C–Cl bonds[32] is expected to be the main distortion to increase distance *d*. The energy corresponding to an in-plane deformation of the C–Cl bond by $\theta°$ is $U = {}^1/_2k \cdot d_{\text{C-Cl}}{}^2\theta^2$, where *k* is the in-plane bending force constant,[33] $k = 0.96 \times 10^5$ dyn cm^{-1}, $d_{\text{C-Cl}}$ is the C–Cl bond distance, 1.71 Å, and θ is the deformation angle. For $\theta = 5$ and 10° one obtains $U = 3.1$ and 12.3 kcal/mol, respectively. This increases the distance *d* by 0.2 and 0.33 Å. The geometry of the interactions in compound II is not so favorable as that in I. First, the decrease in CCCl angle which will result in an increase in *d* requires energy to overcome both the repulsion due to the second chlorine on the exocyclic methylene and to deform the C–Cl bond angles. The two chlorines at the exocyclic methylene group have a "butressing effect" on each other.

An interesting experiment which could contribute to our understanding of the origin of the energy barrier would involve measuring the ring inversion in derivatives of compounds I and II substituted with chlorines in positions 2 and 7. These chlorines would be expected particularly in compound I to inhibit bending of C–Cl bonds through a "butressing effect." Similar effects have been observed in the biphenyl series.[34]

The explanation of the larger barrier to inversion in II when compared to I is relatively simple; the difference undoubtedly arises from the larger size of the bromine atoms in comparison to chlorine atoms. Since the analogy between the gross structure of the transition states in the racemization of optically active biphenyls and the inversion in compounds of the kind exemplified by I, II, and III has been drawn, it is of interest to compare the data for the racemization of 2,2′-dibromo-4,4′-dicarboxybiphenyl (IV) and the inversion data for III. Harris[35] measured the rate constants for the racemization of IV in ethanol and found that the Arrhenius activation energy was 18.9 kcal mol^{-1} while $\Delta S^{\ddagger}$ was −4.9 eu. Using the experimental data $\Delta F^{\ddagger}$ was found to be 20.0 kcal mol^{-1} at 25°. These data compare quite favorably with the $\Delta H^{\ddagger}$ and $\Delta F^{\ddagger}$ for III.

In view of the difficulty with line widths it appears that the errors might have been somewhat alleviated if compounds I, II, and III with one methyl-d_3 had been used. An approach similar to that used for cyclohexane-d_{11}[22d] may have given more reliable values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. It appears that long-range CH$_3$–CH$_3$ coupling would be eliminated; however, in view of the fact that methyl-d_3 has different steric requirements, the populations at sites A and B would not be equal.

Acknowledgment. We wish to thank Dr. D. Y. Curtin of this department for valuable discussions and for his suggestion of this problem to us.

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[32] The suggestion that the aryl chlorines can bend out finds some support from the crystal structure of 1,5-dichloroanthraquinone: M. Bailey, *Acta Crystallogr.*, 11, 102 (1958). In-plane bending, presumably due to steric effects, has been reported for chloronaphthalene derivatives.[5g]

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[35] M. M. Harris, *Proc. Chem. Soc.*, 367 (1959).

Nuclear Magnetic Resonance Studies of Phenoxy Radicals. Spin Delocalization in Cyclic Aliphatic Substituents

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Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627. *Received June 7, 1968*

Abstract: We have taken the nmr spectra of a series of phenoxy radicals with cyclic aliphatic substituents in the free radical solvent di-*t*-butyl nitroxide Rapid spin exchange between solvent and solute molecules allows one to observe relatively sharp lines from the solute radicals in dilute solutions. Spectra from two different geometric isomers were observed in each case. The coupling constants for the various groups of protons in the radicals were found to depend on the relative geometries of the molecules. Long-range couplings through the aliphatic rings were observed in most cases. Electron spin resonance spectra of each of the radicals were taken and were found to be in good agreement with the results predicted from the nmr experiments.

There have been numerous theoretical and experimental studies of π-electron spin densities in aromatic radicals reported in the past few years. In contrast to this there is a relatively meager amount of information available about spin delocalization through aliphatic chains.[1] The resolution of esr spectra is generally too poor to allow one to resolve splittings from protons on carbons removed more than two positions from an aromatic ring, and no information is obtained about the signs of the coupling constants. Most of the information available about long-range coupling through aliphatic chains has been obtained from nmr strudies of transition metal chelates.[2,3] In this article we report nmr studies of a series of phenoxy radicals with cyclic aliphatic substituents. This study has produced information about coupling to protons in

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[1] E. De Boer and H. van Willigen, "Progress in NMR Spectroscopy," Vol. 2, Pergamon Press, New York, N. Y., 1966; E. De Boer and C. MacLean, *Mol. Phys.*, 9, 191 (1965).

[2] D. R. Eaton, A. D. Josey, and R. E. Benson, *J. Amer. Chem. Soc.*, 89, 4040 (1967).

[3] R. J. Fitzgerald and R. S. Drago, *ibid.*, 90, 2523 (1968).

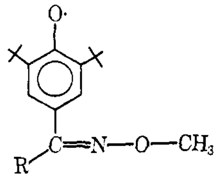
different sized aliphatic rings and information about the dependence of the various coupling constants on the geometries of the molecules.

The signs and magnitudes of electron–nuclei coupling constants can be obtained from nuclear resonance spectra under certain circumstances. Relatively sharp line spectra can be observed if a mechanism is present for rapidly averaging the electron spin states.[4] When this condition is fulfilled one may observe single shifted lines from each set of equivalent protons in the molecule. The relation between the shift, ΔH, and the electron–nuclei coupling constant, a_i, is

$$a_i = -\frac{\Delta H}{(\gamma_e/\gamma_N)\left(\frac{gBH}{4kT}\right)} \qquad (1)$$

The concentration-dependent intermolecular spin exchange reaction provides a mechanism for averaging the electron spin states. In concentrated solutions of organic radicals this reaction may be rapid enough to allow one to observe single lines from each group of nuclei. An alternative approach is to dissolve a given radical in a second free radical solvent.[5] In this case spin exchange between solvent and solute radicals may be rapid enough to allow one to observe the nmr lines of the solute in dilute solutions.

We have used this approach to investigate the nmr spectra of a series of substituted phenoxy radicals. The liquid radical di-*t*-butyl nitroxide (DBNO) was used as a solvent for the phenoxy radicals. Spin exchange was rapid in all cases and lines from most of the protons on the phenoxy radicals were observed. The radicals which were investigated are



1, R = H
2, R = cyclopropy
3, R = cyclobutyl
4, R = cyclopentyl
5, R = cyclohexyl
6, R = cycloheptyl

Each of these radicals can exist in *syn* or *anti* conformations. The favored conformation is probably the one with the methoxy group *anti* to the phenoxy ring. The nmr spectra of the compounds with cyclic substituents showed lines from both conformations. The lines with greater intensities were assigned to the *anti* isomer.

The esr spectra of the radicals were taken in order to obtain the nitrogen coupling constants. The proton coupling constants obtained from the nmr experiments were used to calculate theoretical esr spectra. There was good agreement between theoretical and experimental spectra in each case.

Experimental Section

I. Compounds. A. Radicals. The radicals were made from the corresponding phenols by oxidation with aqueous alkaline $K_3Fe(CN)_6$. The yields of the radicals were very sensitive to the reaction conditions used. The best yields were generally obtained with the following conditions. A solution made from 5 g of KOH and 5.6 g of $K_3Fe(CN)_6$ in 50 ml of distilled water was added as rapidly as possible to a solution of 10^{-3} mol of the appropriate phenol in 125 ml of ether. Nitrogen was bubbled through both solutions for 5 min before mixing and nitrogen was bubbled in the flask during the reaction. The mixture was stirred vigorously for 3–4 min. Longer oxidation times resulted in lower yields of the radicals. The layers were separated and the ether layer was washed with water, dried, and vacuum evaporated. The resulting purple oils were generally 60–70% radical plus the starting phenol and some decomposition material. For esr experiments, the oxidations were carried out in a sealed degassed apparatus with PbO_2. All of the esr spectra were taken with CCl_4 as the solvent.

B. Phenols. The O-methyl oximes were made from the corresponding ketones by methods previously described.[6,7] The ketones were made by the method of Matsuura.[8] Analytical data, melting points, and yields are given in Table I. The chemical shifts of the ketones and oximes are given in Table II. In some instances the oximes were mixtures of *syn* and *anti* isomers which exhibited separate nuclear resonance signals.

II. Instruments. The nmr spectra were run on a JEOLCO 4H-100 100-MHz nmr spectrometer. A broad-line attachment employing 35-Hz field modulation was used in most cases. The spectra were calibrated with an audiooscillator. The esr spectra were taken on a JEOLCO 3BSX esr spectrometer with 100-kHz field modulation. Spectral simulations were done on a JEOLCO RA-1 digital computer.

Table I. Analytical Data, Melting Points, and Yields of Ketones and Oximes

	Theoretical		Found			
R	C, %	H, %	C, %	H, %	Mp, °C	Yield, %
		1.	Ketones			
Cyclopropyl	78.8	9.49	77.9	9.39	141–142	64
Cyclobutyl	79.1	9.74	78.81	9.61	138–139	47
Cyclopentyl	79.5	9.94	79.20	9.98	125–126	58
Cyclohexyl	79.8	10.1	79.66	10.11	126–127	95
Cycloheptyl	80.0	10.3	79.82	10.04	93–94	52
		2.	Oximes			
Cyclopropyl	75.4	9.55	75.43	9.53	133–134	93
Cyclobutyl	75.7	9.80	75.57	9.87	120–122	95
Cyclopentyl	76.2	9.98	76.49	9.98	122–123	96
Cyclohexyl	76.5	10.14	76.49	10.22	128–130	86
Cycloheptyl	76.9	10.6	76.8	10.30	111–113	90

Results and Discussion

The nuclear resonance spectra of the radicals exhibited peaks from most of the protons in the molecules. The spectra observed were superpositions of spectra from the *syn* and *anti* isomers. The peaks with larger areas were assigned to the *anti* isomer. The areas of peaks from the *syn* isomer were 5–20% as large as those from the *anti* isomer. The relative geometries of the isomers and the labeling of the various positions are shown in Figure 1. Representative nmr spectra are shown in Figure 2. Shifts and coupling constants for the various compounds are given in Tables III and IV.

Each of the spectra showed a single line from the aromatic protons shifted to lower field. The low-field shift indicates a positive coupling constant for these protons and negative spin density at the *meta* carbon atoms. The aromatic proton splitting was relatively constant for this series of compounds. Two methoxy lines were observed which were shifted to lower fields in each case. The relative areas of these two peaks were used to estimate the relative percentages of the

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(4) R. W. Kreilick, *J. Chem. Phys.*, **46**, 4260 (1967); **45**, 1922 (1966); H. H. Hausser, H. Brunner, and J. C. Jochims, *Mol. Phys.*, **10**, 253 (1966).

(5) R. W. Kreilick, *ibid.*, **14**, 495 (1968); *J. Amer. Chem. Soc.*, **90**, 2711 (1968).

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(7) R. W. Kreilick, *J. Amer. Chem. Soc.*, **88**, 5284 (1966).

(8) T. Matsuura, A. Nishinaga, and H. Cahnmann, *J. Org. Chem.*, **27**, 3620 (1962).

Table II. Chemical Shifts of Ketones and Oximes[a]

R	*t*-Butyl	R[b]	C–H[b]	OCH_3	OH	Aromatic
			1. Ketones			
Cyclopropyl	1.48	1.14	2.61		5.81	7.95
Cyclobutyl	1.48	2.33	3.98		5.91	7.96
Cyclopentyl	1.48	1.94	3.64		5.83	7.90
Cyclohexyl	1.48	1.88	3.23		5.82	7.85
Cycloheptyl	1.47	1.75	3.41		5.75	7.86
			2. Oximes			
Cyclopropyl	1.42	0.75	2.20	3.96	5.24	7.11
Cyclobutyl	1.42, 1.45	2.20	3.85	3.88, 3.89	5.23	7.12
Cyclopentyl	1.43	1.65	3.43	3.91	5.23	7.15
Cyclohexyl	1.43	1.56	3.17	3.80, 3.90	5.20	7.12, 7.06
Cycloheptyl	1.45	1.67	3.24	3.78, 3.89	5.21	7.13, 7.24

[a] Units are parts per million in $CDCl_3$. [b] Center of groups of lines.

Table III. Shifts[a] and Coupling Constants for the *anti* Isomers

		t-Butyl		Aromatic		OCH_3		β		γ		ϵ	
R	N a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G
H	3.9	0.47	+0.063	13.21	+1.78	6.96	+0.935	17.26[b]	+2.32				
Cyclopropyl	3.78	0.505	+0.068	13.75	+1.85	6.09	+0.82	14.98	−2.02				
Cyclobutyl	3.9	0.505	+0.068	13.43	+1.82	5.19	+0.70	14.79	−1.99	0.772	+0.104	0.190	−0.026
Cyclopentyl	3.8	0.505	+0.068	13.44	+1.82	5.30	+0.715	2.50	−0.338	0.853	+0.115	0.140	−0.019
Cyclohexyl	3.75	0.505	+0.068	13.44	+1.82	4.99	+0.675	2.15	−0.290	1.03	+0.139	0.353	−0.048
Cycloheptyl	3.8	0.505	+0.068	13.52	+1.83	5.31	+0.717	2.58	−0.348	0.763	+0.103	0.104	−0.014

[a] The shifts are from corresponding peaks in the diamagnetic phenols. [b] This shift and coupling constant are for the proton on the α carbon.

Table IV. Shifts[a] and Coupling Constants for the *syn* Isomers

	OCH_3		β		γ		
R	Shift, kHz	a_i, G	Shift, kHz	a_i, G	Shift, kHz	a_i, G	% *syn* isomer
Cyclopropyl	2.90	+0.390	5.43	−0.73			7
Cyclobutyl	2.75	+0.372	8.81	−1.19			10
Cyclopentyl	2.25	+0.304	5.70	−0.77	1.20	+0.162	13
Cyclohexyl	2.17	+0.294	4.47	−0.65			22
Cycloheptyl	2.26	+0.306			0.97	+0.131	5

[a] The shifts are from the corresponding peak in the diamagnetic phenol. The aromatic and *t*-butyl protons show single peaks and the couplings are assumed to be the same in both isomers.

two isomers present. These values are given in Table IV. The sign of the methoxy splitting was positive in each of the radicals. The magnitude of this splitting varied slightly through this series of compounds. The splitting from the *syn* isomer was smaller than that of the *anti* isomer in each case. If one considers these compounds as odd alternate radicals one predicts positive spin density at the nitrogen. The positive splitting observed for the methoxy protons indicates that Q_{OCH_3} is positive. A single peak shifted to low field was observed from the *t*-butyl protons. The *t*-butyl groups are attached to the aromatic ring at positions for which one predicts positive spin densities. The positive splitting found for these protons indicates that $Q_{t\text{-butyl}}$ is also positive.

This series of radicals was investigated in order to obtain information about the variation of the coupling constants with the size of the aliphatic ring. Compound **1** was studied to determine the sign of the spin density at the α carbon atom. The spectra of this compound showed lines from only one of the geometric isomers. The line from the proton connected to the α carbon atom is shifted to low field indicating a positive coupling constant and negative spin density at the α carbon atom.

The lines from the protons at the β position were shifted to high field in each case, indicating negative coupling constants. Peaks from both isomers were observed. The peaks from the γ and ϵ protons were difficult to distinguish. In the case of the cyclopropyl compound we were unable to observe a line from the γ protons and have assumed that it is overlapped with the line from the *t*-butyl protons. In the other compounds, peaks shifted to high and low field were observed. Unfortunately, we were unable to see these lines under the same experimental conditions and therefore we could not compare these areas directly. The line shifted to high field could be seen when samples were run in deuteriochloroform or deuteriobenzene. With these conditions, the line shifted to lower field was broadened and could not be seen. When samples were run in DBNO we were able to observe the low-field line but the high-field peak was overlapped with either the diamagnetic *t*-butyl line or the DBNO line. As a consequence our assignment is not unambiguous. The lines shifted to low field have larger coupling con-

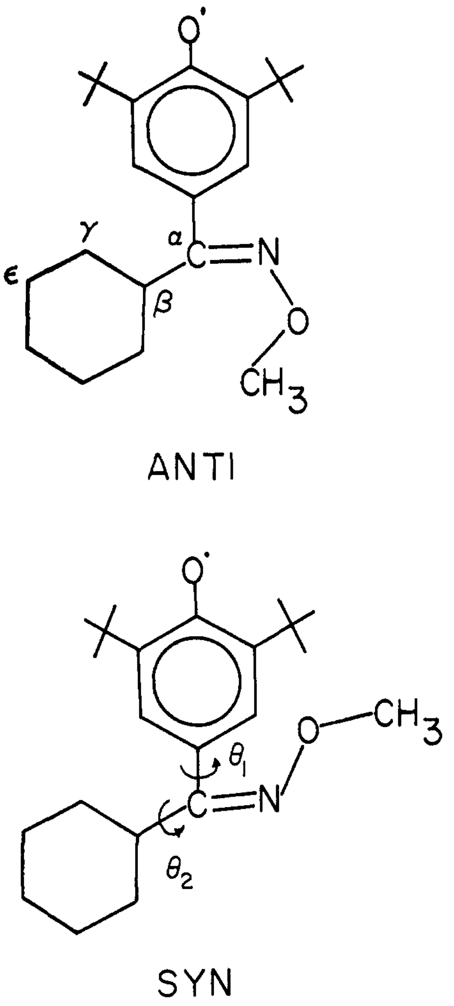

Figure 1. Geometries of *syn* and *anti* isomers and labeling of positions.

stants and were assigned to the γ protons. The high-field lines were assigned to the ϵ protons. If this assignment is correct, the signs of the coupling constants alternate from the α to the ϵ positions.

Electron spin resonance spectra were taken for each of the radicals. Representative spectra are shown in Figure 3. The appearance of the spectra changed markedly between compounds III and IV, reflecting the large change in β proton coupling constants. Lower resolution spectra showing the main groups of lines were obtained in all cases. High-resolution spectra showing the smaller splittings were observed from radicals II, III, and V. Spectra were simulated using the nitrogen coupling constants given in Table III and the proton coupling constants obtained from the nmr experiments. There was good agreement between theoretical and experimental spectra in each case. The esr spectra observed came from the dominant geometric isomer in each case.

The nitrogen coupling constant is reasonably constant throughout this series of compounds. This coupling should depend on the twist angle of the phenoxy ring with respect to the carbon–nitrogen double bond[7] (θ_1 in Figure 1). The similarity in the nitrogen coupling constants suggests that this angle is reasonably constant for this series of compounds. If this is the case, the spin density at the α carbon atoms

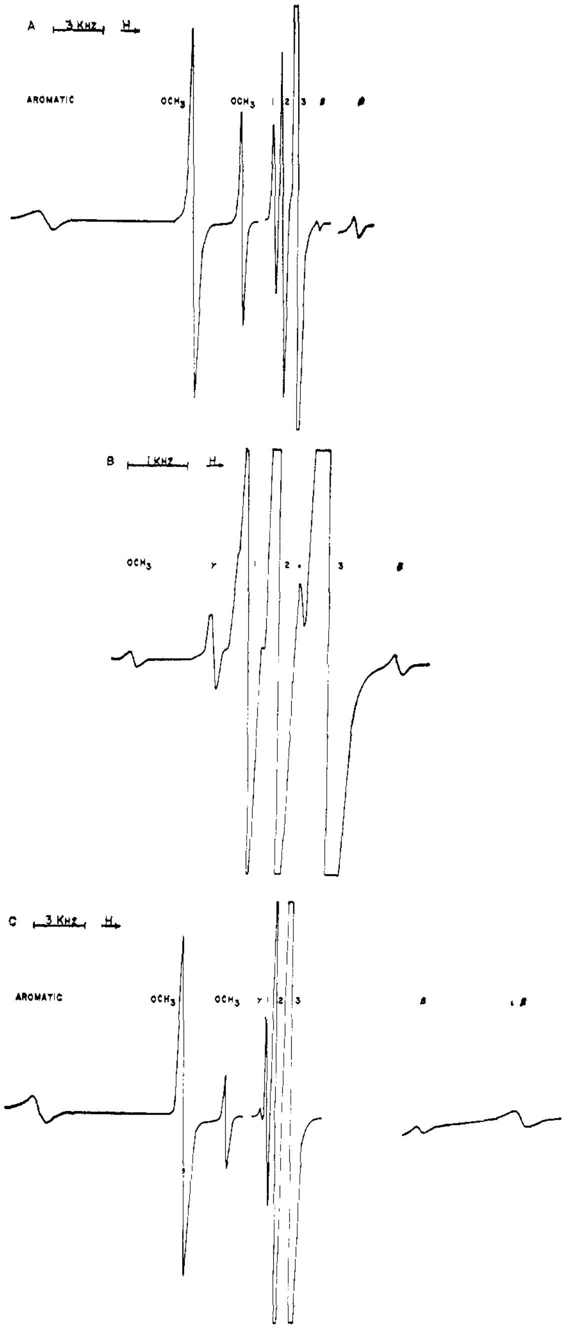

Figure 2. A, Nmr spectrum of radical **5** in DBNO; B, expansion of the center region of the spectrum of radical **5**; C, nmr spectrum of radical **3** in DBNO. The center regions of spectra A and C are recorded at lower gains. Lines 1, 2, and 3 refer to the radical *t*-butyl peak, the diamagnetic *t*-butyl peak, and DBNO, respectively.

should be about the same in each of the radicals. If this argument is correct, the large changes in the β proton coupling constants cannot be explained by changes in the spin density at the α carbon atom.

There are a number of mechanisms which could be proposed to account for the splittings by the protons in the saturated rings. Splittings by methyl groups connected to sp^2-hybridized carbons containing an unpaired electron have been explained by hyperconjugation.[9] This mechanism predicts that the splittings should depend on the angle between the protons in the

(9) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, 5, 31 (1962).

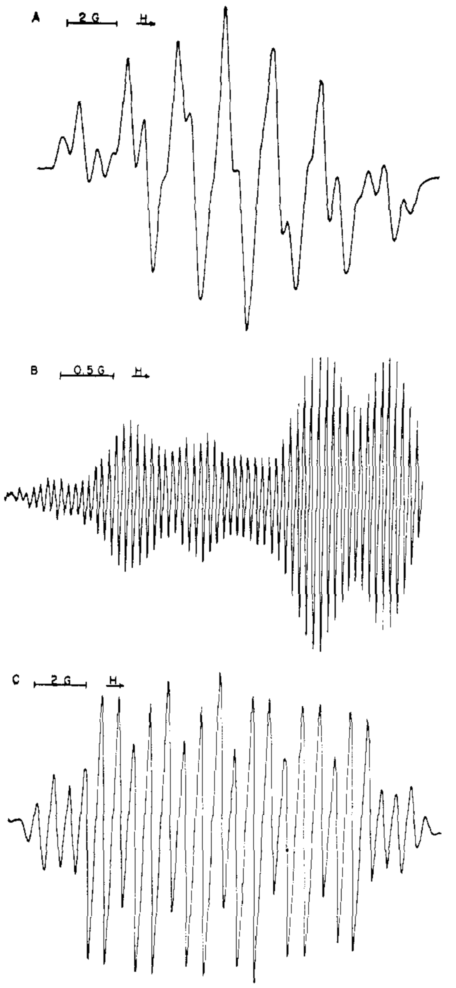

Figure 3. A, Low-resolution esr spectrum of radial **5**; B, high-resolution spectrum of the low-field groups from radical **5**; C, low-resolution esr spectrum of radical **3**.

alkyl group and the p orbital of the carbon containing the spin[10] (θ_2 in Figure 1). The sign of the proton coupling constants should be the same as that of the spin density at the unsaturated carbon. The alkyl proton splittings could also be accounted for by a spin polarization mechanism.[2] In this case one would predict a linear relation between the splittings and the

$$a_i = Q_i\rho_\alpha \qquad (2)$$

spin density at the α carbon. A different polarization constant should be found for each alkyl group depending on its distance from the α carbon atom.

The splittings of the β protons in radicals **2–6** seem to be dominated by a hyperconjugative interaction. The coupling to the γ and ϵ protons appears to be due to spin polarization. The β proton coupling constant decreases sharply in going from radicals **2** and **3** to radicals **4–6**. This change in the coupling constant can be accounted for by a change in the angle, θ_2. Steric hindrance between the methoxy group and the larger saturated rings could explain the changes in the θ_2's in the *anti* isomers. This angle is favorable for a hyperconjugative interaction in the smaller ring compounds and one observes a larger coupling constant. In compounds **4–6** the angle is not favorable for this type of interaction and smaller coupling constants are observed. If θ_2 is large enough the contribution to the coupling from this interaction should be small and spin polarization might be the dominant cause of the smaller splittings.

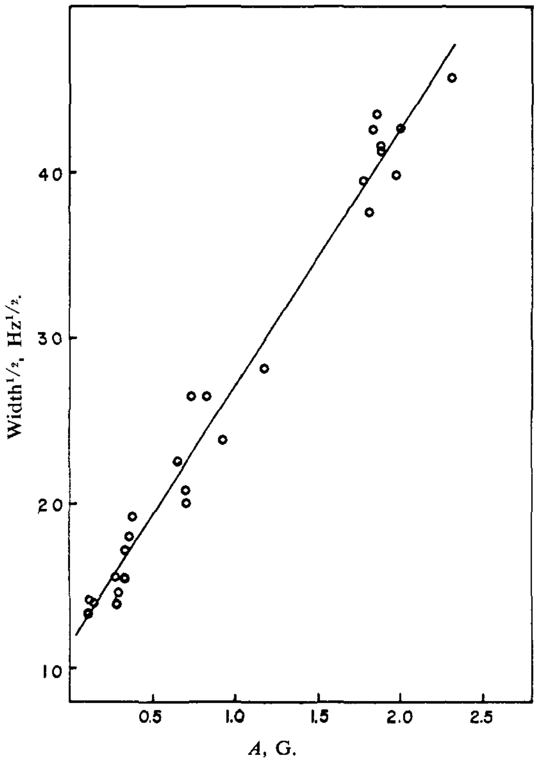

Figure 4. A plot of the square root of the line widths *vs.* the coupling constants.

The large change in the β coupling constant is not reflected in the γ or ϵ coupling constants. This behavior suggests that hyperconjugation is not the predominant interaction producing these splittings. If spin polarization is responsible for these splittings the observed coupling constants should be proportional to the spin density at the α carbon atom. The spin density at the α carbon can be determined for compound **1** [$\rho_\alpha = -0.103$ with $Q_\alpha = -22.5$ G]. The nitrogen coupling of compound **4** is close to that found for compound **1**. If one estimates the spin density at the α carbon atom of compound **4** with the value found for compound **1**, one can approximate the polarization constants. The values for the polarization constants are $Q_\gamma = -1.1$ G, $Q_\epsilon = +0.18$ G). The value for the γ protons is in good agreement with a value determined from ^{13}C splittings of phenoxy radicals.[11]

We were able to determine the methoxy and the β proton coupling constants for the other geometric isomer. The methoxy coupling constant in the *syn* isomers is smaller than that of the *anti* isomers in each case. The decrease in the methoxy splittings probably reflects smaller spin densities at the nitrogen and α carbon because of a change in the angle θ_1. Molecular models indicate that the methoxy group and the aromatic ring interfere with one another in a planar orientation. This interference is minimized in a twisted conformation in which the methoxy group is above the aromatic ring. The β proton coupling constants do

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(10) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960); E. W. Stone and A. H. Maki, *ibid.*, **37**, 1326 (1962).

(11) L. Gilbert and R. Kreilick, *ibid.*, **48**, 3377 (1968).

not show a sharp change in these isomers indicating that θ_2 is similar for each of the molecules.

The line width of the nuclear resonance peaks should be dominated by the Fermi contact interaction and the electron–proton dipole–dipole interaction.[12] The contribution to the line width from both of these interactions should vary as the square of the coupling constant. A plot of the square root of the line widths *vs.* the coupling constants is shown in Figure 4. Within experimental error the predicted linear relation is observed.

Conclusions

The nmr spectra of a series of phenoxy radicals with cyclic aliphatic substituents have been taken. Coupling constants from two geometric isomers were observed. Some of the coupling constants were found to depend on the geometries of the molecules. The couplings to the β protons in the aliphatic rings appear to be dominated by a hyperconjugative interaction while the smaller couplings from the γ and ϵ protons may be due to spin polarization.

Acknowledgments. This work was supported in part by National Science Foundation Grant GP-5482.

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Hydrogen–Deuterium Kinetic Isotope Effects in the Gas Phase Bromination of Monodeuterated Toluene[1]

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Abstract: The intramolecular hydrogen–deuterium kinetic isotope effect in the gas phase bromination of monodeuterated toluene has been determined. The ratio of second-order rate constants obtained over the temperature interval of 120–160° can be expressed in terms of the following equation: $k_H/k_D = (1.08 \pm 0.25) \exp(1430 \pm 110)/RT$. The kinetic isotope effect measured in these gas phase experiments is larger than the corresponding values reported in solution studies. A general discussion of the comparison of the solution and gas phase results is presented.

Some of the interesting aspects of comparing reactions in the gas phase to the same reaction in solution have been pointed out by Mayo in a recent article.[2] In the case of free radical hydrogen atom abstraction reactions, the comparison has been limited mainly to the measurement of selectivity ratios for abstraction from various carbon–hydrogen bonds (*e.g.*, primary *vs.* secondary C–H bonds). For chlorine atom reactions an increased selectivity in the gas phase has been observed.[3] On the other hand, methyl radicals do not exhibit any marked difference in selectivity in comparing gas phase and solution work.[4] In general, differences in selectivity ratios have been explained in terms of cage and solvation effects taking place in the solution reactions.[2]

In our experimental work, the relative rates of abstraction of hydrogen and deuterium atoms by bromine atoms from monodeuterated toluene in the gas phase have been determined. This same kinetic isotope effect was measured previously in carbon tetrachloride solution by Wiberg and Slaugh.[5] The only previous example of the same kinetic isotope effect measured in the gas phase and solution would appear to be the work of Walling and Miller[6] in studying the reaction of chlorine atoms with deuterated toluene.

Experimental Section

All reactions were carried out in a conventional high-vacuum apparatus. Monodeuterated toluene was synthesized *via* the reaction of $C_6H_5CH_2MgCl$ with D_2O. The extent of deuteration was determined mass spectrometrically using a Hitachi RMU-6 mass spectrometer. Analysis showed the toluene to be 95% $C_6H_5CH_2D$, the remaining 5% being $C_6H_5CH_3$. Reagent grade bromine (stated purity 99.9%, Baker Chemical Co.) was left in contact with potassium bromide for several days. A small amount of this bromine was then distilled from the potassium bromide with only the middle fraction being retained for reaction.

The thermal reactions were carried out over a temperature range of 120–160°. The reaction furnace was equipped with three separate windings of Nichrome wire and, in this way, it was possible to obtain a constant temperature across the reaction cell. The cylindrical reaction cell was made of Pyrex and had a volume of approximately 250 cc.

In an experiment, the desired amount of toluene-d_1 was measured in a micropipet and then distilled into the reaction vessel and condensed in a small cold finger at −196°. The bromine was similarly measured in the pipet and then transferred to the cold finger. The stopcock isolating the reaction vessel from the vacuum system (a Kern high-vacuum greaseless stopcock) was then closed. Reaction was initiated by vaporizing the frozen bromine and toluene by warming with hot water; the time required for this was less than 10 sec. The greaseless stopcock plus tubing connecting the reaction cell, cold finger, and stopcock was maintained at 90° by wrapping with insulated heating tape. In this way, condensation of the bromine and toluene was avoided.

It was not possible with this experimental setup to measure the initial amounts of toluene-d_1 or bromine to better than ±15%. However, the kinetic isotope effect measurement is not contingent on an exact knowledge of the amounts of starting materials.

The desired kinetic isotope effect was determined by measuring the amounts of HBr and DBr produced from reactions 2a and 2b.

The HBr and DBr formed in these reactions were separated from the reaction mixture *via* passage through traps at −125° (*n*-pentane

[1] This research was supported by the National Science Foundation, Research Grant GP-4932.

[2] F. R. Mayo, *J. Amer. Chem. Soc.*, 89, 2654 (1967).

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