

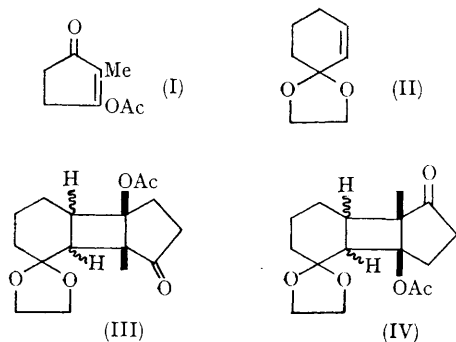
Solvent Effects on the Stereochemistry of a Photocycloaddition

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INTERMOLECULAR photocycloaddition has been used as a synthetic tool for carbocyclic ring formation on several occasions in recent years.¹ A major drawback to a considerable extension of its use is the difficulty in the prediction of the *cis*- or *trans*-direction of addition, *viz.* head-to-head as against head-to-tail. This is evidently a serious problem if both of the molecules are unsymmetrical about the ethylenic linkages concerned. Corey has shown² that the polar nature of the reacting double bonds exerts an influence on the direction of cycloaddition, and, of course, steric effects must be expected. Another effect which has been recognised as active is that due to the interactions of the overall dipoles of the reacting molecules. This interpretation has been used to explain the *syn*- to *anti*-ratios of products from cycloaddition of maleic anhydride to 1,2-dichloroethylene,³ and from the dimerisation of acenaphthylene.⁴ The more relevant variability of the ratio of products from cyclopentenone photodimerisation⁵ has also been attributed, qualitatively, to this phenomenon, although the interpretation in this case is made more complex by the presence of conjugation. We present here a clear demonstration of the importance of this effect.

Cycloaddition of (I) to (II) was used as the first stage of a synthetic sequence leading to β -himachalene.^{1a} The product from this reaction, performed in cyclohexane solvent, was (III), formed



in good yield, and apparently uncontaminated with the other isomers, (IV). Since there appeared to be no strong steric reason for this specificity, and it was demonstrated that the double bond of (II) had very little polar character,^{1a,6} this observation was interpreted as indicating that the dipole moments of (II) and the excited state of (I) were opposed in the transition state.⁷

The hypothesis was tested⁷ by irradiation of (I) and (II) in six solvents, of widely differing dielectric constants. A notable increase in the amount of (IV) produced was observed from irradiations in solvents of high dielectric constant.† In order to eliminate effects caused by the finite concentration of reagents, several different concentrations of (I) and (II) in each solvent were irradiated, and the ratio of (III) to (IV) was extrapolated to zero concentration of (I) and (II). The results are plotted in the Figure.

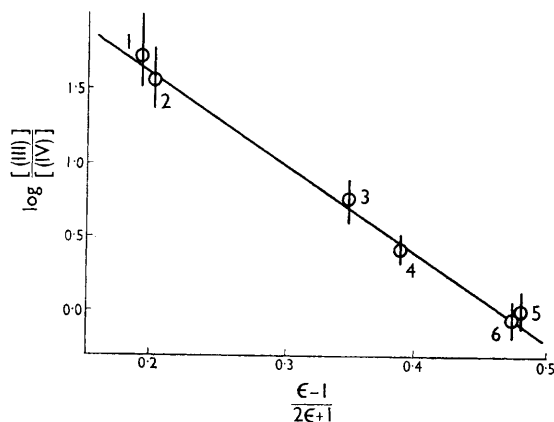


FIGURE. Variation of cycloadduct ratios with solvent dielectric constant (ϵ). The function of dielectric constant is derived from the Kirkwood–Onsager equations, and the method applied is essentially that of Berson.^{6,7}† Solvents used were: (1) iso-octane; (2) cyclohexane; (3) diethyl ether; (4) ethyl acetate; (5) acetonitrile; (6) methanol.

The magnitude of the effect is surprisingly large; the ratio of (III) to (IV) changes from 98:2 in

† Satisfactory analyses were obtained for the cycloadducts. The identity of the isomers of (IV) was established by degradation with mild acid and alkali to chromophores visible in the u.v. region (ref. 6).

‡ In this case it was not necessary to modify the original Onsager equation and invoke the molar volume of the solvent (as distinct from that of the solute). The "cavity radius" of the solute was assumed to be independent of the solvent. The ratio of (III) to (IV) in the product mixture was determined by v.p.c. The large margin of possible error given for the ordinate for hydrocarbon solvents derives from the difficulty of measuring accurately the small proportion of (IV) present.

dilute hydrocarbon solvents, to 45 : 55 in methanol. Even at high concentrations of (II) (e.g. 30% w/w), and the consequent unavoidable change in the dielectric constant of the medium, the change in the ratio is still from 92 : 8 to 60 : 40.

These results clearly indicate that the effect of the dipole interactions is important and suggest that, with an appropriate choice of solvent, stereochemical control of photocycloaddition may be achieved by suitable polar substitution of a

molecule, other than on the reacting double bonds. Such substituents, for instance halogens, may then be removed after having fulfilled their function. Whether the dipole effect can over-ride the more specific interactions discussed by Corey² is the subject of current investigation: at present it can only be noted that in this instance the directing effect is greater than those recorded previously.²

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