The Determination of Inductive Effects by ^{13}C Nuclear Magnetic Resonance Spectrometry

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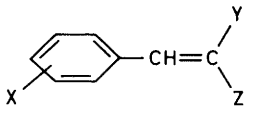
A series of *meta*- and *para*-XCH_2-substituted methyl cinnamates has been prepared and the ^{13}C n.m.r. chemical shifts of the α- and β-side-chain carbons have been determined in ethanol. In the majority of cases the magnitudes of the substituent-induced chemical shifts are directly proportional to the inductive substituent constants of the group X. C–H Hyperconjugation appears to play a significant role in the relay of inductive effects from the substituent to the more distant ethenyl carbon in the *para*-series, but in the other three cases relay appears to be mainly *via* a direct field effect.

In a previous paper [1] the effect of varying *meta*- and *para*-ring substituents on the ^{13}C n.m.r. chemical shifts of the β-carbons of β-substituted styrene derivatives (1) was investigated. It was shown that for varying X, with Y and Z constant, the magnitude of the substituent chemical shift† could be correlated with the electronic effect of the substituent X. The data were satisfactorily interpreted by means of the Hammett equation and there were strong indications that $\rho_{meta} \approx \rho_{para}$. Alternative analysis of data of these types based on Ehrenson, Brownlee, and Taft's dual substituent parameter (DSP) equation [2] appeared to offer no advantage over the simpler Hammett approach.[3]



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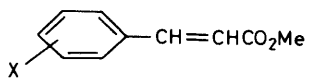

(2)

It was found that if the assumption that $\rho_{meta} = \rho_{para}$ was made, it was possible to vary the apparent degree of resonance interaction between a *para*-substituent and the β-carbon by varying Y and Z. In general, more negative (or less positive) values for σ_{para} were obtained as the total electron-withdrawing power of Y and Z was increased.[1] Unlike the situation observed for Hammett correlations of reactivity data, however, there appeared to be no tendency towards a series of 'discrete' σ_{para} values. The system therefore seemed well suited for the study of resonance effects in aromatic systems.

The major disadvantage is that while changes in σ_{para} can be easily measured, σ_{para} does not represent the operation of a pure resonance effect; there is also an inductive contribution involved. It is possible to eliminate this difficulty by considering instead ($\sigma_{para} - \sigma_{meta}$) values, but it would be much better if it were possible to measure the inductive effect (σ_I) by an independent method and to make an allowance for it.

There have been a number of attempts to obtain quantitative measures of inductive effects, and to place them on the same scale as Hammett σ values. The most widely accepted set of values at present is that of Ehrenson *et al.*,[2] which appears to be derived from data for a number of reactions previously studied, together with a spectroscopic investigation of the ^{19}F chemical shifts of *meta*-substituted fluorobenzenes. This scale, however, is intended primarily for use in aqueous or aqueous organic solvents. The majority of styrene derivatives have only a limited solubility in these, and there is no guarantee that inductive effects are solvent independent. Indeed, a solvent dependence study on the styrenes has shown that they are not.[4] What is needed is a quick way of determining σ_I values that could be applied in non-polar solvents.

A spectroscopic method appeared the most likely to fulfil these conditions. The ^{19}F chemical shift data reported by Taft and his co-workers [5] are not suitable, as close examination reveals that factors other than the inductive effect of substituents are almost certainly contributing to the overall shifts.

As a possible alternative approach we decided to look at the effect of *meta*- and *para*-XCH_2-substituents on the ^{13}C n.m.r. chemical shifts of a styrene derivative.

We were fully aware that in such systems resonance effects were not absent, C–H hyperconjugations between the $-CH_2-$ group and the aromatic nucleus being possible, but hoped that the effect of this on the overall chemical shifts might either be constant or prove proportional to the inductive effects of the substituents involved.

The system chosen for investigation was the *m*- and *p*-XCH_2-substituted β-methoxycarbonylstyrenes (2).‡ The success or failure of the approach should be independent of the nature of any substituent(s) on the β-carbon, and the choice of a single methoxycarbonyl group was based on convenience. The compounds are readily prepared and purified, and, with only a few exceptions, are stable crystalline solids. In addition, the chemical shifts for the carbon adjacent to the methoxycarbonyl group differ sufficiently from those of the other sp^2 carbons for ready identification.

In the course of obtaining the data for the C_β shifts, those for the α-carbons also became available. Brownlee and his co-workers have reported that ^{13}C n.m.r. chemical shifts for carbons of these types are also influenced by the electronic effect of substituents.[6] Analysis of their C_α data using the dual substitution parameter equation of Ehrenson *et al.*[2] led to negative values for ρ_I and ρ_R and these were interpreted in terms of a localized polarisation of the side-chain arising from the direct field effect of the substituent. The explanation is not entirely satisfactory since, while it adequately accounts for the negative values obtained for ρ_I, it does not explain why ρ_R

† The substituent chemical shift (SCS) of a particular carbon is defined as the difference in chemical shift between the substituted and non-substituted derivative.

‡ Because of possible confusion as to which is the α- and which is the β-carbon of the side chain the term β-methoxycarbonylstyrenes will be used instead of the more common methyl cinnamates.

Table 1. Positions of C_β and C_α resonances for *meta*- and *para*-XCH_2- and *meta*-X-substituted β-methoxycarbonylstyrenes in ethanol [a]

	SCS-C_β			SCS-C_α		
X	*m*-X	*m*-XCH_2	*p*-XCH_2	*m*-X	*m*-XCH_2	*p*-XCH_2
H	118.22	117.95	117.09	145.85	146.08	145.91
Me	−0.27	−0.03	0.05	0.23	0.02	0.04
NMe_2	−0.83	0.57	1.05	1.33	−0.46	−0.47
OMe	0.19	0.51	0.99	−0.01	−0.39	−0.42
OPh	0.88	0.62	1.13	−0.77	−0.45	−0.29
F	1.65	0.95	1.67	−1.55	−0.76	−0.72
Cl	1.71	0.95	1.68	−1.86	−0.88	−0.84
Br	1.72	0.96	1.72	−1.86	−0.95	−0.89
I	1.52	0.83		−1.89	−0.81	
CF_3	2.30			−1.95		
CN	2.91	1.27	1.77	−2.72	−1.13	−1.02
NO_2	3.36	1.49	2.57	−2.77	−1.25	−1.19

[a] The positions are given in the form of substituent chemical shifts (see text) except for X = H, for which values are given in p.p.m. downfield of tetramethylsilane.

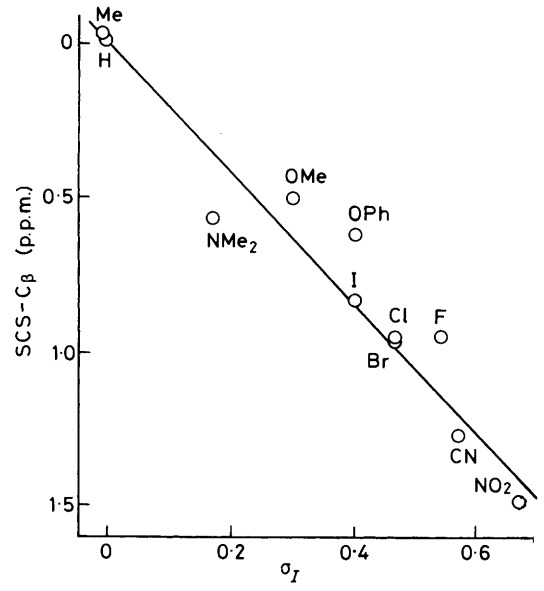

Figure 1. Graph of SCS for C_β of *meta*-XCH_2-substituted β-methoxycarbonylstyrenes against σ_I

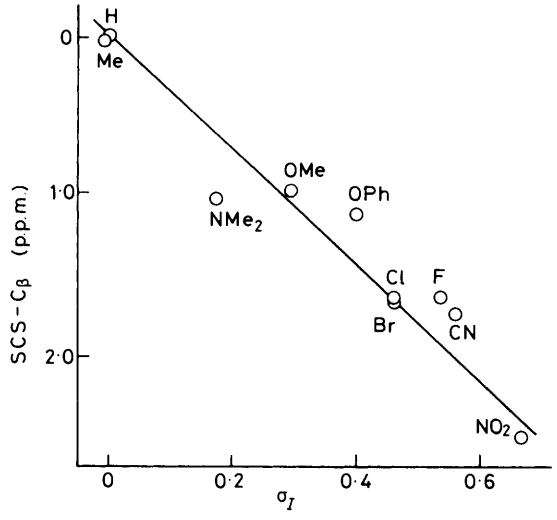

Figure 2. Graph of SCS for C_β of *para*-XCH_2-substituted β-methoxycarbonylstyrenes against σ_I

(the sensitivity of the substituent chemical shifts to resonance effects) should also be negative. The explanation advanced by Brownlee to account for negative values for ρ_R in side-chains containing a carbonyl group is not valid for ethenyl side-chains.

However, since ρ_R is usually much lower in magnitude than ρ_I, for most substituents the resonance contribution to the overall shift is much less than the inductive one. In our system the interposition of a $-CH_2-$ group between the substituent and the π system should eliminate any possibility of direct resonance interaction between the side-chain and X. We would therefore expect to find that the ^{13}C n.m.r. chemical shifts for C_α, like C_β, should be proportional to the inductive effects of the substituents.

In order to minimise any problems arising from the solvent dependence of inductive effects, the spectra were determined as dilute (0.2M or less) solutions in absolute ethanol. Studies of the styrene system have shown that in this solvent σ values appropriate to aqueous systems should apply.[4]

Results and Discussion

The chemical shift data for C_α and C_β of the XCH_2-substituted β-methoxycarbonylstyrenes are listed in Table 1. They are listed in the form of substituent chemical shifts (SCS), which represent the difference in chemical shift between the substituted and unsubstituted derivatives. Also included for the purposes of comparison are data for the corresponding *meta*-X substituted derivatives. Graphs of the SCS of C_α and C_β for the XCH_2-substituted compounds against σ_I are given in Figures 1—4. We have elected to use Charton's σ_I scale [7] in preference to that of Ehrenson *et al.*[2] because of our uncertainty as to the basis of the latter. While some degree of scatter is to be expected due to measurement errors (ρ_I is rather low in all cases) there are a number of discrepancies that appear to arise from other sources. Substituents that can be considered ' well behaved ' in that their shifts are apparently dominated by inductive effects include H, Me, I, Cl, Br, NO_2, and CN (in three of the four series). In addition, if we examine a correlation of the C_β data for the *meta*-X-substituted series against σ^{meta} (where we would expect to find a good correlation) it will be seen (Figure 5) that for the MeO and PhO substituents, the water-based σ_I values used in Figures 1—4 may be inappropriate for use in ethanol. The use of σ_I values *ca.* 0.05 lower than normal for these would add the MeO group to our list of well behaved substituents over the range of solvents studied and reduce discrepancy for OPh substantially, particularly in so far as the C_β shifts are con-

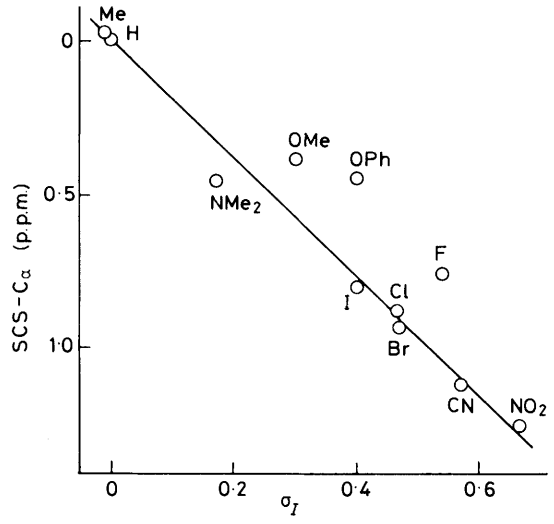

Figure 3. Graph of SCS for C_α of *meta*-XCH_2-substituted β-methoxycarbonylstyrenes against σ_I

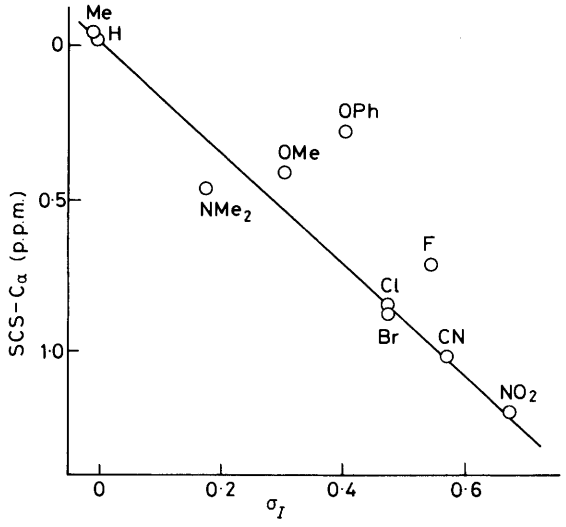

Figure 4. Graph of SCS for C_α of *para*-XCH_2-substituted β-methoxycarbonylstyrenes against σ_I

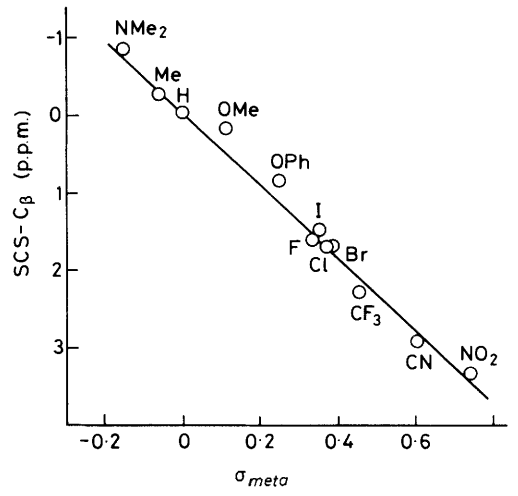

Figure 5. Graph of SCS for C_β of *meta*-X-substituted β-methoxycarbonylstyrenes against σ^{meta}

cerned. Of the remaining substituents, NMe_2 differs from the rest in that the deviations observed are approximately the same in all cases, and are consistent with an apparent σ_I for this substituent of *ca.* +0.27. Such a figure is very high, higher in fact than that observed for the OMe substituent, which we would expect to be more electron-withdrawing of the two. In the *meta*-X series (Figure 5) NMe_2 behaves normally, but in view of the much higher basicity of the $-CH_2NMe_2$ group the comparison may not be a valid one; there are certainly a number of species around capable of interacting with this substituent and increasing its $-I$ effect *e.g.* EtOH, traces of H_2O, CO_2, and the ester group of the compound itself.

This leaves only three substituents, F, OPh, and CN where the observed substituent chemical shifts cannot be adequately accounted for on the basis of the inductive effects of substituents alone, and even in these the inductive effect is the major contributor. Two of them, F and OPh, possess features in common in that discrepancies are significantly greater for C_α than for C_β, and are independent of whether the substituent is *meta* or *para* to the side chain. This is consistent with an effect that discriminates between C_α and C_β mainly on the basis of distance from the substituent and is independent of the nature of the intervening π system, thereby ruling out any type of resonance effect as an explanation. While we are unable to say exactly what factor is involved, it obviously seems very closely related to the inductive effect in so far as its mechanism of transmission is involved, since, like the latter it induces shifts in opposite directions at C_α and C_β. Exactly why it is only significant for these two substituents, which have little else in common, is unknown.

Lastly there is the problem of the apparently anomalous upfield shift of the CN derivative in the *para*-C_β series. It is probably significant that this series is the one where there is greatest potential for resonance interaction between substituent and side-chain. The chemical shift lies nearly 0.5 p.p.m. upfield of its expected position, the direction indicating that it is a stronger electron donor than expected. The possibility of C–C hyperconjugation as an explanation must be considered, but the effect seems too large for this; there is certainly no evidence for abnormal σ values for this substituent in other systems such as benzoic acid [8] or pyridinium ion [9] ionizations. Incidentally, it will be noted that the SCS for the methyl derivative in this particular series lies downfield from that for the parent compound. This behaviour is not easy to explain, but at least is not unexpected, since both in other n.m.r. studies [3] and in reactivity data,[10] it has been observed previously that an ethyl group attached to an aromatic ring can be less electron donating than a methyl. It is likely that resonance effects are involved here also.

Transmission of Inductive Effects.—The efficiency with which the electronic effect of X is relayed to C_α or C_β will depend on the mechanism by which it is relayed. In the case of a direct field effect, the distance between X and the carbon under consideration should be the most important factor although the orientation of the C–X bond can play a significant part. On the other hand, if the effect involves distortion of the σ- or π-electron system, while distance is still important, the effectiveness of transmission should depend to some extent on whether the XCH_2 group is *meta* or *para* to the side-chain.

If we examine the data in Table 1 on this basis, we can see that the substituent chemical shifts for C_α of the *meta*- and *para*-XCH_2-substituted derivatives are relatively independent

Table 2. Hammett σ values for XCH_2-substituents [a]

	Me	NMe_2	OMe	OPh	F	Cl	Br	I	CN	NO_2
σ^{meta}	−0.06	0.07	0.05	0.08	0.15	0.15	0.15	0.12	0.22	0.26
σ^{para}	−0.23	−0.01	−0.03	0.00	0.12	0.12	0.13		0.14	0.31
σ^{meta} [11]	−0.09		0.08	0.11		0.15	0.15	0.13	0.20	0.26
σ^{para} [9]	−0.14		0.01	0.03		0.08	0.09		0.14	0.39 [b]

[a] Calculated σ values are based on ρ 4.706 (see text). Literature values are based on a ρ for ionization of pyridinium ions of 6.01. [b] This figure is abnormally high and was considered by Fischer to be due to tautomerism of the 4-nitromethyl derivative.

of whether the XCH_2 is *meta* or *para* to the side chain. This supports Brownlee's contention [6] that it is the field effect that is responsible for reverse substituent chemical shifts. It also suggests that any affect arising from differing orientations of the C–X bond is only a minor one. A least-squares analysis gives $\rho^{para}/\rho^{meta} = 0.95$, a figure in good agreement with that of 1.14 derived by Exner for the ionization of XCH_2-substituted benzoic acids in aqueous organic solvents,[8] and 1.00 which can be calculated from Fischer's data on the pK_a values of XCH_2-substituted pyridinium ions in aqueous solution.[9,11]

In the case of the C_β shifts, however, there are considerable differences in the efficiencies of transmission from the two positions, least-squares analysis (with CN omitted for correlation purposes) giving $\rho^{para}/\rho^{meta} = 1.69$. It is likely, however, that this apparently high value is misleading, since a dual substituent parameter analysis of C_β data for the closely related *meta*- and *para*-X-substituted β-ethoxycarbonylstyrenes [12] suggests $\rho^{para} \approx \rho^{meta}$, and indeed this seems to be generally the case in systems of this type. This being the case, the enhanced transmission of inductive effects from the *para*-position to the β-carbon of the side-chain cannot represent a π-inductive effect, which would involve merely distortion of the π-system by the field effect of the substituent, but rather a resonance effect, involving a substituent-dependent variation in the extent of hyperconjugative interaction between C_β and the CH_2– group. A similar effect has been observed for the arylazo-substituted β-ethoxycarbonylstyrenes, where a value for ρ^{para}/ρ^{meta} of *ca.* 2 is observed.[12]

Superficially there is no reason why similar apparent enhancements of ρ^{para}/ρ^{meta} should not be found for Exner's and Fischer's data. However in these cases calculated σ^{para} values for the *para*-Me derivatives (−0.14 and −0.16, respectively) are substantially lower than for our system (−0.23) suggesting a much weaker degree of hyperconjugative interaction between the $-CH_2-$ group and the reaction site, and an accordingly lower contribution of resonance to the overall effect.

In another study [13] we have observed that for the ^{19}F n.m.r. chemical shifts of XCH_2-substituted fluorobenzenes ρ^{para}/ρ^{meta} has a value of *ca.* 3.5. It is likely that the origin of this high value is the same as that in the present case.

Hammett σ Constants for XCH_2 *Groups.*—While the primary purpose of obtaining the data in this study was to investigate the inductive effect of substituents, it is possible to use it to determine the electronic effect of XCH_2 groups as substituents. The least-squares line through the data in Figure 5 (omitting the OMe and OPh substituents) has a slope of 4.706 and σ values for the various XCH_2 groups can be calculated from this. The results are summarised in Table 2. Also included in Table 2 are σ values derived from Fischer's data [9,11] for comparison. (These are considered more reliable than those of Exner's because ρ is considerably higher.) Agreement is excellent between the two sets of σ^{meta} values, and would probably be even better if allowance was made for the solvent dependence of σ_I for the OMe and OPh groups. Comparisons of σ^{para} values are more difficult to make since the two series impose considerably different demands on the resonance effects of the CH_2X groups. All our values except that for CH_2CN are considerably more negative than Fischer's.

Finally, comparison of the ρ value for the system with those estimated from Figures 1 and 2 enables us to calculate the attentuating effect of interposing a $-CH_2-$ group between the substituent and the ring. The values obtained are 0.44 and 0.77 for the *meta*- and *para*-series respectively. The latter figure is believed not to represent a true attenuating effect for reasons given earlier, but the first agrees well with Fischer's values of 0.49 and 0.51 and Exner's of 0.47 and 0.58 for the *meta*- and *para*-positions respectively.

Conclusions.—The results of the study show that while the ^{13}C n.m.r. substituent chemical shifts of both C_α and C_β in our series are primarily influenced by the inductive effects of substituents, these in at least some cases are clearly not the only factors involved. For many substituents these factors do not appear to be significant, so that in favourable circumstances measurements on compounds of these types could provide a good way of estimating σ_I values. Unfortunately there appears to be no way of predicting whether a substituent is likely to fall into the ' normal ' or ' abnormal ' class. It is possible that the best way of using the approach as a method of estimating σ_I values would be to examine the effect of solvent on the magnitudes of the shifts and to relate changes in shifts to changes in the magnitude of inductive effects.

Experimental

Preparation of Compounds.—(a) *Methyl* meta-X-*substituted cinnamates.* The methyl esters of cinnamic acid and its *m*-Me, *p*-Me, *m*-OMe, *m*-OPh, *m*-F, *m*-Cl, *m*-Br, *m*-I, *m*-CF_3, *m*-CN, and *m*-NO_2 analogues were prepared by esterification of the appropriate cinnamic acids, which were in turn derived from the corresponding aldehydes by the Knoevenagel method.[14] Methyl *m*-dimethylaminocinnamate was prepared from methyl *m*-aminocinnamate by the method described in Houben-Weyl for ethyl *p*-dimethylaminobenzoate.[15] Only two of the derivatives have not been previously reported: *methyl* 3-*phenoxycinnamate*, oil (Found: M^+, 254.0977. $C_{16}H_{14}O_3$ requires M^+, 254.0943); *methyl* m-*dimethylaminocinnamate*, m.p. 56—58 °C (Found: C, 69.9; H, 7.5. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.4%).

(b) *Methyl* meta- *and* para-XCH_2-*substituted cinnamates.* *Methyl* m-*ethylcinnamate* and *methyl* p-*ethylcinnamate* were prepared from the corresponding aldehydes by the method used for the *meta*-X-substituted derivatives. Both compounds were oils [Found: C, 75.9; H, 7.7 (*meta*-isomer); C, 75.7; H, 7.1 (*para*-isomer). $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%].

Methyl *m*-bromomethylcinnamate. Methyl *m*-methylcinnamate (39 g), *N*-bromosuccinimide (46 g), and dibenzoyl peroxide (5 g) were refluxed in carbon tetrachloride for 90 min. The cooled solution was filtered and the solvent evaporated under reduced pressure. ^1H n.m.r. of the crude product

showed it to contain about equal quantities of the required product and starting material. Neither extending the reaction time nor increasing the molar ratio of *N*-bromosuccinimide improved the yield. The crude product was purified by rapid vacuum distillation and methyl *m*-bromomethylcinnamate was collected as the fraction boiling at *ca.* 160 °C and 0.1 mmHg. Much material was lost by decomposition in the distillation flask. The product was recrystallised from ether to give *crystals* (8.5 g, 15%), m.p. 81—82 °C (Found: C, 51.5; H, 4.7. $C_{11}H_{11}BrO_2$ requires C, 51.8; H, 4.4%).

Methyl *p*-bromomethylcinnamate. The method given above for the *m*-bromomethyl analogue was used. The crude product contained only small amounts of starting material and crystallised on standing. Recrystallisation from ether–light petroleum gave crystals, m.p. 59—60 °C. The overall yield was 41%.

Methyl *m*-chloromethylcinnamate. The *m*-bromomethyl derivative (250 mg) and lithium chloride (330 mg) were stirred in dry Me_2SO (5 ml) for 12 h at room temperature. The Me_2SO solution was poured into water and extracted with chloroform. The extract was evaporated to give methyl *m*-chloromethylcinnamate (180 mg, 87%). Recrystallisation from light petroleum gave *crystals*, m.p. 62—63 °C (Found: C, 62.6; H, 5.3. $C_{11}H_{11}ClO_2$ requires C, 62.7; H, 5.3%).

Methyl *p*-chloromethylcinnamate. This was prepared from methyl *p*-bromomethylcinnamate by the method described above for the *m*-Cl analogue. The product was obtained in 85% yield as *crystals*, m.p. 34 °C (Found: C, 62.8; H, 5.3. $C_{11}H_{11}ClO_2$ requires C, 62.7; H, 5.3%).

Methyl *m*-iodomethylcinnamate. Methyl *m*-bromomethylcinnamate (500 mg) was stirred at room temperature with sodium iodide (1 g) in acetone (10 ml) for 12 h. The solution was then poured into water and extracted with chloroform. The extract was washed with sodium thiosulphate solution and with water, dried, and evaporated. The crude product was further purified by recrystallisation from ether–light petroleum to give cream *crystals*, m.p. 95—96 °C. These darkened rapidly and microanalysis was consistent with some loss of iodine (Found: $M^{+\cdot}$, 301.990. $C_{11}H_{11}IO_2$ requires $M^{+\cdot}$, 301.981).

Methyl *m*-fluoromethylcinnamate. Methyl *m*-bromomethylcinnamate (500 mg) and potassium fluoride (1 g) (dried by heating for 12 h at 200 °C under vacuum) were refluxed together for 7 h in dry *N*-methylpyrrolidone (15 ml). The mixture was cooled, poured into saturated ammonium chloride solution, and the product taken up in ether. The ether solution was dried and evaporated to give a pale yellow oil (370 mg, 84%). Chromatography on Florisil using 5% ether–light petroleum as eluant gave the product as an *oil* (Found: C, 68.0; H, 5.9. $C_{11}H_{11}FO_2$ requires C, 68.0; H, 5.7%).

Methyl *p*-fluoromethylcinnamate. This was prepared in 87% yield from methyl *p*-bromomethylcinnamate by the method above. Recrystallisation from light petroleum gave *crystals*, m.p. 49—50 °C (Found: C, 67.6; H, 6.0. $C_{11}H_{11}FO_2$ requires C, 68.0; H, 5.7%).

Methyl *m*-cyanomethylcinnamate. Methyl *m*-bromomethylcinnamate (250 mg) and sodium cyanide (100 mg) were stirred together in dry Me_2SO for 20 min. The solution was poured into water and the product extracted with chloroform. Evaporation of the chloroform gave a yellow oil (160 mg, 81%) that crystallised on standing. Recrystallisation from ether–light petroleum gave *crystals*, m.p. 73—74 °C (Found: C, 71.5; H, 5.6. $C_{12}H_{11}NO_2$ requires C, 71.6; H, 5.5%).

Methyl *p*-cyanomethylcinnamate. This was obtained in 70% yield from the *p*-bromomethylcinnamate by the above method. Recrystallisation from ether–light petroleum gave cream *crystals*, m.p. 78—79 °C (Found: C, 71.6; H, 5.8. $C_{12}H_{11}NO_2$ requires C, 71.6; H, 5.5%).

Methyl *m*-nitromethylcinnamate. Methyl *m*-bromomethylcinnamate (300 mg) in anhydrous ether (5 ml) was added over 3 h to a stirred slurry of silver nitrate (1 g) and calcium hydride (100 mg) in anhydrous ether. The mixture was stirred for a further 200 h. During the addition and the remainder of the reaction the whole system was kept in the dark at a temperature of *ca.* 3 °C. The mixture was then filtered under suction and the solids washed with more ether. Evaporation of the filtrate and washings gave *crystals* (220 mg, 85%) which on recrystallisation from methanol–water had m.p. 86—87 °C (Found: C, 59.6; H, 5.0. $C_{11}H_{11}NO_4$ requires C, 59.7; H, 5.0%).

Methyl *p*-nitromethylcinnamate. Applying the above method to the *p*-bromomethyl derivative gave the *p*-nitromethyl derivative in 80% yield. The product, on recrystallisation from ether–light petroleum, consisted of *crystals*, m.p. 102 °C (Found: C, 59.8; H, 5.2. $C_{11}H_{11}NO_4$ requires C, 59.7; H, 5.0%).

Methyl *m*-methoxymethylcinnamate. Methyl *m*-bromomethylcinnamate (250 mg) was refluxed in methanol (20 ml) for 45 h. The solution was then concentrated to half its volume, poured into water, and the product taken up into ether. Evaporation of the ether gave a yellow oil (145 mg, 72%). Purification by h.p.l.c. gave an *oil* (Found: C, 69.3; H, 7.1. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%).

Methyl *p*-methoxymethylcinnamate. This was prepared by the above method in 74% yield, as an oil. Purification by h.p.l.c. gave a crystalline *solid*, m.p. 39—40 °C (Found: C, 69.5; H, 7.5. $C_{12}H_{14}O_3$ requires C, 69.9; H, 6.8%).

Methyl *m*-phenoxymethylcinnamate. Methyl *m*-bromomethylcinnamate (250 mg), anhydrous potassium carbonate (250 mg), and phenol (200 mg) were refluxed with stirring for 6 h in acetone (20 ml). The solution was then poured into water and the product taken up in ether. Removal of the ether gave a pale yellow oil (210 mg) that crystallised on standing. Recrystallisation from light petroleum gave *crystals*, m.p. 81—82 °C (Found: C, 76.2; H, 6.4. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%).

Methyl *p*-phenoxymethylcinnamate. The *p*-bromomethylcinnamate, treated as above, gave the *para*-derivative as *crystals* (85%), m.p. 114—116 °C (Found: C 76.1; H, 6.4. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%).

Methyl *m*-dimethylaminomethylcinnamate. Methyl *m*-bromomethylcinnamate (500 mg) was stirred in dry Me_2SO (10 ml) that had been cooled almost to the point of freezing (*ca.* 18 °C). Dimethylamine (0.5 ml) was added and stirring was continued for 30 min. The mixture was then poured into water and the aqueous mixture extracted with ether. Evaporation of the extract gave an oil (370 mg, 86%). This was purified by h.p.l.c. to give an *oil* (Found: $M^{+\cdot}$, 219.128. $C_{13}H_{17}NO_2$ requires $M^{+\cdot}$, 219.126).

Methyl *p*-dimethylaminomethylcinnamate. This was prepared from the *p*-bromomethyl derivative by the above method and purified in the same manner (Found: *M*, 219.127. $C_{13}H_{17}NO_2$ requires $M^{+\cdot}$, 219.126).

The proposed structures of all compounds prepared were confirmed by ^1H and ^{13}C n.m.r. spectrometry. Data are deposited as Supplementary Publication No. SUP 23545 (2 pp.).*

^{13}C *N.m.r. Measurements.*—The ^{13}C n.m.r. measurements were made on dilute (0.2M or less) solutions of the cinnamates in absolute ethanol, using D_2O as an external lock. The instrument used was a Varian CFT-20 and data were obtained at normal probe temperature. Solvolysis of even the more reac-

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index issue.

tive compounds was sufficiently slow relative to data collection times for this not to be a problem.

Acknowledgement

We thank the Research Committee of the University Grants Committee for financial support.

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Received 13*th August* 1982; *Paper* 2/1413