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TRANSMISSION OF SUBSTITUENT EFFECTS THROUGH THE UNSATURATED SYSTEM IN RING-SUBSTITUTED α-METHOXYSTYRENES AND RELATED COMPOUNDS

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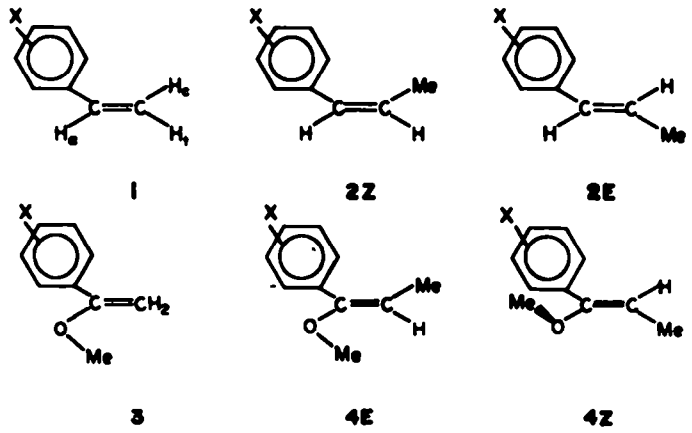
Abstract—A ^{13}C NMR study of the transmission of substituent effects in *m*- and *p*-substituted derivatives of α-MeO-styrene and the E and Z forms of α-MeO-β-Me-styrene has been performed. The C=C bond of vinyl ethers is a considerably weaker transmitter of substituent effects than that of ordinary alkenes, especially if *p*-π conjugation in the vinyloxy system is unhindered. In each series of compounds studied, a fairly good linear correlation exists between the ^{13}C chemical shift of the β carbon and the Hammett σ parameter. The worst linear correlation was obtained for the C-β shifts of α-MeO-styrenes. The shifts concerned, however, were nicely correlated with the Hammett σ° parameter.

A few studies on the transmission of substituent effects through the ring of ring-substituted styrenes (1) to the ethylenic system have been reported, with ^1H NMR[1-3] or ^{13}C NMR[4] spectroscopy as the experimental tools. The ^1H NMR studies have revealed that the polar effects of *m*- and *p*-substituents (X) are nicely transmitted to the β carbon of the ethylenic bond, as judged from good linear correlations between the H_c (and especially, H_t) proton chemical shifts and the Hammett σ parameter (see also Ref. 5). On the other hand, correlation between the α proton chemical shift and σ is less good. The ^{13}C shieldings of the β carbon, but not those of the α carbon, have also been found to be linearly correlated with the Hammett σ values.[4] In addition (and as a consequence of the above facts), good correlations exist between the H_c (and H_t) chemical shifts and the ^{13}C shieldings of the β carbon.

Besides these studies on styrenes with an unsubstituted side chain, a ^{13}C investigation of the transmission of substituent effects in β-Me substituted styrenes (2Z and 2E) has been published.[6] The β carbon ^{13}C chemical shifts were again well linearly correlated with the σ values. The C=C bond of the Z form appeared to be a somewhat less efficient transmitter of substituent effects to the β carbon than that of the E form. This was explained to be caused by some twisting of the aromatic ring in 2Z out of coplanarity with the ethylenic system, leading to reduced overlap between the π orbitals of the adjoining unsaturated moieties.



The present paper describes the results of a ^{13}C NMR study of the transmission of substituent effects in the α-MeO substituted derivatives of 1 and 2 (3 and 4, respectively), compounds that are structurally closely related to the above olefins.

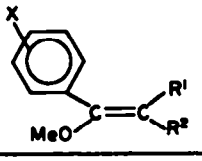
RESULTS AND DISCUSSION

The experimental ^{13}C chemical shifts for some characteristic peaks of the compounds investigated, measured dowfield from internal TMS in $CDCl_3$ solution, are listed in Table 1. Least-squares treatment of the β carbon chemical shifts δ(C-β) against the Hammett σ values[7] gave the following equations:

3: $\delta(C\text{-}\beta) = (3.7 \pm 0.8)\sigma + (81.42 \pm 0.12)$ ppm (correlation coefficient $r = 0.926$).
4E: $\delta(C\text{-}\beta) = (2.6 \pm 0.3)\sigma + (93.94 \pm 0.04)$ ppm ($r = 0.980$).
4Z: $\delta(C\text{-}\beta) = (5.1 \pm 0.7)\sigma + (108.52 \pm 0.12)$ ppm ($r = 0.963$).

The best linear correlation between δ(C-β) and σ was found for 4E, in which the β carbon shift is least sensitive to substituent changes in the aromatic ring

Table 1. ^{13}C chemical shifts (in ppm from internal TMS) for some styrene derivatives in $CDCl_3$ solution

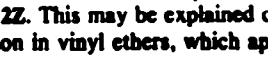


R^1	R^2	X	δ(C-α)	δ(C-β)	δ(MeO)	δ(R^1)	δ(R^2)
H	H	p-MeO	154.13	80.11	55.11		
		p-Me	153.72	80.84	55.11		
		m-Me	153.66	81.54	55.15		
		H	153.72	81.65	55.11		
		p-F	154.96	81.54	55.23		
		p-Cl	155.02	82.06	55.19		
Me	H	p-MeO	155.51	93.18	54.79	12.90	
		p-Me	155.35	93.50	54.79	12.82	
		m-Me	155.75	93.66	54.79	12.82	
		H	155.26	93.91	54.79	12.74	
		p-F	154.95	94.24	55.01	12.86	
		p-Cl	154.37	94.47	54.87	12.82	
H	Me	p-MeO	155.35	106.81	58.11		10.88
		p-Me	155.35	107.79	58.11		10.88
		m-Me	155.51	108.43	58.19		10.88
		H	155.26	108.67	58.19		10.88
		p-F	154.62	108.89	58.35		10.90
		p-Cl	154.37 ?	109.41	58.36		10.96

(from the above equations, the Hammett ρ values are 3.7, 2.6 and 5.1 ppm/σ, respectively, for 3, 4E and 4Z). Generally, linear relationship between δ(C-β) and σ is not as good for the vinyl ethers as for the alkenes and the ρ values are lower for vinyl ethers, as may be seen from the following discussion.

The ^{13}C NMR study of 1 includes the same substituents as used in the present study, with the exclusion of the p-F derivative.[4] However, the ^{13}C shift value given for the β carbon of the p-Me derivative appears anomalous and almost certainly is erroneous. Thus if the shift value of the p-Me derivative is omitted from least-squares treatment of δ(C-β) vs σ, a ρ value of 6.9 ppm/σ and a correlation coefficient of 0.998 are obtained for the β carbon chemical shift relation. For 2Z and 2E, the ρ values are 5.2 and 6.6 ppm/σ and the correlation coefficients 0.992 and 0.991, respectively.[4] The significance of these facts is discussed below.

The ρ values for 3 and 4E are about half as large as those for the corresponding alkenes 1 and 2Z, which shows that the ability of the vinyl ether double bonds in 3 and 4E to transmit substituent effects to the β carbon is only half of that of the "ordinary" C=C bonds in the alkenes 1 and 2Z. This may be explained on the basis of p-π conjugation in vinyl ethers, which apparently leads to a reduced



double bond character of the olefinic linkage and thereby to a weaker transmission ability (single bonds are less effective transmitters of substituent effects than double bonds; see, e.g. Ref. 2 for shift data for substituted styrenes and ethylbenzenes). An interesting comparison is provided by the thermodynamics of isomerization experiments on vinyl ethers, which has shown that the stabilization exerted by alkyl groups on the double bond of vinyl ethers with unhindered conjugation in the vinyloxy system is *ca.* half the stabilization brought about by the same groups on the "ordinary" C=C bond of alkenes,[8,9] which is another indication of the reduced double bond character in vinyl ethers. On the other hand, the ρ value of 5.1 ppm/σ for 4Z is only slightly smaller than that (6.6 ppm/σ) for the corresponding alkene 2E, which shows that p-π conjugation in 4Z is essentially hindered. This means that the MeO group of 4Z assumes mainly the nonplanar gauche configuration, although some contribution from the planar s-*trans* configuration may also be present.[10]

As mentioned above, linear correlations between δ(C-β) and σ are worse for the vinyl ethers than for the alkenes and in the case of vinyl ethers the correlation falls in the sequence 4E > 4Z > 3. MO calculations[11] show that in vinyl ethers conjugation in the vinyloxy moiety leads to excessive positive and negative charges on the O and C-β atoms, respectively, but there is also a small excess of positive charge on the C-α atom, which is directly linked to the phenyl group of the present compounds. Now if there is in the phenyl ring a para substituent which can donate negative charge to the α atom through its resonance effect, negative charge density should increase in the C=C system and accordingly, about the C-β atom, which leads to ^{13}C absorption at higher field. The best conditions for this effect to appear are achieved when the conjugation in the vinyloxy moiety is unhindered and when, moreover, the aromatic ring is coplanar with the ethylenic system. In the present compounds, 3 fulfills these requirement perfectly and the shift values for especially the p-MeO, p-F and p-Cl derivatives, which are electron donators through their resonance effect, are indeed lower than expected from the shifts of the other derivatives. In the vinyloxy system of 4E, conjugation appears to be as unhindered as in 3, but the aromatic ring is tilted out of coplanarity with the olefinic system, probably by 30–35° as in the corresponding alkene 2Z.[12,13] On the other hand, in 4Z p-π conjugation is essentially reduced and therefore the positive charge on the α carbon must be very small, whereby resonance interaction between this charge and the para substituents is negligible. The above reasoning suggests that in cases where linear correlation between δ(C-β) and σ fails, a better correlation might be obtained by representing δ(C-β) as a function of the Hammett σ^+ parameter. Using the σ^+ values given in Ref. 7, the following equations were derived by linear least-squares treatment of δ(C-β) vs σ^+:

3: $\delta(C\text{-}\beta) = (2.15 \pm 0.17)\sigma^+ + (81.69 \pm 0.06)$ ppm (r = 0.988).

4E: $\delta(C\text{-}\beta) = (1.25 \pm 0.37)\sigma^+ + (94.07 \pm 0.13)$ ppm (r = 0.861).

4Z: $\delta(C\text{-}\beta) = (2.76 \pm 0.35)\sigma^+ + (108.85 \pm 0.12)$ ppm (r = 0.969).

The best linear correlation is now obtained for 3, in agreement with the discussion given above.

The β carbon chemical shifts of the Z isomer (4Z) are 13–15 ppm higher than those of the E form, in line with the corresponding shifts for many α,β-disubstituted vinyl methyl ethers.[10] Moreover, in the Z isomer the carbon of the β Me group absorbs *ca.* 2 ppm upfield and that of the MeO group *ca.* 4 ppm downfield from the corresponding carbons of the E form.

EXPERIMENTAL

The preparation of the derivatives of 4E and 4Z has been described previously.[14] The derivatives of 3 were prepared analogously. The following boiling points were observed. X = *p*-MeO, 403 K/2.0 kPa; X = *p*-Me, 377–378 K/2.4 kPa; X = *m*-Me, 376 K/2.0 kPa; X = H, 357 K/1.6 kPa; X = *p*-F, 339–340 K/0.8 kPa and X = *p*-Cl, 372 K/0.9 kPa.

The ^{13}C chemical shifts were measured at 15.03 MHz on a Jeol FX 60 spectrometer. The spectra of 4E and 4Z were recorded on mixtures of isomers. Sample concentration was *ca.* 20% (v/v) in $CDCl_3$ and sample temperature *ca.* 300 K. Peak positions were measured relative to internal TMS.

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