Liquid-phase stereoselective thymol hydrogenation over supported nickel catalysts

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The stereoselective hydrogenation of thymol was studied in liquid phase over several nickel catalysts, modified by coimpregnation of inorganic compounds containing chlorine. The total activity of all catalysts studied was decreased and was on the same order of magnitude, indicating that chlorine even after reduction remains on the surface and is responsible for the poisoning effects. Such blocking of accessible sites results in similar reaction rates for the catalysts studied. Selectivity and stereoselectivity to menthols and menthones changed significantly. The modifiers could influence the rate of keto–enol transformations, which is thought to be the key selectivity and stereoselectivity governing step.

Keywords: thymol; hydrogenation; nickel catalyst; liquid phase

1. Introduction

Promotion in heterogeneous catalysis has been a subject of considerable interest for a long time [1]. Promotion or modification of solids leads to changes in activity, selectivity and catalyst lifetime. However, such studies are rather scarce in stereoselective heterogeneous catalytic reactions, although stereochemical studies can provide additional information on the reaction mechanism [2]. One example of such reactions is the hydrogenation of dialkylphenols with the formation of two stereomer substituted cyclohexanones and four stereomer substituted cyclohexanols. The most frequently studied alkylphenol is thymol, because its liquid-phase catalytic hydrogenation is used in the fragrance industry for the manufacture of menthols. This reaction leads to the formation of a mixture of four diastereoisomers [2]. (Scheme containing reaction products is presented in fig. 1, where the

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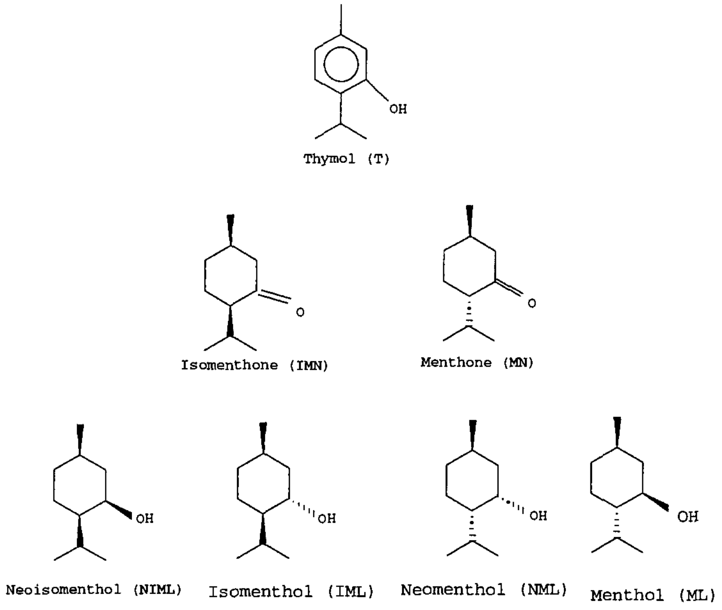

Fig. 1. Chemical substances.

desired product is menthol.) Thus an industrial process needs separation and recycling of useless diastereoisomers. Various catalysts were reported to be active in this reaction [2–6]. Skeletal nickel catalysts were found to be efficient at 423–473 K and hydrogen pressure 2–10 MPa [3] in an alcohol solution of NaOH forming all isomers with stereoselectivity to menthol close to 50%. High selectivity was observed in the case of Co catalysts [4,5]. Although Ni and Co catalysts as well as copper [3–6] showed high activity and selectivity, noble metals were also studied to achieve milder conditions [7–14]. Thymol reduction was conducted in the gas phase [7], liquid phase [7–12] and even in the solid state [13,14].

The objective of these investigations was obtaining information on activity, selectivity and stereoselectivity dependencies on the nature of metal, solvent, pH, etc. Kinetic models, based on either formal considerations [9] or the theory of complex reactions [10,12] were reported and the reaction network, given in fig. 2, was advanced [10].

However, little attention has been focused on thymol hydrogenation over modified catalysts. Therefore, in this paper we studied activity, selectivity and stereoselectivity of different modified supported catalysts. As a base catalyst we chose an industrial nickel–chromium catalyst and the main portion of data to be presented below was obtained with this catalyst. For comparison we also carried out thymol hydrogenation over several supported metal catalysts. All the reactions were studied in the liquid phase under conditions close to industrial ones.

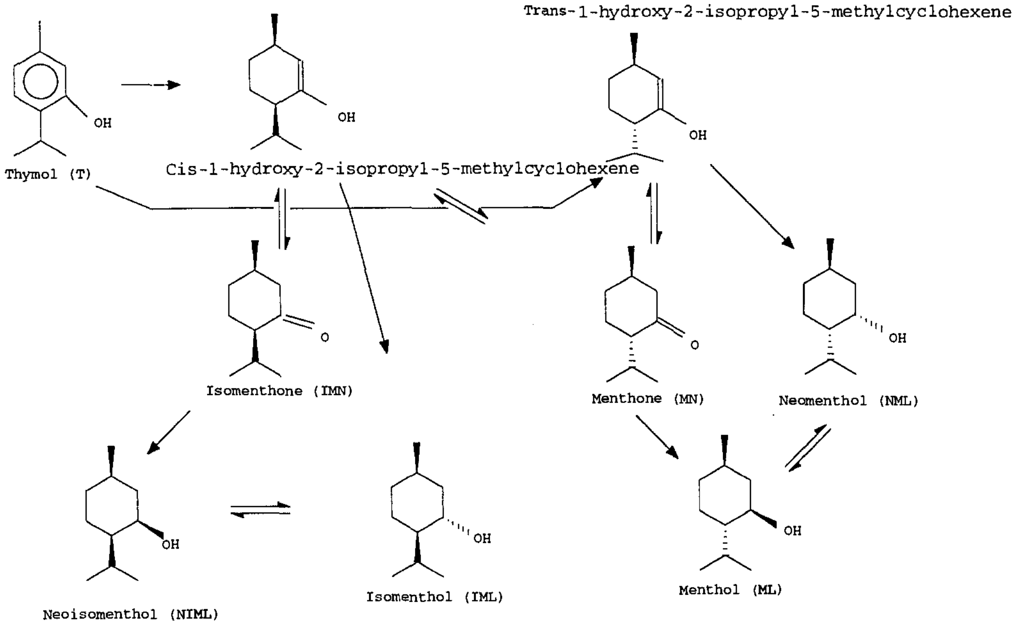

Fig. 2. Reaction scheme.

2. Experimental

2.1. CATALYSTS

The pellets of industrial Ni/Cr_2O_3 [15] were crushed and those less than 50 μm in particle size were taken and reduced in flowing hydrogen at 623 K. In the case of other supported monometallic catalysts the ion-exchange procedure was used. The size of the support was less than 50 μm. Water solutions of $RhCl_3$, $PdCl_2$, H_2PtCl_6, OsO_4, $RuCl_4$, $IrCl_4$ or $Ni(NO_3)_2$ were added to the support to a nominal weight loading. Reduction was performed by HCOOH in the case of noble metals and by hydrogen for Ni catalysts. For chloride containing precursors the catalysts were washed with water until neutral pH.

Modified catalysts were prepared by impregnation. Unreduced Ni/Cr_2O_3 catalyst was impregnated by water solution (4×10^{-4} or 8×10^{-4} mol/ℓ) of corresponding compounds to a nominal loading, then drying in air at 373 K and reducing in a hydrogen flow at 623 K for 2 h and at 673 K for 1 h, and then cooled in hydrogen flow. The specific surface area of the carrier and the catalysts was determined by nitrogen and hydrogen (O_2 for Ni catalysts [16]) chemisorption respectively. Some data are presented in table 1.

2.2. HYDROGENATION PROCEDURE

The kinetic experiments were performed in a shacked reactor with an external heating–cooling system. The volume of the reactor was 75 ml. The frequency of

Table 1
Catalysts used in thymol hydrogenation

Catalyst	Code	Surface area of the metal (m^2/g-cat)	Pretreatment
50% Ni/Cr_2O_3	Ni1	52	
3% Rh/C	Rh1	5.5	
5% Pt/C	Pt1	4.7	
10% Rh/Ni1	MRh11		reduced from $RhCl_3$ before
10% Rh/Ni1	MRh12		reduced from $RhCl_3$
10% Rh/Ni1	MRh13		solution of $RhCl_3$ neutralised by Na_2CO_3 before impregnation and reduced by hydrogen
10% Rh/Ni1	MRh14		solution of $RhCl_3$ neutralised by NH_4OH before impregnation and reduced by hydrogen
5% Rh/Ni1	MRh21		neutralised by Na_2CO_3
20% Rh/Ni1	MRh3		neutralised by Na_2CO_3
5% Cu/Ni1	MCu1	135[a] (130[b])	
10% Cu/Ni1	MCu2	108[a] (106[b])	
15% Cu/Ni1	MCu3	108[a]	
10% Ir/Ni1	MIr		
10% Li/Ni1	MLi		
15% Ag/Ni1	MAg	113[a] (100[b])	
10% Co/Ni1	MCo		
10% Pt/Ni1	MPt		without prereduction of H_2PtCl_6
5% Ru/C	Ru1	5.0	
5% Ir/C	Ir1	3.3	
5% Os/C	Os1	2.2	
5% Pd/C	Pd1	2.8	

[a] Total surface area.
[b] Total surface area after reaction.

vibration of the reactor was 150 min^{-1} and the amplitude was 15 cm. The pressure in the reactor was measured with a standard manometer and was constant during the experiment. The reactor temperature was kept within a range of 1 K of the fixed values. The hydrogenation reactions were carried out between 353 and 463 K and at hydrogen pressures between 2–4 MPa. *n*-hexane and cyclohexane were chosen as solvents and the initial mole fraction of thymol was 0.08. Before an experiment the reactor, containing thymol and catalyst, was flushed with H_2 at room temperature (for 1 h). During the course of the reaction samples of the solution were taken and analyzed by FID gas chromatography (15% LAC-3R-446 on chromosorb W). Menthones and menthols were separated at 413 K (2 m). Thymol was separated using the same phase (1 m) at 458 K. A fresh portion of catalyst was taken for each experiment.

The absence of diffusion limitations was verified using the published procedure [17]. The proportionality of the efficiency of the reactor to the amount of catalyst, the calculation of the rate of diffusion of dissolved hydrogen to the outside surface of the catalyst particles, and the efficiency factor show that the reaction took place in the kinetic region.

3. Results

The activity of the nickel catalyst Ni1 is presented in table 2. Experiments were carried out in *n*-hexane solution at 403–463 K at 2–4 MPa of hydrogen pressure. It can be seen from the data, given in table 2, that at 403 and 433 K in the range of 2–3 MPa the reaction order in respect to hydrogen is more than one, and thereafter is zero order. At higher temperatures, as it was previously observed for benzene hydrogenation over nickel catalyst [18], the zero order limit is reached at lower values of hydrogen pressure. The reaction order towards thymol was found to be equal to zero.

Product distribution as a function of time for a typical kinetic run is shown in fig. 3 and we present some of the data in table 2 as well. The menthol/neomenthol (C) ratio was found to be practically independent of conversion at 403 K and kept its value after total thymol consumption. This observation indicates that the rate of menthol isomerisation into neomenthol is very low. By contrast the ratio of isomenthol/neoisomenthol (D) was seen to decrease, thus the isomerisation reaction in this case takes place. In table 2 ratios ML/NML (C), IML/NIML (D) and (ML+NML)/(IML + NIML + ML + NML) (E) at high values of conversion are given.

After complete hydrogenation of thymol and menthones we could determine isomerisation rates for neoisomenthol–isomenthol and neomenthol–menthol.

Table 2
Activity, selectivity and stereoselectivity in thymol hydrogenation and rates of neomenthol–menthol (r_1) and neoisomenthol–isomenthol (r_2) isomerisation for Ni1 catalyst

T (K)	P_{H_2} (MPa)	Activity (mol/g h)	r_1 (mol/g h)	r_2 (mol/g h)	Conversion α(%)	Production distribution [a]		
						C	D	E
403	2	0.019	b	0.0036	67	1.07	0.72	0.37
403	3	0.038	b	0.0020	77	1.03	0.24	0.214
403	4	0.0325	b	b	76	1.17	0.54	0.36
433	2	0.073	0.0018	0.0018	73	1.14	0.44	0.41
433	3	0.128	0.0034	0.0016	80	1.14	0.22	0.31
433	4	0.129	0.0058	c	97	1.78	c	0.95
463	2	0.114	0.0028	0.0178	87	1.58	2.48	0.57
463	3	0.13	0.0011	0.005	82	1.74	0.57	0.40
463	4	0.1	0.0086	c	91	0.96	c	0.91

[a] C = ML/NML; D = IML/NIML; E = (ML + NML)/(ML + NML + IML + NIML).

[b] Rate is negligible.

[c] No NIML in the reaction mixture.

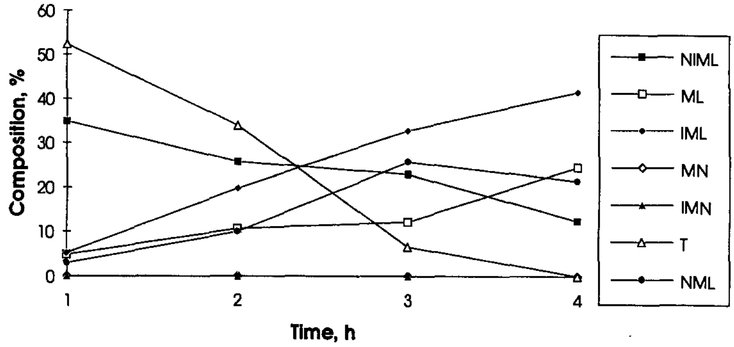

Fig. 3. Thymol hydrogenation over nickel–chromium catalyst at 403 K and 2.0 MPa.

Results given in table 2 reveal that the isomerisation rates are an order of magnitude lower than the rates of hydrogenation of thymol.

The time dependence of thymol conversion and product distribution was also studied at different pressures over promoted nickel catalysts (results are given in figs. 4–6 and table 3) and other supported non-modified catalysts (fig. 7 and table 4).

4. Discussion

Several models of promoter behavior could be invoked in explaining our experimental data. One of the models could be the change in surface area for the supported catalysts studied. However, if this explanation is given it seems difficult to rationalize the kinetic results. One would not expect the same reaction rate for practically all modified catalysts as the activity of non-promoted catalyst is always higher. For instance, in the case of highly active supported platinum and rhodium, as well as for the much less active copper catalyst, activity of modified materials

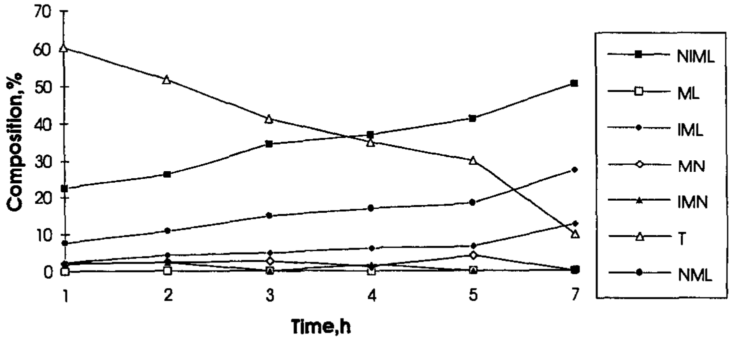

Fig. 4. Thymol hydrogenation over nickel–chromium catalyst modified with copper (MCul) at 403 K and 2.0 MPa.

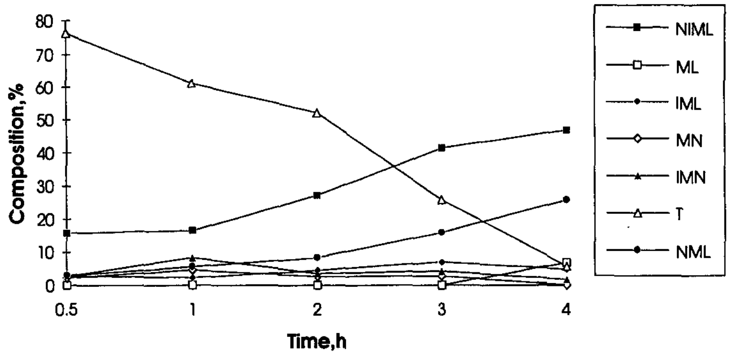

Fig. 5. Thymol hydrogenation over nickel–chromium catalyst modified with platinum (MPt1) at 433 K and 3.0 MPa.

was an order of magnitude lower than for the industrial nickel–chromium catalyst. In table 4 we present activity values of several supported non-modified catalysts and it can be easily seen that they are more active, than nickel–chromium catalyst.

Therefore, an alternative explanation which is consistent with this data has to be argued. It should be noted, that modified catalyst was prepared by impregnation with chlorine containing compounds. It was recently demonstrated by Prins [19], that even after high-temperature reduction chlorine could remain in the catalyst, either on the surface or by migrating into subsurface layers or even into the bulk of the catalyst.

It is known that chlorine can influence activity and selectivity of a particular reaction. Such effects of chlorine were established in the case of ethylene oxidation over silver supported catalysts and are well demonstrated [20–22].

Therefore, because the activity of all the modified catalysts was suppressed, chlorine could be responsible for this deactivation. Different activities could be attributed to different degrees of reduction of the catalyst precursors.

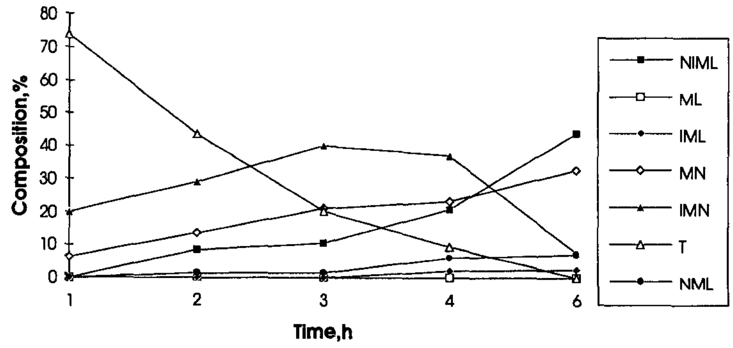

Fig. 6. Thymol hydrogenation over nickel–chromium catalyst modified with rhodium (MRh12) at 433 K and 3.0 MPa.

Table 3
Activity and product distribution for promoted catalysts [a]

Catalysts code	Conditions		Activity (mol/g h)	α (%)	Product distribution [b]				
	T(K)	P(MPa)			A	B	C	D	E
MCu2	433	2	0.0063	28	0.26	0.23	0	0.06	0.09
				84	0.54	0.05	0.47	0.41	0.47
MCu2	433	3	0.018	18	0	0.08	0	0	0.11
				93	0	0.03	1.48	0.29	0.27
MCu2	433	4	0.012	32	0	0.09	0	0.14	0.15
				98	0	0	0.47	0.45	0.54
MCu2	463	2	0.008	60	0.48	0.1	1.12	0.47	0.4
				86	0	0	1.43	3.08	0.69
MCu2	463	4	0.011	68	0.47	0.15	0	0.23	0.24
				88	0	0	0.77	0.76	0.51
MCu3	433	3.5	0.004	40	0.8	0.12	0	0.11	0.21
				90	0	0	0	0.25	0.3
MRh11	433	2	0.015	37	0.38	0.54	0	0.05	0.23
				87	0.56	0.38	0.36	0.12	0.33
MRh12	433	2	0.017	26	0.31	1	–	–	–
				80	0.5	0.75	0	0	0.15
MRh13	433	3	0.01	63	–	0	1.48	0.48	0.82
				87	–	–	2	–	0.86
MCo1	433	3.5	0.006	66	0.45	0.08	0	0.17	0.22
				91	0.37	0.03	0.03	0.43	0.39
MIr1	433	2	0.002	28	0.88	0.58	0	0	0.56
MLi1	463	3.5	0.003	34	0.92	0.23	0	0.1	0.08
MAg1	463	3.5	0.04	95	–	0	0.96	0.83	0.47
MPt1	433	3.5	0.004	85	0.52	0.04	0.5	0.42	0.43

[a] Reaction was carried out in *n*-hexane for MCu2 and in cyclohexane for other catalysts.

[b] Here A=MN/IMN; B=(MN + IMN)/(MN + IMN + ML + NML + IML + NIML); C = ML/NML; D = IML/NIML; E = (ML + NML)/(ML + NML + IML + NIML).

Let us now consider if there are any changes in selectivity and stereoselectivity for the modified catalysts studied. From tables 2 and 3 we can easily see some variation at relatively high conversions. For instance, considerable amounts of menthones were detected, which was not the case for nickel–chromium catalyst.

It can be suspected therefore, that modified metal can influence some of the elementary reactions involved in the reaction mechanism. It is not, however, unexpected, as such types of promotion modes were described in the literature [1]. A question that rises can be formulated in the following way: what elementary reaction could be influenced by the modifier, leading to drastic changes in selectivity and stereoselectivity. In order to answer this we will examine the reaction mechanism advanced from kinetic investigation [10,12].

The hydrogenation of alkylphenols has been a subject of interest for a long time

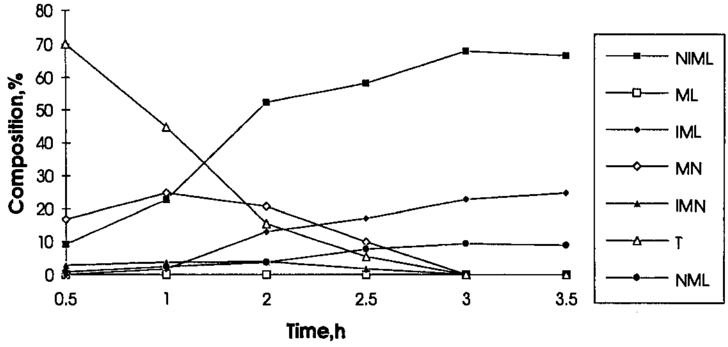

Fig. 7. Thymol hydrogenation over Ru/C at 353 K and 3.0 MPa.

and several reaction networks were proposed in the literature [9,23–25]. Based on kinetic data and taking into account similarity in homogeneous and heterogeneous catalysis, it was proposed [25], that the step which governs the total selectivity and stereoselectivity in alkylphenol hydrogenation is the step of keto–enol transformation in the same way as it is established for acid–base homogeneous catalysed transformation of ketone and enol [26]. Such tautomeric transformation is a key step, which can greatly influence stereoselectivity of the overall complex reaction of alkylphenol hydrogenation. Cis-alkylcyclohexanols were thought to be produced from corresponding cyclohexanones, and trans-alkylcyclohexanols from direct hydrogenation of adsorbed enols (cyclohexen-1-ols). Thus, for thymol menthol and isomenthol are produced from enol forms and neomenthol and neoisomenthol from ketones. We present the reaction network adopted from ref. [25] in fig. 2. It was suggested [25] in the case of phenol hydrogenation, that rates of keto–enol tautomerization greatly depend on the catalyst. In the instance of the nickel catalyst this rate is lowered, leading to trans products. Therefore relatively high amounts of menthols are observed. At the same time the ratio IML/NIML is not high. In promotion we change the product distribution and that can be due to both factors: influence of metal and chlorine. One of the catalysts used, MAg1, was prepared from a non-chlorine containing salt. Therefore, the reaction rate was relatively

Table 4
Activity of supported catalyst in thymol hydrogenation

Catalyst	*T* (K)	Hydrogen pressure (MPa)	Activity, (mol/g h)
Rh1	393	2.4	0.19
Pt1	353	2	0.15
Ru1	353	3	0.037
Ir1	363	2	0.03
Pd1	353	2	0.008
20% Ni/C	403	2.8	0.005

high in comparison with Ni1 catalyst. However, in both cases production of menthones was not observed and the ratio E, (ML + NML)/(ML + NML +IML + NIML), was approximately the same. The selectivity ratios ML/NML and IML/NIML were altered, lowering the amount of trans alcohol–menthol. As for the copper catalyst, selectivity values at high thymol conversions were very close to those of the non-promoted catalyst.

Other modified catalysts showed relatively high selectivity to menthones which was especially high for the Rh modified catalysts. It was previously demonstrated that Rh catalyst was active in 4-tert-butylphenol hydrogenation with formation of cis-4-tert-butylcyclohexanol. We attributed [25] this characteristic evidence to the following properties of Rh: availability of catalysing keto–enol tautomerisation on the one hand and sufficient activity in ketone hydrogenation. At the moment based on our results we can only speculate on the possible nature of this presumably electronic influence. A detailed explanation of the promoter effects was not in the scope of the present communication. The main objective was to report on experimental data, which manifests the importance of investigating the mode of action of promoters in the case of complex reactions with a variety of products of different selectivity and stereoselectivity.

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