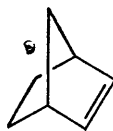


The Mechanism of Epoxide Formation by Peroxy-acids

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THE reaction between olefins and peroxy-acids has been represented for many years by sequence (A).¹ A different mechanism (B), advanced recently by Kwart and Hoffmann,² involves 1,3-dipolar addition to the olefin of a dipolar tautomer derived from the peroxy-acid. Assuming, reasonably, that reactions of type (B) will show the general characteristics of 1,3-dipolar additions, a distinction between the alternative mechanisms can be made.

relief of strain in the transition states leading to the five-membered-ring intermediates. (Although the triazolines are not isolated in the picryl azide reactions, their formation is rate-determining.³) A similar rate enhancement would then be expected in the epoxidation of norbornene if sequence (B) is a valid representation. On the basis of mechanism (A) there should be little or no relief of strain in the transition state, and the epoxidation rate



(I)

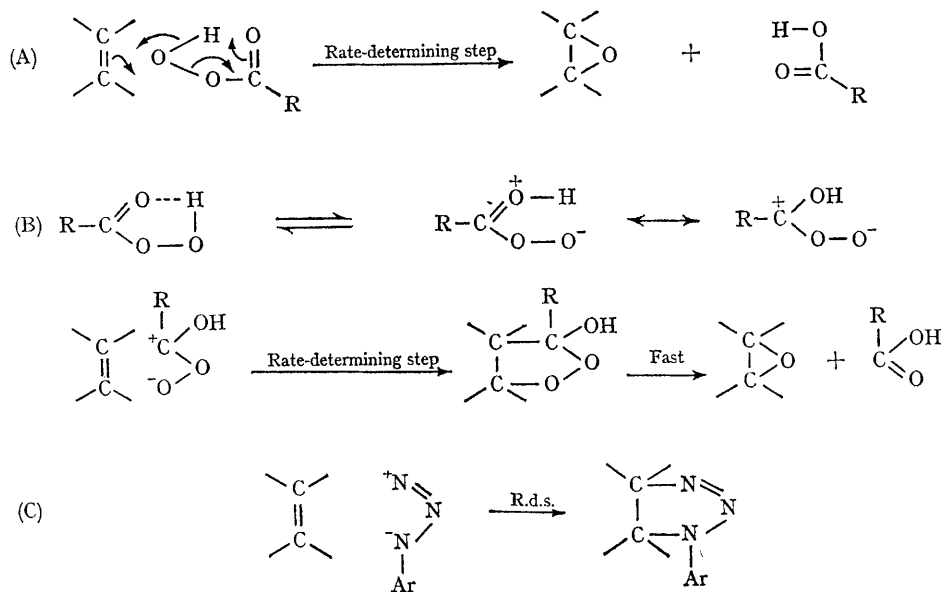


(II)

Reaction with:	k_I/k_{II}
Phenyl azide	6.5×10^3
Picryl azide	8.0×10^3
Perlauric acid	1.2

In 1,3-dipolar additions norbornene (I) is much more reactive than cyclohexene (II). A striking illustration is the ratio of the rate constants (k_I/k_{II}) of the reactions with aromatic azides (C),³ the fast reactions of norbornene stemming from the

should be determined mainly by the degree of hindrance to approach by the peroxy-acid: prediction is difficult, but no spectacular difference between norbornene and cyclohexene would be expected.



Using perlauric acid in chloroform at 25° the second-order rate constants (l.mole⁻¹ sec.⁻¹) were found to be 1.92×10^{-2} for cyclohexene and 2.28×10^{-2} for norbornene. Thus, dipolar addition (B) is not the rate-determining step in the norbornene-perlauric acid reaction.

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