Substituted Peroxycarbamic Acids as Epoxidizing Agents

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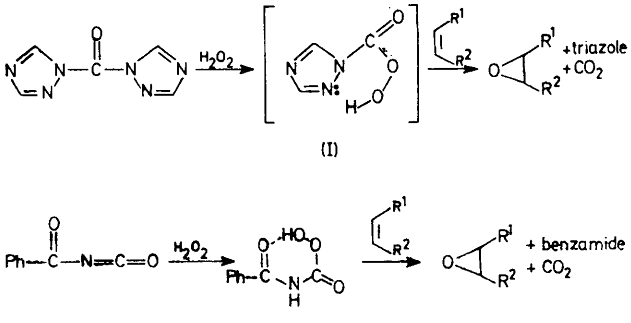
Summary Substituted peroxycarbamic acids have a high reactivity in epoxidation reactions, but can be used under mild conditions.

WE have observed that the action of various dehydrating agents on anhydrous H_2O_2 in the presence of alkenes results in epoxidation. To date the most promising new reagents are the substituted peroxycarbamates (I)[1] and (II),[2] generated *in situ* as in the Scheme. These agents, as with other peroxy-acids, have an intramolecular hydrogen bond[3] but also may cause epoxidation with concomitant CO_2 extrusion.

Reagent (I) epoxidizes cyclohexene, norbornene, cholesteryl acetate, and cyclododecenes at rates some 200 times faster than peroxybenzoic acid in tetrahydrofuran (THF). Unlike conventional peroxyacids, the epoxidation rates observed with (I) are nearly independent of solvent (THF, $CHCl_3$, $HCONMe_2$, and EtOH). Further evidence for the unique hydrogen bond of (I) is provided by the failure of the corresponding imidazole-derived reagent to yield more than traces of epoxide under these conditions.

Reagent (II) has been crystallized and its i.r. spectrum[4] supports the 7-membered hydrogen bonded structure indicated. That CO_2 is formed simultaneously with oxygen transfer with either of these reagents has not been established; however, both (I) and (II) react rapidly with phenanthrene at room temperature to give biphenyl-2,2′-dicarboxylic acid, and (II) appears to react with napthalene under unusually mild conditions.† The products of this reaction have not yet been identified, although the disappearance of naphthalene is shown by g.l.c. This reactivity, combined with the innocuous nature of the other reaction products indicate the synthetic potential of these reagents.



SCHEME

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† Typically, the dehydrating agent is added to a solution of alkene (0·1—0·01M) in THF containing excess of H_2O_2 and a trace of free-radical inhibitor.

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