluated[3] for the addition of CH_3–$O\cdot$ to the nitrone **15** seems to us excessively high.

The oxidation of t-butanol by $K_2S_2O_8$ at 60° in the presence of **15** results in a complex ESR behaviour because more radicals, which change with time, are formed. However, in agreement with the chemical behaviour, the spectral characteristics are different depending on the presence or not of Ag^+. The splitting constant of the main triplet of doublets in the absence of Ag^+ is $a_N = 14.40G$ at both high (0.3 mol/l) and low (10^{-2} mol/l) concentration of nitrone. In the presence of Ag^+ the splitting constant is $a_N = 15.30G$ at high and low nitrone concentration; moreover the spectrum initially obtained at low nitrone concentration (10^{-2} mol/l) changes on warming giving a triplet with $a_N = 8.17G$. That means that the nitroxide of the type **16** initially formed further reacts losing the β H atom.

The oxidation of ethyleneglycol by $K_2S_2O_8$ at 60° in the presence of **15** initially gives under all the conditions (presence or not of Ag^+ at high and low nitrone concentration) an identical spectrum ($a_N = 14.84$–$14.90G$; $a_{\beta_H} = 3.00$–$3.07G$) not differing substantially from that obtained from methanol. The spectrum, obtained at low nitrone concentration (10^{-2} mol/l) however changes by warming giving a different triplet of doublets ($a_N = 15.88G$ and $a_{\beta_H} = 3.38$).

In conclusion the spin-trapping technique by the nitrone **15** leaves doubts regarding the radicals formed in the oxidation of the alcohols with $K_2S_2O_8$, even if in some cases the difference, due to the presence of Ag^+, clearly appears, in agreement with the chemical evidence. This is not surprising because the information regarding the nature of the radical trapped is difficult to obtain from the spectrum of the spin adduct. The spectrum always consists of a triplet of doublets due to the nitrogen and β-H coupling of the spin adduct. Although the magnitudes of both coupling constants depend on the bulk and electronegativity of the radical added, the differences in N and β-H couplings between various spin adducts are small and serious overlap occurs when more than one spin adduct is present in solution.

EXPERIMENTAL

GLC were performed on a "Hewlett Packard" 5750 G instrument using a 6 ft, $\frac{1}{8}$" steel column, packed with 10% U.C.C.-W-982 on chromosorbW a.w. DMCS, 80–100 mesh.

Oxidation of t-butanol in the presence of protonated quinoline

(A) *By* $Na_2S_2O_8$ *and* Ag^+. To a soln of quinoline (10.3 g), conc H_2SO_4 (2.2 ml), $AgNO_3$ (1.35 g) in 90 ml t-BuOH and 30 ml water, heated to 80°, a soln of $Na_2S_2O_8$ (9.5 g) in 20 ml water was added under stirring (*ca* 10 min). The mixture was kept at 80° for 1 hr, made alkaline and extracted with $CHCl_3$. 12.7 g of basic product were obtained. GLC analysis revealed, in addition to unreacted quinoline, 2 main reaction products: 2-methylquinoline (42%) and 4-methylquinoline (58%). Traces of 2,4-dimethylquinoline and of the compounds **4** and **5** were also obtained. All the products were identified by comparison with authentic samples (GLC, NMR, MS). Conversion 20%; yield based on converted quinoline 95%.

(B) *By* $Na_2S_2O_8$ *without* Ag^+. The reaction was carried out as in (A). No trace of methylquinolines was revealed by GLC. The two main products were **4** (63%) and **5** (27%). The compounds were identified by MS: significant peaks at *m/e*: 182 (M^+–H_2O), 167, 143, 129, 102. Conversion 3%.

(C) *By* $Na_2S_2O_8$ *and* Fe^{2+}. The reaction was carried out as in (B) in the presence of $FeSO_4$ (0.3 g). No substantial change in the nature of the products and conversion compared with (B) was observed.

(D) *By* H_2O_2 *and* Fe^{2+}. H_2O_2 (3.5 ml; 36%) and $FeSO_4$ (4.5 g) in 18 ml water were simultaneously added under stirring and cooling (5–10°) to a soln of quinoline (2.6 g) and 1.2 ml conc H_2SO_4 in 30 ml t-BuOH and 10 ml water. The mixture was made alkaline and extracted with $CHCl_3$. The compounds **4** (71%) and **5** (29%) were obtained with 12% conversion. No trace of methylquinolines was observed by GLC.

Oxidation of 2,3 - dimethyl - 2 - butanol in presence of protonated quinoline

(A) *By* $Na_2S_2O_8$ *and* Ag^+. A soln of $Na_2S_2O_8$ (2.4 g) in 5 ml water was added under stirring (*ca* 10 min) to a soln of quinoline (1.3 g), conc H_2SO_4 (0.6 ml), $AgNO_3$ (0.3 g) in 15 ml 2,3 - dimethyl - 2 - butanol, 4 ml acetonitrile and 5 ml water, heated to 80°. The mixture was kept for 1 hr at 80–90°, made alkaline and extracted with ether. GLC revealed, in addition to unreacted quinoline, 5 compounds: 2-Methylquinoline (1.72%), 4-methylquinoline (2.3%), 2-isopropylquinoline (43.6%), 4-isopropylquinoline (48.6%) and 2,4-diisopropylquinoline (4.3%). All the compounds were identified by comparison with authentic samples. Conversion 38%, yield on converted quinoline 96%.

(B) *By* $Na_2S_2O_8$ *without* Ag^+. The reaction was carried out as in (A). No trace of isopropyl or methylquinolines was revealed by GLC. Most of quinoline (>97%) was unchanged.

Oxidation of ethyleneglykol in presence of protonated quinoline

(A) *By* $Na_2S_2O_8$ *and* Ag^+. A soln of $Na_2S_2O_8$ (1.2 g) in 5 ml water was added under stirring in 15 min to a soln of quinoline (2.6 g), conc H_2SO_4 (1.2 ml), $AgNO_3$ (0.34 g) in 30 ml ethyleneglycol and 10 ml water, heated to 80°. The mixture was stirred for additional 3 hr at 85–90°, made alkaline and extracted with ether. GLC revealed, in addition to unreacted quinoline, 2-hydroxymethyl-**11** (36.2%), 4-hydroxymethyl **12** (32.9%), and 30.9% of an unidentified product. **11** and **12** were identified by comparison with authentic samples (GLC, NMR, MS). Conversion of quinoline 11%.

(B) *By* $Na_2S_2O_8$ *without* Ag^+. The reaction was carried out as in (A). No trace of **11** and **12** was revealed by GLC. The glycols **9** and **10** were the main products. They were identified by MS (*m/e*: 189 (M^+), 158, 143 and 129) and NMR 2.1–2.2δ (m 2H), 3.5–4.3δ (m 2H) 5.5–5.7δ (m 1H) and 7.5–8.8δ (m 6H); conversion on quinoline 6%.

Oxidation of 1-hexanol in presence of protonated quinoline

(A) *By* $Na_2S_2O_8$ *and* Ag^+. A soln of $Na_2S_2O_8$ (9.6 g) in 20 ml water was added under stirring to a soln, heated to 65°, of quinoline (5.2 g), conc H_2SO_4 (2.4 ml), $AgNO_3$ (1.2 g) in 50 ml 1-hexanol, 15 ml water and 15 ml acetonitrile. The mixture was heated for 4 hr to 65–75°, made alkaline and extracted with ether. GLC revealed the presence of unreacted quinoline and the isomer **13** (48%) and **14** (52%). The latter were separated by SiO_2 chromatography (hexane–EtOAc) and analysed by NMR and MS. **13**—MS *m/e*: 229 (M^+), 228, 200, 199, 171, 170, 156, 155, 142, 127, 110. NMR: 0.6–0.9δ (t 3H), 1.1–1.9δ (m 6H), 2.6–3.1δ (q 1H), 3.3–3.7δ (t 2H), 4.4δ (s 1H), 7.0–8.2δ (m 6H). **14**—MS *m/e*: 229 (M^+), 213, 199, 183, 181, 171, 167, 154, 141, 129, 114. NMR: 0.5–0.9δ (t 3H), 1.2–2.0δ (m 6H), 3.2–3.8δ (m 3H) 4.6δ (s 1H), 7.2–8.9δ (m 6H). Conversion of quinoline 34%. Yield on converted quinoline 94%.

(B) *By* $Na_2S_2O_8$ *without* Ag^+. The reaction was carried out as in (A). Conversion of quinoline was 12%. A mixture of at least 6 hydroxyhexyl isomer derivatives of quinoline in comparable amounts were revealed by GLC (all show the molecular ion of 229 in MS). No attempt was made to isolate the single isomers.

Spin-trapping experiments. A Varian E-4 spectrometer was employed. In all experiments four spectra of the resulting nitroxide adduct were measured and averaged to give the nitrogen and hydrogen coupling constants reported; standard deviation are 0.04 g. Some experiments were carried out *in situ* by using a variable temperature unit for heating the sample.

REFERENCES

[1] Part XI—F. Minisci, A. Citterio, M. Perchinunno and F. Bertini, *Gazz. Chim. Ital.* **105**, 1083 (1975).

[2] D. A. House, *Chem. Rev.* **62**, 185 (1962); J. E. Issac and J. O. Edwards, *J. Org. Chem.* **34**, 2565 (1969); L. Dogliotti and E. Hayon, *J. Phys. Chem.* **71**, 2511 (1967).

[3] A. Ledwith, P. J. Russell and L. H. Sutcliffe, *Chem. Comm.* 964 (1971); *Proc. Roy. Soc.* A, **332**, 151 (1973).

[4] A Ledwith, P. J. Russell and L. H. Sutcliffe, *J. Chem. Soc.* Perkin II, 630 (1973).

[5] J. K. Kochi, *Free Radicals* (Edited by J. K. Kochi), Vol. II, p. 676. Wiley, New York (1973).

[6] R. O. C. Norman, P. M. Storey and P. R. West, *J. Chem. Soc.* B, 1087 (1970); R. O. C. Norman and P. M. Storey, *Ibid.* 1099 (1970).

[7] F. Minisci, *Synthesis* 1 (1973); F. Minisci and O. Porta, *Advances in Heterocyclic Chemistry* (Edited by A. R. Ketritzky), Vol. 16, p. 123. Academic Press, New York (1974); F. Minisci, *Topics in Current Chemistry* **62**, 1 (1976).

[8] F. Minisci, R. Mondelli, G. P. Gardini and O. Porta, *Tetrahedron* **28**, 2403 (1972); T. Caronna, G. Fronza, F. Minisci and O. Porta, *J. Chem. Soc.* Perkin II, 1477, 2035 (1972); A. Clerici, F. Minisci and O. Porta, *Tetrahedron* **29**, 2775 (1973); *Ibid.* **30**, 4201 (1974); *J. Chem. Soc.* Perkin II, 1699 (1974).

[9] T. Caronna, R. Galli, V. Malatesta and F. Minisci, *Ibid.* C, 1747 (1971); F. Bertini, T. Caronna, L. Grossi and F. Minisci, *Gazz. Chim. Ital.* **104**, 471 (1974); F. Minisci, A. Citterio, M. Perchinunno and F. Bertini, *Ibid.* **105**, 1083 (1975); A. Citterio, M. Ghirardini and F. Minisci, *Tetrahedron Letters* 203 (1976).

[10] Unpublished results from this laboratory.

[11] W. Buratti, G. P. Gardini, F. Minisci, F. Bertini, R. Galli and M. Perchinunno, *Tetrahedron* **27**, 3655 (1971).

[12] C. Walling and A. Padwa, *J. Am. Chem. Soc.* **85**, 1593 (1963); D. G. Hoare and W. A. Waters, *J. Chem. Soc.* 2552 (1964).

[13] A. Clerici, F. Minisci and O. Porta, *Tetrahedron Letters* 4183 (1974).

[14] H. Lemaire and A. Rossat, *J. Chem. Physique* **61**, 1580 (1964).