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.

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

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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

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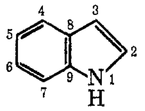
TABLE I

THE CHEMICAL SHIFTS[a] AND ASSIGNMENTS FOR THE ^{13}C SPECTRA OF INDOLES



Compd	C-2	C-3	C-4	C-5	C-6	C-7	C-9	C-9	Methyl
Indole	67.63	90.16	71.54	70.49	72.54	80.95	64.04	56.65	
1-Methyl-	63.48	91.48	71.51	70.91	73.03	83.02	63.39	55.27	160.71
2-Methyl-	57.10	92.40	72.75	71.70	72.93	81.90	62.90	55.70	179.40
3-Methyl-	70.07	81.36	73.39	70.54	73.20	81.06	63.61	55.49	182.95
4-Methyl-	68.62	91.73	62.58	70.61	72.67	83.51	64.11	56.26	171.19
5-Methyl-	67.81	90.69	69.06	64.00	72.01	81.50	63.65	57.57	171.31
6-Methyl-	68.49	90.48	72.07	70.94	61.30	81.20	66.15	55.49	171.08
7-Methyl-	68.03	89.81	73.92	70.08	72.48	71.93	64.38	56.42	176.15
1,2-Dimethyl-	54.74	92.78	72.80	72.08	73.19	83.58	63.94	55.75	164.13 180.55
2,3-Dimethyl-	61.44	85.97	74.41	71.66	73.51	82.07	62.54	56.55	181.67 184.32
2,7-Dimethyl-	57.65	91.83	75.14	71.13	72.95	72.87	63.34	56.28	176.16 179.40
2,3,5-Trimethyl-	61.58	86.48	70.31	65.01	74.67	82.60	62.35	58.21	171.25 181.66 184.40

[a] In parts per million upfield from carbon disulfide.

TABLE II

THE INCREMENTAL CHANGES IN CHEMICAL SHIFT OF THE RING CARBONS IN INDOLES UPON METHYL SUBSTITUTION

Compd	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9
Indole[a]	67.63	90.16	71.54	70.49	72.54	80.95	64.04	56.65
1-Methyl-	−4.15	+1.32	−0.03	+0.42	+0.49	+2.07	−0.65	−1.38
2-Methyl-	−10.53	+2.24	+1.21	+1.21	+0.39	+0.95	−1.14	−0.95
3-Methyl-	+2.44	−8.80	+1.85	+0.05	+0.66	+0.11	−0.43	−1.16
4-Methyl-	+0.99	+1.57	−8.96	+0.12	+0.13	+2.56	+0.07	−0.39
5-Methyl-	+0.18	+0.53	−2.48	−6.49	−0.53	+0.55	−0.49	+0.92
6-Methyl-	+0.86	+0.32	+0.53	+0.45	−11.24	+0.25	+2.11	−1.16
7-Methyl-	+0.40	−0.35	+2.38	−0.41	−0.06	−9.02	+0.34	−0.23

[a] Relative to carbon disulfide.

are observed in such spectra and direct ^{13}C–H couplings are reduced to 20–40 Hz while still providing favorable Overhauser enhancement[3,8] of the signal intensity. In the indoles we have studied, off-resonance proton decoupling yielded fairly clean doublets for the ring carbons bearing a proton and singlets for the quaternary carbons. An additional aid in assigning the quaternary carbons was the observation that the quaternary carbons bearing a methyl group appeared to be slightly more intense (about 10%) than the carbons at the ring junction (C-8 and C-9).

Exact proton-decoupling frequencies for each carbon were also an aid in making the chemical-shift assignments. Because the protons at C-2, C-3, and C-4 can be easily assigned in the proton spectra of these indoles,[9] this technique was used exclusively where applicable.

Discussion of Spectra. A. Indole.—The fully-proton-decoupled cmr spectrum of indole (Figure 1) consists of eight nearly equally intense peaks which, with narrower sweeps, become six sharp, equally intense, singlets and two smaller, broader singlets. The off-resonance decoupled spectrum showed the broad singlets to be the quaternary carbons, C-8 and C-9. The low-field singlet at 56.65 ppm was assigned to C-9 since carbons adjacent to nitrogen in pyrroles[10] and pyridines[11] have been shown to appear at lower field than those in a β position. The singlet at 64.04 ppm is then assigned to C-8.

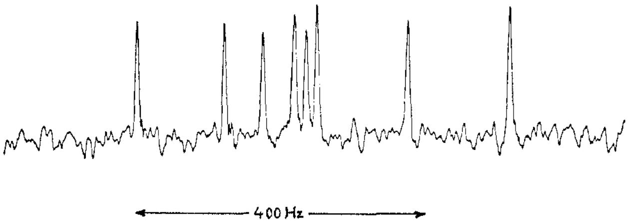


Figure 1.—Noise-decoupled, natural-abundance cmr spectrum of indole at 15.1 MHz. The field increases to the right and the farthest right-hand peak (C-3) is 90.16 ppm upfield from CS_2.

Because the protons at C-2, C-3, and C-4 can be readily assigned in the proton spectrum, single-frequency decoupling was employed to assign C-2 at 67.63 ppm, C-3 at 90.16 ppm, and C-4 at 71.54 ppm. Three singlets, 70.49, 72.54, and 80.95 ppm, then remained unassigned. The identities of the unassigned singlets were established by comparison with the spec-

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tra of 5-, 6-, and 7-methylindole. Thus, C-5 appears at 70.49 ppm in indole, C-6 at 72.54 ppm, and C-7 at 80.95 ppm.

B. 1-Methylindole.—In the spectrum of 1-methylindole, C-2 and C-9 both undergo downfield shifts of 4.15 and 1.38 ppm, respectively, compared with the corresponding carbons of indole, presumably owing to a slight difference in polarization of the C–N σ bonding electrons. The chemical shifts of the other carbons remain essentially unchanged with the exception of C-7 which is shifted 2.07 ppm upfield. This shift may be the result of a steric interaction between the C-7H and 1-methyl group which could cause some steric compression at C-7.[12] An electron-releasing effect from the five-membered ring into the six-membered ring on N-methyl substitution seems to be small because there is very little change at the other carbons in the six-membered ring as is observed on methylation of anilines.

C. 2-Methylindole.—Substitution of a methyl group at C-2 causes two large changes in the spectrum, relative to indole. C-2 undergoes a large downfield shift of 10.53 ppm while C-3 shifts upfield by 2.24 ppm. Both of these changes are about the same as those found for methyl substitution in alkanes[3a] and pyrrole, furan, and thiophene.[4a] The changes in the chemical shifts of C-4, C-5, C-6, and C-7 are in the upfield direction indicating some electron release into the six-membered ring upon methyl substitution at carbon in the five-membered ring. Both C-8 and C-9 shift slightly downfield.

D. 3-Methylindole.—The spectrum of 3-methylindole is very similar to that of 2-methylindole with the changes in shifts of C-2 and C-3 reversed. C-3 undergoes an 8.80-ppm downfield shift relative to indole, while C-2 is shifted upfield 2.44 ppm. The upfield shifts at C-5, C-6, and C-7 are smaller than in the case of 2-methylindole, while C-4 is shifted to even higher field, perhaps owing to a steric interaction between the hydrogen at C-4 and the methyl group.

E. 4-Methylindole.—The major changes in the spectrum of 4-methylindole, relative to indole, are at C-4 and C-7. C-4, as expected, is shifted downfield by 8.96 ppm upon methyl substitution. The change in chemical shift at C-7 is almost identical with that observed between benzene and the *para* position of toluene, 2.56 ppm upfield.[12] On this basis, it appears that a *para* effect is operative in the six-membered ring and a large upfield shift should generally be expected at the carbon "*para*" to the one bearing the methyl group.

F. 5-Methylindole.—The indole which deviates most from the general pattern is 5-methylindole. The downfield shift of the resonance of C-5 is only 6.49 ppm and there is a large, unexplained downfield shift of C-4 (but not C-6) by 2.48 ppm. The effect at C-5 may be the result of some sort of an electron saturation effect because C-5 is "*para*" to the nitrogen. A similar effect is evident at C-9 where there is an upfield shift of 0.9 ppm instead of the expected 2 ppm.

G. 6-Methylindole.—Introduction of a methyl group at C-6 causes reasonably expected changes. The downfield shift of C-6 is somewhat larger than expected, 11.24 ppm, and there is a sizable upfield shift of 2.11 ppm at C-8 which corresponds to the *para*-methyl effect.

H. 7-Methylindole.—The only significant changes in the chemical shifts in 7-methylindole, relative to indole, occur at C-7, whose resonance is shifted downfield by 9.02 ppm, and at C-4, which is upfield by 2.38 ppm as the result of the *para* effect.

Methyl Groups.—The chemical shifts of the methyl groups appear to be typical for their particular environment. Those attached to the five-membered ring, with the exception of the N-methyl group, are at slightly higher field than those in the six-membered ring and are in agreement with the values found in methylpyrroles.[10] The methyls attached to the six-membered ring appear at the same position as those in toluene, the xylenes, etc.[13]

Additive Effects.—If the chemical shifts of the carbons at each position in the seven monomethylindoles are compared with the chemical shifts of the corresponding carbons in indole, the incremental change in chemical shift at each carbon for each type of methyl substitution can be calculated (Table II) and used to predict by simple additivity the chemical shifts of indoles containing more than one methyl group. The predicted and observed chemical shifts for three dimethylindoles and 2,3,5-trimethylindole are shown in Table III. The

Table III

Observed and Predicted Chemical Shifts for Some Methyl-Substituted Indoles

Carbon	Obsvd	Predicted	Difference[a]
	1,2-Dimethylindole		
2	54.74	52.95	+1.79
3	92.78	93.72	−0.94
4	72.80	72.72	+0.08
5	72.08	72.12	−0.04
6	73.19	73.42	−0.23
7	83.58	83.97	−0.39
8	63.95	62.25	+1.70
9	55.75	54.32	+1.43
	2,3-Dimethylindole		
2	61.44	59.54	+1.90
3	85.97	83.60	+2.37
4	74.40	74.60	−0.20
5	71.66	71.75	−0.09
6	73.51	73.59	−0.08
7	82.07	82.01	+0.07
8	62.54	62.47	+0.07
9	56.55	54.54	+2.01
	2,7-Dimethylindole		
2	57.65	57.50	+0.15
3	91.83	92.05	−0.22
4	75.14	75.13	+0.01
5	71.13	71.29	−0.16
6	72.95	72.87	+0.08
7	72.87	72.88	−0.01
8	63.34	63.24	+0.10
9	56.28	55.47	+0.81
	2,3,5-Trimethylindole		
2	61.58	59.72	+1.86
3	86.48	84.13	+2.35
4	70.31	72.12	−1.81
5	65.01	65.26	−0.25
6	74.67	73.06	+1.61
7	82.60	82.56	+0.04
8	62.35	61.98	+0.37
9	58.21	55.46	+2.75

[a] Observed chemical shift minus that predicted.

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chemical shifts of these four indoles were assigned using techniques described earlier in this paper.

The quality of the predictions appear to be good to excellent. For 2,7-dimethylindole, the difference between the predicted and observed values is only about 0.1 ppm, except at C-9 where the difference is somewhat greater but still less than 1.0 ppm. This could be expected to provide a favorable case because the two methyl groups are not close to one another and their mutual interactions should be small.

With the 1,2- and 2,3-dimethylindoles, the 1,2-methyl interactions should be roughly the same and as a result the deviations from the predicted shifts should be about the same. This is apparent from the resonance of C-2 which is upfield for both compounds by 2.0 ppm from what is predicted. The C-2 shift may be the result of methyl–methyl repulsions causing slight lengthening of the 1,2-ring bond in 1,2-dimethylindole and the 2,3-ring bond in 2,3-dimethylindole.[7] There is also an upfield shift at C-9 for both compounds, possibly because the methyl–methyl repulsions deform the five-membered ring with resultant lengthening of the 1,9 bond.

The worst agreement between prediction and experiment is seen for 2,3,5-trimethylindole. The previously discussed effects at C-2, C-3, and C-9 are present in about the same magnitude but the resonances at C-4 and C-6 show rather large unexplained deviations from prediction. These may be connected with the abnormalities of 5-methylindole itself as discussed above.

Experimental Section

The indoles used in this study were commercial materials and were used without further purification.

The chemical shifts were measured using the digital frequency sweep spectrometer[4a] with pseudo-random, noise-modulated, proton decoupling[6a] as previously described. The samples were dissolved in dioxane, usually at concentrations of 1.0 g/1.5 ml at which it was usually only necessary to average 10 to 15 scans to obtain adequate signal-to-noise ratios. Sweep rates of 2- or 4-Hz/sec at 50- or 100-Hz sweep widths were generally employed. The peak widths were usually on the order of from 1 to 3 Hz. The off-resonance, proton-decoupled spectra usually required 30 to 40 time-averaged scans although it was possible in most cases to identify the quaternary carbons after 10 to 15 scans.

Registry No.—Indole, 120-72-9; 1-methylindole, 603-76-9; 2-methylindole, 95-20-5; 3-methylindole, 83-34-1; 4-methylindole, 16096-32-5; 5-methylindole, 614-96-0; 6-methylindole, 3420-02-8; 7-methylindole, 933-67-5; 1,2-dimethylindole, 875-79-6; 2,3-dimethylindole, 91-55-4; 2,7-dimethylindole, 5621-13-6; 2,3,5-trimethylindole, 21296-92-4.

Diazo Alkane Adducts of Thiete Sulfone (Thiacyclobutene 1,1-Dioxide) in Synthesis of Thiabicyclopentane Dioxides, Pyrazoles, and Tetrahydrothiophene Sulfones[1-3]

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Diazoalkanes have been added to the double bond of thiete sulfone (thiacyclobutene 1,1-dioxide) to yield 1- or 2-pyrazolines. Adducts of diphenyldiazomethane or methylphenyldiazomethane lose nitrogen on heating or on irradiation with ultraviolet light to give 2-thiabicyclo[2.1.0]pentane 2,2-dioxides. In contrast, the adducts of phenyldiazomethane and *p*-methoxyphenyldiazomethane lose sulfur dioxide to give pyrazoles. A route to thiophane (tetrahydrothiophene) sulfones from the thiabicyclopentane sulfones is shown.

Thiete sulfone has a reactive double bond; it and substituted thiete sulfones add anions readily and are dienophiles in the Diels–Alder reaction.[4] 1,3-Cycloadditions of diazo alkanes with acyclic[5a] and cyclic[5b] α,β-unsaturated sulfones are known. Adducts of diazo alkanes with thiete sulfone may be potentially useful intermediates in the synthesis of highly strained systems (such as bicyclobutanes) if the simultaneous or stepwise loss of both nitrogen and sulfur dioxide can be effected from the adducts. Cyclopropanes are formed by loss of nitrogen from 1-pyrazolines[6] and by loss of sulfur dioxide from certain four-membered cyclic sulfones (thietane sulfones).[7]

Addition of Diazo Alkanes to Thiete Sulfone.—Thiete sulfone yields crystalline adducts with various diazo alkanes. All of the adducts are 1-pyrazolines[8] with the exception of the adduct obtained from ethyl diazoacetate which forms a 2-pyrazoline. Table I lists the pyrazolines prepared. Where R and R′ are different groups, the stereochemistry (*syn,anti*) of the adducts was not determined although it is reasonable to assume

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[1] This work was aided by Grant 5R01 CA 08250 of the National Institutes of Health, for which we are grateful.

[2] Reported at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstracts of Papers, Division of Organic Chemistry, No. 178.

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[8] Infrared absorption at 1540 cm^{-1} and ultraviolet absorption at 335 nm for $-N{=}N-$; no absorption for N—H in the infrared.