

Stereochemistry of the Transition State of Hydrogen Abstraction by Vinyl Radicals

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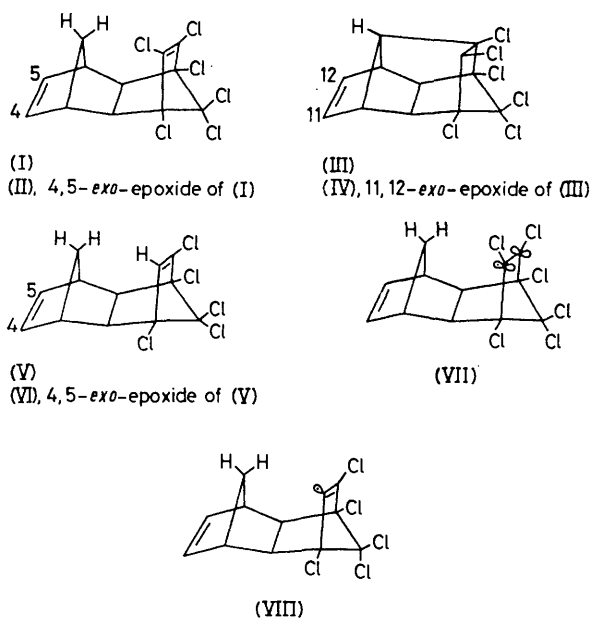
Summary Reduction of vinyl radicals, generated by photochemical dechlorination of polycyclic chlorinated pesticides, shows that the process of hydrogen abstraction must occur by a co-linear arrangement of reacting centres.

THE stereochemistry of the transition states of hydrogen abstraction by an alkyl radical,¹ the addition of a radical to an olefin,² and the ground state S_N2 displacement reaction³ are all described as proceeding *via* an arrangement of reacting centres which maximize orbital overlap. We describe here some experiments which we interpret as indicating that hydrogen abstraction by the vinyl radical must also proceed by such a mechanism.

The photochemical behaviour of the polycyclodiene pesticides, aldrin (I) and dieldrin (II), is known to be sensitive to reaction conditions.⁴ Irradiation in the presence of triplet sensitizers leads to the rapid production of the bridged isomeric photoproducts (III) and (IV), respectively, whereas irradiation under conditions where the triplet state is inaccessible leads to sequential dechlorination of the dichloroethylene bridge to give (V) and (VI), respectively. In general, bridge formation in norbornyl systems is associated with the triplet state while dechlorination is ascribed to the singlet state.⁵

Photoisomerization must proceed intramolecularly, presumably *via* the triplet state of the dichloroethylene function. Proton abstraction can occur from the suitably opposed methylene bridge by one of the carbons of the excited dichloroethylene function. In this excited state (VII), with one of the π -electrons promoted into another orbital, the remaining electron in the π -bonding orbital is co-linear with the bridge methylene hydrogen. This is close to the six-membered chair configuration usually described for this type of intramolecular process.³ After hydrogen abstraction (or the displacement of hydrogen by the radical) has occurred, bond formation between the resultant radical centres occurs to produce the σ -bond between the two bridges forming the photoproduct.

The unsensitized reaction, because of the formation of a different product, must proceed by way of a different



intermediate. The dechlorinated product presumably does not arise by hydrogen abstraction from the solvent followed by β -cleavage. The radical so formed by such an intermolecular process would have its lone electron in an orbital co-linear with the bridge methylene hydrogen, an arrangement which resulted in an intramolecular reaction involving these centres to produce the photoisomer in the triplet sensitized reaction. Another possible reaction for this hypothetical intermediate is to undergo a second hydrogen abstraction from the solvent to yield the dihydro-derivative. More plausible is the occurrence of homolytic cleavage of the carbon-chlorine bond from the excited singlet dichloroethylene chromophore. The vinyl radical thus resulting is so constituted that its half-filled orbital is almost exactly orthogonal to the methylene bridge and so constrained so as to be held in this position without the possibility of any isomerization (VIII). This is in extreme

contrast with the stereo-electronic configuration of the intermediate resulting in photoisomerization.

Irradiation of dieldrin or aldrin in deuteriated cyclohexane to *ca.* 50% conversion results in the mono-dechloro-vinyl isomer being the only product formed and with deuterium only at this position. This is easily seen by the complete absence of any proton resonance at δ 6.00 for the dieldrin derivative or at δ 5.93 for the aldrin example. The photochemical reduction has thus occurred exclusively

intermolecularly, without any involvement of the methylene bridge.

It seems reasonable to ascribe the clear preference for intermolecular reaction to the lack of intramolecular interaction because of the directional characteristics of the vinyl radical orbital and the requirement for maximum interaction of the orbitals involved during reaction.

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