Response of Acidity and Magnetic Resonance Properties to Aryl Substitution in Carbon Acids and Derived Carbanions: 2- and 3-Arylindenes

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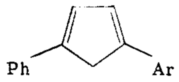
Substitution in the aryl ring of 2- and 3-arylindenes has been used to examine the acidity of these hydrocarbons and the charge density and ion pair structure of their anions. Acidities were measured for the 2-arylindenes both in pure Me_2SO and in a Me_2SO–H_2O mixture. After allowance for the different acidities of the indicators used in the two media, the acidities of the indenes are higher in pure Me_2SO (the pK_a's are lower by 1–2 units). The dispersion forces of Me_2SO are more effective in stabilizing the delocalized charge of the anion than are the more localized interactions of the hydroxyl groups in the mixed solvent. The pK_a's in both solvents exhibit a linear response to the Hammett σ constant. Substituents that are electron withdrawing through resonance are better correlated by the σ^- constant, suggestive of a strong resonance interaction between the aryl group and the indene ring. Such an interaction is substantiated by the chemical shift changes on deprotonation. The ^1H resonance of $H_{4'}$ (para position) in the unsubstituted 2-arylindenyl anion and the ^{13}C resonance of $C_{4'}$ in all the 2-arylindenyl anions are shifted upfield in comparison to the neutral hydrocarbons, as a result of negative charge delocalization into the aryl ring. The sigmoidal shape of the plot of ^{13}C chemical shifts of certain atoms in the 2-arylindenyl anions vs. σ gives evidence for a structural change within the anion. Only the carbons with very high charge density exhibit this behavior ($C_{1,3}$). Observations in the indene series generally parallel those in the 1-aryl-4-phenylcyclopentadienes. The annelated phenyl ring in the indenes therefore causes effects similar to those of the simply bound phenyl ring in the cyclopentadienes.

In a recent study we utilized the high acidity of 1-aryl-4-phenylcyclopentadienes (**1**) to investigate the response of both thermodynamic (acidity) and extrathermodynamic (^1H and ^{13}C shielding) parameters to remote substitution.[3] Synthetic limitations prevented the examination of mesomerically electron-withdrawing substituents on the aryl ring. Annelation of the unsubstituted phenyl ring in **1** can produce either the 2- or the 3-arylindene (**2**, **3**). We present herein the results of acidity and magnetic resonance studies of these indenes. A direct examination of the annelation effect is possible by comparison of the indenes with the 1-aryl-4-phenylcyclopentadienes.[3] The availability of the two different indenes (**2** and **3**) provides a flexible probe to assess the inductive and resonance interactions between the aryl substituent and the five-membered ring. Furthermore, we have been able to obtain a few electron-withdrawing substituents in the indene series. Again our attention will be focused on the response of the acidity to remote substitution and on the dependence of the acidity on the medium, either nonhydroxylic (pure Me_2SO) or hydroxylic (Me_2SO–H_2O). The response of the NMR probes will be evaluated in terms of the ion-pair structure of the anion at the high concentrations required for the magnetic resonance experiment.



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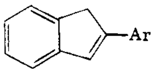

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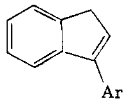

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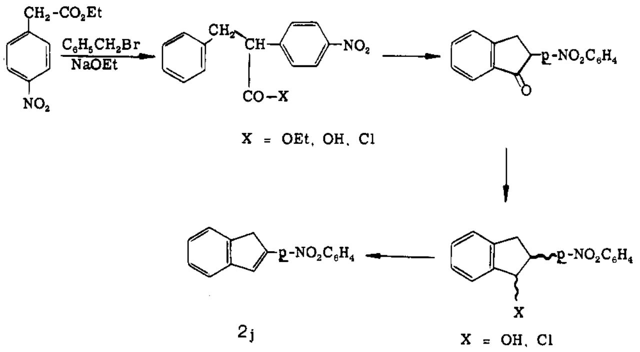
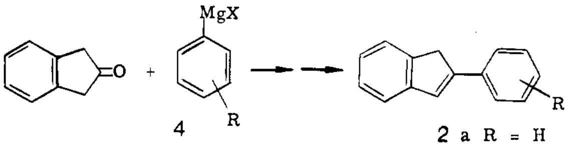
Results

Synthesis of the 2-Arylindenes. The 2-arylindenes **2a–g** were prepared through the action of substituted arylmagnesium bromides (**4**) on 2-indanone and subsequent dehydration of the tertiary alcohol (eq 1).[4] 2-(*p*-Acetylphenyl)indene (**2i**) was available through a modification of this route by the reaction of the Grignard reagent of *p*-bromoacetophenone ethylene ketal with 2-indanone. Acidic treatment of the resulting alcohol removed the ketal protection and induced dehydration.

Scheme I





(1)

a - f X = Br
g X = I

2 a R = H
b R = p-Me
c R = m-Me
d R = p-OMe
e R = p-F
f R = p-Cl
g R = p-Br

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[3] Greifenstein, L. G.; Lambert, J. B.; Nienhuis, R. J.; Pagani, G. A. *J. Am. Chem. Soc.*, in press. The reliability of the H_- method is discussed extensively.

[4] Galton, S. A.; Kalafer, M.; Beringer, F. M. *J. Org. Chem.* **1970** *35*, 1–6.

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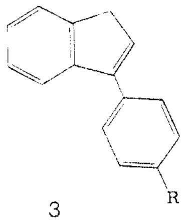
Table I. Acidifying Effect of Phenyl Substituents on Indene

	pK_a			
	Me_2SO	Me_2SO-H_2O	X_{H_2O}[c]	indicator (pK_a)
indene	20.12[a]	19.28 ± 0.03[b]	0.29	NAH (18.91)
2-phenyl	19.36[a]	18.62 ± 0.07	0.47	NAH (18.91)
3-phenyl	17.3 ± 0.2[a]	17.12 ± 0.10	0.57	CNAH (17.08)

[a] Reference 8. [b] In Me_2SO-H_2O with X_{H_2O} = ca. 0.18, pK_a = 20.25 relative to 9-phenylfluorene with pK_a = 18.59 from: Goutines, G.; Mathiew, A. *Analusis* **1973**, *2*, 584. [c] Mole fraction of water.

2-(*p*-Cyanophenyl)indene (**2h**) was prepared by the copper-catalyzed cyanide displacement of bromide from 2-(*p*-bromophenyl)indene (**2g**).[5] A novel route was devised for preparing 2-(*p*-nitrophenyl)indene (**2j**, Scheme I). Benzylation with benzyl bromide of ethyl *p*-nitrophenylacetate gave the ester, which was converted into the acid chloride via the carboxylic acid. Internal Friedel–Crafts acylation afforded 2-(*p*-nitrophenyl)indan-1-one, which was reduced to the alcohol, and this in turn was converted to the diasteroisomeric mixture of the *E* and *Z* chlorides. Dehydrohalogenation of the chlorides with quinoline afforded **2j** in high yield.

Synthesis of the 3-Arylindenes. The 3-Arylindenes **3a–e** were prepared through the action of the appropriate arylmagnesium bromide on 1-indanone via the tertiary alcohols, analogous to eq 1. 3-(*p*-Cyanophenyl)indene (**3f**) was prepared by the copper-catalyzed cyanide displacement of bromide ion from 3-(*p*-bromophenyl)indene (**3e**). While the 2-arylindenes are all stable, crystalline compounds, many 3-arylindenes are poorly stable, liquid products that rapidly turn brown on standing. Extensive chromatography thus was needed to obtain pure compounds.



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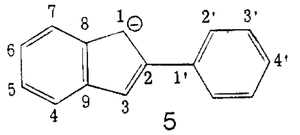
a R = H
b R = NMe$_2$
c R = OMe
d R = Me
e R = Br
f R = CN

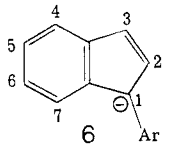
Acidity Measurements. Because of the poor stability of 3-arylindenes, great difficulties were met in measuring their ionization constants. For this reason, although acidities of all the 2-arylindenes have been determined, for the 3-aryl series we have restricted the determination to the parent compound only. Table I reports the pK_a's of indene and of the parent systems **2a** and **3a** in Me_2SO and in Me_2SO-H_2O to help evaluate the effect of a phenyl group in positons 2 and 3, respectively. Table II reports the pK_a data for the full series of the 2-arylindenes. The basic solutions for the chlorine and bromine substituents (**2f** and **2g**) gave clear evidence for instability. For this reason these measurements possess a larger standard deviation.

Methodology both in Me_2SO and in Me_2SO-H_2O is strictly analgous to that described by us previously.[3] Relative to the procedure used for 1-aryl-4-phenylcyclopentadienes,[3] two major differences concern the water mole fraction (X_{H_2O}) of the Me_2SO-H_2O mixed solvent and the use of two amine indicators instead of only one. The X_{H_2O} had to be decreased (from 0.70 to 0.3–0.5) because of the lower acidities of compounds **2** and **3** in comparison to those of the arylphenylcyclopentadienes.[3] Two amine indicators had to be use since the range of pK_a's is considerably larger than before and could not be covered by NAH (*p*-nitroaniline) or CNAH (4-chloro-2-nitroaniline) alone.

NMR Parameters. Table III reports the ^1H shifts in pure Me_2SO for the 2-arylindenyl anions **5** and Table IV for the 1-arylindenyl anions **6** (from the 3-arylindenes), recorded under the same conditions as those previously described.[3] In both the 2-aryl- and the 3-arylindenyl series, the halophenyl-substituted indenyl anions appear to be somewhat unstable, the solutions turning brown rather rapidly (10–60 min). The 2-(*p*-nitrophenyl)indene gave, under standard concentration conditions, a deep purple suspension totally unsuitable for NMR analysis. Although unfortunate, this observation was not totally unexpected since difficulties are known to arise when nitroaryl-activated carbon acids are treated with oxidizable bases (MeO^-, dimsyl anion).[6] In fact, deprotonation can be competitive with radical anion forming processes. For the anions **5** the benzo portion of the spectrum is AA′BB′. The shifts for H_5 and H_6 are given as the center of the BB′ portion. The absolute shift is somewhat in error systematically, but the relative displacements in the series caused by the substituent effects are not affected. Unfortunately, substituent chemical shift changes are small, and thus the percent error may not be negligible. For the anions **6** the benzo pattern is ABCD, with the chemical shifts of H_5 and H_6 almost coincident. In this case too, the data refer to the weight center of the $H_{5,6}$ portion. Resonances H_4 and H_7 are sizably spaced, both being to low field of $H_{5,6}$, the latter more than the former because of the deshielding effect of the aryl ring. The H_4 and H_7 parameters obtained by a first-order analysis should be very close to the real ones.



5



6

The ^{13}C chemical shifts for the potassium salts of the 2-arylindenyl anions (**5**) in Me_2SO are given in Table V. The ^{13}C assignments were made in the same fashion as for the 1-aryl-3-phenylcyclopentadienides.[3] The ^{13}C chemical shifts for the neutral 2-arylindenes **2** could not be measured in Me_2SO because of limited solubility. As before,[3] the neutral compounds were examined in tetrahydrofuran, and these results are recorded in Table VI.

Linear Relationships. Results of correlative analysis of the data are reported in Table VII. In accord with previous results[3] the pK_a sensitivity in the mixed solvent is smaller than in pure Me_2SO (entries 1 and 2). Inclusion of halo substituents in the correlation of entry 2 (entries 3–5) confers a worse degree of precision to the fit, although it does not alter the slope. This reduced precision is no doubt attributable to the higher degree of uncertainty associated with pK_a's of the halogenated precursors, in turn associated with the greater instability of the anions.

Despite the limited number of points available for the 1-arylindenyl anions (**6**), several linear relationships appear to hold. Proton H_2 is linearly correlated with H_3 (entry 12); inclusion of the *p*-CN substituent (entry 13) makes the correlation worse. It appears that H_2 responds better to σ (compare entries 15 and 16), whereas H_3 requires σ^-

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[5] Pizey, J. S. "Synthetic Reagents"; Wiley: New York, 1974; Vol. 1, p 41.

[6] Guthrie, R. D.; Cho, N. S. *J. Am. Chem. Soc.* **1975**, *97*, 2280–2281.

Table II. Acidities of the 2-Arylindenes (2) in Me_2SO and in Me_2SO-H_2O

substituent[a]	Me_2SO[b]	Me_2SO-H_2O[c]	X_{H_2O}[d]	indicator	slope (r)[f]	$r(A^-)$[g]	$r(In^-)$[h]
H	19.4	18.62 ± 0.07	0.47	NAH	1.06 (0.994)	0.999	0.997
OMe	20.1	19.10 ± 0.02	0.32	NAH	0.978 (0.994)	0.995	0.978
Me	19.7	18.93 ± 0.01	0.36	NAH	0.993 (0.997)	0.998	0.992
m-Me		18.83 ± 0.03	0.36	NAH	1.02 (0.992)	0.995	0.992
SMe		18.93 ± 0.03	0.36	NAH	1.05 (0.988)	0.997	0.998
F	19.3	18.64 ± 0.01	0.37	NAH	0.982 (0.999)	0.998	0.998
Cl	18.7	17.99 ± 0.04	0.45	CNAH	1.08 (0.940)	0.944	0.997
Br		18.26 ± 0.04	0.41	NAH	1.05 (0.980)	0.990	0.990
COMe		17.52 ± 0.06	0.52	CNAH	1.04 (0.957)	0.982	0.991
CN		17.61 ± 0.07	0.53	CNAH	1.11 (0.925)	0.973	0.965

[a] Substituents are para unless otherwise indicated. [b] Reference 5. [c] Uncertainties originated from $1/\epsilon$ as determined by a linear regression of a plot $1/c_{\mathrm{base}}$ vs. $1/\epsilon_{\mathrm{anion}}$. [d] X_{H_2O} = water mole fraction. [e] NAH = 4-nitroaniline, pK_a (Me_2SO-H_2O) = 18.91; CNAH = 4-chloro-2-nitroaniline, pK_a (Me_2SO-H_2O) = 17.08. From: Dolman, D.; Stewart, R. *Can. J. Chem.* **1967**, *45*, 911-924. [f] Slope of the line log $[A^-]/[HA]$ vs. H_- and its correlation coefficient. [g] Correlation coefficient of the plot $1/\epsilon$ vs. $1/c_{\mathrm{base}}$ for HA. [h] Correlation coefficient of the plot $1/\epsilon$ vs. $1/c_{\mathrm{base}}$ for HIn.

Table III. Proton Chemical Shifts for the 2-Arylindenyl Anions (5)[a]

	shift, ppm	
X[b]	$H_{5,6}$	$H_{1,3}$
H	6.255	6.168
F	6.253	6.103
m-Me	6.222	6.126
OMe	6.227	6.062
Cl	6.250	6.133
Me	6.233	6.119

[a] In Me_2SO relative to (trimethylsilyl)propanesulfonic acid sodium salt. [b] All substituents are para unless otherwise indicated.

Table IV. Proton Chemical Shifts for the 1-Arylindenyl Anions (6)[a]

	shift, ppm				
X[b]	H_2	H_3	H_4	$H_{5,6}$	H_7
H	6.79	5.90		6.41	7.63
NMe_2	6.65	5.82	7.12	6.33	7.56
OMe	6.69	5.85	7.14	6.36	7.57
Me	6.75	5.88	7.14	6.38	7.61
CN	6.95	6.07	7.22	6.59	7.67

[a] In Me_2SO relative to (trimethylsilyl)propanesulfonic acid sodium salt. [b] All para substituents.

for *p*-CN (compare entries 18 and 19). If so, the different response of the *p*-CN point in the intermonitor correlation of H_2 and H_3 (entry 13) is readily understandable. The linear response of $H_{5,6}$ in 6 appears to indicate again a preference for a σ^- requirement (compare entries 21 and 22; although neither the slope nor the correlation coefficient is greatly affected, the standard deviation of entry 22 is remarkably better).

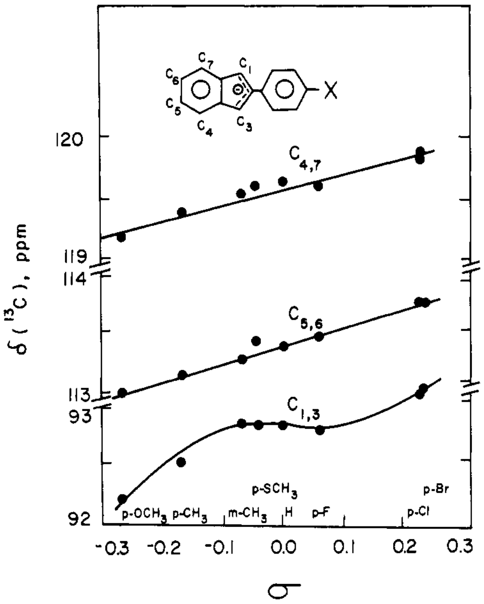

Figure 1. Carbon-13 chemical shift of $C_{1,3}$, $C_{4,7}$, and $C_{5,6}$ of the 2-arylindenyl anion (potassium salt) as a function of the Hammett substituent constant σ.

Of the ^{13}C shifts obtained for the neutral hydrocarbons, the 2-arylindenes (2), it appears that only C_4 responds linearly to substituent effects (entry 6), although the C_6 correlation is not bad. Linear correlations, of course, are not expected for the aryl ring, because of direct effects of the substituent. The correlations for the carbons in the anions 5 are illustrated in Figure 1. The best linear correlation is for $C_{5,6}$ (entry 10), although the $C_{4,7}$ correlation (entry 9) is fair. For $C_{1,3}$, a well-defined S-shaped

Table V. Carbon-13 Chemical Shifts for the Potassium 2-Arylindenyl Anions (5)[a,b]

	substituent							
carbon	Cl	Br	F	SCH_3	H	*m*-CH_3[b,c]	CH_3	OCH_3
1,3	93.08	93.10	92.79	92.84	92.83	92.85	92.54	92.24
2	131.92	130.40	131.10	131.02	132.52	132.39	131.99	132.16
4,7	119.81	119.91	119.61	119.63	119.64	119.56	119.40	119.19
5,6	113.73	113.73	113.46	113.48	113.39	113.28	113.17	113.02
8,9	132.42	132.38	132.58	132.53	132.07	132.15	132.38	132.45
1′	143.00	142.70	140.68	131.31	144.14	144.01	141.31	137.18
2′	127.28	128.01	126.99	131.02	126.03	126.79	126.00	126.89
3′	129.18	132.20	115.92	128.96	129.38	137.71	130.00	115.01
4′	130.45	122.30	160.53	141.83	123.57	124.31	132.10	156.68
CH_3, XCH_3				17.88		22.97	22.21	56.43
Me_2SO	42.03	42.15	42.10	42.00	41.85	42.08	42.08	41.85

[a] In Me_2SO in parts per million relative to (trimethylsilyl)propanesulfonic acid sodium salt. [b] The substituent is in the para position unless designated otherwise. [c] For *m*-CH_3, $C_{5'}$ resonates at 129.20 ppm and $C_{6'}$ at 123.33 ppm.

Table VI. Carbon-13 Chemical Shifts for the Neutral 2-Arylindenes (2)[a,b]

	substituent					
carbon	Cl	Br	F	H	*m*-CH_3[b,c]	CH_3
1	129.39	129.55	129.22	129.23	129.09	129.58
2	135.58	136.01	136.89	136.93	136.78	137.78
3	39.42	39.34	39.40	39.44	39.46	39.58
4	121.68	121.67	121.53	121.50	121.42	121.32
5	125.62	125.63	125.35	125.35	125.23	125.14
6	127.69	127.97	127.12	126.29	126.93	126.30
7	124.20	124.20	124.18	124.18	124.11	124.11
8	146.03	145.74	145.56	146.26	146.28	146.48
9	144.03	143.98	144.03	144.06	143.98	143.95
1′	145.86	145.74	144.90	147.30	147.36	143.95
2′	127.23	127.19	127.27	126.29	127.09	126.30
3′	127.91	132.36	115.94	127.12	138.56	127.13
4′	133.58	124.20	166.20	128.04	128.80	134.32
CH_3					21.42	21.18
THF	68.10	68.06	68.13	68.11	68.06	68.13
THF	26.26	26.21	26.29	26.24	26.21	26.28

[a] In THF in parts per million relative to (trimethylsilyl)propanesulfonic acid sodium salt. [b] The substituent is para unless otherwise indicated. [c] For *m*-CH_3, $C_{6'}$ resonates at 123.50 ppm and $C_{5'}$ at 127.09 ppm.

Table VII. Fitting Parameters for Correlations

entry	system	ordinate	abscissa	slope	intercept	*r*	*n*	substituents
1	2	pK_a (Me_2SO)	σ	−2.60 ± 0.24	19.36	0.988	5	H, OMe, Me, F, Cl
2	2	pK_a (Me_2SO–H_2O)	σ	−1.35 ± 0.07	18.73	0.992	8	H, OMe, Me, F, *m*-Me, SMe, COMe, CN
3				−1.36 ± 0.08	18.71	0.988	9	as entry 2 + Br
4				−1.375 ± 0.14	18.68	0.964	9	as entry 2 + Cl
5				−1.38 ± 0.14	18.67	0.963	10	as entry 4 + Br
6	2	C_4	σ	0.87 ± 0.06	121.48	0.992	6	H, *m*-Me, Me, F, Cl, Br
7	2	C_6	σ	5.98 ± 1.37	126.49	0.952	4	H, F, Cl, Br
8				4.24 ± 1.02	126.78	0.923	5	as entry 7 + Me
9	5	$C_{4,7}$	σ	1.22 ± 0.16	119.60	0.954	8	H, OMe, *m*-Me, SMe, F, Cl, Br, Me
10	5	$C_{5,6}$	σ	1.41 ± 0.04	113.40	0.998	7	H, OMe, *m*-Me, Me, F, Cl, Br
11				1.38 ± 0.13	113.41	0.974	8	as entry 10 + SMe
12	6	H_3	H_2	0.56 ± 0.04	2.09	0.996	4	H, NMe_2, Me, OMe
13				0.83 ± 0.08	0.298	0.985	5	as entry 12 + CN
14	6	H_2	σ	0.33 ± 0.04	6.79	0.984	4	as entry 12
15				0.27 ± 0.02	6.78	0.992	5	as entry 14 + CN (0.66)
16				0.22 ± 0.02	6.77	0.983	5	as entry 14 + CN (0.88)
17	6	H_3	σ	0.19 ± 0.02	5.90	0.987	4	as entry 14
18				0.23 ± 0.01	5.91	0.996	5	as entry 14 + CN (0.66)
19				0.19 ± 0.005	5.90	0.999	5	as entry 14 + CN (0.88)
20	6	$H_{5,6}$	σ	0.183 ± 0.003	6.41	0.999	4	as entry 14
21				0.24 ± 0.01	6.42	0.995	5	as entry 14 + CN (0.66)
22				0.198 ± 0.003	6.41	0.999	5	as entry 14 + CN (0.88)
23	5/7	$H_{1,3}$	$H_{2,3}$	1.13 ± 0.20	−0.57	0.957	5	H, F, OMe, NMe_2, Me
24				0.967 ± 0.21	0.36	0.919	6	as entry 23 + Cl

curve is obtained, and further examination of the $C_{4,7}$ plot shows that the relatively poor correlation is caused by some sigmoidal character. Sigmoidal plots were also obtained for the 1-aryl-3-phenylcyclopentadienides.[3] The present results with the 2-arylindenyl anions confirm the earlier cyclopentadienyl results and will be interpreted in a similar fashion.

Discussion

Acidities. Bordwell[7] has recently pointed out the difficulties in comparing acidities obtained in different solvents and with different indicators and the futility of anchoring acidities in aqueous solvents to water as a "standard state". Nonetheless, it is instructive to compare the acidities in Me_2SO and in Me_2SO–H_2O of indene, 2-phenylindene, 3-phenylindene, and (from the previous paper[3]) 1,4-diphenylcyclopentadiene.

From inspection of Table I, the carbon acids in the indene series appear to be more acidic (lower pK_a) in the mixed aqueous solvent than in anhydrous Me_2SO by 0.84, 0.74, and 0.18 pK_a unit, respectively, whereas 1,4-diphenylcyclopentadiene[3] is less acidic by 1.1 units. It should be kept in mind, however, that the scale in Me_2SO is absolute, whereas that in Me_2SO–H_2O is to a large extent relative. Comparison between the scales are improved when the acidity changes of the appropriate amine indicators in the two media are taken into consideration. For the indicators, the change in pK_a from Me_2SO to Me_2SO–H_2O [$\Delta pK_a = pK_a(Me_2SO\text{–}H_2O) - pK_a(Me_2SO)$] becomes increasingly more negative as the mole fraction of water increases (acidities are higher and pK_a's lower in the mixed solvent).[8] The ΔpK_a depends both on the water content of the mixture and on the structure of the amine indicator. The ΔpK_a for NAH is larger (−2.09) than that for 4-NO_2-DPA (−1.2), even though the higher pK_a of NAH requires a Me_2SO–H_2O solution with a higher H_- and hence a lower water content. The value for CNAH is −1.8.

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[7] Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325–3328.

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Although there are these individual differences, the negative sign of ΔpK_a for all the indicators is consistent with a greater stabilization by the pair InH/In^- in the aqueous solvent than in anhydrous Me_2SO (higher acidity or lower pK_a in the mixed solvent).

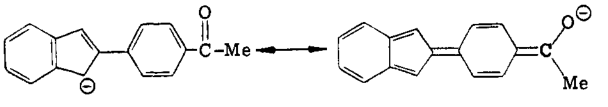
Correction of the changes in pK_a between solvents for the carbon acids for these changes exhibited by the indicators [$\Delta\Delta pK_a = \Delta pK_a$ (HA) - ΔpK_a (HIn)] represents the energy balance for the pair of acids HA and HIn upon transfer from Me_2SO to Me_2SO–H_2O. The positive value for indene [$\Delta\Delta pK_a = -0.84 - (-2.09) = 1.25$] indicates that the ionization of indene is favored by water less than the ionization of NAH. The larger values for 2-phenylindene [$-0.74 - (-2.09) = 1.35$], 3-phenylindene [$-0.18 - (-1.8) = 1.62$], and 1,4-diphenylcyclopentadiene [$1.1 - (-1.2) = 2.3$] indicate even less favoring of ionization by water for HA compared to HIn. Thus, the lower the pK_a of the carbon acid (higher the acidity), the smaller is the stabilization by water relative to the indicator. For 1,4-diphenylcyclopentadiene, the relatively high acidity (low pK_a) results in a destabilization of the ionization process, *relative to the indicator*. Direct comparison of these systems, however, is tenuous, because the pK_a's were not measured at the same mole fraction of water. The lower acidity of the indenes (higher pK_a) than of the diphenylcyclopentadiene in part arose from the lower water content for Me_2SO–H_2O (X_{H_2O} = 0.3 vs. 0.7). Since the addition of water does not induce a monotonic variation of the solvation shell of the carbanion,[9] the relative sensitivities of the ionization of the indenes and the diphenylcyclopentadiene cannot be ascribed simply to relative susceptibilities to hydrogen bonding.

The results in all three systems, after adjustment for indicator differences, fit well with the general picture, according to which carbanions are better stabilized in Me_2SO by dispersion forces than in hydroxylic solvents by hydrogen bonding.[10] In terms of the HSAB theory, the soft carbanion base interacts more facorably with soft dipoles than with the hard hydroxylic proton. The unfavorable effect of water on the ionization constants of these carbon acids is not in accord with the reported higher acidity by 3 pK_a units of cyclopentadiene in water relative to Me_2SO.[11] This difference, however, did not take into account the variation of the pK_a of the indicator used in Me_2SO upon transfer to water.[12] Furthermore, the pK_a determination of cyclopentadiene in water is far from being a "thermodynamic" or absolute value, because of the extremely high ionic strength of the solution and deviation from ideality of the ionic activities.

Substitution of phenyl for H at position 2 of indene induces an increase in acidity of 0.7 and 0.66 pK_a units in Me_2SO and Me_2SO–H_2O, respectively. the increase in acidity upon phenyl substitution for H at position 3 is considerably larger (2.8 and 2.16 pK_a units in Me_2SO and Me_2SO–H_2O, respectively), but not so large as that reported for phenyl substitution for H at position 9 of fluorene (4.7 pK_a units).[13] These observations are in accord with the prediction of the reactivity–selectivity principle, according to which in two series of carbon acids the same substituent will induce greater stabilizing effects on acidity for the less acidic substrate.

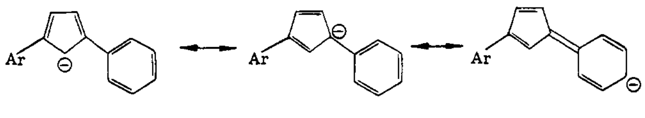
The water component in Me_2SO–H_2O affects not only the acidity of carbon acids relative to pure Me_2SO but also their sensitivity to substituent effects, as measured by the ratio of Hammett slopes. The 2-arylindenes show a sensitivity that is lower by almost a factor of 2 in the mixed solvent relative to that in pure Me_2SO. The fact that the leveling effect of water in the mixed solvent is smaller here than for the 1-aryl-4-phenylcyclopentadienes, for which a factor of 3 was found, is no doubt attributable to the smaller X_{H_2O} (0.30–0.50 vs. 0.70) used for the 2-arylindenes. Noncoincidence of the sensitivities in the two solvents is clear evidence for a breakdown of the Hammett acidity function concept,[14] on which the Me_2SO–H_2O acidities were based.

Acidities of the 2-arylindenes (**2**) respond linearly with a considerable degree of precision to the Hammett substituent constants (Table VII). A very interesting feature of the response is that para electron-withdrawing substituents (COMe, CN) require the larger σ^- constants. Thus, a direct, phenyl-mediated conjugation of the substituent with the negative charge occurs. In terms of the VB approach, this is to say that quinoidal structures **5′** contribute appreciably to the description of the system.



5i 5i′

The fact that a sizable amount of negative charge resides at the para position of the phenyl ring is substantiated by the remarkable high-field shift suffered by $H_{4'}$ (6.85 ppm), at least 0.4 ppm to higher field than that of the neutral precursor (see below). Its pattern is strongly reminiscent (triplet of triplets) of that of benzyl carbanions.[15] The benzyl carbanide nature of the anions **5** is further supported by the almost identical sensitivity in Me_2SO of the response to substituent effects of 1-aryl-3-phenylcyclopentadienides (**7**) and of 2-arylindenides (**5**). The cyclopentadiene series lacked mesomerically electron-withdrawing groups because of synthetic difficulties.[3] Since the distance of the substituent from the carbanion cavity is the same in the two series (**5** and **7**), the observed similar sensitivity must be taken as evidence for analogous quinoid conjugation of the negative charge with the substituent (**5′** and **7′**). Therefore, delocalization prefers to be as extensive as possible. The stabilization gained in the process more than counterbalances the adverse effect associated with the quinoidal structure of the benzene ring annelated to the cyclopentadiene moiety.



7 7′

Proton Spectra. It should be borne in mind that the much higher concentrations for the NMR spectra than for the acidity measurements mean that a different sort of anion (paired or aggregated) is under investigation. One characteristic feature of the ^1H NMR spectra of the anions

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(10) Ritchie, C. D. In "Solute-Solvent Interactions"; Coetzee, J. R., Ritchie, C. D., Eds.; Marcel Dekker: New York, 1969.

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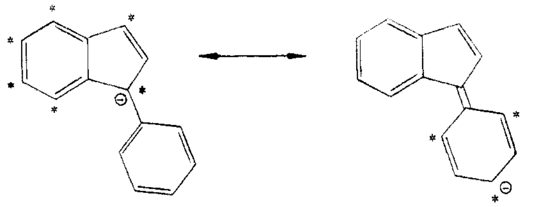
(14) Reference 10, pp 243–244. Gutbezahl, B.; Grunwald, E. *J. Am. Chem. Soc.* **1953**, *75*, 559–565. Kreevoy, M. M.; Baughman, E. H. *Ibid.* **1973**, *95*, 8178–8179. Cox, R. A.; Stewart, R. *Ibid.* **1976**, *98*, 488–494.

(15) Sandel, V. R.; Freedman, H. H. *J. Am. Chem. Soc.* **1963**, *85*, 2328–2329. Bradamante, S.; Gianni, F.; Pagani, G. A. *J. Chem. Soc., Chem. Commun.* **1976**, 478–479. House, H. O.; Auerbach, R. A.; Gale, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514–522.

5a and **6a** is the high-field shift of $H_{4'}$ relative to the neutral precursors. The similar ^1H shifts for all these anions (**5a**, δ 6.85; **6a**, δ 6.59; **7**, δ 6.53) suggest a benzyl carbanionic nature. The $C_{4'}$ resonances in the anions **5** were also all shifted upfield from the respective resonances in the neutral compounds **2**.

None of the proton resonances of the 2-arylindenyl anions **5** responds linearly to substituent parameters, although protons $H_{1,3}$ of **5** do not vary unsystematically. Their chemical shifts are linearly correlated with those of $H_{2,3}$ of the 1-aryl-3-phenylcyclopentadienyl anions **7** (Table VII, entries 23 and 24).

Because of the limited number of points available for the 1-arylindenyl anions (**6**), the interpreation of the response of the ^1H monitors is subject to great caution. All nine carbons in the indenyl rings can carry a formal negative charge, but those starred in **6** are predicted by VB theory to carry the largest amount of negative charge. The protons attached to these carbons, e.g., $H_{5,6}$ and H_3, respond better to the σ^- scale. Furthermore, H_5 and H_6 in anion **6** are analogous in terms of negative charge delocalization and distance from the para substituent X to proton $H_{4'}$ of the 1-aryl-3-phenylcylclopentadienyl anions (**7**).[3] It is interesting to note that they have very similar sensitivities in the response (0.20 and 0.16 ppm/σ, respectively).


6 6'

Carbon-13-Spectra. In our study of the 1-aryl-3-phenylcyclopentadienyl anions (**7**), we found that the ^{13}C chemcial shifts of the secondary carbons in the five-membered ring exhibited a sigmoidal response to the Hammett σ constants.[3] Such behavior was not exhibited by the analogous carbons in the neutrals or by the carbons bearing little negative charge in the anions. It is extremely significant that analogous behavior is observed with the 2-arylindenyl anions in the present study. The plot of the shifts of $C_{1,3}$ is noticeably sigmoidal, whereas those for $C_{4,7}$ or $C_{5,6}$ are nearly linear (Figure 1). These confirming observations suggest that the phenomenon may have some generality. Our original explanation in terms anion structure applies equally well to the present situation.[3]

We appear to be observing a change in the ion pair or aggregation structure with the substituent. Contact ion pairs exhibit higher field (more shielded) resonances than solvent-separated ion pairs.[16-19] A less polarized, wider distribution of negative charge in the solvent-separated anion results in less charge and hence less shielding at the carbons that, in the contact ion pair, are closest to the cation. If only a single ion-pair structure were present in solution, we would expect a linear response of the ^{13}C chemical shift to the change in substituent. Temperature variation has already been well established as a means to alter the ion-pair structure.[16-19] Such an experiment yields a sigmoidal plot of the chemical shift as a function of temperature. In this fashion a dual ion-pair structure has already been established for the parent indenyl anion.[19]

In the 2-aryl series for a common temperature, introduction of an electron-donating substituent such as p-OCH_3 appears to increase the proportion of the solvent-separated ion pair. The higher electron density is better stabilized by the more delocalized structure. The chemical shift for $C_{1,3}$ is pushed above the line passing through the point for H (no substituent) and parallel to either end of the sigmoidal curve. Upward movement of the point corresponds to a downfield shift, which is characteristic of a larger proportion of the solvent-separated ion pair.[16-19] Introduction of an electron-withdrawing substituent such as p-chloro pushes the chemical shift for $C_{1,3}$ downward on the plot, representing an upfield shift. Such a change is consistent with a higher proportion of the contact ion pair. Electron withdrawal from the five-membered ring permits greater localization of charge, as in the more polarized contact ion pair. The shieldings may also be interpreted in terms of changes in the extent of aggregation.

The remaining carbons in the ion do not exhibit the sigmoidal behavior. Similarly in the 1-aryl-3-phenylcyclopentadienyl anion, sigmoidal behavior was not observed in the phenyl ring nor for the quaternary carbons in the five-membered ring.[3] The nearly linear plots for $C_{5,6}$ and $C_{4,7}$ (Figure 1) have a lower slope than the ends of the sigmoidal plot for $C_{1,3}$, indicating lower sensitivity to substituent, presumably because of lower charge density. With a smaller amount of negative charge, the carbons are less sensitive to ion-pair or aggregation effects. It is possible that $C_{4,7}$ exhibits a small degree of sigmoidal behavior. The quaternary carbons ($C_{8,9}$) have very low charge density and do not respond sigmoidally to substituent change. The chemical shifts of the carbons in the aryl ring are dominated by the α, β, and γ effects of the X substituent and consequently do not exhibit the same linear or sigmoidal behavior of the indenyl carbons. Their behavior, however, parallels that of the aryl carbons in the 1-aryl-3-phenylcyclopentadienyl anions **7** or, for that matter, that of simple monosubstituted benzenes.[3] The chemical shifts of the carbons in the neutral hydrocarbons **2** do not exhibit the sigmoidal behavior of the shifts in the anion **5**.

The sigmoidal dependence of the ^{13}C shifts of carbons bearing high negative charge density on the Hammett substituent constants has now been established in two systems, the cyclopentadienyl and the indenyl anions. The dependence of anion structure on the nature of aryl substituents may be a general phenomenon for delocalized anions at NMR concentrations.[20]

Summary and Conclusions

In both the arylindenes and the 1-aryl-4-phenylcyclopentadienes,[3] we have been studying the effect of remote aryl substitution on negative charge that has been created in a cyclopentadienyl ring. Whereas the unsubstituted phenyl ring is free to rotate in the cyclopentadiene series, it has been annelated to the five-membered ring in the indene series. Nonetheless, we make very similar observations in the two series.

Acidities were measured for the 2-arylindenes in pure Me_2SO and in a Me_2SO–H_2O mixture. The measured acidities were lower (pK_a's higher) in Me_2SO (Table I), but

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(19) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661–666.

(20) After completion of this paper, a report was published describing a dependence of 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 $\Delta H°$ roughly parallel our results. Unfortunately, the quoted 7% error on $\Delta H°$ and $\Delta S°$ renders any calculation of $\Delta G°$ statistically unreliable.

Table VIII. Melting [Boiling] Points (°C) of the 2- and 3-Arylindenes[a]

substituent[b]	2-Ar[c]	3-Ar
H	164-165[d]	[105-107 (0.1 mm)][e,f]
OMe	206-207[g]	50-52[h]
Me	181-183	[110-112 (0.1 mm)][e]
m-Me	94-96	
SMe	205-207	
F	150-152	
Cl	170-171	
Br	158-160	92-93[j]
COMe	158-160	
CN	154-156	[138-145 (0.05 mm)][e]
Me_2N		48-50[k]

[a] Products gave satisfactory analytical data. [b] Para substitution unless otherwise indicated. [c] Crystallized from ethanol unless otherwise indicated. [d] Lit. mp 165-166 °C: Dubois, J. E.; Hegarty, A. F. *J. Chem. Soc. B* **1969**, 638-643. [e] Kugelrohr distillation. [f] Lit. bp 158 °C (7 mm): Galton, S. A.; Kalafer, M.; Beringer, F. M. *J. Org. Chem.* **1970**, *35*, 1-6. [g] From benzene. [h] Crystallized spontaneously after chromatography (benzene as eluant). [i] From acetic acid. [j] Crystallized spontaneously after chromatography (petroleum ether as eluant). [k] Crystallized spontaneously after chromatography (petroleum ether/CH_2Cl_2, 1/1).

allowance for differences in the acidities of the indicators in the two solvents confirms that the relative acidities are actually higher in Me_2SO. As with the cyclopentadienes, the dispersion forces in Me_2SO more effectively stabilize the highly delocalized negative charge than do the hydrogen-bonding interactions in the hydroxylic medium. In both media, the acidities showed a linear response to the Hammett σ constant. The sensitivity to σ was almost twice as large in pure Me_2SO relative to that in the mixed solvent. The different sensitivities result from a breakdown in the Hammett acidity function concept.[14]

Strongly electron-withdrawing substituents provided a better linear correlation in the Hammett plot when σ^- constants were used. Thus, the aryl ring must have a strong resonance interaction with the five-membered ring. The electron-withdrawing substituents were not available in the 1-aryl-4-phenylcyclopentadiene series,[3] so that this observation was not previously possible. Delocalization of negative charge from the indenyl ring into the aryl ring is substantiated by significant upfield shifts of the hydrogen resonance ($H_{4'}$ in **5a**) and the carbon resonances ($C_{4'}$ in the series **5**) at the para position.

For the ^{13}C resonances of carbons with high charge density in the cyclopentadienyl anions,[3] we observed unusual sigmoidal Hammett plots, whose nonlinear behavior we attributed to a dependence of the ion pair or aggregated structure on the nature of the aryl substituent. These observations have now been confirmed in the indenyl series. Again, the sigmoidal behavior is observed only for the carbons with very high negative charge density, in this case $C_{1,3}$ (Figure 1). The structure of the plot is very reminiscent of plots of temperature vs. chemical shift for various carbanions.[16-19] The plots may be explained in terms of the existence of two types of ion pairs or variable degrees of aggregation.

Experimental Section

Uncorrected melting points are given in Table VIII. All new compounds gave satisfactory elemental analyses and ^1H NMR spectra in accord with the expected structure. Electronic spectra are summarized in Table IX. Bromobenzene, *p*- and *m*-bromotoluene, *p*-bromoanisole, *p*-bromofluorobenzene, *p*-bromochlorobenzene, and *p*-dibromobenzene were commercially available. *p*-Bromophenyl methyl sulfide was prepared by methylation of the commercially available *p*-bromobenzenethiol; *p*-bromo-*N*,*N*-dimethylaniline was prepared according to known methods.[21] Detailed procedures have already been given for the pK_a measurements and for NMR sample preparation.[3]

General Synthesis of 2-Arylindenes. A small portion of the properly substituted bromobenzene was added to a suspension of Mg turnings (2.02 g, 80 mmol) in anhydrous ethyl ether (60 mL). Gentle warming initiated the reaction, and the remaining bromobenzene (90 mmol) in ether (40 mL) was added at such a rate as to maintain gentle reflux (ca. 45 min). After another 30 min of reflux, 2-indanone[22] (10 g, 76 mmol) in ether (50 mL) was added dropwise to the stirred brown reaction mixture. The resulting milky mixture was refluxed another hour. The mixture was cooled and poured into aqueous NH_4Cl (4.3 g, 80 mmol, in 20 mL of H_2O). The ether layer was separated, dried (Na_2SO_4), and evaporated. The residue was then poured into a stirred, cold solution of H_2SO_4 (8 mL) in acetic acid (32 mL), and H_2O was added. The solid was separated, thoroughly washed with H_2O, dried in air, and subsequently either crystallized (twice) or chromatographed (silica gel, 150 g, $CHCl_3$ or CH_2Cl_2).

2-(*p*-Acetylphenyl)indene (2i). A small portion of *p*-bromoacetophenone ethylene ketal was added to a suspension of Mg turnings (0.93 g, 38.5 mmol) in anhydrous THF (20 mL).[23] Gentle warming initiated the reaction. The remainder of the ketal (10.4 g, 43 mmol) in THF (30 mL) was then added with the temperature maintained at 45–50 °C during addition and for another 45 min after addition. 2-Indanone[22] (4.9 g, 37 mmol) in THF (10 mL) was then added dropwise. The reaction mixture was stirred for another 2 h and then treated with aqueous NH_4Cl (4 g in 20 mL of H_2O). The organic phase was separated, washed with brine, dried (Na_2SO_4), and evaporated. The residue was poured into a solution of H_2SO_4 (8 mL) in acetic acid (32 mL). Water was then added (80 mL), and the solid was isolated by filtration and crystallized first from EtOH and then from dilute acetic acid to give 0.6 g (7%) of the product: NMR δ ($CDCl_3$) 7.95 (2, AA′ part of the *p*-acetylphenyl ring), 7.65 (2, BB′ part of the same), 7.6–7.1 (5, m, aromatic and =CH), 3.8 (2, br s, CH_2), 2.58 (3, s, $COCH_3$).

2-(*p*-Cyanophenyl)indene (2h). A vigorously stirred slurry in anhydrous DMF (5 mL) of 2-(*p*-bromophenyl)indene (**2g**, 1.5 g, 5.5 mmol) and freshly prepared CuCN (0.6 g, 6.7 mmol) was heated to reflux under N_2 for 8 h. The reaction mixture was then cooled and poured into a warm (60 °C) solution of $FeCl_3$ (1.7 g) in 6% HCl (12 mL). The mixture was maintained at this temperature, with stirring for 30 min. The still-warm (45–50 °C) mixture was then extracted with benzene (6 × 30 mL), and the combined extracts were washed with 18% HCl (2 × 100 mL), H_2O (100 mL), 10% NaOH (100 mL), and brine, dried (Na_2SO_4), and evaporated under reduced pressure. The brown residue was chromatographed (SiO_2, 30 g, 1/1 benzene/cyclohexane), yielding 0.35 g (30%) of pure product: NMR δ ($CDCl_3$) 7.55 (4, s, aromatic), 7.4–7.2 (5, m, aromatic and =CH), 3.7 (2, br s, CH_2).

General Synthesis of 3-Arylindenes. The arylmagnesium bromide was prepared analogously to the procedure described for the 2-arylindenes by starting from the substituted bromobenzene (39 mmol) in THF (20 mL) and Mg (38 mmol) in the same solvent (10 mL). 1-Indanone (5 g, 38 mmol) in THF (15 mL) was added, and stirring was continued overnight. The reaction mixture was then hydrolyzed with aqueous NH_4Cl (4 g in 20 mL of H_2O). The organic phase was separated, washed with brine, dried (Na_4SO_4), and evaporated. The oily residue was taken up in acetic acid (16 mL) and refluxed for 15 min. The solvent was evaporated, the residue was dissolved in CH_2Cl_2 (30 mL), and the organic phase was washed with saturated aqueous $NaHCO_3$ (20 mL) and with H_2O, dried, and evaporated. The residue was then distilled (in the case of 3-phenyl- and 3-*p*-tolylindene) or chromatographed (SiO_2, 150 g, eluant specified in Table VIII).

3-(*p*-Cyanophenyl)indene. 3-(*p*-Bromophenyl)indene (1.5 g, 5.5 mmol) was treated with CuCN (0.58 g, 6.5 mmol) in anhydrous DMF (20 mL) for 16 h at reflux. After a workup analogous to that described above for 2-(*p*-cyanophenyl)indene,

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(22) Horan, J. E.; Schiessler, R. W. "Organic Synthesis"; Baumgarten, H. E., Ed.; Wiley: New York, 1973; Collect. Vol. V, pp 647–649.

(23) Feugeas, C. *Bull. Soc. Chim. Fr.* **1963**, 2568–2579.

Table IX. Electronic Spectra of the 2-Arylindenes[a] and Conjugated Anions

	carbon acid		carbanion	
	λ, nm	$10^{-4}\epsilon$ (λ, nm)	$10^{-3}\epsilon$	X_{H_2O}
H	332 (sh), 315, 305	2.35 (316), 1.74 (325)	4.5 (360)	0.47
OMe	335 (sh), 323, 315	2.22 (323), 1.55 (335)	10.1 (370)	0.32
Me	330 (sh), 319, 307	2.66 (319), 2.11 (325)	14.2 (360)	0.33
m-Me	335 (sh), 319, 307	2.45 (318), 1.85 (325)	15.2 (360)	0.36
SMe	350 (sh), 335	3.63 (335), 2.45 (350)	22.5 (382)	0.36
F	330 (sh), 315, 306	2.14 (300), 2.25 (306), 1.93 (320)	11.0 (360)	0.37
Cl	330 (sh), 320, 310	2.15 (300), 2.65 (310), 1.99 (330)	8.4 (360)	0.45
Br	335 (sh), 323, 307	2.19 (300), 2.84 (323)	11.5 (375)	0.41
COMe	356 (sh), 340	2.31 (342), 2.11 (350)	9.6 (425)	0.52
CN	345 (sh), 335	2.98 (335), 2.57 (345)	2.98 (408)	0.53

[a] Para substitution unless otherwise indicated.

the residue was chromatographed (SiO_2, 80 g, CH_2Cl_2) and distilled to give the product (0.14 g), which was slightly (4–5%) contaminated with the starting material: NMR δ ($CDCl_3$) 7.52–6.98 (8, m, aromatic), 6.50 (1, t, *J* = 2 Hz, =CH), 3.40 (2, d, *J* = 2 Hz, CH_2); IR (film) 2230 cm^{-1} (CN).

2-(*p*-Nitrophenyl)-3-phenylpropionic Acid. To a solution of NaOEt prepared from Na (3.45 g, 0.150 mol) in absolute ethanol (180 mL) was added ethyl (*p*-nitrophenyl)acetate (31.5 g, 0.150 mol) in ethanol (500 mL) dropwise. To the deep purple solution was added benzyl bromide (23.1 g, 0.135 mol) in ethanol (110 mL) slowly with stirring. After 60 h at room temperature with stirring, the yellow solution was evaporated under reduced pressure, and the residue was taken up with $CHCl_3$ and 5% HCl. The organic phase was separated, washed with H_2O, dried (Na_2SO_4), and evaporated. The reddish brown oil (31 g) was taken up in a mixture of acetic acid (230 mL), H_2O (150 mL), and concentrated H_2SO_4 (30 mL) and refluxed for 15 min. The pink precipitate that formed when the mixture cooled was filtered off, dissolved in 5% NH_4OH (200 mL), boiled, and filtered hot with charcoal. Acidification with HCl produced 60% of the crude product: mp 157–158 °C (from EtOH); NMR δ ($CDCl_3$) 3–3.6 (m, CH_2), 4 (m, CH), 7–8.2 (9, aromatic).

2-(*p*-Nitrophenyl)indan-1-one. 2-(*p*-Nitrophenyl)-3-phenylpropionic acid (22 g, 0.081 mol) was slowly added in portions to a suspension of PCl_5 (16.7 g, 0.081 mol) in $CHCl_3$ (185 mL). The solution was then refluxed for 30 min, evaporated to dryness, and taken up with CH_2Cl_2 (200 mL). This solution was added dropwise to a stirred suspension of $AlCl_3$ (12 g, 0.090 mol) in CH_2Cl_2 (150 mL). Stirring was continued overnight at room temperature. The solution was then poured onto a 50/50 mixture (300 g) of crushed ice and concentrated HCl. The organic phase was separated, washed (3 × 150) with 15% HCl, with aqueous $NaHCO_3$, and with H_2O, dried (Na_2SO_4), and evaporated to give the crude product: 68%; mp 134–136 °C (AcOH); NMR δ ($CDCl_3$) 3.31–4.03 (3, ABX system, $\nu_A = 3.76$, $\nu_B = 3.31$, $\nu_X = 4.03$, $J_{AX} = 8.25$ Hz, $J_{BX} = 3.25$ Hz, $J_{AB} = -17$ Hz, CH–CH_2), 7.3–8.3 (8, m, aromatic).

2-(*p*-Nitrophenyl)indene (2j). A solution of sodium borohydride (1.37 g, 0.036 mol) in H_2O (20 mL) was added slowly to a stirred suspension of 2-(*p*-nitrophenyl)indan-1-one (13.8 g, 0.054 mol) in 20% (v/v) aqueous ethanol (500 mL). The mixture was stirred overnight, a few drops of acetic acid were added to lower the alkaline pH of the solution, and another portion of sodium borohydride (1.3 g) was added. Stirring was continued for another 12–18 h. Acetic acid was then added to decompose the excess borohydride, and the solution was evaporated to dryness. The semisolid, oily residue was dissolved in $CHCl_3$ (50 mL), filtered, and treated with $SOCl_2$ in $CHCl_3$ (40 mL). After 7 h, the solution was evaporated to dryness, taken up with $CHCl_3$, washed with H_2O, dried, and evaporated to dryness to give a solid (12 g), which from NMR analysis proved to be a mixture of 2-(*p*-nitrophenyl)indene (**2j**) and the (*E*)- and (*Z*)-1-chloro-2-(*p*-nitrophenyl)indans in a ratio (over several preparations) of 1/4: NMR δ ($CDCl_3$) 8.2 (2, AA′ part of the *p*-nitrophenyl ring of both the indene and the (*E*)- and (*Z*)-indans), 7.7 (0.4, BB′ part of the indene only), 7.6–7.2 (5.8, m, other aromatic protons and =CH), 5.56 (0.26, d, *J* = 5.5 Hz, H_1 in the (*E*-indan), 5.34 (0.37, d, *J* = 8 Hz, H_1 in the (*Z*)-indan), 4–3 (2.8, m, ABX system of H_2, H_3, and $H_{3'}$ of both (*E*)- and (*Z*)-indans and H_3 and $H_{3'}$ of **2j**, which emerges as a br s at 3.80). From the intensities of the δ 7.74, 5.56, and 5.34 peaks the composition was calculated: **2j**, 20%; *Z* isomer, 47%; *E* isomer 33%. This mixture was suspended in quinoline (80 mL), preheated at 80 °C, and then kept at 120 °C for 15 min. The solid that separated when the mixture cooled was filtered, washed with dilute HCl and then with MeOH, and crystallized from acetic acid to give pure **2j**: 6 g (46% overall yield); mp 237–239 °C; NMR δ ($CDCl_3$) 8.2 (2, AA′ part of the *p*-nitrophenyl ring), 7.7 (2, BB′ part of the *p*-nitrophenyl ring), 7.6–7.2 (5, m, aromatic and =CH), 3.81 (2, br s, CH_2).

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Registry No. 2a, 4505-48-0; **2b**, 79449-05-1; **2c**, 79449-06-2; **2d**, 54288-29-8; **2e**, 1512-69-2; **2f**, 23909-29-7; **2g**, 38453-87-1; **2h**, 79449-07-3; **2i**, 79449-08-4; **2j**, 79449-09-5; **2** (R = *p*-SMe), 79449-10-8; **3a**, 1961-97-3; **3b**, 79449-11-9; **3c**, 38199-92-7; **3d**, 57803-87-9; **3e**, 66648-21-3; **3f**, 79449-12-0; **5a**, 78525-48-1; **5b**, 79449-13-1; **5c**, 79449-14-2; **5d**, 79449-15-3; **5e**, 79449-16-4; **5f**, 79449-17-5; **5g**, 79449-18-6; **5h**, 79466-82-3; **5i**, 79449-19-7; **5** (R = *p*-SMe), 79449-20-0; **6a**, 78525-49-2; **6b**, 79449-21-1; **6c**, 79449-22-2; **6d**, 79449-23-3; **6f**, 79466-55-0; bromobenzene, 108-86-1; *p*-bromotoluene, 106-38-7; *m*-bromotoluene, 591-17-3; *p*-bromoanisole, 104-92-7; *p*-bromofluorobenzene, 460-00-4; *p*-bromochlorobenzene, 106-39-8; *p*-dibromobenzene, 106-37-6; *p*-bromophenyl methyl sulfide, 104-95-0; *p*-bromo-*N*,*N*-dimethylaniline, 586-77-6; 2-indanone, 615-13-4; *p*-bromoacetophenone ethylene ketal, 4360-68-3; 1-indanone, 83-33-0; 2-(*p*-nitrophenyl)-3-phenylpropionic acid, 50434-43-0; ethyl (*p*-nitrophenyl)acetate, 5445-26-1; benzyl bromide, 100-39-0; 2-(*p*-nitrophenyl)indan-1-one, 79466-83-4; *trans*-1-chloro-2-(*p*-nitrophenyl)indan, 79449-24-4; *cis*-1-chloro-2-(*p*-nitrophenyl)indan, 79449-25-5; indene, 95-13-6.