Asymmetric Induction in the Epoxidation of Alkenes by Optically Active Peroxy-acids

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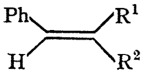
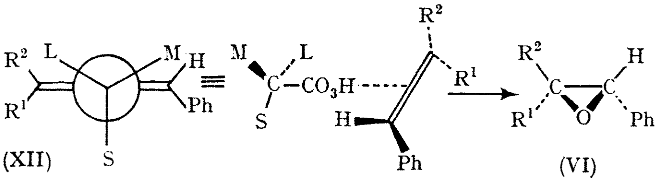
In the study of asymmetric syntheses the reliability and limitations of the empirical models which define the topology of the transition state are of importance. Asymmetric oxidations of aryl alkyl sulphides and sulphoxides with optically active peroxy-acids had been interpreted in terms of eclipsing effects between the groups bonded to sulphur and the groups of small (S), medium (M), and large (L) size bonded to the asymmetric carbon of peroxy-acid.[1] Since the mechanism of these reactions (electrophilic attack by the peroxy-acid on the substrate)[2] is largely identical to that proposed for the epoxidation of olefins with peroxy-acids, it is important to check whether the proposed model remains valid in the latter case too.

Asymmetric inductions have been observed[3,4] in the epoxidation of mono-substituted and αα-disubstituted olefins with optically active peroxy-acids. We oxidised styrene (I) and *trans*- and *cis*-olefins (II)—(V) to the corresponding oxirans (VI) with (1*S*)-(+)-peroxycamphoric acid (VII), (*S*)-(+)-2-phenylperoxypropionic acid (VIII), (*R*)-(−)-2-(α-naphthyl)peroxypropionic acid (IX), (*R*)-(−)-2-cyclohexylperoxypropionic acid (X) and (*S*)-(+)-2-methylperoxybutyric acid (XI). All the peroxy-acids (VII)—(XI), prepared as previously described,[1c,5] lack polar substituents and correspond to the general formula SMLC·CO_3H. The oxidations were carried out in chloroform solution at 0° and the products (50—96%) were always optically active. As in the oxidations at sulphur, the optical yields were rather low (maximum 7·5%), but in all the cases examined the chirality of the oxiran (VI) was always correlated to that of the peroxy-acid (Table).

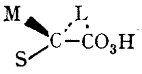
Model (XII), analogous to that proposed[1] for oxidations at sulphur, allows prediction of the correct configuration of the prevalent enantiomer (VI).† The topology of the transition state is represented in such a way that the bulkier alkene-bonded group faces the least hindered region of the peroxy-acid, between groups S and M and near group S, while the less bulky group faces the medium-hindered region, between groups S and L.



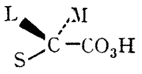
(I) $R^1=R^2=H$ (II) $R^1=Me, R^2=H$
(III) $R^1=H, R^2=Me$ (IV) $R^1=H, R^2=Ph$
(V) $R^1=H, R^2=Bu^t$



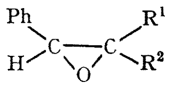
(XII) (VI)



(A)



(B)



(VIa)

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† Model (XII) applies equally to the asymmetric epoxidations of mono- and αα-di-substituted alkenes described by other authors (ref. 3).

Asymmetric epoxidation of substituted alkenes[a]

	Peroxy-acids				Epoxides (VIa)		
	Chirality	Absolute configuration	R¹	R²	$[\alpha]^{20}_{350}$	Optical yield (%)	Found Absolute[b] configuration
(VII)	(A)	(1*S*)-(+)	H	H	−5·7°[c,d]	4·6[d]	(*S*)
(VIII)	(A)	(*S*)-(+)			−2·1	1·7	(*S*)
(IX)	(B)	(*R*)-(−)			+4·8	3·9	(*R*)
(X)	(B)	(*R*)-(−)			+4·3	3·5	(*R*)
(XI)	(A)	(*S*)-(+)			−1·8	1·5	(*S*)
(VII)	(A)	(1*S*)-(+)	Me	H	+3·5[e]	2·2	(1*S*,2*R*)
(VIII)	(A)	(*S*)-(+)			+3·1	1·9	(1*S*,2*R*)
(X)	(B)	(*R*)-(−)			−2·7	1·7	(1*R*,2*S*)
(XI)	(A)	(*S*)-(+)			+1·0	0·6	(1*S*,2*R*)
(VII)	(A)	(1*S*)-(+)	H	Me	−20·2[c]	5·1	(1*S*,2*S*)
(VIII)	(A)	(*S*)-(+)			−7·4	1·8	(1*S*,2*S*)
(X)	(B)	(*R*)-(−)			+19·7	4·9	(1*R*,2*R*)
(XI)	(A)	(*S*)-(+)			−7·2	1·8	(1*S*,2*S*)
(VII)	(A)	(1*S*)-(+)	H	Ph	−109·0[f]	7·5	(*S*,*S*)
(VIII)	(A)	(*S*)-(+)			−46·0	3·2	(*S*,*S*)
(XI)	(A)	(*S*)-(+)			−51·0	3·5	(*S*,*S*)
(VII)	(A)	(1*S*)-(+)	H	Bu^t	−12·0[c]	—	(1*S*,2*S*)[g]
(VIII)	(A)	(*S*)-(+)			−3·5	—	(1*S*,2*S*)
(XI)	(A)	(*S*)-(+)			−6·1	—	(1*S*,2*S*)

[a] In chloroform solution at 0°; values corrected for optically pure peroxy-acids; [b] in all cases equal to the known configurations; [c] pure liquid; [d] see also ref. 4; [e] chloroform solution; [f] ethanol solution; [g] absolute configuration not known before.

Model (XII) implies the existence of a fairly symmetrical transition state,[2a] as it is normally accepted[2b] for these processes. However, in the epoxidation of other olefins stereoelectronic factors may shift the mechanism towards polar, non-symmetrical transition states. In this case the model could lead to erroneous predictions.

Model (XII) does not necessarily mean that asymmetric induction is due to direct sterical interactions between the groups S, M, and L of the peroxy-acid and those of the alkene. In fact, as has already been shown,[1c,3] it is likely that in these oxidations asymmetric induction is transmitted through a solvent shell. This hypothesis is supported by the activation parameters for the various solvents, measured in both the epoxidation of alkenes[3] and the oxidation of sulphides to sulphoxides.[6]

This work was supported by a grant from the Consiglio Nazionale delle Richerche, Rome.

(*Received, September* 23*rd*, 1968; *Com.* 1285.)

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