

Response of Acidity and Magnetic Resonance Properties to Aryl Substitution in Carbon Acids and Derived Carbanions: 1-Aryl-4-phenylcyclopenta-1,3-dienes. Dependence of Ionic Structure on Aryl Substitution

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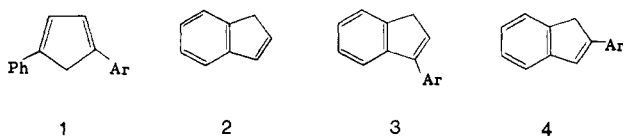
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Abstract: Monosubstitution on one aryl ring of 1,4-diphenylcyclopenta-1,3-diene provides a probe for studying anion stability, charge density, and ionic structure. We have measured the pK_a 's of several members of this series in both pure Me_2SO and Me_2SO-H_2O . Acidities are stronger by 1-2 pK_a units in pure Me_2SO , as a consequence of greater stabilization by dispersion forces in Me_2SO than by hydrogen bonding in the H_2O mixture. Both sets of acidity constants provide a linear response to the Hammett σ constants. The sensitivity of pK_a to σ is about 3 times larger in pure Me_2SO because of the leveling effect of H_2O and the breakdown of the H_- function concept. These results suggest that there is hydrogen bonding between H_2O and the cyclopentadienyl anions. The ^{13}C chemical shifts in pure Me_2SO provide insight into the ionic structure of the anions. The carbons in the unsubstituted phenyl ring and the quaternary carbons of the five-membered ring exhibit a small but generally linear response to σ . The much larger response of the tertiary carbons (C_2 , C_3 , C_5) in the five-membered ring is sigmoidal. The aryl substituent alters the ion pair or aggregated nature of the anion. The sigmoidal behavior is not observed for the neutral hydrocarbons and is less pronounced for the lithium anions. Spin-lattice relaxation times (T_1) of (1,3-diphenylcyclopentadienyl)potassium are consistent with an aggregated or multisolvated structure, since the effective molecular weight is almost twice that of the anion-cation monomer.

The high energy content of carbanions represents a major difficulty in the systematic study of substituent effects on carbon acids and conjugated anions. Proton-transfer equilibria can be readily observed in dipolar, nonhydroxylic solvents for many carbon acids that are α functionalized with a strongly electron-withdrawing substituent ($-NO_2$, $-COR$, $-SO_2R$). For electron-donating or weakly electron-withdrawing substituents, ionization can sometimes be observed, particularly in apolar solvents, in which ion pairing and aggregative processes become important. The fact that α substitution also can influence hybridization of the adjacent carbanion adds further complexity to the analysis of substituent effects.²⁻⁶

Because of the difficulties associated with α functionalization, our approach has been to use the more remote functionalization offered by a substituted phenyl ring. With a few exceptions, somewhat less attention has been devoted to remote substituent effects on carbon acid ionization equilibria and carbanion stability.⁷ Such studies depend on the availability of a series of remotely substituted carbon acids of reasonable strength. Derivatives of cyclopentadiene appear to be suitable, and in this paper we are concerned with the ionization equilibria of 1-aryl-4-phenylcyclopenta-1,3-dienes (1). In a related work,⁸ we have also been



concerned with the indene derivatives 2-4. These series, 1-4,

provide a systematic variation of phenyl substitution within the cyclopentadienyl framework.

To probe substituent effects, we have investigated the equilibrium acidities of the neutral hydrocarbons in pure Me_2SO and in a Me_2SO-H_2O mixture, and we have obtained the NMR parameters (1H and ^{13}C chemical shifts and ^{13}C relaxation times) of the conjugate carbanions.

Several methods have been developed to estimate relative acidities in a series of carbon acids. Streitwieser proposed an acidity scale based on equilibria between the carbon acid and lithium or cesium cyclohexylamide in cyclohexylamine (CHA).⁹ Using a glass electrode, Ritchie determined pK_a 's potentiometrically in Me_2SO .¹⁰ Bordwell has measured equilibrium acidities in pure Me_2SO spectrophotometrically.¹¹

We have used the Bordwell procedure in pure Me_2SO . For Me_2SO-H_2O , we have used the H_- approach, which is applicable to single or mixed solvents that are sufficiently basic to ionize weak acids. These functions measure the ionizing ability of such solutions and are defined by eq 1. In dilute aqueous solutions, H_-

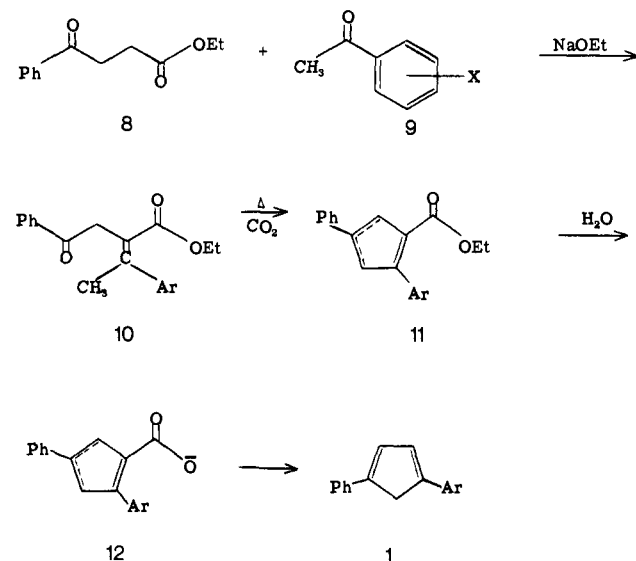
$$H_- = pK_a - \log ([HA]/[A^-]) \quad (1)$$

is equivalent to the pH. For a series of indicator acids, H_- is defined for various solutions of differing base concentration (or composition), and the ionization ratio of the unknown acid is measured spectrophotometrically to obtain the pK_a . The necessary assumptions underlying the method have been based on the pK_a in water and have required similar activity coefficient behavior for the indicators and the unknown acid.^{12,13} Comparison of pK_a 's obtained in pure Me_2SO (Bordwell's procedure¹¹) and in Me_2SO-H_2O (Dolman and Stewart's H_- scale¹⁴) was expected to be useful

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Scheme I

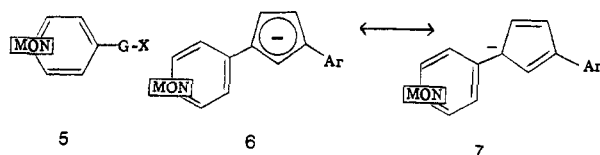


a, X = H; b, X = *p*-NMe₂; c, X = *p*-Me; d, X = *m*-Me; e, X = *p*-OMe; f, X = *m*-OMe; g, X = *p*-F; h, X = *p*-Cl; i, X = *p*-Br; j, X = *p*-Ph; k, X = *p*-SMe; l, X = *p*-NO₂; m, X = *p*-CN;

in testing the assumptions on which the *H*-acidity function is based and in determining the effect of water on these equilibria.

Among NMR parameters, ¹³C shifts have been used to probe the distribution of π -electron density in aromatic systems via a linear relationship. The spin-lattice relaxation time (*T*₁) depends on the effective molecular size of the species under study, so that aggregation phenomena can be examined. In the present study, we utilize these ¹³C probes to study the anion structure.

We have recently shown that the shifts of para spin active nuclei in systems **5** monitor the type and extent of interaction of group



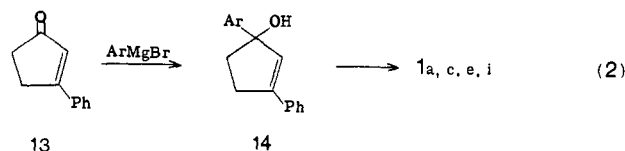
G with the substituent X.¹⁵ 1-Aryl-3-phenylcyclopentadienyl anions **6** can be regarded in the limiting structure **7** as ω -substituted benzyl carbanions (analogous to **5**, G = CH⁻), in which the electron demand of the substituent is regularly varied at a remote position. Thus arylphenylcyclopentadienides **6** can be submitted to the correlative treatment developed for series **5**.

Results

Synthesis of Substrates. Two different routes have been used for preparing the 1-aryl-4-phenylcyclopenta-1,3-dienes **1**. Both routes, however, presented a limited range of applicability. The first approach (Scheme I) follows closely the method of Drake and Adams.¹⁶ Aryl methyl ketones **9** were condensed in two steps with ethyl 3-benzoylpropionate (**8**) to the intermediate arylphenylcyclopentadiene carboxylic esters **11**, which on heating undergo hydrolysis and decarboxylation to the final compounds **1a-k**. This procedure applied successfully, albeit with very modest overall yields (5–15%), to a number of substituted acetophenones **9a-k** but fails totally whenever the substituents present on the aryl methyl ketone are strongly electron withdrawing (**11,m**). The 3-benzoylpropionate **8** is first deprotonated α to the carboxy group to form the carbanion, which then condenses with the carbonyl group of the aryl methyl ketone. We believe that the failure observed for electron-withdrawing substituted aceto-

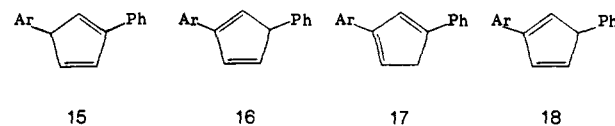
phenones (**9l,m**) is due to the fact that they are more acidic than the ethyl 3-benzoylpropionate (**8**), thus causing proton transfer between the anion of **8** and the acetophenone **9** to compete with nucleophilic attack of the anion on the same ketone.

In an effort to increase the overall yields of cyclopentadienes **1**, we investigated an alternative route.¹⁷ Arylmagnesium bromides were condensed with 3-phenylcyclopent-2-enone (**13**) to the corresponding cyclopentenols **14**, which were anticipated to provide arylcyclopentadienes **1** by dehydration (eq 2). Dis-



appointingly, this alternative route met two major difficulties: (i) the production of 3-phenylcyclopent-2-enone in relatively large amounts and (ii) dehydration of the cyclopentenols under conditions that were destructive of the final cyclopentadienes. Although we found experimental conditions that allowed the satisfactory preparation of 3-phenylcyclopent-2-enone, we succeeded by this route in isolating final cyclopentadienes **1** only with very poor yields (1–2%).

Physical properties of the isolated arylphenylcyclopentadienes are given in the Experimental Section. It should be noted that some melting points varied slightly from sample to sample, although the ¹H NMR analysis and TLC did not offer evidence for the presence of impurities. We believe this behavior should be ascribed to the possible presence of minor amounts of at least one of the other four double-bond isomers (**15-18**) of 1-aryl-4-



phenylcyclopenta-1,3-diene **1**. This possibility is supported by the frequent observation of a triplet upfield from the ring CH₂ triplet (intensity ratio with the latter ranging from 0.05 to 0.10), which could be ascribed to either isomer **16** or **17**.

Despite our interest in synthesizing substrates **1** with an electron-withdrawing group in the aryl ring, neither of the synthetic routes was compatible with such substituents. Efforts to substitute the bromine residue of **1i** with CuCN in DMF failed,¹⁸ probably because under the severe reaction conditions the starting diene did not survive. Negative results were also obtained when the Grignard reagent from *p*-bromoacetophenone ethylene ketal was reacted with 3-phenylcyclopent-2-enone (**13**). We did, however, succeed in placing electron-withdrawing substituents on the aryl rings of the indenenes **3** and **4**.⁸

Acidity in Me₂SO-H₂O. Ionization constants of the arylphenylcyclopentadiene carbon acids (AH) were determined spectrophotometrically by monitoring the ratio of [AH] and [A⁻] in Me₂SO-H₂O-Me₄NOH solutions of different base strength (*H*₋). Five determinations were done for each carbon acid. The base strength of each of the five basic solutions was obtained by measuring the ionization ratio of an amine of known reported p*K*_a in Me₂SO-H₂O. The limited range of p*K*_a variation within the series (0.60 p*K*_a unit) allowed the use of only one indicator (*p*-nitrodiphenylamine, p*K*_a = 15.67)¹⁴ for all six compounds whose acidity has been measured. In the majority of cases reported in the literature, different base strengths for solutions of mixed aqueous solvents are obtained by varying the water content of the mixture and keeping constant the base concentration. Such a procedure could not be utilized in the present case for two reasons. (i) The absorptions of the anions A⁻ are dependent upon the composition of the solvent mixture, being blue-shifted with an increase of the water content.¹⁹ (ii) Absorption maxima of the

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Table I. Acidity Constants of 1-Aryl-4-phenylcyclopenta-1,3-dienes

X	pK _a ^a	pK _a ^b	X _{H₂O} ^c	slope (r) ^d	r(A ⁻) ^e	r(In ⁻) ^f
H	14.28	15.38 ± 0.02	0.710	1.01 (0.996)	0.999	0.997
p-OMe	15.16	15.64 ± 0.05 ^g	0.705	0.989 (0.996)	0.996	0.984
p-Me	14.80	15.53 ± 0.03	0.717	0.995 (0.996)	0.999	0.999
p-F	14.12	15.27 ± 0.07	0.734	1.02 (0.994)	0.987	0.991
p-Cl	13.50	15.03 ± 0.07 ^h	0.738	1.14 (0.986)	0.996	0.999
p-Br		15.10 ± 0.07	0.735	1.047 (0.931)	0.975	0.956

^a Measured in pure Me₂SO. ^b Measured in Me₂SO-H₂O relative to *p*-nitrodiphenylamine (pK_a = 15.67). ^c Mole fraction of H₂O. ^d Slope for the plot of log [A⁻]/[HA] vs. H₋ (correlation coefficient r). ^e Correlation coefficient for the plot of 1/ε vs. 1/c_{base} for HA. ^f Correlation coefficient for the plot of 1/ε vs. 1/c_{base} for HIn. ^g Four point plot. ^h Three-point plot.

anions are close enough to the peak maxima of the precursor to merge into a single broad envelope. The above two difficulties were circumvented as follows. (i) Goutines and Mathieu²⁰ have reported the graphical variation of H₋ as a function of the base concentration [Me₄NOH] in a Me₂SO-5% H₂O mixture. Since preliminary results showed that the base concentration affects only the ionization ratio [A⁻]/[HA] but not the position of the absorption peak, we performed the five determinations of the ratio [A⁻]/[HA] for each carbon acid in five Me₂SO-H₂O-Me₄NOH solutions differing in the base concentration but of identical water content. Particular efforts were made to avoid, within the six carbon acid series, too large a variation of the water mole fraction (X_{H₂O} = 0.714 ± 0.077). Thus pK_a's of arylcyclopentadienes were determined relative to one single indicator (*p*-nitrodiphenylamine) in solutions of strictly comparable water content. (ii) The increase in carbanion concentration [A⁻] on increasing the base strength was monitored at a wavelength at which the carbanion but not the precursor absorbs. At this λ (≠ λ_{max} of the anion) the ε was unknown. We extrapolated its value for each of the carbanions from a five-point plot of 1/ε vs. 1/[Me₄NOH] at the point for which 1/[Me₄NOH] = 0. The relationship H₋ = 15.67 + log [A⁻]/[HA] requires that the five-point plots of H₋ vs. log [A⁻]/[HA] be of unit slope. Table I reports the average pK_a's for the six 1-aryl-4-phenylcyclopenta-1,3-dienes **1a,c,e,g,h,i**, the X_{H₂O} at which the determinations were made, slopes and correlation coefficients of the lines H₋ vs. log [A⁻]/[HA], and correlation coefficients of the lines 1/ε vs. 1/[Me₄NOH].

The method just described is somewhat laborious and possibly subject to errors originating from the extrapolation of the molar absorptivities of the anions (both for the indicator and for the carbon acids). This method was chosen because it is particularly applicable to cases for which the absorptivities of the ionized species are not available directly. It is essentially the same as that authoritatively proposed by Schaal²¹ and subsequently described in detail for aqueous media by Albert and Serjeant.²² Nonetheless, we were concerned about the reliability of the resulting pK_a's in Table I and endeavored to establish their credibility by a series of internal checks, which are described in detail in the Experimental Section: (1) comparison of extrapolated absorptivities of indicator anions with available literature data; (2) comparison of the total concentration of {[HIn] + [In⁻]} from direct weighings with calculations from the extrapolated absorptivities; (3) demonstration of the linearity of H₋ with log c_{base} by evaluation of the correlation coefficient of the line and by comparison of the slopes and intercepts of the line for each carbon acid investigated; (4) comparison of H₋ values calculated from the carbon acids 1 themselves as indicators ([Me₄NOH] = 0.011 M) with H₋ values predicted by Dolman and Stewart¹⁴ at the appropriate X_{H₂O}. All these checks responded very favorably and, taken together, constitute strong support for the reliability of the pK_a's in Me₂SO-H₂O listed in Table I. The standard deviations for these values were obtained from the average of the five figures for each run from the five different base concentrations and may

Table II. Proton Chemical Shifts^a (δ) of Sodium 1-Aryl-3-phenylcyclopentadienides

X ^b	H ₄ ^{''}	H _{2,3}	H ₅
NMe ₂	6.442	5.860	6.204
OMe	6.545	5.893	6.244
Me	6.559	5.934	6.309
<i>m</i> -Me	6.561	5.952	6.339
H	6.534	5.983	6.365
F	6.592	5.946	6.303
Ph	6.607	6.049	6.438
<i>m</i> -OMe	6.592	5.973	6.359
Br	6.614	5.981	6.354
Cl	6.612	5.981	6.352

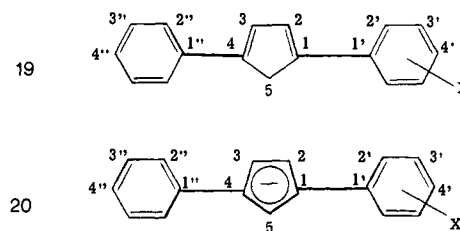
^a In parts per million downfield from (trimethylsilyl)propane-sulfonic acid sodium salt. ^b Para substitution unless otherwise indicated.

be underestimates. Dolman and Stewart¹⁴ pointed out this possibility. If the actual error is larger, it would produce scatter in pK_a plots rather than an expansion or compression of the pK_a range. Thus the slope of the plot of pK_a in Me₂SO-H₂O vs. pK_a in pure Me₂SO should not be significantly affected.

Acidity in Me₂SO. Acidity constants of the arylphenylcyclopentadienes were also measured in pure Me₂SO, using the indicator method of Bordwell.^{11,23} These values may be found in the first column of Table I.

Proton NMR Parameters. Shifts reported in Table II are derived from a first-order interpretation of the spectra. Substituents do not induce an appreciably different shift between H₂ and H₃. These resonances appear as a doublet at higher field than the triplet of H₅ (J_{(2,3)-5} = 2.1 Hz). Resonances of the two aryl rings are not easily and unambiguously assigned in each case, with the exception of H₄^{''}, which appears always as a triplet of triplets and comes at a slightly lower field than H₅. The pattern shown by the phenyl ring is typical of that presented by benzyl carbanions.^{15,24-26}

The numbering system used in Table II is appropriate for the neutral acid, which is a 1,4-substituted cyclopentadiene (**19**). In



order to have the same system for the neutral and the anion, we have numbered the positions in the anion as if it also were 1,4-substituted (**20**). We appreciate that the anion is a 1,3-disubstituted cyclopentadienide, but we feel that it is more important

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Table III. Carbon-13 Chemical Shifts (δ) of Potassium 1-Aryl-3-phenylcyclopentadienides in $\text{Me}_2\text{SO}^a, b$

	Cl	Br	F	SMe	H	<i>m</i> -Me	CH_3	OMe
C_1^c	123.73	122.96	122.21	122.24	123.11	123.17	122.76	122.96
C_2	108.28	108.32	107.68	107.68	107.68	107.60	107.39	106.93
C_3	108.08	108.09	107.55	107.68	107.68	107.72	107.39	106.79
C_4	123.63	121.29	120.49	123.19	123.11	123.17	122.76	122.38
C_5	103.26	103.29	102.71	102.76	102.79	102.88	102.51	101.89
C_1'	142.67	143.77	140.81	142.05	143.96	143.96	141.41	137.24
C_1''	143.56	141.51	144.06	143.63	143.96	144.09	141.19	143.89
C_2'	124.28	124.82	123.96	123.40	123.11	123.91	123.16	124.14
C_2''	123.30	123.36	123.21	122.96	123.11	122.97	123.28	122.96
C_3'	129.01	131.84	115.74	129.98	129.20	137.43	129.94	115.04
C_3''	129.25	129.27	129.29	128.99	129.20	129.23	129.26	129.23
C_4'	120.75	111.58	158.60	126.22	120.36	121.33	128.71	154.87
C_4''	120.84	120.80	120.49	120.29	120.36	120.34	120.26	120.21
XCH_3				18.73		23.05	22.14	56.46
Me_2SO	42.10	41.97	42.13	42.05	42.07	42.14	42.10	42.36

^a Relative to (trimethylsilyl)propanesulfonic acid sodium salt. ^b Para substitution unless otherwise indicated. ^c See structure 20 for the numbering system.

to be able to refer to analogous positions by the same numerical index.

Carbon-13 NMR Parameters. The ^{13}C chemical shifts were measured for the potassium salts of eight of the arylphenylcyclopentadienyl anions (Table III). The shift assignments were made by off-resonance decoupling techniques and by comparison with monosubstituted benzene assignments in the literature.²⁷ The ^{13}C - ^{19}F coupling constants in the *p*-F compound were unambiguous. The shift difference between the corresponding positions in the aryl and phenyl rings, e.g., 3' vs. 3'', was always very close to the analogous difference between benzene and monosubstituted benzene (same substituent). The carbons in the five-membered ring formed three well-defined sets, in which C_5 always stood alone near δ 102, C_2 and C_3 were near 108, and C_1 and C_4 were near 122.

The ^{13}C spectra of the neutral hydrocarbons were obtained in THF (Table IV), because some of the substrates were quite insoluble in Me_2SO , CHCl_3 , CCl_4 , hydrocarbons, and other ethers.

In order to obtain qualitative information about aggregate size, we measured the spin-lattice relaxation time (T_1) for the unsubstituted diphenylcyclopentadienyl anion. The effective molecular weight M is related to the dipolar T_1 by eq 3,²⁸ in which

$$1/T_1(\text{DD}) \propto nM\eta/\rho \quad (3)$$

n is the number of protons attached to the relaxing carbon, η is the solution viscosity, and ρ is the solution density. The ratio of the dipolar T_1 for the neutral acid and the anion should give the ratio of the effective molecular weights, provided other factors are constant. In order to ensure the η and ρ , as well as the temperature and any other factors, are identical, we measured T_1 for the neutral and the anion in a common solution. Under these circumstances, the following relationship holds (eq 4).²⁹ A

$$T_1(\text{neutral})/T_1(\text{anion}) = M(\text{anion})/M(\text{neutral}) \quad (4)$$

solution 0.3 M in anion and 0.3 M in neutral was prepared from 0.3 M dimethyl in Me_2SO with 0.6 M neutral added. For molecules of this size, it can be assumed that the dipolar relaxation mechanism dominates the overall spin-lattice relaxation, so that corrections via nuclear Overhauser effects are probably not necessary. The resulting relaxation times are given in Table V.

Linear Relationships. Results of correlative analysis of the foregoing data are reported in Table VI. 1-Aryl-4-phenylcyclopenta-1,3-dienes **1** are more acidic in Me_2SO than in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$. Acidities in both media respond linearly to the σ constants of substituents, but the sensitivity in the mixed solvents is almost one-third of that in Me_2SO (entries 1, 2). Acidities in

Table IV. Carbon-13 Chemical Shifts (δ) for the Neutral 1-Aryl-4-phenylcyclopenta-1,3-dienes in Tetrahydrofuran^a

	Cl	F	H	<i>m</i> -Me ^b	Me	OMe ^c
C_1	135.68	136.94	136.96	136.89	136.85	136.5
C_2	127.45	127.29	127.23	127.19	127.09	126.9
C_3	128.53	127.29	127.23	128.06	127.68	128.5
C_4	136.80	136.94	136.96	138.51	137.06	136.6
C_5	41.42	41.54	41.37	41.43	41.39	41.4
C_1'	145.29	143.34	146.68	146.51	146.08	141.4
C_1''	147.28	145.82	146.68	146.89	146.60	145.4
C_2'	126.93	127.25	125.53	126.25	125.48	126.6
C_2''	125.61	125.56	125.53	125.51	125.48	125.4
C_3'	129.46	115.98	129.15	128.51	129.83	114.7
C_3''	129.22	129.20	129.15	129.17	129.14	129.6
C_4'	132.64	162.67	128.56	129.17	134.80	157.2
C_4''	129.22	128.53	128.56	128.59	128.63	128.7
CH_3					21.18	55.3
OCH_3						
THF	68.13	68.13	68.10	68.13	68.10	68.1
THF	26.29	26.29	26.26	26.29	26.26	26.3

^a Para substitution unless otherwise indicated. ^b For *m*-Me, C_6' resonated at 122.79 and C_5' at 129.08. ^c The assignments for the *p*- OCH_3 substituent may not be exact because of drifts in the resolution during the long accumulation time that was required. ^d See structure 19 for the numbering system.

Table V. Spin-Lattice Relaxation Times for 1,3-Diphenylcyclopenta-1,3-diene and Its Potassium Salt

carbon	neutral T_1	anion T_1	neutral T_1 / anion T_1
1'	5.5	3.5	1.6
3'	1.3	1.1	1.2
4'	1.8	0.7	2.6
2,3	0.9	0.4	2.3

both Me_2SO and $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ are linearly correlated with the shift of $\text{H}_{4''}$ of anions **6** (entries 3,4). Thus, $\text{H}_{4''}$ responds to σ values (entry 7), but in this case the number of available points is considerably higher than for the pK_a correlations. The slope of entry 7 can be compared with that of entry 9, which refers to the $\text{H}_{4''}$ response of 1-aryl-3-phenylallyl anions.³⁰ In this latter case, the response is more than three times larger.

Protons of the five-membered ring of anions **6** do not respond linearly to σ values of substituents. Variations, however, are not unsystematic, since the shifts of $\text{H}_{2,3}$ and H_5 are linearly correlated with a high degree of precision (entry 8). Some of the ^{13}C shifts exhibit linear correlations (C_3'' , C_4''), whereas others have S-shaped curves (C_2 , C_3 , C_5) (Figures 1 and 2). This sigmoidal behavior will be examined in the Discussion. Interestingly, there are no good correlations between the ^1H and ^{13}C monitors, in contrast

(27) Details may be found in: Nienhuis, R. J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1979.

(28) Lambert, J. B.; Netzel, D. A.; Sun, H.-n.; Lilianstrom, K. K. *J. Am. Chem. Soc.* 1976, 98, 3778-3783.

(29) Edlund, U. *Org. Magn. Reson.* 1977, 9, 593-595.

(30) Bushby, R. J.; Ferber, G. J. *J. Chem. Soc., Perkin Trans. 2* 1976, 1688-1695.

Table VI. Fitting Parameters for Correlations

entry	sys-tems	y(A)	x(B)	slope	intercept	r	n	substituents ^a
1	1	pK _a (Me ₂ SO)	σ	-3.26 ± 0.08	14.27	0.999	5	H, Me, OMe, Cl, F
2	1	pK _a (Me ₂ SO/H ₂ O)	σ	-1.17 ± 0.07	15.34	0.993	6	as entry 1 + Br
3	1	pK _a (Me ₂ SO)	H ₄ '', ^b	-23.88 ± 1.36	171.47	0.995	5	as entry 1
4	1	pK _a (Me ₂ SO/H ₂ O)	H ₄ '', ^b	-8.51 ± 0.70	71.35	0.987	6	H, OMe, Me, F, Cl, Br
5	6	C ₄ '', ^c	H ₄ '', ^c	5.16 ± 1.25	86.41	0.922	5	H, F, OMe, Me, <i>m</i> -Me
6	6	C ₄ '', ^c	H ₄ '', ^c	7.90 ± 1.44	68.48	0.938	6	as entry 5 + Br
7	6	H ₄ '', ^c	σ	16.03 ± 0.74	658.03	0.991	10	NMe ₂ , <i>m</i> -Me, Me, OMe, <i>m</i> -Me, F, Cl, Br, Ph, H
8	6	H _{2,3} '', ^c	H ₅	1.25 ± 0.06	-1.10	0.990	10	as entry 7
9	d	H ₄ '', ^c	σ	52.69 ± 6.35	596.71	0.959	8	NMe ₂ , <i>t</i> -Bu, OMe, Me, H, F, <i>m</i> -F, Cl
10	d	C ₄ '', ^c	H ₄ '', ^c	11.87 ± 0.82	41.05	0.986	8	as entry 9

^a Para substitution unless otherwise indicated. ^b In δ (ppm). ^c In δ (ppm) × 10². ^d 1-Aryl-3-phenylallyl anions.²⁸

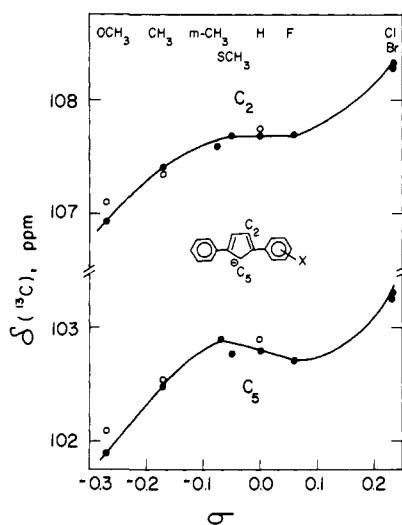


Figure 1. The ¹³C chemical shift of C₂ and C₅ of (1-aryl-3-phenylcyclopentadienyl)potassium as a function of aryl substitution (closed circles and curve). The open circles are for the analogous lithium salt.

with earlier observations.^{28,30,31}

Discussion

Acidities. Examination of the effect of proton donors on the pK_a's of carbon acids and on their sensitivity to remote substitution is hampered by two opposing factors. On the one hand, the pK_a of the hydrocarbons must be low enough to allow the anion to survive a high concentration of proton donor. In general, stabilization is achieved by delocalization of the negative charge over a large molecular framework. On the other hand, delocalization substantially decreases the tendency of the carbanion to interact with the proton donor through hydrogen bonding. Accordingly, several failures have been reported in attempts to observe sizable effects of proton donors on the properties of delocalized carbanions such as those derived from fluorene³² and fluoradene³³ in the unpaired or solvent-separated ion-pair form. Our choice of diphenylcyclopentadiene appears to be fortunate, since this system offers a compromise between delocalization and proton acceptance. The anion is stable enough to survive aqueous media and still entertain rather strong hydrogen bonding. In media of low water content, water interacts preferentially with the cosolvent Me₂SO rather than with the carbanion. In media of high water content (X_{H₂O} > 0.5), the carbanion interacts appreciably with the proton donor.¹⁹ Therefore, electronic properties of the anion do not vary monotonically with changes in the solvent composition. The stability of the anion and hence the pK_a are expected to respond to the change in interactions on going from anhydrous to aqueous Me₂SO.

Direct comparison of the measured pK_a of 1,4-diphenylcyclopentadiene (1a) in Me₂SO (14.28) and in Me₂SO-H₂O (15.38)

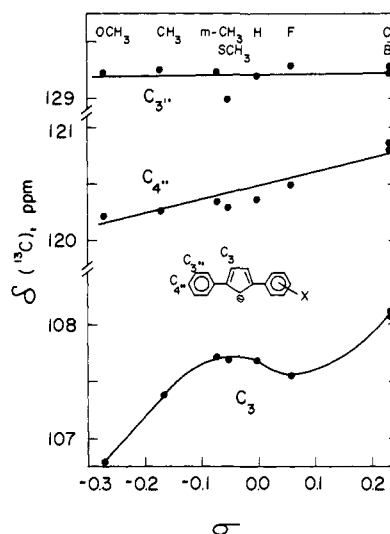


Figure 2. The ¹³C chemical shift of C₃, C₃'', and C₄'' of (1-aryl-3-phenylcyclopentadienyl)potassium as a function of aryl substitution.

(ΔpK_a = (pK_a)_{Me₂SO-H₂O} - (pK_a)_{Me₂SO} = 1.1 units) is difficult because the Me₂SO figure is based on Bordwell's absolute scale but the Me₂SO-H₂O figure is based on a relative scale. Some comparison is possible if allowance is made for ΔpK_a of the reference indicator, 4-nitrodiphenylamine (4-NO₂-DPA). The pK_a of this indicator was measured to be 16.85 in Me₂SO²³ and 15.67 in Me₂SO-H₂O,¹⁴ ΔpK_a = -1.2. The standard deviation for these measurements was about 0.02. Correction for this factor brings the ΔpK_a of 1,4-diphenylcyclopentadiene to 2.3 (+1.1 - (-1.2)). Diphenylcyclopentadiene is indeed more acidic in Me₂SO than in Me₂SO-H₂O, although the reference indicator is less acidic in pure Me₂SO. Water favors ionization of 4-NO₂-DPA but disfavors ionization of the carbon acid.

The higher acidity of 1a in anhydrous Me₂SO than in Me₂SO-H₂O is consonant with previous results with carbon acids that produce highly delocalized carbanions. Fluoradene, for instance, is more acidic in Me₂SO than in MeOH by at least 6.5 pK_a units.³⁴ This behavior was interpreted³⁴ as evidence that such carbanions are substantially more stabilized by dispersion forces promoted by Me₂SO than by hydrogen bonding to MeOH. Definitive support for this type of interaction between Me₂SO and the cyclopentadienyl anion came from thermochemical investigations carried out by Arnett and his group.³⁵ The analysis of effects exerted by proton donors on the UV properties of the 1,3-diphenylcyclopentadienyl anion (6) and some other carbanions and nitranions is analogously in line with this overall picture.¹⁹

The sensitivity of acidity within the series 1 to the Hammett substituent constants shows a threefold decrease in Me₂SO-H₂O compared to pure Me₂SO (ρ_{Me₂SO}/ρ_{Me₂SO-H₂O} = 3.26/1.17 = 2.79). Although this ratio gets around the problem of relative scaling,

(31) Bradamante, S.; Pagani, G. *J. Org. Chem.* **1980**, *45*, 105-114.

(32) Ford, W. T. *J. Am. Chem. Soc.* **1970**, *92*, 2857-2861.

(33) Hogen-Esch, T. E. *J. Am. Chem. Soc.* **1973**, *95*, 639-641.

(34) Reference 6, p 232.

(35) Arnett, E. M.; Johnston, D. E.; Small, L. E. *J. Am. Chem. Soc.* **1975**, *97*, 5598-5600.

it is subject to error associated with the larger uncertainty of the acidities in the mixed solvent. As discussed above and in greater detail in the Experimental Section, the acidities in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ are sufficiently reliable to support a case that the sensitivity difference between the two solvents is real. Error in the acidities would increase the scatter for the mixed solvent but could not expand the range from about 0.60 $\text{p}K_a$ unit in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ to the 1.60 measured in anhydrous Me_2SO .

This leveling effect of water is not unprecedented. Bordwell, on comparing his $\text{p}K_a$'s for a series of 2-substituted fluorenes in Me_2SO ³⁶ with those of Bowden and Cockerill³⁷ in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$, noted that the identity of the ρ values was fortuitous and that there was a compression of the $\text{p}K_a$ range in the mixed solvent. The work of Ford³² and of Hogen-Esch³³ demonstrated that fluorene is scarcely capable of hydrogen bonding, so a similarity of sensitivities to σ might be expected for that substrate in the two solvents. The larger ratio of sensitivities that we observe for the arylphenylcyclopentadienes is consistent with stronger hydrogen-bonding interactions between the anions and water. The ratio (2.79) is very close to that observed for the sensitivities of benzoic acids in Me_2SO and in H_2O ($X_{\text{H}_2\text{O}} = 1.0$) ($\rho_{\text{Me}_2\text{SO}}/\rho_{\text{H}_2\text{O}} = 2.7$).³⁸ Since our aqueous solvent ($X_{\text{H}_2\text{O}} = 0.7$) is not pure water, the ratio of sensitivities of arylphenylcyclopentadienes in Me_2SO and in pure H_2O would be even larger than 2.79. Although the sensitivity ρ of the acidities in Me_2SO can be analyzed in terms of anion response to the substituent, it is seen that the sensitivity in the mixed solvent $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ must be interpreted for a large part in terms of solvation effects.

Several years ago Ritchie³⁹ recognized that a change in dispersion stabilization of anions in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ leads to changes in the activity coefficient ratios and consequently to a breakdown of the H scale. He pointed out that solvent sensitivity of substituent effects is indicative of solvent effects on activity coefficients. Grunwald⁴⁰ discussed the solvent dependence of ρ values in a similar vein. Our observations are consonant with these conclusions.

Carbon-13 Spectra. The carbon monitor was expected to exhibit a linear response to aryl substitution, since changes in electron density should parallel the defining phenomena for σ . The plots of the ^{13}C shifts vs. σ for the potassium anions (Figures 1 and 2, closed circles), however, have a sigmoidal shape for the carbons in the five-membered ring (C_2 , C_3 , C_5). Further from the five-membered ring, the response is more nearly linear (C_4') or level (C_3''). Response in the substituted aryl ring is not relevant, since these carbon shifts are dominated by the α , β , and γ effects of the X substituent. These latter effects in fact directly parallel those in simple, monosubstituted benzenes.

The sigmoidal shape of the five-membered ring carbon response to substitution is also observed in the indenyl anion described in a related paper.⁸ Consequently, some sort of systematic structural effect seems to be operative in these systems. Previous workers have observed temperature variation of ^{13}C shifts that could be attributed to ion-pair effects.⁴¹⁻⁴⁴ For a given carbon, contact ion pairs exhibit higher field (more shielded) resonances. The propinquity of the cation polarizes charge toward the carbon. In the solvent-separated ion pair, the carbon is at lower field (less shielded) because a wider distribution of charge throughout the anion reduces the charge at the position(s) of closest approach in the contact ion pair.

The sigmoidal behavior in figures 1 and 2 can be understood

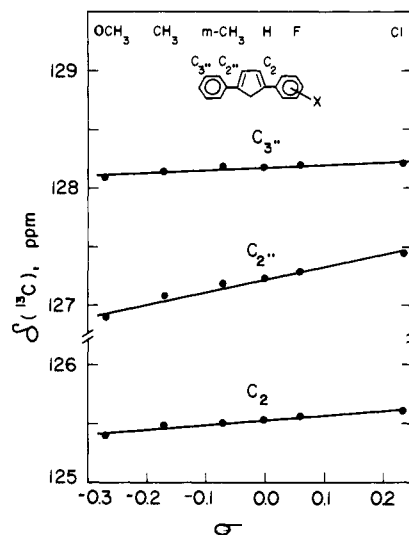


Figure 3. The ^{13}C chemical shift of C_2 , C_2'' , and C_3'' of 1-aryl-4-phenylcyclopentadiene as a function of aryl substitution.

in terms of a change over from one type of ion pair to another. A single ionic species should have exhibited linear behavior. Introduction of a $p\text{-OCH}_3$ group pushes the data point for C_2 , C_3 , or C_5 above the line that passes through H and is parallel to either end of the sigmoidal curve. This direction represents a larger downfield shift than expected or an increase in the amount of solvent-separated ion pair for the electron-donating substituent. Conversely, introduction of $p\text{-Cl}$ at the opposite extreme pushes the carbon resonances below the H line, representing an upfield shift. The electron-withdrawing substituents must favor the contact ion pair. One possible explanation for these observations is that the systems with electron donation have a higher net electron density in the five-membered ring, which is better stabilized in the more delocalized solvent-separated ion pair. Electron withdrawal decreases the electron density in the five-membered ring, which can then be more easily polarized to form the contact ion pair.

It is especially significant that the quaternary carbons in the five-membered ring of the anion show linear rather than sigmoidal behavior ($\text{C}_{1,4}$ vs. σ). These atoms must bear little negative charge, so that their chemical shifts are not sensitive to the type of ion pairing. The low or linear response of the carbons in the unsubstituted phenyl ring also reflects low negative charge and hence the relative insensitivity to the ion-pair structures. The slopes of these plots represent the sensitivity to substitution and must reflect the negative charge density on the carbon. Thus the plots for C_1 , C_4 , C_3'' , and C_4' have a much lower slope than those for the linear portions at the ends of the plots for C_2 , C_3 , and C_5 .

It should be noted that the sigmoidal behavior is not observed in the neutral arylphenylcyclopentadienes, in which C_2 , C_2'' , and C_3'' give nicely linear plots vs. σ and C_3 gives a very scattered plot (Figure 3). In the neutral series, C_5 is not saturated, so the correlation for this atom is no longer relevant. The carbons in the substituted phenyl ring again follow the shifts of monosubstituted benzenes very closely. The sigmoidal behavior is uniquely a characteristic of the anion series.⁴⁵

In order to test the effect of cation on the sigmoidal behavior, we prepared the lithium salts for three of the systems. As expected, the greater part of the sigmoidal behavior has been lost (see the open circle points in Figure 1). A comparison of the absolute shifts from Li to K is not possible because it is not known if the cation itself exerts an electric field that could influence ^{13}C shifts, aside

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 (37) Bowden, K.; Cockerill, A. F. *J. Chem. Soc. B* **1970**, 173-179.
 (38) Kreevoy, M. M.; Baughman, E. H. *J. Am. Chem. Soc.* **1973**, *95*, 8178-8179. Cox, R. A.; Stewart, R. *Ibid.* **1976**, *98*, 488-494.
 (39) Reference 6, pp 243-244.
 (40) Gutbezahl, B.; Grunwald, E. *J. Am. Chem. Soc.* **1953**, *75*, 559-565.
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 (42) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 7427-7429.
 (43) O'Brien, D. H.; Russell, C. R.; Hart, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 633-639.
 (44) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661-666.

(45) After completion of this paper, a report was published describing a dependence of the ion-pair structure for 1,5-diarylpentadienyl anions on aryl substitution: Parkes, H. M.; Young, R. N. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1137-1140. Their observations on ΔH° roughly parallel our results. Unfortunately, the quoted 7% error on ΔH° and ΔS° renders a calculation of ΔG° statistically unreliable.

from the effects of ion-pair differences. The more nearly linear plot for Li^+ is consistent with a greater proportion of a single ion pair (contact) for all aryl substituents.

Although our results are consistent with a change in ion-pair structure with substituent, this explanation is not proved. The foregoing arguments could also apply to changes in aggregation rather than in ion pairing. Shielding changes can also take place within aggregates. The spin-lattice relaxation time experiments provided confirming evidence for aggregation. The ratio of T_1 's for the neutral vs. the anion varies from 1.2 to 2.6, with an average of about 2.0 (Table V). The variation may reflect anisotropy of motion or different NOE's. When adjusted for molecular weight (218 for the neutral diphenylcyclopentadiene; 256 for (diphenylcyclopentadienyl)potassium), either an aggregation of about 1.7 or an average of 2.3 solvating molecules per anion is indicated for these 0.3 M solutions. One structure that is reasonably consistent with these observations is a double ion pair. At the concentration levels necessary for the ^{13}C NMR experiments, it seems that both ion pairing and aggregation might be present. At UV concentrations, some 4 orders of magnitude more dilute, the observations are relatively independent of cation, so that ion pairs appear not to be present.¹⁹

Because we cannot distinguish between shielding effects of ion pairing and aggregation, our most conservative conclusion is that we are observing a change in the ionic structure with aryl substitution. The change can involve aggregation or at least two types of ion pairs.

Summary and Conclusions

Acidity studies of 1-aryl-4-phenylcyclopenta-1,3-dienes demonstrate the sensitivity of the $\text{p}K_a$ to the solvent and to the mode of measurement. Generally higher acidities (lower $\text{p}K_a$'s) in pure Me_2SO than in a mixture of Me_2SO with H_2O result from superior stabilization of the delocalized anion by the dispersion forces of the Me_2SO molecules, in comparison to the more localized stabilization provided by H_2O molecules through hydrogen bonding. As measured from the Hammett σ plot, acidities are about 3 times more sensitive to substitution in pure Me_2SO than in the $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ mixture. Water appears to provide a leveling effect. A similar difference in sensitivity to substitution observed in benzoic acid ionizations has been attributed to a breakdown in the Hammett H concept.³⁸⁻⁴⁰ The data indicate that hydrogen bonding to water is important for these cyclopentadienyl anions.

At the concentrations necessary to obtain good ^{13}C spectra, the anions are present as ion pairs or aggregates. At the higher dilutions used for UV experiments, the anions are essentially free.¹⁹ The spin-lattice relaxation times (T_1) of the anion of 1,4-diphenylcyclopenta-1,3-diene, compared to that of the neutral, indicate either aggregation at approximately the level of a dimer or the attachment of about two molecules of solvent (Me_2SO). The ^{13}C chemical shifts, particularly those of the five-membered-ring carbons, give evidence for structural changes within the ion pair or aggregate, as a function of aryl substitution. The ^{13}C shifts of the unsubstituted phenyl ring ($\text{C}_{3'}$ and $\text{C}_{4'}$) and of the quaternary carbons in the five-membered ring (C_1 , C_4) exhibit a small but linear response to aryl substitution (vs. σ). The amount of negative charge on these carbons is small and is not appreciably altered by changes in the ion-pair structure. The ^{13}C shifts of the tertiary carbons of the five-membered ring (C_2 , C_3 , and C_5) show a large and sigmoidal dependence on σ . This behavior can be attributed to a change in the nature of the ion pair, from contact to solvent separated, as a function or aryl substitution, or to changes in the level of aggregation. Replacement of the potassium ion with lithium largely removes the sigmoidal behavior. The lithium salt is probably present predominantly as the contact ion pair, so that substitution does not perturb the anion structure. The neutral acid exhibits linear rather than sigmoidal behavior.

Experimental Section

General Synthesis of 1-Aryl-4-phenylcyclopenta-1,3-dienes (1). (A) **From Substituted Acetophenones.** Ethyl 3-benzoylpropionate (8, 14.0 g, 68 mmol) was added under N_2 to a stirred suspension of dry sodium ethoxide (9.39 g, 13.6 mmol) in anhydrous benzene (100 mL). The red

Table VII. Melting Points for Compounds 1

X^a	mp, °C	solvent ^c
H	156-157	A
Me	151-152	A
<i>m</i> -Me	119-120	B
F	157-158	A
Cl	160-161	A
Br	165-166	C
OMe	166-167	A
<i>m</i> -OMe	99-100	A
NMe ₂	162-164	A
Ph	210-212	C
SMe	154-155	C

^a Para substitution unless otherwise indicated. ^b A = ethanol; B = sublimed (0.1 mmHg); C = benzene/petroleum ether.

Table VIII. Electronic Spectra of 1-Aryl-4-phenylcyclopenta-1,3-dienes and Their Anions

X^a	carbon acid		carbanion	
	λ_{max}	$10^{-4}\epsilon$ (λ)	λ_{max}	$10^{-3}\epsilon$ (λ)
H	362, 352	1.12 (375) 1.54 (352)	387	13.6 (410)
Me	367, 352	1.75 (375) 2.07 (360) 1.91 (345)	377	7.19 (415)
OMe	365, 351	1.80 (375) 1.76 (345)	382	2.07 (425)
Br	365, 352	1.34 (380) 1.67 (365) 1.49 (340)	397	9.52 (425)
Cl	360, 350	1.71 (375) 1.92 (360) 1.78 (345)	392	13.6 ^b (415)
F	360, 350	1.17 (375) 1.65 (360) 1.70 (345)	375	6.94 (412)

^a All para substituents. ^b Three-point plot.

solution was stirred for 10 min, and the acetophenone (9, 6.8 mmol) was then added. The flask was stoppered, and the red-brown reaction mixture was stirred at 40 °C for 24 h. After the solution was cooled in an ice bath, water (400 mL) was added and the mixture was stirred at room temperature for 0.5 h. The mixture was then extracted with ethyl ether, and the aqueous layer was warmed at 70 °C until bubbling and solid formation were complete. The solid product was isolated by filtration and recrystallized.^{46,47} All products gave satisfactory analytical data (elemental, ^1H NMR). The physical properties have been collected in Tables VII and VIII.

(B) **From 3-Phenylcyclopent-2-enone.** (*m*-Methoxyphenyl)magnesium bromide was prepared from Mg turnings (0.85 g, 35 mmol) in THF (15 mL) and *m*-bromoanisole (5.80 g, 31 mmol) in THF (20 mL). 3-Phenylcyclopent-2-enone (5.0 g, 31 mmol) in THF (20 mL) was added dropwise with stirring. After 2 h, the mixture was warmed gently (ca. 50 °C) for 15 min and cooled. A saturated (20%) NH_4Cl solution (20 mL) was added. The THF was separated and evaporated under reduced pressure. The residue was then chromatographed (120 g of silica, 9/1 petroleum ether/benzene). The compound was finally recrystallized from EtOH (mp 96-97 °C).

3-Phenylcyclopent-2-enone. To a stirred suspension of dry sodium methoxide (13 g, 240 mmol) in ethyl ether (100 mL) was added slowly ethyl acetoacetate (31.5 g, 242 mmol). After 1 h of stirring at room temperature, phenacyl bromide (47.9 g, 240 mmol) in ethyl ether (200 mL) was also added, and stirring was continued for 24 h. The reaction mixture was then filtered and evaporated at reduced pressure. The residue was taken up with 2% NaOH (400 mL) and, under vigorous mechanical stirring, was warmed to 60 °C and kept at this temperature for 15 min. The solution was diluted with 200 mL of toluene, and NaOH in pellets (32 g) was gradually added. Heating was continued to reflux and maintained for 2 h. The cooled organic portion was separated, dried (Na_2SO_4), and concentrated. Crystallization of the residue was induced by addition of *tert*-butyl methyl ether (10-15 mL). The solid was filtered and recrystallized from EtOH; mp 80-81 °C (lit.⁴⁸ 83 °C).

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Acidity Measurements in Me₂SO-H₂O. General Data. Ionization constants of carbon acids HA were determined spectrophotometrically at 25 °C from the ratio of [HA]/[A⁻] in Me₂SO-H₂O-Me₄NOH solutions of known base strength (*H_a*). The base strength of each of the five solutions was obtained by measuring the ionization ratio [HIn]/[In⁻] of an amine indicator HIn of known (reported) p*K_a* in Me₂SO-H₂O. Experimental data thus consisted of UV spectra of mixtures of HA and A⁻ in a series of five solutions of varying base strength and the parallel spectra of the amine indicator and the amine anion in the same solutions. The base strength of the five pairs of solutions was varied regularly along the series, while both the water mole fraction (*X_{H₂O}*) and the molarity either of [HA] + [A⁻] or of [HIn] + [In⁻] was kept virtually constant.

Solvents. Me₂SO was distilled from CaH₂ under vacuum (after 2 h at 70 °C under N₂) and stored under N₂ in a flask equipped with serum caps. Water was distilled and stored under N₂ in a flask fitted with serum caps to allow transfer by syringe. All solutions were transferred by syringe under a slight N₂ pressure. Oxygen contamination was scrupulously avoided in every flask or container that was going to be filled with solvents or solutions destined for the UV cuvette and spectrophotometric determination. UV cuvettes also were fitted with serum caps. Usually a cycle of five vacuum evacuations (to at least 10⁻² torr) and five fillings with ultrapure N₂ was performed before transfer into empty receivers. Weight rather than volumetric determinations were done. Thus molarities of solutes in samples obtained upon mixing weighted amounts of solutions were obtained by transforming weight determinations of Me₂SO and Me₂SO-H₂O mixtures into volumetric data from the interpolated density of the solvent in question and the known graphic relationship of density vs. *X_{H₂O}* in Me₂SO-H₂O mixtures.⁴⁹

Procedures. A stock Me₂SO-H₂O mixture was first prepared by mixing under N₂ appropriate weighed amounts of Me₂SO and water. The water mole fraction (*X_{H₂O}*) in the mixture was predetermined so that the final desired *X_{H₂O}* in the cuvette solution to be submitted to UV determination was obtained upon mixing ca. 1 mL of Me₂SO with ca. 1 mL of the stock Me₂SO-H₂O mixture. Then a mother solution of base of known titer in Me₂SO-H₂O was prepared by mixing in a volumetric flask a weighed amount of Me₄NOH-5H₂O and a weighed amount of the stock Me₂SO-H₂O mixture. Five samples of Me₂SO-H₂O-Me₄NOH differing only in [Me₄NOH] were then prepared by mixing weighed aliquots of the Me₂SO-H₂O-Me₄NOH mother solution and of the Me₂SO-H₂O stock mixture. Five solutions containing both HA and A⁻ were then prepared directly in the UV cells by mixing a precisely weighed amount of a Me₂SO solution (ca. 1 mL) of one of the five Me₂SO-H₂O-Me₄NOH solutions at different base strength. Analogously, five different samples of Me₂SO-H₂O-Me₄NOH solutions containing HIn and In⁻ were prepared directly in the UV cells by mixing a precisely weighed amount (ca. 1 mL) of a Me₂SO solution of known content in *p*-nitrodiphenylamine (*p*-NO₂-DPA) and a precisely weighed amount (ca. 1 mL) of one of the five Me₂SO-H₂O-Me₄NOH solutions of base at different base strength. Values of 1/ε for A⁻ and In⁻ at a certain λ were respectively extrapolated from two five-point plots of 1/absorbance (at a λ at which both the amine and the carbon acid have absorbance equal to 0) vs. 1/*c_{base}*, from the solutions containing HA/A⁻ and HIn/In⁻, at the point at which 1/*c_{base}* = 0. Since [HA + A⁻] and [HIn + In⁻] were known from weighing data and since [A⁻] and [In⁻] were determined from the absorbances of A⁻ and In⁻, then [HA], [HIn], and [In⁻] were known for each of the five solutions. From the usual formulas, *H_a* and hence the p*K_a* of HA for each of the five solutions were determined.

Reliability of the Method. (1) Absorptivities of the Indicators. Table IX⁵⁰ lists absorptivities for the anion of the 4-nitrodiphenylamine indicator. Such values vary widely from solvent to solvent and cannot be compared directly with those obtained by extrapolation of 1/ε vs. 1/*c_{base}* for the five different basic solutions in which the p*K_a*'s of the aryl-substituted carbon acids were determined. In our work, the maximum deviation is 7% (between 2.86 and 3.08 × 10⁴). A more direct comparison can be made for the anion of 4-nitroaniline, an indicator we used elsewhere.⁸ Table X⁵⁰ shows that our extrapolated values are identical with those of Dolman and Stewart.¹⁴

(2) Composition of the Solutions. Comparison was made of the total concentration of {[HIn] + [In⁻]} from weight data and from absorbance of the solution. Run H₂ for diphenylcyclopentadiene, for example, gave a total concentration of 2.07 × 10⁻⁵ M from weight data and of 2.15 × 10⁻⁵ M from the absorptivities (In⁻ at 498 nm, HIn at 391 nm, ε_{HIn} = 1.955 × 10⁴, from which [In⁻] = 0.78 × 10⁻⁵ M and [HIn] = 1.36 × 10⁻⁵ M). The difference between these two approaches is 0.08 × 10⁻⁵ M or 3.7%.

(3) Linearity of *H_a* vs. Log *c_{base}*. In order that 1/*c_{base}* be linear with 1/ε, it is necessary that *h_a* = constant/*c_{base}*, i.e., that *H_a* = constant × log *c_{base}*. Table XI⁵⁰ shows that the plots are nicely linear for all the aryl-substituted systems. The correlation coefficients all exceed 0.991, and the slopes and intercepts are nearly constant.

(4) Comparison of *H_a* of Dolman and Stewart with Values from the Carbon Acids 1 as Indicators. The p*K_a*'s in Table I can be used to evaluate *H_a* values in basic solution (Table XII).⁵⁰ For each carbanion, values of [A⁻]/[HA] at *c_{base}* = 0.011 M, and the p*K_a* can give *H_a* from eq 1, *H_a* = p*K_a* + log ([A⁻]/[HA]). Comparison with the compilation of Dolman and Stewart¹⁴ at the appropriate base concentration and mole fraction of H₂O shows that three cases are exceptionally good (*H*, *p*-Cl, and *p*-Br) and three cases are fair (*p*-OMe, *p*-Me, and *p*-F). Since the scatter for the last three cases is both positive and negative, it cannot produce an overall compression in the range of p*K_a*'s.

Preparation of the Dimsyl Solution for Magnetic Resonance Experiments. The dimsyl solution was prepared from KH and twice-distilled Me₂SO. The concentration of the first solution that was prepared was measured by titration to be 0.60 M. The same solution was measured by the spectrophotometric method to be 0.59 M. Because of the excellent agreement between the two methods, all other solutions that were prepared were checked only by titration. Mallinckrodt analytical reagent grade Me₂SO was distilled from CaH₂ (1.5 g/25 mL of Me₂SO) after stirring for 1 h at 70 °C under 1 atm of dry N₂. The second distillation was from NaH (1.5 g/25 mL of Me₂SO). The KH was obtained from the Ventron Corp. as a 20–25% dispersion in oil. The KH dispersion was placed in a tared 125-mL Schlenk flask, which was fitted with an air-tight septum cap and stopcock. The oil was removed by washing ten times with dry pentane under an atmosphere of dry N₂. The Schlenk flask was then evacuated and weighed to determine the actual amount of dry KH inside. An appropriate amount of twice-distilled Me₂SO was added by syringe. Complete reaction was ensured by using vacuum to remove the H₂ gas byproduct. The flask was then wrapped in Al foil and stored under N₂ at 0 °C. The dimsyl solution was also prepared from NaH or KNH₂. The dimsyl solutions prepared from NaH were not so clear as those prepared from KH, and small amounts of solid were present that would not dissolve at this concentration of dimsyl. For these reasons, KH was used almost exclusively to generate the dimsyl solution.

Preparation of the Anions. The anion samples were prepared for ¹³C analysis directly in the 10-mm NMR tubes by the addition of 2.0 mL of 0.6 M dimsyl solution to 0.6 mmol of organic substrate. The resulting solution was 0.6 M in base and 0.3 M in substrate. This twofold excess of base was used to ensure complete deprotonation of the substrate. The organic substrates were recrystallized from EtOH or THF prior to usage. For ¹H spectra, the 5-mm tubes contained 0.5 mL of a Me₂SO solution that was 0.2 M in anion. The ¹³C NMR spectra were obtained at 20 MHz with a Varian CFT-20 spectrometer. Chemical shifts (δ) of the anions are reported in parts per million downfield from the methyl resonance of the sodium salt of (trimethylsilyl)propanesulfonic acid (Me₃SiNa) (Tables II and III). To obtain adequate sensitivity of the methyl resonance, 25 mg of Me₃SiNa was required per 2 mL of solution. The deuterium lock required by the CFT-20 was provided by D₂O in a sealed, internal, coaxial 4-mm NMR tube. The 4-mm tube was held in place inside the 10-mm tube by a Teflon spacer. The spacers were vertically notched in three places so that the dimsyl solution could flow past the spacer. The spacer was positioned in the 4-mm tube so that it would be just above the level of the solution. Into the 10-mm NMR tube were placed 0.6 mM of substrate, 25 mg of Me₃SiNa, and the 4-mm D₂O tube with its Teflon spacer. The 10-mm tube was capped with a rubber septum cap, and the septum cap-tube interface was wrapped in Parafilm. The atmosphere within the 10-mm tube was then replaced with dry N₂ via syringe through the septum cap by alternating between vacuum and N₂, both of which were connected to the syringe through a three-way stopcock. The 2 mL of 0.06 M dimsyl solution was then syringed directly into the 10-mm tube, and the N₂ vacuum cycles were repeated several times to remove the H₂ gas byproduct and to ensure complete deprotonation. The ¹H spectra were obtained on a Varian HA-100 or XL-100 spectrometer with similarly constituted samples (5-mm tubes).

Carbon-13 T₁ Measurements. Since the anions were prepared under O₂-free conditions, these preparations were suitable for the T₁ measurements. Because of the low concentration of the anion (0.3 M), 300 scans were necessary to obtain a high enough signal-to-noise ratio. This time-consuming requirement was offset, however, by the short pulse delay that was used. Since the longest T₁ was only 1.8 s, the required pulse delay (τ) was only 9.0 s. In this manner a T₁ could be measured in a 16-h time period. The standard inversion recovery method (90°-τ-180°-τ) was used.

Sample Preparation of the Neutrals. All of the compounds were recrystallized from EtOH or THF prior to usage. The 0.6 mmol of compound was dissolved in 2.0 mL of THF, to which 16 drops of C₆D₆

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(50) This material is found in the microfilm version of this paper.

and 5 drops of Me_4Si were added. The resulting solution was nearly 0.3 M. The small quantity of C_6D_6 was enough to provide the deuterium lock for the Varian CFT-20 but not enough to interfere with the ^{13}C resonances of the compounds.

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Supplementary Material Available: Table IX, absorptivity of the 4-nitrodiphenylamine anion, Table X, absorptivity of the 4-nitroaniline anion in $\text{Me}_2\text{SO}-\text{H}_2\text{O}$, Table XI, plots of H_{ν} vs. $\log c_b$ for 4- NO_2 -DPA indicator, and Table XII, comparison of H_{ν} values from Table I with those predicted by Dolman and Stewart (4 pages). Ordering information is given on any current masthead page.

Homolytic Addition to Benzene. Rate Constants for the Formation and Decay of Some Substituted Cyclohexadienyl Radicals^{1a}

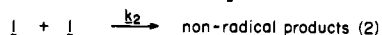
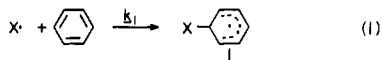
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Abstract: Addition to benzene of $\text{Et}_3\text{Si}\cdot$, $(\text{EtO})_2\dot{\text{P}}\text{O}$, and $\text{C}_6\text{H}_5\cdot$ led to cyclohexadienyl radicals which were detected by EPR and optical modulation spectroscopy. The rate constants for addition of $\text{Et}_3\text{Si}\cdot$ and $(\text{EtO})_2\dot{\text{P}}\text{O}$ were found to be $\geq 10^5$ and $2.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, respectively, while the rate constants for self-reactions of the resulting cyclohexadienyl radicals were found to be 8.9×10^8 and $6.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. EPR parameters and UV-visible spectra of the cyclohexadienyl radicals were reported.

Homolytic aromatic substitution has been the subject of extensive investigation since 1937, when Hey and Waters reviewed the mechanism for the phenylation of aromatic substrates.² In its simplest form, the mechanism involves addition of a radical $\text{X}\cdot$ to benzene (reaction 1) to form a substituted cyclohexadienyl



- a, X = Et_3Si ;
b, X = Me_3Si ;
c, X = $(\text{EtO})_2\text{PO}$;
d, X = Ph

radical, 1. Self-reactions of 1 lead to nonradical products, (reaction 2), amongst which are cyclohexadienes and the X-substituted benzene. It is the rate of generation of $\text{X}\cdot$, the concentration of benzene, and the magnitudes of k_1 , k_{-1} , and k_2 which determine the reaction products. However, essentially all of the research in this area has been based upon product studies alone^{3,4} and rate constants for the elementary reactions of the substituted cyclohexadienyls have rarely been measured or estimated.³

In this work, we have used both electron paramagnetic resonance (EPR) and optical modulation spectroscopy to characterize the spectra of the substituted cyclohexadienyl radicals, 1a-d, and to measure some of the rate constants for their formation and decay.

Experimental Section

Materials. All materials were commercially available and, with the following exceptions, were used as received. Benzene (Aldrich, Gold Label) was treated with concentrated sulfuric acid, neutralized with aqueous sodium carbonate, and washed with distilled water. It was then dried over magnesium sulfate before being distilled from calcium hydride. Di-*tert*-butyl peroxide (K & K) was washed with aqueous silver nitrate and water, to remove olefinic impurities. It was dried over magnesium sulfate and was finally passed through alumina to remove hydroperoxide impurities. Diethyl phosphite was purified by distillation.

Apparatus. EPR spectra were recorded by using a Varian E104 spectrometer. Radicals were generated by direct photolysis of samples placed in the EPR cavity. The photolysis source was a 500-W mercury arc lamp, and the output of the lamp was filtered through an aqueous solution of cobalt and nickel sulfates which removed much of the visible and most of the infrared radiation. Radical concentrations were measured by double integration of appropriate lines in the EPR spectra and were calibrated against the signal obtained from a standard, benzene solution of diphenylpicrylhydrazyl. The EPR signal produced by a ruby disk placed inside the cavity was used to correct for differences in sensitivity of the spectrometer to the different solutions. The techniques of kinetic EPR spectroscopy have been described in detail elsewhere.⁷

The optical modulation spectrometer used in this work follows closely upon the design developed by Huggenberger and Fischer^{8,9} and has been described elsewhere.¹⁰ Briefly, radicals were generated by photolysis of a solution which was flowed slowly through a standard fluorescence cell. The photolysing light (1000-W Hg/Xe) was modulated as a sin wave by

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