

OXIDATION OF SUBSTITUTED 2-METHYL BENZOIC ACIDS AND ACRYLIC ACIDS BY  $S_2O_8^{=}$  - Ag(I) ;  
 THEIR CONVERSION TO PHTHALIDES AND BUTENOLIDES THROUGH REARRANGEMENT OF ACYLOXYL RADICALS.

M.P. BERTRAND, H. OUMAR-MAHAMAT and J.M. SURZUR

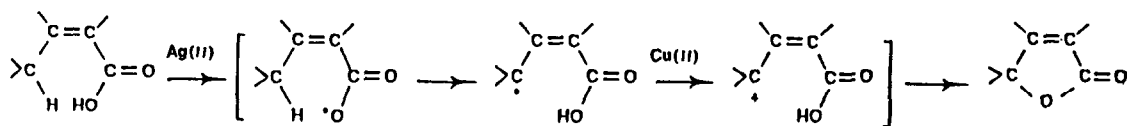
Université Aix-Marseille III - Laboratoire de chimie organique B - Associé au CNRS n° 109 -  
 rue H. Poincaré - 13397 MARSEILLE, Cedex 13.

*Abstract : Ag (I) mediated persulphate oxidation of various 2-methyl benzoic acids and acrylic acids, co-catalysed by Cu (II), leads to unsaturated  $\gamma$ -lactones, together with decarboxylation products. Lactonisation proceeds through 1,5 hydrogen transfer from intermediate acyloxy radical.*

Acyloxy radicals are known to decarboxylate readily. Starting from the statement that the rate constant  $k$  for this process is sensitive to hybridization in the R-CO<sub>2</sub> bond<sup>(1)</sup> ( $k$  being lowered by an increased  $s$  character) and to conjugation, we decided to investigate the ability of  $\alpha,\beta$ -unsaturated acyloxy radicals to undergo 1,5 hydrogen transfer and determine to what extent this reaction could compete with decarboxylation. If this rearrangement was shown to be the major pathway for 2-methyl<sup>(2)</sup> and 2-benzyl<sup>(3)</sup> benzoyloxy radicals, only one example of such a reaction has been reported in the literature for acryloyloxy radicals<sup>(4)</sup>.

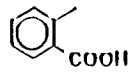
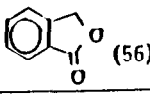
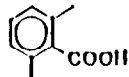
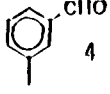
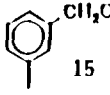
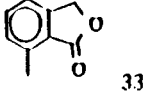
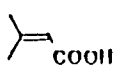
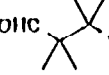
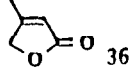
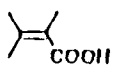
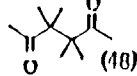
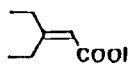
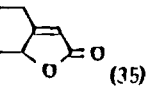
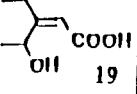
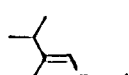
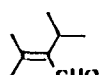
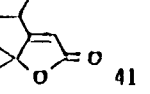
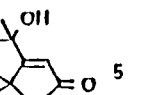
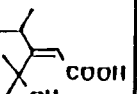
Furthermore, since acyloxy radicals are effective intermediates in the  $S_2O_8^{=}$  - Ag (I) oxidation of carboxylic acids<sup>(5)</sup>, this oxidising system, combined with Cu (II) (more prone than Ag (II) to oxidise alkyl radicals, once formed in the medium<sup>(5)</sup>) would provide, if it works as presumed on scheme 1, a good method to convert, in one step,  $\alpha,\beta$ -unsaturated acids to the corresponding  $\alpha,\beta$ -unsaturated lactones<sup>(6)</sup>.

Scheme 1



In this paper are reported preliminary results obtained from 2-methyl benzoic acids and acrylic acids (cf. Table 1). Typical experiments were realised as follows : the carboxylic acid (0.02 mol),  $Na_2S_2O_8$  (0.025 mol),  $AgNO_3$  (0.004 mol),  $CuX_2$  (0.004 mol), were dissolved together in 50 ml of solvent ( $CH_3CN-H_2O$  ; 1-1 ratio) and heated at 80°C for a variable period. Extraction and following treatment, afforded neutral and acidic products which were analysed separately.

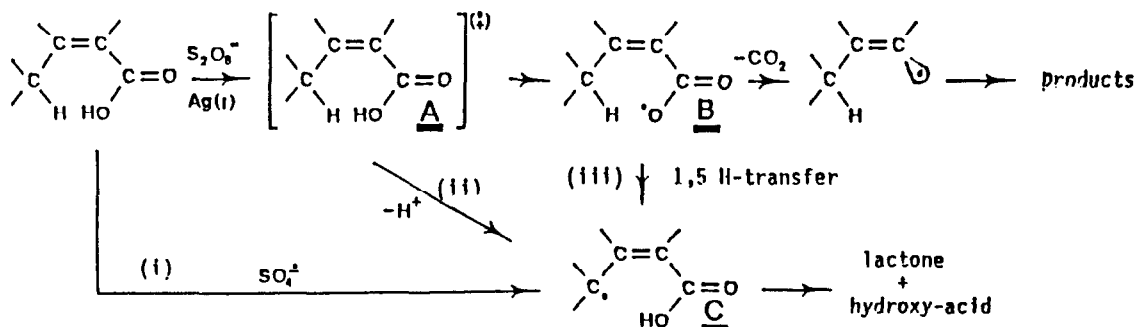
Table 1

Entry	Acid	Conversion %	Products % (7)	
a		93		 (56)
b		80	 4  15	 33
c		75	 7	 36
d		92	 (18)	
e		81		 (35)  19
f		73	 1	 41  5  23

$CuX_2 = CuCl_2$  (a-b) ;  $CuX_2 = CuSO_4$  (c-d-e-f).

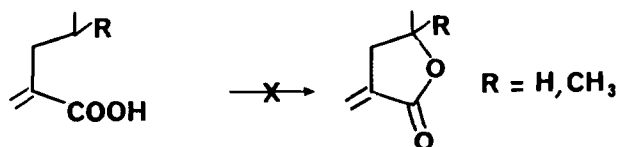
$S_2O_8^{2-}$  with or without metal catalysts has been shown to oxidise both aromatics (or olefins), and carboxylic acids<sup>(8)</sup>. Substrates which present simultaneously the two functions, follow different paths depending on reaction conditions. This is illustrated by the behaviour of  $\gamma$ -phenyl butyric acid<sup>(9)</sup>. Our substrates are somewhat different since the two functional groups are conjugated.

Scheme 2



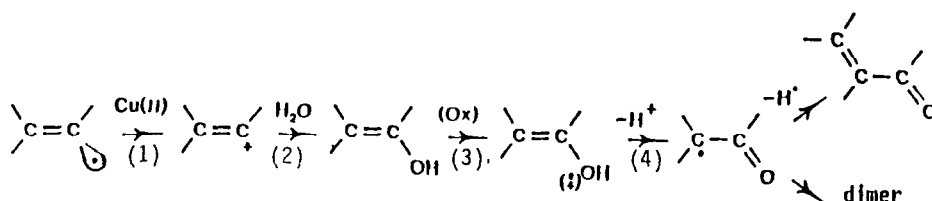
Intermediate C explains both lactonic products and hydroxy-acids (cf. scheme 2). It can be formed by at least three ways : (i) H-abstraction by  $\text{SO}_4^{\cdot-}$  ; (ii) loss of a benzylic<sup>(2c)</sup> (or allylic) proton from radical-cation A ; (iii) 1,5 H-transfer from acyloxy radical B. The following arguments agree with the latter proposal : - if formed by either path (i) or (ii), A would be expected as a cis-trans mixture and hence would lead to trans hydroxy-acids which have not been observed ; - the drop in lactone's yield (cf. experiments a/b and c/d) seems difficult to explain, if either paths (i) or (ii) are followed. On the contrary, steric effects (probably by inhibiting delocalisation of  $\Pi$ -system), have been shown to favour decarboxylation of conjugated acyloxy radicals<sup>(1,10)</sup>. Our results fit well with this steric influence, and strongly suggest that lactonic products are formed through path (iii), with B as an intermediate.

Acceleration of decarboxylation due to an alkyl substituent on the  $\alpha$  carbon in acryloyloxy radicals, explains the failure to detect any trace of  $\alpha$ -methylene  $\gamma$ -butyrolactone among the very numerous oxidation products of  $\alpha$ -butyl acrylic acids.



The other products can be ascribed to the competitive decarboxylation process, leading to phenyl or vinyl radicals. The first would undergo H-abstraction from the solvent, and then would give the expected oxidation products of alkyl-aromatics<sup>(8)</sup>. We suggest that 1-4 dicarbonylated compounds and  $\alpha,\beta$ -unsaturated aldehydes, derive from vinyl radicals through successive oxidations steps (scheme 3).

Scheme 3



Step (3) should be more rapid than keto-enol equilibration, since from d, the more substituted  $\alpha$ -keto radical is formed selectively. The less substituted one is favoured when oxidation is performed on the ketone or its enolate<sup>(11)</sup>.

As a conclusion, this work shows that acryloyloxy radicals (intermediates in the Ag

(I) mediated persulfate oxidation of acrylic acids) can undergo intramolecular reactions other than decarboxylation. The 1,5 hydrogen transfer reaction provides a very simple route to 2-butenolides, although in moderate yields, from readily available precursors. It should be compared to the method recently described by COREY starting from  $\alpha,\beta$ -unsaturated aldehydes<sup>(12)</sup>.

## REFERENCES AND NOTES

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- 6) Lactonisation of saturated aliphatic acids has been reported, using as reagent,  $S_2O_8^{=}$  in the absence of Ag (I) (G.I. NIKISHIN, I.V. SVITANKO and E.I. TROYANSKY, *JCS Perkin II*, 595 (1963). Starting from  $\alpha,\beta$ -ethylenic acids, we did not observe any lactone by this method.
- 7) Yields are based on reacted starting material. They are estimated from chromatographic data, except those in parentheses, which correspond to pure isolated products. Isolated products did not account for 100% of transformed acids, owing to untractable materials and probably to light products which have been trapped.
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