Electron-transfer Processes: Metal Salt Catalysed Oxidation of Olefins by Peroxydisulphate

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The reaction of simple olefins (oct-1-ene, oct-2-ene, cyclohexene, cycloheptene) with peroxydisulphate has been investigated under several conditions: (i) in aqueous medium and catalysis by Ag^{I}, Fe^{II}, and Cu^{II}; (ii) in acetic medium and catalysis by Cu^{II}, Fe^{III}; (iii) in the presence of traps of nucleophilic alkyl radicals (protonated heteroaromatic bases and 1,4-benzoquinone either in water or in acetic acid). The catalyst and the radical trap govern the selectivity and allow a variety of new synthetic achievements. Evidence for a unified initial mechanism of electron transfer with formation of a radical cation from the olefin is reported to explain all the results. In water the radical cation gives a β-hydroxyalkyl radical, which, depending on the nature of the catalyst and the trap, can give the corresponding saturated alcohol by hydrogen abstraction, the products of Cu^{II} oxidation, or β-hydroxyalkylation of the heteroaromatic compound or 1,4-benzoquinone. In acetic acid the radical cation gives a β-acetoxyalkyl radical, which is oxidized to the corresponding allylic acetate by copper(II) acetate or trapped by the heteroaromatic base.

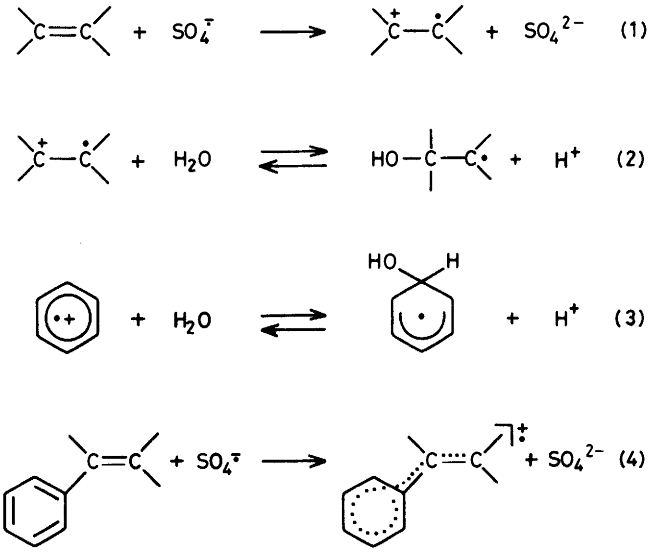
The ability of the radical anion $SO_4^{\cdot -}$, which arises easily from thermal, photochemical, radiolytic, or redox decomposition of peroxydisulphate, to oxidize a variety of organic compounds by electron-transfer processes has recently received increasing support.[1]

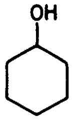
In preliminary reports we have shown the possibility of β-hydroxyalkylation of heteroaromatic bases[2] and 1,4-benzoquinone[3] by oxidation of olefins with peroxydisulphate in water, suggesting, among possible mechanisms, the intermediate formation of a radical cation [equation (1)]. This, according to recent reports,[4] would be in equilibrium with a β-hydroxyalkyl radical [equation (2)] as would also be the case with aromatic radical cations[1] [equation (3)].

Moreover the oxidation of aryl-substituted olefins by peroxydisulphate in acetic acid leads in good yield to the diacetoxylation of the double bond with evidence that an intermediate radical cation is involved[5] [equation (4)].

Since interactions of types (1) and (4) are well documented[1] for aromatic compounds with ionization potentials close to those of the olefins (*i.e.* 8.8 eV for toluene and 8.9 eV for cyclohexene), it was of particular interest to obtain a deeper knowledge of the reactivity of simple olefins with peroxydisulphate, particularly in the presence of metal salt catalysis.

The problem has been investigated by several approaches, which have led to new synthetic developments and to chemical evidence for an electron-transfer mechanism [equation (1)]: (i) oxidation of olefins by peroxydisulphate in aqueous solution and catalysis by Ag^{I}, Fe^{II}, and Cu^{II} salts; (ii) oxidation in acetic acid medium and catalysis by Cu^{II} and Fe^{III} salts; (iii) trapping of the intermediate nucleophilic radicals obtained in (i) and (ii) by protonated heteroaromatic bases and 1,4-benzoquinone.

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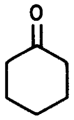
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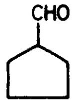
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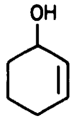
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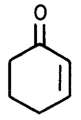
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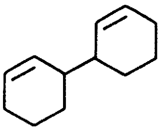
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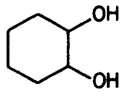
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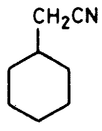
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Results

Oxidation in Aqueous Medium.—When the olefin was oxidized in aqueous medium the reaction took place in a two-phase system (aqueous and organic) even if a co-solvent (acetonitrile) was used. Most of the work was carried out with cyclohexene: compounds (1)—(8) account for the reacted cyclohexene in aqueous acetonitrile medium.

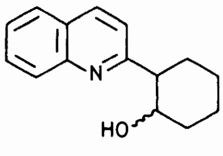
The results for Ag^{I}, Fe^{II}, and Cu^{II} salts, as catalyst, are summarized in Table 1. The behaviour of cycloheptene is quite similar; in the presence of Cu^{II} salt cyclohexancarbaldehyde was obtained in 70% yield.

Qualitative investigations have shown that the behaviour of acyclic olefins, such as oct-1- and -2-ene is similar for catalysis by Ag^{I} and Fe^{II} salts, but no rearrangement to carbonyl compounds was observed in the presence of Cu^{II} salt and epoxides and 1,2-*trans*-diols were the major reaction products. The asymmetrical structures, however, lead to a

Table 1. Reaction products (%) in the metal salt catalysed oxidation of cyclohexene by peroxydisulphate in aqueous acetonitrile

Metal salt	Reaction products (%)[a] (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Olefin conversion (%)[b]
Ag^+	49	2	1.5	4.5	1	16	5	20	90
Fe^{2+}	40	3	1	20	1.5	4	6	14	20
Cu^{2+}		2	80	7					50

[a] mmol per mmol of reacted olefin. [b] mmol per mmol peroxydisulphate used.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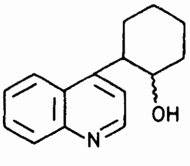
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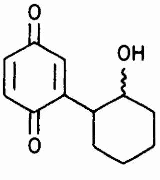
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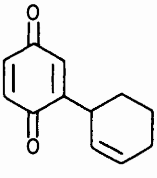
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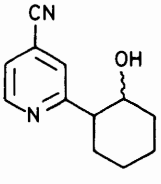
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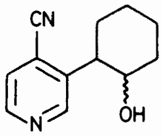
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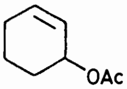
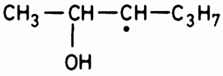
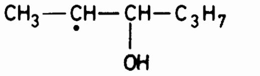

(17)

$AcO{-}CH_2{-}CH{=}CH{-}C_5H_{11}$

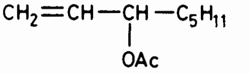
(18)


$CH_3{-}\underset{OH}{CH}{-}\dot{C}H{-}C_3H_7$

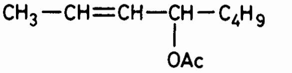
(13)


$CH_3{-}\dot{C}H{-}\underset{OH}{CH}{-}C_3H_7$

(14)


$CH_2{=}CH{-}\underset{OAc}{CH}{-}C_5H_{11}$

(19)


$CH_3{-}CH{=}CH{-}\underset{OAc}{CH}{-}C_4H_9$

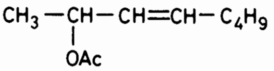
(20)

more complex mixture of the reaction products (both olefinic carbon atoms and both allylic positions are involved) with a considerable reduction in synthetic interest.

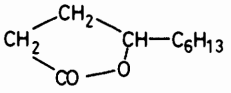
Oxidation in Aqueous Medium in the Presence of Protonated Heteroaromatic Bases.—When the oxidation of cyclohexene in the presence of quinoline was carried out in water by $S_2O_8^{2-}$–Ag^+ under the same experimental conditions in which compounds (1)—(8) are formed, the substituted quinolines (9) and (10) were obtained. Both products (9) and (10) (40 : 60) were mixtures of *trans-* (85%) and *cis-* (15%) isomers. Analogous behaviour takes place in the presence of 4-cyanopyridine: a mixture of *trans-* and *cis-* (90 : 10) isomers of (11) was obtained along with a small amount of (12).

Asymmetrical olefins, such as oct-2-ene, also give the corresponding products of β-hydroxyalkylation, but the number of the isomers is increased. Thus with oct-2-ene and 4-methylquinoline four isomers were detected by g.l.c.–mass spectrometry. The molecular weight and the fragmentation pattern indicate that the four isomers arise from the substitution of position 2 of quinoline by the two β-hydroxyalkyl radicals (13) and (14) and formation of *threo-* and *erythro*-derivatives.

Oxidation in Aqueous Medium in the Presence of 1,4-*Benzoquinone.*—1,4-Benzoquinone behaves similarly to the protonated bases. With cyclohexene compounds (1)—(8) were formed only in traces and the 2-hydroxycyclohexyl-1,4-benzoquinone (15) was the major reaction product along with a small amount of cyclohex-2-enyl-1,4-benzoquinone (16). (15) is a mixture of *trans-* and *cis-* (83 : 17) derivatives.


$CH_3{-}\underset{OAc}{CH}{-}CH{=}CH{-}C_4H_9$

(21)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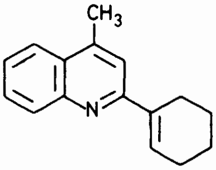
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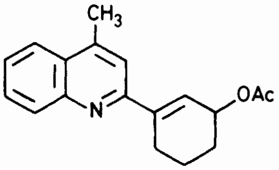
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Oxidation in Acetic Medium.—Potassium peroxydisulphate has very low solubility in acetic acid and the reaction is very slow in the absence of catalyst even at the boiling temperature of the solvent. In the presence of copper(II) acetate the reaction, however, becomes relatively fast and clean for the olefin. Cyclohexene gives the cyclohexenyl acetate (17), whereas oct-1- and -2-ene give all possible allylic acetate isomers (18)—(21). The results are summarized in Table 2. With oct-1-ene, KOAc, and iron(III) acetate the lactone (22) is the major reaction product, whereas the allyl acetates (18)—(21) are minor products. Under the same conditions in which (17) is the only reaction product, but in the presence of 4-methylquinoline, the olefinic derivative (23) is the main reaction product, (24) being the only significant by-product.

Table 2. Allylic acetoxylation of olefins (0.04 mol) by $K_2S_2O_8$ (0.02 mol) and $Cu(OAc)_2$ in AcOH (50 ml)

Olefin	$Cu(OAc)_2$ (mmol)	t/h	Conversion of olefin (%)	Allyl acetates yield (%) [a]	Other products (%)
Cyclohexene	5	6	78	83	
Cyclohexene	20	2	44	90	
Cyclohexene	21	5	89	87	
Cyclohexene	40	6	85	96	
Oct-1-ene	24	5	22	80 [b]	
Oct-2-ene	21	5	50	65 [c]	6% Octan-2-one and 6.2% octan-3-one

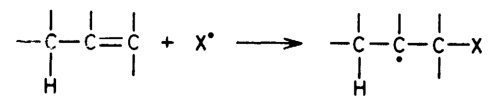
[a] Yields are based on converted olefin. [b] Isomer distribution: (18) 55% and (19) 45%. [c] Isomer distribution: (18) 16%, (19) 25%, (20) 22%, (21) 37%.

Table 3. Oxidation of cyclohexene in aqueous acetic acid by sodium or potassium peroxydisulphate with or without copper(II) acetate catalysis

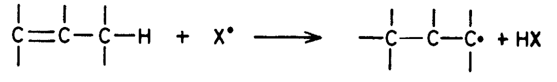
					Products (mol %)						
Cation (mmol)	Olefin (mmol)	Acetic acid (ml)	H_2O (ml)	$Cu(OAc)_2$ (mmol)	$-\overset{\vert}{\underset{\text{OAc}}{C}}-\overset{\vert}{\underset{\text{OAc}}{C}}-$	$-\overset{\vert}{\underset{\text{OH}}{C}}-\overset{\vert}{\underset{\text{OAc}}{C}}$	$-\overset{\vert}{\underset{\text{H}}{C}}-\overset{\vert}{\underset{\text{OAc}}{C}}-$	$-\overset{\vert}{\underset{\text{H}}{C}}-\overset{\vert}{\underset{\text{OH}}{C}}-$	(6)	(17)	Olefin conversion (% on $S_2O_8^{2-}$)
Na^+ (25)	50	30	10		23	48	16	4	12		78
Na^+ (25)	50	30	10	25		1				67	70
K^+ (25)	50	30	10		4	40	20	3	17	9	40
K^+ (25)	50	30	10	25		2				71	74
K^+ (20) *	40	50		5						81	85

* In the absence of water.

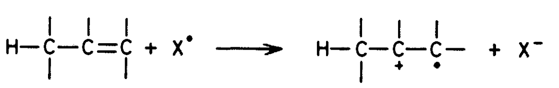
$$S_2O_8^{2-} \longrightarrow SO_4^{\cdot-} \xrightarrow{H_2O} \cdot OH \qquad (5)$$



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}=\overset{|}{C} + X^{\bullet} \longrightarrow -\underset{H}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{\cdot}{C}}-\overset{|}{\underset{|}{C}}-X \qquad (6)$$



$$\overset{|}{C}=\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H + X^{\bullet} \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{\underset{|}{C}}{\bullet} + HX \qquad (7)$$



$$H-\overset{|}{\underset{|}{C}}-\overset{|}{C}=\overset{|}{\underset{|}{C}} + X^{\bullet} \longrightarrow H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{+}{C}}-\overset{|}{\underset{\bullet}{C}}- + X^- \qquad (8)$$

Oxidation in Aqueous Acetic Medium.—The uncatalysed oxidation of cyclohexene by $Na_2S_2O_8$ and $K_2S_2O_8$ in AcOH–H_2O (3 : 1) leads to a mixture of cyclohexane-1,2-diol mono- and di-acetate, cyclohexanol, cyclohexyl acetate, dicyclohexenyl, and cyclohex-3-enyl acetate. In the presence of $Cu(OAc)_2$ practically only cyclohex-3-enyl acetate is formed. The results are summarized in Table 3.

Discussion

Three basic interactions can be envisaged in the reaction of the free radicals ($X\cdot = SO_4^{\cdot-}$, $HO\cdot$) arising from peroxydisulphate [equation (5)] with olefins: (i) addition to the olefinic bond [equation (6)], (ii) abstraction of allylic hydrogen [equation (7)], (iii) electron-transfer [equation (8)]. The results for most of the reactions reported above can be reasonably explained by, at least, two of the interactions (6)—(8), but only the electron-transfer process (8) can explain at the same time all the results by a unified mechanism.

Thus, with cyclohexene in aqueous solution the results obtained with very efficient nucleophilic alkyl radical traps, such as protonated heteroaromatic bases [6] and 1,4-benzoquinone,[7] unequivocally show that the only significant primary intermediate is the 2-hydroxycyclohexyl radical (25) [trapped to give in good yield compounds (9)—(12) and (15), respectively, equations (9) and (10)]. Reactions (9) and (10) are much faster [6,7] than all other possible reactions of the 2-hydroxycyclohexyl radical and therefore only traces of compounds (1)—(8) are formed.

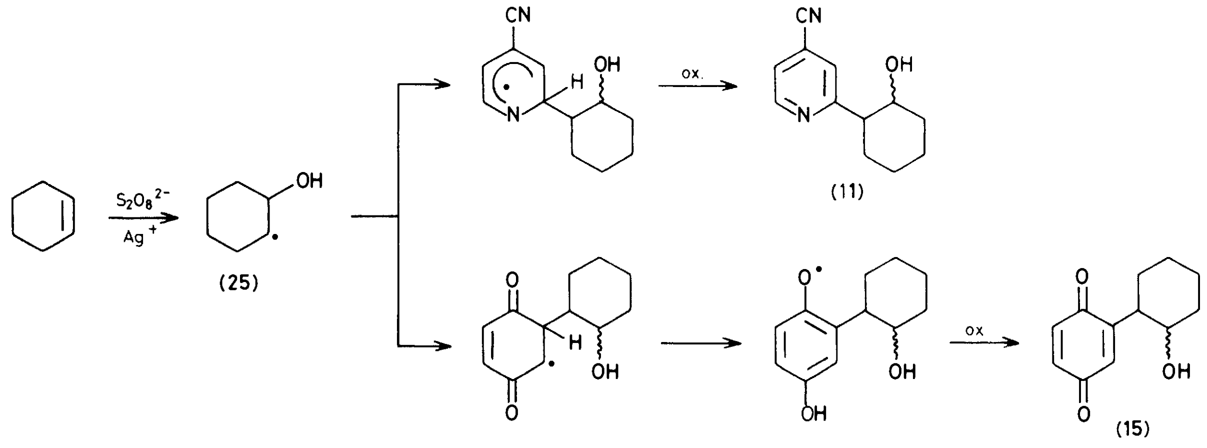
Besides mechanistic considerations both types of reaction have undoubted synthetic potential.

The formation of (25) can be explained by the addition of the hydroxyl radical [equation (6; X = OH)], as well as by an electron-transfer process followed by water addition [equation (11)]. The involvement of hydroxyl radical in the primary interaction can be ruled out owing to the very low amount of allylic hydrogen abstraction observed (a significant side-reaction of these intermediates with olefins [8]).

However, when the oxidation was carried out in acetic acid, only allylic acetoxylation was observed. Also the formation of the cyclohexenyl acetate (17) can be explained by two different mechanisms: hydrogen abstraction [equation (7; $X = SO_4^{\cdot-}$)] followed by the oxidation of the allyl radical [equation (12)] as well as addition of acetic acid to the radical cation and subsequent oxidation [equations (13) and (14)].

The cyclohexenyl acetate (17) cannot be formed by an interaction of the type (6), even if the acetoxyl radical is formed by a competitive process of oxidation of the acetate ion [9] [equation (15)]. The high decarboxylation rate [10] (1.6×10^9 s^{-1} at 60 °C) of the acetoxyl radical [equations (16)] prevents intermolecular reactions from outside the solvent cage. Allylic hydrogen abstraction does not occur through the methyl radical [equation (17)] arising from equation (16) because the Cu^{II} salt is a very effective trap of methyl radical [11] [equation (18)] and the formation of allylic acetates is more selective at higher Cu^{II} salt concentrations (Table 2).

Evidence that the compounds (17)—(21) are formed by processes (13) and (14) was further obtained by carrying out



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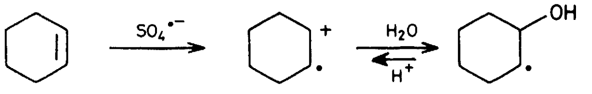


(11)

the reaction under the same conditions, but in the presence of 4-methylquinoline. The formation of (23) does not arise from isomerization of the corresponding allyl derivative (27) [equation (19)] since it was verified that, under the reaction conditions, (27) does not isomerize to (23). Moreover the oxidation of the allylic cyclohex-3-enyl radical by Cu^{II} salt is too fast to give a significant amount of (27); this was verified by generating cyclohex-3-enyl radical by equation (20) in the presence of 4-methylquinoline and Cu^{II} salt. On the contrary, attempts to acetylate the 2-hydroxycyclohexyl derivative (28) by acetic anhydride, acetyl chloride, and acetic acid–dicyclohexylcarbodi-imide lead to the olefinic derivative (23) [equation (21)]. This means that (23) probably arises by elimination of acetic acid from the acetoxy-derivative (29). Compound (24) probably arises from allylic acetoxylation of (23). Thus 2-acetoxyalkyl radicals (26) are the primary intermediate formed in the oxidation in acetic acid, and if we want to explain the different behaviour in water and acetic acid by a unified initial mechanism, we can only invoke the electron-transfer mechanism [equation (10)] with formation of a radical cation and subsequent reaction with the nucleophilic solvent.

The reaction of the olefins in acetic acid are clean because allylic acetates are practically the only products. With cyclohexene the yields based on peroxydisulphate are in the range 75—80%; the simple experimental conditions and the high yields based on converted cyclohexene confer synthetic interest on the reaction; reactions (15) and (18) account for the balance of the peroxydisulphate.

Actually, when terminal olefins, such as oct-1-ene, with an ionization potential somewhat higher than cyclohexene (9.46 and 8.94 eV, respectively)[12] are oxidized in acetic acid with catalysis by iron(III) acetate, which is not able to oxidize the methyl radical,[13] lactone (22) is obtained as well as the allylic acetate isomers (18)—(21). Lactone (22) is formed because the methyl radical is not trapped by the Fe^{III} salt and it abstracts a hydrogen atom from acetic acid with formation of a carboxymethyl radical [equation (22)], which adds to the olefin leading to the lactone (22) [equation (23)].[9] The yields of lactone (22) increase and those of the acetates (18)—(21) decrease by adding the olefin to the reaction medium slowly in order always to keep low the olefin concentration, thus minimizing reaction (1) and increasing the concentration of AcO^- in order to favour reaction (18). In the presence of Cu^{II} salt no lactone is formed, all the methyl radicals are oxidized to methyl acetate [equation (18)], and the main products arising from the olefin are the allylic acetates (18)—(21). The ratios of the allylic acetate isomers observed with unsymmetrical olefins (Table 2) are not significant because isomerization occurs under the reaction conditions.

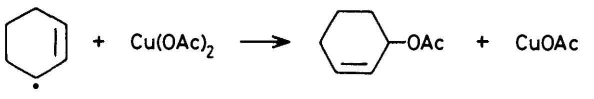
It is noteworthy that with propenylbenzene derivatives the reaction, under the same conditions, leads in high yield to diacetoxylation of the double bond[5] and only to traces of allylic acetoxylation. A possible reason is that the oxidation of a benzylic radical by $Cu(OAc)_2$ leads to a benzylic acetate[7] [equation (24)] and not to the olefin. It is not easy to establish that the initial β-acetoxyalkyl radical has structure (30) or (31), but from analogous systems[14,15] we would expect that (30) rearranges to (31) [equation (25)]. The formation of the compounds (1)—(8) in water can be explained by the further reaction of the 2-hydroxycyclohexyl radical (25). The metal salt plays two roles in catalysis, which both sustain a redox chain. The reducing form decomposes the peroxydisulphate in the redox process (26). The oxidized form determines the selectivity of the process. Thus the system $S_2O_8^{2-}$–Ag^+ is not able effectively to oxidize alkyl and allyl radicals[1] because the stationary concentrations of the radicals and Ag^{2+} are always low, whereas the Ag^{2+} salt can compete with the radical anion $SO_4^{\bullet-}$ in oxidizing the olefinic bond [equation (27)].

The 2-hydroxycyclohexyl radical (25) therefore reacts further by hydrogen abstraction from cyclohexene and the solvent (CH_3CN) giving cyclohexanol and cyclohex-3-enyl (32) and cyanomethyl radical (33), respectively (Scheme 1). The cyclohexenyl radical mainly dimerizes to dicyclohexenyl (6) and, to a minor extent, it is oxidized to cyclohexenol (4) and cyclohexenone (5). The cyanomethyl radical adds to cyclohexene and the resulting radical adduct leads to (8) by hydrogen abstraction. It is noteworthy that cyclohexanol formed by hydrogen abstraction from (25) is oxidized to cyclohexanone only to a small extent. That means that cyclohexene is much more reactive than cyclohexanol towards Ag^+–$S_2O_8^{2-}$, particularly taking into account the fact that the reaction was carried out in a two-phase system (aqueous–organic) and that cyclohexanol is much more soluble in water than cyclohexene.

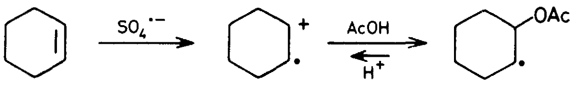
We have reported[16] unequivocal evidence for the oxidation of alcohols by Ag^+–$S_2O_8^{2-}$ to the corresponding alkoxyl radical [equation (28)]. Moreover in a preliminary report[2] we have shown that unsaturated alcohols give rise, in the presence of protonated heteroaromatic bases (**B**), to products of intramolecular addition [equation (29)].

The present results suggest that the nucleophilic radicals (34) and (35), intermediates in these oxidations, can arise from intramolecular nucleophilic addition of the intermediate radical cation [equation (30)].

This mechanism would explain the different regioselectivity observed in these cyclizations by comparison with an actual intramolecular addition of an alkoxyl radical.[17] We can, however, expect that the predominant oxidation of the hydroxy-


(12)

(17)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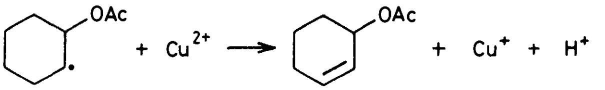
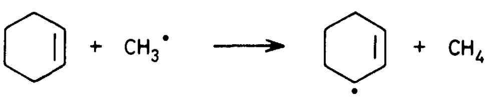
(26)


(14)

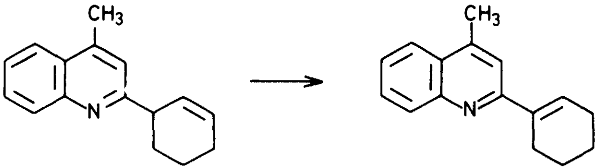
(17)

$$AcO^- + SO_4^{\bullet -} \longrightarrow AcO^\bullet + SO_4^{2-} \qquad (15)$$

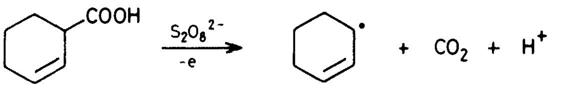
$$AcO^\bullet \xrightarrow{o} CH_3^\bullet + CO_2 \qquad (16)$$


(17)

$$CH_3^\bullet + Cu(OAc)_2 \not\longrightarrow CH_3OAc + CuOAc \qquad (18)$$


(19)

(27) (23)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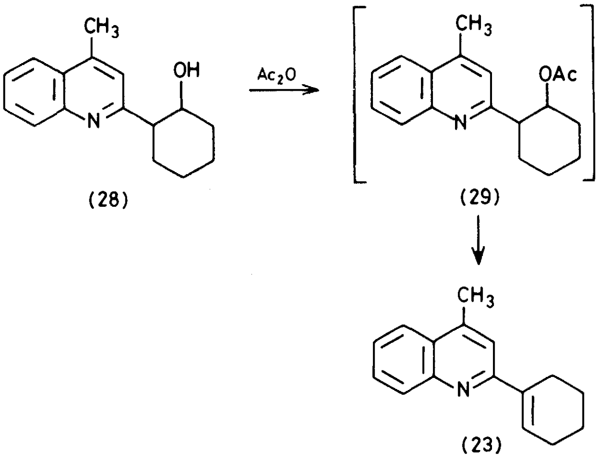

(21)

(28) (29) (23)

group or the olefinic bond by Ag^+–$S_2O_8^{2-}$, when both functions are present, is strictly related to the ionization potential of the olefin. When an Fe^{II} salt is used in water instead of Ag^I salt only a minor modification occurs because the Fe^{III} salt is not able to oxidize [13] the 2-hydroxycyclohexyl radical (25) but oxidizes the cyclohexenyl radical more efficiently [equation (31)]. Thus the amount of cyclohexenol (4) and cyclohexenone (5) increases and that of dicyclohexenyl (6) decreases. Copper(II) salt completely changes the reaction course because it selectively oxidizes the 2-hydroxycyclohexyl radical to cyclopentanecarbaldehyde (3) [equation (32)].

Oxidative rearrangement by Cu^{2+}–$S_2O_8^{2-}$ is far the predominant reaction pathway observed with cyclic olefins, whereas with acyclic olefins formation of epoxides and *trans*-1,2-diols prevail.

Kochi *et al.*[18] have shown that the oxidation of alkyl radicals by Cu^{II} salts generally procedes *via* the formation of an alkylcopper intermediate [equation (33)] which can then undergo either β-proton elimination to form an alkene [equation (34)], or electron-transfer to form a carbonium ion [equation (35)]. For β-hydroxyalkyl radicals the reaction sequence would be shown by equations (34)—(36). The β-elimination (34) was, however, never observed with β-hydroxyalkyl radicals. Walling *et al.*[19] found evidence only of glycol production, whereas Buxton *et al.*[20] reported high yields of epoxide. These results, obtained for different radical sources, agree with our results for acyclic olefins and the epoxide is probably the precursor of the glycol.

The formation of the aldehyde from cyclic olefins involves a Wagner–Meerwein type rearrangement with ring contraction. It was important to establish if aldehydes were primary oxidation products of cyclic olefins or if they arose from rearrangement of the epoxides or the glycols first formed. It was therefore verified that under the reaction conditions neither cyclohexene oxide nor cyclohexane-1,2-diol rearrange to cyclopentanecarbaldehyde. Thus we suggest that the aldehydes are formed by oxidative rearrangement of the alkylcopper intermediate (35), favoured by a suitable conformation [equation (37)].

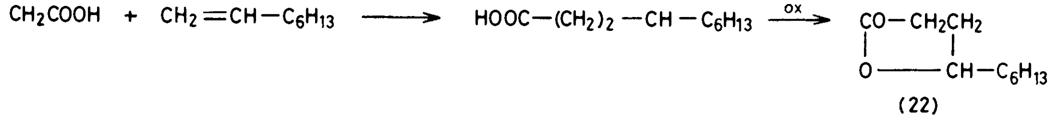
This interpretation is also supported by the oxidative rearrangement of cyclohexene to cyclopentanecarbaldehyde with Hg^{II},[21] Pb^{IV},[22] and Tl^{III} [23] salts. In these cases electrophilic addition to the double bond occurs with formation of an organometallic intermediate similar to (35) [equation (38)].

The analogy between Cu^{2+}–$S_2O_8^{2-}$ and Hg^{II} salts in the oxidation of cyclic olefins is even closer. In fact, whereas with $HgSO_4$ cyclohexene is oxidized to cyclopentanecarbaldehyde [equation (39)], with $Hg(OAc)_2$ it gives the allylic ester [equation (40)]. The behaviour is identical to that of Cu^{2+}–$S_2O_8^{2-}$: with $CuSO_4$ cyclopentanecarbaldehyde is obtained in good yield [equation (4)], whereas with $Cu(OAc)_2$ cyclohex-2-enyl acetate is the only reaction product [equation (42)].

These results strongly imply that similar organometallic intermediates are involved in both cases and provide further evidence of the Kochi's rationalization [11,18] of the interactions between alkyl radicals and copper(II) salts. They also suggest that probably the acetoxy-moiety bonded to a mercury or copper organometallic intermediate plays a role in the β-proton elimination [equation (43)].

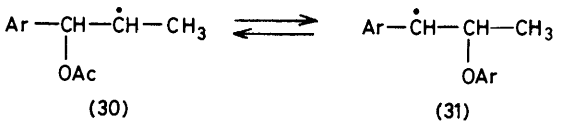
The results reported by Russian workers [24] for the oxidation of olefins by peroxydisulphate in acetic acid–water (molar ratio 1 : 1) in the absence of metal salts merits comment. Instead of the good selectivity observed by us for Cu^{II} catalysis, a complex mixture of products has been reported.[24] Two aspects of their results, however, are surprising by comparison with ours (Tables 1 and 2), even if the amount of reacted olefin is poor: the absence of monofunctional alcohols, which are the main reaction products in the absence of Cu^{II} salts but in the presence of Ag^+ and Fe^{2+} (Table 1) and the predominance of 1,2-dihydroxy-acetate and -diacetate when no transition metal salt is added. In our opinion these results can be explained by the fact that the reaction of the initially formed

$$CH_3^{\bullet} + CH_3COOH \longrightarrow CH_4 + {}^{\bullet}CH_2COOH \qquad (22)$$



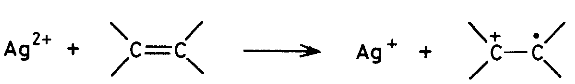
$$CH_2COOH + CH_2{=}CH{-}C_6H_{13} \longrightarrow HOOC{-}(CH_2)_2{-}CH{-}C_6H_{13} \xrightarrow{ox} \text{(22)} \qquad (23)$$

$$Ar{-}\dot{C}H{-}CH(OAc){-}CH_3 + Cu(OAc)_2 \longrightarrow Ar{-}CH(OAc){-}CH(OAc){-}CH_3 + CuOAc \qquad (24)$$

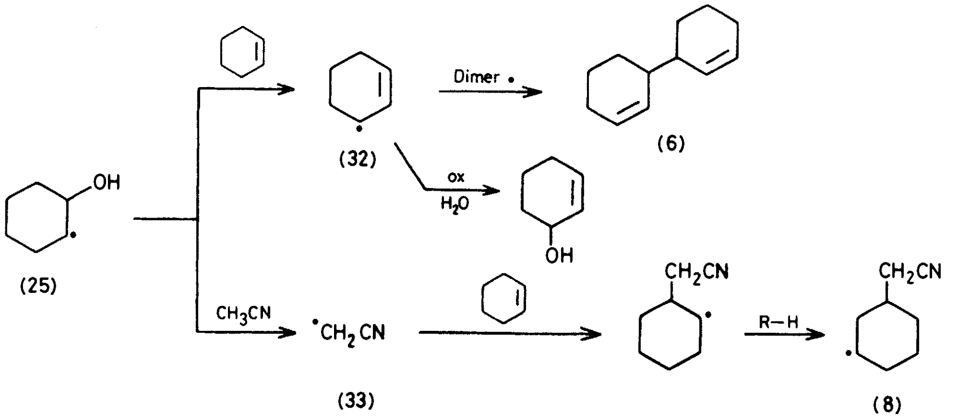


$$Ar{-}CH(OAc){-}\dot{C}H{-}CH_3 \rightleftharpoons Ar{-}\dot{C}H{-}CH(OAr){-}CH_3 \qquad (25)$$

$$S_2O_8^{2-} + M^{+} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} + M^{2+} \quad (M^{+}{=}Ag^{+}, Cu^{+}, Fe^{2+}) \qquad (26)$$



(27)



Scheme 1.

radical cation with water is a reversible process [4] [equation (2)] whereas the reaction of the radical cation with acetic acid could proceed irreversibly according to Scheme 2.[24] The cyclic radical (36) should be much more oxidisable than the β-hydroxyalkyl radical (25) so that bifunctional oxygenated products are obtained.

The mechanism in Scheme 2 could be invalidated by the work of Beckwith and his co-workers [14] on the mechanism of rearrangement of β-acetoxyalkyl radicals, even though we do not consider that their kinetic and e.s.r. evidence is conclusive.* In any case, the only reasonable alternative to the mechanism in Scheme 2 is that, contrary to β-hydroxyalkyl radicals, β-acetoxyalkyl radicals are easily oxidized by peroxydisulphate [equation (44)]. Evidence that the 2-acetoxycyclohexyl radical is oxidized by peroxydisulphate according to equation (44) was obtained by comparing the results with sodium and potassium peroxydisulphate and cyclohexene under the same experimental conditions in acetic acid–water (3 : 1) (Table 3). With $Na_2S_2O_8$ the 1,2-hydroxy-acetates and -diacetates are the major reaction products, whereas with $K_2S_2O_8$ cyclohexyl acetate and dicyclohexenyl are formed in increasing amounts. This behaviour can be related to the large difference of solubility of sodium and potassium peroxydisulphate in water–acetic acid (3 : 1). The sodium salt is soluble enough to allow predominant oxidation according to equation (44), whereas the low solubility of potassium salt makes this oxidation less favourable and β-acetoxycyclohexyl radical abstracts hydrogen from cyclohexene [equation (45)] leading to cyclohexyl acetate and cyclohexenyl radical which mainly dimerize to dicyclohexenyl.

The problem is why β-acetoxycyclohexyl radical is easily oxidized by peroxydisulphate, whereas β-hydroxycyclohexyl,

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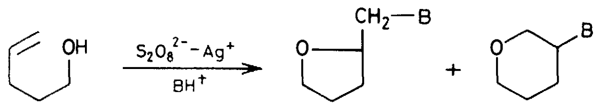
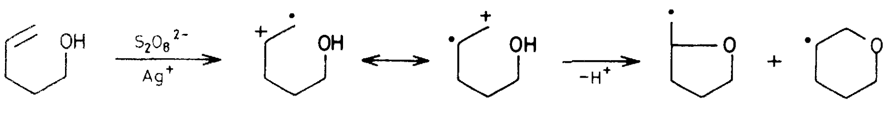
* *Note added in proof:* Rate constant for the free-radical rearrangement $RC(O)O(CH_3)_2{-}CH_2^{\bullet} \rightarrow RC(O)OCH_2{-}\dot{C}(CH_3)_2$, and for the ring-opening reaction $R{-}\dot{C}OCH_2C(CH_3)_2O \rightarrow RC(O)OCH_2{-}\dot{C}(CH_3)_2$ have been measured by kinetic e.s.r. spectroscopy (L. R. C. Barclay, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, 1982, **104**, 4399). On this basis, the formation of a 1,3-dioxolan-2-yl radical as an intermediate in these rearrangements cannot be ruled out.

$$R-OH + Ag^{+} \longrightarrow R-O^{\bullet} + Ag^{+} + H^{+} \qquad (28)$$



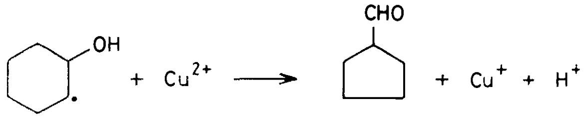
(29)



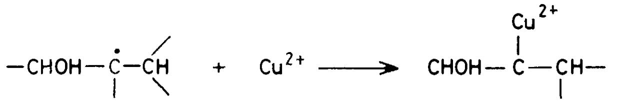
(34) (35)

(30)

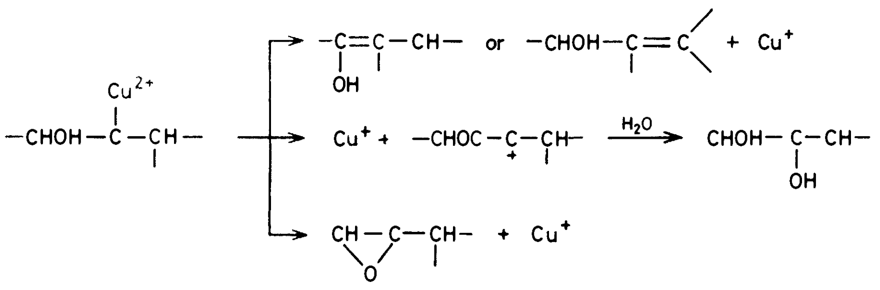
(31)



(32)



$$-CHOH-\dot{C}-CH + Cu^{2+} \longrightarrow CHOH-C(Cu^{2+})-CH- \qquad (33)$$



(34)

(35)

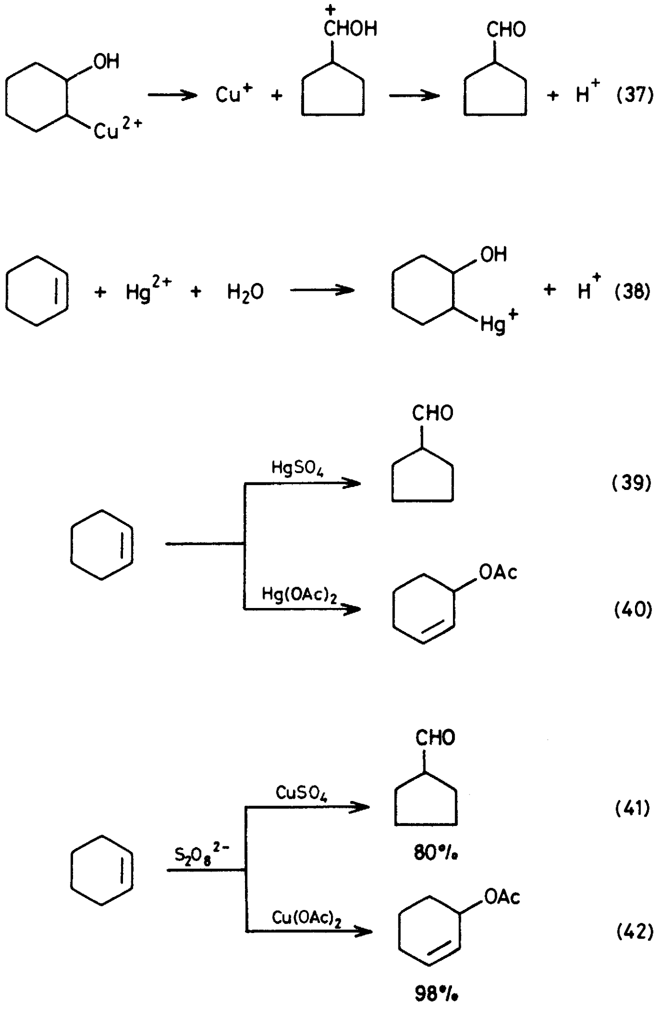
(36)

cyclohexyl, and in general primary, secondary, and tertiary alkyl radicals are not so oxidized.[1] If we exclude the intermediate formation of the cyclic radical (26), this easy oxidability can be explained by neighbouring group participation in the oxidation, the limiting case being the formation of a cyclic carbonium ion [equations (46) and (47)]. In the presence of $Cu(OAc)_2$ with both sodium and potassium peroxydisulphate in aqueous acetic acid the main reaction product is cyclohexenyl acetate as in acetic acid solution [equation (17)]. That is surprising because H_2O is a better nucleophile than AcOH; it, however, can always be explained by the fact that the addition of water to the radical cation is reversible [equation (2)] and the oxidative elimination of the intermediate β-acetoxyalkyl radical by Cu^{2+} [equation (14)] is faster than the intramolecular process in Scheme 2. Actually when the interactions of the nucleophilic solvents are irreversible [equations (47) and (48)] the formation of hydroxy-derivatives becomes important (Table 3).

Experimental

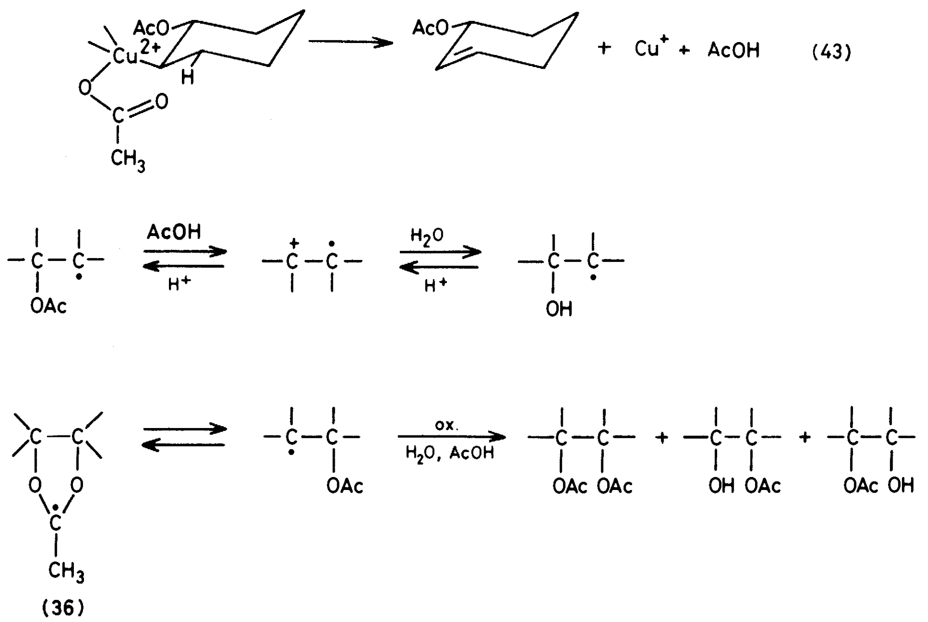
M.p.s are uncorrected. I.r. spectra were recorded for liquid films or KBr pellets on a Perkin-Elmer E-177 spectrometer. N.m.r. spectra were obtained for $CDCl_3$ solutions (Me_4Si as internal standard) on Varian A90 or A100 spectrometers. Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6D spectrometer at 70 eV. G.l.c.-m.s. analyses were performed on a Finnigan 4021 spectrometer equipped with capillary column (20 m) packed with Carbowax 20M. G.l.c. analyses were performed on a Carlo Erba 4200 instrument with flame ionization detector using a glass column (2m) packed with (A) 10% UCC 289 on Chromosorb W-AW-DMCS (80—100 mesh), (B) Carbowax 20M on Chromosorb W-DMCS (80—100 mesh), or (C) OV 101 on Chromosorb W-DMCS (80—100 mesh), using the internal standard method after calibration for the products determined.

Materials.—All the olefins were distilled before use. 1,4-Benzoquinone was sublimed before use. $K_2S_2O_8$, $Cu(OAc)_2 \cdot H_2O$, $CuSO_4 \cdot 5H_2O$, and $AgNO_3$ were Carlo Erba products. Basic iron(III) acetate was a Redel-Hanegen product. Quinoline, 4-methylquinoline, 4-cyanopyridine, cyclohexanol, cyclohexanone, cyclohex-2-enol, cyclohex-2-enone, and octan-2- and -3-one, and *cis*- and *trans*-cyclohexane-1,2-diols were Aldrich products. The following compounds were prepared according to literature methods: *trans*-2-hydroxycyclohexyl acetate, b.p. 130—131 °C at 15 mmHg); [25] *trans*-cyclohexane-1,2-diyl diacetate, b.p. 126—128 °C at 15 mmHg; [25] cyclohex-2-enyl acetate, b.p. 75—76 °C at 20 mmHg; [26] octenyl acetates (18)—(21), b.p. 90—95 °C at 13 mmHg; [27] cyclohexene oxide, b.p. 131 °C; [28] oct-1-ene oxide, b.p. 64—65 °C at 20 mmHg; [28] oct-2-ene oxide, b.p. 71—72 °C at 20 mmHg; [28] cyclopentanecarbaldehyde, b.p. 77—78 °C at 100 mmHg; [29] cyclohexanecarbaldehyde, b.p. 72—73 °C at 20 mmHg.[29]

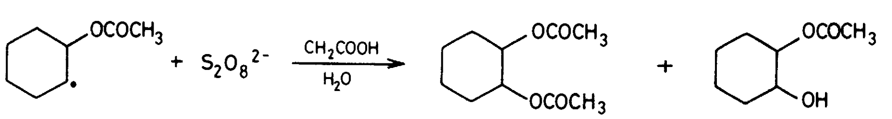


Oxidation of Cyclohexene and Cycloheptene in Aqueous Media.—General procedure. A mixture of $K_2S_2O_8$ (5.4 g, 0.02 mol), cyclohexene (10.1 ml, 0.1 mol), and the appropriate metal salt (0.008 mol) in water (50 ml) and acetonitrile (50 ml) was stirred for 6 h at 60 °C. The aqueous layer was saturated with Na_2SO_4 and the organic layer was separated, dried, and analysed in g.l.c. after addition of dec-1-ene as internal standard. The aqueous solution was continuously extracted with diethyl ether and the organic extract dried and analysed as previously by g.l.c. All compounds were identified by comparison with authentic samples. The results are summarized in Table 1. Under the experimental conditions used, 1,2-epoxycyclohexane and *trans*-1,2-dihydroxycyclohexane do not rearrange to cyclopentanecarbaldehyde. Cycloheptene was oxidized under the same conditions in the presence of $CuSO_4$; the yield of cyclohexanecarbaldehyde based on converted cycloheptene is 70%.

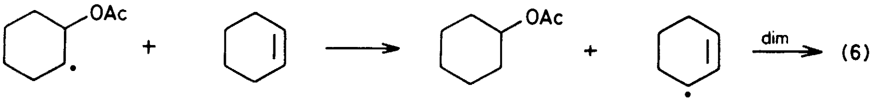
Oxidation of cyclohexene in aqueous medium in the presence of heteroaromatic bases. $K_2S_2O_8$ (5.4 g, 0.02 mol) in water (20 ml) were added over 1 h with stirring to a refluxing mixture of quinoline (2.68, 0.02 mol), concentrated H_2SO_4 (1 ml, 0.02 mol), $AgNO_3$ (0.34 g, 0.002 mol), and cyclohexene (16.2 ml, 0.16 mol) in water (25 ml)–acetonitrile (25 ml). The mixture was refluxed for an additional 2 h, then cooled at 20 °C. The organic layer was separated and extracted with 36% HCl (5 ml). The acid solution was added to the aqueous phase and the precipitated AgCl was filtered. The resulting solution was basified with 30% NaOH at pH 9 and extracted with $CHCl_3$ (4 × 50 ml). The extract was washed with saturated NaCl solution, dried, and concentrated to 100 ml. This solution (10 ml) was analysed quantitatively by g.l.c. after addition of 2,4-dimethylquinoline as internal standard. The remaining solution was concentrated and the residue was chromatographed through a silica gel column (Merck; 0.032—0.063 mesh) using the flash chromatography technique and eluting with a 3% gradient of ethyl acetate in hexane. The separation gave four pure compounds, identified by spectral data as *cis*- and *trans*-(9) and *cis*- and *trans*-(10). The conversion of quinoline was



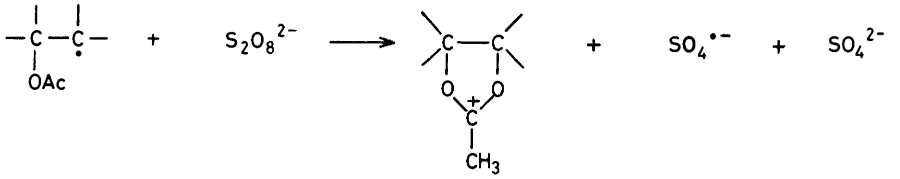
Scheme 2.



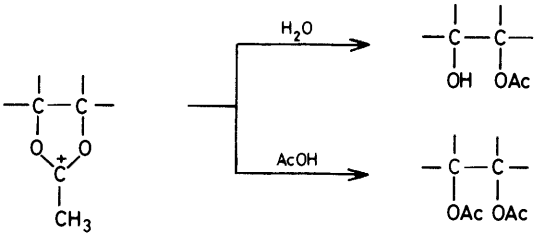
(44)



(45)



(46)



(47)

(48)

51%. The yield in (9) and (10) based on converted quinoline was 100%. The isomer distribution was *cis*-(9) 6.4%, *trans*-(9) 36.2%, *cis*-(10) 4.3%, *trans*-(10) 53.1%. *cis*-(2-Hydroxycyclohexyl)quinoline *cis*-(9) had m.p. 126 °C (from di-isopropyl ether); $\nu_{\text{max.}}$ 3 300br cm^{-1}; *m/e* 227 (M^+), 226, 210, 199, 184, 170, 156 (100%), 143, 128, 115, 101, and 77; δ 0.9—2.2 (8 H, m, aliph.), 2.9 (1 H m, C*H*Ar), 4.5 (1 H, m, C*H*OH), 7.25 (1 H, d, 3-H), 7.4—7.8 (3 H, m, 5—7-H), 8.05 (1 H, dd, 8-H), 8.1 (1 H, d, 4-H), and 12.0br (1 H, OH). *trans*-(9) had m.p. 134 °C (from diethyl ether–chloroform); $\nu_{\text{max.}}$ 3 400br cm^{-1}; *m/e* 227 (M^+, 8%), 226 (7), 225 (5), 210 (12), 199 (23), 184 (10), 170 (10), 156 (100), 143 (21), and 130 (50); δ 1.2—2.3 (8 H, m, aliph.), 2.8 (1 H, ddd, CHAr), 4.1 (1 H, ddd, C*H*OH), 4.6br (1 H, D_2O exchangeable, OH), 7.3 (1 H, d, 3-H), 7.4—7.8 (3 H, m, 5—7-H), 7.95 (1 H, dd, 8-H), and 8.0 (1 H, d, 4-H). *cis*-4-(2-Hydroxycyclohexyl)quinoline *cis*-(10) had m.p. 134 °C (from di-isopropyl ether); $\nu_{\text{max.}}$ 3 300 cm^{-1}; *m/e* 227 (M^+, 20%), 199 (8), 180 (12), 172 (10), 170 (8), 156 (100), 143 (28), and 128 (16); δ 1.2—2.0 (8 H, m, aliph.), 2.9 (1 H, m, C*H*Ar), 3.8 (1 H, m, C*H*-OH), 4.2br (1 H, OH), 7.4 (3-H), 7.5—7.8 (6-, 7-H), 8.00 (1 H, dd, 5-H), 8.2 (1 H, dd, 8-H), and 8.6 (1 H, d, 2-H). *trans*-(10) had m.p. 127—128 °C (from diethyl ether); $\nu_{\text{max.}}$ 3 240 cm^{-1}; *m/e* 227 (M^+, 27%), 199 (9), 198 (7), 180(7), 170 (8), 156 (100), 154 (18), 143 (28), 130 (17), 115 (10), 83 (12), 45 (30), and 39 (28); δ 1.2—2.2 (8 H, m, aliph.), 3.4 (1 H, m, C*H*Ar), 3.92 (1 H, m, C*H*OH), 4.35br (1 H, D_2O exchangeable, OH), 7.3 (1 H, d, 3-H), 7.6—7.8 (2 H, m, 6-, 7-H), 7.97 (1 H, dd, 5-H), 8.27 (1 H, dd, 8-H), and 8.56 (1 H, d, 2-H).

Using the same procedure 4-cyanopyridine gives the following results: conversion 30%; yield of (11) and (12) based on converted 4-cyanopyridine 93%; isomer distribution, *cis*-(11) 8.7%, *trans*-(11) 80.6%, *trans*-(12) 10.7%. *cis*-4-Cyano-2-(2-hydroxycyclohexyl)pyridine *cis*-(11) had m.p. 130 °C (from diethyl ether); $\nu_{\text{max.}}$ 3 300 and 2 235 cm^{-1}; *m/e* 202 (M^+, 4%), 201 (2), 183 (10), 174 (32), 169 (8), 157 (8), 155 (20), 145 (10), 131 (100), and 77 (30); δ 1.3—2.2 (8 H, m, aliph.), 2.7 (1 H, m, C*H*Ar), 3.9 (1 H, m, C*H*OH), 7.4 (1 H, d, 5-H), 7.5 (1 H, s, 3-H), and 8.8 (1 H, d, 6-H). *trans*-(11) had m.p. 135—136 °C (by sublimation); $\nu_{\text{max.}}$ 3 400 and 2 240 cm^{-1}; *m/e* 202 (M^+, 2%), 201 (3), 184 (10), 183 (9), 174 (30), 169 (5), 159 (9), 157 (6), 155 (15), 145 (15), 143 (14), 142 (13), 131 (100), 118 (20), and 77 (26); δ 1.3—2.2 (8 H, m, aliph.), 2.71 (1 H, m, C*H*Ar), 3.6br (1 H, D_2O exchangeable, OH), 3.94 (1 H, m, C*H*OH), 7.41 (1 H, d, 5-H), 7.5 (1 H, s, 3-H), and 8.78 (1 H, d, 6-H). *trans*-4-Cyano-3-(2-hydroxycyclohexyl)pyridine *trans*-(12) had m.p. 149—150 °C (from diethyl ether); $\nu_{\text{max.}}$ 3 320br and 2 235 cm^{-1}; *m/e* 202 (M^+, 52%), 184 (4), 183 (5), 174 (26), 173 (12), 169 (7), 159 (6), 157 (10), 155 (8), 145 (12), 133 (27), 132 (100), 118 (38), 93 (12), and 77 (14); δ 1.2—2.3 (8 H, m, aliph.), 2.9 (1 H, m, C*H*Ar), 3.85 (1 H, m, C*H*OH), 7.5 (1 H, d, 5-H), 8.7 (1 H, s, 2-H), and 8.8 (1 H, d, 6-H).

Under the same conditions 4-methylquinoline gives the following results: conversion 55%; yield of (28) based on converted 4-methylquinoline 90%; isomer distribution, *cis*-(28) 13%, *trans*-(28) 87%. *trans*-2-(2-Hydroxycyclohexyl)-4-methylquinoline *trans*-(28) had m.p. 118—119 °C (from propan-2-ol); $\nu_{\text{max.}}$ 3 220 cm^{-1}; δ 1.2—2.3 (8 H, m, aliph.), 2.7 (3 H, s, CH_3), 2.9 (1 H, m, C*H*Ar), 4.1 (1 H, m, C*H*OH), 4.5br (1 H, D_2O exchangeable, OH), 7.25 (1 H, s, 3-H), 7.5—7.8 (2 H, m, 6-, 7-H), 8.0 (1 H, dd, 5-H), and 8.3 (1 H, dd, 8-H); *m/e* 241 (M^+), 240, 224, 213, 198, 184, 170 (100%), 143, 130, and 76. *cis*-(28) had m.p. 106—107 °C (from propan-2-ol), $\nu_{\text{max.}}$ 3 300 cm^{-1}; *m/e* 241 (M^+), 240, 224, 213, 184, 170 (100%), 142, 129, 128, and 77.

*Oxidation of oct-*1- *and -*2-*ene in aqueous media.* $Na_2S_2O_8$ (2.25 g, 0.01 mol) and water (10 ml) were added over 1 h to a refluxing mixture of octenes (2.5 ml, 6.2 mmol) and $AgNO_3$ (0.170 g, 1 mmol) in water (20 ml)–acetonitrile (40 ml). Acetonitrile and octenes were distilled off and the aqueous phase was extracted with ether. G.l.c. revealed, as main reaction products, octan-1- and -2-ol from oct-1-ene and octan-2- and -3-ol from oct-2-ene. The compounds were identified by comparison with authentic samples.

Oxidation of oct-2-ene in aqueous medium in the presence of

4-*methylquinoline*. $(NH_4)_2S_2O_8$ (4.6 g, 20 mmol) and water (10 ml) were added at 70 °C over 20 min to a mixture of 4-methylquinoline (2.65 ml, 20 mmol), oct-2-ene (25 ml, 62 mmol), H_2SO_4 (0.8 ml, 15 mmol), and $AgNO_3$ (0.689, 5 mmol) in water (20 ml) and acetonitrile (10 ml). The mixture was stirred for 4 h at 70 °C, then diluted with water, basified at pH 9 and extracted by CH_2Cl_2. Analysis by g.l.c. (capillary columns)–mass spectra revealed the presence of four 2-(β-hydroalkyl)-4-methylquinoline isomers, *m/e* 259 (M^+), 258, 241, 188, 170 (100 %), and 142.

Oxidation of cyclohexene in water in the presence of 1,4-*benzoquinone*. $K_2S_2O_8$ (5.4 g, 0.02 mol) was dissolved in water (25 ml) and a mixture of cyclohexene (8.2 ml, 0.1 mmol) and 1,4-benzoquinone (2.16 g, 0.02 mol) in acetonitrile (25 ml) was added. The mixture was vigorously stirred and warmed at 50 °C; the reaction was started by addition of a solution of $AgNO_3$ (0.34 g, 2 mmol) in water (1 ml). The reaction was run for 3 h, then cooled and the organic layer separated; the water layer, saturated with Na_2SO_4, was extracted with diethyl ether (2 × 50 ml). The combined organic extracts were dried and concentrated to 100 ml; 2,3,5-trimethyl-1,4-benzoquinone was added as internal standard and the solution was analysed by g.l.c. on the OV17 and SP 2250 columns. In a parallel experiment, the extracts were concentrated at room temperature, most of the unchanged 1,4-benzoquinone was vacuum sublimed and the residue was chromatographed on SiO_2 (hexane–hexyl acetate 7 : 3). The results of the analyses and the analytical data for the compound isolated were: olefin conversion 14%; quinone conversion 60%; yield of (15) (*trans* 82%, *cis* 18%) 90% on converted olefin and 68% on quinone; yield of (16) 12% on converted quinone. 2-(Cyclohex-2-enyl)-1,4-benzoquinone (16) had $\nu_{max.}$ 1 660 and 1 600 cm^{-1}; δ 1.2—2.1 (6 H m, aliph.), 3.56 (1 H, m, CHAr), 5.41 (1 H, m, *J* 7.5 Hz, cyclohexyl 2-H), 5.94 (1 H, m, cyclohexyl 3-H), 5.58 (1 H, s, 3-H), and 5.73 (2 H, s, 5-, 6-H); *m/e* 188 (M^+), 173, 160, 147, 91, 67, and 55. *trans*-2-(2-Hydroxycyclohexyl)-1,4-benzoquinone (15) had m.p. 87—88 °C (from hexane); $\nu_{max.}$ 3 500, 1 660, and 1 600 cm^{-1}; δ 1.1—2.2 (8 H, m, aliph.), 2.7 (1 H, m, C*H*Ar), 353 (1 H, m, C*H*OH), 661 (1 H, s, 3-H), 6.76 (2 H, 5-, 6-H), and 11.0br, (1 H, OH); *m/e* 206 (M^+, 11%), 188 (10), 162 (50), 160 (21), 149 (38), 147 (36), 123 (100), 94 (40), 82 (30), 77 (26), and 39 (60). *cis*-2-(Hydroxycyclohexyl)-1,4-benzoquinone (15) had m.p. 112—113 °C (from hexane); $\nu_{max.}$ 3 500, 1 660, and 1 600 cm^{-1}; δ 1.2—2.0 (8 H, m, aliph.), 2.9 (1 H, m, C*H*Ar), 3.95 (1 H, m, C*H*OH), 6.66 (1 H, s, 3-H), and 7.75 (2 H, s, 5-, 6-H); *m/e* 206 (M^+, 31%), 204 (10), 188 (10), 176 (12), 162 (100), 160 (30), 149 (80), 147 (55), 123 (75), and 83 (60).

Oxidation of Olefins in Acetic Acid Solution.—Procedure 1. A mixture of olefin (0.04 mol), $Cu(OAc)_2 \cdot H_2O$ (0.998 g, 0.005 mol), AcOK (11.78 g, 0.12 mol), and $K_2S_2O_8$ (5.4 g, 0.02 mol) in acetic acid (50 ml) was refluxed (118 °C) for 3 h under nitrogen. The mixture was cooled at 0 °C, dec-1-ene (1 g) was added as internal standard and concentrated H_2SO_4 (2.3 ml, 0.025 mol) was then added. The precipitated K_2SO_4 and $CuSO_4$ were filtered off and the acetic solution was directly analysed by g.l.c.

Procedure 2. A mixture of olefin (0.04 mol), $Cu(OAc)_2 \cdot H_2O$ (3.81 g, 0.021 mol), and $K_2S_2O_8$ (5.4 g, 0.02 mol) in acetic acid (50 ml) was refluxed for 4—8 h. Dec-1-ene was added as internal standard and the solution was directly analysed by g.l.c. Alternatively the solution was basified with 10% NaOH solution at −10° (pH 9) and the mixture extracted with CH_2Cl_2 (3 × 50 ml). The combined extracts were washed with water, dried, and analysed as previously. The results are summarized in Table 2.

*Oxidation of oct-*1*-ene in acetic acid in the presence of* $Fe(OAc)_2OH$. A mixture of $Fe(OAc)_2OH$ (0.93 g, 4.8 mmol), KOAc (15.7 g, 0.16 mol), $K_2S_2O_8$ (2.7 g, 0.01 mol), and oct-1-ene (2.18 g, 0.02 mol) in acetic acid (50 ml) was refluxed (115 °C) under nitrogen for 5 h. Ethyl phenylacetate was added as internal standard and the solution was analysed by g.l.c. The lactone (22) and the acetates (18) and (19) were identified by comparison with authentic samples. Yields based on peroxydisulphate were (22) 63% and (18) + (19) 5%. n-Decanoic acid (10%) was present in the reaction mixture.

Oxidation of cyclohexene in acetic acid in the presence of 4-*methylquinoline*. A mixture of 4-methylquinoline (1.32 ml, 10 mmol), cyclohexene (2.02 ml, 20 mmol), $K_2S_2O_8$ (2.71 g, 10 mmol), KOAc (0.98 g), $Cu(OAc)_2 \cdot H_2O$ (0.182 g), Ac_2O (0.2 ml), and AcOH (25 ml) was refluxed for 2 h. The mixture was diluted with water, basified with 30% NaOH at pH 9, and extracted with CH_2Cl_2. G.l.c. quantitative analysis, after addition of 2,4-dimethylquinoline as internal standard, give a 47% conversion of the 4-methylquinoline, and a yield (on converted base) of 70% for (23) and 15% for (24). The two products were isolated by silica gel chromatography (hexane–ethyl acetate 8 : 2). 2-(Cyclohex-1-enyl)-4-methylquinoline (23) had δ ($CDCl_3$) 7.8—8.1 (4 H, m, Ar), 7.35 (1 H, s, 3-H), 6.68 (1 H, m, CH=C), 2.65 (2 H, m, $CH_2C=C$), 2.6 (3 H, s, CH_3), 2.30 (2 H, m, $CH_2C=C$), and 1.6—1.9 (4 H, m, aliph.); $\nu_{max.}$ (liquid film) 3 050 (=C−H), 1 600 (C=C), 1 550, 1 500, and 750 cm^{-1}; *m/e* 223 (M^+, 100%), 222, 208, 194, 181, 180, 167, 157, and 115.

2-(3-Acetoxycyclohex-1-enyl)-4-methylquinoline (24) had δ ($CDCl_3$) 7.4—8.1 (4 H, m, Ar), 7.46 (1 H, s, 3-H), 6.62 (1 H, m, CH), 5.3 (1 H, m, C*H*OAc), 2.7 (2 H, m, $CH_2C=$), 2.6 (3 H, s, CH_3), 2.08 (3 H, s, $COCH_3$), and 1.9 (4 H, m, aliph.); $\nu_{max.}$ (liquid film) 3 060 (=CH−), 1 735 (C=O), 1 600, 1 550, 1 500, and 1 230 cm^{-1}; *m/e* 281 (M^+), 222, 208, 194, 180, 167 (100%), 152, 138, and 115.

Oxidation of Cyclohexene in Aqueous Acetic Acid.—General Procedure. A mixture of peroxydisulphate (2.5 mmol) and cyclohexene (5.07 ml, 50 mmol) in water (10 ml) and acetic acid (30 ml) was refluxed for 5 h. The mixture was directly analysed by g.l.c. on columns A and C, after addition of phenylethyl acetate as internal standard and drying with Na_2SO_4. The results are summarized in Table 3. All compounds were identified by comparison with authentic samples.

Attempts to Acetylate Compound (28).—All attempts to acetylate compound (28) by Ac_2O–pyridine or acetyl chloride led to olefin (23).

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