

# Electron-transfer Processes: Oxidation of $\alpha$ - and $\beta$ -Alkenylbenzenes by Peroxydisulphate in Acetic Acid

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Oxidation of  $\alpha$ - and  $\beta$ -unsaturated alkylbenzenes by peroxydisulphate in acetic acid gives side-chain acetoxylation with formation of the corresponding glycol diacetates and compounds (10), respectively. The reaction is catalysed by transition-metal salts, among which cupric acetate gives the best results. Generally, electron-releasing substituents on the benzene ring increase the yield and improve the selectivity. The same substrates are oxidized in water under  $\text{Ag}^+$  catalysis to the corresponding aldehydes. The different behaviour in the two solvents is ascribed to the difference in reactivity between the primary oxidation products and the starting olefin, whereas the initial oxidation step is suggested to occur in both cases *via* an electron-transfer process from the olefin to the sulphate radical anion.

The oxidation of aromatic substrates by peroxydisulphate has been extensively investigated.<sup>1</sup> Recently, these oxidations carried out in organic solvents, such as aliphatic carboxylic acids, have attracted our attention because of their synthetic significance.<sup>2-7</sup> Generally, the oxidation is carried out in the presence of transition-metal salts, which catalyse the peroxydisulphate decomposition and increase the reaction selectivity. A general mechanism involving the formation of a radical cation *via* electron transfer from the aromatic substrate to the sulphate radical anion ( $\text{SO}_4^{\cdot-}$ ) has been postulated.<sup>1</sup>

The different reaction products come from different position of attack of the nucleophile on the radical-cation intermediate as well as from the efficiency of the metal salts in oxidizing the carbon-centred radical intermediates.

The interest in the reactivity of radical cations<sup>8,9</sup> and the possibility that the sulphate radical anion could prove to be a very selective agent in promoting electron-transfer processes prompted us to extend the study on peroxydisulphate oxidation to benzene derivatives having one double bond in the side-chain.

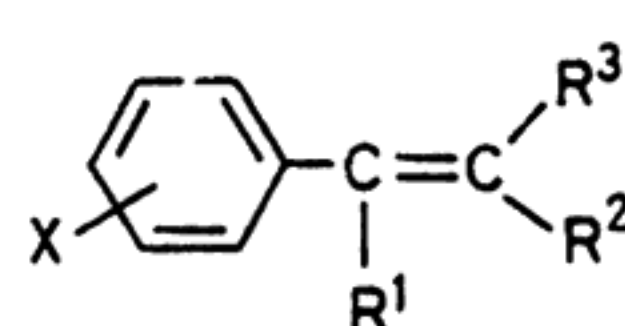
## Results

The oxidation of *trans*-1-(4-methoxyphenyl)propene (1a) in acetic acid in the presence of copper(II) acetate was selected for a preliminary study on the basis of the following considerations: (a) the low ionization potential of the propene (1a) should reduce the competitive oxidation of the solvent; (b) copper(II) acetate, a good scavenger of alkyl radicals,<sup>10</sup> should avoid the reactions between radicals (*i.e.* methyl, from the oxidation of acetic acid) and the substrate; (c) moreover, acetic acid is fairly resistant to the peroxydisulphate oxidation.<sup>2-7</sup>

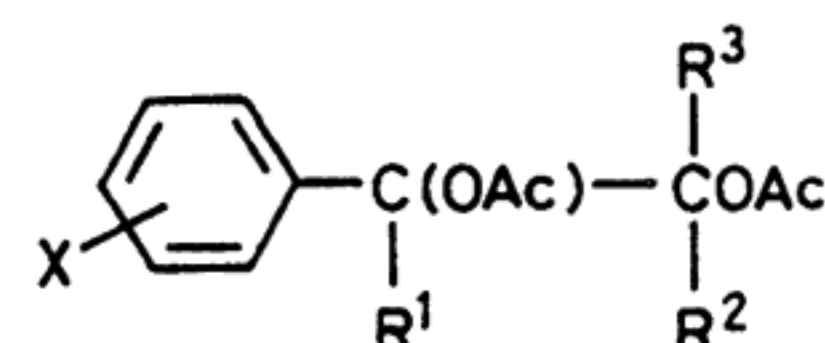
Compound (1a) was easily oxidized at 118 °C by potassium peroxydisulphate in acetic acid in the presence of monohydrate copper(II) acetate and potassium acetate to give 1-(4-methoxyphenyl)propane-1,2-diyl diacetate, as a mixture of *erythro* (2a) and *threo* (3a) isomers (1 : 1), in 84% yield.

Minor amounts of *trans*-3-(4-methoxyphenyl)prop-2-en-1-yl acetate (4a) (1.5%), 2-hydroxy-1-(4-methoxyphenyl)propan-1-yl acetate (5a), 1-hydroxy-1-(4-methoxyphenyl)propan-2-yl acetate (6a) (8%), and 4-methoxybenzaldehyde (7a) (3%) were formed, while no nuclear substitution was observed. The reaction was relatively fast, being complete within 50 min.

The reaction was also catalysed by other transition-metal



(1)



(2) *erythro*  
(3) *threo*

	X	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
a;	4-OMe	H	H	Me
b;	H	H	H	Me
c;	3,4-(OMe) <sub>2</sub>	H	H	Me
d;	4-Cl	H	H	Me
e;	4-Me	H	H	Me
f;	3-OMe, 4-OAc	H	H	Me
g;	3,4-(-OCH <sub>2</sub> O-)	H	H	Me
h;	H	H	H	H
i;	4-OMe	H	H	H
j;	H	Me	H	H
k;	H	H	H	Ph
l;	H	-(CH <sub>2</sub> )-		H
m;	2-OMe	H	H	Me

acetates (*e.g.*  $\text{Pb}^{\text{IV}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$ ,  $\text{Ce}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ , and  $\text{Ag}^{\text{I}}$ ) (Table 1).

The yield of the glycol diacetates (2a) and (3a) varied depending upon the experimental conditions; the best results were obtained using a catalytic amount of monohydrate copper(II) acetate in the presence of potassium acetate as buffer (method A) or anhydrous copper(II) acetate (2 mol per mol of peroxydisulphate) (method B). In the latter case a significant increase in the yield of (4a) was observed.

The presence of water in the media affects the product selectivity, and leads to the formation of compounds (5a) and (6a). Under anhydrous conditions these compounds were formed only in trace amounts (<1%).

In the absence of transition-metal salts, the peroxydisulphate decomposition was slow and the reaction gave a complex mixture of products, in which (2a) and (3a) (41%

yield at 75% conversion of the olefin after 6 h) were still present (Table 1).

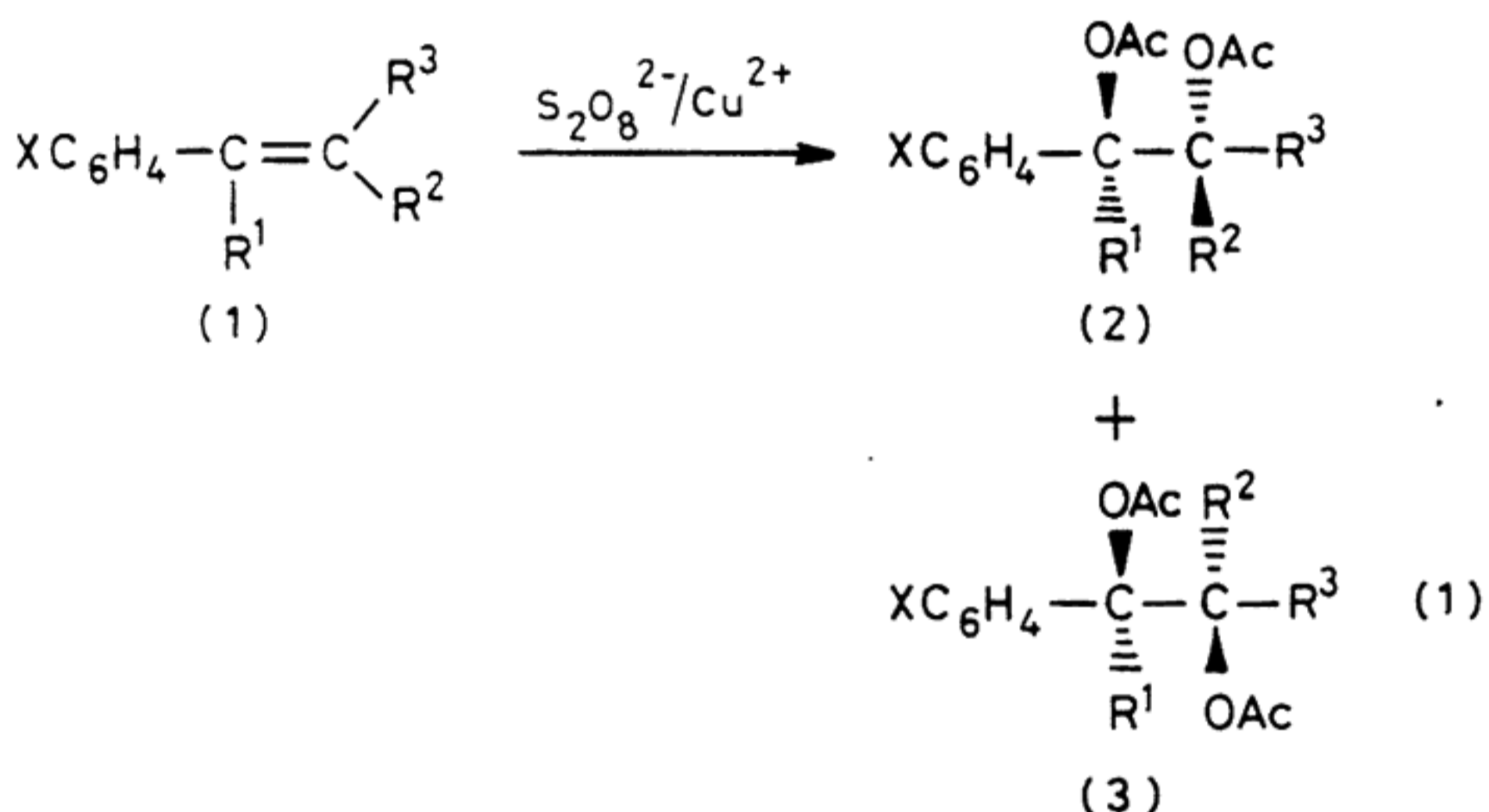
The best conditions found for the propene (1a) were used also in the oxidation of other substituted *trans*- $\alpha$ -alkenylbenzenes (1b–m), and all the reactions provided glycol diacetates as the prevalent products [equation (1)].

In Table 2 are reported the analytical data, conversions,

**Table 1.** Oxidation of 1-(4-methoxyphenyl)propene (1a) by peroxydisulphate in acetic acid in the presence of metal acetates (in molar ratio with the oxidant)

Metal acetate	Olefin conversion (%)	(2) + (3) (Yield/%) <sup>a</sup>	Reaction time (h)
	75	41	6
Cu <sup>II</sup> (0.1 mol)/AcOK	97	84 <sup>b</sup>	1.5
Cu <sup>II</sup>	96	90 <sup>c</sup>	1
Cu <sup>II d</sup>	88	52 <sup>d</sup>	1
Co <sup>II</sup>	98	77	2
Ag <sup>I</sup>	100	50	0.6
Pb <sup>IV</sup>	95	75	3
Mn <sup>II</sup>	98	75	3

<sup>a</sup> Based on peroxydisulphate. <sup>b</sup> Other products identified were: (4a) 1.5%, (5a) + (6a) 8%, and (7a) 3%. <sup>c</sup> Other products identified were: (4a) 5%, and traces of (5a) and (6a). <sup>d</sup> Experiment carried out using procedure B in the presence of water (1 ml); other products identified were (4a) 3%, (5a) + (6a) 13%, and (7a) 10%.

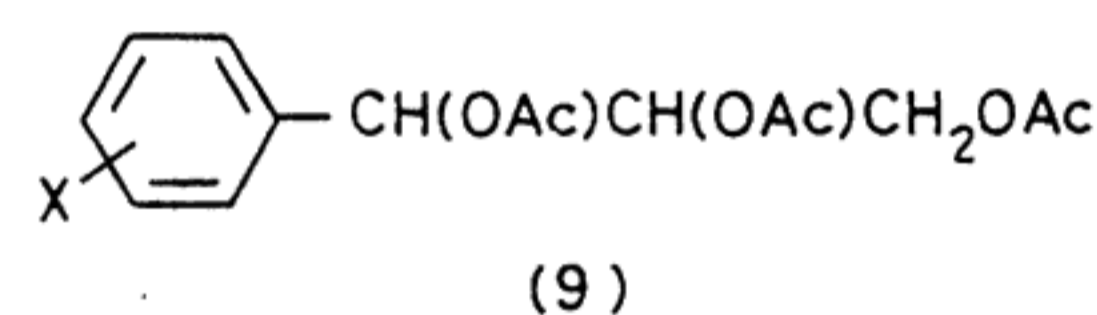
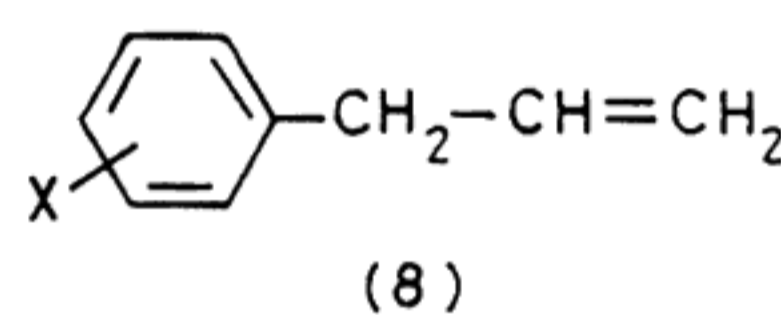
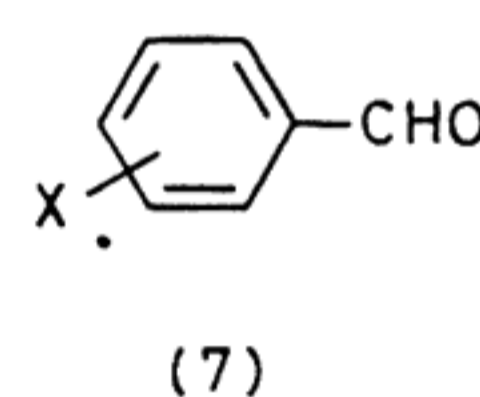
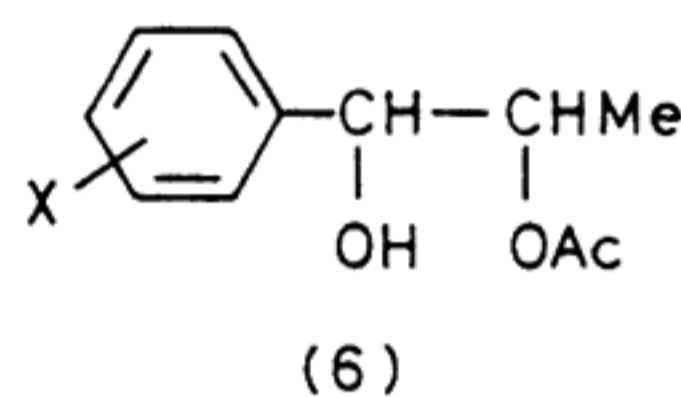
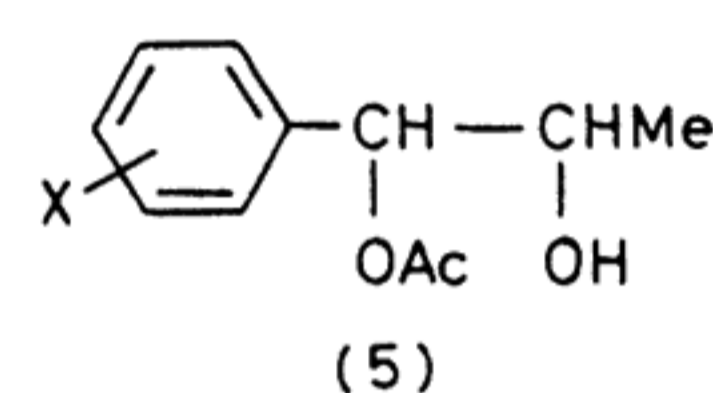
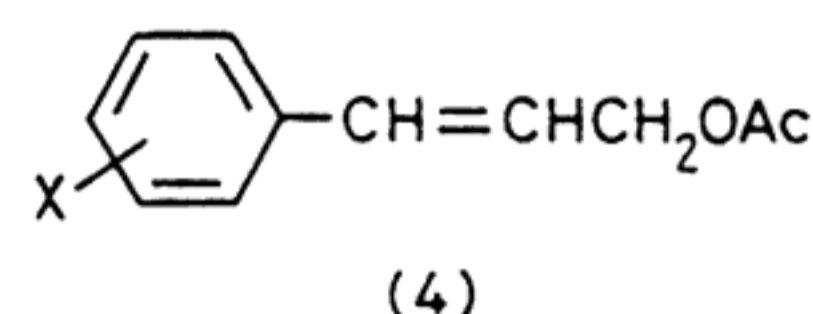


yields, and the distribution of the diastereoisomers [(2) : (3)] for all the substrates examined.

Methoxy- and acyloxy-substituents give good results; moreover, significant yields were obtained with unsubstituted, halogeno and methyl substituted  $\alpha$ -alkenylbenzenes. With the 4-methyl derivative (1c) (using the conditions of method B), no benzylic acetoxylation on the methyl group was found, and only minor amounts of 3-(4-methoxyphenyl)prop-2-enyl acetate (9%) and 4-methylbenzaldehyde (5%) were isolated in addition to the isomers (2c) and (3c) (57%), the major products.

Olefins having an alkyl group in position 1 [(1j) and (1m)] give only minor amounts of glycol diacetates, and 2-acetoxy-1-hydroxy-derivatives were instead formed. It is possible that these compounds were formed from the corresponding diacetates during the work-up of the reaction mixture.

Peroxydisulphate oxidation of styrene and propenylbenzene without any transition-metal salt added resulted in a very complex mixture of products containing telomers, benzylic dimers, and glycol diacetates in low yields (10 and 21%, respectively).



a; X = 4-OMe  
 b; X = H  
 c; X = 3,4-OMe  
 m; X = 2-OMe

**Table 2.** Peroxydisulphate oxidation of X-substituted  $\alpha$ -alkenylbenzenes in acetic acid under copper(II) catalysis

Olefin	Method	Conversion	(2) + (3) (Yield/%)	(2) : (3)	(2) ( <i>erythro</i> ) B.p. (°C/mmHg)	(3) ( <i>threo</i> ) B.p. (°C/mmHg)
(1a)	A	97	84	1	130–131/0.5	127–120/0.5
(1a)	A <sup>a</sup>	75	41	1		
(1b)	A	70	57	1	111–112/0.5	110–112/0.5
(1b)	A <sup>a</sup>	80	21	1		
(1c)	A	98	87	1	146–147/0.5	149–150/0.5
(1d)	B	61	36	1	118–119/0.5	118/0.5
(1e)	B	70	57	1	113–114/0.5	114/0.5
(1f)	A	82	80	1	129–130/0.05	126/0.06
(1g)	A	96	71	1	140–142/0.6	137–139/0.6
(1h)	B	68	33		106–107/0.5	
(1h)	A <sup>a</sup>	100	10			
(1i)	B	87	60		121–123/0.5	
(1j)	B	70	45		90–92/0.2	
(1k)	A	79	60	0.3	117 (M.p.)	135 (M.p.)
(1l)	A	60	33	0.2	[isolated as (5l) and (6l)]	

<sup>a</sup> Experiments carried out in the absence of cupric salt. In each experiment a considerable amount of telomer [particularly with (1h)] and benzylic dimer was observed; the structure was not investigated.

**Table 3.** Reactivity of some *p*-substituted *trans*-propenylbenzenes and 4-methoxyalkylbenzenes, in the oxidation by peroxydisulphate (relative to propenylbenzene)

Substrate X	(1b) H	(1e) 4-Me	(1d) 4-Cl	(1a) 4-OMe	(1c) 3,4-(OMe) <sub>2</sub>	(2a)	(8a)	4-Methoxy-toluene
Rel. rate	1	3.3	0.59	6.1	8.2	0.32	0.5	0.39

**Table 4.** Peroxydisulphate oxidation of some substituted 3-phenylprop-1-enes in acetic acid

Compound	(9a) (Yield/%) <sup>a</sup>	(4a) (Yield/%) <sup>a</sup>	Olefin conversion (%)
(8a)	54	8	82
(8b)	20	8	70
(8c)	62	5	90
(8m)	60	4	95

<sup>a</sup> Based on peroxydisulphate.

The trend of yields reported in Table 2 parallel that of substrate reactivity in electron-transfer oxidations. We investigated this point and analysed the products formed in competitive oxidation experiments with some *p*-substituted propenylbenzenes using method B and carrying out the reactions at low conversion (<15%). The relative reactivities so deduced for five substrates, along with those of 4-methoxytoluene and 4-methoxyallylbenzene, are reported in Table 3.

In competitive experiments between 4-methoxytoluene and the diacetate (2a), the main oxidation products were 4-methoxybenzyl acetate<sup>5</sup> and 4-methoxybenzaldehyde, respectively. Moreover, the allyl derivative (8a) gave 1-(4-methoxyphenyl)propane-1,2,3-triyl triacetate (9a), as a mixture (1 : 1) of the *erythro*- and *threo*-isomers.

The oxidation of other  $\beta$ -alkenylbenzenes provided compounds (9) in yields which varied from good to moderate depending on the substituent on the phenyl (Table 4); the corresponding substituted 3-phenylprop-2-enyl acetates (4) were observed in any case in low yield.

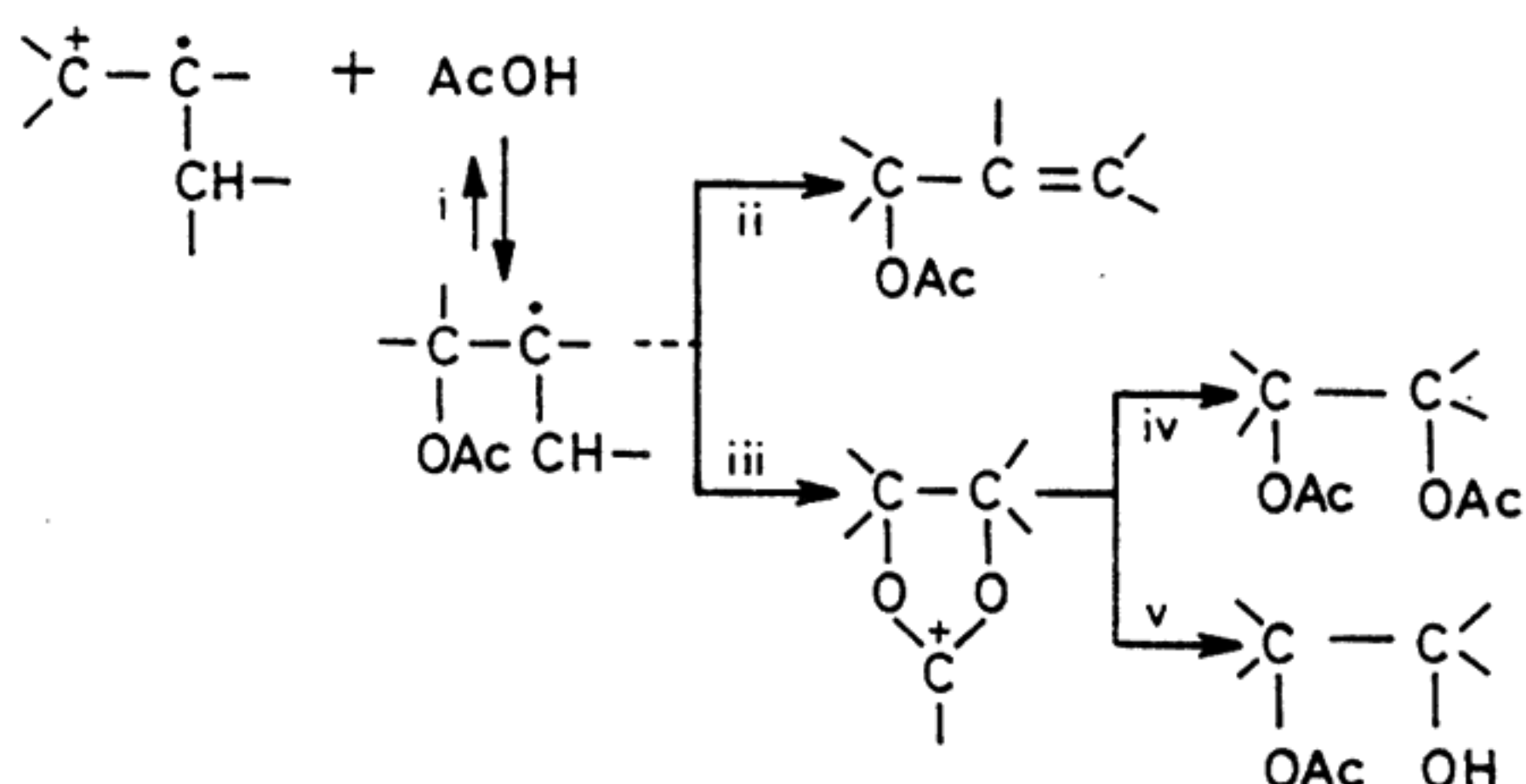
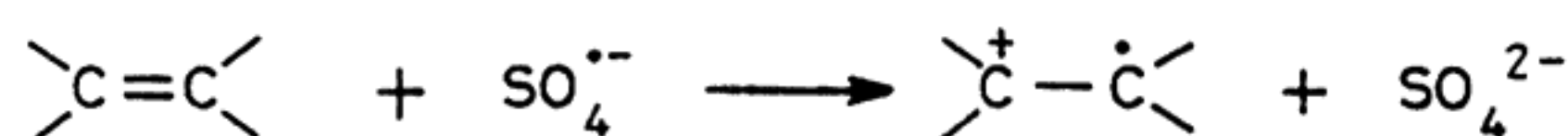
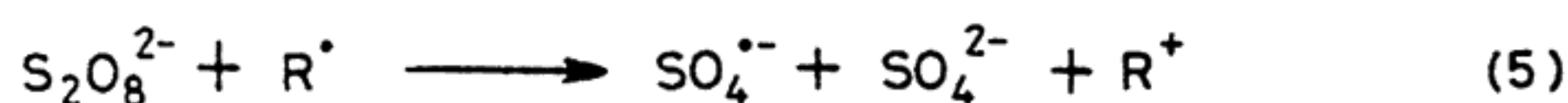
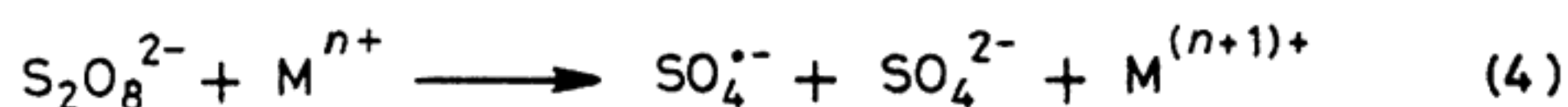
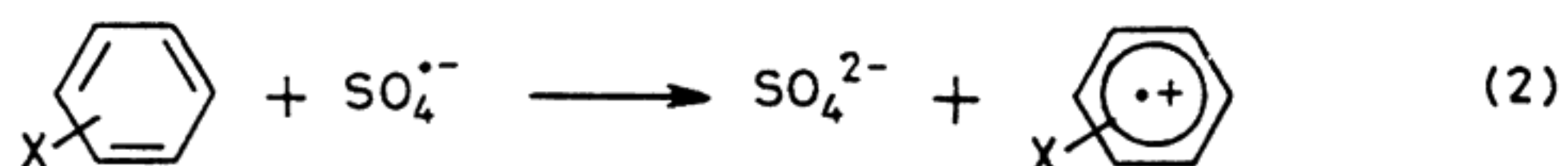
The derivatives (1a), (1b), (1e), (8a), (8m), and (4a) were also oxidized under heterogeneous conditions in water-acetonitrile (9 : 1) by peroxydisulphate in the presence of a catalytic amount of silver nitrate (5% on peroxydisulphate). All compounds gave the corresponding benzaldehydes with high selectivity (75–95% yield at 40–45% conversion). These results agree with the previously reported ones.<sup>11</sup> With the 2-methoxyphenyl derivative (8m), small amounts of benzylic dimers were detected; however, the addition of copper(II) sulphate (1 mol to 50 mol peroxydisulphate) prevented their formation.

## Discussion

The oxidation of aromatic substrates by peroxydisulphate has been considered to occur *via* an electron-transfer mechanism involving the sulphate radical anion [equation (2)] as suggested by pulse radiolysis<sup>12</sup> and e.s.r.<sup>13</sup> experiments where aromatic radical cations were detected. The radical anion  $\text{SO}_4^{\cdot-}$  can be generated in the reaction medium by thermal [equation (3)], metal-catalysed [equation (4)], or induced [equation (5)] decomposition of peroxydisulphate.

In several cases the oxidation products were similar to those obtained in oxidations of the same substrates by metal salts [ $\text{Ce}^{\text{IV}}$ ,<sup>14</sup>  $\text{Mn}^{\text{III}}$ ,<sup>15</sup>  $\text{Co}^{\text{III}}$ ,<sup>16</sup>  $\text{Ag}^{\text{I}}$ <sup>17</sup>] which are considered to promote the oxidation *via* an electron-transfer mechanism.

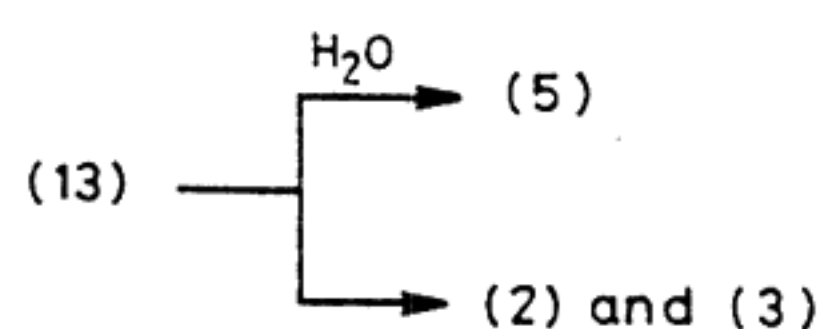
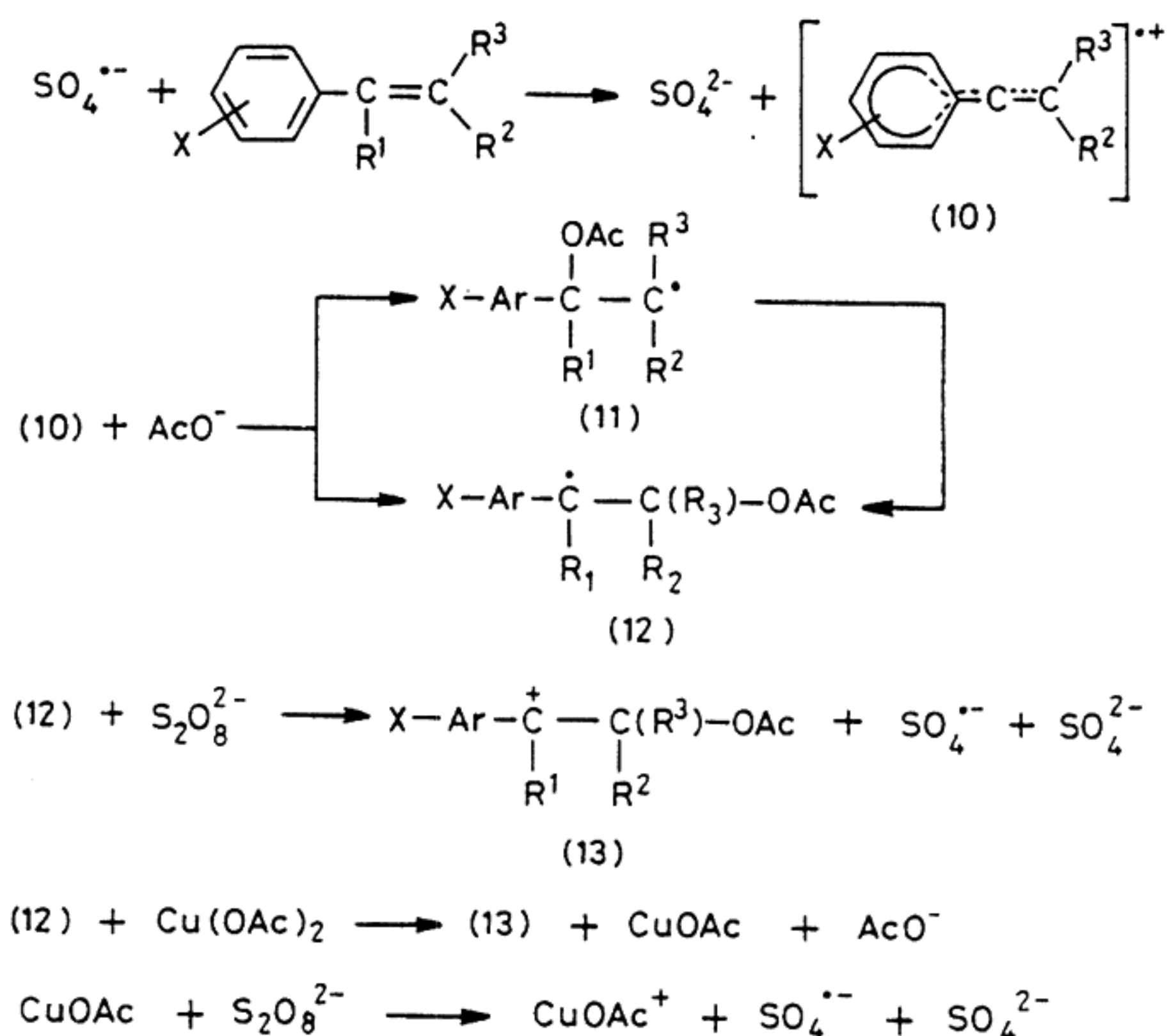
Recently, it has also been suggested that the peroxy-

**Scheme 1.** Reagents: i,  $\text{H}^+$ ; ii,  $\text{Cu}(\text{OAc})_2$ ; iii,  $\text{S}_2\text{O}_8^{2-}$ ; iv,  $\text{AcOH}$ ; v,  $\text{H}_2\text{O}$ 

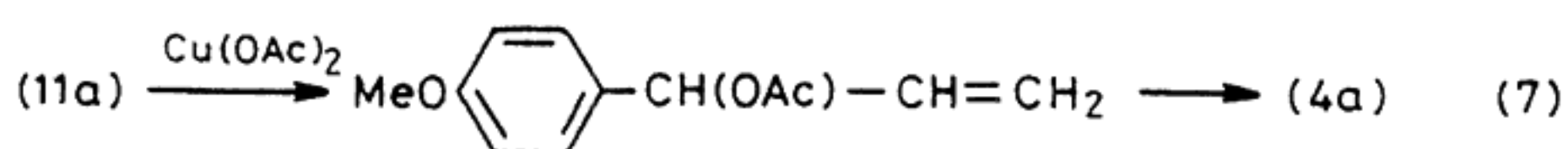
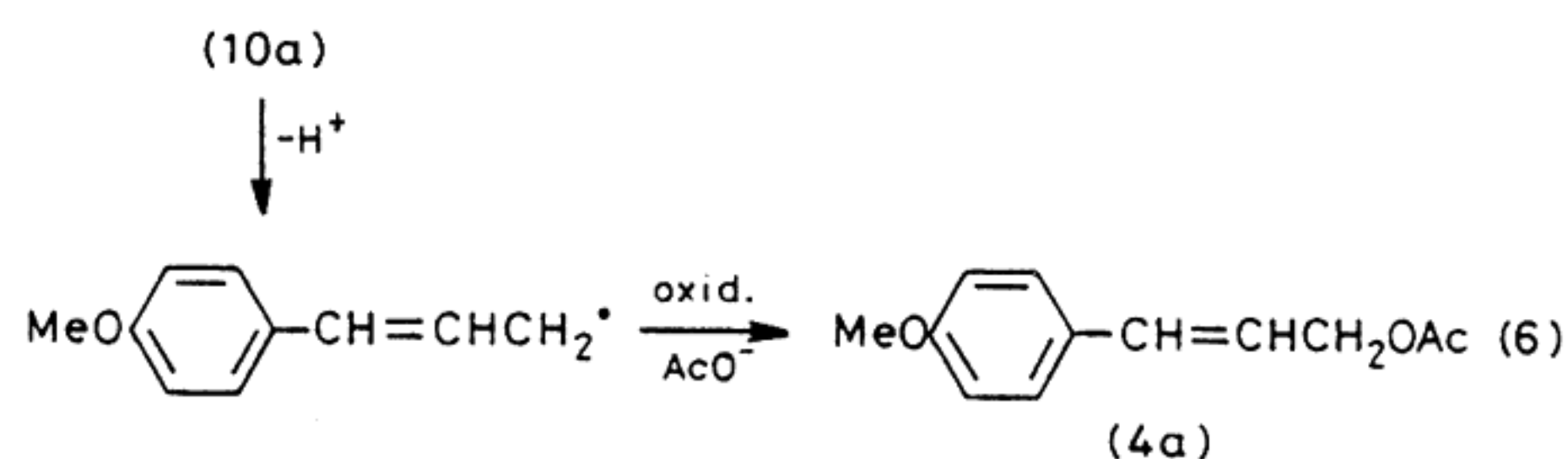
disulphate oxidation of olefins occurs by an electron-transfer mechanism,<sup>18,19</sup> but quite different behaviour was observed with or without  $\text{Cu}^{\text{II}}$  catalysis: in the absence of  $\text{Cu}^{\text{II}}$  in mixture of acetic acid and water, glycol mono- and di-acetates were obtained as predominant products;<sup>18</sup> in the presence of copper(II) acetate, allylic acetoxylation selectively occurs.<sup>19</sup> The results have been explained by the mechanism summarized in Scheme 1, in which the 2-acetoxyalkyl radical, formed by addition of acetic acid to the radical cation, undergoes oxidative elimination with copper(II) acetate and oxidative substitution with peroxydisulphate. In the latter case, anchimeric assistance of the acetoxy-group in the oxidation by  $\text{S}_2\text{O}_8^{2-}$  has been postulated.<sup>19</sup> Also the results of the oxidations of  $\alpha$ - and  $\beta$ -alkenylbenzenes agree with the electron-transfer hypothesis.

The oxidation of  $\alpha$ -alkenylbenzenes in acetic acid gives rise only to minor oxidation of the solvent or the acetate ion, the olefins being preferentially attacked. However, the oxidation products varied depending upon the experimental conditions. In the absence of metal salts, products from dimerization and telomerization of the olefin were observed, whereas the glycol diacetates (2) and (3) were formed in yields which increased with the electronic availability of the olefin or its substituents [Table 1, experiments with substrates (1a), (1b), and (1h)]. These last products were, instead, selectively obtained in the presence of copper(II) acetate (or other transition-metal salts).

The behaviour observed is related to the reactivity of the



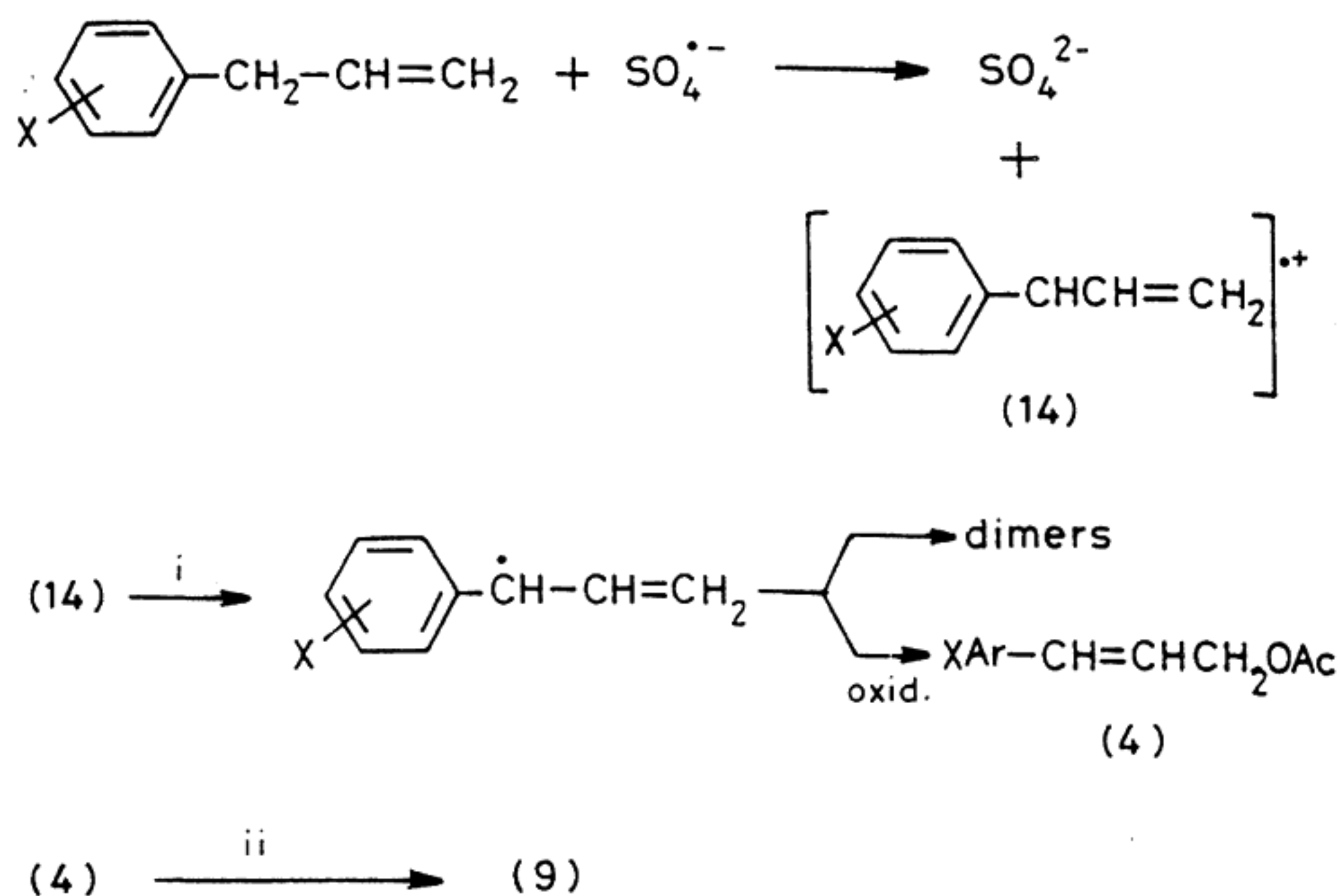
Scheme 2.



benzyl radicals (12), which are selectively oxidized by cupric salts<sup>20</sup> but not by peroxydisulphate.<sup>1</sup> The  $\beta$ -acetoxyalkyl radical (12) cannot be formed by addition of the acetoxy-radicals to the double bond, owing to the known fast decomposition to methyl radical and  $\text{CO}_2$ ;<sup>21</sup> thus nucleophilic addition to a radical cation appears to be a reasonable explanation if only one mechanism is operating in all cases (Scheme 2). Two peculiar aspects characterize conjugated olefins in comparison with simple olefins. They are more reactive towards both oxidation and radical addition reactions, so significant results are obtained only in the presence of cupric salts; however, the intermediate benzyl radical (12) undergoes selective oxidative substitution by cupric salts whereas 2-acetoxyalkyl radicals from simple olefins give oxidative elimination.

Scheme 2 explains also the minor amounts of side-products (4a), (5a), (6a), and (7a) which occur. In fact, compounds (5), (6) and (7) are formed in significant amounts only if water [arising from hydrated copper(II) acetate or used as co-solvent] is present in the reaction medium; under anhydrous conditions only traces were detected. The results of Table 1 suggest, furthermore, that benzaldehydes (7) are formed by further oxidation of compounds (5); thus, the presence of water affects the product selectivity.

As far as the increasing yield of (4a) with cupric salt concentration is concerned, the two different reaction paths of equations (6) and (7) can be considered.

Scheme 3. Reagents: i,  $-\text{H}^+$ ; ii,  $\text{K}_2\text{S}_2\text{O}_8\text{-Cu}(\text{OAc})_2$ 

The dependence of the yield of (4a) on the copper(II) concentration would support the mechanism of equation (8); at higher  $\text{Cu}^{\text{II}}$  concentration, the oxidation of (11a) to (4a) becomes more effective, thus reducing the possibility of the rearrangement (11)  $\longrightarrow$  (12).<sup>22</sup>

Of the investigated catalysts, copper(II) acetate proved to be the best. Its role involves three aspects of the whole process: it catalyses the peroxydisulphate decomposition in a redox chain process; it efficiently oxidizes all alkyl radical intermediates, increasing the selectivity; and it inhibits, in particular, the formation of by-products arising from the interaction of the methyl radical (from the oxidation of acetate ion by  $\text{SO}_4^{\bullet-}$ ) with the aromatic substrate.

The electron-transfer mechanism proposed in Scheme 2 is also supported by the results of the competitive experiments in Table 3. Electron-releasing groups and conjugated double bonds appear to increase the reactivity of the aromatic moiety towards peroxydisulphate indicating a significant polar effect from the aromatic substituents. This behaviour parallels the effect of substituents on the ionization potential of aromatics in which a free radical cation is formed. However, the relative rates obtained are only indicative because they reflect the ratios of product yields in competitive experiments and can therefore be influenced by equilibria between aromatic radical cations [equation (8)], which are known to be very fast.<sup>23</sup>

The oxidation products of allylbenzenes (8) in acetic acid can similarly be explained (Scheme 3) by the observation that compound (4), present in all cases as a minor component in the reaction mixture, is oxidized to (9) in good yield, analogously to the other  $\beta$ -alkenylbenzenes. The difference in reactivity between (9) and (8) is responsible for the observed product distribution. The formation of compound (4) can be considered both as benzylic or allylic acetoxylation. Under the conditions used both reactions are well documented.<sup>3,19</sup>

Finally, the oxidation of the same substrates in water by the couple  $\text{Ag}^+/\text{S}_2\text{O}_8^{2-}$  suggests that a similar mechanism works in the two solvents. The glycol (15) is certainly an intermediate in the oxidation of  $\alpha$ -alkenylbenzenes to the corresponding benzaldehydes (7) [equation (9)]. A sequence analogous to that reported in Scheme 2 could well explain its formation. Three routes can be envisaged for the oxidation of the diol (15) to the aldehyde (7) in water, as shown in Scheme 4. There is good evidence for each of the interactions (a),<sup>1</sup> (b),<sup>1,17</sup> and (c).<sup>24</sup>



m, Ar), 6.4 (1 H, d,  $J$  7 Hz, CH-Ar), 5.44 (1 H, m, CHOAc-CH<sub>2</sub>), 3.8 (3 H, s, OCH<sub>3</sub>), 2.05 (3 H, s, OCOCH<sub>3</sub>), and 1.9 (6 H, s, OCOCH<sub>3</sub>);  $m/z$  324 ( $M^+$ , 1), 264 (4), 221 (10), 179 (19), 163 (16), 137 (100), 107 (20), 91 (10), and 43 (95); *erythro*-3-(3,4-dimethoxyphenyl)propane-1,2,3-triyl triacetate (9c),  $m/z$  354 ( $M^+$ , 5), 294 (8), 251 (33), 167 (100), and 43 (60); *threo*-3-(3,4-dimethoxyphenyl)propane-1,2,3-triyl triacetate (9c),  $m/z$  354 ( $M^+$ , 3), 294 (5), 251 (10), 250 (12), 167 (100), and 43 (66).

*Oxidation of Alkenylbenzenes with Peroxydisulphate.*—

*Procedure A. Oxidation with catalytic copper(II) acetate and potassium acetate.* 1-(3,4-Dimethoxyphenyl)propene (1c) (20 g, 0.112 mol), copper(II) acetate hydrate (0.011 mol), anhydrous potassium acetate (33 g, 0.337 mol), and potassium peroxydisulphate (30 g, 0.112 mol) were added at room temperature to acetic acid (500 ml) and acetic anhydride (20 ml). The vessel was flushed with nitrogen and was heated under nitrogen by an electric mantle at reflux temperature (118 °C) with vigorous stirring. The reaction was stopped after 2 h and the mixture was distilled at 40 mmHg to remove the acetic acid (350 ml); the cold residue was taken up with ethyl acetate (250 ml) and 1% HCl (250 ml), the organic layer separated, washed with aqueous NaHCO<sub>3</sub> until pH reached 8, then with water, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated. The residue was distilled under reduced pressure. 1-(3,4-Dimethoxyphenyl)propane-1,2-diyl diacetate, b.p. 148—152 °C/0.5 mmHg, was obtained as a 1 : 1 mixture of *threo*- and *erythro*-diastereoisomers [28 g, 84% yield, 96% purity by g.l.c. analysis on the column (a)]. The isomers (5.8 g) were separated by liquid chromatography on a preparative Miniprep Jobin Iyon instrument on silica gel [0.023—0.063 mm (Merck)] (100 g), eluting with hexane-ethyl acetate (9 : 1), to give a fraction of the pure *threo*-isomer (2.4 g; b.p. 147—148 °C/0.5 mmHg), a mixture of the *erythro*- and *threo*-derivatives (1.2 g) and a fraction of the pure *erythro*-derivative (2.1 g; b.p. 149—150 °C/0.5 mmHg).

*Procedure B. Oxidation with anhydrous copper(II) acetate.* 4-Methoxystyrene (2.68 g, 0.02 mol) was added to a mixture of anhydrous copper(II) acetate (4.18 g, 0.023 mol) and potassium peroxydisulphate (5.4 g, 0.02 mol) in acetic acid (50 ml). The reaction was heated under reflux with stirring for 2 h. The resulting solution was cooled, poured into water, basified with saturated aqueous NaHCO<sub>3</sub> until the pH reached 8, and extracted with diethyl ether (2 × 40 ml). The extracts were washed with water, dried and analysed by g.l.c. on columns (a) and (b) for the yield and conversion determination (after addition of biphenyl as internal standard). The solution was then concentrated on a rotary evaporator and the residue was chromatographed on silica gel using hexane-ethyl acetate (9 : 1—7 : 3, gradient 1%) as eluant. 1-(4-Methoxyphenyl)-ethyl acetate was the first eluted product (5% on starting olefin) followed by 1-(4-methoxyphenyl)ethane-1,2-diyl diacetate (2i). Distillation of this fraction give pure compound (2i), b.p. 121—123 °C/0.5 mmHg, in 60% yield.

The experimental conditions for procedures A and B were used in all the runs in Table 1, varying the metal salt and the amount used. In Table 2 are reported the results of the reactions carried out with different  $\alpha$ -alkenylbenzenes using the A or B procedure.

*Peroxydisulphate Oxidation of  $\alpha$ -Alkenylbenzenes in Water.*—Silver nitrate (84 mg,  $5 \times 10^{-4}$  mol) was added to an heterogeneous mixture of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.35 g, 4.85 mmol) in water-acetonitrile (45 : 5, w/w) and the alkenylbenzene ( $\alpha$  or  $\beta$ ) (3 ml), and the solution vigorously stirred at 40 °C for 3 h under N<sub>2</sub>. Diethyl ether was added (50 ml), and the organic layer separated, dried and analysed by g.l.c. on columns (a)

and (b). Compounds (1a—f) afforded the corresponding benzaldehydes in 80—90% yield.

*Competitive Experiments.*—Two aromatic substrates (20 mmol) were added to a mixture of anhydrous copper(II) acetate (0.3 mmol) and potassium peroxydisulphate (0.2 mmol) in acetic acid (30 ml). The mixture was stirred and heated under reflux for 3 h. After addition of biphenyl and separation as above, the analyses were carried out on column (b). The results are summarized in Table 3.

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