Tetrahedron Letters, Vol.22, No.44, pp 4359 - 4362, 1981
Printed in Great Britain

0040-4039/81/444359-04$02.00/0

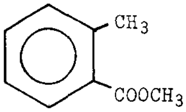
A NOVEL METHOD FOR CORRELATION OF SUBSTITUENT CONSTANTS IN SOME AROMATIC ESTERS USING THE SHIFT REAGENT $Eu(fod)_3$

K.Ranganayakulu, Ranjana Dubey, and K.Rajeswari
Department of Chemistry, Banaras Hindu University
Varanasi-221005, U.P., India

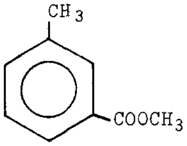
Department of Chemistry, University of Calgary
Calgary, Alberta, T2N 1N4, Canada

Summary: The lanthanide induced chemical shifts of the ester methyl group were studied in eighteen m-, and p-substituted aromatic methyl esters with varying amounts of added shift reagent, $Eu(fod)_3$. *Each time the lanthanide induced shift (LIS) was plotted against the molar ratio of shift reagent (SR)/substrate and a straight line was obtained upto one mole ratio of added shift reagent. The slopes of these plots correlated well with the Hammett's* σ *constants and yield a value of -4.95 for the reaction constant* ρ . *The method is therefore one of the simplest ways of correlating the substituent constants in aromatic esters.*

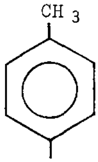
Since the first introduction of shift reagents to nmr spectroscopy[1] a number of articles dealing with the application of shift reagents in resolving structure of organic molecules have appeared in the literature[2]. Recently we have studied the estimation of isomer ratios in some substituted aromatic alcohols, amines, amides and esters using the shift reagent $Eu(fod)_3$[3] . We have noticed during our investigations the ester methyl signals of isomeric methyl toluates (Ia-c) have different chemical shifts in the presence of $Eu(fod)_3$. Fig. I depicts the nmr spectrum of ester methyl signals for a mixture of o-, m-, and p-toluates both in the presence and the absence of $Eu(fod)_3$.



Ia



Ib



Ic COOCH$_3$

Since the distance between the ester methyl protons and the complexing site to the metal ion (structure II) is the same in all the above three esters one expects the lanthanide induced shift to be similar for all the three esters in the absence of any other structural effects. Apparently some other factor(s) is responsible in these systems and this causes the ester methyl signals to have different chemical shifts in the presence of $Eu(fod)_3$. Hence, it is of interest to see whether the complexing ability of an ester is dependent on the nature of the substituent present in the aromatic ring and whether any correlation exists between the extent of the lanthanide induced chemical shifts of ester methyl group and the nature of substituent.

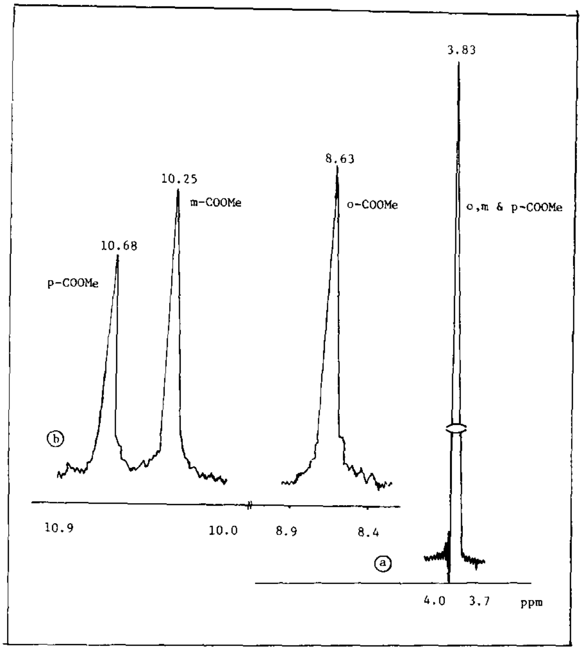
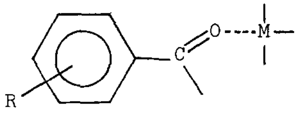
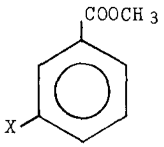


Fig. I NMR SIGNALS OF THE ESTER METHYL GROUPS IN A MIXTURE OF o-, m- & p-TOLUIC ESTERS a) IN THE ABSENCE & b) IN THE PRESENCE OF 0.55 MOLE OF SR

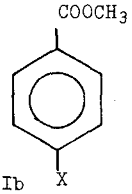


II

For our study we have chosen a series of m- and p-substituted methyl benzoates of the general formula IIIa, b as depicted below:



IIIa



IIIb

X = CH_3-, CH_3O-, NH_2-, Br-, Cl-, H-, NO_2-, -C≡N, -$COOCH_3$.

The lanthanide shift reagent Eu(fod)$_3$ was preferred for our study over the other available shift reagents because, not only is it highly soluble in $CDCl_3$, the solvent used for our nmr spectral measurements, but it is also very suitable for molecules with weak basic sites such as the ester functions. The lanthanide induced chemical shifts of ester methyl signal versus molar ratio of shift reagent to substrate were plotted for the series of esters IIIa, b. In each case a straight line was obtained and their slope values along with the Hammett σ constants are given in Table 1. The slope indicates the lanthanide induced shift of ester methyl group per mole ratio of added shift reagent. As can be seen, the slope is greatest for the ester with the -NH_2 substituent and is least for the ester with the -NO_2 substituent. It appears that the complexing ability of an ester is dependent on the nature of the substituent present in the aromatic ring, and this has the effect of changing the lanthanide induced shift of the ester methyl group. Further, we have plotted the slope values against Hammett σ constants and observed a straight line (Fig. II). The reaction constant ρ was calculated from this plot to be -4.95.

Two factors have emerged from these studies 1) a large reaction constant suggesting the

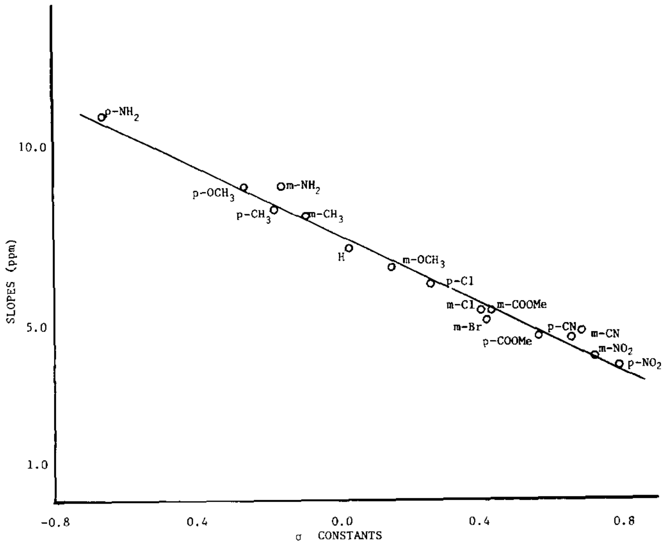


Fig. 11 PLOT OF SLOPES VS σ CONSTANTS

Table 1

Comparison of slopes obtained from lanthanide induced chemical shift of ester methyl group of various meta and para substituted methyl benzoates with Hammett σ Constants

Substituent	Slope = LSR induced shift of ester methyl group (ppm)/mole of SR.		Hammett σ Constants	
	m-	p-	m-	p-
$-NH_2$	9.0[a]	11.0[a]	-0.16	-0.66
$-OCH_3$	6.5	8.8	0.12	-0.27
$-CH_3$	8.0	8.3	-0.07	-0.17
-H	7.1	7.1	0.0	0.0
-Cl	5.4	6.1	+0.37	+0.23
-Br	5.2	6.0	+0.39	+0.23
-CN	5.0	4.8	+0.68	+0.63
$-NO_2$	4.1	3.85	+0.71	+0.78
$-COOCH_3$	5.3[a]	4.8[a]	+0.40	+0.52

a) Values are after making necessary correction for more than one complexing site.

sensitivity of the method compared to other methods 2) a nice correlation of substituent constants with the lanthanide induced shifts of the ester methyl signal in m- and p-substituted aromatic esters.

We investigated the effect of temperature on the lanthanide induced shifts of the ester methyl group to establish the fact that an equilibrium situation is involved between the complexed and the uncomplexed ester function in the presence of shift reagent. The measured ratio (Km) for the complexed-uncomplexed species at each temperature can be calculated using the relationship (eq. I)[4]:

$$Km = \frac{\delta o - \delta u}{\delta c - \delta o} \qquad \ldots \qquad \text{eq. I.}$$

If K_{real} is the real equilibrium constant, then $Km[Eu(fod)_3] = K_{real}$ where $[Eu(fod)_3]$ is the concentration of uncomplexed lanthanide shift reagent. The quantities δu refer to the chemical shift of the uncomplexed ester methyl group, δc to the chemical shift of the fully complexed ester methyl group, and δo to the chemical shift of the ester methyl group at a particular temperature for a certain mole ratio of the shift reagent. From the plots of ln Km Vs. 1/T the -ΔH values for 0.2 mole ratio of shift reagent were obtained for three esters namely methyl p-toluate, methyl benzoate and methyl m-cyanobenzoate and these values are in the expected order, viz. 2.8 kcals., 1.7 kcals., and 1.0 kcals., per mole respectively, indicating a stronger complex formation between $Eu(fod)_3$ and methyl p-toluate relative to the other two. The entropies are -10.8 e.u, -7.8e.u, and -5.0 e.u, for the above three esters, and these are also in the expected order indicating a better complex formation with methyl p-toluate. Other factors like the change in exchange process of substrate with the shift reagent and the paramagnetic effects of the excited state in Eu^{3+} are responsible for the temperature dependence of chemical shifts of the protons in the presence of shift reagent[5]. These effects are common to all the esters under study and any variation must be attributed to the shift in equilibrium depending on the nature of the ester.

We also studied the lanthanide induced chemical shifts of the ester methyl signal in ortho substituted methyl benzoates and found no regular pattern in these series, apparently due to the complicating steric effects.

References

1. C.C.Hinckley, J.Am.Chem.Soc., 91, 5160 (1969).
2. a) B.C.Mayo, Chem.Soc. Reviews, 2, 49 (1973), b) A.F.Cockerill, G.L.O. Davies, R.C. Harden, and D.M.Rackham, Chem. Reviews, 73, 533 (1973), c) J.Briggs, G.H.Frost, F.A.Hart, G.P.Moss, and M.L.Stainforth, Chem.Commun., 749 (1970), d) R.E.Rondeau, and R.E.Sievers, J.Am.Chem. Soc., 93, 1522 (1971).
3. K.Rajeswari, Ranjana Dubey, and K.Ranganayakulu, Indian J.Chem., 17B, 504 (1979)
4. E.Breitmaier and W.Voelter, ^{13}C NMR spectroscopy, Methods and applications, Verlag Chemi., 80 (1974).
5. Yu. Yu. Samitov and Sh.S. Bikeey, Org. Magnetic Resonance, 7, 467 (1975).

(Received in USA 11 February 1981)