

Focusing attention on the 9-Ph-Fl⁻ family, where the data are likely to be more reliable, we find that β_{Nu} decreases from 0.31 for PhCH₂Cl to 0.28 for PhCH₂Br. This change can have a substantial effect on the k^{Br}/k^{Cl} rate ratios as may be seen by comparing the ratios 435, 389, and 310 in the 9-Ph-Fl⁻ family for the *p*-MeSO₂, *m*-Cl, and H substituents, respectively (Table IV).

Interpretation of k^{Br}/k^{Cl} leaving-group effects is rendered difficult because of the large differences (a) in Cl and Br electronegativities, (b) in C-Cl and C-Br bond lengths and bond strengths, and (c) in solvation of the incipient Cl⁻ and Br⁻ ions. We hope to obtain additional information concerning leaving-group effects in S_N2 reactions by studying systems where the nature of the atoms in the bond broken is kept constant.

The Reactivity-Selectivity Principle (RSP). A controversy has arisen recently over the validity of the so-called reactivity-selectivity principle (RSP), which states that a more reactive species will be less selective in choosing its reaction partner and vice versa.¹² The data in Table III contain many exceptions to RSP. For example, 9-Me-Fl⁻ reacts with PhCH₂Cl over 8000 times as rapidly as does 9-CN-Fl⁻.¹ According to RSP, the highly reactive 9-Me-Fl⁻ ion should be less selective in choosing *m*-ClC₆H₄CH₂Cl vs. PhCH₂Cl than will the less reactive 9-CN-Fl⁻ ion. We see from Table III, however, that in a competition for equal amounts of these reagents 9-Me-Fl⁻ would choose *m*-ClC₆H₄CH₂Cl over PhCH₂Cl in a ratio of 4.9 to 1.0, compared to 2.5 to 1.0 for 9-CN-Fl⁻. The constancy of β_{Nu} for large changes in ΔG° brought about by increased nucleophile basicities or decreased leaving-group basicities, which was discussed in the previous paper,¹ constitutes an even greater challenge to RSP. It must be remembered that RSP has its origin in the Leffler-Grunwald rate-equilibrium relationship.¹³ The experimental

support for RSP rests primarily, therefore, on the observation of a variation of Brønsted β 's in proton-transfer reactions, i.e., curved Brønsted plots, and a variation in β_{Nu} in Brønsted-type plots for S_N2 reactions.¹⁴ We have argued elsewhere that curved Brønsted plots are at least as likely to arise from failure to keep steric effects constant and the use of different kinds of donor and acceptor atoms (causing solvation effects of change) as from changes in the extent of bond making and bond breaking in the TS.¹ The failure to observe curvature in Brønsted-type plots for S_N2 reactions¹ supports this view. We agree with the conclusion that RSP should be abandoned.⁶

Acknowledgment. We are grateful to the National Science Foundation for the support of this work.

Registry No. 1, 1529-40-4; 1 anion, 12564-43-1; 2, 73636-50-7; 2 anion, 73872-40-9; 3, 789-24-2; 3 anion, 31468-22-1; 4, 2523-37-7; 4 anion, 31468-21-0; 9-*p*-MeC₆H₄SO₂-2-PhSO₂-Fl, 73838-64-9; 9-C₆H₅SO₂-2-Br-Fl, 73838-65-0; 9-*p*-BrC₆H₄SO₂-Fl, 73838-66-1; 9-C₆H₅SO₂-Fl, 22010-78-2; 9-*p*-MeC₆H₄S-2-PhSO₂-Fl, 73838-67-2; 9-C₆H₅S-2-Br-Fl, 29800-84-8; 9-*p*-BrC₆H₄S-Fl, 73855-17-1; 9-C₆H₅S-Fl, 28114-92-3; 9-*p*-MeSO₂C₆H₄-Fl, 73872-41-0; 9-*m*-ClC₆H₄-Fl, 32377-11-0; 9-*p*-MeC₆H₄-Fl, 18153-43-0; 9-Me-2,7-Br₂-Fl, 73872-42-1; 9-Me-2-Cl-Fl, 73872-43-2; 9-*p*-MeC₆H₄SO₂-2-PhSO₂-Fl⁻, 73838-72-9; 9-C₆H₅SO₂-2-Br-Fl⁻, 73838-73-0; 9-*p*-BrC₆H₄SO₂-Fl⁻, 73838-74-1; 9-C₆H₅SO₂-Fl⁻, 71805-74-8; 9-*p*-MeC₆H₄S-2-PhSO₂-Fl⁻, 73838-75-2; 9-C₆H₅S-2-Br-Fl⁻, 73838-76-3; 9-*p*-BrC₆H₄S-Fl⁻, 73838-77-4; 9-C₆H₅S-Fl⁻, 71805-72-6; 9-*p*-MeSO₂C₆H₄-Fl⁻, 73872-44-3; 9-*m*-ClC₆H₄-Fl⁻, 73872-45-4; 9-*p*-MeC₆H₄-Fl⁻, 42730-14-3; 9-Me-2,7-Br₂-Fl⁻, 73872-46-5; 9-Me-2-Cl-Fl⁻, 73872-47-6; *p*-MeOC₆H₄CH₂Cl, 824-94-2; *p*-MeC₆H₄CH₂Cl, 104-82-5; *m*-MeC₆H₄CH₂Cl, 620-19-9; C₆H₅CH₂Cl, 100-44-7; *p*-FC₆H₄CH₂Cl, 352-11-4; *p*-ClC₆H₄CH₂Cl, 104-83-6; *m*-ClC₆H₄CH₂Cl, 620-20-2; *m*-CF₃C₆H₄CH₂Cl, 705-29-3; *m*-NO₂C₆H₄CH₂Cl, 619-23-8; *p*-NO₂C₆H₄CH₂Cl, 100-14-1; PhCH₂Br, 100-39-0.

(14) Following the original suggestion of Leffler and Grunwald,¹³ comparisons of rate and product data from solvolysis reactions have often been used in support of RSP. The mechanistic complexity of these reactions, wherein products can arise from at least two types of ion pairs, as well as free cations, renders them unsuitable, however, as a testing ground for RSP.^{12a}

(15) **Note Added in Proof.** Additional work with these and other substrates suggests that, in general, the β_{Nu} values for RCl and RBr do not differ significantly.

(12) (a) Ritchie, C. D. *Acc. Chem. Res.* 1972, 5, 348-354. (b) Johnson, C. D. *Chem. Rev.* 1975, 75, 755-765. (c) Pross, A. *Adv. Phys. Org. Chem.* 1977, 14, 69-132. (d) Giese, B. *Angew. Chem., Int. Ed. Engl.* 1977, 16, 125-136. (e) McLennan, D. J. *Tetrahedron* 1978, 34, 2331-2342.

(13) Leffler, J. E.; Grunwald, E. "Rates and Equilibria in Organic Reactions"; Wiley: New York, 1964; pp 156-168.

Acidities of Indene and Phenyl-, Diphenyl-, and Triphenylindenes

F. G. Bordwell* and George E. Drucker

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received January 24, 1980

Equilibrium acidities in Me₂SO for indene and 2-phenyl-, 3-phenyl-, 1,3-diphenyl-, 2,3-diphenyl-, and 1,2,3-triphenylindenes are reported. The pK_a values for indene and 1,3-diphenylindene agree reasonably well with literature values once the latter are corrected to an absolute basis. It is urged that henceforth acidities of weak acids in Me₂SO or other dipolar nonhydroxylic solvents be referred to an absolute base rather than an arbitrary reference standard. 2-Phenylindene was found to be only 0.7 pK_a unit more acidic than indene, and 2-Ph substitution into 3-phenyl- and 1,3-diphenylindenes caused a decrease in acidity for steric reasons. The 7.6 pK_a units greater acidity of 1,3-diphenylindene, relative to indene, is attributed mainly to charge delocalization in the anion.

Phenyl substitution for hydrogen has been found to increase the acidity of carbon acids in solution substantially. In the absence of steric effects, the size of the phenyl acidifying effect has been shown to decrease with a decrease in the size of the negative charge on the carbon atom to which the phenyl group is attached (resonance-saturation effect).¹ When phenyl groups are substituted suc-

cessively for hydrogen, there is a progressive decrease in the size of the acidifying effects. For example, in the gas phase, phenyl substitution into methane increases the

(1) Bordwell, F. G.; Bares, J. E.; Bartmess, J. E.; McCollum, G. J.; Van Der Puy, M.; Vanier, N. R.; Matthews, W. S. *J. Org. Chem.* 1977, 42, 321-325.

Table I. Acidities of Indene and Phenylindenes in Dimethyl Sulfoxide Solution

compd	indicator	runs	pK_a	selected pK_a
indene	NPANH ^a	2	20.13	20.12
	CNAH ^b	2	20.11	
2-phenylindene	PSO,PFH ^c	2	19.38	19.37
	PFH ^d	3	19.36	
3-phenylindene	(EtSO ₂) ₂ CHCH ₃	2	17.23	17.3 ± 0.2
	PSO,PFH ^c	1	17.42	
	PSFH ^d	2	17.43	
2,3-diphenylindene	PSO,PFH ^c	2	17.74	17.71
	(EtSO ₂) ₂ CHCH ₃	2	17.69	
1,3-diphenylindene	(PhSO ₂) ₂ CH ₂	2	12.79	12.77
	FMY33 ^e	2	12.75	
1,2,3-triphenylindene	(MeSO ₂) ₂ CH ₂	2	15.18	15.20
	(<i>i</i> -PrSO ₂) ₂ CH ₂	2	15.22	

^a 2-Naphthylacetonitrile. ^b 4-Chloro-2-nitroaniline.

^c 2-(Phenylsulfonyl)-9-phenylfluorene. ^d 9-Phenylfluorene. ^e 2-(Phenylsulfonyl)-9-(*p*-tolylthio)fluorene.

acidity by 37 kcal/mol (27 pK_a units), and a second phenyl substitution causes a further increase in acidity of 15 kcal/mol (11 pK_a units).² In Me₂SO solution the comparable phenyl acidifying effects are estimated to be about 13 and 10 pK_a units, respectively.³ A third phenyl substitution causes only a 1.8- pK_a -unit further increase in acidity.¹ The decreasing phenyl acidifying effects are due in part to a resonance-saturation effect, and in part to steric hindrance to resonance in the anion. Successive substitution of phenyl groups into the 1-, 2-, and 3-positions of indene would be expected to have these, and other, effects on the acidity of indene.

The acidity of indene has been measured by a variety of methods in a variety of solvents including benzene (or ether),⁴ cyclohexylamine (CHA),⁵ dimethyl sulfoxide (Me₂SO),⁶⁻⁸ and MeOH-Me₂SO.⁹ The acidity of 1,3-diphenylindene has been measured in CHA¹⁰ and in Me₂SO;¹⁰ that of 1,2,3-triphenylindene has been measured in DME-*t*-BuOH.¹¹ In this paper we report acidity data in Me₂SO for these and other phenylindenes obtained by the overlapping-indicator method.¹²

Results and Discussion

Acidities of Indenes in Various Media. The pK_a values for indene and five phenyl-substituted indenenes, measured in Me₂SO solution by the overlapping-indicator method,¹² are summarized in Table I. These values are anchored on acidities in the low- pK_a region (4-8) where the acids are strong enough to be partially ionized by the Me₂SO solvent. The latter acidities are absolute in the

sense that they are measured directly by using classical methods (spectrophotometric, potentiometric, or conductometric). Our Me₂SO acidity scale therefore rests on an absolute base.^{12,16}

Comparison of the results in Table I with those in the literature is complicated because most previous investigators have tried to relate their acidities to a "water acidity scale" ("water as the standard state"). The concept of placing all acids on a single scale has turned out to be an illusion, however. Since most organic compounds are insoluble in water, the acidities of the reference standards chosen were usually determined in aqueous-organic mixtures by using the H_- technique. For example, Bowden and Stewart used CH₂(CN)₂ ($pK_a = 11.1$ in H₂O) as their starting point.¹³ The pK_a for 9-cyanofluorene in Me₂SO-EtOH was found to be 11.41, which is 3.1 pK_a units higher than the pK_a in pure Me₂SO.¹² Since Kuhn and Rewicki used $pK_a = 11.41$ as a reference for many of the compounds in their Table X,¹⁴ including indene, the fact that the pK_a of indene listed by them for "high dielectric constant solvents" (20.1) is identical with that in Table I is fortuitous. The pK_a determined by the H_- method in Me₂SO-MeOH is actually 1.9 pK_a units lower.⁹

Steiner chose the pK_a of 4-nitroaniline of 18.4,⁵ determined by the H_- method in mixed aqueous media, as his reference standard for pK_a 's in Me₂SO, whereas the pK_a anchored on an absolute base is 2.6 units higher.¹² When his pK_a for indene is corrected to our absolute scale, it agrees reasonably well with ours.

Shatenshtein⁷ based his Me₂SO acidity scale on the pK_a of 18.5 for 9-phenylfluorene determined by the H_- method in aqueous sulfolane, whereas the pK_a anchored on an absolute base in pure Me₂SO is 0.6 pK_a unit lower.¹² When his pK_a for indene is corrected to our absolute scale, it agrees exactly with ours. (Agreement to within ±0.3 pK_a unit with Shatenshtein's values is observed for 15 compounds covering the pK_a range 11-32.)

The value for indene determined by the potentiometric method in Me₂SO⁸ is 1.6 pK_a units lower than our value. Discrepancies of this order of magnitude between the potentiometric and overlapping-indicator methods are not unusual above $pK_a = 14$.¹² For compounds with pK_a values of 14 and above, slow electrode response apparently makes accurate determinations by the potentiometric method difficult.^{12,15}

A pK_a of 15.40 for 1,3-diphenylindene in Me₂SO was obtained previously by equilibration against indicators developed by Kuhn and Rewicki¹⁴ for the Pr₃N-Me₂SO system.¹⁰ Correction of this value to our absolute scale by subtraction of 3.1 units (see above) brings the number down to 12.3, which is reasonably close to our value of 12.8 (Table I).

It is evident from the above discussion that much confusion has arisen from the practice of trying to base acidities on water as a "standard state". This is a futile exercise in any event, since for the ionization of a weak acid, HA, by a solvent, S (eq 1), we can expect each solvent to have a unique ability to solvate the proton, the neutral acid, and the acid anion, A⁻. No single acidity scale will suffice.



In order to make direct comparison of acidities, we must anchor acidity scales on an absolute base. This is possible

(2) Bartmess, J. E.; McIver, R. T. "Gas-Phase Ion Chemistry"; Bowers, M. T. Ed; Academic Press: New York, 1979; Vol. 2, Chapter 11.

(3) Algrim, D.; Bares, J. E.; Branca, J. C.; Bordwell, F. G. *J. Org. Chem.* **1978**, *43*, 5024-5026.

(4) McEwen, W. K. *J. Am. Chem. Soc.* **1936**, *58*, 1124-1129.

(5) Streitwieser, A.; Ciuffarin, E.; Hammons, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 63-67.

(6) Steiner, E. C.; Gilbert, J. M. *J. Am. Chem. Soc.* **1965**, *87*, 382-384.

(7) Terekhova, M. I.; Petrov, E. S.; Mesyats, S. P.; Shatenshtein, A. I. *J. Gen. Chem. USSR*, **1975**, *45*, 1499-1501.

(8) Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.*, **1967**, *89*, 2752-2753.

(9) Bowden, K.; Cockerill, A. F.; Gilbert, J. R. *J. Chem. Soc. B* **1970**, 179-184.

(10) Streitwieser, A.; Chang, C. J.; Hollyhead, W. B. *J. Am. Chem. Soc.* **1972**, *94*, 5292-5296.

(11) Mazur, S.; Breslow, R. *J. Am. Chem. Soc.* **1973**, *95*, 584-585.

(12) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006-7014.

(13) Bowden, K.; Stewart, R. *Tetrahedron* **1965**, *21*, 261-266.

(14) Kuhn, D.; Rewicki, D. *Prog. Org. Chem.* **1967**, *7*, 116-161.

(15) Ritchie, C. D. "Solute-Solvent Interactions", Ritchie, C. D., Coetzee, J. F., Eds.; Marcel Dekker: New York, 1976; Vol. 2, Chapter 12.

for water, for certain other hydroxylic solvents, and for some dipolar nonhydroxylic solvents including Me_2SO and *N*-methylpyrrolidin-2-one (NMP).¹⁶ We recommend that the practice of relating acidities in such solvents to an arbitrary standard be abandoned.

For weakly polar nonhydroxylic solvents, such as benzene, DME, and CHA, absolute acidity measurements are difficult or impossible because of ion association, even in dilute solutions. Here it is necessary to use an arbitrary reference standard, such as the $\text{p}K_a$ of MeOH in (MeOH), chosen by McEwen⁴ for the benzene (or ether) acidity scale, or the $\text{p}K_a$ of 9-phenylfluorene in aqueous sulfolane (18.5), chosen by Streitwieser for the CHA scale.¹⁰ It must be emphasized, however, that the "ion-pair $\text{p}K_a$ values" in these scales have no absolute meaning and that comparisons of the numbers in C_6H_6 with those in CHA or with $\text{p}K_a$ values in H_2O , Me_2SO , NMP, or the like are not valid. (We urge chemists to stop the common practice of giving the $\text{p}K_a$ of a weak acid without reference to solvent.) For example, it is meaningless to compare the ion-pair $\text{p}K_a$ of 13.92 for 1,3-diphenylindene in CHA¹⁰ with the $\text{p}K_a$ of 12.8 in Me_2SO (Table I) which rests on an absolute base.¹² This point is made clear by the report that the "absolute ion pair" $\text{p}K_a$ of 1,3-diphenylindene in CHA is lower by 11.7 units.^{10,22} For hydrocarbons forming highly delocalized anions, the relative acidities in Me_2SO and CHA often agree remarkably well.¹² For 1,3-diphenylindene, however, the $\Delta\text{p}K_a$, relative to indene, is 5.5 units in CHA and 7.6 units in Me_2SO . Since the latter $\Delta\text{p}K_a$ represents the stabilizing effect of the two phenyl groups on the indenyl anion in the absence of the counterion, it appears that in CHA the Cs^+ counterion is less effective in stabilizing the 1,3-diphenylindenyl anion than it is in stabilizing the indicator ions with which it is being equilibrated.¹⁰ In other words, "tighter" ion pairing with the Cs^+ cation causes the equilibrium to shift toward the side of the indicator anions, in which the anion center is flat [e.g., the anion derived from 1,1,3,3-bis(biphenylene)propene],¹⁰ and away from the 1,3-diphenylindenyl anion wherein access to the anionic sites is blocked by the twisted phenyl rings.

A " $\text{p}K_a$ " for 1,2,3-triphenylindene of 17.8 ± 3 in DME-*t*-BuOH, relative to the $\text{p}K_a$ of 9-phenylfluorene (18.5), determined in aqueous sulfolane by the H_- method, has been estimated by equilibrating the lithio derivatives of the hydrocarbons and quenching with acetic acid-*O-d*.¹¹ For the reasons given above, we do not believe that a comparison of this value with the $\text{p}K_a$ of 1,2,3-triphenylindene given in Table I is meaningful.

Changes in the Acidity of Indene Caused by Phenyl Substitution. These effects are summarized in Figure 1. Note first that Ph substitution at C-2 of indene causes an increase in acidity of only 0.7 $\text{p}K_a$ unit (Figure 1). A smaller effect is expected for Ph substitution at C-2 as compared to C-3 (or C-1) since the negative charge in the anion cannot be effectively delocalized into the phenyl ring. Also, the negative charge density at C-2 is less than half that at C-3 (or C-1) according to MO calculations. The effect is also small because Ph substitution at C-2 introduces a conjugative stabilizing effect between the Ph group and the π bond in the neutral acid.¹⁷ This effect is present also in the anion but is diminished because of cross conjugation.

Phenyl substitution at C-3 of indene causes a 2.5- $\text{p}K_a$ -unit increase in acidity (Figure 1). Here conjugation between the Ph group and the π bond is inhibited sterically

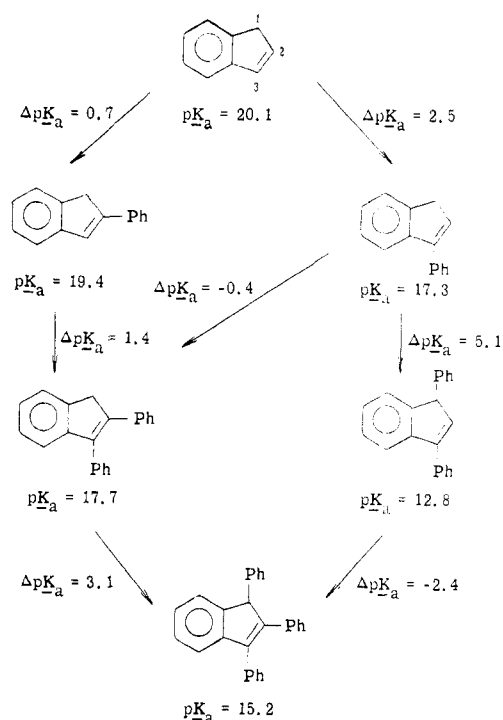
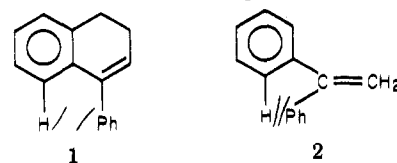


Figure 1. Changes in acidity caused by substitution of one or more phenyl groups into the 1-, 2-, or 3-positions of indene. (The $\Delta\text{p}K_a$ values are statistically corrected for the number of acidic protons and the symmetry of the indenyl and 2-phenyl-, 1,3-diphenyl-, and 1,2,3-triphenylindenyl anions.)

in both the neutral acid and the anion. The steric effect is appreciable, judging from data for 4-phenyl-1,2-dihydronaphthalene (1) and 1,1-diphenylethylene (2), which



can be considered as models for 3-phenylindene.^{18,19} In 1 and 2 the phenyl groups are twisted out of the plane of the $\text{C}=\text{C}$ bond by about 50° ¹⁸ and 30° (each),¹⁹ respectively. However, since the conjugative stabilization is believed to be proportional to the square of the cosine of this angle,²⁰ a significant amount of stabilization would be present even with this degree of twist.

1-Phenylindene is isomerized completely to 3-phenylindene under base catalysis in CDCl_3 .²¹ This is no doubt due in part to the conjugation between the phenyl group and the π bond in the latter, which is not possible in the former. Since 1-phenyl- and 3-phenylindene form the same anion, we can place the $\text{p}K_a$ of 1-phenylindene at a minimum of 2 $\text{p}K_a$ units below that of 3-phenylindene (assuming that the equilibrium favors the latter in Me_2SO by at least 100:1). This means that the $\Delta\text{p}K_a$ between indene and 1-phenylindene must be at least 4.5 units. The effect of Ph substitution at C-1 in 3-phenylindene is of a comparable order of magnitude ($\Delta\text{p}K_a = 5.1$), as expected.

(18) Dubois, J. E.; Hegarty, A. F. *J. Chem. Soc. B* 1969, 638-643.

(19) Hegarty, A. F.; Lomas, J. S.; Wright, W. V.; Bergmann, E. D.; Dubois, J. E. *J. Org. Chem.* 1972, 37, 2222-2228.

(20) Dewar, M. J. S. *J. Am. Chem. Soc.* 1952, 74, 3341-3345.

(21) Kende, A. S.; Bogard, T. L. *Tetrahedron Lett.* 1967, 3383-3388.

(22) Spectroscopic determination of the concentration of the anion formed upon solution of 1,3-diphenylindene in CHA leads to an ion-pair $\text{p}K_a$ of 2.2.¹⁰ The higher acidity of weak acids in ammonia or amine solvents like CHA is due primarily to the high basicity of the solvent; e.g., the $\text{p}K_a$ of PhNH_2 in liquid NH_3 is 21.2²³ compared to 30.6 in Me_2SO .

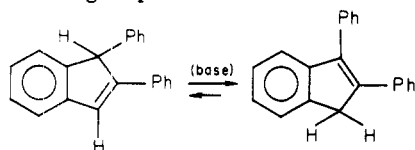
(23) Lagowski, J. J. *J. Chem. Educ.* 1978, 55, 752-759.

(16) Olmstead, W. N.; Branca, J. C.; Hughes, D.; Bordwell, F. G. *J. Org. Chem.*, accompanying paper in this issue.

(17) Haselbach, E.; Heilbronner, E. *Helv. Chim. Acta* 1968, 51, 16-33.

Introduction of a Ph group into a position adjacent to one already present has a diminished or even a negative acidifying effect (Figure 1). Thus, 3-Ph substitution into 2-phenylindene and 1-Ph substitution into 2,3-diphenylindene cause smaller increases in acidity, by 1.1 and (at least) 1.4 p*K*_a units, respectively, than do the comparable substitutions into indene.

The increases in acidity observed (1.4 and 3.1 p*K*_a units, respectively) are in part caused by stabilization of the negative charge by delocalization into a 3-Ph or 1-Ph substituent. These effects are moderated, however, by steric inhibition of resonance caused by the presence of the adjacent Ph group.



1,2-Diphenylindene must have an energy about 2.7 kcal/mol higher than that of 2,3-diphenylindene, since the latter is formed almost completely on isomerization with base.²⁴ This strain energy must also be present in 1,2,3-triphenylindene, and is a contributing factor in causing it to be 3.1 p*K*_a units more acidic than 2,3-diphenylindene.

The 2.4-p*K*_a-unit decrease in acidity for 2-Ph substitution into 1,3-diphenylindene points to appreciable steric inhibition of resonance in the anion, which completely overshadows the (acid strengthening) inductive effect of the 2-Ph substituent. A similar, but much smaller, acid-weakening effect is observed for 2-phenyl substitution into 3-phenylindene (Figure 1) and for phenyl substitution into benzyl phenyl ketone.¹

Experimental Section

Indene (Chemical Intermediates) was vacuum distilled twice through a vacuum-jacketed Vigreux column [bp 97–98 °C (48 mm) [lit.²⁵ bp 182.2–182.4 °C (761 mm)]] and then further purified by preparative GLC on a 7/8 in. × 12 ft column packed with 10% Carbowax 20-M on acid-washed Chromasorb W at 130 °C. After Kugelrohr distillation [bp 50 °C (0.2 mm)] the purity as determined by GLC was >99.9%.

1,3-Diphenylindene was prepared from 3,3-diphenylpropionic acid by a minor modification of the procedure of Streitwieser.¹⁰ Cyclization of the acid by treatment with 10 times its weight of polyphosphoric acid for 4 h at steam-bath temperatures with occasional stirring, aqueous workup, and Kugelrohr distillation of the resulting crude brown solid gave 3-phenyl-1-indanone. This was subsequently treated with phenyllithium in anhydrous Et₂O, and the crude 1,3-diphenyl-1-indanol was dehydrated by two treatments of the neat oil with excess anhydrous MgSO₄ at 110–130 °C (for 1.5 and 1 h, respectively). Aqueous workup and ether extraction was followed by brine wash, drying (MgSO₄), and

concentration in vacuo of the combined ether extracts to give an orange paste. Recrystallization from acetic acid followed by preparative thick-layer chromatography on silica gave 1,3-diphenylindene: mp 64–67 °C (lit.¹⁰ mp 69–70 °C); greater than 99.5% pure by GLC; TLC on silica showed only one spot; NMR (CDCl₃) δ 4.6 (1 H, d, Ph-CH), 6.5 (1 H, d, vinylic H), 7.0–7.7 (14 H, br m, aromatic hydrogens).

2-Phenylindene was prepared by the method of Braun and Manz.²⁶ Crude 2-phenylindan-2-ol prepared from 2-indanone and excess phenylmagnesium bromide in dry THF was refluxed for 3 h in 50 mL of 20% aqueous sulfuric acid, cooled, poured into 50 mL of cool water, and extracted with ether. The combined ether extracts were washed with H₂O, saturated NaHCO₃, and brine, dried (MgSO₄), and concentrated in vacuo to give reddish crystals. Repeated recrystallization from acetone gave white flakes, mp 167.5–168 °C (lit.²⁷ mp 167.5 °C). TLC on silica gave only one spot. The NMR agreed with that previously reported.²⁷

3-Phenylindene. Crude 1-phenylindan-1-ol (prepared from 1-indanone and excess phenyllithium in dry Et₂O) was treated with excess anhydrous MgSO₄ at 110–120 °C (bath temperature) for 1.5 h. Aqueous workup and ether extraction were followed by concentration in vacuo to give 3-phenylindene as a crude brown oil. Short-path distillation [bp 100–108 °C (0.2 mm) [lit.¹⁸ bp 158 °C (7 mm)]] gave a slightly yellow oil only ~95% pure by GLC analysis. Column chromatography was carried out on silica gel with hexane as eluent. Kugelrohr distillation of the combined purified product caused decomposition. Repetition of the chromatography gave the light-sensitive product >99% pure by GLC: NMR (CDCl₃) δ 3.4 (2 H, d, CH₂-CH), 6.45 (1 H, t, CH₂-CH), 7.0–7.6 (9 H, m, aromatic hydrogens).

2,3-Diphenylindene. 2,3-Diphenylindene (Aldrich) was refluxed in 50 mL of ethylene glycol with a large excess of 85% aqueous hydrazine hydrate (periodically replenished) for 24 h, allowed to cool, and extracted with a large volume of hexane. The combined hexane extracts were washed with water and brine, dried (MgSO₄), and concentrated in vacuo to give reddish crystals. Two recrystallizations from methanol gave pink crystals (mp 107–109 °C) which gave only one spot on TLC upon silica. Two more recrystallizations from hexane with Darco treatment gave yellow crystals: mp 107.5–108.5 (lit.²⁴ mp 108 °C); NMR (CDCl₃) δ 3.8 (2 H, s, CH₂), 7.1–7.4 (14 H, m, aromatic hydrogens).

1,2,3-Triphenylindene (Alfred Bader Chemicals) was repeatedly recrystallized from acetone to give pale yellow crystals: mp 131.0–131.5 °C (lit.²⁸ mp 135 °C); TLC on silica gave only one spot; NMR (CDCl₃) δ 5.0 (1 H, s, Ph-CH), 7.0–7.5 (19 H, m, aromatic hydrogens).

Acknowledgment. We are grateful to the National Science Foundation for support of this research.

Registry No. Indene, 95-13-6; 2-phenylindene, 4505-48-0; 3-phenylindene, 1961-97-3; 2,3-diphenylindene, 5324-00-5; 1,3-diphenylindene, 4467-88-3; 1,2,3-triphenylindene, 38274-35-0; 3,3-diphenylpropionic acid, 606-83-7; 3-phenyl-1-indanone, 16618-72-7; 1,3-diphenyl-1-indanol, 73940-73-5; 1-phenylindan-1-ol, 36374-47-7.

(26) V. Braun, J.; Manz, G. *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 1059–1065.

(27) Galton, S. A.; Kalafer, M.; Beringer, F. M. *J. Org. Chem.* **1970**, *35*, 1–6.

(28) Schlenk, W.; Bergmann, E. *Justus Liebigs Ann. Chem.* **1928**, *463*, 1–322.

(24) Shiner, R.; Knox, W. R. *J. Org. Chem.* **1951**, *16*, 1064–1068.

(25) Spilker, A.; Dombrowsky, A. *Chem. Ber.* **1909**, *42*, 572–573.