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# Para-Substituted Toluenes. Evaluation of Long-Range Carbon–Hydrogen Coupling Constants

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*Received May 13, 1977*

Carbon-13 NMR spectra for a series of para-substituted toluenes were obtained and the proton-coupled spectra were analyzed. It is shown that the coupling patterns observed are characteristic for each type of carbon signal and can be used as "fingerprints". One-bond carbon–hydrogen coupling constants $J_{77}$ and $J_{22}$ were found to vary systematically and were analyzed using the Swain–Lupton $\mathcal{F}$ and $\mathcal{R}$ treatment. Chemical-shift substituent effects were found to be similar in direction and magnitude to those obtained for monosubstituted benzenes.

A great number of studies concerning the carbon-13 NMR spectral properties of aromatic compounds, particularly benzenoid systems, have been reported over the last few years.[1b–e] While considerable attention has been devoted to chemical-shift data and substituent effects, natural-abundance carbon-13–hydrogen coupling constant data have been generally neglected.[2] (In favorable instances, one-bond carbon–hydrogen coupling constants have been obtained from the carbon-13 satellites appearing in proton NMR spectra.[3]) Natural-abundance long-range carbon-13–hydrogen coupling-constant investigations of benzene derivatives are indeed rare, limited only to benzene,[4] halobenzenes,[5] toluene[6] and some substituted phenols.[7] The major problem associated with obtaining proton-coupled carbon-13 spectra is inherent in the nature of the carbon-13 nucleus.[8] However, recent advances in instrumentation, especially the introduction of "gated-decoupling,"[9] have facilitated the measurement of proton-coupled spectra. Additionally, a spectrometer system equipped with a crystal filter[10a] or quadrature detection[10b] can reduce the total time necessary to obtain a spectrum by ca. one-half.

The information contained in the proton-coupled spectrum can be perceived in a study of ortho-disubstituted benzenes, whereby carbon-13 shift assignments were made by simple inspection of the coupling "fingerprint."[11] (The use of "fingerprints" in proton NMR aromatic shift assignments is exemplified in an investigation by Zanger.[12]) While the above example represents the ideal situation, careful inspection of the more complex proton-coupled spectrum of monosubstituted benzenes can often lead to the carbon-shift assignments.[7,13] The purpose of the present report is to evaluate the proton-coupled carbon-13 spectra for a series of para-substituted toluenes.

## Experimental Section

All compounds used in this study were commercially available materials requiring no further purification as indicated by the lack of significant additional signals in both the proton and carbon-13 NMR spectra. Sample concentrations, in deuteriochloroform, were ca. 20% w/v for chemical-shift determinations, and ca. 60% w/v for coupling-constant data. Sample tubes with an o.d. of 10 mm were used. The carbon-13 magnetic resonance spectra were obtained in the Fourier transform mode on a JEOL FX-60 spectrometer system operating at 15.03 MHz, and equipped with a Texas Instruments computer with 24K memory.

General NMR spectral and instrumental parameters used were: internal deuterium lock to solvent, spectral width of 2500 Hz for decoupled spectra and 500 Hz for proton-coupled spectra, a pulse width of 4 $\mu$s, corresponding to a 36° pulse angle, and a pulse repetition time of 1.8 s. All proton-coupled spectra were obtained in the "gated" mode, and the free induction decay signal was worked up without a window function. For all decoupled spectra 8K data points were used, while for proton-coupled spectra 16K data points were employed.

All chemical shifts are referenced to internal $Me_4Si$ and are esti-

**Table I. Carbon-13 Chemical Shift Values ($\delta_c$) for a Series of Para-Substituted Toluenes[a]**

| X | Registry no. | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_7$ |
|---|---|---|---|---|---|---|
| H | 108-88-3 | 137.8 | 129.3 | 128.5 | 125.6 | 21.3 |
| F | 352-32-9 | 133.4 | 130.4 | 115.0 | 161.3 | 20.5 |
| Cl | 106-43-4 | 136.2 | 130.4 | 128.3 | 131.2 | 20.7 |
| Br | 106-38-7 | 136.5 | 130.7 | 131.1 | 119.0 | 20.8 |
| I | 624-31-7 | 136.9 | 130.9 | 136.9 | 90.2 | 20.9 |
| OH | 106-44-5 | 130.2 | 130.2 | 115.4 | 152.8 | 20.3 |
| OMe | 104-93-8 | 129.7 | 129.9 | 113.8 | 157.7 | 20.4 |
| SH | 106-45-6 | 126.7 | 129.7 | 129.7 | 135.2 | 20.8 |
| $NH_2$ | 106-49-0 | 127.5 | 129.7 | 115.2 | 144.0 | 20.5 |
| CN | 104-85-8 | 143.8 | 130.0 | 131.9 | 109.3 | 21.7 (119.1) |
| $NO_2$ | 99-99-0 | 146.2 | 129.9 | 123.4 | 146.2 | 21.5 |
| $CH_3$ | 106-42-3 | 134.6 | 129.0 | 129.0 | 134.6 | 20.9 |

[a] In parts per million from internal $Me_4Si$.

Table II. Substituent Chemical Shifts for a Series of Para-Substituted Toluenes

| X | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_7$ |
|---|---|---|---|---|---|
| F | −4.4[a] | 1.1 | −13.5 | 36.7 | −0.8 |
| Cl | −1.4 | 1.1 | −0.2 | 5.6 | −0.6 |
| Br | −1.3 | 1.4 | 2.6 | −6.6 | −0.5 |
| I | −0.9 | 1.6 | 8.4 | −35.4 | −0.4 |
| OH | −7.6 | 0.9 | −13.1 | 27.2 | −1.0 |
| OMe | −8.1 | 0.6 | −14.7 | 32.1 | −0.9 |
| SH | −11.1 | 0.4 | 1.2 | 9.6 | −0.5 |
| $NH_2$ | −10.3 | 0.4 | −13.3 | 18.4 | −0.8 |
| CN | 6.0 | 0.7 | 3.4 | −16.3 | 0.4 |
| $NO_2$ | 8.4 | 0.6 | −5.1 | 20.6 | 0.2 |
| $CH_3$ | −3.2 | −0.3 | 0.5 | 9.0 | −0.4 |

[a] Negative numbers indicate an upfield shift.

mated to be accurate to ±0.05 ppm. Coupling-constant data were measured from expanded spectra, and relative line positions are believed to be accurate to ±0.06 Hz. The observed coupling constants themselves are probably accurate to at least ±0.2 Hz.

## Results and Discussion

**Chemical-Shift Values.** The carbon-13 chemical shift values for the para-substituted toluene series are given in Table I, and the substituent chemical shifts ($\Delta\delta = \delta_{\text{toluene}} - \delta_{\text{obsd}}$, negative sign indicates upfield shift) are listed in Table II. The substituent effects are not greatly affected by the *p*-methyl moiety and compare well with the substituent effects reported for monosubstituted benzenes.[1d] Carbon assignments were made on the basis of the substituent effects and of the appearance of the proton-coupled spectrum (vide infra). In a recent investigation, Taft et al. suggested that caution should be exerised when making carbon-13 assignments simply from substituent effect additivity based solely on monosubstituted benzene data because the substituent shifts depend upon the nature of the fixed substituent.[14] However, the fixed methyl substituent does not cause any large deviations from the monosubstituted benzene data.

**Coupling-Constant Data.** For ease of discussion, the coupling-constant data obtained for each carbon type will be presented separately (see Table III). Certain coupling-con-

Table III. Carbon-13–hydrogen Coupling Constants in Para-Substituted Toluenes

| | | *J*, Hz | | |
|---|---|---|---|---|
| $C_1$ | $C_{2(6)}$ | $C_{3(5)}$ | $C_4$ | $C_7$ |
| | | H[a] | | |
| −6.0 ($H_7$) | 4.6 ($H_7$) | 157.6 ($H_3$) | 0.8 ($H_7$) | 126.0 ($H_7$) |
| 0.5 ($H_2$) | 155.9 ($H_2$) | 7.9 ($H_5$) | 7.8 ($H_2$) | 5.0 ($H_2$) |
| 7.6 ($H_3$) | 6.6 ($H_6$) | | 1.1 ($H_3$) | −0.4 ($H_3$) |
| | | Cl | | |
| 6.4 ($H_7$) | 4.9 ($H_7$) | 163.4 ($H_3$) | 1.1 ($H_7$) | 126.4 ($H_7$) |
| | 160.0 ($H_2$) | 4.6 ($H_5$) | 10.6 ($H_2$) | 4.3 ($H_2$) |
| 6.4 ($H_3$) | 6.6 ($H_6$) | | 0.6 ($H_3$) | 0.4 ($H_3$) |
| | | Br | | |
| 6.2 ($H_7$) | 5.0 ($H_7$) | 165.2 ($H_3$) | 1.1 ($H_7$) | 126.4 ($H_7$) |
| | 159.1 ($H_2$) | 6.3 ($H_5$) | 10.5 ($H_2$) | 4.3 ($H_2$) |
| 6.2 ($H_3$) | 6.7 ($H_6$) | | 0.6 ($H_3$) | 0.4 ($H_3$) |
| | | I | | |
| 6.3 ($H_7$) | 4.9 ($H_7$) | 165.2 ($H_3$) | 1.1 ($H_7$) | 126.4 ($H_7$) |
| 1.2 ($H_2$) | 158.6 ($H_2$) | 6.3 ($H_5$) | 10.5 ($H_2$) | 4.3 ($H_2$) |
| 6.3 ($H_3$) | 6.5 ($H_6$) | | 0.6 ($H_3$) | 0.4 ($H_3$) |
| | | OH | | |
| 6.3 ($H_7$) | 5.0 ($H_7$) | 158.5 ($H_3$) | | 125.8 ($H_7$) |
| | 157.1 ($H_2$) | 3.8 ($H_5$) | 7.4 ($H_2$) | 4.0 ($H_2$) |
| 6.3 ($H_3$) | 6.2 ($H_6$) | | | 0.6 ($H_3$) |
| | | SH | | |
| 6.2 ($H_7$) | 4.8 ($H_7$) | 158.0 ($H_3$) | | 125.4 ($H_7$) |
| | 157.9 ($H_2$) | 4.9 ($H_5$) | 7.2 ($H_2$) | 4.4 ($H_2$) |
| 6.2 ($H_3$) | 5.7 ($H_6$) | | | |
| | | $NH_2$ | | |
| 6.2 ($H_7$) | 4.9 ($H_7$) | 161.2 ($H_3$) | | 125.7 ($H_7$) |
| 0.6 ($H_2$) | 155.3 ($H_2$) | 5.4 ($H_5$) | 8.4 ($H_2$) | 4.3 ($H_2$) |
| 6.2 ($H_3$) | 7.1 ($H_6$) | | | 0.4 ($H_3$) |
| | | OMe | | |
| 6.4 ($H_7$) | 5.0 ($H_7$) | 159.3 ($H_3$) | | 126.0 ($H_7$) |
| 0.8 ($H_2$) | 156.2 ($H_2$) | 4.5 ($H_5$) | | 4.3 ($H_2$) |
| 6.4 ($H_3$) | 6.8 ($H_6$) | | | 0.4 ($H_3$) |
| | | CN | | |
| 6.5 ($H_7$) | 5.1 ($H_7$) | 164.6 ($H_3$) | | 126.9 ($H_7$) |
| 0.8 ($H_2$) | 161.7 ($H_2$) | 5.8 ($H_5$) | 8.0 ($H_2$) | 4.3 ($H_2$) |
| 6.5 ($H_3$) | 5.3 ($H_6$) | | | 0.7 ($H_3$) |
| | | $NO_2$ | | |
| 6.2 ($H_7$) | 5.0 ($H_7$) | 162.7 ($H_3$) | | 127.1 ($H_7$) |
| 0.7 ($H_2$) | 162.7 ($H_2$) | 4.5 ($H_5$) | | 4.3 ($H_2$) |
| 6.0 ($H_3$) | 6.8 ($H_6$) | | | 0.6 ($H_3$) |

[a] M. Hansen and H. J. Jakobsen, *J. Magn. Reson*, **20**, 520 (1975).

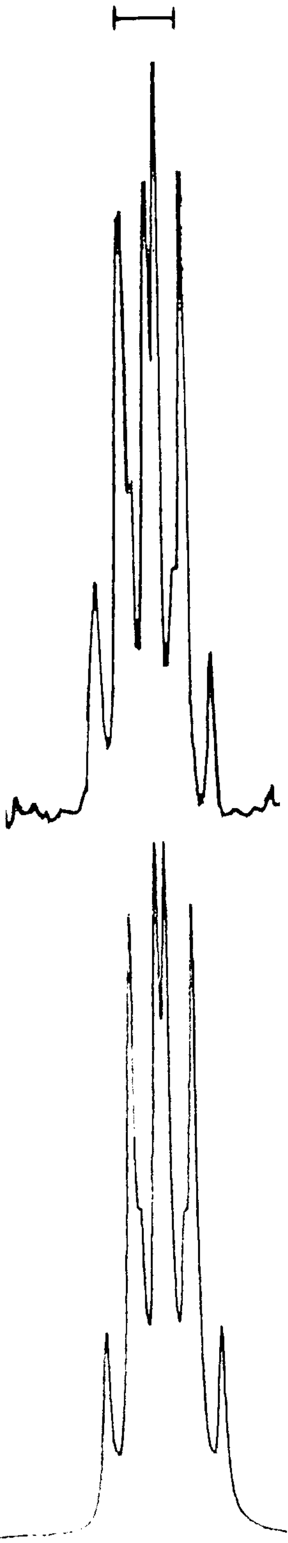
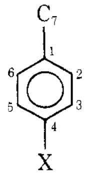


Figure 1. Top: lower-field half of the proton-coupled carbon-13 spectrum of $C_2$ in p-chlorotoluene. Bottom: calculated spectrum for $C_2$ using p-chlorotoluene data. Measure bar is 10 Hz.

stant data were unobtainable even at spectral widths that would allow better than 0.06-Hz data-point resolution. These carbon–hydrogen coupling constants were of the two or four bond variety, whose magnitudes in this type of aromatic system are generally on the order of 1 Hz or less.[4-6] The numbering sequence is shown below.



Before proceeding with the discussion concerning the carbon–hydrogen coupling constants, an understanding of the method used to obtain those values is warranted. The carbon-13 proton-coupled spectrum of the methyl carbon $C_7$ and ring carbons $C_1$ and $C_4$ represent the X part of separate AA′-BB′$M_3$X spin systems, while ring carbons $C_2$ ($C_6$) and $C_3$ ($C_5$) represent the X part of separate ABCD$M_3$X spin systems. Because of the unobservable long-range couplings of the two and four bond variety, these complex spin systems were found to be amenable to analysis by a more simplified notation. For example, the $C_2$ spin system was analyzed assuming it to be an AB$M_3$X system, while $C_1$ simplifies to AA′$M_3$X. In *principle*, the $J_{AX}$ and $J_{BX}$ values can not be obtained directly from the relative line positions, only the sum ($J_{AX} + J_{BX}$) can be directly measured, the true values being obtained by computer simulation. However, there is strong precedence in the literature indicating that in certain systems direct measurement of observed spectral splittings of the proton-coupled carbon-13 spectrum yields excellent values for the coupling constants.[7,15] Under such conditions (AA′X type spin systems), Roberts et al. obtained the coupling-constant values for benzene.[4] In addition, the directly observed values should be of more use to the practicing organic chemist.

In order to substantiate the premise that useful coupling constants for the para-substituted toluenes could be read directly from the spectrum, noniterative spectral analysis of the $C_2$ coupling pattern was performed. $C_2$ was chosen because its coupling pattern was of reasonable complexity. If the values obtained by first-order analysis are useful, then there should be little difference between the directly measured splittings and splittings dictated by the input data. In all of the instances (including selected examples involving $C_1$ and $C_3$), the correlation between measured splittings and input data was excellent, within the ±0.1 Hz experimental accuracy. A comparison of the observed and calculated spectrum for $C_2$ is shown in Figure 1. It may be noted that there is some intensity skewing in the observed spectrum, indicating that these systems are not strictly first order.

A less extensive study done in this laboratory of unsymmetrical meta-disubstituted benzenes indicates a limitation on the use of first-order rules. The apparent problem associated with the meta series lies in the nonsymmetrical nature of the paired splitting patterns. The coupling patterns in the para series did not suffer from this problem and in view of the above discussion the values obtained by first-order analysis are believed to be useful.

**Methyl Carbon ($C_7$).** The proton-coupled carbon-13 spectrum of the methyl carbon $C_7$ appears grossly as a quartet of triplets, arising from a large one-bond coupling to the three directly attached protons, $J_{77}$, and a three-bond coupling to the protons at carbons 2 and 6, $J_{72}$. Inspection of the triplets at a larger sweep width indicates further coupling arising from protons on carbons 3 and 5, $J_{73}$. From the data in Table III, it is noticed that the size of the one-bond coupling $J_{77}$ is affected by the para substituent. Analysis of the $J_{77}$ values using a dual substituent parameter equation[16] with the Swain–Lupton $\mathcal{F}$ and $\mathcal{R}$ values[17] yields regression coefficients of 0.88 and 0.84, respectively, $\bar{r}$ = 0.98, average error 0.07 Hz. This result is consistent with the values recently reported by Yoder et al.[18] The $J_{72}$ value appears to be unaffected by the para substituent.

**Carbon 1.** Carbon 1 is a nonprotonated center and appears in the proton-coupled spectrum as a first-order sextet with peak-area ratios of almost exactly 1:5:10:10:5:1. This spectral pattern arises as a consequence of the equality of the coupling constants to the methyl protons, $J_{17}$, and the three-bond coupling to the protons on carbons 3 and 5, $J_{13}$. In some cases,

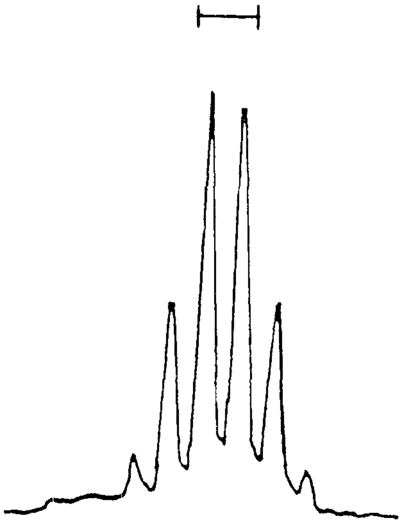


**Figure 2.** Proton-coupled carbon-13 spectrum of $C_1$ in *p*-chlorotoluene. Measure bar is 10 Hz.

careful inspection of the central two peaks (because of their greater intensity) reveals another small coupling attributable to protons on carbons 2 and 6, $J_{12}$; thus, each peak in the sextet is further split into a triplet. The data in Table III indicate that $J_{17}$ and $J_{13}$ remain fairly constant, with $J_{13}$ reduced in magnitude vs. the analogous coupling constant found for toluene and $J_{17}$ being slightly larger than the toluene value.

**Carbon 2 (6).** Each half of the proton-coupled spectrum of carbon 2 (6) appears as an octet. This pattern arises from the coupling with the methyl protons, $J_{27}$, being further split by the coupling of the ring protons 2 (6) and 6 (2). In the instance of *p*-cyanotoluene, this spectral pattern appears as a quintet owing to the near equality of the $J_{27}$ and $J_{26}$ coupling constants. From the coupling-constant data given in Table III, it can be seen that $J_{27}$ is larger than that found for toluene and this value remains fairly constant. This result is consistent with recent theoretical calculations which indicate that para substitution increases the $J_{27}$ coupling constant.[20] The coupling constant across the methyl moiety, $J_{26}$, varies from 5.3 to 7.1 Hz with an average value of 6.4 Hz. No apparent trend (correlation with dual substituent shift equation or with group electronegativity is poor) is observed for the $J_{26}$ coupling constant values.

The one-bond carbon–hydrogen coupling, $J_{22}$, is seen to vary in a regular manner. Using the Swain–Lupton $\mathcal{F}$ and $\mathcal{R}$ values and the dual substituent parameter equation, a regression coefficient of 5.5 $\mathcal{F}$ and 2.7 $\mathcal{R}$ is obtained, $\bar{r} = 0.98$, average error 0.4 Hz. This result may be rationalized as follows. The presence of an electron-withdrawing group increases the effective electronegativity of the aromatic ring which causes increased polarization of the C–H bond, resulting in a larger coupling constant.[21] Conversely, for electron-donating groups a decrease in the s character of the C–H bond occurs and a smaller coupling constant is obtained. This observation is seen to parallel the data for $J_{77}$, the one-bond methyl coupling constant.

**Carbon 3 (5).** Each half of the proton-coupled spectrum of $C_{3\ (5)}$ appears as a sharp doublet owing to a three-bond coupling to the proton on $C_{5\ (3)}$. (Under a number of different spectral parameter conditions, no other long-range couplings to this carbon could be observed.) All of the one-bond coupling constants, $J_{33}$, are seen to be larger than that found for toluene. The long-range coupling constant $J_{35}$ varies from 3.8 to 6.3 and is smaller than the analogous toluene values. This reduction in the coupling constant across an electronegative moiety parallels the calculated reduction of the analogous coupling in fluorobenzene.[20] No correlation with the Swain–Lupton values was obtained.

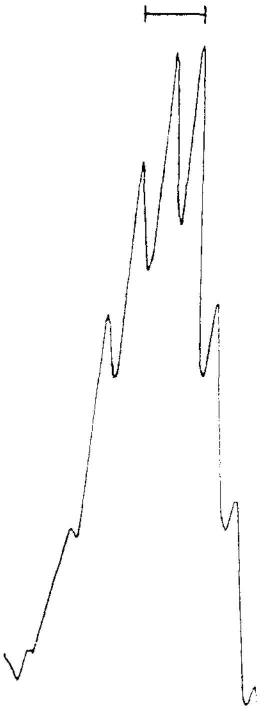


**Figure 3.** Expanded view of the central peak of the proton-coupled carbon-13 spectrum of $C_4$ in *p*-iodotoluene. Measure bar is 1 Hz.

**Carbon 4.** The coupling pattern for $C_4$, by preliminary inspection, appears as a simple triplet; however, an expanded spectrum reveals, in some cases, a very complex pattern. In the instance of para-halo toluenes, long-range coupling to the methyl protons could clearly be observed. The central peak of the proton-coupled pattern for carbon 4 in *p*-iodotoluene is shown in Figure 3. No general trends were observed in the $J_{42}$ coupling constant.

**Conclusions.** It has been found that the proton-coupled carbon-13 spectra of para-substituted toluenes yield "fingerprint" patterns which can be readily utilized for making signal assignments. In the instance of para-substituted toluenes, the proton–carbon coupling constants can be read directly from the spectrum. The coupling constants $J_{22}$, $J_{33}$, $J_{35}$, and $J_{24}$ are substantially influenced by the nature of the para substituent. This can be rationalized, in part, to be due to changes in the hybridization of the individual C–H bonds. It is clear, however, that other factors such as changes in excitation energy[22] and $\pi$-bond orders[15b] play an important role in determining the magnitude of these long-range coupling constants.

**Acknowledgments.** The financial support of this work by the Robert A. Welch Foundation is gratefully acknowledged. In addition, the author thanks Professor Paul D. Bartlett for his encouragement during the course of this research.

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$$\delta = f\mathcal{F} + r\mathcal{R} = i$$

where $i$ is the intercept of the equation and $f$ and $r$ are the regression coefficients; see ref 18. $\mathcal{F}$ and $\mathcal{R}$ are contributions arising from field and inductive effects taken together and resonance effects, respectively.

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# Highly Stereoselective Methanolysis of Diazaoxyphospholenes

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*Received May 24, 1977*

When the diazaoxyphospholene *cis*-**2** is placed in a neutral absolute methanol solution, it gives both isomerization to *trans*-**2** and ring opening with exclusive formation of only one (**3b**) of the four possible diastereomeric β-phenylhydrazone methylphosphinates **3**. In the same conditions the isomer *trans*-**2** gives the same diastereomer **3b**. The relative configuration of the two chiral centers in **3b** is tentatively assigned. The high stereoselectivity is explained in terms of pentacoordinate phosphorus intermediates, in which steric factors have a considerable influence on their stability.

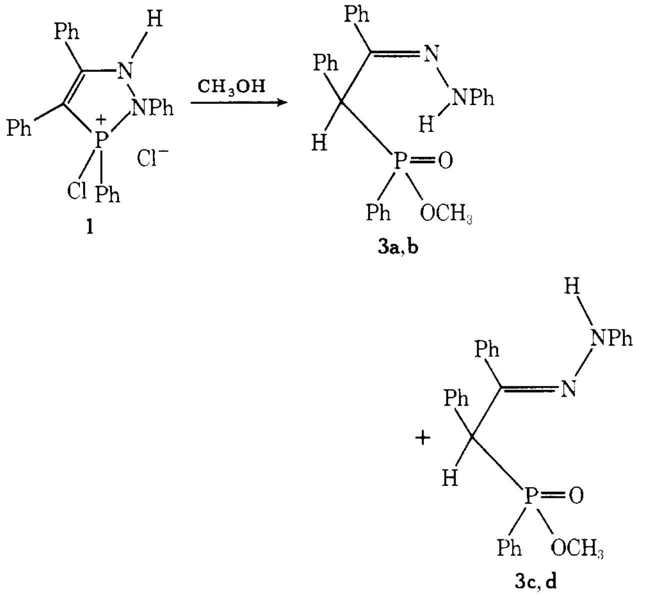
The discovery of the role played by a small ring containing phosphorus in determining the behavior of the nucleophilic displacement reaction at a phosphoryl center has led to wide research in this field.[1-5] Generally these attacks on phosphorus contained in a five- or four-membered ring are rationalized by assuming the formation of intermediates with pertacoordinated phosphorus.[5,6]

Considerable information is now available[6-8] on the factors which effect the stability of such phosphorane derivatives and control the process of ligand reorganization within them. Two factors turn out to be important in this connection: (a) the preference of electronegative groups for the apical positions and (b) the preference of a small-membered ring for an apical-equatorial situation.[7-10] However, the reaction stereochemistry may also be dependent on the steric interactions as well as on the specific reaction conditions.

In this paper we report a case in which a steric effect is the main factor in highly stereoselective stereochemical results.

## Results

In previous communications we reported that the diazaphospholene cycloadduct **1** undergoes exclusive ring opening when treated with neutral absolute methanol,[11] while ring retention was observed when the adduct was treated with water under the same reaction conditions.[12] This unexpected behavior was rationalized[11] on the basis of the relative apicophilicities of hydroxyl and methoxy groups compared to the diaza group. Each one of the four diastereomeric β-phenylhydrazone methyl phosphinates **3** was isolated in pure form.



Configurational assignment about the C=N has been determined by proton NMR spectroscopy. From the data presented in Table I, it should be noted that the methine proton in isomers **3a** and **3b** resonates at lower magnetic fields (deshielded) than that of **3c** and **3d,** suggesting[13] that isomers **3a** and **3b** have the syn configuration defined as that in which the anilino and benzylic groups are on the same side of the C=N bond. Moreover, our NMR data were in good agreement with Karabatsos[14] on the analysis of the anisotropic effects of the benzene ring on the syn and anti methinic hydrogens.

Another NMR correlation which is potentially useful for configurational assignments involves the chemical shift difference in the NH proton resonance of diastereomers **3.** The NH of **3a** and **3b** is strongly intramolecularly bonded as evidenced from the low-resonance value.

In contrast the NH of the other forms **3c** and **3d,** incapable of this hydrogen bonding, resonates at higher magnetic field (masked by aromatic protons). Hence, in the diastereomers

0022-3263/78/1943-0216$01.00/0