Abstraction of Methyl Hydrogen of Substituted Anisoles by *t*-Butoxy Radicals[1a]

HIDEKI SAKURAI,[1b] AKIRA HOSOMI, AND MAKOTO KUMADA

Department of Synthetic Chemistry, Kyoto University, Sakyo-ku, Kyoto 606, Japan

Received June 2, 1969

Relative reactivities of the methyl hydrogens of eight ring-substituted anisoles toward *t*-butoxy radicals were determined in 1,1,2-trichlorotrifluoroethane at 45.0°. Di-*t*-butyl peroxyoxalate was used as a source of *t*-butoxy radicals. One methyl hydrogen of anisole was slightly less reactive than that of toluene. The logarithms of the relative reactivities of anisoles show a good $\rho\sigma$ correlation, the ρ value being -0.41. This figure indicates that the transmitting efficiency of polar effects of anisoles toward hydrogen abstraction is rather unexpectedly high compared with that of toluene. An attempt to correlate the reactivities of anisoles and toluenes in various reactions was made in terms of transmission of polar effects.

In a previous paper,[2] we have indicated that abstraction of benzylic hydrogen atoms of substituted toluenes by *t*-butoxy radicals gives rise to rate data better correlated with σ^+ parameters than with σ. It follows, therefore, that rates of abstraction of benzylic[3] and phenolic[4] hydrogens by electron-seeking radicals are generally correlated with σ^+ parameters. It is very interesting to compare these results with the facts that ionization potentials of substituted benzyl[5] and phenoxy[6] radicals as well as solvolytic rates in benzylic systems follow the $\rho\sigma^+$ relationship.

We now report relative reactivities of methyl hydrogens of substituted anisoles toward *t*-butoxy radicals in the same reaction conditions for substituted toluenes.[2] These data are discussed in terms of transmission of polar effects and comparison of other pertinent data.

Results and Discussion

The relative reactivities of the *t*-butoxy radical toward hydrogen donors can be measured by the following competition.

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_a} (CH_3)_3COH + R\cdot$$

$$(CH_3)_3CO\cdot \xrightarrow{k_d} (CH_3)_2CO + CH_3\cdot$$

Thus the ratio of the rate constant, k_a/k_d, can be calculated from the *t*-butyl alcohol/acetone ratio by the equation[7]

$$[(CH_3)_3COH]/[CH_3COCH_3] = (k_a/k_d)[RH]$$

By comparing the ratios of k_a/k_d for substituted anisoles, the relative reactivities of these compounds may be obtained.

As pointed out by Walling and Wagner[8] and by us in the previous paper,[2] the effects of solvents (or reactants in the case of neat states) on these competitions could be quite significant. However, in a common solvent at high dilution, k_d must be kept constant no matter how large the solvent effect may be. Thus, if the rate expression is valid, the experimental points of the plot of the resulting *t*-butyl alcohol/acetone ratios against the initial concentration of each substrate should lie on a straight line with a slope equal to k_a/k_d. Experiments indicate that this is true. The *t*-butyl alcohol/acetone ratios do not depend on the substrate/peroxide ratio but on the concentration of the substrate.

The relative reactivities of substrates toward *t*-butoxy radicals may be determined by competitive chlorination with *t*-butyl hypochlorite.

$$(CH_3)_3COCl \longrightarrow (CH_3)_3CO\cdot + Cl\cdot$$

$$(CH_3)_3CO\cdot + R^1H \longrightarrow (CH_3)_3COH + R^1\cdot$$

$$(CH_3)_3CO\cdot + R^2H \longrightarrow (CH_3)_3COH + R^2\cdot$$

$$R^1\cdot + (CH_3)_3COCl \longrightarrow (CH_3)_3CO\cdot + R^1Cl$$

$$R^2\cdot + (CH_3)_3COCl \longrightarrow (CH_3)_3CO\cdot + R^2Cl$$

Relative rates of abstraction for R^1H and R^2H may be measured directly from the R^1Cl/R^2Cl ratio. This method has been accepted widely. However, as pointed out earlier,[2] chlorination by *t*-butyl hypochlorite can involve chlorine atoms instead of *t*-butoxy radicals as the chain carrier. This view has been once rejected,[9] but quite recently, Walling and McGuinness[10] have recognized properly that *t*-butyl hypochlorite chlorinations actually involve chlorine-atom chains in certain substrates, especially in compounds having benzylic hydrogens. Therefore, the present method seems at this time to be most reliable to estimate reactivities toward the *t*-butoxy radicals.

The relative reactivities of substituted anisoles for hydrogen abstraction are determined in 1,1,2-trichlorotrifluoroethane (Freon-113) at 45.0° using di-*t*-butyl peroxyoxalate[11] as the source of *t*-butoxy radicals. Di-*t*-butyl peroxyoxalate was decomposed in excess of substituted anisole of varying concentrations, and *t*-butyl alcohol/acetone ratios were determined by gas chromatography. The plots of *t*-butyl alcohol/acetone *vs.* concentration of the substrates gave excellent straight lines, as shown in Figure 1. The ratios of k_a/k_d were calculated by the method of least squares, the results being listed in Table I. Figure 2 represents the relationship between log (k_a/k_d) and Hammett's σ values.[12]

---

[1] (a) Presented in part at the 8th Symposium on Free-Radical Reactions, Nagoya, Japan, Oct 1967, Preprints, p 14. (b) To whom correspondence should be addressed: Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai, Japan.

[2] H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, **89**, 458 (1967).

[3] G. A. Russell and R. C. Williamson, Jr., *ibid.*, **86**, 2357 (1963).

[4] K. U. Ingold, *Can. J. Chem.*, **41**, 1744, 2816 (1963).

[5] A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961).

[6] J. M. S. Tait, T. W. Shannon, and A. G. Harrison, *ibid.*, **84**, 4 (1962).

[7] A. L. Williams, E. A. Oberright, and J. W. Brooks, *ibid.*, **78**, 1190 (1956).

[8] C. Walling and P. Wagner, *ibid.*, **86**, 3368 (1964).

[9] D. J. Calsson and K. U. Ingold, *ibid.*, **89**, 4885, 4891 (1967).

[10] C. Walling and J. A. McGuinness, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. ORGN-61; *J. Amer. Chem. Soc.*, **91**, 2053 (1969).

[11] P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960).

[12] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 334 (1964).

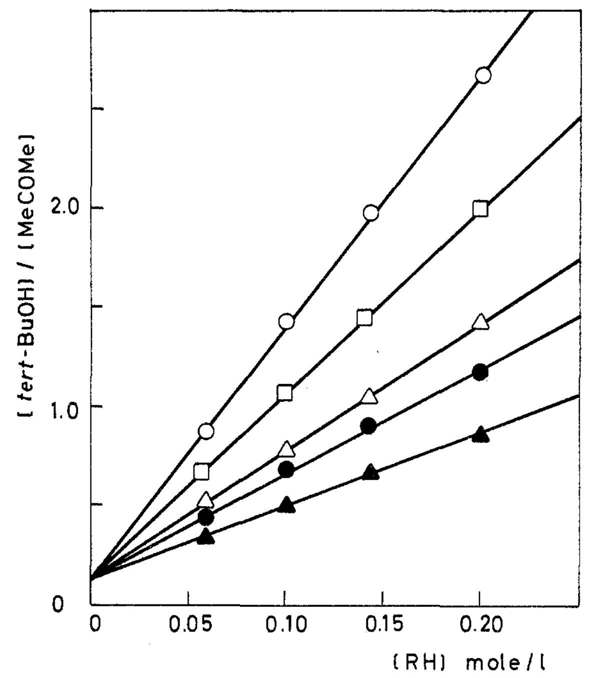


Figure 1.—Typical examples of *t*-butyl alcohol/acetone ratios in hydrogen abstraction from anisoles in Freon-113 at 45.0°: —○—○—, *m*-methoxy; —□—□—, *p*-phenoxy; —△—△—, unsubstituted; —●—●—, *m*-chloro; —▲—▲—, *p*-cyano.

TABLE I

RELATIVE REACTIVITIES OF ONE METHYL HYDROGEN (k_a/k_d) OF SUBSTITUTED ANISOLES TOWARD *t*-BUTOXY RADICALS IN FREON-113 AT 45.0°

Substituent	k_a/k_d[a]
p-C_6H_5O	2.65 ± 0.02[b]
p-CH_3O	2.59 ± 0.01
H	1.99 ± 0.05
m-CH_3O	1.98 ± 0.01
p-Cl	1.94 ± 0.07
m-C_6H_5O	1.74 ± 0.04
m-Cl	1.44 ± 0.04
p-CN	0.99 ± 0.01

[a] The k_a/k_d value for one aromatic ring hydrogen was estimated as 0.14–0.16 in Freon-113 using $C_6H_5OC_6H_5$ or C_6H_5Cl as model substrates. Results in this table are corrected for the reactivities of ring hydrogens. [b] Deviation listed for two or three runs.

As anticipated, the relative reactivities are correlated with σ. These results clearly demonstrate that electron availability plays an important role in determining the relative rates in reactions of this type.[3]

Recently, Mulcahy, Tucker, Williams, and Wilmshurst[13] have observed that a phenoxymethyl radical produced in the gas phase gave benzaldehyde, presumably by a mechanism involving simultaneous phenyl migration and hydrogen-atom ejection.

$$PhOCH_2\cdot \longrightarrow O{=}CHPh + H\cdot$$

However, the main fate of phenoxymethyl radicals in solution was revealed to be dimerization to give 1,2-diphenoxyethane.

$$2PhOCH_2\cdot \longrightarrow PhOCH_2CH_2OPh$$

The latter compound has been characterized by comparison of its physical properties with those of an authentic sample. This observation is in accord with the fact that chlorination of anisole by *t*-butyl hypochlorite gave chloromethyl phenyl ether.[14]

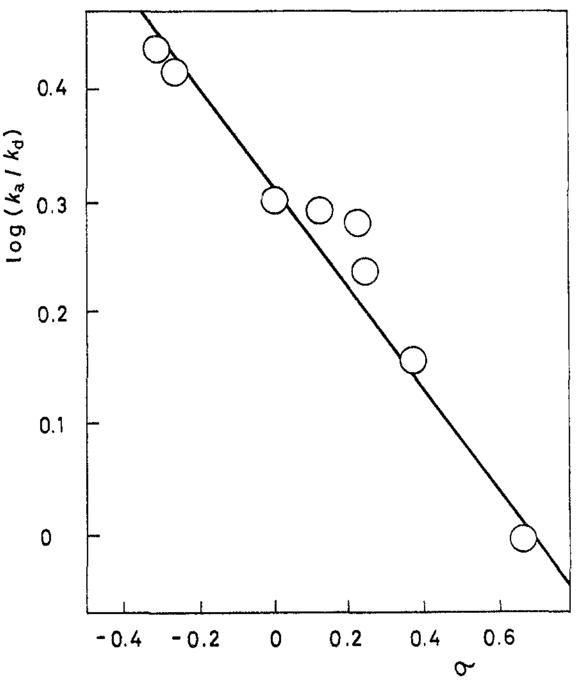


Figure 2.—Correlation of log (k_a/k_d) + 1 and σ for abstraction of methyl hydrogen of substituted anisoles by the *t*-butoxy radical in Freon-113 at 45.0°.

The k_a/k_d value of anisole, 1.99, indicates that one methyl hydrogen of unsubstituted anisole is slightly less reactive than that of unsubstituted toluene (k_a/k_d = 2.19 in Freon-113).[2] However, the transmitting efficiency of polar effects of anisole toward hydrogen abstraction appears unexpectedly high. Thus the ρ value of anisoles (−0.41) is rather large in absolute magnitude compared with those of toluenes (−0.35 with σ^+ or −0.40 with σ)[2] in spite of the circumstance that the substituent-carrying benzene ring of the former is separated by one more atom, oxygen, from the reaction center. It is well established that the interposition of a methylene group decreases the ρ value by a factor of *ca.* 2.3. Such "superconducting effect" of oxygen was observed also in nmr data.[15]

Now it appears of interest to compare ρ values of appropriate reactions in which stabilization of the benzylic carbonium ions plays a crucial role with that of the corresponding reaction of the phenoxymethyl systems under the same reaction conditions. Table II lists some data, including the present study, and contains also the Hammett correlations observed on nmr chemical shifts for anisoles[16] and toluenes.[15]

For *t*-butyl phenoxyperacetates, only half-lives of unimolecular decomposition were reported;[17] however, the data fit satisfactorily with the $\rho\sigma$ relationship and the ρ value is calculated by the method of least squares. Although the mechanism of the decomposition of *t*-butyl phenoxyperacetates have not been fully elucidated, the fact that α-alkoxyperalkanoic esters decomposed by

---

[13] M. F. R. Mulcahy, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Aust. J. Chem.*, **20**, 1155 (1967).

[14] C. Walling and M. J. Minz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).

[15] S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

[16] C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962).

[17] C. Rüchardt, H. Bock, and I. Rüchardt, *Angew. Chem.*, **78**, 267 (1966).

TABLE II

COMPARISON OF ρ VALUES FOR ANISOLES AND TOLUENES IN SOME REACTIONS

No.	Reactant	Reaction	ρ (σ or σ^+)	$\rho_{anisole}/\rho_{toluene}$	Ref
1	$4\text{-X-}C_6H_4OCH_3$	*a*	16.2 (cps/σ)	1.27	*b*
	$4\text{-X-}C_6H_4CH_3$	*a*	12.8 (cps/σ)		*c*
2	$\text{X-}C_6H_4OCH_3$	*d*	0.41 (σ)	1.17	*e, f*
	$\text{X-}C_6H_4CH_3$	*d*	0.35 (σ^+)		*g*
3	$\text{X-}C_6H_4OCH_2CO_3C(CH_3)_3$	*h*	1.18 (σ)	1.08	*i*
	$\text{X-}C_6H_4CH_2CO_3C(CH_3)_3$	*j*	1.09 (σ^+)		*k*
4	$\text{X-}C_6H_4OCH{=}CH_2$	*l*	1.7 (σ)	0.84	*m*
	$\text{X-}C_6H_4CH{=}CH_2$	*l*	2.03 (σ^+)		*n*
5	$\text{X-}C_6H_4OCH{=}CH_2$	*o*	2.2 (σ)	0.65	*p*
	$\text{X-}C_6H_4CH{=}CH_2$	*q*	3.42 (σ^+)		*r*

[a] Chemical shifts of methyl protons in CCl_4 at 60 MHz. [b] C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962). [c] Reference 15. [d] Hydrogen abstraction by *t*-butoxy radicals at 45.0° in Freon-113. [e] This study. [f] K. Uneyama, H. Namba, and S. Oae have reported $\rho = -0.38$ in the reaction of six anisoles with di-*t*-butyl peroxide at 130° in chlorobenzene: Preprints, 8th Symposium on Free-Radical Reactions, Nagoya, Japan, Oct 1967, p 15. [g] Reference 2. [h] Spontaneous decomposition at 70.5° in ethylbenzene. [i] C. Rüchardt, H. Bock, and I. Rüchardt, *Angew. Chem.*, **78**, 267 (1966). [j] Spontaneous decomposition at 90.7° in chlorobenzene. [k] P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960). [l] Cationic copolymerization. [m] T. Okuyama, I. Matsumura, T. Fueno, and J. Furukawa, Preprints, 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1966, IV, p 107. [n] C. G. Overberger, L. H. Arond, D. Tanner, J. J. Taylor, and T. Alfrey, Jr., *J. Amer. Chem. Soc.*, **74**, 4848 (1952); J. P. Kennedy in "Copolymerization," G. E. Ham, Ed., Interscience Publishers, New York, N. Y., 1964, p 308. [o] Hydrolysis at 35.0° in 0.2 *N* HCl–dioxane (80)–water (20). [p] T. Fueno, I. Matsumura, T. Okuyama, and J. Furukawa, Preprints, 17th Symposium on Organic Reaction Mechamisms, Tokyo, Oct 1966, p 121. [q] Hydration at 25.0° in 3.83 *M* $HClO_4$. [r] W. M. Schubert, B. Lam, and J. Reefe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964).

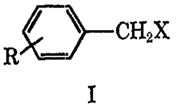
a concerted mechanism[18] indicates that phenoxyperacetates also decompose in a concerted fashion like phenylperacetates.[19]

$$PhCH_2CO_3(CH_3)_3 \longrightarrow [PhCH_2\cdots\cdots\cdots CO_2\cdots\cdots OC(CH_3)_3] \longrightarrow \text{products}$$

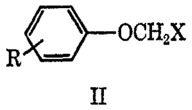
$$PhOCH_2CO_3C(CH_3)_3 \longrightarrow [PhOCH_2\cdots\cdots\cdots CO_2\cdots\cdots OC(CH_3)_3] \longrightarrow \text{products}$$

These results demonstrate a marked similarity in the polar substituent effects between homolytic processes, such as hydrogen abstraction and unimolecular bond breaking, and a cationic process, such as hydration of olefins. The gradual change of ρ values seen in Table II originates naturally in the difference of capability to transmit the polar effects.

The difference in the capability to transmit the polar effects between benzyl systems (I) and phenoxymethyl systems (II) results in such a gradual change of relative ρ values according to increasing ionic characters of the transition state. Thus, the greater the electron demand at the transition state, the smaller should be the $\rho_{anisole}/\rho_{toluene}$ ($\equiv \rho_{II}/\rho_{I}$), since the interposition of an oxygen atom leads to suppression of direct conjugation between the benzene ring and the electron-deficient reaction center. The data in Table II now serve to draw a comparison of efficiency to transmit the polar effects between I and II.



I



II

A plot of (ρ_{II}/ρ_{I}) *vs.* $|\rho_{I}|$ is shown in Figure 3. Very remarkably, a good linear relationship was obtained. It is interesting to note that the nmr data coincide very closely to the value corresponding to $\rho_{I} = 0$, indicative of the nmr data to be concerned with the characters of the ground states.

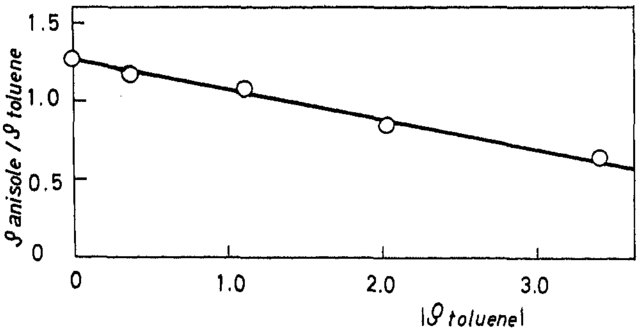


Figure 3.—Correlation of $\rho_{anisole}/\rho_{toluene}$ with $\rho_{toluene}$ of some homolytic and cationic reactions.

Several conclusions may be obtained from the relation; *e.g.*, (a) hydrogen abstaction by *t*-butoxy radicals leads to less polar transition states, (b) the ionic characters of the transition states of decomposition of peresters develop more than those of hydrogen abstractions, and (c) the carbonium-ion character of cationic polymerizations is less than that of hydration of olefins.

The results now demonstrate a marked parallelism in reactivities of homolytic with cationic processes on the polar substituent effects. For structural changes of the substrates in these reactions, for which the Hammett equation is applicable, differences in the bond dissociation energies of R–X bonds in question are less important[20] than those of ionization potentials of R· radicals. It should be emphasized that the $\rho\sigma^+$ rela-

---

(18) D. R. Dixonand and A. Pajaczkowski, *Chem. Commun.*, 337 (1966).

(19) P. D. Bartlett and C. Rüchardt, *J. Amer. Chem. Soc.*, **82**, 1756 (1960).

(20) M. Szwarc, C. H. Leigh, and A. H. Sehon [*J. Chem. Phys.*, **19**, 675 (1951)] have recorded the influence of aromatic substitution on the C–Br bond dissociation energy in benzyl bromides. The magnitude of the effect is rather comparable with the experimental errors.

tionship observed in hydrogen abstraction reactions is concerned with the polar effects of substituents in stabilization of the benzylic carbonium ions and not with the resonance stabilization of the benzylic radicals.[21] No extra-delocalization effect of substituents is therefore required to express the reactivities of hydrogen abstraction in benzylic systems.

Experimental Section

Materials.—Di-*t*-butyl peroxyoxalate was prepared by the method of Bartlett, *et al.*[11] Freon-113 was commercially available and was used after distillation. Anisole and three derivatives, *p*-methoxy-, *p*-chloro-, and *p*-cyanoanisole, were commercial samples and were used after purification by usual way.

***p*-Phenoxyanisole.**—This compound was prepared from the potassium salt of *p*-methoxyphenol and bromobenzene by refluxing in the presence of copper powder: bp 136° (6 mm) [lit.[22] bp 186° (32 mm)]; $n^{20}{}_{\mathrm{D}}$ 1.5781; d^{20} 1.1201.

***m*-Phenoxyanisole and *m*-Dimethoxybenzene.**—To the ethanol solution of resorcinol (220 g, 2.0 mol) and dimethyl sulfate (260 g, 2.06 mol) was added aqueous potassium hydroxide (112 g, 2.0 mol) with cooling by ice bath. By distillation, *m*-methoxyphenol (126 g, 1.02 mol, 51.0% yield) was obtained: bp 138° (27 mm) (lit.[23] bp 240–242°); $n^{20}{}_{\mathrm{D}}$ 1.5492; $d^{20}{}_4$ 1.1490. In addition, *m*-dimethoxybenzene (38 g, 0.275 mol, 13.8% yield) was obtained: bp 107° (27 mm) [lit.[24] bp 213–213.6° (753 mm)]; $n^{20}{}_{\mathrm{D}}$ 1.5252; d_4^{20} 1.0721. *m*-Phenoxyanisole (23 g, 0.115 mol) was then prepared from *m*-methoxyphenol (50 g, 0.403 mol), bromobenzene (62 g, 0.395 mol), and potassium hydroxide (22 g, 0.393 mol) in the presence of a catalytic amount of copper powder in 28.5% yield: bp 134° (15 mm) [lit.[22] bp 175° (20 mm)]; $n^{20}{}_{\mathrm{D}}$ 1.5798; $d^{20}{}_4$ 1.1164.

***m*-Chloroanisole.**—This was prepared from the sodium salt of *m*-chlorophenol (25 g, 0.194 mol) by treating it with dimethyl sulfate (31.5 g, 0.25 mol) in water: yield 23.5 g (0.165 mol, 85.1% yield); bp 85° (27 mm) (lit.[25] bp 193–194°); $n^{20}{}_{\mathrm{D}}$ 1.5359; $d^{20}{}_4$ 1.1737.

Procedure for Kinetic Runs.—The reaction mixtures of varying concentrations (0.05–0.20 *M*) were made of samples of substituted anisole and di-*t*-butyl peroxyoxalate in Freon-113 which were accurately weighed. A reactant ratio of substituted anisole to di-*t*-butyl peroxyoxalate of 5:1 was employed. The reaction mixtures were then placed in a glass tube and were degassed by repeated freezing and melting under vacuum. The tubes were then sealed under vacuum and were immersed in a constant-temperature bath kept at 45.0 ± 0.1° for 7.5 hr. After being cooled in a Dry Ice–methanol bath, the tubes were opened and the *t*-butyl alcohol/acetone ratios were determined by glpc on a column packed with polyethylene glycol 1500 using helium as a carrier gas. The ratios of the rate constant k_a/k_d were calculated from the plots of *t*-butyl alcohol/acetone *vs.* concentration of the substrates by the method of least squares.

Registry No.—*p*-Phenoxyanisole, 1655-69-2; *p*-methoxyanisole, 150-78-7; anisole, 100-66-3; *m*-methoxyanisole, 151-10-0; *p*-chloroanisole, 623-12-1; *m*-phenoxyanisole, 1655-68-1; *m*-chloroanisole, 2845-89-8; *p*-cyanoanisole, 874-90-8.

---

(21) H. Sakurai and K. Tokumaru, "Chemistry of Free Radicals," H. Sakurai and K. Tokumaru, Ed., Nankodo, Tokyo, 1967, Chapter 17.

(22) T. R. Lea and R. Robinson, *J. Chem. Soc.*, 412 (1926).

(23) W. H. Parkin, J. N. Ray, and R. Robinson, *ibid.*, 941 (1926).

(24) J. K. Marsh, *ibid.*, 125, 420 (1924).

(25) F. Reverdin and F. Eckhard, *Chem. Ber.*, **32**, 2626 (1899).

Nuclear Magnetic Resonance Spectroscopy. ^{13}C Spectra of Indole and Methylindoles[1]

Richard G. Parker and John D. Roberts

Contribution No. 3939 from the Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California 91109

Received September 8, 1969

The natural-abundance ^{13}C nmr spectra of indole, the seven monomethylindoles, and some di- and trimethylindoles have been determined at 15.1 MHz. The chemical shifts of the ring carbons in these compounds were found to range over 50 ppm, and with the aid of complete proton decoupling it was possible to resolve all of the carbon resonances. Single-frequency and off-resonance proton-decoupling techniques were employed to assign the resonances to specific carbons.

Instrumentation is now available for relatively routine determination of high-resolution ^{13}C nmr (cmr) spectra in natural abundance in organic compounds.[2–5] Noise-modulated proton decoupling[6] is of special utility for organic structural analysis because it permits measurement of fully proton-decoupled spectra consisting of sharp singlets when other nuclei with nonzero spin are either absent or undergo rapid quadrupole relaxation.

No reports on the ^{13}C nmr spectra of indoles have appeared in the literature. As a part of our continuing efforts to measure and interpret the ^{13}C spectra of organic aromatic heterocyclic compounds,[4a] the chemical shifts of the carbons of indole and its seven monomethyl derivatives have been measured and assigned (Table I). From these data, it was found possible to compile a table of additivity parameters (Table II) for use in predicting the chemical shifts of some di- and trimethyl derivatives which were available for comparison.

Carbon spectra in which the protons were not at least partially decoupled were found to be unsatisfactory in this work because of their complexity and the long scanning times required.[6a] Off-resonance, single-frequency decoupled spectra, in which the sample is irradiated strongly at a frequency several hundred hertz from the region of proton resonance frequencies were found to be very helpful.[7] No long-range couplings

---

[1] Supported by the National Science Foundation and the Public Health Service, Research Grant GM-11072-07 from the Division of General Medical Sciences.

(2) J. B. Stothers, *Quart. Rev.*, **19**, 144 (1965).

(3) (a) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); (b) D. K. Dalling and D. M. Grant, *ibid.*, **89**, 6612 (1967).

(4) (a) F. J. Weigert and J. D. Roberts, *ibid.*, **89**, 2967 (1967); **90**, 3543 (1968); F. J. Weigert, Ph.D. Thesis, California Institute of Technology, 1968. (b) F. J. Weigert, M. Winokur, and J. D. Roberts, *ibid.*, **90**, 1566 (1968).

(5) (a) J. J. Burke and P. C. Lauterbur, *ibid.*, **86**, 1870 (1964); (b) R. A. Friedel and H. L. Retcofsky, *ibid.*, **85**, 1300 (1963).

(6) (a) F. J. Weigert, M. Jautelat, and J. D. Roberts, *Proc. Nat. Acad. Sci., U. S.*, **60**, 1152 (1968); (b) F. L. Johnson and M. E. Tate, *Can. J. Chem.*, **47**, 63 (1969); (c) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(7) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, **92**, 1338 (1970).