

MULTIFUNCTIONAL CATALYSIS XI : ASYMMETRIC CATALYSIS OF THE MUTAROTATION  
OF TETRAMETHYLGLUCOSE BY OPTICALLY ACTIVE PHOSPHINOTHIOIC ACIDS.

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*Abstract* : Catalytic activities of R(+) and racemic *t*-butylphenylphosphinothioic acids on the mutarotation of 2,3,4,6 tetramethyl-d-glucose are studied in benzene.

In previous studies of the catalytic activity of multifunctional compounds in benzene two cases of asymmetrical catalysis were reported :

1) - In the catalysis of the mutarotation of tetramethylglucose (TMG) by the enantiomeric R(+) and S(-) ( $\beta$ -naphthoxy)-2 propionic acids (1), a slight difference in the values of the activation parameters may be noted (2) :

$$\delta \Delta H^\ddagger = 0.4 \text{ Kcal.mole}^{-1}$$

$$\delta \Delta S^\ddagger = 1 \text{ e.u.}$$

The difference of  $0.1 \text{ Kcal.mole}^{-1}$  in the free energy of activation indicates an optical yield of 8 %.

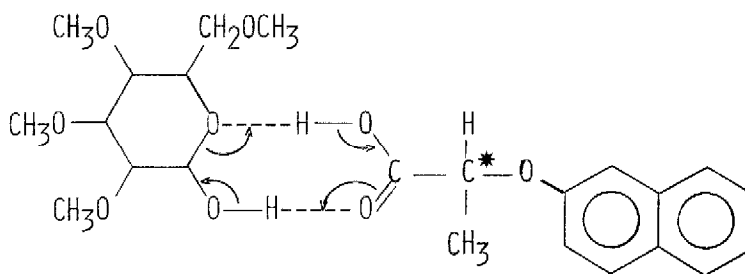


Figure 1

2) - In the isomerisation of  $\Delta$ -5 cholestenone by mixtures of 3-nitro phenol and the optically active tertiary amines R(+) and S(-) N,N dimethyl 1-phenyl ethylamines (3), the difference in the values of the activation parameters is more significant :

$$\delta \Delta H^\ddagger = 1.5 \text{ Kcal.mole}^{-1}$$

$$\delta \Delta S^\ddagger = 5 \text{ e.u.}$$

However, the free energies of activation  $\Delta G^\ddagger$  have neighbouring values : the existence of an isokinetic point has been observed at 30°C.

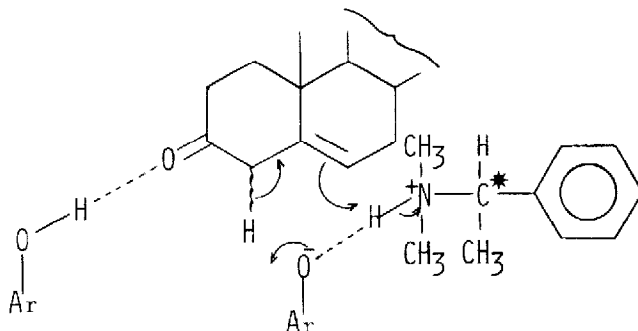


Figure 2

Figures 1 and 2 show the proposed reaction mechanisms : the asymmetric centre of these catalysts is farther away from the nearest reaction site in the case of TMG (oxygen of carbonyl group) than in the case of the steroid (nitrogen of amino group). These results suggested studying the catalytic activity of enantiomeric compounds whose asymmetric centre would be directly linked to the nearest reaction site.

By analogy with phosphinic acids which catalyse the two previous reactions (4), optically active monothiophosphinic acids should be bifunctional catalysts. Like phosphinic acids too, such compounds are likely to be dimerized at high concentrations in benzene. Hence, their catalytic activity was investigated on mutarotation of TMG (acid concentration  $10^{-4}$  M) rather than on isomerisation of  $\Delta$ -5 cholestenone (acid concentration  $10^{-1}$  M).

The rate law obtained with t-butylphenylphosphinothioic acids of known configurations, R(+) and racemic (5), is identical to that obtained with oxyacids (4,6).

$$v = k_{\text{ex}} (\text{TMG}) = k' (\text{TMG}) (\text{acid monomer})$$

The rate constant for each acid was determined at various temperatures (Table I) (7).

Table 1 : Values of rate constant  $k'$ , in  $\text{mole.l}^{-1}.\text{s}^{-1}$ , for the catalysis of the mutarotation of TMG by R(+) and racemic t-butylphenylphosphinothioic acids.

T°C	R(+) acid	Racemic
20	0.74	0.50
25	1.14	0.82
30	1.75	1.24
35	2.83	2.00
40	4.20	2.78
45	6.31	4.11

These values give the activation parameters of the reaction for the two studied acids and allow the corresponding values to be calculated for the S(-) acid (Table II).

Table II : Activation parameters.

Catalyst	$\Delta H^\ddagger$ Kcal.mole <sup>-1</sup>	$\Delta S^\ddagger$ e.u.	$\Delta G^\ddagger$ at 25°C Kcal.mole <sup>-1</sup>
Racemic	14.9 ± 0.3	- 8.8 ± 0.5	17.5 ± 0.3
R(+) acid	15.4 "	- 6.6 "	17.3 "
S(-) acid	14.4 "	- 11.1 "	17.7 "

The differences between the values of the activation parameters for the two enantiomers are notable and similar to that obtained with enantiomeric tertiary amines on isomerisation (3). Furthermore, the difference in free energy of activation  $\Delta G^\ddagger_{S(-)} - \Delta G^\ddagger_{R(+)}$ , of about 0.4 Kcal.mole<sup>-1</sup>, corresponds, according to PRELOG (8), to an optical yield of more than 50 %.

These examples of asymmetrical catalysis illustrate the greatly accrued importance of group interactions in the diastereoisomeric transition states, when the asymmetric centre is very close to a reaction site, Figure 3.

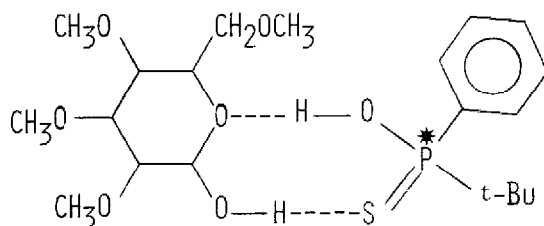


Figure 3

References and Notes :

- 1 - A. KERGOMARD and M.F. RENARD, Tet. Letters, 1969, 3041.
- 2 - The values of the activation parameters given in reference (1) were determined by plotting  $\log \frac{k}{t}$  v.  $f \left(\frac{1}{t}\right)$ . Using linear regression of least squares, it was possible to obtain a greater degree of precision and thus to separate the values of the activation parameters obtained for each acid.
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