Hydrolysis of a solution of $C_3Cl_5^+SbCl_6^-$ in dichloromethane and similar work-up gave only hexachloropropene in 98% yield.

Potassium Hexachloroantimonate. The procedure of Jander and Swart[17] was followed. Potassium chloride (1.51 g, 0.02 mole) was added to 17 ml of melted antimony(III) chloride and heated gently until the potassium chloride completely dissolved. Antimony(V) chloride (6.10 g, 0.021 mole) was added dropwise and the resulting brown solution was allowed to cool, whereupon solidification took place. The solid mass was ground and washed with three 50-ml portions of carbon disulfide to dissolve the antimony(III) chloride and any excess antimony(V) chloride. The light gray solid residue was dried under vacuum.

Anal. Calcd for $KSbCl_6$: K, 10.5; Sb, 32.6; O, 0.00; Cl, 56.9. Found: K, 10.2; Sb, 32.4; O, 0.00; Cl, 57.0.

A mineral oil mull smeared between CsI plates gave a single infrared absorption band at 346 cm^{-1}.

Acknowledgments. The authors thank the National Science Foundation for a grant in support of this research.

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[17] G. Jander and K. H. Swart, *Z. Anorg. Allgem. Chem.*, **301**, 54 (1959).

Conformational Variation in the Electron Spin Resonance Spectra of Some Phenoxy Radicals

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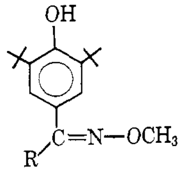
Abstract: We have examined the esr and optical spectra of a series of 4-substituted 2,6-di-*t*-butylphenoxy radicals. The magnitude of the coupling constant of the 4 substituent is shown to depend on the conformation of the radical. The extinction coefficient and position of the ultraviolet maximum are also related to the radical's conformation. The nmr and ultraviolet spectra of the phenols, from which the radicals were made, show that these compounds also exist in different conformations.

Electron spin resonance spectroscopy can be used to obtain information about the conformational identity of organic free radicals. Geske's group has studied a series of nitrobenzene anion radicals, and found that the nitrogen coupling constants increase as the nitro group twists from coplanarity with the aromatic ring.[1] Tetraisopropylnitrobenzene shows two different nitrogen splittings which have been shown to come from two different conformation isomers.[2] The nitrogen splitting in these radicals depends on the angle of twist between the nitro group and the plane of the aromatic ring. Substituents on the aromatic ring affect this angle and change the nitrogen coupling constant.

We have conducted a study to examine how steric hindrance affects the spin distribution in a series of conjugated phenoxy radicals. The odd electron spin was introduced into the phenoxy ring, and the coupling constants of groups of nuclei connected in the *para* position were determined. The radicals which we have studied were derived from phenols of the general structure



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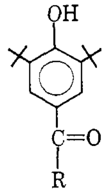

II

+ = *t*-butyl

a, R = H
b, R = CH_3
c, R = *t*-butyl
d, R = phenyl

The radicals were made by removal of the hydroxyl hydrogen atom by oxidation. Conjugation between the phenoxy ring and the *para* substituent depends on the angle, θ, between the plane of the aromatic ring and a plane projected through the RC=R group. If this twist angle is large, conjugation between the two parts of the molecules is reduced.

The coupling constant of the nitrogen, in compounds Ia–d, should depend on the value of the resonance integral of the Ar–C bond (β_{Ar-C}). The magnitude of β_{Ar-C} depends on the twist angle θ[3] and the Ar–C bond length.[4] The variation of β_{Ar-C} with the twist angle, θ, can be written as

$$\beta_{Ar-C} = \beta_0 \cos\theta \tag{1}$$

where β_0 is the normal resonance integral. Bulky substituents on the oximido carbon should increase the twist angle and decrease the value of β_{Ar-C}. This change will be reflected in a decrease of the nitrogen coupling constant if the phenoxy ring has a higher electron affinity than the oxime group.

The radicals with a carbonyl group rather than the oxime group should show the same general behavior. It is interesting to compare the splitting of the R group in the ketones and aldehyde with those of the corresponding groups in the oximes. Some idea of the relative twist angles in the two series of compounds can be obtained by comparison of these splittings.

Experimental Section

A. Magnetic Resonance Measurements. The esr spectra were taken on a Jeolco 3BSX, esr spectrometer with 100-kc field

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[1] D. H. Geske, J. L. Ragle, M. A. Bambenek, and A. L. Balch, *J. Am. Chem. Soc.*, **86**, 987 (1964).

[2] T. M. McKinney and D. H. Geske, *J. Chem. Phys.*, **44**, 2277 (1966).

[3] R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950).

[4] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* (London), **A251**, 172 (1961).

modulation. Variable temperature measurements were made by blowing heated or cooled N_2 gas over the samples. Samples were prepared by oxidizing the parent phenols with PbO_2 in a sealed, degassed apparatus. Nmr spectra were taken on a Varian Associates A-60 nmr spectrometer.

B. Spectral Simulation. The esr coupling constants were determined by simulation of the spectra with a Jeolco RA-1 digital computer. The computed spectra fit the experimental spectra within experimental error.

C. Solvents. The solvents used were 2-methyltetrahydrofuran (MTHF), methylene chloride, carbon tetrachloride, and dimethyl sulfoxide. MTHF was distilled from CaH and stored in a vacuum bottle over a Na–K alloy. Methylene chloride and carbon tetrachloride were distilled into vacuum bottles and stored over potassium carbonate. Dimethyl sulfoxide was distilled from CaH, transferred to the vacuum apparatus, and degassed on the vacuum line.

D. Optical Spectra. The optical spectra were taken on a Cary Model 11 recording spectrophotometer. Extinction coefficients were determined by the following procedure. Samples of the parent phenols of known concentration were made by standard volumetric procedures. These samples were oxidized with PbO_2 and centrifuged, and the spectra of the radicals recorded immediately. Various oxidation times were tried. It was found that after a 90-sec oxidation the peaks had reached a maximum value. The samples decayed slowly, and the spectra of the radicals were gone in about 12 hr. Samples were run in duplicate and various concentrations were used. There is some error in determining the molar extinction coefficients in this manner. Unfortunately, because of the low melting points of the radicals, we were unable to obtain crystalline solids with which more precise measurements could be made. All of the measurements were made in Eastman spectroanalyzed cyclohexane.

E. Compounds. (1) Aldehyde and Ketones. Compound IIa was made by the method of Coppinger and Campbell.[5] Compounds IIb and c were made by the method of Matsuura.[6] Compound IId was made by the method of Cook and Gilmour.[7] Compound IIc has not been previously reported. The yield of the reaction between 2,6-di-*t*-butylphenol, trimethylacetic acid, and trifluoroacetic anhydride was 66% (mp 133–134° from CCl_4). *Anal.* Calcd for $C_{20}H_{30}O_2$: C, 78.4; H, 10.3. Found: C, 77.2; H, 9.8. Nmr (ppm) in $CDCl_3$, carbonyl *t*-butyl 1.40, ring *t*-butyls 1.48, hydroxyl 5.66, aromatic 7.82.

(2) O-Methyl Oximes. All of the oximes, compounds Ia–d, were prepared by the method of Muller.[8] In a typical preparation, 2×10^{-2} mole of ketone or aldehyde and 3×10^{-2} mole of O-methylhydroxylamine hydrochloride were dissolved in 40 ml of methanol and 3 ml of pyridine. The mixture was refluxed for 20 hr, diluted with water, and extracted with ether. The ether layer was washed with dilute HCl and water, dried, and vacuum evaporated. The resulting oils were carefully recrystallized from aqueous methanol. Seeding was required to obtain well-formed crystals. The yields, melting points, and analysis of the new oximes are listed below. Compound Ia had properties identical with those given by Muller.

Compound Ib, mp 64°, yield 64%. *Anal.* Calcd for $C_{17}H_{27}NO_2$: C, 73.5; H, 9.75. Found: C, 73.1; H, 9.78.

Compound Ic, mp 64°, yield 63%. *Anal.* Calcd for $C_{20}H_{33}NO_2$: C, 75.3; H, 10.3. Found: C, 74.9; H, 10.5.

Compound Id, mp 73°, yield 66%. *Anal.* Calcd for $C_{22}H_{29}NO_2$: C, 77.9; H, 8.6. Found: C, 77.8; H, 8.9.

Results and Discussion

A. Phenoxy Oximes. The esr spectra of the four phenoxy oxime radicals (radicals Ia–d) are shown in Figure 1. The spectrum of radical Ia has previously been reported by Muller.[8] With better resolution we find that the spectrum can be fit with the coupling constants given in Table I. The coupling constants for the other phenoxy oxime radicals are also found in Table I. The major splitting in radicals Ia, b, and d is produced by the nitrogen. In radical Ic, the coupling constant of the *meta* ring protons is greater than that of the nitrogen. There is a gradual decrease in the nitrogen coupling constant, as the alkyl group connected to the oximino carbon becomes more bulky:

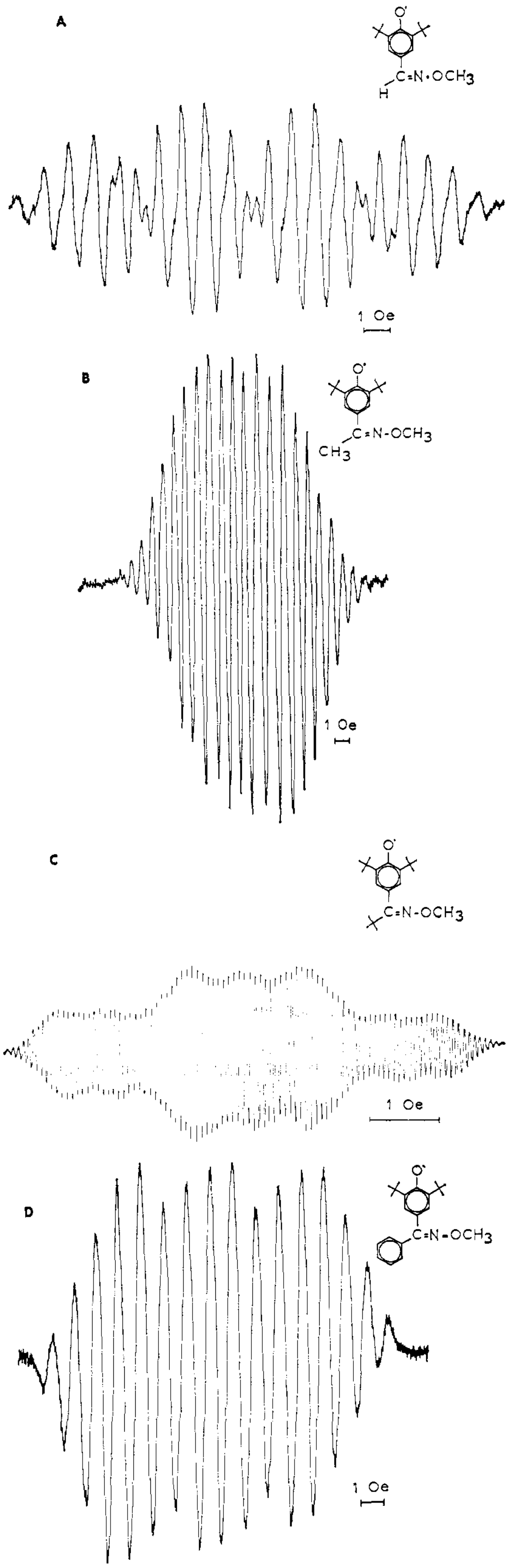

Figure 1. Esr spectra of phenoxy oximes at 20°. Compounds A, B, and D in MTHF; compound C in CCl_4.

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(5) G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

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

(7) C. D. Cook and N. D. Gilmour, *ibid.*, **25**, 1429 (1960).

(8) E. Muller, R. Mayer, B. Narr, A. Rieker, and K. Scheffler, *Ann.*, **645**, 19 (1961).

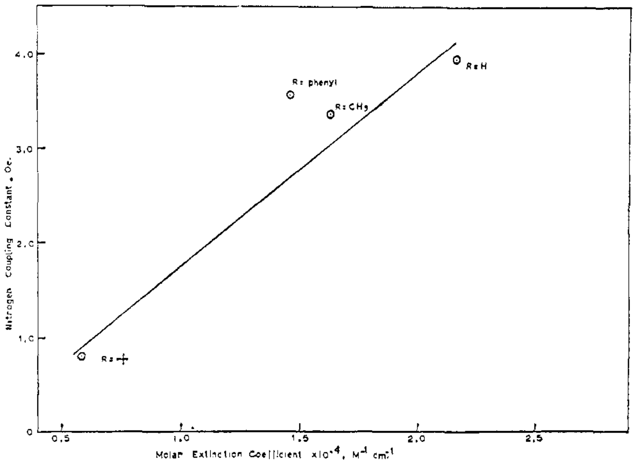
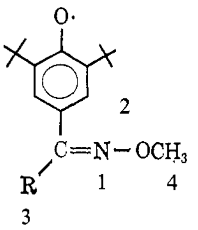


Figure 2. Plot of molar extinction coefficient *vs.* nitrogen coupling constant for phenoxy oximes.

a_N(C–H) > a_N(C–CH$_3$) > a_N(C–*t*-butyl). Radical Id's nitrogen coupling constant falls between that of radicals Ia and b.

Table I. Esr Coupling Constants and Wavelengths of Optical Transitions and Molar Extinction Coefficients of



Esr coupling constants			Optical transitions	
Compound	Position	a, oersteds	Position, mμ	ϵ, M^{-1} cm^{-1}
R = H	1	3.96	597	1.2×10^3
	2	1.72	547	1.0×10^3
	3	2.28	511	7.6×10^2
	4	0.92	340	2.2×10^4
			320	Shoulder
			297	Shoulder
R = CH$_3$	1	3.46	591	8.2×10^2
	2	1.72	535	8.9×10^2
	3	1.77	342	1.6×10^4
	4	0.92	336	1.6×10^4
			319	Shoulder
			306	Shoulder
R = *t*-butyl	1	0.84	600	4.8×10^2
	2	1.72	392	6.8×10^2
	3	?	377	6.8×10^2
	4	0.08(?)	305	5.9×10^3
			265	7.6×10^3
R = phenyl	1	3.60	601	1.0×10^3
	2	1.72	550	9.6×10^2
	3	Small	334	1.5×10^4
	4	0.92	305	7.6×10^3

The coupling constants of the *meta* aromatic protons were identical in this series of radicals. The coupling constants of the OCH$_3$ group attached to the nitrogen were also the same for radicals Ia, b, and d. We were unable to determine either the methoxy or *t*-butyl coupling constant of radical Ic because of the complexity of the spectrum. From the number of lines and their relative intensities it appears that the *o*-*t*-butyl groups produce a measurable splitting. No splitting was observed from the *o*-*t*-butyl groups of any of the other radicals. We were also unable to detect any splitting from the unsubstituted phenyl ring of radical Id.

The change in the nitrogen coupling constants with increased steric bulk can be explained by a change in the twist angle. As the steric bulk of the R substituent increases, the twist angle becomes greater and the nitrogen coupling constant decreases. The nitrogen splitting, in these radicals, is small in comparison to that of nitroxide radicals or anion radicals containing nitro groups. This small coupling constant, along with the manner of change with increased steric bulk, indicates that the phenoxy ring contains most of the spin.

The spectra were taken in a number of different solvents. Radicals Ia, b, and d were studied in MTHF and methylene chloride. The spectrum of compound Ic was taken in these solvents and in DMSO and CCl$_4$. The coupling constants of all of these radicals were independent of the solvent. The resolution of the *t*-butyl splitting in compound Ic was better in CCl$_4$ than in the other solvents.

The spectra of the radicals were also studied over a wide range of temperatures. The spectra were recorded in 10° increments from 20 to −120° (in MTHF). The spectrum of compound Ic was also studied in 10° increments from 20 to +120° (in DMSO). No changes in the isotropic coupling constants of radicals Ib, c, and d were observed over these temperature regions. The spectrum of compound Ia changed slowly with temperature. Because the spectrum contains so many overlapped lines it was impossible to tell which coupling constant(s) were changing. It appeared that either the nitrogen or oximino proton increased by about 0.1 oersted when the temperature was lowered by 80°.

The optical spectrum of each of these radicals was taken and molar extinction coefficients were determined. Suzuki[9] and others[10] have proposed that the position and intensity of the optical transitions, in molecules of this type, should be affected by changes in the twist angle. The molar extinction coefficient and wavelength of the transitions should both decrease as the twist angle becomes larger. This series of radicals shows the predicted behavior, as there is a decrease in the molar extinction coefficients of the ultraviolet maxima as the steric bulk of the R group increases. There is also a shift of this transition to lower wavelength. Figure 2 shows that there is a rough correlation between the value of the extinction coefficients and the nitrogen coupling constant. The values of the molar extinction coefficients and positions of the transitions are given in Table I.

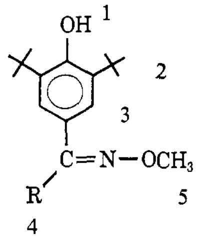
The ultraviolet and nmr spectra of the parent phenols show that these compounds also exist in different conformations. There is a decrease in the chemical shift of the hydroxyl proton as the size of the R group becomes larger (Table II). Dilution studies were made over a tenfold concentration range for each phenol with no measurable change in chemical shift for the hydroxyl protons. The chemical shifts of the methoxy and aromatic protons in compound Ic are smaller than those of the same protons in compounds Ia and b.

(9) H. Suzuki, *Bull. Chem. Soc. Japan*, **32**, 1340 (1959).

(10) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

This upfield shift can be accounted for by a conformation in which the methoxy protons lie above the plane of the aromatic ring.[11] A conformation of this sort is present when the twist angle is large. The nmr spectrum of compound Id shows two lines for each group of protons except the unsubstituted phenyl ring. The doubling of these lines may be due to two different conformations.

Table II. Chemical Shifts and Wavelengths of Optical Transitions and Extinction Coefficients of



Chemical shifts			Optical transitions	
Compound	Position	Shift, ppm	Position, mμ	ε, M^{-1} cm^{-1}
R = H	1	5.25	227	1.5×10^4
	2	1.44	294	Shoulder
	3	7.31	303	Shoulder
	4	7.86		
	5	3.86		
R = CH_3	1	5.13	266	1.35×10^4
	2	1.45		
	3	7.37		
	4	2.12		
	5	3.90		
R = *t*-butyl	1	5.05	272	1.5×10^3
	2	1.44	278	1.4×10^3
	3	6.68		
	4	1.11		
	5	3.64		
R = phenyl	1	5.15, 5.2	242	1.27×10^4
	2	1.38, 1.44	271	1.04×10^4
	3	7.06, 7.20		
	4	7.30		
	5	3.83, 3.86		

The variation in the molar extinction coefficients of the ultraviolet maximum also supports the idea that different conformations are present in this series of phenols (Table II). The molar extinction coefficient decreases as steric bulk increases. Compound Id shows a double maximum which may be due to two different conformations.

The esr spectra of radicals IIa–d are shown in Figure 3. The major splitting in each of these radicals comes from the two *meta* aromatic protons. The splittings from the R protons in radicals IIa and b are extremely small (0.4 and 0.28 oersted, respectively). *para* substituents in other phenoxy radicals have relatively large coupling constants (*i.e.*, *para* substituent: CH_3, 10.3 oersteds;[12] O–CH_3, 1.6 oersteds;[13] O=SCH_3, 2.0 oersteds).[13] A possible explanation for the small coupling constant in radicals IIa and b is a large twist angle.

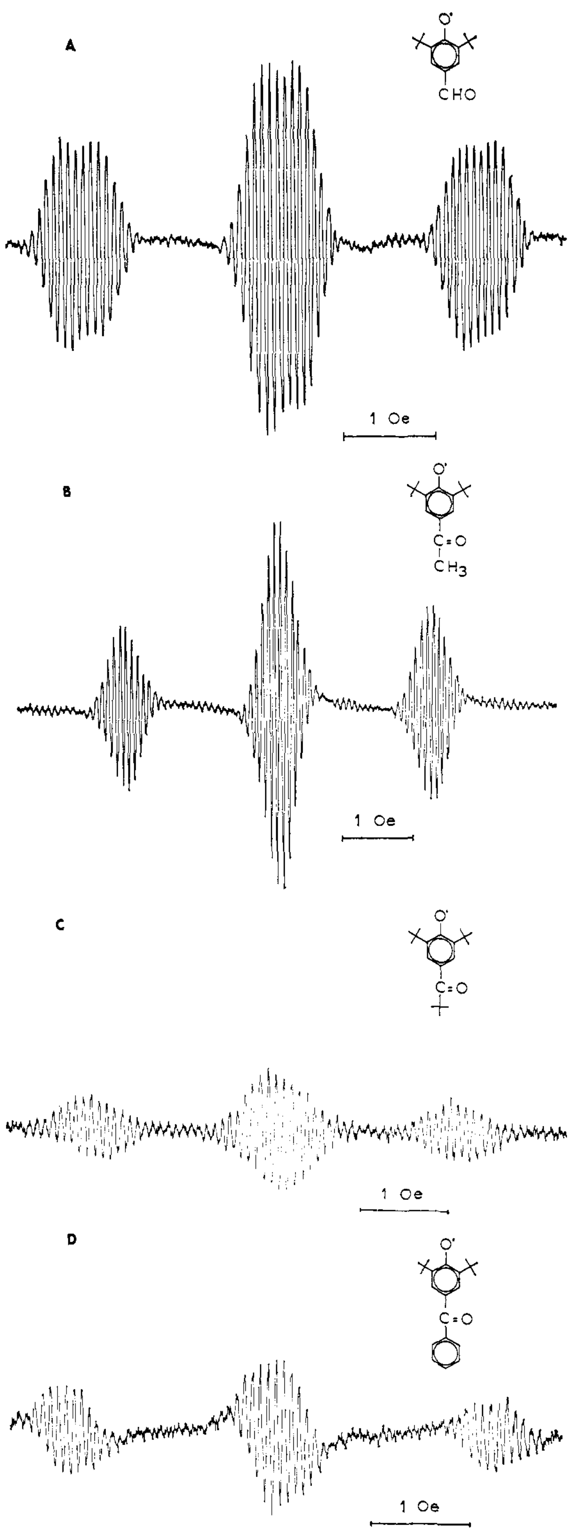


Figure 3. Esr spectra of phenoxy ketones in CCl_4 at 20°.

The spin distribution in radicals IIa, b, and d appears to be somewhat different from that in radicals Ia, b, and d. The splitting of the *o*-*t*-butyl groups is resolvable in the phenoxy ketones, varying from 0.08 to 0.095 oersted. The line widths of the phenoxy oximes show that the splitting from the *o*-*t*-butyl groups must be less than 0.08 oersted. The R groups in radicals Ia and b produce a splitting about five times greater than the corresponding R groups in radicals IIa and b. It is difficult to be certain of the

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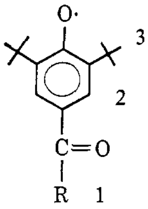
(11) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
(12) J. Becconsall, S. Clough, and G. Scott, *Trans. Faraday Soc.*, **56**, 459 (1960).
(13) K. Scheffler, *Z. Elektrochem.*, **65**, 439 (1961).

Table III. Esr Coupling Constant of



Compound	Position	*a*, oersteds
R = H	1	0.4
	2	2.2
	3	0.08
R = CH_3	1	0.28
	2	2.2
	3	0.09
R = *t*-butyl	1	0.17(?)
	2	2.2
	3	0.09
R = phenyl	1	Small
	2	2.2
	3	0.08

coupling constants of the two different types of *t*-butyl protons in radical IIc, because of the large number of overlapping lines and the relatively poor resolution of the esr spectrum. It appears, however, that the splitting from the *t*-butyl group attached to the carbonyl has about twice the coupling constant of the *t*-butyl groups on the aromatic ring. No splitting was observed from the unsubstituted phenyl group in either radical Id or IId. Coupling constants for the phenoxy ketones are given in Table III.

Radicals IIa–d dimerize in solution and exist entirely as dimers in the solid state.[14] Radicals Ia–c appeared to be entirely monomeric in solution. These radicals had a normal Curie temperature dependence as far as we could tell. The dimerization of the phenoxy ketones made it impossible to determine the molar extinction coefficients of the optical transitions.

Conclusion

The change in the nitrogen coupling constants of radicals Ia–d appears to be due to changes in the angle between the plane of the phenoxy aromatic ring and the plane formed by the RC=N group. As the steric bulk of the R group increases, this angle becomes larger and the nitrogen coupling constant decreases. This variation in twist angle is also reflected in the decrease of the molar extinction coefficients of the optical spectra, with an increase of steric bulk of the R groups. The nmr and ultraviolet spectra of the phenols, from which these radicals were made, indicate that these compounds also exist with different twist angles.

The small splittings from the CHO and O=CCH_3 protons in radicals IIa and b might be explained by twisted conformations. Protons in the same positions on compounds Ia and b have coupling constants about a factor of five larger. Although other factors may determine the relative magnitudes of the coupling constants of the R groups, a possible explanation is a large difference in twist angles.

Acknowledgments. This work was supported in part by National Science Foundation Grant GP-5482. The author wishes to thank Mr. M. Sakamoto for assistance in the calculations of the theoretical spectra.

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(14) We shall discuss the structures of the dimers and the radical-dimer equilibria in a later publication.

Solvent Effects in Nuclear Magnetic Resonance Spectroscopy. IX.[1] A Variable-Temperature Study of α,β-Unsaturated Ketones in Toluene-d_8 Solution

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Contribution from the University Chemical Laboratory, Cambridge, England.
Received July 5, 1966

Abstract: A variable-temperature proton magnetic resonance study of a series of α,β-unsaturated ketones (fixed *s-trans* and *s-cis* systems, as well as mobile systems) has been made in toluene-d_8 solution. Stereospecific complexing between the α,β-unsaturated ketones and the toluene-d_8 solvent results in temperature-dependent chemical shifts of the proton resonances. The direction of change of the temperature-dependent chemical shift (upfield or downfield) is dependent on the location of the proton with reference to a plane drawn through the carbonyl carbon atom and perpendicular to the C–O bond. This generalization may be utilized in both structural and conformational studies of α,β-unsaturated ketones.

Recently it has been shown[2,3] that the solvent shifts ($\Delta = \delta_{CDCl_3} - \delta_{C_6H_6}$ ppm) induced by benzene (relative to deuteriochloroform) in the proton magnetic resonance spectra of saturated ketones are positive for protons lying behind a reference plane drawn through the carbonyl carbon atom and perpendicular

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(1) Part VIII: J. H. Bowie, J. Ronayne, and D. H. Williams, *J. Chem. Soc., Sect. B*, 785 (1966).

(2) J. D. Connolly and R. McCrindle, *Chem. Ind.* (London), 375 (1965).

(3) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).