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CHIRAL SOLVENT-INDUCED ASYMMETRIC SYNTHESIS OF SULPHOXIDES IN THE METAL-CATALYSED OXIDATION OF SULPHIDES BY t-BUTYL HYDROPEROXIDE.

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OUR interest[1] in the elucidation of the mechanism of alkene and sulphide oxidations by t-butyl hydroperoxide catalysed by vanadyl and molybdenyl acetylacetonates[2], $VO(acac)_2$ and $MoO_2(acac)_2$ respectively, led us to examine the effect of changing the nature of the solvent on the general features of the reactions. As we moved from ethanol as solvent to benzene-alcohol mixtures, we observed a remarkable asymmetric induction by some optically active alcohols in the oxidation of organic sulphides. We report here the results for p-tolyl methyl sulphide and phenyl methyl sulphide.

The reactions were carried out in benzene or benzene-toluene, with 2.5 to 30% w:v added alcohol in the temperature range 25° to -10°. Equimolar amounts of substrate and t-BuOOH (0.3 - 0.5 M) were allowed to react in the presence of the catalyst (see the Table for details) until completion (6 to 12 hours). The sulphoxide was isolated and purified by column chromatography. The optical activity was measured in acetone or in ethanol and the enantiomeric excess was evaluated in the usual way on the basis of literature data $[\alpha]_D^{20}$ (acetone) +145.5 and -145.5 for the R and S optically pure p-tolyl-SO-Me[3] and $[\alpha]_D^{20}$ (ethanol)+146.2 for Phenyl-SO-Me[4].

The stereoselectivity of the reaction seems to depend on the alcohol, but not so much on its concentration, and on the catalyst. Vanadyl acetylacetonate proves to be significantly better than molybdenyl acetylacetonate. Under the best conditions so far tried, which may well yet be improved upon, the enantiomeric excesses observed compare well with the best results reported for the asymmetric oxidations of sulphides by chiral peroxyacids[5]. This method should also be valuable for the epoxidation of alkenes[6] and related reactions, and may represent an useful alternative to other methods of asymmetric oxidation.

As far as the mechanistic aspects are concerned, the fairly large asymmetric induction observed would suggest, rather than a simple solvent effect[7], the entering of one or more chiral alcohol molecules in the metal coordination sphere. From this point of view the use of chiral alcohols may result in an useful tool for understanding the intimate structure of the catalyst.

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TABLE

Asymmetric Induction in the Oxidation of p-Tolyl Methyl Sulphide (1) and Phenyl Methyl Sulphide (2) by t-Butyl Hydroperoxide in Benzene-12% Toluene Containing Chiral Alcohol.

Substrate	Catalyst			Alcohol[a]		Sulphoxide		
	Type	10^4Conc.,M	Temp.	Type	%	$[\alpha]_D^{20}$	% e.e.	Conf.[b]
1[c]	$MoO_2(acac)_2$	0.10	25°	(-)-2-octanol	2.5	0.9	0.62	R(+)
1[c]	"	0.65	12°	(-)-menthol	5	2.	1.4	R(+)
1	"	0.20	-10°	(-)-menthol	5	2.2	1.5	R(+)
1	"	7.5	-10°	(-)-menthol	5	1.9	1.3	R(+)
1	"	0.95	0°	(-)-borneol	6	0.3	0.2	S(-)
2	"	3.3	-10°	(-)-menthol	12	1.9	1.3	R(+)
1	$VO(acac)_2$	13.5	0°	(-)-menthol	5	7.	4.8	R(+)
1	"	25.	0°	(-)-menthol	15	12.9	8.9	R(+)
1	"	25.	0°	(-)-menthol	30	14.4	9.8	R(+)
1	"	24.5	-10°	(-)-menthol	5	9.2	6.3	R(+)
1	"	17.5	0°	(-)-borneol	6	1.7	1.2	S(-)
2	"	27.	0°	(-)-menthol	30	6.7	4.7	R(+)
1	H^+ [d]	890.	0°	(-)-menthol	5	-	-	-

[a] All the alcohols used have R configuration at the carbinol carbon. [b] Ref. 3. [c] Solvent benzene. [d] From CH_3SO_3H catalyst.

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