

SILVER-MEDIATED OXIDATIVE DECARBOXYLATION OF CARBOXYLIC ACIDS BY PEROXOCOMPOUNDS
NEW SOURCES OF CARBON-CENTERED RADICALS FOR HETEROAROMATIC SUBSTITUTION

Francesco Minisci and Elena Vismara^x

Dipartimento di Chimica del Politecnico, piazza Leonardo da Vinci 32, 20133 Milano, Italy

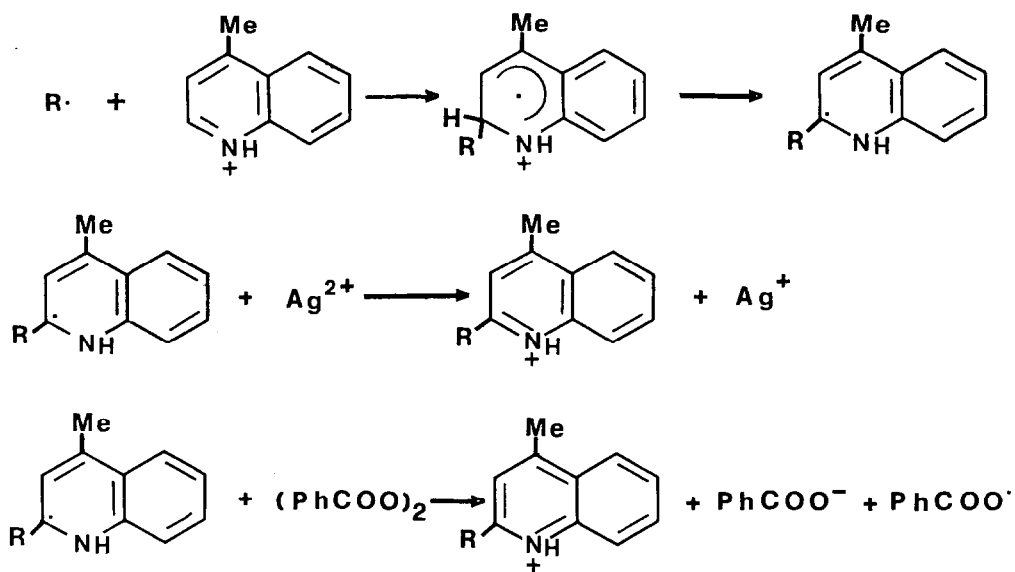
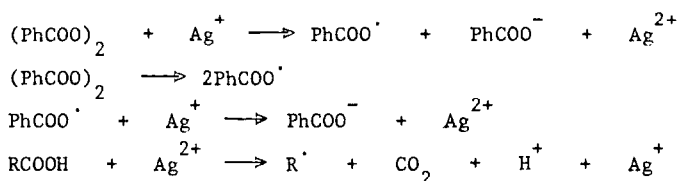
Ugo Romano

ENICHEM SINTESI, S. Donato Milanese (Mi)

Abstract- The silver catalyzed oxidative decarboxylation of carboxylic acids by aroylperoxides, percarbonates and perborate provides new sources of alkyl radicals useful for selective substitution of lepidine.

Metal salts of high electrode potential (Ag^{2+} , Co^{3+} , Ce^{4+} , Mn^{3+} , Pb^{4+} etc) are often selective oxidants of organic compounds¹. Their stoichiometric use, however, is not always convenient because of their expensive reagents, the high molecular weight of the salts and the experimental difficulties of their use. An alternative approach is to use the metal salts as catalyst in the presence of a different oxidant, whose only function is to reoxidize the metal salt to the higher oxidation state². We now report for the first time, as far as we know, the oxidation of Ag(I) to Ag(II) by peroxocompounds, such as aroyl peroxides, alkyl percarbonate, perborate. That allows the use of the silver salt in catalytic amount for the oxidation of organic substrates.

Thus when benzoyl peroxide is decomposed in acidic medium in the presence of a carboxylic acid and an heteroaromatic base the phenylation of the base occurs according to the classical homolytic aromatic substitution³ without any involvement of the carboxylic acid. Under the same conditions in the presence of catalytic amount of Ag(I) nitrate or acetate (~20%) a dramatic change occurs: only traces of phenylation are observed and the alkylation by the alkyl radical arising from decarboxylation of the carboxylic acid is almost the only reaction of the base. We explain the results by the following mechanism⁴:



With less catalyst both alkylation and phenylation are competitive processes (Table). Alkyl percarbonates are even more effective in determining the oxidative decarboxylation of carboxylic acids and the heteroaromatic alkylation. Some results utilizing lepidine, as typical heteroaromatic base, are reported in the Table. The reaction has, however, general character for the heteroaromatic bases. Methyl, primary, secondary and tertiary alkyl radicals can be easily obtained by this procedure, which is selective towards carboxylic acids of different structure. Thus acetic acid is decarboxylated to methyl radical but solutions of pivalic acid and phenoxyacetic in acetic acid lead practically only to *t*-butyl or phoxymethyl radicals. That indicates that the oxidation of pivalic and phenoxyacetic acids are much faster than that of acetic acid in agreement with the known behaviour of oxidative decarboxylation⁵ and that the formation of a mixed peranhydride catalyzed by the silver salt, can be excluded as responsible for the decarboxylation. Moreover there is e.s.r. evidence for the formation of the Ag(II) salt under the reaction conditions. We have previously reported the alkylation of heteroaromatic bases by decarboxylation of carboxylic acids by peroxydisulphate catalyzed by a silver salt⁶. The use of organic peroxides further increases the synthetic potentiality,

Table- Alkylation of position 2 of protonated lepidine by decarboxylation of carboxylic acids^a

Acid	Radical	Peroxide	Ag ⁺ % ^b	Solvent	Yields of ^c Phenyllepidine	Yields of ^c Alkyllepidine	Recovered ^c Lepidine%
t-C ₄ H ₉ COOH	t-C ₄ H ₉	(PhCOO) ₂ ^a	23	CH ₃ CN	3	35	78
t-C ₄ H ₉ COOH	t-C ₄ H ₉	(PhCOO) ₂ ^a	10	CH ₃ CN	9	14	73
t-C ₄ H ₉ COOH	t-C ₄ H ₉	(PhCOO) ₂ ^a	5	CH ₃ CN	11	5.5	66
t-C ₄ H ₉ COOH	t-C ₄ H ₉	(PhCOO) ₂ ^a	23	CH ₃ COOH	6	23	71
C ₆ H ₁₁ COOH	C ₆ H ₁₁	(PhCOO) ₂ ^a	23	CH ₃ CN	3	29	78
CH ₃ COOH	CH ₃	Percadox ^{d,e}	15	CH ₃ COOH	-	12	50
n-C ₃ H ₇ COOH	n-C ₃ H ₇	Percadox ^a	10	CH ₃ CN	-	15	85
i-C ₃ H ₇ COOH	i-C ₃ H ₇	Percadox ^a	10	CH ₃ CN	-	29	82
C ₆ H ₁₁ COOH	C ₆ H ₁₁	Percadox ^a	10	CH ₃ CN	-	24	76
t-C ₄ H ₉ COOH	t-C ₄ H ₉	Percadox ^e	10	CH ₃ CN	-	40	81
C ₆ H ₅ OCH ₂ COOH	C ₆ H ₅ OCH ₂	Percadox ^f	28	CH ₃ CN	-	71	82
C ₆ H ₅ OCH ₂ COOH	C ₆ H ₅ OCH ₂	Percadox ^f	28	CH ₃ COOH	-	58	73
C ₆ H ₅ OCH ₂ COOH	C ₆ H ₅ OCH ₂	NaBO ₃ ·4H ₂ O ^e	18	CH ₃ CN/H ₂ O	-	14	79

a- ratio lepidine : peroxide 1:1

b- based on lepidine

c- based on isolated compounds

d- percadox: bis(4 tert.butylcyclohexyl)peroxydicarbonate

e- ratio lepidine : peroxide 1:2

f- ratio lepidine : peroxide 1:1.5

considering the low solubility of the peroxydisulphate in organic solvents. The fact that hydrogen peroxide, alkyl hydroperoxides and alkyl peroxides are not effective for the oxidation of Ag(I) suggests that the reaction is connected with the nature of the peroxide (peroxide (peroxide of carboxylic, carbonic and sulphuric acids.)

That induced us to investigate the behaviour of sodium perborate. Actually this peroxide in the presence of silver salt is able to decarboxylate carboxylic acids. It is however less effective than peroxydisulphate and percarbonates.

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