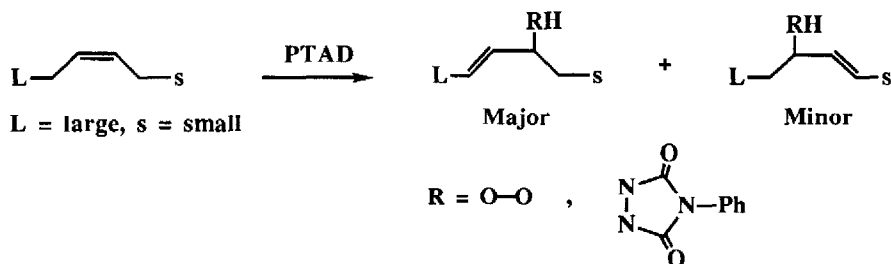


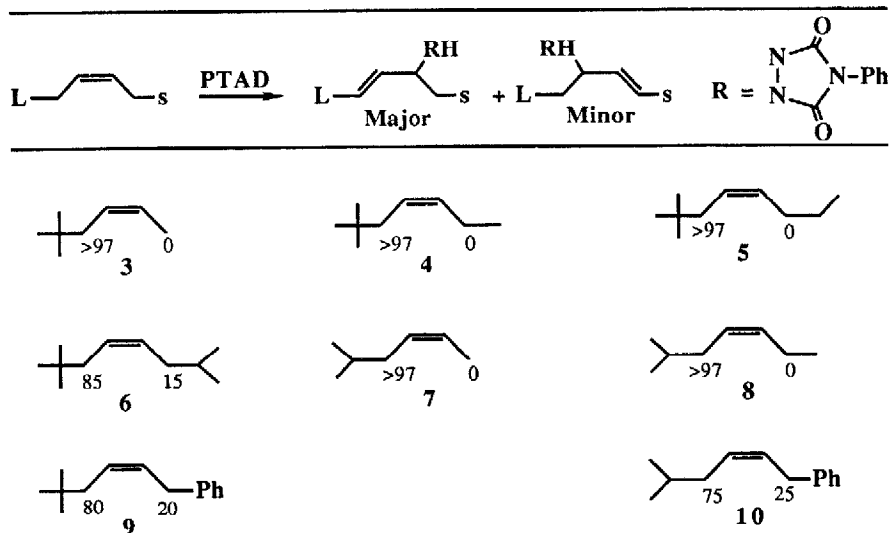
reaction of PTAD with similar substrates. We report here a new type of regioselective ene reaction of PTAD with unsymmetrical *cis*-alkenes. This reaction is stereospecific and shows a general preference for hydrogen abstraction from the larger group of the double bond. Unlike the reaction of PTAD with trisubstituted olefins (scheme I), or allylsilanes, this reaction shows product selectivity in the same direction as that of $^1\text{O}_2$ but to a greater extent. The results are summarized in Table I.



The reaction of PTAD with *cis*-alkenes gives ene adducts by preferential abstraction of allylic hydrogens from the carbon next to the larger group. For example, when L (larger group) is *tert*-butyl and s (smaller group) is hydrogen, compound **5**, the preference for abstraction of hydrogens adjacent to the *tert*-butyl group is greater than 97%, making this reaction highly regioselective. When the size of the s group becomes larger, the selectivity toward the *tert*-butyl group is still high. This is demonstrated with substrates **4**, **5**, **6**, **7** and **8**, where the preferential hydrogen abstraction is greater than 85% on the *tert*-butyl or isopropyl sides.

Similarly, alkenes **9** and **10** give again as a major product the ene adduct with the double bond next to the *tert*-butyl and isopropyl groups. The ene adducts of **9** and **10** substrates were purified by flash chromatography and gave 60% and 55% overall isolated yields respectively. Some other products are present in small amounts as indicated by TLC and ^1H NMR analysis. No attempt was made to identify the minor products. They are most probably formed the following way: The minor ene adducts of **9** and **10** with the double bond conjugated to the phenyl ring, react with one more PTAD molecule in a Diels-Alder fashion to form the 2PTAD:1 adduct. A further addition to the newly formed diene can yield a 3PTAD:1 adduct. It is interesting to note that we were not able to observe any ene adduct of PTAD with *cis*-1-phenyl-2-pentene or *cis*-1-phenyl-2-butene, even though there are four and five available allylic hydrogens respectively. Instead Diels-Alder adducts are formed. This result suggests that PTAD reacts more rapidly in a [4+2] fashion than in an ene reaction. The addition of PTAD or $^1\text{O}_2$ to the double bond and the ortho position of an aryl ring in

Table I. Regioselective Reaction^a of PTAD with *cis*-Alkenes¹⁰

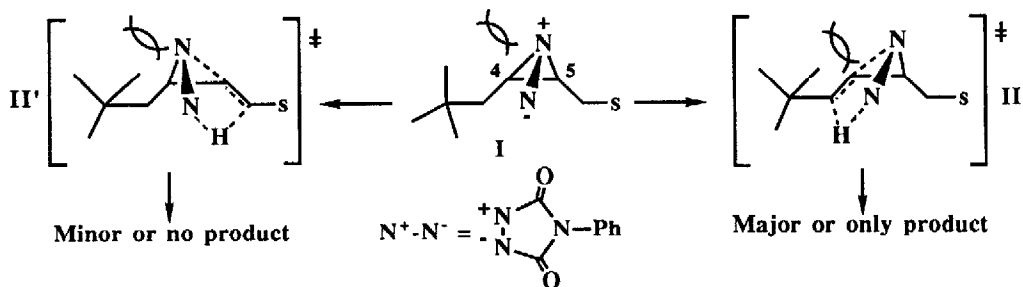


^a Product ratio was determined on Bruker (250 or 500MHz) spectrometers with TMS internal standard in CDCl_3 . Numerical values below substrates represent percent of hydrogen abstraction.

styrene or stilbene type of molecules is well documented¹¹.

Although the selectivity of this reaction can be rationalized either by the intermediacy of an aziridinium imide **2**, or a 1,4 dipolar intermediate we prefer the AI. Such an intermediate in the ene reaction of PTAD with alkenes has found strong support from isotope effect studies^{1a,4a}, direct spectroscopic observations¹², and in some cases from experimental and theoretical calculations with dienes⁵.

For the unsymmetrically disubstituted alkenes the AI, **I** is probably unsymmetrical, due to non-bonding interactions, with $\text{N}-\text{C}_4$ bond being longer and weaker than $\text{N}-\text{C}_5$ bond.



The lack of a substantial effect of solvent polarity on rates^{1a}, suggests that transition states do not have much dipolar character. In the transition state (II) leading to the major (or only) product, the non-bonding interactions involving the large (*tert*-butyl) group and triazolinedione moiety are much smaller than those in transition state (II') leading to the minor or absent product. Therefore transition state (II) is expected to have lower energy than (II'). The selectivity of PTAD is in the same direction with that of ¹O₂, but greater. This may be expected from the fact that the phenyltriazolinedione moiety is much larger than oxygen and therefore more sensitive to steric interactions.

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