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CHIRAL RECOGNITION OF ALKENE AND ARENE HYDROCARBONS BY ^{1}H AND ^{13}C NMR. DETERMINATION OF ENANTIOMERIC PURITY[1]

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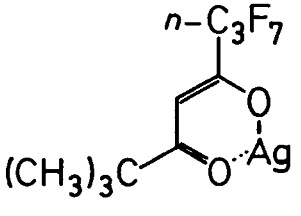
Simultaneous presence of the silver salt 1 and one of the lanthanide complexes (+)-2, (+)-3, or (+)-4 splits ^{1}H or ^{13}C NMR signals of the chiral alkenes 5, 6, and 8 as well as of the chiral arene 7; the enantiomeric purity of a mixture of (+)- and (-)-8 was determined successfully.

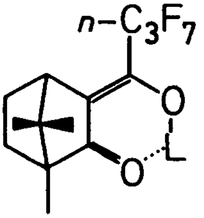
NMR in the presence of optically active auxiliary compounds has contributed to stereochemistry mainly by differentiation between chiral and achiral substrates, determination of enantiomeric purity and relative configuration[4] and by measurement of rates[3] of intramolecular processes. The required signal splittings are effected by chiral association complexes betweeen substrate and auxiliary. The interactions are of the following types: Hydrogen bonding, coordination to a lanthanide complex, cation-anion attraction[2], and electron-donor-acceptor interaction[5]. *Hydrocarbons* are insensitive[6] to these mechanisms and have therefore not been amenable substrates for the above stereochemical investigations. We report here the first signal splittings of some chiral alkenes and arenes, generated by optically active additives.

Auxiliary compounds used. To this end we have utilized Sievers' silver(I) compound 1 which, in an equilibrium, forms complexes with alkenes or arenes in solution[7,8], association and dissociation being fast on the NMR time scale[9].



1

	L
(+)-2	Yb/3
(+)-3	Eu/3
(+)-4	Pr/3



Thereby, silver shifts the substrate signals, always to lower field in ^{1}H NMR[10], but carbon shifts are variable[11]. These silver induced shifts multiply upon addition of lanthanide complexes[7,8,12,13], although lanthanides alone apparently do not interact with alkenes[12,14]. The chiral recognition (*vide infra*) was achieved by mixtures of 1 and one of the lanthanide *D*-camphorates (+)-2, (+)-3, or (+)-4. The achiral silver compound 1 was chosen because it is more readily available than optically active alternatives[15]. In spite of the resulting "dilution" of the optically active environment around the substrate molecule in the association complexes, we observed significant signal splittings.

Signal splittings by 1 and an optically active additive. The signs of our values in Fig.1 represent absolute assignments of the signals to the enantiomers and were determined by studying non-racemic mixtures. ^{1}H signal splittings of α-pinene (5) (Fig.1a) could be clearly seen despite broadening due to the additives and, in some cases, spin-spin interactions. Such phenomena obscure any additional signal splittings for the protons of 5 which are not shown in Fig.1a. The value of $\bar{\delta}_{(-)} - \bar{\delta}_{(+)} = +0.48$ ppm for the alkene proton on C-2, generated by 1 and the europium complex (+)-3, is noteworthy. However, this value is higher ($\bar{\delta}_{(-)} - \bar{\delta}_{(+)} = +1.03$ ppm) in the presence of only 0.48 equivalents of 1 and 1.78 equivalents of the *ytterbium* complex (+)-2. The superiority of ytterbium over europium in this regard seems to be general and parallels its greater shifting power[8]. In our ^{1}H NMR studies, a series of four to ten spectra with increasing reagent-to-substrate ratios had to be recorded for each substrate in order to distinguish reagent from substrate signals and to assign the latter. In this fashion, the resonances of (+)- and (−)-H_Z on C-9 in limonene (6) could be separated by as much as 1.63 ppm (Fig.1c), while the (+)- and (−)-H_E signal remained unsplit[16]. A comparison of Fig.1c with the results for 3,4,5,6-tetramethylphenanthrene[17] (7) (Fig.1d) and similar compounds indicates that the splittings $|\bar{\delta}_{(-)} - \bar{\delta}_{(+)}|$ for such arenes are much smaller than for alkenes. They also show that 7 is chiral and does not enantiomerize rapidly ($\Delta G^{\ddagger} > 68$ kJ/mol, +25 °C), as expected from the investigation[18] of another 4,5-dimethylphenanthrene.

In ^{13}C{^{1}H} NMR spin-spin coupling does not interfere. The splittings observed for the enantiomers of 5 (Fig.1a) are relatively small, perhaps due to the high substrate concentration (hence low reagent-to-substrate ratio) required by the low ^{13}C receptivity. The ^{13}C and ^{1}H splittings (Fig.1a) of α-pinene (5) suggest preferential association at the least hindered face of the C=C bond, i.e. at the "upper" face (see formula) in 5. In camphene (8) only C-2 is split by 1 and (+)-4 (Fig.1b).

The optical purity of a sample of 8 is $P_o = 0.22 \pm 0.01$ according to polarimetry[19]. The ^{1}H signals of =CH$_E$H$_Z$ were both split (Fig.1b), albeit not completely base-line resolved. From the relative intensities we calculate P = 0.21.

Future possibilities. Further experiments will test different combinations and concentrations of auxiliary compounds. Although we have demonstrated the versatility of this method, the scope of substrates will be expanded, to inclu-

(−)-(4*S*,6*S*)-5

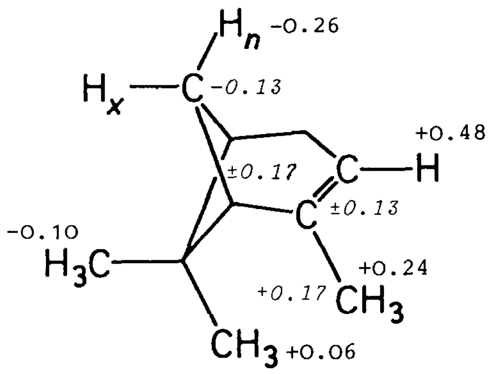


Fig.1a.

^{1}H. Ca. 0.1M α-pinene (5); (−)-5/(+)-5 = 1.5; 1/5 = 0.90 (H$_n$: 0.16); (+)-3/5 = 2.18 (H$_n$: 0.70).

^{13}C, 7700 scans. Ca. 0.64M 5; (−)-5/(+)-5 = 1.64; 1/5 = 0.07; (+)-2/5 = 0.25. All other splittings <0.15.

(+)-(1*R*,4*S*)-8

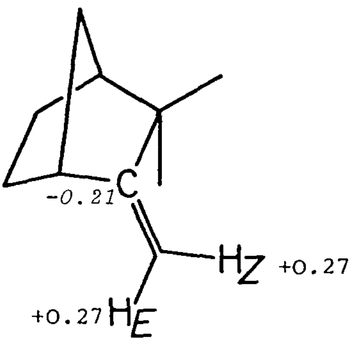


Fig.1b.

^{1}H, 200 scans. Ca. 0.12M camphene (8); (−)-8/(+)-8 see text; 1/8 = 0.40; (+)-2/8 = 0.51.

^{13}C, 14000 scans. Ca. 1.5M 8; (−)-8/(+)-8 see text; 1/8 = 0.11; (+)-4/8 = 0.10. All other splittings <0.25.

(+)-(*R*)-6

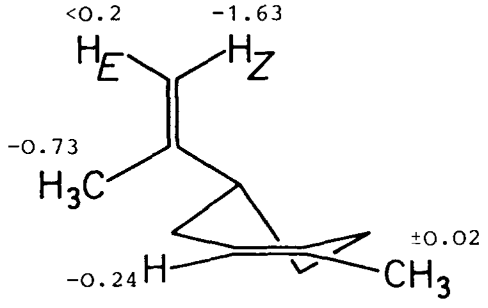


Fig.1c.

^{1}H, 1300 scans. Ca.0.02M limonene[16] (6); (−)-6/(+)-6 = 1.1; 1/6 = 1.85; (+)-2/6 = 3.91.

(−)-(*M*)-7

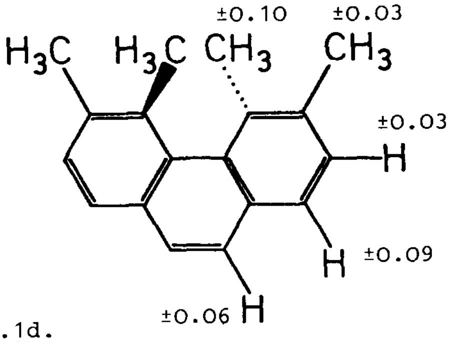


Fig.1d.

^{1}H, 1200 scans. Ca. 0.02M (*MP*)-3,4,5,6-tetramethylphenanthrene (7); 1/7 = 6.1; (+)-2/7 = 7.7.

Fig.1. Splittings $\delta_{(-)} - \delta_{(+)}$ in ppm generated by 1 and a lanthanide complex ((+)-2, (+)-3, or (+)-4) in CDCl$_3$. A positive sign means that the signal of the (+)-enantiomer resonates at higher field. ^{1}H at 60 MHz (CW) and 33°C or at 90 MHz (PFT) and 25°C; ^{13}C at 22.64 MHz and 35°C.

de molecules such as substituted butadienes20) which form thermally *interconvertible* enantiomers. Since it has been shown that alkynes8), phosphines7), and some alkylhalides8) exhibit shifts induced by silver/lanthanide complexes, it will be worthwhile to study chiral recognition for these classes of compounds as well as others which do not interact sufficiently with lanthanide complexes alone.

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