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OPTICAL INDUCTION - IV[1]

Optical Induction by Using Homogeneous Catalyst

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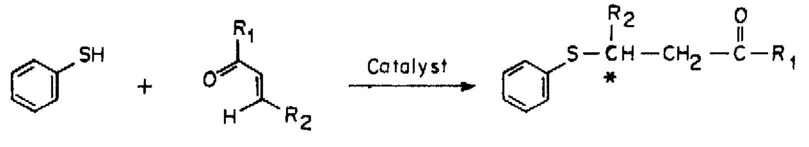
SUMMARY - Better optical induction during Michael addition has been achieved by using new homogeneous catalysts based on quinine and quinidine.

Michael addition of thiophenol I to α,β-unsaturated ketones such as II, when carried out in presence of catalytic amount of quinine (Qn) and quinidine (Qd) and their derivatives leads to β-ketosulphides III in which one of the optical enantiomer predominates[2,3]. In a pursuit of preparing optically pure ketosulphides, we have now found that, when the same reaction is carried out in presence of new homogeneous catalysts based on quinine [Qn homo-cat] and quinidine [Qd homo-cat], there is a manifold increase in the optical induction [Table 1 for comparative studies]. The concentration of the catalysts [Qn homo-cat and Qd homo-cat] mentioned in the Table are optimum for a particular set of reactions.



I II III

A - $R_1 = CH_3$; $R_2 = C_6H_5$
B - $R_1 = C_6H_5$; $R_2 = CH_3$

* depicts optical centre

These new homogeneous catalysts were prepared by interacting quinine/quinidine with $MoO_2(acac)_2$[4]. The utility of incorporation of quinine/quinidine as fixed ligand for the preparation of this catalyst for optical induction was evident from the fact that $MoO_2(acac)_2$ alone does not induce any optical activity[5] in the resulting product.

In a typical experiment[6], thiophenol (1.1 g; 0.01 M) was added to a solution of IIA, (1.46 g; 0.01 M) and Qn homo-cat (8.6 mg; 16×10^{-6} gM) in dry benzene (10 ml). The mixture was refluxed for 3 hr. It was cooled to room temperature and benzene was removed at reduced pressure. The mixture was fractionated to remove Ph_2S_2 formed in the reaction and IIIA was collected at 120-130°/3×10^{-3} mm. It was twice crystallised from pet.ether to give white needles (2.1 g; 82%), m.p. 58°C. The purity of the products and absence of Ph_2S_2 and catalysts was ensured by TLC. The results obtained in this reaction and with different concentrations of the catalysts were found to be reproducible.

TABLE 1 Set.I — I + IIA[8] $\longrightarrow$ IIIA

Catalyst used	gM of catalyst	Molecular Rotation	Enantiomeric Excess[7] Ee(%)
Qn	16×10^{-6}	$+ 30.71^{o}$	14.15
Qn Homo-cat.	16×10^{-6}	$+ 72.21^{o}$	33.27
Qd	64×10^{-6}	$- 5.2^{o}$	2.40
Qd Homo-cat.	64×10^{-6}	$- 42.54^{o}$	19.60
	Set. II - I + IIB[8] $\longrightarrow$ IIIB		
Qn	32×10^{-6}	+ 2.52	3.99
Qn Homo-cat.	32×10^{-6}	+ 18.89	29.98
Qd	64×10^{-6}	- 1.31	2.07
Qd Homo-cat.	64×10^{-6}	- 21.76	34.53

It is premature to speculate any mechanism which will explain all the experimental facts. A systematic study of the mechanism of the catalytic action and the utilisation of these catalysts for better optical yields in other reactions are in progress.

REFERENCES AND NOTES

1 NCL Communication No. 2647.

2 K. Hermann and H. Wynberg, J.Org.Chem. 44, 2238 (1979); B. Marsmann and H. Wynberg, J.Org.Chem. 45, 158 (1980) and references cited therein.

3 S. Bhole and V.N. Gogte, Indian J.Chem. (in press); S. Bhole "Optical Induction" a thesis submitted to Poona University (1979).

4 The preparation and spectral data is being published elsewhere.

5 R.R. Ahuja, A.A. Natu and V.N. Gogte (Unpublished results).

6 a) Fore-run of the distillation contains Ph_2S_2 along with some amount of IIA and IIIA.

b) Since IIIB is liquid it was purified by repeated distillations.

7 Enantiomeric excess was determined by PMR measurements (in CCl_4) using $Eu(hfc)_3$ as shift reagent. The results were in good agreement with observed optical rotations.

8 IIA and IIB were prepared according to procedures, A.I. Vogel "Practical Organic Chemistry" Longman Group Ltd., London (1976), p. 716; R.R. Fuson, R.E. Christ, G.M. Whitman, J.Amer.Chem.Soc., 58, 2450 (1936).

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