

## A Solvent Trend in the Epoxidation of Substituted Alkenes

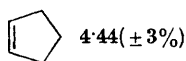
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THE symmetrically substituted cycloalkenes (I)—(IV) were prepared and their rates of epoxidation (using peroxylic acid) were determined to obtain quantitative information concerning the

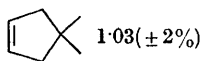
rate values (in benzene at 20°) demonstrate the retarding effect of the *gem*-dimethyl groups.

The effect of the *gem*-dimethyl group is greater in (II) (relative to cyclopentene) than in (IV)



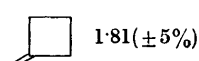
4.44(±3%)

(I)



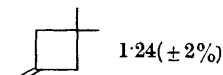
1.03(±2%)

(II)



1.81(±5%)

(III)



1.24(±2%)

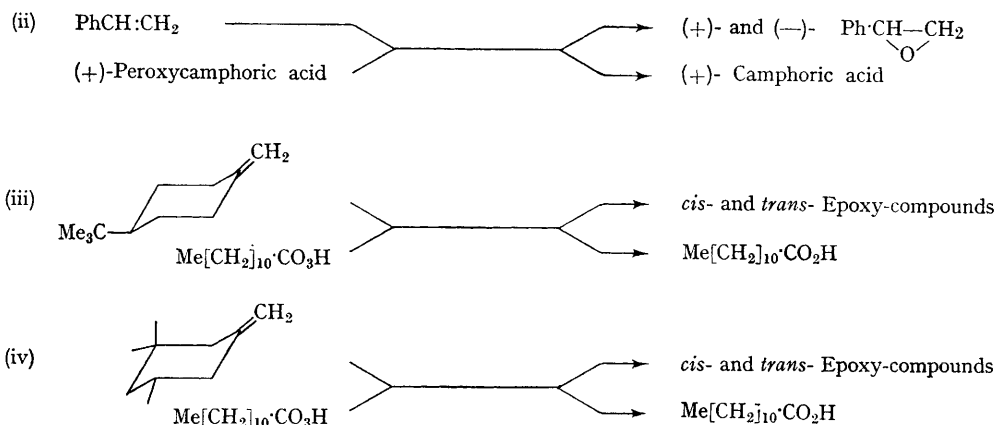
(IV)

Rates of epoxidation ( $k \times 10^3$ ; l. mole<sup>-1</sup>sec.<sup>-1</sup>)

effect of *gem*-dimethyl groups upon the rates in different solvents. The following second-order

(relative to methylenecyclobutane) in keeping with the smaller distance (by *ca.* 15%) between

TABLE



Solvent	(i) $k/k_s$	(ii) <sup>a</sup> Asymmetric induction (optical purity of epoxide)	(iii) Proportions of <i>cis</i> -product (equatorial approach of $\text{RCO}_3\text{H}$ )	(iv)
Ether .. .. .	—	2.0	15	65
Cyclohexane .. .. .	3.9	—	—	—
Carbon tetrachloride .. .. .	4.0	2.0	15	75
Toluene .. .. .	4.2	2.4	—	—
Benzene .. .. .	4.3	2.5	18	80
Chlorobenzene .. .. .	4.7	—	—	—
Dichloromethane .. .. .	5.3	3.5	21	83
Bromotrichloromethane .. .. .	5.3	—	—	—
Chloroform .. .. .	5.7	4.4	21	83

<sup>a</sup> Values for the epoxidation of oct-1-ene were 1.0 (ether) and 2.5 (chloroform), the *S*-epoxide again being the major product.

the methyl substituents and the transition state in the former compound. However the distances between the methyl groups and the transition state for the compounds (II) and (IV) are large enough to make an explanation based solely on steric interactions uncertain; solvent molecules in the vicinity of the substituents and the transition state also need to be considered. Epoxidations of compounds (I) and (II) were carried out in various solvents, the relative rates [ $k$  for (I), and  $k_s$  for (II)] being given as ratios ( $k/k_s$ ) in column (i) of the above Table.

The  $k/k_s$  values for the epoxidation of the cycloalkenes (I) and (II) represent an external comparison of rates. Internal comparisons of rates were made by using the following (hydrocarbon) substituted alkenes and reactions (ii)—(iv). In reaction (ii), the *S*(-)-epoxide was the major product.

Although the range of liquids used for reactions

(ii), (iii), and (iv) is less than that used for the pair of reactions (i), the trend of the solvent effect is the same for the internal comparisons as for the external comparison. The differences in the directive and kinetic effects, arising from the presence of hydrocarbon substituents in the alkene molecules, are greatest in polar halogenated solvents. A factor contributing to this result may be the presence, during the reactions of the substituted alkenes in these solvents, of less favourable nonbonded interactions between the substituent(s) and the solvated transition state; *cf.* the appreciable positive deviation from non-ideal behaviour of mixtures of hydrocarbons, especially alkanes, with halogenated solvents. The firmness and the extent of the solvation shell around each transition state may also need to be considered.

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