ROBERT R. FRASER

ABSTRACT

The complete results of analysis of the N.M.R. spectra of twelve 2,6-dimethyl-1-substituted benzenes are reported. The results are interpreted as evidence that the ability of the substituent to donate or withdraw electrons by resonance interaction with the benzene ring is a major factor in determining the position of absorption of the protons attached to the ring. The chemical shifts and coupling constants for nitroethylene are also reported.

The study of the effect of a substituent on the position of absorption in the N.M.R. spectra of protons attached to a benzene ring has been greatly hindered by the complexity of the spectra of monosubstituted benzenes. These spectra generally fall in the classification AB_2C_2 following the nomenclature of Bernstein, Pople, and Schneider (1). Analysis of such a five-spin system is extremely tedious even in the case of pyridine, which belongs to the slightly simpler AB_2X_2 system (2). For this reason little work has appeared in the literature on the correlation of chemical shifts of protons on a benzene ring with substituents since the first report by Corio and Dailey (3). These authors reported the values δ_{0} , δ_{m} , δ_{p} for the chemical shifts of the ortho, meta, and para protons in the N.M.R. spectra of 22 monosubstituted benzenes. Their analysis was of a qualitative nature on spectra whose resolution was limited by the use of a transmission frequency of 30.00 Mc/sec. Furthermore Bothner-By and Glick subsequently showed that solvent effects were responsible for inaccuracies of as much as 0.07 p.p.m. in the values for δ_p (4). Correlation of their δ values with Hammett's σ constants gave only rough agreement although Taft later showed that agreement to within 0.07 p.p.m. could be obtained employing the equation^{*} $\delta_{\mathbf{p}} = +0.40\sigma_{\mathrm{I}} + 1.04\sigma_{\mathrm{R}}^{0} + 0.02$ (5). In this equation σ_{I} is the inductive substituent constant of Taft (6) and $\sigma_{\rm R}^0$ is the resonance substituent constant corrected for isovalent conjugation (5). Taft has interpreted this agreement to be an indication that polarization effects in the transition state are sufficiently similar to those in the ground state to give the correlation between σ and δ_{p} (7).

An alternative theory of the origin of chemical shift differences in the ring protons of monosubstituted benzenes has been suggested in a recent article by Buckingham (8). He proposes that the screening constant for each proton is determined by the "internal electric field" of the molecule. In addition polarization of the surrounding solvent by the solute produces a "reaction field" whose effect combines with that of the electric field to give the total effect on the screening constants. He has derived expressions for these two fields in terms of the dipole moment of the solute, its refractive index, and the dielectric of the solution from which screening constants can be directly calculated. Calculations for nitrobenzene gave values of -0.69, -0.40, and -0.51 p.p.m. relative to benzene for the ortho, meta, and para protons in fair agreement with the values -0.97, -0.30, and -0.42 observed by Corio and Dailey. In order to provide data which might aid in the elucidation of the cause of chemical shift differences with different substituents, a series

¹Manuscript received June 29, 1960.

Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Ontario. This paper was presented at the 43rd Annual Conference of the Chemical Institute of Canada, Ottawa, June 13–15, 1960. *It should be noted that Corio and Dailey employ $\delta_{\rm p} = 10^6 \{(H_{\rm ref} - H)/H_{\rm ref}\}$, which causes negative signs to represent shifts to higher field.

Can. J. Chem. Vol. 38 (1960)

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 129.12.217.83 on 11/10/14 For personal use only.

FRASER: SUBSTITUTED XYLENES

of 2,6-dimethyl-1-substituted-benzenes were synthesized and their spectra obtained with a Varian V-4302 spectrometer using a 60 Mc/sec r.f. unit. These xylene derivatives were selected for study since they provide spectra which can be accurately analyzed.

RESULTS AND DISCUSSION

The results of analysis of the spectra of 12 substituted xylenes are given in Table I.

Results of analysis of twelve 2,6-dimethyl-1-substituted benzenes (substituent o values are also given)

Substituent	$\Delta {\nu_{\rm m}}^*$	$\Delta \nu_{\mathbf{p}}^{*}$	$\Delta \nu_{\rm m}'$	σm	σ_{p}	$\sigma_{\rm R}$	<i>т</i> сн ₃ †
CN Br I F OH NH ₂ NO ₂ COOH OCH ₃ NHCH ₃	$12.9 \\ 16.8 \\ 18.4 \\ 22.5 \\ 24.8 \\ 25.8 \\ 29.0 \\ 12.5 \\ 16.0 \\ 23.5 \\ 25.5 \\ 26.5 \\ 26 \\ 26 \\ 26 \\ 26 \\ 26 \\ 26 \\ 26 \\ 2$	$\begin{array}{c} 0.3\\ 16.8\\ 14.4\\ 26.5\\ 14.5\\ 39.0\\ 47.2\\ 5.2\\ 7.0\\ 29.0\\ 35.8\\ 26\end{array}$	$\begin{array}{c} 2.6\\ 6.5\\ 8.1\\ 12.2\\ 14.5\\ 15.5\\ 18.7\\ 2.2\\ 5.7\\ 13.2\\ 15.2\\ 15.7\end{array}$	$\begin{array}{c} 0.62\\ 0.39\\ 0.35\\ 0.35\\ 0.00\\ 0.08\\ -0.15 \end{array}$	$\begin{array}{c} 0.68\\ 0.23\\ 0.28\\ 0.08\\ 0.00\\ -0.35\\ -0.66\end{array}$	$\begin{array}{c} 0.10 \\ -0.22 \\ -0.11 \\ -0.44 \\ 0.00 \\ -0.60 \\ -0.76 \\ +0.05 \\ +0.06 \\ -0.20 \\ -0.39 \\ -0.21 \end{array}$	$\begin{array}{c} 7.52\\ 7.61\\ 7.54\\ 7.76\\ 7.73\\ 7.88\\ 7.89\\ 7.68\\ 7.55\\ 7.75\\ 7.76\\ 7.76\\ 7.76\end{array}$

NOTE: All the σ values for the first seven substituents are taken from R. W. Taft, Jr., N. C. Deno, and A. S. Skell. Ann. Rev. of Phys. Chem. 9, 292 (1958). The $\sigma_{\rm R}$ values for the last five substituents are calculated from normal $\sigma_{\rm R}$ values by correcting for the percentage of steric inhibition of resonance. The percentage inhibition was taken from the following sources: R. W. Taft, Jr. and H. D. Evans, J. Chem. Phys. 27, 1427 (1957), who reported NO₂ (67%), OCH₃ (59%), and N(CH₃)₂ (75%); B. M. Wepster. Rev. trav. chim. 76, 335, 357 (1957), who found NO₂ (69%), N(CH₃)₂ (80%), and NHCH₃ (60%); A. Burawoy and J. T. Chamberlain, J. Chem. Soc. 2310 (1952), from whose results the value 62% is calculated for OCH₃; and G. M. Moser and A. I. Kohlenburg, J. Chem. Soc. 805 (1957), from whose data the value 50% is estimated for COOH. For a discussion of steric inhibition of resonance in these compounds see B. M. Wepster. Progress in stereochemistry. Vol. 2. Edited by W. Klyne and P. B. D. de la Mare. Butterworths Scientific Publications, London. 1958.

 $\Delta \nu_m$ and $\Delta \nu_p$ are the chemical shifts in cycles/sec at 60 Mc/sec relative to the internal reference benzene for the meta and para protons.

 $\dagger \tau_{CH_3}$ gives the chemical shift of the ortho methyls expressed as parts per million with tetramethylsilane assigned a value 10.00.

The protons attached to the aromatic ring appeared in all but three cases as an AB_2 pattern whose general solution has been reported in reference 1. The spectrum consists of eight transitions whose energies and intensities are dependent only on the ratio $J_{AB}/\Delta\nu_{AB}$. In Fig. 1 the spectra of 2,6-dimethylphenol, 2,6-dimethylanisole, and N,N-dimethyl-2,6dimethylaniline are shown. They illustrate cases where the ratio is less than one, about one, and much greater than one, respectively. In 2,6-dimethylphenol, as in all AB_2 systems, line 3 gives the position of chemical shift for the 4 nucleus, unmodified by spin coupling. The corresponding position for the B nuclei is the mean of transitions 5 and 7. Thus $\Delta \nu_{AB} = \Delta \nu_{\rm p} - \Delta \nu_{\rm m}$ can be obtained directly from the spectrum. In the spectrum of this compound transitions 5 and 6 could not be resolved. To insure accurate results, theoretical spectra were calculated for various ratios of $J/\Delta \nu_{AB}$ until agreement with the observed spectra to within 0.4 cycle/sec for each transition was obtained. In most spectra the agreement was within 0.2 cycle/sec for each transition. In all spectra J_{AB} was found to be 7.7 cycles/sec. The spectra of N,N-dimethyl-2,6-dimethylaniline and 2,6-dimethylbromobenzene showed only a single observable peak under high gain and it is estimated that the chemical shift of the meta and para protons in these two compounds is the same to within 3.0 cycles/sec.

* J_{AB} is the coupling constant between the para (A) and meta (B) protons. $\Delta \nu_{AB} = \nu_A - \nu_B$ represents the chemical shift between the meta and para protons. The symbol $\Delta \nu$ is used to denote chemical shifts in units of cycles per second as recommended by Pople, Schneider, and Bernstein (11).



FIG. 1. (A) Aromatic proton absorption of 2,6-dimethylphenol (side bands at 40.0 cycles/sec) as a 10% solution in carbon tetrachloride. (B) Aromatic protons of 2,6-dimethylanisole (side bands at 35.1 cycles/sec) and (C) N,N-dimethyl-2,6-dimethylaniline (side bands at 25.0 cycles/sec) as 10% solutions in carbon tetrachloride.

In 2,6-dimethylfluorobenzene coupling of the fluorine atom with the meta and para protons resulted in the more complex spectrum shown in Fig. 2. By neglecting coupling of the methyl groups with the ring protons we can classify the aromatic protons and the fluorine nucleus as an AB_2X system. In order to simplify the calculations we have considered the aromatic proton spectrum as the sum of two AB_2 systems. This type of simplification has been employed previously by Anet in the analysis of the 2,3-dibromobutanes (9). When the X nucleus, fluorine, has a spin of +1/2 the aromatic protons will form one AB_2 system. When fluorine has a spin of -1/2 the aromatic protons comprise

2228

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 129.12.217.83 on 11/10/14 For personal use only.

2229



FIG. 2. Aromatic absorption of 2,6-dimethylfluorobenzene (side bands at 30.0 cycles/sec) as a 10% solution in carbon tetrachloride.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 129.12.217.83 on 11/10/14 For personal use only.

a second AB_2 system of equal total intensity. From the experimentally determined spectrum we found the chemical shift for the widely separated AB_2 system to be 8.6 cycles/sec. Using the values $J_{FHB} = 7.0$ cycles/sec, $J_{FHA} = \pm 2.2$ cycles/sec, and $J_{AB} = 7.7$ cycles/sec, it was then possible to calculate the complete spectrum for the aromatic protons. Two solutions were obtained, one for the case where the coupling constants between fluorine and the meta and para protons are of opposite sign (Fig. 3A) and one where the coupling constants are of the same sign (Fig. 3B). The numerical values for the fluorine-hydrogen coupling constants were chosen from the results of Gutowsky, Holm, Saika, and Williams, who observed the coupling between the ring protons and fluorine in fluoromesitylene to be 7.0 cycles/sec and the coupling between fluorine and a para proton to be 2.2 cycles/sec in several fluorinated benzenes (10). The line width of the strongest peak in the observed spectrum suggests that it is due to an AB_2 system having a very large ratio of $J/\Delta\nu_{AB}$ as depicted in Fig. 3A. In addition failure to observe the transition at +2.2 cycles/sec shown in Fig. 3B further indicates that the observed spectrum is due to a system in which the two fluorine-proton coupling constants are of opposite sign. Unfortunately an element of doubt remains as the differences between the two theoretical spectra are not large. The spectrum of 2,6-dimethylfluorobenzene was also measured in acetone, methylene iodide, dimethylsulphoxide, and aqueous methanol. Only in acetone was the spectrum altered significantly, $\Delta \nu_{AB}$ for the well-resolved AB_2 system being increased to 10.1 cycles/sec. Again better agreement between observed and calculated spectra was obtained assuming the fluorine-hydrogen coupling constants to be of opposite sign. With the values chosen in Fig. 3A, the chemical shift difference between the meta and para protons is found to be 4.0 cycles/sec with the para proton at higher field. The alternative assumption increases the difference to 6.2 cycles/sec. The methyl groups in 2,6-dimethylfluorobenzene appeared as a doublet of spacing 2.05 cycles/ sec due to coupling with the fluorine nucleus.

Before the results are examined it is necessary to make a correction in the $\Delta \nu_m$ values. The spectrum of 2,6-dimethyldeuterobenzene shows that the meta protons are shifted 10.3 cycles/sec more to high field than the para ones by the methyl groups. Whatever



FIG. 3. Theoretical spectra of aromatic protons in 2,6-dimethylfluorobenzene.

(A) For $J_{AB} = 7.7$ cycles/sec, $J_{\mathbf{F}-\mathbf{H}_B} = 7.0$ cycles/sec, $J_{\mathbf{F}-\mathbf{H}_A} = -2.2$ cycles/sec, $\Delta \nu_{obs} = 8.6$ cycles/sec. (B) For $J_{AB} = 7.7$ cycles/sec, $J_{\mathbf{F}-\mathbf{H}_B} = 7.0$ cycles/sec, $J_{\mathbf{F}-\mathbf{H}_A} = 2.2$ cycles/sec, $\Delta \nu_{obs} = 8.6$ cycles/sec. In this diagram transitions of intensity less than 40% of band at +5.6 are not included. The positions of the A and B nuclei in the absence of coupling are shown below the abscissa.

Н

the origin of this preferential shift, it is necessary to assume that it remains constant throughout the series of compounds measured. If this is true we can assign $\Delta \nu_{m}'$ values = $\Delta \nu - 10.3$ to the meta protons. Now the effect of the methyls is removed and the substituent

2230

FRASER: SUBSTITUTED XYLENES

2231

effect of a deuterium atom appears the same at the meta and para positions. The $\Delta \nu_m$ values are also given in Table I. Let us now consider the chemical shifts observed in 2,6dimethylaniline and its N,N-dimethyl derivative. The para proton in 2,6-dimethylaniline occurs at 47.2 cycles/sec relative to benzene, the meta proton at 29.0 cycles/sec relative to benzene. The value $\Delta \nu_{\rm p} - \Delta \nu_{\rm m}'$ shows that the amino substituent causes the para proton to be shifted 28.5 cycles/sec to higher field relative to the meta, which is corrected for the effect of the methyl group. On the other hand the dimethylamino substituent can be seen to cause only a 10.3 cycles/sec preferential shift of the para proton to higher field. It has been established by ultraviolet spectroscopy and by chemical reactivity (see references 1 and 2 in Table I) that two methyl groups ortho to a dimethylamino group greatly inhibit its resonance interaction with the benzene ring by preventing it from attaining coplanarity with the ring. The large difference in chemical shifts in 2,6-dimethylaniline can be explained by a resonance effect. That is to say the nitrogen atom donates its electrons to the para position more than to the meta position in the ground state and the increase in electron density results in a shift to higher field. The resonance interaction of the dimethylamino group with the ring is greatly decreased and so the effect on the shielding of the para and meta protons is also greatly diminished. The screening at the meta and para positions in the two compounds was calculated from the equations derived by Buckingham. The values 1.62 and 0.94, which Fischer found (12) for the dipole moments of 2,6-dimethylaniline and N,N-dimethyl-2,6-dimethylaniline, were used in the calculation. The dielectric constants for 5% solutions in carbon tetrachloride were estimated to be 2.5 and 2.4 respectively.

For 2,6-dimethylaniline the equations of Buckingham give values for $\Delta \nu_{\rm m}'$ and $\Delta \nu_{\rm p}$ of 6.4 cycles/sec and 7.2 cycles/sec. For the N,N-dimethyl derivative values of 3.7 and 4.1 cycles/sec were obtained. When these are compared with our experimental results it can be seen that the agreement is very poor.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 129.12.217.83 on 11/10/14 For personal use only.

A more obvious contradiction of the electric field effect is seen in the data for 2,6dimethylfluorobenzene. Its dipole moment will most certainly be greater than zero with the negative end directed away from the ring.* Electric field theory then predicts that the para protons will be less screened than the meta when, in fact, the opposite situation has been found.

A plot of $\Delta \nu_{\rm m}'$ and $\Delta \nu_{\rm p}$ against the Hammett sigma constants for each substituent is shown in Fig. 4. No linear relationship is seen as the strongly electron-donating substituents appear at too high field. The same type of behavior was found for the F¹⁹ chemical shifts determined by Gutowsky (14). However, Taft later showed that the observed chemical shifts could be correlated with the inductive and resonance substituent constants $\sigma_{\rm I}$ and $\sigma_{\rm R}$ (7). The measured chemical shifts for the seven compounds whose substituents are free of steric inhibition of resonance were tested for correlation by the equation $\Delta \nu = \alpha \sigma_{\rm I} + \beta \sigma_{\rm R} + \gamma$ where α and β represent the susceptibility of the chemical shift to inductive and resonance effects of the substituent, respectively, and γ represents the constant methyl group effect. The chemical shifts for the meta protons are correlated by the equation $\Delta \nu_{\rm m}' = 14.5 - 17\sigma_{\rm I} - 10\sigma_{\rm R}$, with the maximum error being 2.4 cycles/sec in the case of the bromo compound. The equation $\Delta \nu_{\rm p} = 14.5 - 17\sigma_{\rm I} - 46\sigma_{\rm R}$ gives a better correlation, the maximum error being 1.7 cycles/sec in the iodo compound. As an illustration of the greater susceptibility of the para protons to $\sigma_{\rm R}$, the value $\Delta \nu_{\rm p} - \Delta \nu_{\rm m}'$ for each

*The only available dipole moment data on fluorobenzenes is that of Everard, Kumar, and Sutton (13), who found the dipole moment of fluorobenzene to be 1.48 Debye units. The introduction of two methyl groups could lower the dipole moment by no more than 0.6 Debye unit which would lead to a minimum estimate of 0.88 Debye unit for 2,6-dimethylfluorobenzene.



FIG. 4. Correlation of the shielding of the meta and para protons expressed in cycles per second at 60 Mc/sec from benzene by Hammett's σ 's. FIG. 5. Correlation of the separation in cycles per second at 60 Mc of the meta and para protons by Taft's $\sigma_{\rm R}$.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 129.12.217.83 on 11/10/14 For personal use only.

compound is plotted against the $\sigma_{\rm R}$ value of the substituent in Fig. 5.* The linear relationship is obeyed to within 2.5 cycles/sec for those substituents free from resonance inhibition by the adjacent methyl groups. The substituents for which there is experimental evidence of steric inhibition of resonance are also plotted on the graph using $\sigma_{\rm R}$ values corrected for the percentage of inhibition as listed in Table I. The points for these substituents do not give a good linear plot, which might be interpreted as failure of the spectral and chemical methods to give a quantitative measure of the steric inhibition of resonance. Indeed the theoretical interpretation of the observed decrease in intensity of the ultraviolet absorption spectrum with increasing resonance inhibition, which was proposed by Braude, Sondheimer, and Forbes (15), has been invalidated by the recent work of Waight and Erskine (16). They observed no change in intensity of the ultraviolet spectra of a series of ortho-methylacetophenones with a 216° temperature change, a finding which contradicts Braude and co-worker's theory. It would be too presumptuous on the basis of our limited findings to propose corrected values for resonance inhibition by assuming the linear relationship to be valid for our compounds. It is sufficient to say that the deviation of these compounds from linearity does not refute the proposal that chemical shifts are determined by the inductive and resonance effects of the substituents.

Our findings can be compared with those of Corio and Dailey for the meta and para protons. The absence of ortho protons in our spectra is unimportant as Jackman has pointed out that the ortho shieldings are in many instances misleading (17). Jackman has found that each of the groups CN, Br, COOH, COCl, COCH₃, CHO in 2-substituted-1-propenes causes a shift of the proton cis to it to lower field relative to the trans proton.

*If $\Delta \nu_{\mathbf{m}}' = \alpha \sigma_{\mathbf{I}} + \beta \sigma_{\mathbf{R}} + \gamma$ and $\Delta \nu_{\mathbf{p}} = \alpha \sigma_{\mathbf{I}} + \beta' \sigma_{\mathbf{R}} + \gamma$ then $\Delta \nu_{\mathbf{p}} - \Delta \nu_{\mathbf{m}}' = (\beta' - \beta) \sigma_{\mathbf{R}}$ and so a linear relationship between $\Delta \nu_{\mathbf{p}} - \Delta \nu_{\mathbf{m}}'$ and $\sigma_{\mathbf{R}}$ should be found.

FRASER: SUBSTITUTED XYLENES

2233

The magnitude of the effect varies from 0.05 to 0.5 p.p.m. We have found that the nitro group has an even greater effect. Nitroethylene as a 10% solution in carbon tetrachloride gave a spectrum with well-separated absorption peaks. Assignments were made by assuming the coupling to be greater between protons trans to one another than cis and the results of analysis by first-order perturbation theory are given in Fig. 6. The



FIG. 6. Chemical shifts (τ values) and coupling constants for nitroethylene.

proton cis to the nitro group appears 0.68 p.p.m. to lower field than the proton trans to the nitro group. This effect of substituents will undoubtedly also be present in monosubstituted benzenes and will result in ortho protons appearing to lower field than in the absence of the effect. In instances where the effect is large, e.g. nitro, it could also be significant in the meta position even though it should fall off with the cube of the distance (11, p. 176). Our results are generally in agreement with those of Corio and Dailey although they show much greater sensitivity. For example, phenol showed no resolvable fine structure at 30 Mc/sec whereas 2,6-dimethylphenol showed signals for the meta and para protons separated by 13.2 cycles/sec. There is a discrepancy in the case of the iodo substituent. The values assigned to the para and meta protons in iodobenzene were \pm .10 and \pm .17 p.p.m. or 6.0 and 10.2 cycles/sec at 60 Mc/sec respectively. By subtracting the effect of the methyl groups our results for iodobenzene would be -0.1 and -6.4 cycles/sec respectively. Presumably, the discrepancy is due to those factors mentioned earlier, solvent effects and approximate analysis.

In conclusion it can be stated that our findings are not explainable by the Buckingham electric field theory. They are in agreement with the proposal of Taft that the observed shifts at the meta and para positions are determined by both the inductive and resonance effects of the substituent. The theoretical basis for such a relationship has been clearly discussed by Taft (7). In spite of our findings it should be emphasized that the quantitative value of the correlations is questionable. The meta protons are subject to only small shifts which could easily be overwhelmed by solvent or anisotropy effects. Indeed the recent work of Schneider (18) points out the need for caution. He found that the chemical shifts of the C¹³ nuclei in monosubstituted benzenes show appreciable variation due to resonance at the para position and even larger variation due to resonance and anisotropy effects at the ortho positions. At the meta position the variation in chemical shift was extremely small and not interpretable by resonance effects.

EXPERIMENTAL

The spectra were measured with a Varian V-4302 high-resolution N.M.R. spectrometer. Every result reported is the average of at least three determinations. Peak separations were determined by the side-band technique (11, p. 74) employing a Hewlett-Packard wide-range oscillator. The frequency of the side band was counted after each determination with a Hewlett-Packard 521C frequency counter with an accuracy of ± 0.1 cycle/sec. If a broad peak was being measured the calibration was carried out by superposition of the reference signal on the desired peak. Alternatively, several of the spectra were calibrated by recording the spectrum of the reference and aromatic compound and their

CANADIAN JOURNAL OF CHEMISTRY. VOL. 38, 1960

side bands, then measuring the separation by interpolation. Both methods were used on 2,6-dimethylphenol and were found to agree to within 0.2 cycle/sec. All calibrations with respect to the internal reference were made employing 5% solutions of the aromatic compound in carbon tetrachloride containing 1% of benzene as internal reference. Measurements of the aromatic proton absorption of 2,6-dimethylanisole were made on 20%, 10%, and 5% solutions in carbon tetrachloride. From complete analysis of the multiplet system it was found that the chemical shift between the meta and para protons changed only 0.4 cycle/sec over the range studied. The check on effect of dilution was made since it was necessary to employ a concentration of 10% of some compounds in order to get reproducible measurements of the AB_2 system. For analysis of the deutero, dimethylamino, carboxyl, bromo, and methoxy compounds 5% solutions were employed. It is estimated from the average standard deviation for all compounds that the measured chemical shift between meta and para protons is accurate to within 0.4 cycle/sec and that the same accuracy was obtained for reference measurements. This would lead to a maximum possible error of ± 0.8 cycle/sec for the chemical shifts in Table I. The τ values for the methyl groups as listed in the table were obtained from measurements on 5%solutions in carbon tetrachloride containing 1% of tetramethylsilane. The nitroethylene spectrum was obtained from a 10% solution in carbon tetrachloride containing 1% of tetramethylsilane.

2,6-Dimethylaniline

Reagent grade 2,6-dimethylaniline (Eastman Kodak Co.) was freshly distilled from zinc dust to give a liquid, b.p. 79–80°, 6 mm, $n_{\rm D}^{25}$ 1.5588 (literature b.p. 216°, 747 mm, $n_{\rm D}^{20}$ 1.5602 (19)).

2,6-Dimethylnitrobenzene

Practical grade 2,6-dimethyl-1-nitrobenzene (Eastman Kodak Co.) was distilled before use to give a light yellow liquid, b.p. 81°, 7 mm, $n_{\rm D}^{25}$ 1.5203 (literature b.p. 225°, 744 mm (20, Vol. 3, p. 815)).

2,6-Dimethylphenol

Reagent grade 2,6-dimethylphenol (Eastman Kodak Co.) was twice sublimed before use to give white crystals, m.p. 43-44.5° (literature m.p. 49° (20, Vol. 4, p. 680)).

2,6-Dimethylanisole

Methylation of 2,6-dimethylphenol with dimethyl sulphate in alkali (21, p. 58) gave 69% of product from which a portion was redistilled to give a colorless liquid, b.p. 54°, 6 mm, $n_{\rm D}^{23}$ 1.5024 (literature b.p. 66–67°, 11 mm, $n_{\rm D}^{25}$ 1.5003 (22)).

N-Methyl-2,6-dimethylaniline

A mixture of 2.55 g (0.021 mole) of 2,6-dimethylaniline and 3.2 g (0.023 mole) of methyl iodide was heated under reflux for 30 minutes. The solid which formed was recrystallized from chloroform and acetone. The purified solid, 2.7 g, was then dissolved in 10% sodium bicarbonate and the solution extracted twice with ether. The ether extracts were dried over magnesium sulphate, then filtered, and the filtrate was distilled to remove the ether. The residue, 1.1 g (37%), was distilled through a Holtzmann column to give N-methyl-2,6-dimethylaniline, b.p. 73.5–74°, 6 mm, $n_{\rm D}^{25}$ 1.5347 (literature b.p. 87°, 13 mm (12)).

N,N-Dimethyl-2,6-dimethylaniline

Following the procedure of Brown and Grayson (19), N,N-dimethyl-2,6-dimethylaniline was prepared in 41% yield. The product distilled at 64–64.5°, 5 mm, $n_{\rm D}^{24}$ 1.5136 (literature b.p. 195°, 740 mm, $n_{\rm D}^{25}$ 1.5133 (19)).

2234

FRASER: SUBSTITUTED XYLENES

2,6-Dimethylbenzonitrile

The nitrile was obtained in 37% yield from 2,6-dimethylaniline by diazotization and treatment with cuprous cyanide (21, p. 514). The product melted from 88–89.3° (literature m.p. 90–91° (23)).

2,6-Dimethylbenzoic Acid

The nitrile was converted to the amide by treatment with concentrated sulphuric acid and thence to the acid by heating with 100% phosphoric acid as described by Berger and Olivier (24). The acid after recrystallization from benzene melted from $115.5-116.5^{\circ}$ (literature m.p. $115-116^{\circ}$ (24)).

2,6-Dimethyliodobenzene

Following the procedure used for the preparation of iodobenzene (25, p. 351), 2,6-dimethylaniline was converted to the iodo compound in 14% yield. The product was a liquid, b.p. 98–99°, 9 mm (literature b.p. 228–230° (20, Vol. 3, p. 49)). Calc. for C_8H_9I : C, 41.4; H, 3.9. Found: C, 41.6; H, 3.7.

2,6-Dimethylbromobenzene

The procedure used for the conversion of *o*-toluene to *o*-bromotoluene (21, p. 135) was employed to convert 2,6-dimethylaniline into 2,6-dimethylbromobenzene in 15% yield. The product was a liquid, b.p. 74.5–75°, 7 mm, $n_{\rm D}^{25}$ 1.5532 (literature b.p. 206° (20, p. 379)). Calc. for C₈H₉Br: C, 51.8; H, 4.9. Found: C, 52.4, 51.9; H, 5.0, 5.0.

2,6-Dimethylfluorobenzene

This compound, although not previously prepared, was readily obtained from 2,6-dimethylaniline following exactly the procedure for the conversion of aniline to fluorobenzene (25, p. 295). The product was obtained in 40% yield as a liquid, b.p. 85°, 115 mm, $n_{\rm p}^{28}$ 1.4762. Calc. for C₈H₉F: C, 77.4; H, 7.3. Found: C, 77.6; H, 7.4.

2,6-Dimethylbenzene-1-d

The procedure for the preparation of this compound was kindly provided by Dr. L. C. Leitch (26). A mixture of 5 g of 2,6-dimethylaniline and 8 ml of heavy water (99.9%) containing a pellet of sodium hydroxide was stirred for 8 hours at 80°. The heavy water was separated in a separatory funnel and the exchange procedure was repeated twice more with fresh heavy water. The amine, 4.18 g (0.035 mole), was added to 12.1 ml of completely deuterated 50% hypophosphorous acid and 6.2 ml of heavy water and the mixture was cooled to -5° in an ice-salt bath. To this was added dropwise a solution of 2.38 g (0.035 mole) of sodium nitrite in 4.2 ml of heavy water keeping the temperature below 0°. The resultant solution was kept at 0° for 20 hours then extracted with ether. The extracts were dried over magnesium sulphate, filtered, and after removal of the ether under reduced pressure, distillation of the residue gave 0.7 g of colorless liquid, b.p. 65° (80 mm), whose N.M.R. spectrum gave no indication of contamination by other products.

Nitroethylene

This compound was prepared by the sequence recommended by Noland (27). The product was a lachrymatory yellow liquid, b.p. 43°, 90 mm, (literature b.p. 38–39°, 80 mm (28)).

ACKNOWLEDGMENTS

The author is grateful to Dr. W. G. Schneider for his helpful discussions. The author wishes to thank Dr. L. C. Leitch for providing the method of preparation of 2,6-dimethylbenzene-1-*d* and for a gift of deuterated hypophosphorous acid. The financial assistance

2235

CANADIAN JOURNAL OF CHEMISTRY. VOL. 38, 1960

of the National Research Council of Canada is gratefully acknowledged. The author is also indebted to Mrs. V. Nicolson for technical assistance and to Miss E. Busk for the microanalyses.

REFERENCES

REFERENCES
1. H. J. BERNSTEIN, J. A. POPLE, and W. G. SCHNEIDER. Can. J. Chem. 35, 65 (1957).
2. W. G. SCHNEIDER, H. J. BERNSTEIN, and J. A. POPLE. Ann. N.Y. Acad. Sci. 70, 806 (1958).
3. P. L. CORIO and B. P. DALLEY. J. Am. Chem. Soc. 78, 3043 (1956).
4. A. A. BOTHNER-BY and R. E. GLICK. J. Chem. Phys. 26, 1651 (1957).
5. R. W. TAFT, JR., S. EHRENSON, J. C. LEWIS, and R. E. GLICK. J. Am. Chem. Soc. 81, 5352 (1959).
6. R. W. TAFT, JR. In Steric effects in organic chemistry. Edited by M. S. Newman. John Wiley and Sons, Inc., New York. 1956. p. 594.
7. R. W. TAFT, JR. J. Am. Chem. Soc. 79, 1045 (1957).
8. A. D. BUCKINGHAM. Can. J. Chem. 38, 300 (1960).
9. F. A. L. ANET. Proc. Chem. Soc. 327 (1959).
10. H. S. GUTOWSKY, C. H. HOLM, A. SAIKA, and G. A. WILLIAMS. J. Am. Chem. Soc. 79, 4596 (1957).
11. J. A. POPLE, W. G. SCHNEIDER, and H. J. BERNSTEIN. High-resolution nuclear magnetic resonance. McGraw-Hill Book Co., Inc., New York. 1959. p. 88.
12. I. FISCHER. Acta Chem. Scand. 4, 1197 (1950).
13. K. B. EVERARD, L. KUMAR, and L. E. SUTTON. J. Chem. Soc. 2807 (1951).
14. H. S. GUTOWSKY, D. W. MCCALL, B. R. MCGARVEY, and L. H. MEYER. J. Am. Chem. Soc. 74, 4809 (1952).

- H. S. OUTOWSKI, D. W. BROCHE, Z. T. AND MARKEN, D. W. BROCHE, Z. T. M. LACEMAN, Applications, Butterworths Scientific Publications, London. 1958. p. 75.
 J. M. LACEMAN, Applications of nuclear magnetic resonance spectroscopy in organic chemistry.

L. M. JACKMAN. Applications of nuclear magnetic resonance spectroscopy in organic chemistry. Pergamon Press, New York. 1959. p. 123.
 W. G. SCHNEIDER. To be published.
 H. C. BROWN and M. GRAYSON. J. Am. Chem. Soc. 75, 20 (1953).
 I. HEILBRON and H. M. BUNBURY. Dictionary of organic compounds. Eyre and Spottiswoode Ltd., Lorder 1962.

- London. 1953.
- ORGANIC SYNTHESES. Coll. Vol. I, p. 58.
 ORGANIC SYNTHESES. Coll. Vol. I, p. 58.
 D. Y. CURTIN and R. R. FRASER. J. Am. Chem. Soc. 80, 6016 (1958).
 R. SCHOLL and F. KACER. Ber. 36, 327 (1903).
 G. BERGER and S. C. J. OLIVIER. Rec. trav. Chim. 46, 600 (1927).
 ORGANIC SYNTHESES. Coll. Vol. II. p. 351.
 C. LEVEL. Private communication

- L. C. LEITCH. Private communication.
 W. E. NOLAND, H. I. FREEMAN, and M. S. BAKER. J. Am. Chem. Soc. 78, 188 (1956).
 N. LEVY and C. W. SCAIFE. J. Chem. Soc. 1471 (1947).

2236

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 129.12.217.83 on 11/10/14 For personal use only.