

Carbon Acids. 12. Acidifying Effects of Phenyl Substituents

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Results of the replacement of one or two hydrogen atoms in CH₃EWG carbon acids (EWG = CH₃SO, CN, PhSO₂, CH₃CO, F₃CSO₂, and the like) by phenyl on equilibrium acidities in Me₂SO are reported. The progressive decrease in phenyl acidifying effects with a progressive increase in acidity of the CH₃EWG parent acids is interpreted as a resonance saturation effect. The acidifying effects of phenyl on PhCH₂EWG, 9,10-dihydroanthracene, and xanthene are found to be severely attenuated by steric inhibition of resonance. Similar effects were observed on substitution of a second Ph group into PhCH₂EWG to give Ph₂CHEWG. The ratios of resonance to polar contributions to the acidifying effect of Ph were estimated by (a) removing the resonance contribution through steric inhibition of resonance and (b) by using the Me₃N⁺ group as a model for polar effects. The first method indicated a ratio of 4:1, the second a ratio of 4.6:1 to 6.6:1 depending on the nature of EWG. The resonance to polar ratio for phenyl was found to be larger than that for PhCO (or CH₃CO), which, in turn, is much larger than that for NO₂, CN, or PhSO₂.

α -Phenyl substitution has been shown to increase the equilibrium acidities of a variety of parent carbon acids in a number of different solvent systems. Some of these data are summarized in Table I in terms of ΔpK units (the increase in acidity relative to that of the parent acid). It will be observed that the effects range from a few negative values to positive values as high as 4.4, and that ΔpK values in solvents as different as benzene, cyclohexylamine (CHA), dimethyl sulfoxide (Me₂SO), and Me₂SO-H₂O sometimes agree surprisingly well. We have pointed out previously that agreement of this kind between acidities in solvents of low dielectric constant (C₆H₆, CHA, etc.) and high dielectric constant (Me₂SO, Me₂SO-H₂O, etc.) occurs only, however, when the compounds and the reference indicators have similar structures.²

There is also an abundance of kinetic evidence to show that α -phenyl substitution increases the acidity of a hydrogen atom attached to carbon. Estimates of equilibrium acidities have often been made on the basis of such data. For example, from relative rates of lithium or cesium cyclohexylamide catalyzed tritium exchange rates in CHA, the relative "pK" of toluene in CHA has been placed at 41, and that of methane at a value higher by 5-8 pK units.^{3,4}

Using equilibrium and kinetic acidity data of this type as a basis, molecular orbital calculations point to a pK for methane from 3 to 10 units higher than that of toluene.^{5,6} Results of extrapolations from equilibrium acidities in Me₂SO show, however, that the difference in pK between toluene and methane is much greater than indicated by these estimates. (In Me₂SO toluene has a pK of ca. 44 and methane has a minimum pK of ca. 60.)⁷

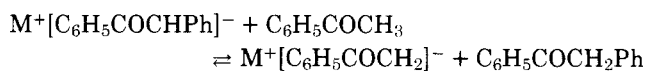
The data in the present paper demonstrate that, in the absence of steric effects, α -phenyl substitution increases the acidity of parent acids to a much greater extent than suggested by the earlier data (Table I). The increases observed vary from 4.4 to 10.6 pK units, depending on the pK of the parent acid (Table II).

Results and Discussion

Comparison with Data in Other Solvents. Table II presents the pK's of a number of parent acids and their α -phenyl derivatives measured in Me₂SO by the method described previously.² Table II also shows the increase in acidity (change to lower pK values) caused by α -phenyl substitution, relative to a hydrogen atom in methane carbon acids (ΔpK_H) and relative to a methyl group in ethane carbon acids (ΔpK_{Me}). Comparison of the ΔpK 's in Table II with those in Table I shows that the α -phenyl effects are generally much

larger for the parent acids that we have examined in Me₂SO than for those reported in other solvent systems. In fact, the *smallest* ΔpK recorded in Table II for an unhindered system (4.4) is as large as any previously recorded in solution, and the largest ΔpK recorded in Table II (10.6) is 6.2 pK units larger than any previously observed. In many instances the smaller effects recorded in Table I are caused by steric inhibition of resonance in the carbanion, which prevent the phenyl group from exerting its maximum effect. Such steric effects are minimized for substitution of phenyl for a hydrogen atom in methane carbon acids, CH₃EWG, or for a methyl group in ethane carbon acids, MeCH₂EWG. For three carbon acids of this type for which comparable data are available (acetophenone, fluorene, and nitromethane) the effects in Me₂SO of substituting phenyl for hydrogen are somewhat larger than in other solvents.

For acetophenone α -Ph substitution increases the acidity in Me₂SO by 7.2 pK units (Table II) as compared to only 3.2 pK units in diglyme (Table I). Evidently in diglyme the ion pair (or ion aggregate), M⁺[C₆H₅COCH₂]⁻, is stabilized relative to the ion pair (or ion aggregate), M⁺[C₆H₅COCHPh]⁻, causing the equilibrium



to shift to the right so as to partially compensate for the delocalizing ability of the phenyl group.²

For fluorene the phenyl effect is only ca. 0.6 pK units greater in Me₂SO than in benzene or CHA. This good agreement is apparently a consequence of the similarity of the stabilities of the two hydrocarbon ion pairs, M⁺[In]⁻ and M⁺[In']⁻, that are being balanced against one another in benzene or CHA.² (In⁻ and In'⁻ are highly delocalized indicator anions.)

For nitromethane the phenyl effect in Me₂SO is 1.6 units greater than that in water. This is not due to differences in stability of salt aggregates since ion association effects are absent in these solvents of high dielectric constant.² The larger ΔpK in Me₂SO in this instance can probably be attributed mainly to a relatively higher negative charge density on carbon in the nitronate ion, PhCH=NO₂⁻, in Me₂SO than in water caused by the weak H-bond donor properties of Me₂SO. It is also possible that Me₂SO may be better than water at stabilizing the negative charge delocalized to the phenyl group in the nitronate ion.⁸

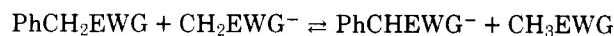
Comparison of Phenyl Effects in the Gas Phase and in Solution. The effect of phenyl substitution on the acidity of

Table I. Effect of α -Phenyl Substitution on Equilibrium Acidities of Carbon Acids

Parent acid ^a	ΔpK^b			
	C ₆ H ₆ ^c	CHA ^d	Me ₂ SO-HOH	Me ₂ SO ^e
Nitromethane			3.6 ^f	
7 <i>H</i> -Dibenzo[<i>c,g</i>]fluorene			1.2 ^g	
13 <i>H</i> -Dibenzo[<i>a,i</i>]fluorene			0.5 ^g	
Fluorene	4.3	4.4	3.8 ^h	4.4
Acetophenone	3.2 ⁱ			
Phenylacetophenone	-0.2 ⁱ			
Xanthene	0.3		3.2 ^h	
9,9-Dimethyl-9,10-dihydroanthracene		1.8		
5 <i>H</i> -Dibenzo[<i>a,d</i>]cycloheptadiene		-0.4		
Diphenylmethane	2.8	2.0	1.7 ^h	2.0

^a The acidities decrease as one proceeds down the table. ^b The (statistically corrected) increase in acidity caused by α -phenyl substitution. ^c W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936). ^d A. Streitwieser, Jr., J. R. Murdoch, G. Häfelfinger, and C. J. Chang, *ibid.*, **95**, 4248 (1973). ^e Data of E. C. Steiner and C. D. Ritchie given in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 4, Table 4-2. ^f In water; from data compiled by A. T. Nielsen, "The Chemistry of Nitro and Nitroso Groups", H. Feuer, Ed., Wiley-Interscience, New York, N.Y., 1969, Chapter 7, Table 5. ^g H. Fischer and D. Rewicki, *Prog. Org. Chem.*, **7**, 116 (1968). ^h K. Bowden and A. F. Cockerill, *J. Chem. Soc. B*, 173 (1970). ⁱ In diglyme: H. D. Zook, W. L. Kelly, and I. Y. Posey, *J. Org. Chem.*, **33**, 3477 (1968).

methane carbon acids can be discussed in terms of the equilibrium

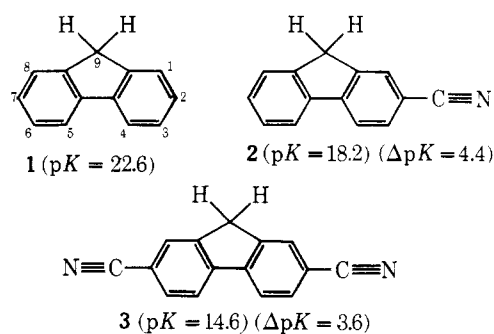


Although the relative stabilities of the undissociated acids, PhCH₂EWG and CH₃EWG, will surely be of importance, it seems likely that the position of equilibrium will be determined primarily by the relative stabilities of the anions, CH₂EWG⁻ and PhCHEWG⁻. The anions are stabilized by a combination of resonance and polar effects. Molecular orbital calculations indicate that the benzyl anion has a resonance energy of 0.72 β ,⁹ which is equivalent to a minimum resonance energy of 13 kcal/mol. Gas-phase acidity data indicate that substitution of a phenyl group into methane may increase the stability of the anion by as much as 33 kcal/mol.¹⁰ Phenyl effects on the gas-phase acidities of the methane carbon acids, acetone and acetonitrile, are much smaller, however, being comparable in magnitude to those shown in Table II. In fact, in view of the linear relationship with near unit slope between acidities in the gas phase and in Me₂SO for two series of compounds, (a) CH₃CN, PhCH₂CN, CNCH₂CN, and (b) CH₃COCH₃, CH₃COPh, PhCH₂COCH₃, PhCOCH₂COCH₃, CH₃COCH₂COCH₃,¹¹ it would appear that the size of the phenyl effects for the methane carbon acids, CH₃EWG, may approach those observed in the gas phase.

Effects of Methyl Substitution. Comparison of the pK 's of the parent methane carbon acids, HCH₂EWG, and ethane carbon acids, MeCH₂EWG, in Table II shows that substitution of a methyl group for a hydrogen atom causes a small increase in acidity for CH₃NO₂ and CH₃COPh (0.7 and 0.5 pK units, respectively), a small decrease in acidity for CH₃COCH₃ (0.3 pK unit), and a sizable decrease in acidity for the sulfone carbon acids, CH₃SO₂Ph, and CH₃SO₂CF₃ (1.7 and 1.4 pK units). The acidity of CH₃CH₂CN is too high to permit accurate measurement by our method, but it is definitely a weaker acid than CH₃CN. Judging from the fact that substitution of

a methyl group for an α -hydrogen atom in PhCH₂CN or H₂C(CN)₂ causes a decrease in acidity of slightly over 1 pK unit in each instance, a pK of 32.5 seems reasonable for MeCH₂CN.¹² (A detailed discussion of these methyl effects will be given in a later paper.)

Saturation of the Phenyl Effect. The carbon acids in Table II are arranged in order of increasing acidity, the strongest acid, nitromethane, being 18.2 pK units stronger than the weakest acid, dimethyl sulfoxide.² The most striking feature of Table II is the progressive decrease in the size of the acid-strengthening effect of the phenyl group (ΔpK_H or ΔpK_{Me}) as we proceed down the series from the weakest parent acid to the strongest CH₃EWG or MeCH₂EWG parent acid. In a previous paper in this series we showed that a strong electron-withdrawing group (EWG) such as CN caused a large (4.4 unit) increase when substituted for a hydrogen atom in the 2 position of the fluorene nucleus (1), but that when a



second CN group was substituted into an equivalent position in the other benzene ring, the 7 position, the acidifying effect was smaller (3.6 pK units).¹³ It was suggested that the first cyano group decreases the charge density at the acidic site in the anion by charge delocalization, and that the stabilizing effect of substituting a second cyano group is less than that of the first because of this delocalizing effect. This was termed a *resonance saturation effect*. For our present purpose we can define a resonance saturation effect as the extent to which depletion of the negative charge at a given site in a carbanion by resonance causes an attenuation in the stabilizing (or destabilizing) effect of a group when substituted into that ion.

We believe that the resonance saturation effect is a general phenomenon in chemistry,¹³ and that this is the primary reason for the decreasing acidifying effect of the phenyl group observed in Table II with increasing parent acid acidity. In other words, the stronger the parent acid, the greater the delocalization of the negative charge in the anion, the smaller the charge density in the anion on the carbon atom to which the phenyl group is attached, and the greater the resonance saturation effect. The operation of the saturation effect is shown graphically in Figure 1, where the pK of the parent methane carbon acids is plotted against ΔpK_H (Table II). [A similar plot is obtained for pK of MeCH₂EWG vs. pK (MeCH₂EWG) - pK (PhCH₂EWG).] Examination of Figure 1 shows that the points for the "planar" EWG's (CN, COCH₃, COPh, and NO₂) and the "tetrahedral" EWG's (SOCH₃, SO₂CH₃, SO₂Ph, and SO₂CF₃) appear to fall on separate lines. The fall-off is much steeper for the "planar" EWG's (ΔpK_H decreases by ca. 5 pK units for a 14 pK increase in acidity for the former vs. ca. 2 pK units for a 17 pK unit increase in acidity for the latter). The fall-off for the "planar" EWG's is also somewhat greater than for substitution of CN into the 2 and 7 positions of fluorene (1-3), where a fall-off of only 0.8 pK unit was observed for an increase in parent acid acidity of 3.6 units (i.e., a fall-off of ca. 3 for a 14 pK unit increase in parent acid acidity). This is understandable since in the fluorene system the resonance saturation effect must operate through a benzene ring whereas in Table II the substituent

Table II. Effect on the Acidities in Me₂SO for Carbon Acids of Replacing a Hydrogen Atom or a Methyl Group by a Phenyl Group

Registry no.	Parent acid	pK ^a	pK- (α -Ph) ^b	ΔpK_H^c	Registry no.	Parent acid ^b	pK	ΔpK_{Me}^f
67-68-5	CH ₃ SOCH ₃	35.1	29.1	6.5				
75-05-8	CH ₃ CN	31.3	21.9	9.6	107-12-0	MeCH ₂ CN ^d	~32.5 ^d	10.6
67-71-0	CH ₃ SO ₂ CH ₃	31.1	25.6	5.8	597-35-3	(MeCH ₂) ₂ SO ₂	~32.8 ^e	7.2
120-12-7	9,10-Dihydroanthracene	30.1	28.8	1.6				
92-83-1	Xanthene	30.0	27.9	2.4				
3112-85-4	CH ₃ SO ₂ Ph	29.0	23.4	5.8	599-70-2	MeCH ₂ SO ₂ Ph	31.0	7.6
67-64-1	CH ₃ COCH ₃	26.5	19.8	7.2	96-22-0	(MeCH ₂) ₂ C=O	27.1	7.3
98-86-2	CH ₃ COPh	24.7	17.7	7.2	93-55-0	MeCH ₂ COPh	24.4016.7	
421-82-9	CH ₃ SO ₂ CF ₃	18.8	14.6	4.4	13003-57-1	MeCH ₂ SO ₂ CF ₃	20.4	5.8
75-52-5	CH ₃ NO ₂	17.2	12.2	5.2	79-24-3	MeCH ₂ NO ₂	16.7	4.5

^a See ref 2. ^b Runs against at least two indicators; standard deviations within runs are generally less than ± 0.05 pK unit. ^c Statistically corrected for the number of acidic protons. ^d Decomposition occurs; pK estimated from the Me effects observed with PhCH₂CN or CH₂(CN)₂ as parent acids. ^e Assuming that the Me effect is the same as observed with CH₃SO₂Ph or CH₃SO₂CF₃ as parent acids. ^f $\Delta pK_{Me} = pK(\text{MeCH}_2\text{EWG}) - pK(\text{PhCH}_2\text{EWG})$.

is being introduced directly at the acidic site.¹⁴ The latter effect is larger, but also more complex. In the fluorene system (1-3) complications arising from solvent effects, steric effects, and polar effects are eliminated by the remote positioning of the substituents,¹³ but in replacing H in CH₃EWG or Me in MeCH₂EWG by Ph all of these factors must be considered.

Replacement of a hydrogen atom in a methane carbon acid, CH₃EWG, by a phenyl group will certainly lead to changes in solvation, particularly in the anion. A methyl group is a much better model in this respect than a hydrogen atom, but is far from ideal. A methyl group is also a better model for phenyl with regard to steric effects. Steric effects between phenyl and EWG are not expected to be large. They should be minimal for anions containing the (linear) cyano group, and will probably be somewhat greater in anions containing the (tetrahedral) sulfone group. The phenyl group must, of course, have its π system parallel to the lobes of the p orbital of the carbanion for maximum overlap. In this respect its steric demands differ from those of methyl, and we can expect some variation in steric effects for the different PhCHEWG⁻ anions. The variations in solvation and steric factors, just discussed, are likely to be small and relatively constant; therefore, they will probably not interfere seriously with the determination of the size of the resonance saturation effect in the PhCH₂EWG series. The major factor affecting the size of the fall-off factor is likely to be the ratio of resonance to polar contributions for each EWG; steric interactions between Ph and EWG in the anion need to be considered as a possible perturbing factor, particularly in the more crowded systems. Since the ratio of resonance to polar contributions will be different for each EWG, we cannot expect the resonance saturation effect to be directly proportional to the parent acid acidity but instead to vary with the change in the ratio of resonance to polar effects.

The rather steep fall-off in the size of the Ph effect from CH₃CN to CH₃COPh (or CH₃COCH₃) to CH₃NO₂ (the "planar" functions) brought out in Figure 1 is believed to be due principally to the increasing degree to which the negative charge in the anion is located on the heteroatom, rather than on carbon. In CH₂=C=N⁻ the negative charge on the nitrogen atom is less than that on the (more electronegative) oxygen atom in CH₂=C(O⁻)Ph, and in CH₂=NO₂⁻ the charge is distributed over two oxygen atoms. The result is a progressive decrease in the charge density on carbon, and a progressively smaller Ph effect. Some steric interactions may be present, but these are believed to be of minor consequence.

The sulfoxide and sulfone functions differ from the "planar" functions in that the carbanion carbon is linked to a large

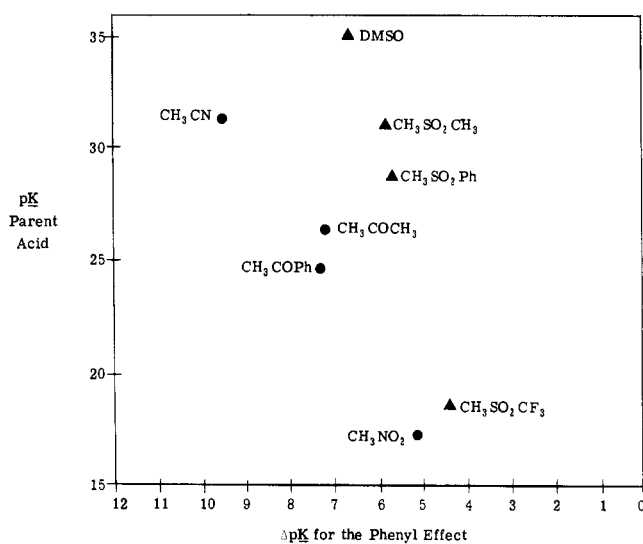


Figure 1. Plot of the acidifying effect of the phenyl group vs. the pK of the parent acid: ●, for "planar" functions; ▲, for "tetrahedral" functions.

second-row element, which is attached to four ligands in a tetrahedral arrangement. Steric effects are obviously important in these systems, but may be relatively constant. This would explain why the points for the "planar" and "tetrahedral" functions fall on different lines. The relatively small fall-off factor for the "tetrahedral" functions, as compared to the "planar" functions (Figure 1) suggests that the ratio of contribution of resonance to polar effects for these functions is relatively small, and that the marked increase in acidity on replacing Ph in SO₂Ph by CF₃ is primarily the result of an increase in the polar factor.

Steric Inhibition of Resonance in Phenyl-Substituted Carbanions. Since the phenyl group has a relatively small polar effect ($\sigma_I = 0.10^{15}$), one would anticipate that the large acidifying effects observed (Table II) must be due primarily to its ability to stabilize the anion by delocalization of charge. This view is supported by the relatively small acidifying effects of phenyl that have been observed in molecules where steric crowding prevents effective overlap between the p orbital of the carbanion and the π system of the phenyl group (Table I). Taking examples of this kind from our work in Me₂SO, we find that 9-phenyl-9,10-dihydroanthracene and 9-phenylxanthene are only 1.6 and 2.4 pK units more acidic, respectively, than their parents, 9,10-dihydroanthracene and xanthene (Table

Table III. Effect of a Second α -Phenyl Group on the Acidities of Carbon Acids in Me₂SO

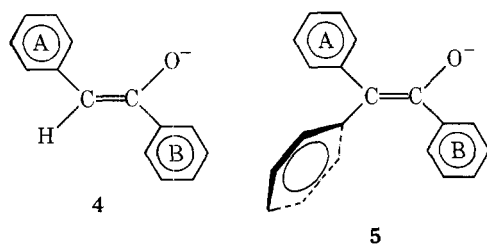
Registry no.	Diphenyl-substituted acid	pK ^a	Δ pK ^b
86-29-3	Diphenylacetonitrile	17.5	4.7
1733-63-7	α,α -Diphenylacetophenone	18.7 ₅	-0.8
102-04-5	α,α -Diphenylacetone	19.4	0.7
7476-11-1	$\alpha,\alpha,\alpha',\alpha'$ -Tetraphenylacetone	17.6 ₅	
5433-76-1	Diphenylmethyl phenyl sulfone	22.3	1.4
19552-15-9	Bis(diphenylmethyl) sulfone	21.9	
5427-04-3	Diphenylmethyl phenyl sulfoxide	24.5	3.0
519-73-3	Triphenylmethane	30.6	2.0

^a Absolute values, not statistically corrected. ^b Relative to the monophenyl carbon acid (Table II); statistically corrected.

II). Examination of scalar molecular models shows that the π systems of the phenyl groups in the anions derived from 9-phenyl-9,10-dihydroanthracene or 9-phenylxanthene are at almost right angles to the p orbital of the carbanion. Delocalization of the charge into the phenyl groups in these anions must be strongly inhibited, and the acidifying effect of the phenyl groups must be largely polar in nature.

The acidifying effect of phenyl groups is also attenuated by steric effects when phenyl is substituted for hydrogen in carbon acids of the type PhCH₂EWG (Table III).

Examination of Table III shows that the phenyl substituent produces its largest acidifying effect (Δ pK = 4.7) when substituted for a hydrogen atom in phenylacetonitrile, i.e., PhCH₂CN \rightarrow Ph₂CHCN. (This is not surprising since the cyano group has the smallest steric demands of any of the common EWG functions.) Nevertheless, this acidifying effect is 4.9 pK units smaller than that produced by replacing a hydrogen atom in CH₃CN by a phenyl substituent (Table II). Most of the smaller effect must be due to a resonance saturation effect since the PhCH₂CN parent acid has a 9.6 pK unit greater acidity than the CH₃CN parent acid. Using Figure 1 as a guide, we find that the 4.7 pK unit acidifying effect is only about 1.5 pK units smaller than expected. Examination of scalar molecular models indicates that the phenyl groups in the Ph₂CHCN⁻ anion need to be twisted only slightly out of the plane of C=C=N⁻ function. On the other hand, twisting of the phenyl groups must be severe in the Ph₃C⁻, Ph₂CSOPh⁻, Ph₂CSO₂Ph⁻, Ph₂CHSO₂CPh₂⁻, Ph₂CHCOCPPh₂⁻, CH₃COCPPh₂⁻, and Ph₂CCOPh⁻ anions.¹⁶ The greatest steric inhibition of resonance is encountered with the ketones. Examination of scalar molecular models shows that the phenyl groups in the enolate ion from acetophenone can achieve the *trans*-stilbene conformation, **4**, with minimal steric interference. Phenyl ring A is close to the enolate oxygen atom, but hindrance can be relieved by bending the bond to the hydrogen atom. Substitution of the hydrogen atom on the C=C bond in **4** by phenyl can be achieved only by bringing



the phenyl group in at right angles to the plane of the enolate ion, as in **5**. Even so, it is necessary to twist ring A. The loss in resonance energy from twisting ring A (or rings A and B) is evidently greater than the polar effect contributed by the third phenyl ring, and Δ pK is negative (Table III). (α,α -Diphe-

nylacetophenone has also been found to be less acidic than α -phenylacetophenone in diglyme.¹⁹) A Δ pK of ca. 5 is predicted for the phenyl effect on α -phenylacetophenone from the correlation of Δ pK with parent acid acidities in Figure 1. A loss in resonance energy corresponding to 5 pK units is 6.8 kcal/mol, which is comparable to the difference in resonance energies between *trans*- and *cis*-stilbenes, as it should be.

Resonance vs. Polar Contributions for the Anion-Stabilizing Effect of Phenyl. In an earlier section we saw that substitution of a phenyl group for a hydrogen atom in the 9 position of 9,10-dihydroanthracene or xanthene caused only a 1.6 and 2.4 pK unit increase in acidity, whereas an increase of 8 or 9 pK units might have been anticipated for such weak parent acids in the absence of steric effects. If we assume that these small acidity increases provide an estimate of the size of the polar effect, it would appear that the ratio of resonance to polar contributions for phenyl is about 4:1.

The ratio of resonance to polar contributions for G in GCH₂EWG systems, where EWG is CN, SO₂Ph, and COPh, can be estimated by using the effect of Me₃N⁺ as a model for the polar effect.²⁰ For the GCH₂SO₂Ph system the resonance to polar ratios determined in this way for G are PhCO (3.7) > NO₂ (1.5), CN (1.4), PhSO₂ (1.3). For the GCH₂CN system the ratios are 4.2 for PhCO, 1.6 for CN, and 1.5 for PhSO₂. The agreement for the two systems is reasonably good, suggesting that steric inhibition of resonance is not a serious problem. With G = Ph the resonance to polar ratio is 6.6 when EWG is PhSO₂, 6.1 when EWG is CN, and 4.6 when EWG is PhCO.²¹ The latter value is near the ratio of 4:1 estimated for Ph from the data for the 9,10-dihydroanthracene and xanthene systems where the resonance effect was damped out by steric effects thus allowing an estimate of the polar effect to be made (see above). The results indicate that the resonance to polar ratio for phenyl is much larger than for any of the strong electron-withdrawing groups, only the PhCO group approaching it in this respect. This was not anticipated from other estimates of the relative size of resonance and polar effects for Ph. For example, the $\sigma_{R(A^-)}$ value for Ph, which is a measure of the resonance effect of a *p*-Ph on the acidity in the ArNH₃⁺ (or ArOH) system, is only 0.04, whereas σ_1 for Ph, which measures the polar contribution, is 0.10.²² [Similarly, Swain and Lupton in their analysis assign a larger polar constant to phenyl ($\mathcal{F} = 0.139$) than a resonance constant ($\mathcal{R} = -0.088$).²³] Part of the difference can be ascribed to the fact that the $\sigma_{R(A^-)}$ value is derived from data for a nitrogen or oxygen acid, rather than a carbon acid. Thus the σ_p^- for Ph derived for the ArCH₂CN system is 0.17,²⁴ as compared to σ_p^- for Ph of 0.11 derived from phenols.²⁵ Nevertheless, it would appear that the resonance effect of Ph is severely damped by transmission across a benzene ring, and that the magnitude of its resonance stabilizing effect on carbanions has not been fully appreciated hitherto.

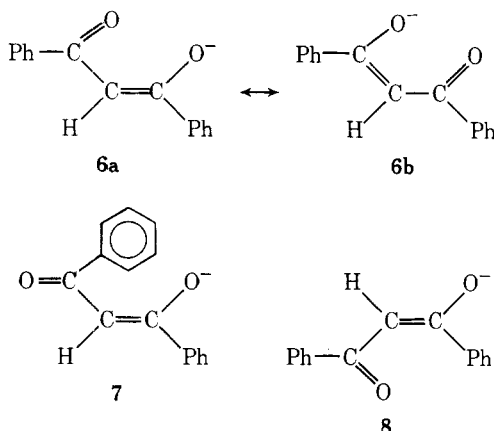
Judging from the GCH₂CN system (see Table II and ref 20) the resonance stabilizing effect of Ph (relative to Me) is 9.1 pK units (12.5 kcal/mol) as compared to 12.2, 13.3, and 18.0 pK units for the PhSO₂, CN, and PhCO groups, respectively. In the GCH₂COPh system the acidifying resonance effects of PhSO₂, CN, and PhCO have decreased to 6.2, 7.5, and 7.7 pK units, respectively, whereas that of Ph has decreased to only 5.5 pK units. In this system the resonance acidifying effect of Ph is of a magnitude comparable to that of a strong electron-withdrawing group. The diminution of effects in the GCH₂COPh system is in part due to a resonance saturation effect,¹³ but this should affect Ph to at least as great a degree as for other substituents. It seems most likely that the unusually severe steric requirements of the GCH₂COPh system (see above) are mainly responsible for the diminution of the effects of PhSO₂, CN, and PhCO. For these dipolar substituents there are no doubt substantial repulsive interactions

Table IV

Compd	Mp or bp, °C	Lit. value, °C	Ref
9-Phenyl-9,10-dihydroanthracene	mp 88–89 ^a	89	27
9-Phenylxanthene	mp 145 ^a	145	2
Phenylnitromethane	bp 99–102 (5 mm)	93–97 (3 mm)	28
α,α -Diphenylacetophenone	mp 136.5–137.5 ^a	135–137	29
$\alpha,\alpha,\alpha',\alpha'$ -Tetraphenylacetone	mp 134–134.5 ^a	133–134	30
Diphenylmethyl phenyl sulfone	mp 187–188 ^a	187–188	31
Bis(diphenylmethyl) sulfone	mp 192–193 ^{a,c}	185–186	32
Diphenylmethyl phenyl sulfoxide	mp 138–139 ^b	137–138	33

^a Recrystallized from 95% EtOH. ^b Recrystallized from CH₃OH/H₂O. ^c Decomposes on melting.

between the negative charge on the enolate oxygen atom and that on the oxygen atom of the carbonyl group, e.g., as in **6**. (Steric hindrance is severe in conformation **7** and in the *Z* isomer, **8**.) On the other hand, when G = Ph the steric interactions are less severe (see **4**).



Steric inhibition of resonance in the GCH₂COPh systems causes the resonance to polar ratios, as determined by the use of Me₃N⁺ as a model for the polar effect,²⁰ to drop to 2.1 for PhCO, 2.5 for CH₃CO, 1.1 for CN, 0.91 for PhSO₂, and 1.1 for NO₂. The resonance to polar ratio for Ph drops to 4.6, but this is believed to be due primarily to a resonance saturation effect, rather than to steric inhibition of resonance. This view is supported by the parallel effects in GCH₂EWG systems reported in this series for Ph and PhS;⁷ steric effects for PhS groups are shown in this paper to be minimal.

Experimental Section

The equilibrium acidity measurements were carried out as previously described.^{2,13} With the exception of the trifluoromethyl sulfones and the compounds listed in Table IV, all compounds in Tables II and III are commercially available from the Aldrich or Parish Chemical Co. Samples of methyl, ethyl, and benzyl trifluoromethyl sulfone were kindly provided by J. B. Hendrickson and P. L. Skipper of Brandeis University. The remaining compounds are listed in Table

IV along with a reference to their method of preparation. All samples were 99+% pure as judged by TLC or GLC analyses.

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