

NMR SPECTRA OF CHIRAL OLEFIN (E)-1-BENZYLIDEN-2,3,4R(S), 5R(S)- TETRABENZYLCHYCLOPENTA-2-EN IN THE PRESENCE OF A CHIRAL LANTHANIDE SHIFT REAGENT AND SILVER AUXILIARY COMPOUND

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ABSTRACT

The chiral olefin (E)-1-Benzyliden-2, 3, 4R(S), 5R(S)-tetrabenzylcyclopenta-2-en was studied by NMR method in the presence of chiral lanthanide shift reagent Ytterbium(III)[tris[3-(heptafluoropropylhydroxymethylene)-l-camphorate] and the auxiliary silver compound (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedion) silver(I) in order to find out the effectiveness of this combination on the enantiomeric resolution in NMR-spectrum.

I - INTRODUCTION

We have reported so far the research of silver compound containing shift reagents that are effective for NMR spectral resolution of a chiral olefin (E)-1-Benzyliden-2,3,4R(S), 5R(S)-tetrabenzylcyclopenta-2-en (Abbreviation: E1) [1]. The binuclear shift reagents are complexes, which are formed in the solution of lanthanide (III)- β -diketonates and auxiliary silver (I) β -diketonates compounds. The silver cation is capable of bonding to a soft Lewis base such as an olefin while the paramagnetic lanthanide ion results in the shift of olefin signals in NMR spectrum [2 - 5].

We now report continuously our new results on the study of the effect of shift reagent Ytterbium(III)[tris[3-(heptafluoropropylhydroxymethylene)-l-camphorate] (Yb(hfc)₃) and silver auxiliary compound (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedion) silver(I) (Ag(tt)) to NMR spectra

of E1, which contains five aromatic rings, two double bonds (one internal and one terminal to the cyclopenta-ring). The ¹H-NMR spectrum of the olefins is separated into two regions of aliphatic and aromatic proton signals. Through the use of binuclear shift reagents it is possible to spread out the NMR spectra, moreover the combination of chiral lanthanide shift reagent (LSR) with silver compound can resolve the resonance of enantiomeric olefinic pairs. Some papers describing the application of binuclear lanthanide shift complexes with chiral olefin compounds were published [3-6]. However, this article describes our new results in order to resolve NMR spectrum of E1 compound by adding chiral lanthanide shift reagent Yb(hfc)₃ in combination with Ag(tt).

II - EXPERIMENTAL

Apparatus. Proton NMR spectra were recorded with a BRUKER AMX spectrometer at 300MHz.

Reagents. Chloroform-d/TMS 0.03% was obtained from Euriso-Top, Group CEA. The AgNO_3 , and (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedion) was obtained from Lancaster Synthese. $\text{Yb}(\text{hfc})_3$ from Aldrich Chem., Co., Milwaukee, WI. All chemicals were used as received without further purification.

Preparation of (E)-1-Benzyliden-2,3, 4R(S), 5R(S) – tetrabenzylcyclopenta-2-en

(E)-1-Benzyliden-2,3,4R(S),5S(R)-tetrabenzylcyclopenta-2-en was isolated from 1,2,3,4,5-Pentabenzylcyclopenta-1,2-dien as described in our previous research [1].

Preparation of (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedion) silver(I) (Ag(ttb))

To a solution of 1 g of AgNO_3 in 100 mL of distilled water added a suspension of 1.2 g of $\text{Na}(\text{ttb})$ in 100 mL of methanol. The solution immediately turned brown and a light brown precipitate separated. After the solution was stirred for 5 min., the solid was collected by suction filtration and dried in vacuum over P_4O_{10} for 24 h. Obtained $\text{Ag}(\text{ttb})$ was then kept in a light-proof container and over P_4O_{10} [2].

NMR measurement. Required amounts of the LSR, the silver auxiliary compound and the olefinic substrate were added to a 0.75 mL

solution of chloroform-d/TMS 0.03% and shaken for 2 min. The mixture was then decanted into an NMR tube for analysis through a cotton-plug filter Pasteur pipett. During these procedures and up until recording the spectrum, the solutions were kept covered with aluminum foil to exclude light [1 - 6].

III - RESULTS AND DISCUSSION

The NMR spectrum of E1 (without shift reagent) was shown in Figure 1a with the overlapping of resonances protons H7, H8, H8'. Following the addition of increasing amounts of $\text{Yb}(\text{hfc})_3$ and $\text{Ag}(\text{ttb})$, a series of spectra was obtained (Figures 1b-c).

In the figure captions the concentration shown are those calculated based on what was added but represent only upper limits since some insoluble material was removed in most cases.

The applied binuclear shift complex of $\text{Yb}(\text{hfc})_3$ and $\text{Ag}(\text{ttb})$ caused not only the shift and spectral dispersion of complete spectrum to downfield but also the partially enantiomeric resolution of resonances H10, H10'. The resonances of H9, H7', H8, H8' and H6 were resolved as well (Fig. 1).

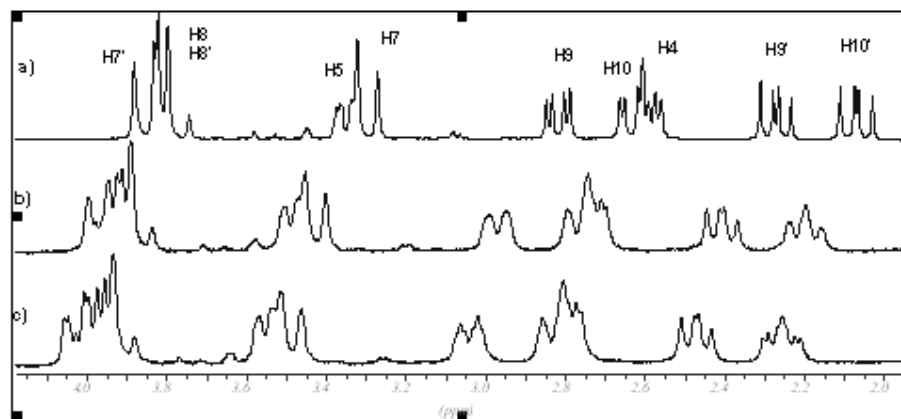


Figure 1: ^1H -NMR Spectra of 0,08 M E1 in CDCl_3 with a) no binuclear shift reagent, b) 0,02 M $\text{Yb}(\text{hfc})_3$ /0,02 M $\text{Ag}(\text{ttb})$ and c) 0,03 M $\text{Yb}(\text{hfc})_3$ /0,03 M $\text{Ag}(\text{ttb})$

In shifted spectra, the large geminal coupling constants have been defined, and the magnitude depends upon the H-C-H angle [2 - 4].

By adding Yb(hfc)₃/Ag(ttb), proton H7' of two enantiomers become chemically non-equivalent and splitted into two signals on ¹H spectrum. One proton H7' of one enantiomer appears at chemical shift of 4.035 ppm while this proton of the opposite enantiomer appeared at chemical shift of 4.025 ppm. Therefore, the difference of resulting Lanthanide Induced Shifts (LIS) of two enantiomers is 0.010 ppm. From this enantiomeric resolution, the coupling constant of H7 to H7' in each enantiomer can be defined ca. 15.0 Hz. The similar analysis was carried out for the enantiotopic protons H9 and H10' and the results were shown in Tab.1.

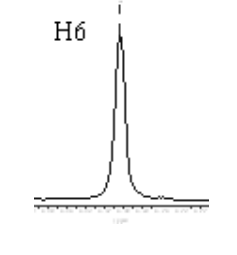
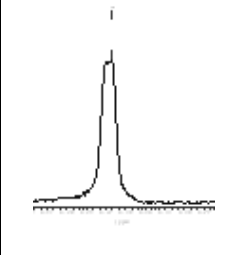
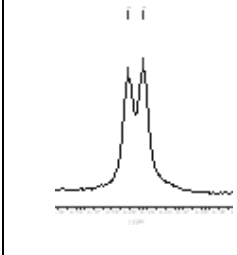
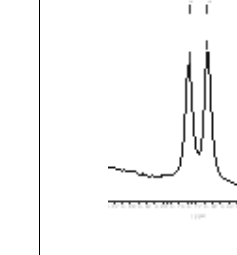
The most interesting is that this silver-compound causing the enantiomeric resolution of H6 resonance even at room temperature (RT). While the combination of Yb(hfc)₃/Ag(fod) brings the enantiomeric resolution of H6 only at lower temperature.

The resolution of H6 resonance is higher by adding more binuclear Yb(hfc)₃/Ag(ttb) complex into the measured solution. At RT, the H6 resonance appears as singlet when the concentration ratio of Yb(hfc)₃/Ag(ttb) is as 0.01 M/0.01M. But it becomes a broad singlet like a coalescence by the ratio of 0,02 M/0.02 M and as two separate singlets by 0.03 M/0.03 M. The distance between those two singlets is largest when the concentration ratio of Yb(hfc)₃/Ag(ttb) reaches 0.1 M/0.1 M, but the resulting NMR signals become more broaden (Fig. 2).

These results show that the sulphur atom may have strong effect on the protons at other site of cyclopentadienyl ring of E1 molecule. This sulfur atom in the ligand (ttb) posses free electron pairs, which may play an important role in the ability to alter the NMR spectra of olefins and aromatics. The different geometry of complex, in which silver ion bonded differently to the double bond of each enantiomer, brings the resolution in NMR spectra.

Table 1: Lanthanide induced shifts in the spectra of 0.08 M E1 with different concentration ratios of binuclear Lanthanide/Silver complex Yb(hfc)₃/Ag(ttb)

Proton	no LSR	0.02 M/0.02 M	$\Delta\delta$ (ppm)	0,03 M/0,03 M	$\Delta\delta$ (ppm)	Enantiomeric resolution
H4	2.59	2.72	0.13	2.79	0.2	
H5	3.35	3.49	0.14	3.55	0.2	
H6	6.30	6.41	0.11	6.47	0.17	
H7	3.3	3.43	0.13	3.48	0.18	
H7'	3.86	3.96	0.1	4.03	0.17	H7'(a) 4.035 ppm (² J _{H7(a)-H7'(a)} = -15Hz) H7'(b) 4.025 ppm (² J _{H7(b)-H7'(b)} = -15Hz)
H8/H8'	3.81	3.9	0.09	3.94	0.13	
H9	2.82	2.97	0.15	3.05	0.23	H9(a) 3.035 ppm (² J _{H9(a)-H9'(a)} = -13.5Hz)
H9'	2.27	2.41	0.14	2.48	0.21	H9(b) 3.055 ppm (² J _{H9(a)-H9'(a)} = -13.5Hz)
H10	2.64	2.78	0.14	2.84	0.2	H10'(a) 2.24 ppm (² J _{H10(a)-H10'(a)} = -13.4Hz)
H10'	2.07	2.2	0.13	2.26	0.19	H10'(b) 2.28 ppm (² J _{H10(b)-H10'(b)} = -13.4Hz)

			
Yb(hfc) ₃ /Ag(tt) 0,01 M/0,01 M one Singlet ($\delta = 6,3057$ ppm)	Yb(hfc) ₃ /Ag(tt) 0,02 M/0,02 M Pseudosinglet (coalescens) ($\delta = 6,4111$ ppm)	Yb(hfc) ₃ /Ag(tt) 0,03 M/0,03 M Two Singlets $\delta_1 = 6,4816$ ppm $\delta_2 = 6,4651$ ppm ($\Delta\delta\delta = 0,0165$ ppm)	Yb(hfc) ₃ /Ag(tt) 0,1 M/0,1 M Two separate Singlets $\delta_1 = 6,7363$ ppm $\delta_2 = 6,6914$ ppm ($\Delta\delta\delta = 0,0449$ ppm)*

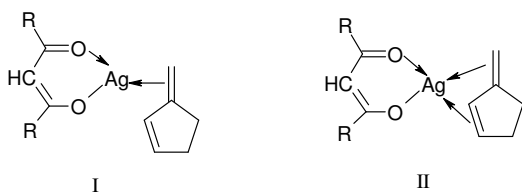
* δ : chemical shift of the ¹H-NMR signal.

$\Delta\delta$: lanthanide induced shift of the ¹H-NMR signals of 1 enantiomer.

$\Delta\delta\delta$: lanthanide induced shift of one ¹H-NMR signals of 2 enantiomer.

Figure 2: Resolution of H6-resonance causing by different concentration ratios of Yb(hfc)₃/Ag(tt) complexes

There are two possible ways, by which the silver can bind to the double bonds of E1-olefin as shown in scheme 1:



Scheme 1: Bonding possibilities of the double-bond in E1-olefin to the silver β -diketonate cation

The Cyclopentadienyl derivative E1 can bind to silver ion through the terminal (exo-) double bond (I) or through both endo- and exo double bonds in the molecule (II).

By the first bonding possibility, free electron pairs of the sulphur atom have electrostatic field effect on the bonding orbital of protons in E1 molecule. Meanwhile, shift induced center of ytterbium causes the change of magnetic field, which lead to the changing in chemical shifts of protons H7, H7', H8, H8' It can be illustrated in Fig. 3.

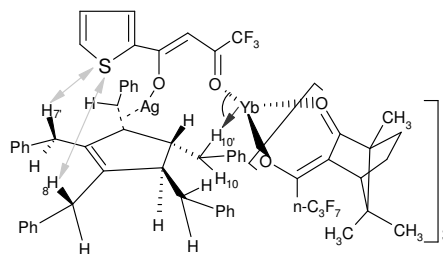


Figure 3: Bonding possibility I, by which the silver atom binds to exo-cyclopenten ring double bond

By the second bonding possibility, the interaction of silver ion to the endo-double bond is very weak (Fig. 4).

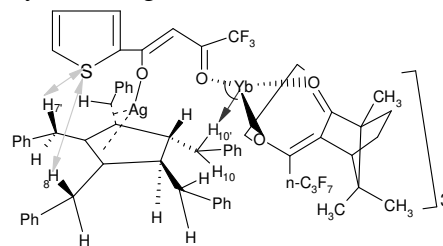
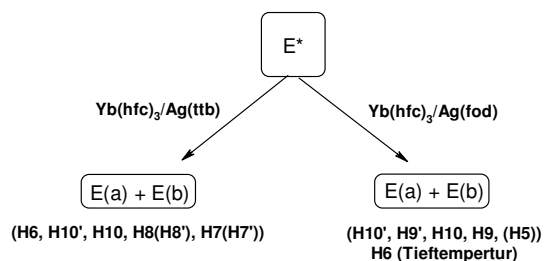


Figure 4: Bonding possibility II, by which the silver atom binds to both endo- and exo- double bonds of cyclopenten ring of E1 molecule

In addition, the silver ion bonding to the terminal double bond of cyclopenten ring leads to larger staying possibilities of H6 resonance in different chemical shift at RT, and the NMR-spectroscopy can record the resolved resonances of H6. Therefore, the first bonding possibility of silver to E1 molecule is more prefer to that of second one.

The distance from lanthanide ion to the olefin in binuclear lanthanide / silver complex is much larger than that of Nitrogen- and Oxygen-containing compounds bonding direct to the LSR. When this distance is reduced, the NMR spectral dispersion and enantiomeric resolution of weak Lewis –base olefin can be found. Although the interaction mechanisms of lanthanide shift reagents to silver species are still unclear, our results have shown that we can use Ag(ttb) and Ag(fod) for the purpose of enantiomeric resolution in NMR-spectra of olefin E1 as showing in Scheme 1.



Scheme 2: Partially enantiomeric resolution in NMR-spectra of E1-compound by the binuclear shift reagent with two different silver auxiliary complexes

These silver compounds are both silver β -diketonate [1 - 12], which associate easily with lanthanide shift reagents and the distance between lanthanide ion and olefin consequently is available [1-8].

The forming complex of 3 components should be stable in the solution. The longer life time of the complex, the larger possibilities it can be detected by NMR spectrometer on its time scale and the more different (if yes) in the geometry of enantiomer complexes can be found out.

VI - CONCLUSION

The $^1\text{H-NMR}$ spectra of chiral olefin E1 have been studied in CDCl_3 solution in the presence of chiral LSR $\text{Yb}(\text{hfc})_3$ and silver β -diketonates Ag(ttb). By changing the ratio of $\text{Yb}(\text{hfc})_3$ and Ag(ttb), a series of resolved spectra of E1 was obtained, the results dedicated that combination of $\text{Yb}(\text{hfc})_3$ and Ag(ttb) is useful for the purpose of enantiomeric resolution in NMR spectra of a chiral olefin.

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