

## ASYMMETRIC REACTIONS. XLVII.\*

## NMR-SHIFT DIFFERENCES OF ENANTIOTOPIC PROTON SIGNALS IN SOME ALKYLARYLMETHANOLS INDUCED BY TRIS[3-TRIFLUOROACETYL-(+)-CAMPHORATO]EUROPIUM(III)

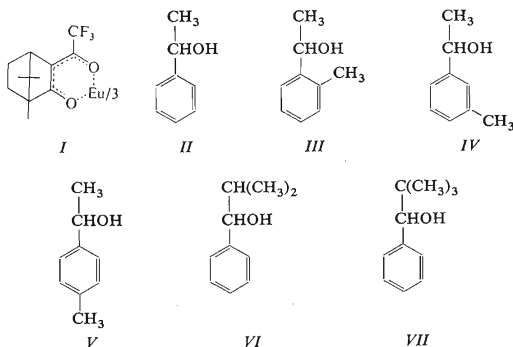
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The use of NMR spectroscopy for determination of optical purity and absolute configuration of alkylarylmethanols with the help of chiral complex of europium is described.

Tris[3-trifluoroacetyl-(+)-camphorato]europium(III) (I) is reported to show high efficiency in direct determining the enantiomeric compositions using  $^1\text{H}$  NMR spectroscopy<sup>1-3</sup>. We have tested the utility of this method on a series of partially optically active alkylarylmethanols II-VII.



According to measurements of Goering and coworkers<sup>1</sup> the enantiotopic  $\alpha$ -H signals of 1-phenylethanol (II) can be resolved up to 0.30 p.p.m. supposed that the

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molar ratio  $[I]/[II]$  is higher than 0.6. The determination of optical purity in the region of high molar ratios mentioned above is accompanied by difficulties arising from the line broadening caused by too high concentration of paramagnetic ions in the sample.

We have found, that a sufficient resolution of the  $\alpha$ -H signals ( $\sim 0.1$  p.p.m.) may be obtained at an approximative molar ratio  $[I]/[II] = 0.18$  if the spin decoupling technique for cancelling the interactions of neighbouring protons is used. The  $\alpha$ -H signals are then observed as two singlets (Fig. 1). Under these conditions

TABLE I  
Optical Purities of Alkylarylmethanols II—VII

Compound	$[\alpha]_D^{20}$	Molar ratio	$\Delta\delta$ p.p.m.	Optical purity, %	
				found	known
II	+18.70°	0.19	0.12	41	44 (ref. <sup>5</sup> )
III	+10.30°	0.18	0.08	14	—
IV	+ 7.24°	0.20	0.12	14	—
V	+12.45°	0.19	0.07	26	—
VI	+ 0.90°	0.21	0.16	4.8	3.4 (ref. <sup>6</sup> )
VII	- 0.79°	0.13	0.09	4	2 (ref. <sup>6</sup> )

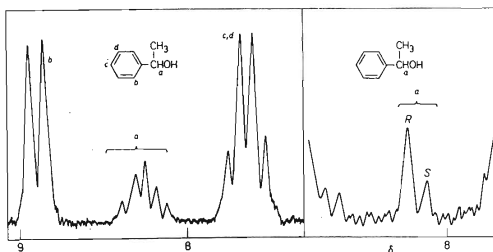


FIG. 1

Part of the NMR Spectrum of Partially Optically Active II in the Presence of I

‡ Molar ratio  $[I]/[II] = 0.19$ . The spectrum on the right side was obtained when protons of the methyl group had been decoupled.

a single measurement may be realized upon using less than 20 mg of *I*. It was convenient to choose the molar ratio within the scope 0.175 and 0.250 where  $\alpha$ -H signals are not overlapped by the signals belonging to the phenyl group (Fig. 2).

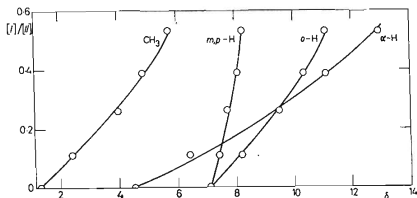


FIG. 2

The Shifts of  $^1\text{H}$  Signals of *II* Induced by Various Molar Concentrations of *I*

The results are summarized in Table I. In all the cases studied we have found the  $\alpha$ -H signal of *R* enantiomer at lower field. This interesting result conforms with the observations of Whitesides and Lewis<sup>4</sup> who noted that *R* enantiomer of 1-phenylethylamin preferentially coordinates to tris[3-(tert-butylhydroxymethylene)-(+)-camphorato]europium(III). It is worth emphasizing that this correlation might be found useful in determining the absolute configuration in some special cases.

The chelate *I* was prepared and purified according to the both procedures described in literature<sup>1,3</sup>. The samples of partially resolved optically active alcohols were obtained by asymmetric reductions<sup>5</sup>. NMR measurements were carried out using Varian XL-100 spectrometer. Tetrachloromethane was used as a solvent and tetramethylsilane as an internal standard.

#### REFERENCES

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