

THE RESOLUTION OF SOME RACEMIC α -OLEFINES BY STEREO-SELECTIVE COMPLEXATION.

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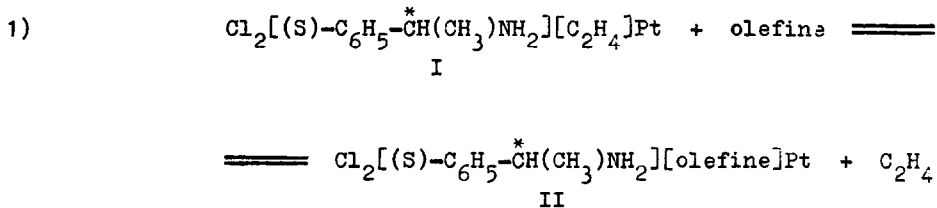
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The resolution of cycloolefines using platinum complexes⁽¹⁾⁽²⁾ as well as diisopinocampheylborane⁽³⁾ has already been achieved, but no resolution of aliphatic racemic α -olefines has been described up to now in literature.

We have observed that such a type of resolution occurs readily using both cis- and trans-dicloro[(S)- α -phenylethylamine][olefine]platinum complexes at least in the α -olefines in which the asymmetric carbon atom is in α or β position to the double bond.

In fact, by reacting cis- or trans-dicloro[(S)- α -phenylethylamine][ethylene]platinum with a solution of a racemic α -olefine, the known⁽⁴⁾ reversible reaction 1 occurs; when an excess of olefine is used the recovered α -olefine is optically active and from its optical activity, the optical purity of the α -olefine bound in the complex present in solution can be evaluated.



As shown in Table 1 operating in solution without crystallizing the complexes, the enantiomer of the α -olefine whose chirality is the same as that of the amine present in the complex, is preferentially bound to the metal atom of the cis platinum complexes; the opposite holds when using the trans platinum complexes.

TABLE 1

Stereoselective Complexation of Racemic α -olefines in solution using cis- or trans-dichloro[(S)- α -phenylethylamine][olefine] platinum Complexes.

α -olefine		Pt complex		recovered α -olefine			α -olefine bound in the dissolved complexes	
Type	m.moles	type	m.moles	m.moles	$[\alpha]_D^{25}$	chirality	chirality	optical purity %
3-methyl-1-pentene	5.0	<u>cis</u>	1.0	3.8	-0.37	R a)	S a)	4
3,7-dimethyl-1-octene	5.0	<u>cis</u>	1.0	3.7	-0.33	R b)	S b)	3
4-methyl-1-hexene	11.4	<u>cis</u>	3.8	6.7	+0.03	R c)	S c)	1
3-methyl-1-pentene	10.5	<u>trans</u>	1.5	7.9	+0.11	S a)	R a)	2
3,7-dimethyl-1-octene	10.5	<u>trans</u>	1.5	7.4	+0.11	S b)	R b)	5

a) P.Pino, L.Lardicci and L.Centoni, J.Org.Chem., 1399 (1959).

b) F.Ciardelli and P.Pino, Ric.Sci., 34(IIA), 694 (1964).

c) P.Pino, L.Lardicci and L.Centoni, Gazz.Chim.Ital., 91, 428 (1961).

The optical purity of the complexed olefine can be greatly increased by crystallization of the complex obtained from the cis form of the complex I. In the Table 2 the melting point and analyses of the crystalline complexes are reported.

TABLE 2

α -olefine	optical purity of the complexed olefine %	<u>cis</u> Pt complexes (II)					
		M.p. °C	Formula	Analyses (%)			
				Calcd. C	Calcd. H	Found C	Found H
3-methyl-1-pentene	24	140-141	$C_{14}H_{23}NCl_2Pt$	35.66	4.92	35.80	4.87
3-methyl-1-hexene	36	151-152	$C_{15}H_{25}NCl_2Pt$ x)	37.11	5.19	36.98	5.11
3,4-dimethyl-1-pentene	93	165-166	$C_{15}H_{25}NCl_2Pt$	37.11	5.19	37.15	5.09
4-methyl-1-hexene	2	112-114	$C_{15}H_{25}NCl_2Pt$	37.11	5.19	37.27	5.16
5-methyl-1-heptene	~ 0	122-124	$C_{16}H_{27}NCl_2Pt$	38.47	5.45	38.60	5.29
3,7-dimethyl-1-octene	42	125-126	$C_{18}H_{31}NCl_2Pt$	40.98	5.92	40.83	5.83

x) Cl calcd. : 14.61, found : 14.80

The optical purity obtained by a single crystallization (Table 3) is strongly dependent on the structure of the α -olefine and, in the case of 3,4-dimethyl-1-pentene, the optical purity of the complexed olefine, after one crystallization, was as high as 93%. No definite relationship seems to exist between chirality of the amine present in the solid complex and chirality of the α -olefine complexed preferentially.

TABLE 3

Resolution of Racemic α -olefines by Crystallization of cis-dichloro[(S)- α -phenyl-ethylamine][olefine] platinum Complexes.

α -olefine		<u>cis</u> Pt complex		olefine recovered from the Pt complex			
Type	m.mo-les	m.mo-les	crystallized from	m.mo-les	$[\alpha]_D^{25}$	chirality	optical purity %
$C_2H_5-\underset{\substack{ \\ CH_3}}{CH}-CH=CH_2$	5	1.0	methanol	0.62	- 9.0	R ^{x)}	24
$CH_3-(CH_2)_2-\underset{\substack{ \\ CH_3}}{CH}-CH=CH_2$	50	10.0	acetone	8.0	+10.4	S ^{a)}	36
$CH_3-\underset{\substack{ \\ CH_3}}{CH}(CH_2)_3-\underset{\substack{ \\ CH_3}}{CH}-CH=CH_2$	46	9.2	acetone	7.5	+ 6.9	S ^{x)}	42
$CH_3-\underset{\substack{ \\ CH_3}}{CH}-\underset{\substack{ \\ CH_3}}{CH}-CH=CH_2$	40	10.0	methanol	6.5	+41.0	R ^{b)}	93
$CH_3-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_2-CH=CH_2$	4.4	1.1	methanol	0.81	+ 0.06	R ^{x)}	2
$CH_3-CH_2-\underset{\substack{ \\ CH_3}}{CH}-(CH_2)_2-CH=CH_2$	20.0	5.0	acetone	4.7	~ 0	-	~ 0

x) See Table 1

a) As shown by hydrogenation with H_2 in the presence of Raney Nickel of the (+) enantiomer to (-)(R)-3-methylhexane [L.Lardicci, P.Salvadori and P.Pino, Ann.Chim., 52, 652 (1962)].

b) As shown by hydrogenation with H_2 in the presence of Raney Nickel of the (+) enantiomer to (+)(R)-2,3-dimethylpentane [L.Lardicci, R.Rossi, S.Pucci, M.Aglietto, G.Botteghi and P.Pino, Chim.Ind. (Milan) in press.].

The present method of resolution is particularly suitable from the preparative point of view as, by simple treatment with ethylene (20-40 atm.) of a solution of the complexes in CH_2Cl_2 or CH_3OH , it is possible to recover quantitatively the resolved olefine as well as the complex I which is sparingly soluble in the above solvents.

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