# $^{13}$C N.M.R. STUDIES

## PART V.[1] CARBON-13 SPECTRA OF SOME SUBSTITUTED STYRENES[2]

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Received September 30, 1964

### ABSTRACT

The 15.1 Mc/s $^{13}$C n.m.r. spectra of 23 substituted styrenes have been examined and the shieldings of the various carbon nuclei determined. Several meta- and para-substituted derivatives were included to study the effects of polar substituents on the vinyl carbon chemical shifts. In agreement with previous proposals, a linear correlation with the Hammett $\sigma$ parameter is found for the $\beta$-carbon shieldings, but not for those of the $\alpha$-carbons. Nine ortho-substituted examples and two $\alpha$-substituted compounds were investigated to compare their chemical shifts with results for related carbonyl compounds. While the $^{13}$C data exhibit marked differences in the hindered compounds, the variations differ from those observed in the more polar carbonyl systems.

### INTRODUCTION

In previous papers of this series we have presented the results of an extensive survey of organic carbonyl compounds by carbon-13 nuclear magnetic resonance (n.m.r.) spectroscopy (1, 2, 3). These investigations have revealed a number of factors which contributed to the shieldings of carbon nuclei in groups bonded to aromatic rings. To gain a fuller understanding, and to test previous interpretations (1), of the effects of polar substituents on these chemical shifts, we have chosen to study a series of substituted styrenes which will allow an examination of two unsaturated centers in a group capable of conjugative interaction with the ring. Ten monosubstituted meta- and para-derivatives were included to compare variations of the vinyl carbon shieldings with the polar character of substituents covering the range $p$-NMe$_2$ to $p$-NO$_2$. Another facet of this investigation was the examination of the chemical shift parameters for nine compounds, bearing one or two ortho-groups, and two examples with $\alpha$-substituents. The analyses of these spectra were performed by methods which have been described (2). More extensive use of spin-decoupling experiments, however, was required than in the previous work, particularly to establish the location of the vinyl carbon signals with certainty for several cases.

The results for the meta- and para-substituted styrenes show that the $\beta$-carbon shieldings are sensitive to the effects of polar substituents and a linear correlation of these values is obtained with the Hammett $\sigma$ parameters. These shifts also correlate with the $^{19}$F shieldings for similarly substituted fluorobenzenes (4), although different slopes are found for the meta- and para-cases. While the variation in the shieldings for the $\alpha$-carbon nuclei are slightly larger than the experimental uncertainty, no similar correlations were found. The ortho-substituted examples extend our studies of hindered systems and the results are qualitatively comparable to those found for the carbonyl compounds. There are significant quantitative differences, however, and estimates of the extent of steric inhibition of conjugation for these styrenes are not possible by the methods previously proposed (2, 3, 5). An approximate correlation has been found for the chemical shifts of the $\beta$-carbon nucleus in the hindered compounds with the molar extinction coefficient of

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[1] *Part IV. Reference 3.*
[2] *These results were reported in part at the 47th Annual Conference of the Chemical Institute of Canada, Kingston, June 1964.*
[3] *Petroleum Research Fund Predoctoral Fellow, 1962–1964.*

the electronic transition involving the conjugated chromophore (6, 7). In addition, these examples provide further tests of the applicability of the additive relation of substituent effects on aromatic carbon shieldings, originally noted by Lauterbur (8). Since the only previously reported study of unsaturated hydrocarbons did not include styrene (9), this paper represents the first investigation of aromatic olefins.

## EXPERIMENTAL

### *Nuclear Magnetic Resonance Spectra*

The $^{13}$C spectra were obtained at 15.085 Mc/s using samples which contained carbon-13 in natural abundance. The detailed procedure employed in this study has been described (2).

### *Materials*

Most of the substituted styrenes were obtained from commercial sources as listed in the following: Matheson, Coleman and Bell, styrene and α-methylstyrene; Aldrich Chemical Co. Inc., the 4-methyl-, 3-nitro-, 2,4-dimethyl-, 2,5-dimethyl-, 2,6-dimethyl-, 2,4,6-trimethyl-, and 2,3,5,6-tetramethyl-derivatives; Columbia Organic Chemicals, 2-bromo-, 3-bromo-, 4-bromo-, 2-chloro-, 3-chloro-, 4-chloro-, 2-methyl-, and 3-methyl-derivatives. A sample of 3,4-dichlorostyrene was kindly provided by Prof. K. Yates. The remaining examples included in this investigation, one of which is a new compound, were prepared by well-known methods. The physical constants (uncorrected) and the syntheses employed for these materials are outlined in Table I together with their reported physical data and the analytical results for 2,4,6-triisopropylstyrene. The microanalysis was performed by Alfred Bernhardt and Associates, Mulheim, Germany. Infrared and proton spectra were determined for each sample before its $^{13}$C spectrum was obtained as a check of the purity. The ultraviolet spectra for a few examples were determined to measure their molar extinction coefficients. These were obtained with a Bausch and Lomb 505 spectrophotometer.

TABLE I

Physical properties of some substituted styrenes prepared for this study

| | | Physical constants | | | | |
|---|---|---|---|---|---|---|
| | | Observed | | Reported | | |
| Substituent | Method of preparation† | b.p./mm (m.p.) | $n_D$ ($t^0$) | b.p./mm (m.p.) | $n_D$ ($t^0$) | Ref. |
| 4-N$(CH_3)_2$ | A-1 | 45–50/0.05 | 1.6112 (20) | — | 1.6110 (20) | 10 |
| 4-$CH_3O$ | B | 57–58/0.9 | 1.5885 (24) | 76–80/8 | 1.5586 (20) | 11 |
| 4-$NO_2$ | C | (∼ 20) | — | (21.5) | — | 10 |
| 2,4,6-($i$-$C_3H_7$)$_3$* | A-2 | 85–86/0.4 | 1.5045 (25) | | | |
| α-$C_2H_5$ | D | 177–180/atm | 1.5262 (22) | 177–180/742 | 1.5262 (22) | 12, 13 |

*Found: C, 88.35; H, 11.45. Calcd. for $C_{17}H_{26}$: C, 88.62; H, 11.30.

†Methods used: A-1, Grignard reaction of MeMgI + ArCHO, spontaneous dehydration of carbinol (10). A-2, Grignard reaction of MeMgI + ArCHO, followed by dehydration on $KHSO_4$ (14). B, dehydration of carbinol on $KHSO_4$ (14). C, from $\phi CH_2CH_2Br$, following the method of Strassbourg, Gregg, and Walling (10). D, from $CH_3CH_2CH(\phi)COOH$ by reduction followed by dehydration over KOH (12, 13).

## RESULTS AND DISCUSSION

The observed chemical shifts for the carbon nuclei in the meta- and para-substituted styrenes are listed in Table II, while the data for the ortho-derivatives appear in Table III. For purposes of the discussion, these will be considered separately. For clarity, the various types of nuclei will be discussed under individual subheadings in the following. Finally, the evidences provided by the spectra of the ortho- and α-substituted cases for the existence of steric inhibition of conjugation of the vinyl group in the hindered systems are considered.

### *Meta- and Para-Substituted Styrenes*

#### *Aromatic Carbons*

The assignments of chemical shifts for the aromatic nuclei in styrene shown in Table II have been made by analogy with the results for other aromatic hydrocarbons (2, 15, 16).

TABLE II

$^{13}C$ chemical shifts of some meta- and para-substituted styrenes (in p.p.m. from $CS_2$)

| | Vinyl carbons | | Aromatic carbons | | | | |
|---|---|---|---|---|---|---|---|
| Substituent | α-C | β-C | C-1 | C-2,6 | C-3,5 | C-4 | Others |
| H | 57.0 | 80.5 | 56.4 | 56.4 | 65.8 | 67.5 | — |
| 4-$CH_3$ | 56.2 | 79.7 | 56.0 | 64.8 | 64.8 | 56.0 | 172.4 |
| 4-$CH_3O$ | 57.2 | 82.3 | 62.4 | 66.0 | 79.2 | 33.8 | 138.7 |
| 4-$N(CH_3)_2$ | 56.4 | 85.0 | 68.2 | 66.8 | 81.0 | 43.4 | 153.4 |
| 4-Cl | 57.0 | 78.9 | 56.2 | 64.7 | 64.7 | 59.3 | — |
| 4-Br | 57.5 | 78.6 | 56.3 | 65.4 | 61.7 | 70.6 | — |
| 3,4-$Cl_2$* | 61.1 | 78.0 | 55.9 | —‡ | —‡ | —‡ | |
| 4-$NO_2$† | 57.8 | 74.7 | 48.9 | 66.5 | 69.4 | 46.0 | — |
| 3-$CH_3$ | 56.4 | 81.1 | 56.3 | 65.3 (C-2) | 56.3 (C-3) | 65.3 | 172.5 |
| | | | | 70.0 (C-6) | 65.3 (C-5) | | |
| 3-Cl | 59.1 | 78.7 | 55.0 | 66.9 (C-2) | 59.1 (C-3) | 66.9 | — |
| | | | | 69.1 (C-6) | 64.5 (C-5) | | |
| 3-Br | 60.6 | 78.3 | 54.5 | 63.6 (C-2) | 69.1 (C-3) | | |
| | | | | 68.4 (C-6) | 63.6 (C-5) | 63.6 | — |
| 3-$NO_2$ | 58.8 | 77.1 | 56.1 | 71.9 (C-2) | 45.3 (C-3) | | |
| | | | | 58.8 (C-6) | 64.1 (C-5) | 71.9 | — |

*In $CS_2$ solution (saturated).
†In 1,4-dioxane solution.
‡Reliable data could not be obtained due to the low concentration attainable.

TABLE III

$^{13}C$ chemical shifts of some ortho-substituted styrenes (in p.p.m. from $CS_2$)

| | Vinyl group | | Aromatic nuclei | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Substituent(s) | α-C | β-C | C-1 | C-2 | C-3 | C-4 | C-5 | C-6 | Other nuclei |
| H | 57.0 | 80.5 | 56.4 | 65.8 | 65.8 | 67.5 | 65.8 | 65.8 | — |
| 2-Cl | 58.2 | 77.7 | 58.6 | 61.2 | 64.2 | 66.0 | 66.0 | 64.2 | — |
| 2-Br | 56.2 | 76.5 | 56.2 | 70.1 | 60.8 | 65.0 | 65.0 | 65.0 | — |
| 2-$CH_3$ | 57.3 | 79.1 | 59.1 | 58.2 | 65.1 | 67.5 | 67.5 | 65.1 | 174.0 |
| 2,4-$(CH_3)_2$ | 58.1 | 80.4 | 58.7 | 58.7 | 62.7 | 58.7 | 67.5 | 62.7 | 172.9 |
| 2,5-$(CH_3)_2$ | 58.8 | 80.0 | 58.7 | 58.7 | 64.2 | 66.4 | 58.7 | 64.2 | 173.5 |
| 2,6-$(CH_3)_2$ | 58.3 | 74.3 | 56.8 | 58.5 | 65.4 | 65.4 | 65.4 | 58.5 | 172.4 |
| 2,4,6-$(CH_3)_3$ | 58.0 | 74.7 | 58.5 | 58.5 | 64.0 | 58.5 | 64.0 | 58.5 | 172.5 |
| 2,3,5,6-$(CH_3)_4$ | 58.6 | 74.2 | 55.6 | 61.0 | 61.0 | 62.8 | 61.0 | 61.0 | 173.1 |
| 2,4,6-$(i\text{-}C_3H_7)_3$ | 58.0 | 74.6 | 59.6 | 47.6 | 73.3 | 47.6 | 73.3 | 47.6 | 177.3<br>163.3<br>169.5<br>167.4 |
| α-$CH_3$ | 50.6 | 81.3 | 52.1 | 65.8 | 65.8 | 67.8 | 65.8 | 65.8 | |
| α-$C_2H_5$ | 43.7 | 82.8 | 52.0 | 66.1 | 66.0 | 67.1 | 66.0 | 66.0 | |

While the assignment for C-1 is unambiguous, the others are not unequivocal although support for the present assignment is provided by the results for the meta-substituted cases. The values for styrene indicate that the substituent effect of the vinyl group on the aromatic shieldings is very similar to that of the methyl group. At the para-position, an up-field shift of 2.5 p.p.m. relative to benzene is observed, whereas the C-1 nucleus is deshielded by 8.6 p.p.m. The comparable figures for the methyl group are +2.8 and −9.1 p.p.m., respectively, (16). Directionally the effects at the ortho- and meta-positions are opposite for these two groups but the changes are less than 1 p.p.m. and, therefore, within experimental uncertainty. According to previous results (16, 17), the observed shielding for the para-carbon indicates an increased π-electron density at this position which is due, presumably, to electron release by the vinyl group to the ring.

An examination of the aromatic shieldings for the meta-derivatives given in Table II shows that bands are observed whose positions are in good agreement with calculated values assuming additivity of substituent effects at these nuclei. The latter values may be calculated from the substituent effects found for monosubstituted cases (16) and the present styrene data. In general, the differences are less than 1.5 p.p.m. with two exceptions, the C-4 and C-3 nuclei in the 3-methyl and 3-bromo derivatives, respectively. The present assignments are based on the assumption that additivity of substituent effects holds. For the para-derivatives, the situation is significantly different. In general, the observed transitions appear at positions which are up to 3.5 p.p.m. from those calculated. To compare the results for the meta- and para-substituted systems, the deviations between the observed and calculated chemical shifts are shown in Fig. 1 for the methyl, bromo, and nitro groups. The assignments indicated in Table II for the aromatic nuclei have been made by assuming a minimum difference between the calculated and observed values, since no other approach is available without resorting to the use of labelled compounds. It is possible, of course, that the deviations are even larger than these but evidence is lacking.

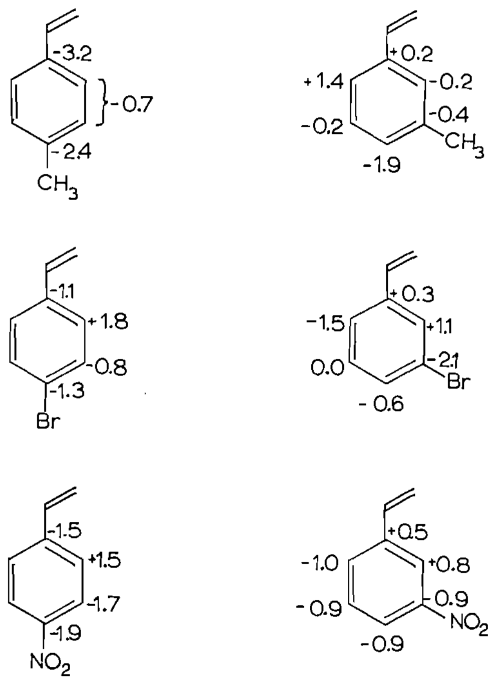


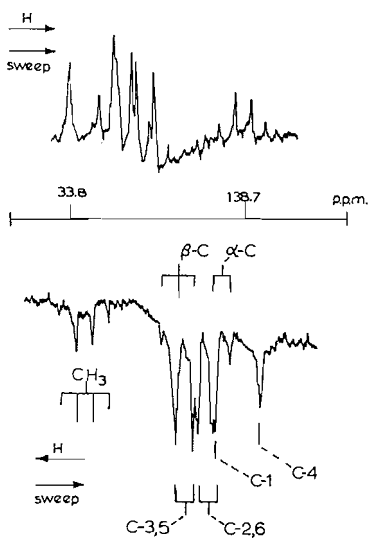
FIG. 1. Differences between the observed and calculated chemical shifts for the aromatic carbon nuclei of some meta- and para-substituted styrenes.

The fact that much better agreement is found for the meta-substituted compounds seems entirely reasonable, since conjugative interactions between the vinyl group and a meta-substituent will be minimal. In cases with significant resonance interaction between two groups on an aromatic ring, it would not be surprising to find greater deviations for the aromatic shieldings, since one or both of the substituent effects could be altered by conjugation. This situation has been discussed in general (18). In the present system, the vinyl group is capable of either electron release to, or withdrawal from, the ring depending on the influence of other polar substituents in conjugation with it. Consequently, the substituent effects of the vinyl group at the aromatic carbon nuclei would be expected to depend strongly on the demands of para-substituents. In styrene itself, it appears that the vinyl group releases electrons to the ring, but this tendency may be reversed if an electron-releasing group is at the para-position such that the vinyl group tends to gain electrons from the ring. Support for this argument is provided by the chemical shift results for the $\beta$-carbon of the vinyl group discussed below. Since the electronic characteristics of the vinyl substituent are subject to these two extremes, it is hardly surprising that the observed values for the aromatic carbons in the para-substituted examples differ from those calculated by substantially greater amounts than the corresponding figures for the meta-systems. For each example having a para-substituent capable of electron release by resonance, the deviations at the C-4 nucleus are large, ranging up to 3.5 p.p.m. for the para-methoxyl case, and all are negative (i.e. the observed shift is at *lower* field than that calculated). This observation is consistent with the reversal of the polar tendencies of the vinyl group in these compounds relative to styrene and reflects a reduced $\pi$-electron density at this position.

### *Vinyl Carbons*

The first investigation of $^{13}$C spectra of olefins, reported by Holm (19), established that olefinic carbons absorb in the same general region as aromatic carbon nuclei. A recent detailed study of $^{13}$C olefinic n.m.r. absorption (9) in aliphatic compounds has clearly defined the effects of alkyl substitution on these shieldings. Since the conjugated systems examined in the aliphatic series showed no marked differences from the corresponding non-conjugated cases, these results suggest the most probable regions of absorption for the vinyl carbons in styrene. Without exception, the bands overlap with the aromatic signals but the patterns due to spin coupling provide an essential clue for the detection of the $\beta$-carbon absorption since it is a triplet with a coupling constant in the range 161 ± 4 c/s. The $\alpha$-carbon band is a doublet with a similar spacing. In most instances, the triplet is readily distinguished since it appears in the higher field portion of this spectral region and overlap with other bands was found to be less serious. The $\alpha$-carbon resonances, however, present a problem in several instances, due to their appearance in a more congested region of the spectrum and the presence of other doublets with comparable coupling constants. Spin-decoupling experiments proved to be extremely valuable in aiding identifications and allowing more precise measurements of these bands. Owing to the above complications, it is necessary to note that the assignments given in Table II appear to be the most reasonable and internally consistent, but they are not unequivocal for all cases, and, lacking measurements of labelled materials, it is conceivable that a few of these figures may be interchanged with certain of the aromatic shifts, the rationale for which was discussed in the previous section. To illustrate the type of spectrum which is obtained for these compounds, that of 4-methoxystyrene is illustrated in Fig. 2 and the assignments are indicated. This case was chosen to show an example in which the $\beta$-carbon signals are not well separated and to illustrate the effect of double irradiation at the proton resonance frequency for the aromatic region (Fig. 3). The origins of the singlets in the decoupled spectrum are indicated since the two traces were obtained at slightly different sweep rates. The effect of sweep direction on the shapes of multiplets is apparent in Fig. 2 and the signal enhancement due to a nuclear Overhauser effect (20) may be seen in Fig. 3 by comparison of the intensities of the absorption due to the C-4 and $\alpha$-C nuclei, for example. Both of these effects prove to be useful as aids for the analyses of these spectra.

The chemical shift values for the vinyl carbons in styrene have been found to be 57.0



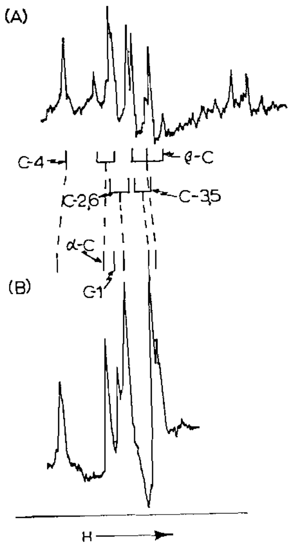


FIG. 2. 15.085 Mc/s $^{13}$C spectra of para-methoxystyrene.

FIG. 3. (A) Normal 15.085 Mc/s $^{13}$C spectrum of para-methoxystyrene; (B) decoupled $^{13}$C spectrum of aromatic region obtained by simultaneous irradiation at the resonance frequencies of the various protons (near 60 Mc/s).

(α-C) and 80.5 (β-C) p.p.m., which may be compared to shifts of 55.2 and 79.3 p.p.m. for the C-2 and C-1 nuclei, respectively, of 1-pentene and 55.6 and 76.2 p.p.m. for C-2 and C-1 in 1,3-butadiene (9). Clearly, the aliphatic shifts are comparable with those for the aromatic system although the latter appear at slightly higher field. Any contribution from a ring-current effect in styrene, an effect which is absent in the other systems, would tend to decrease the vinyl shieldings; thus these data provide another piece of evidence indicating that ring-current effects in carbon spectra are of secondary importance.

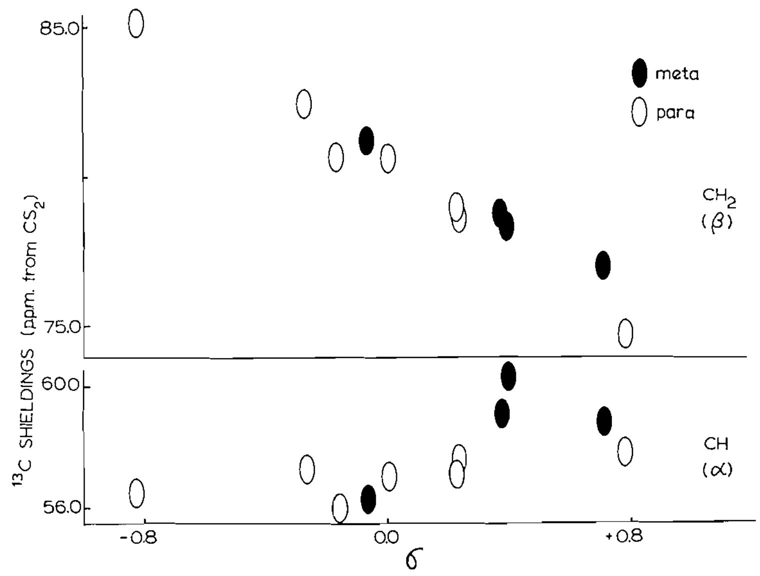
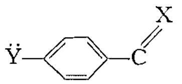


FIG. 4. Plot of vinyl $^{13}$C shieldings of meta- and para-substituted styrenes vs. Hammett σ parameters.

An inspection of the $\beta$-carbon shieldings for the meta- and para-substituted compounds reveals that these nuclei absorb over a total range of 10.3 p.p.m. and that the shifts appear to be dependent on the polar characteristics of the substituent groups. A reasonably linear correlation of the $\beta$-carbon chemical shifts with the Hammett $\sigma$ parameters is obtained as illustrated in Fig. 4. The variation of the $\alpha$-carbon shifts with the same parameters is included to show the marked difference for this nucleus. The scatter of the $\alpha$-carbon shielding values is significantly larger than the experimental error of the measurements but there is no apparent trend with polarity of substituent. In fact, the total variation for the para-derivatives is just greater than the experimental uncertainty while the meta-substituted examples exhibit somewhat larger differences. Perhaps this indicates the presence of a field effect operative at the $\alpha$-carbon due to groupings at the meta-position. The uniform change in the $\beta$-carbon shifts, however, fits well with our previous interpretation of the observed absence of substituent effects on carbonyl carbon shifts in acetophenones (1, 2). The explanation of the latter result was based on a consideration of the contributions to the ground state of conjugated molecules by various resonance forms. As an example, consider a conjugated molecule (I) bearing an electron-releasing group in the para-position. Resonance form II (as well as others) will contribute to the electronic distribution in the ground state. Analogous structures with reversed charges may be written for examples bearing electron-withdrawing substituents. The polarized form (II) illustrates an important difference between the $\alpha$- and $\beta$-nuclei of the sidechain (i.e. C and X, respectively) in that the latter nucleus is at a terminus of the resonance system while the $\alpha$-carbon is not. It appears reasonable to suggest, therefore, that the electron density changes will be most pronounced at the $\beta$-position and minimal at the $\alpha$-nucleus. Our present investigation was prompted by this proposal which was used to explain the carbonyl shieldings of acetophenones, since the styrene series provides a close analogy to the carbonyl systems and permits $^{13}$C studies of the $\beta$-nucleus. $^{19}$F spectral studies (4, 21) on an extensive series of substituted fluorobenzenes has established the marked dependence of $^{19}$F shieldings on substituent polarities. It is interesting to compare the $\beta$-carbon chemical shift values with the $^{19}$F results for the corresponding fluorobenzene derivatives as illustrated in Fig. 5. The meta and para cases appear to follow different correlations. Taft (4) has shown that $^{19}$F data for the two types of substituted systems require different correlation equations using the separated parameters $\sigma_I$ and $\sigma_R$, and therefore, the present result is not unexpected, although difficult to explain. One surprising feature is the excellent plot obtained for the para-substituted derivatives except for the result for styrene itself. The range of values which the meta-series includes is small. The available evidence, however, indicates that the $\beta$-carbon shieldings are approximately one-third as sensitive to substituent polarity as the $^{19}$F nuclei in the para-derivatives, but in the meta-compounds the $\beta$-carbon and $^{19}$F nuclei respond similarly.



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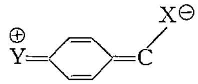

II

*Other Carbons*

The observed chemical shifts for the methyl carbon nuclei in the various substituents agree well with those reported previously by Lauterbur for the corresponding monosubstituted benzenes: toluene, 171.8 (15), anisole, 138.4 (4), and N,N-dimethylaniline, 152.6 p.p.m. (22). It is evident that the vinyl group exerts no significant effect on these

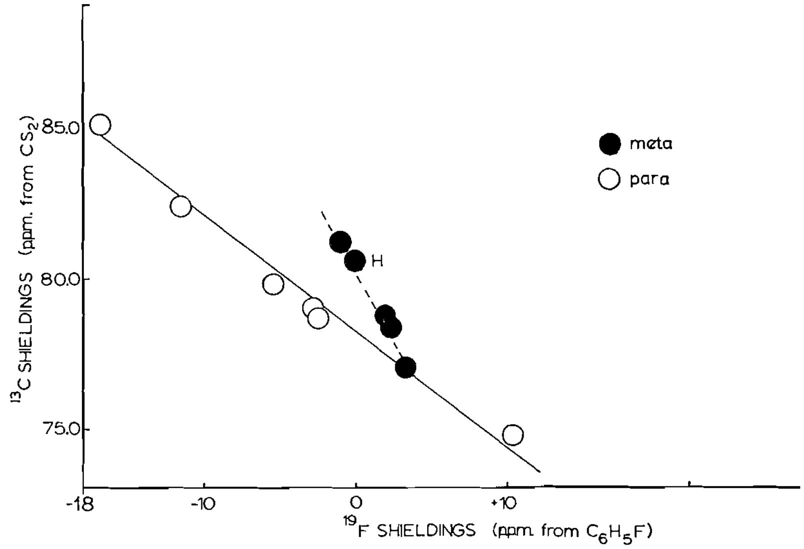

FIG. 5. Plot of β-carbon shieldings for meta- and para-substituted styrenes vs. $^{19}$F shieldings of similarly substituted fluorobenzenes.

nuclei for the meta- and para-derivatives. The observed coupling constants are also similar to the earlier results (4, 15, 22).

### *Ortho-Substituted Styrenes*

#### *Aromatic Carbons*

We have assigned the chemical shifts for the aromatic carbons as listed in Table III by again assuming an additive relation for substituent effects. Since the deviations are greater for ortho-substituted compounds in general (2, 3, 8, 15, 22, 23), there is more uncertainty in all of these cases. Qualitatively, two features are consistent with previous results for the carbonyl systems. Ortho-substitution tends to reduce the deshielding effect of the vinyl group at C-1. To show this for each example it is necessary to allow for the effects of the other substituents but, having done this, it can be seen that for most cases the observed shift is at higher field than that calculated. While the opposite effect is not found consistently for the C-4 nucleus, its absence is not particularly surprising in view of the relatively small change at this position in styrene itself relative to benzene. The second point concerns the aromatic shieldings in vinyldurene for which the "normal" deshielding effect of methyl at the substituted aromatic nuclei is absent. It is curious that the shielding at the C-1 nucleus, however, is very close to that expected if the substituent effects were additive. As in our other recent investigations, present knowledge does not permit an adequate explanation of these aromatic shieldings to be offered.

#### *Vinyl Carbons*

From the data for the first four entries in Table III, it can be seen that the α-carbon chemical shifts for the ortho-substituted styrenes show small variations with the nature of the ortho-group relative to the value for styrene itself, but no pronounced changes are found. These results are similar to those for the meta- and para-derivatives. The α-carbon shieldings for the compounds bearing two or more alkyl substituents are the same within experimental error and indicate that these nuclei are slightly shielded by the ortho-alkyl carbons, although to a lesser extent than carbonyl or methyl carbons in corresponding environments (2, 15). The situation at the β-carbon in these compounds is distinctly different, since the signals due to these nuclei appear at lower fields than those for the β-carbon in styrene. For the 2-chloro-, 2-bromo-, and 2-methyl-derivatives the observed shieldings are reduced by 0.5–2 p.p.m. relative to the corresponding 3- and 4-substituted examples. In the diortho-substituted systems, a further reduction of ca. 5 p.p.m. is apparent. This trend is consistent with the presence of steric interference to coplanarity of the vinyl group in this series. In the alkylated cases, for example, the aromatic ring is electron-rich relative to styrene due to electron release by the alkyl substituents and, in the absence of steric inhibition of conjugation, the vinyl group would be expected to act as an electron-withdrawing substituent from the results discussed above for the meta- and para-derivatives. In this event, the β-carbon nucleus should exhibit an increased shielding with the signal shifted to higher field. In fact, the observed effect is the reverse and, therefore, would appear to indicate that there is steric inhibition of resonance in these systems. It is unfortunate that $^{13}$C data are not available for lower molecular weight olefins with which the values for the hindered styrenes might be compared.

A closer examination of the trends exhibited by the β-carbon shifts of the methylated derivatives shows the following pattern. The β-carbon nucleus in 2-methylstyrene appears at 79.1 p.p.m., which is 1.4 p.p.m. to lower field from its position in styrene. The introduction of the 4-methyl group tends to increase its shielding by 1.3 p.p.m. suggesting that this substituent increases the conjugative interaction of the ring with the vinyl group, an effect that was found for the carbonyl carbon resonances in similarly substituted aromatic ketones. A second ortho-methyl group (e.g. 2,6-dimethylstyrene) shifts the β-carbon signal to 74.3 p.p.m. Further methyl substitution on the ring does not affect the observed shift, nor does this shielding differ for the 2,4,6-triisopropyl derivative. These variations of the β-carbon shieldings are similar to those observed for the carbonyl carbon in the corresponding acetophenones with two important differences. These two nuclei are in different positions relative to the aromatic ring and the carbonyl carbon in the polysubstituted cases is affected by increased substitution. The α-carbon shielding which might be expected to undergo changes similar to those exhibited by the carbonyl carbon nucleus remains essentially constant for this series. In the case of the ketones, however, the α-nucleus (carbonyl carbon) is doubly bonded to an electronegative element, oxygen, whose polarizing effect on the C=O bond will be more pronounced at the α-position for the hindered ketones since the electron supply from the ring is reduced by steric inhibition of conjugation. In the styrene system, both nuclei of the vinyl carbon have comparable electronegativities and no strong polarization of the C=C bond would result from a reduced conjugative interaction with the ring, instead, the shielding at the β-carbon would be decreased relative to the unhindered systems since the conjugative electron release by the ring to the vinyl group is less efficient. We suggest, therefore, that the nature of the double bond in conjugation with the aromatic system is the major controlling factor for determining the shieldings at these side-chain nuclei in the hindered systems and is responsible for the observed differences between the carbonyl and olefinic systems.

Correlations of the shieldings of the β-carbon vinylic grouping with other physical properties would be expected if the above interpretations are valid. In particular, the intensities of the electronic transitions for the fully conjugated chromophores are believed to reflect the extent of steric inhibition of resonance in hindered systems such as these (6, 7, 24). While only limited data are available, an approximate correlation between these two parameters is found as illustrated in Table IV. There is a marked decrease in the

TABLE IV

Comparison of $\beta$-$^{13}$C shielding and ultraviolet data for some substituted styrenes

| Substitution | $\delta_c^{\beta-C}$ (p.p.m.) | $\epsilon_{max}$ | Estimated angle of twist* (°) | |
|---|---|---|---|---|
| Nil | 80.6 | 15 600 | 0 | 0 |
| 2-$CH_3$ | 79.1 | 12 000 | 28 | 31 |
| 2,6-$(CH_3)_2$ | 74.3 | 5 400 | — | 54 |
| 2,4,6-$(CH_3)_3$ | 74.7 | 7 000 | 54 | 49 |
| 2,3,5,6-$(CH_3)_4$ | 74.2 | 4 000 | — | — |
| 2,4,6-(*i*-Pr)$_3$ | 74.6 | 5 800 | — | — |

*First column from ref. 6, second column, ref. 24.

extinction coefficients with increased ortho-substitution which roughly parallels the change in $\beta$-carbon chemical shifts, although the $\epsilon_{max}$ values vary somewhat for the various diortho-substituted derivatives. All of the latter variation may not be real due to the difficulty in locating and measuring the appropriate ultraviolet band precisely. A few of the intensity figures were not available in the literature and were determined for this comparison. The ultraviolet spectral data have been utilized by others to calculate the angles of twist for sterically hindered systems (6, 24) and these estimates are included in Table IV. Lacking the figures for suitable model compounds, we hesitate to perform a similar analysis of the $^{13}$C data. Qualitatively, however, the observed $^{13}$C shifts provide strong evidence of steric inhibition of conjugation of the vinyl group.

### *Other Carbons*

The chemical shifts for the carbon nuclei of the substituent groups are found to correspond well with those observed for the corresponding substituted acetophenones (2). The carbons bonded directly to the ring and ortho to the vinyl group tend to absorb at slightly higher field than those in less hindered positions. The most striking example of this feature is provided by vinyldurene for which two methyl groups appear at 177.3 p.p.m. and these signals have been assigned to the 2- and 6-groups, for reasons discussed previously (2).

## *α-Substituted Styrenes*

### *Aromatic Carbons*

The effects of the isopropenyl and 2-butenyl groups on the aromatic shieldings are found to be closely similar to those exhibited by the vinyl group (last two entries in Table III). The major difference is a greater decrease in shielding at the substituted carbon (C-1) which is found to be 13 p.p.m. for these two groups compared to the −8.6 p.p.m. decrease caused by the vinyl substituent. Apart from this change, the effects at the other aromatic nuclei are the same within experimental error.

### *Vinyl Carbons*

The shielding effects at the olefinic carbon nuclei by methyl substitution on double bonds have been established by Friedel and Retcofsky (9) for aliphatic systems. In general, the changes are opposite at the two centers with the signal for the substituted nucleus moving to lower field and the $\beta$-carbon absorption to higher. Qualitatively, the vinyl carbon shifts for 2-methylstyrene undergo similar changes. The closest model system included in the aliphatic series, is that of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene for which the shift of the internal olefinic carbon (C-2 and C-3) change by −5.2 p.p.m. and the terminal nuclei (C-1 and C-4) are shielded by +5.0 p.p.m. by methyl substitution

(9). For $\alpha$-methylstyrene relative to styrene, the corresponding changes are $-6.4$ and $+0.8$ p.p.m. Introduction of the ethyl group instead of methyl was found to cause changes of $-6.5 \pm 1.3$ and $+1.1 \pm 1.1$ p.p.m. for the substituted and $\beta$-carbon nuclei, respectively, relative to the shifts in the methyl derivative, in some aliphatic olefinic systems (9). Although none of these are closely related to the present cases, the observed changes for $\alpha$-ethylstyrene are remarkably close to these values, $-6.9$ and $+1.5$ p.p.m., respectively. The two $\alpha$-substituted styrenes, therefore, are additional examples showing the same general variations as aliphatic olefins.

The most interesting feature of these observations is the very much reduced shielding at the $\beta$-carbon caused by $\alpha$-methyl substitution. A possible explanation of this could invoke steric inhibition of conjugation such that there is a reduced effect of the aromatic ring at this center. Suzuki has concluded this to be the case from the ultraviolet spectra and has estimated the angle of twist to be 33°(24). Our study of the $^{13}$C results for this system, however, is not nearly extensive enough to corroborate or refute his conclusion.

## ACKNOWLEDGMENTS

We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this investigation through the provision of operating funds and the Ontario Research Foundation for a grant to purchase the 15.1 Mc/s oscillator unit.

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