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THE REACTION OF ACYL PEROXIDES WITH 2,2,6,6-TETRAMETHYLPIPERIDINYL-1-OXY

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Abstract: Benzoyl and lauroyl peroxides undergo induced decomposition by 2,2,6,6-tetramethylpiperidinyl-1-oxy to form acyloxy radicals and carboxylic acid in equimolar amounts. Formation of the carboxylic acid does not involve free acyloxy radicals.

In connection with studies of the interaction of vinyl monomers with acyloxy radicals using nitroxides as radical trapping agents[1,2] we have investigated the reactions of benzoyl and lauroyl (dodecanoyl) peroxides with 2,2,6,6-tetramethylpiperidinyl-1-oxy (1).

The nitroxide (1) (0.005 - 0.05M) reacts with benzoyl peroxide (0.002 - 0.02M) in degassed styrene at 60° C to form the nitrone (5), benzoic acid, and products derived from the interaction of benzoyloxy radicals with monomer in the ratio 0.3:1:1.[3] Similar use of lauroyl peroxide affords the nitrone (5) and lauric acid amongst other products. Examination of the reaction in styrene or benzene by EPR or UV shows that the rate of disappearance of the nitroxide is a function of the concentration of both nitroxide and peroxide.

The identity of the nitrone (5) was confirmed by comparison (MS, NMR, HPLC, GC, IR.) with an authentic sample prepared using the procedure developed by Keana et al.[4] Oxidation of the hydroxylamine (4) formed by the Grignard reaction of isopropenyl magnesium bromide with 5,5-dimethyl-1-pyrroline-N-oxide gave the nitrone (5) in 80% yield. The nitrone (5) has NMR ($CDCl_3$) δ6.45 (1H, br s, =CH), 5.4 (1H, br s, =CH), 2.7 (2H, br t, J=7Hz, allylic CH_2), 2.1 (3H, br s, allylic CH_3), 2.0 (2H, br t, J=7Hz, CH_2), 1.4 (6H, s, 2 x CH_3); IR(CCl_4) 1605, 1535 cm^{-1}. Anal. Calcd. for $C_9H_{15}NO$: m/e 153.1153. Found: 153.1149.

It has recently been reported[5,6] that benzoyl peroxide undergoes a facile reaction in di-t-butylnitroxide solvent to afford a near quantitative yield of benzoic acid plus isobutylene and 2-methyl-2-nitrosopropane. The mechanism proposed[5-7] for this process involved induced decomposition (homosolvolysis) of benzoyl peroxide to give benzoyloxy radicals and a labile O-benzoyloxyhydroxylamine (2b) (the latter compound was assumed to be in equilibrium with nitroxide and benzoyloxy radicals) with hydrogen abstraction from the nitroxide by benzoyloxy radicals then affording the observed products.

Our experiments show that a mechanism involving a reaction of free benzoyloxy radicals with nitroxide cannot account for all the benzoic acid formed when the reaction is conducted in the presence of vinyl monomer solvent. If this were the case, benzoyloxy radicals would be partitioned between nitroxide and monomer and, consequently, the yield of benzoic acid relative to the yield of products derived from the interaction of benzoyloxy radicals with monomer would be a function of nitroxide concentration. In fact, this ratio remains essentially constant over a wide range of nitroxide concentrations (0.005 - 0.05M).

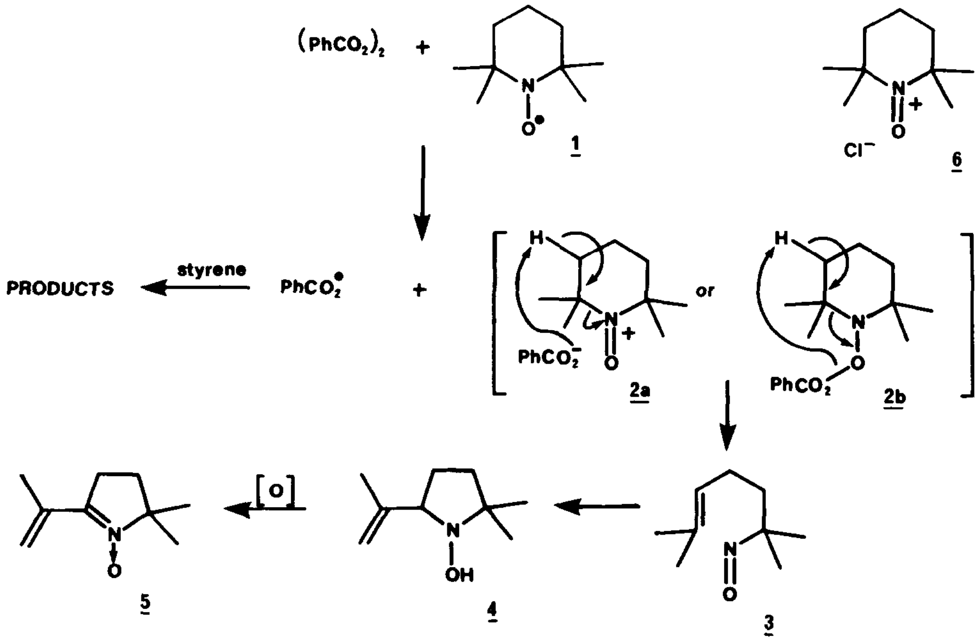
Similarly, free lauroyloxy radicals are almost certainly not involved in the formation of lauric acid from lauroyl peroxide. The decarboxylation of aliphatic acyloxy radicals has been extensively studied[8] and is known to be an extremely facile process; few, if any, of these radicals escape the solvent cage. Therefore, it seems unlikely that any reaction between lauroyloxy radicals and the nitroxide (1) (e.g. hydrogen abstraction) could compete with the decarboxylation of lauroyloxy radicals and account for the observed yield of lauric acid.

Finally, it is notable that the nitrone (5) is not formed when other radicals with known propensities for involvement in abstraction reactions are generated in the presence of the nitroxide (1) in a vinyl monomer solvent; for example, when *t*-butoxy and phenyl radicals are generated from di-*t*-butylperoxalate and triphenylmethylazobenzene respectively.[1,2]

The following mechanism is proposed to explain the yield of benzoic acid and to account for the transformation of the nitroxide (1) into the nitrone (5) (Scheme 1). The nitroxide (1) induces the decomposition of benzoyl peroxide forming one equivalent of benzoyloxy radicals and undergoing concomitant conversion into the intermediate (2). The present data do not allow the nature of this species to be precisely defined (it may be written as an oxo-ammonium salt (2a)[9] or as a covalent adduct (2b)). What is certain, however, is that benzoic acid and the nitrone (5) must be formed without the intermediacy of free benzoyloxy radicals. It is therefore proposed that (2) decomposes directly to benzoic acid and the unsaturated nitroso compound (3).[9,10] This could occur by an ionic mechanism similar to that invoked in the oxidative degradation of other nitroxides[11-15] or by an electrocyclic mechanism as shown for (2b). The nitroso compound (3) can then undergo an intramolecular 'ene' reaction to give the hydroxylamine (4),[16-18] oxidation of which affords the nitrone (5).

The most likely oxidant for (4) is benzoyl peroxide.[18] The induced decomposition of benzoyl peroxide by hydroxylamines is known to be an extremely facile reaction.[19] This process would lead to the formation of a further two equivalents of each benzoyloxy radicals and benzoic acid which is in keeping with the observed stoichiometry for the overall reaction (*i.e.* formation of *ca.* three equivalents of benzoic acid for every one of nitrone).

The nitroxide induced decomposition of benzoyl peroxide by the above mechanism affords directly a 50% yield of benzoic acid. If, as seems likely, the same mechanism is involved in the previously reported[5,6] reaction of nitroxides with benzoyl peroxide in neat nitroxide (*vide supra*), then the interaction of benzoyloxy radicals with nitroxide can account for at most 50% of the near quantitative yield of benzoic acid observed.



Scheme 1

Evidence that the species (2) can break down as shown in Scheme 1 was obtained by examining the reaction between the oxoammonium chloride (6)[20] and benzoate ions. Treatment of (6) with sodium benzoate or silver benzoate in dichloromethane leads to a rapid reaction giving benzoic acid, the nitrone (5), and the nitroxide (1) as the only products. The formation of the latter two compounds presumably involves an oxidation/reduction reaction between hydroxylamine (4) and the species (6) and/or (2).

Under our usual reaction conditions (involving 0.002 - 0.05M (1) in a monomer solvent) acyloxy radicals do not react with the nitroxide (1). Product analyses show that these radicals either react with monomer or decarboxylate to give alkyl or phenyl radicals which may in turn undergo reaction with monomer, else they are trapped by the nitroxide as stable alkoxyamines.[1,2] The relative importance of the latter two processes is a function of the concentration of monomer and nitroxide.

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References and Notes

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9 The intermediates (2a) and (3) can have only transient existence since there is no evidence of the characteristic absorptions of these compounds when the reaction is followed by UV.

10 The decomposition of (2) could proceed with loss of a β-methyl hydrogen rather than a β-methylene hydrogen as shown (cf. Scheme 1). While the unsaturated nitroso compound formed in this way cannot yield (3) by an intramolecular 'ene' reaction, an alternative cyclisation mechanism may be possible (cf. ref. 15).

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