Lanthanide Shift Reagents for Alkenes

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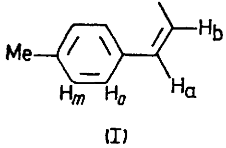
Summary Equimolar mixtures of Ln(fod)$_3$ (fod = $C_3F_7COCHCOCMe_3$) and $C_3F_7CO_2Ag$ act as shift reagents for alkenes in CCl_4 or $CDCl_3$ solution.

Lanthanide shift reagents[1] cannot be used directly to simplify the n.m.r. spectra of molecules in which a carbon–carbon double bond is the only function.[2] However, possible systems for this purpose are of the type $\geqslant$M-X $\cdots$ R, where M is a transition metal such as Ag, Pd, or Rh which can complex alkenes, and X is a group which can co-ordinate to the shift reagent R. We present results obtained using CF_3CO_2Ag or $C_3F_7CO_2Ag$ as the transition-metal complex. Typically, for mono- or di-substituted alkenes, equimolar amounts of $C_3F_7CO_2Ag$ and Ln([$^2H_9$]-fod)$_3$ were shaken in an n.m.r. tube with 1·5—2·0 equiv. of alkene in CCl_4 or $CDCl_3$ solution until all the silver salt had dissolved. With a trisubstituted alkene (α-pinene), *ca.* 4 equiv. of substrate were required, with a corresponding reduction in the induced shifts. As usual, Eu([$^2H_9$]fod)$_3$ and Pr([$^2H_9$]fod)$_3$ caused shifts to low- and to high-field respectively. Yb([$^2H_9$]fod)$_3$ usually, but not invariably, gave rise to low-field shifts, and seems less useful than the other two reagents.



(I)

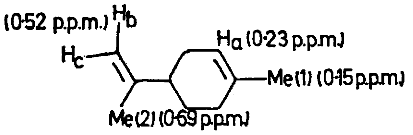
Table

Induced shifts (p.p.m.) for 4-methylstyrene (I) with lanthanide shift reagents in CCl_4 solution.

Shift reagent[a]	H_a	H_b	H_c	H_o	H_m	Me
(A)	+1·29	+1·66	+1·61	+0·90	+0·42	+0·23
(B)	−0·97	−0·75	−0·86	−0·54	−0·27	−0·15
(C)	−1·40	−1·09	−0·70	−1·07	−0·61	−0·40

[a] (A): 0·200 M $C_3F_7CO_2Ag$, 0·175 M Pr([$^2H_9$]fod)$_3$, 0·400 M substrate; (B): 0·200 M $C_3F_7CO_2Ag$, 0·200 M Eu([$^2H_9$]fod)$_3$, 0·400 M substrate; (C): 0·200 M $C_3F_7CO_2Ag$, 0·203 M Yb([$^2H_9$]fod)$_3$, 0·400M substrate.

The induced shifts obtained for 4-methylstyrene (I) with the three shift reagents are given in the Table. In the absence of Ln([$^2H_9$]fod)$_3$, only very small shifts were observed ($\leqslant$ 0·07 p.p.m. at an alkene : Ag$^+$ ratio of 4 : 1), and more alkene was needed to dissolve the silver salt. With limonene (II), the observed shifts {0·10 M $C_3F_7CO_2Ag$, 0·10 M Eu([$^2H_9$]fod)$_3$, 0·2 M limonene in CCl_4} indicate that Ag$^+$ co-ordinates preferentially to the terminal double bond. This was confirmed by using Gd([$^2H_9$]fod)$_3$ as a 'relaxation' reagent,[3] when much more extensive broadening was observed for the Me(2) resonance than for the Me(1) resonance. This preference of Ag$^+$ for the less highly substituted double bond is consistent with the results obtained by Muhs and Weiss[4] for complexation of Ag$^+$ with a wide variety of alkenes in ethanediol solution.



(II)

The induced shifts for alkenes, although useful, are clearly considerably smaller than those normally observed with other substrates.[1] This is presumably due to the appreciable Ag$^+$–Ln^{3+} distance (the two ions are separated by three atoms). More effective shift reagents for alkenes might be found with suitable hydroxy-complexes of other transition metals such as rhodium.

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