Asymmetric Isomerization of Racemic α-Olefins by Titanium Tetra-(−)-menthoxide–Tri-isobutylaluminium

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Summary The homogeneous catalytic system obtained from $AlBu^i_3$ and an optically active titanium alkoxide [titanium tetra-(−)-menthoxide] effects asymmetric isomerization of racemic α-olefins into *Z*- and *E*-2-olefins, whereas no asymmetric transformation occurs in the hydrogenation.

HYDROCARBON-SOLUBLE Ziegler–Natta catalysts obtained by reaction of titanium alkoxides with alkylaluminiums have been reported to effect hydrogenation[1,2] and isomerization[2] of unsaturated hydrocarbons.

In connection with our investigations[3,4] on the stereoelective polymerization of racemic α-olefins by heterogeneous Ziegler–Natta catalysts prepared from optically active metal alkyls, it was interesting to know whether these soluble hydrogenation and isomerization catalysts were able to effect asymmetric (stereoelective[4]) transformations[5] of racemic α-olefins.

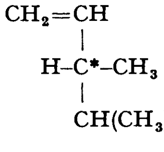
The dark brown solution obtained by reaction of titanium tetra-(−)-menthoxide[6] ($[\alpha]^{25}_D$ − 96·2; *c* 4·2 in benzene†) with tri-isobutylaluminium in benzene or toluene gives, at room temperature and under dry nitrogen, a slow isomerization of α-olefins into *cis*-(*Z*) and *trans*-(*E*) 2-olefins. Under similar conditions, but under dry hydrogen (*ca.* 860 Torr), both hydrogenation and isomerization take place, the former reaction being faster than the latter. In the case of racemic 3,4-dimethylpent-1-ene (I) and 3,7-dimethyloct-1-ene (II) the unreacted α-olefin and the paraffin are optically active, the sign of optical rotation[9] indicating that the latter is formed by hydrogenation of α-olefin in which the same antipode prevails as in the unreacted α-olefin. Furthermore, the paraffin has an optical purity slightly lower than that of the unreacted α-olefin (Table 1). No optical activity measurements on isomerization products can be performed as the 2-olefins are non-dissymmetric.‡

TABLE 1

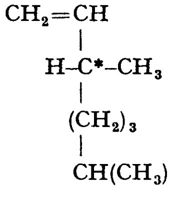
Optical activity[a] of unreacted α-olefin and reaction products in the isomerization and hydrogenation of racemic α-olefins by titanium tetra-(−)-menthoxide–tri-isobutylaluminium

		Products[b]								
		Unreacted α-olefin			Paraffin			Mixtures of 2-olefins		
Starting α-olefin	Gas	%	$[\alpha]^{25}_D$	Optical purity %	%	$[\alpha]^{25}_D$	Optical purity %	%	$[\alpha]^{25}_D$	Optical purity %
(I)[c]	H_2	65	+0·98	2·20	27	+0·18	1·6	8	nondissymmetric	
(II)[d]	H_2	59	+0·12[e]	0·74[e]	22	—[f]	n.d.	19	nondissymmetric	
(III)	N_2	92	+0·10	0·36	3	n.d.	n.d.	5	nondissymmetric	
(IV)	N_2	77	+0·018	0·60	6	n.d.	n.d.	17	+1·04	2·6

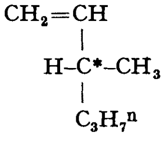
[a] Neat. [b] Qualitative and quantitative analysis of crude reaction mixture was performed by g.l.c. on 2m columns packed with $AgNO_3$+ ethylene glycol on Chromosorb. In order to recover pure reaction products and unreacted α-olefin, preparative chromatography, fractional distillation, and selective reactions with bromine and R_2AlH were used. [c] Hydrogenation of (+)-(*R*)-(I) by Raney Ni gives (+)-(*R*)-2,3-dimethylpentane.[9a] [d] Hydrogenation of (+)-(*S*)-(II) by Raney Ni gives (−)-(*R*)-2,6-dimethyloctane.[9b] [e] Minimum value, as the α-olefin contained about 10% of paraffin having negative optical activity. [f] Negative optical rotation.


$CH_2{=}CH{-}C^*H(CH_3){-}CH(CH_3)_2$

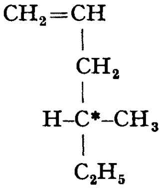
(−)-(*S*)-(I)


$CH_2{=}CH{-}C^*H(CH_3){-}(CH_2)_3{-}CH(CH_3)_2$

(−)-(*R*)-(II)


$CH_2{=}CH{-}C^*H(CH_3){-}C_3H_7^n$

(−)-(*R*)-(III)


$CH_2{=}CH{-}CH_2{-}C^*H(CH_3){-}C_2H_5$

(+)-(*R*)-(IV)

In the absence of hydrogen racemic 3-methylhex-1-ene (III) and 4-methylhex-1-ene (IV) are isomerized into *Z*- and *E*-2-olefin, and a small amount of paraffin is also formed;§ both unreacted α-olefins are optically active. In the case of (IV) where the asymmetric carbon atom is at

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† A sample of this titanium tetra-(−)-menthoxide gives on hydrolysis (−)-menthol [(1*R* : 3*R* : 4*S*)-4-isopropyl-1-methylcyclohexan-3-ol] having $[\alpha]^{25}_D$ − 43·8 (*c* 5·0 in benzene); the value $[\alpha]^{25}_D$ − 47·2 has been reported[7] for the same alcohol considered a optically pure.[8]

‡ *R*-(II), optical purity 48%, gives under the same conditions a paraffin with 49% optical purity, showing that no hydrogenation of 2-olefins has taken place.

§ Formation of paraffin in the absence of molecular hydrogen is known[10] to occur during polymerization of α-olefins by $TiCl_4$ (or $TiCl_3$) and AlR_3.

C-4, the mixture of Z and E (1 : 3) 4-methylhex-2-ene has positive optical activity (Table 1), indicating that (S)-(IV)[11] has been preferentially isomerized.

Taking into account this last result, as well as the optical purity and configurational relationships between the unreacted α-olefin and the corresponding paraffin, it seems reasonable to conclude that hydrogenation is practically non-asymmetric, isomerization being the only asymmetric transformation.

Fischer projection formulae of the α-olefins (I—IV) and optical activity data (Tables 1 and 2) show that the catalyst, in which the asymmetric carbon atom closest to titanium has absolute configuration (R), isomerizes preferentially the antipode having the same arrangement of groups around the asymmetric carbon atom in case of (I), (II), and (III). The opposite takes place in case of (IV) in which the asymmetric carbon atom is at C-4.

The ratio R_i between the isomerization rates of the two antipodes is 1·67 for (I) (Table 2) and only 1·05 for (IV), as observed in the stereoelective polymerization of the same racemic α-olefins.[12]

TABLE 2

Ratio (R_i) *between isomerization rate of the antipodes of some racemic α-olefins by titanium tetra-*(−)*-menthoxide–tri-isobutylaluminium*

		Unreacted α-olefin		
Starting α-olefin	Conversion (C) into 2-olefins (%)	Absolute configuration	Optical purity (%) (P_1)	R_i[a]
I	8	R	2·20	1·67
III	5	S	0·36	1·15
IV	17	R	0·60	1·05

[a] $R_i = [100\,C + P_1\,(100 - C)]/[100\,C - P_1\,(100 - C)]$.

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