

# Steric, Conformational, and Electronic Effects as Revealed by Acidities of Substituted Xanthenes and Reactions of Substituted Xanthenyl and Related Carbanions with Benzyl Chloride

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Received October 20, 1982

Equilibrium acidities in Me<sub>2</sub>SO solution for 9-substituted xanthenes (9-G-XnH) with G = H, CN, PhS, PhSO<sub>2</sub>, CO<sub>2</sub>Me, and Ar are reported. Comparison of these acidities with those of related compounds, GCH<sub>2</sub>CN, 9-G-FlH (9-substituted fluorenes), and GCHPh<sub>2</sub>, shows that CN and PhS groups have minimal steric demands whereas CO<sub>2</sub>Me, PhSO<sub>2</sub>, and Ar groups have stereoelectronic requirements that cause anion destabilization of 9-G-Fl<sup>-</sup>, 9-G-Xn<sup>-</sup>, and GCHPh<sub>2</sub><sup>-</sup> ions, relative to GCHCN<sup>-</sup> ions. Similar destabilization of ions is evident from lower than expected acidities from a number of other compounds including 1,2,3-triphenylindene, 1,1,3,3-tetraphenylpropene, and 1,1,3,3-tetraphenyl-2-azapropene. Rates for all of these carbanions reacting with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO solution are reported. Reactivity values, *r*, for carbanions, relative to a 9-MeFl<sup>-</sup> ion of equal basicity, were calculated by using equations of the type  $r = \beta(\Delta pK_a) - \log(k_{\text{Fl}}^{\text{Me}}/k_{\text{Xn}}^{\text{G}})$ . These *r* values reveal rate accelerations for 9-CN-Xn<sup>-</sup> and 9-PhS-Xn<sup>-</sup> ions and rate retardations for 9-PhSO<sub>2</sub>-Xn<sup>-</sup> and 9-Ar-Xn<sup>-</sup> ions. An unexpectedly large rate retardation was observed for substitution of a *p*-PhSO<sub>2</sub> or *p*-MeSO<sub>2</sub> group into Ph in the 9-Ph-Xn<sup>-</sup> ion, which is interpreted as indicating a conformational change. The *r* values for 9-G-Xn<sup>-</sup> ions, relative to a 9-MeFl<sup>-</sup> ion of comparable basicity (*r* = 0.0), are CN (1.7) > PhS (0.65) > CO<sub>2</sub>R (-0.12) > SO<sub>2</sub>R (-0.66) > Ar (-0.82), and a similar order with more negative *r* values (larger steric factors) was observed for Ph<sub>2</sub>CG<sup>-</sup> ions: CN (-0.19) > CO<sub>2</sub>R > (-1.9) > SO<sub>2</sub>R (-2.6). The most negative *r* value was observed for the Ph<sub>2</sub>C=NCPPh<sub>2</sub><sup>-</sup> ion (-3.0).

In the accompanying paper we have shown that large, flat carbanions such as 9-substituted fluorenyl ions, 9-G-Fl<sup>-</sup> (G = H, Me, CN), the 9-cyano-9,10-dihydrophenanthrenyl ion, and ArC(Me)CN<sup>-</sup> ions exhibit remarkably small steric effects in S<sub>N</sub>2 reactions of PhCH<sub>2</sub>Cl.<sup>1</sup> In S<sub>N</sub>2 reactions with the more hindered electrophiles *i*-BuBr, *i*-PrBr, and *c*-C<sub>6</sub>H<sub>11</sub>Br, 9-MeFl<sup>-</sup> ions actually give smaller rate retardations, relative to *n*-BuBr, than do N<sub>3</sub><sup>-</sup> or I<sup>-</sup> ions.<sup>2</sup> (Estimates made for rates at equal basicities indicate, however, that 9-MeFl<sup>-</sup>, N<sub>3</sub><sup>-</sup>, and I<sup>-</sup> ions all exhibit about equal sensitivities to retarding effects of α- or β-alkyl branching in RBr.<sup>2</sup>) Reactivity values, *r*, calculated from eq 1 by using rate constants for reactions of 9-G-Fl<sup>-</sup> ions

$$r = \beta(\Delta pK_a) - \log(k^{\text{Me}}/k^{\text{G}}) \quad (1)$$

with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO solution, allowed comparisons of the effect of a variety of substituents, G, to be made at the same basicity, relative to the 9-MeFl<sup>-</sup> ion family line in a Brønsted plot.<sup>1</sup>

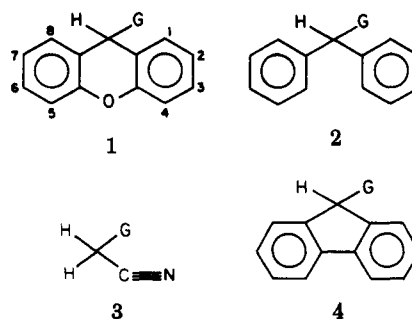
These calculations showed that when the group G protrudes from both sides of the fluorene ring, rate constants calculated at the same basicities were decreased, for steric reasons, moderately for G = Ph (*r* = -0.58) but substantially for G = *o*-tolyl, *t*-Bu, or mesityl (*r* = -2.2, -2.6, and -3.1, respectively). On the other hand, CO<sub>2</sub>Me and CN substituents caused mild accelerating effects (*r* = 0.45) for electronic reasons.

In this paper we extend these studies to a variety of other carbanions, including 9-substituted xanthenyl ions (9-G-Xn<sup>-</sup>), diphenylmethyl ions (Ph<sub>2</sub>CG<sup>-</sup>), and some related di-, tri-, and tetraphenyl systems, examining the effect of PhS, PhSO<sub>2</sub>, CN, CO<sub>2</sub>Me, and Ar substitution on carbon acid equilibrium acidities and on carbanion reactivities toward PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO solution.

## Results and Discussion

**Equilibrium Acidities of 9-Substituted Xanthenes, 9-G-XnH.** NMR studies have shown that xanthenes with

hindered 9-aryl substituents and 9-alkyl-9,10-dihydroanthracenes exist in boat conformations.<sup>3,4</sup> From alkylation studies it has been concluded that the anions derived from the latter exist in a flattened boat conformation with the 9-alkyl group in a pseudoaxial position.<sup>4</sup> By analogy, one might expect xanthenyl carbanions bearing hindered 9-substituents to exist in boat conformations for steric reasons. On the other hand, if the substituent, G, conjugates with the carbanion, one would expect the entire xanthenyl moiety to be as planar as possible in order to maximize overlap between the π orbitals of the benzene rings and the anion p orbital. Some insight into the magnitude of steric and conformational effects in 9-G-Xn<sup>-</sup> ions and Ph<sub>2</sub>CG<sup>-</sup> ions (the latter are expected to be propeller shaped) can be gained by comparing substituent effects on the acidities of substituted xanthenes (1) and diphenylmethanes (2) with those of similarly substituted acetonitriles (3) and fluorenes (4) both of which form flat carbanions.



Substrates 1-3 with G = H all have acidities in the 30-32 pK<sub>a</sub> unit range, whereas that for 4 is much lower (22.6). The higher acidity of 4 is due to unusual stabilization in the anion caused partly because the two benzene rings are constrained to be coplanar and orthogonal to the carbanion p orbital and partly because of the aromaticity of the

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Table I. Equilibrium Acidities of Acetonitriles (GCH<sub>2</sub>CN), Xanthenes (9-G-XnH), Fluorenes (9-G-FIH), and Diphenylmethanes (GCHPh<sub>2</sub>) in Dimethyl Sulfoxide Solution at 25 °C

G	$\Delta pK_a^a$			
	GCH <sub>2</sub> CN (3) <sup>b</sup>	9-G-XnH (1) <sup>h</sup>	9-G-FIH (4) <sup>k</sup>	GCHPh <sub>2</sub> (2) <sup>m</sup>
H	(0.0)	(0.0)	(0.0)	(0.0)
CN	20.4 <sup>c</sup>	16.7	14.6	14.7 <sup>f</sup>
PhS	10.7 <sup>d</sup>	7.5	6.9	5.9 <sup>d</sup>
PhSO <sub>2</sub>	19.5 <sup>c</sup>	9.0 <sup>i</sup>	11.3	9.9 <sup>f</sup>
CO <sub>2</sub> Me	18.7 <sup>e</sup>	11.9	12.5	10.3 <sup>n</sup>
C <sub>6</sub> H <sub>5</sub>	9.6 <sup>f</sup>	2.4 <sup>f</sup>	5.0	1.8 <sup>f</sup>
<i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	2.4 <sup>g</sup>	1.3 <sup>j</sup>	1.1 <sup>l</sup>	2.0 <sup>o</sup>
<i>p</i> -PhSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	6.1 <sup>g</sup>	4.8 <sup>j</sup>		7.0 <sup>o</sup>
<i>p</i> -MeSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>		3.75 <sup>j</sup>	2.7 <sup>l</sup>	

<sup>a</sup>  $\Delta pK_a$  values are statistically corrected. <sup>b</sup>  $\Delta pK_a = 31.3 - pK_a$  (GCH<sub>2</sub>CN). <sup>c</sup> Reference 7. <sup>d</sup> Reference 8. <sup>e</sup> Reference 9. <sup>f</sup> Reference 6. <sup>g</sup>  $\Delta pK_a$  relative to C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CN.<sup>10</sup> <sup>h</sup>  $\Delta pK_a = 30 - pK_a$  (9-G-XnH).<sup>11</sup> <sup>i</sup>  $\Delta pK_a = 22.6 - pK_a$  (9-G-FIH).<sup>12</sup> <sup>j</sup>  $\Delta pK_a$  relative to 9-C<sub>6</sub>H<sub>4</sub>XnH. <sup>k</sup>  $\Delta pK_a = 22.6 - pK_a$  (9-G-FIH).<sup>12</sup> <sup>l</sup> Relative to 9-C<sub>6</sub>H<sub>4</sub>FIH.<sup>12</sup> <sup>m</sup>  $\Delta pK_a = 32.2 - pK_a$  (GCHPh<sub>2</sub>). <sup>n</sup> Reference 14. <sup>o</sup> Relative to C<sub>6</sub>H<sub>5</sub>CHPh<sub>2</sub>.<sup>15</sup>

fluorenyl anion, which has been estimated to be about 14.5 kcal/mol.<sup>5</sup> The presence of the oxygen atom in xanthene could conceivably cause destabilization of the anion by an antiaromaticity effect. This does not occur, however, since xanthene is actually 0.4 pK<sub>a</sub> unit *more* acidic than its carbon analogue, 9,10-dihydroanthracene.<sup>6</sup> Evidently the HXn<sup>-</sup> ion can adopt a puckered conformation where overlap including 16  $\pi$  electrons is avoided and the effect of the C–O dipole can exert a stabilizing influence. The acidities of the GCH<sub>2</sub>CN, 9-G-XnH, 9-G-FIH, and GCHPh<sub>2</sub> carbon acids are compared in Table I with those of the parent acids [G = H;  $\Delta pK_a = pK_a$  (parent) –  $pK_a$  (substituted acid)] statistically corrected for the number of acidic hydrogen atoms.

We assume that the G substituents exert their major influence on acidity through their ability to stabilize or destabilize the carbanion. The size of  $\Delta pK_a$  is then determined primarily by two factors: (a) the extent to which the charge density at the carbanion site is decreased by charge delocalization (the resonance saturation effect<sup>16</sup>) and (b) steric effects that cause inhibition of resonance in the anion or prevent an optimum alignment of the anion pole with dipoles in the substituents. The extent of delocalization into the benzene rings of the carbanions derived from fluorenes 4 and diphenylmethanes 2 can be judged by the size of the Hammett  $\rho$  for equilibrium

Table II. Acidifying Effects of PhS, CO<sub>2</sub>Me, and PhSO<sub>2</sub> Functions Relative to that of the CN Function in Acetonitrile, Xanthene, Fluorene, and Diphenylmethane Substrates

substrate	$\Delta \Delta pK_a^a$			
	PhS	CO <sub>2</sub> Me	PhSO <sub>2</sub>	Ph
GCH <sub>2</sub> CN (3)	9.7	1.7	0.9	10.8
9-G-XnH (4)	9.2	4.8	7.7	14.3
9-G-FIH (5)	7.7	2.1	3.3	9.6
GCHPh <sub>2</sub> (6)	8.8	4.4	4.8	12.9

<sup>a</sup>  $\Delta \Delta pK_a = \Delta pK_a$  (G = CN) –  $\Delta pK_a$  (G);  $\Delta pK_a$  values are taken from Table I.

acidities in Me<sub>2</sub>SO for 2-substituted fluorenes (~7.5)<sup>16</sup> and for meta- and para-substituted diphenylmethanes (5.7).<sup>17</sup> The limited information available indicates that  $\rho$  values for xanthene and fluorene are probably similar since  $\Delta pK_a$  for 2,7-Br<sub>2</sub>-9-CO<sub>2</sub>MeXnH and  $\Delta pK_a$  for 2,7-Br<sub>2</sub>-9-CO<sub>2</sub>MeFIH vs. the unsubstituted parents are similar (3.7 and 3.85, respectively).

The GCH<sub>2</sub>CN substrate (3) differs from the 9-G-XnH (1), 9-G-FIH (4), and Ph<sub>2</sub>CHG (2) hydrocarbon substrates in that there is essentially no steric effect in the GCHCN<sup>-</sup> ion and because a large part of the stabilizing effect of CN is caused by its sizable dipole, which means that there is a relatively high charge density on the adjacent carbon atom in the parent CH<sub>2</sub>CN<sup>-</sup> ion (G = H). For these reasons substituent effects are maximal for this substrate (note the high  $\Delta pK_a$  values in column 1 of Table I for CN, PhS, PhSO<sub>2</sub>, CO<sub>2</sub>Me, and C<sub>6</sub>H<sub>5</sub> substituents). For G = CN the relative sizes of  $\Delta pK_a$  values in the four substrates are GCH<sub>2</sub>CN (20.4) > 9-G-Xn- (16.7) > Ph<sub>2</sub>CHG (14.6), 9-G-FIH (14.7). Since steric effects are absent or small for G = CN, these  $\Delta pK_a$  values suggest that the relative charge densities in the parent ions are CH<sub>2</sub>CN<sup>-</sup> > HXn<sup>-</sup> > Ph<sub>2</sub>CH<sup>-</sup> or HF<sup>-</sup>. The  $\Delta pK_a$  values for the PhS function, which also has minimal steric demands, show a somewhat similar order. On the other hand, the  $\Delta pK_a$  values for the functions PhSO<sub>2</sub>, CO<sub>2</sub>Me, and Ph, which are subject to steric inhibition of resonance by virtue of their stereoelectronic requirements, all show the order 3 > 4 > 1, 2. Steric restraints on these functions are evidently greatest in the 9-G-Xn<sup>-</sup> and Ph<sub>2</sub>CG<sup>-</sup> anions.

In order to examine further the size of stereoelectronic effects of these functions in destabilizing the anion, it may be helpful to relate their  $\Delta pK_a$  values to those of CN, which will help to factor out the charge density effect. The  $\Delta \Delta pK_a$  values in Table II are meant to serve this purpose.

Since  $\Delta \Delta pK_a$  is defined as the difference between  $\Delta pK_a$  with G = CN and  $\Delta pK_a$  for the function in question, large  $\Delta \Delta pK_a$  values correspond to small stabilizing effects of the function on the anion, relative to the CN function. Even though reference to the CN function allows us to ignore steric effects, CN is not an ideal model since its effect depends on the orientation of its dipole as well as its ability to delocalize the charge. The other functions, PhS, Ph, CO<sub>2</sub>Me, and SO<sub>2</sub>Ph, may differ appreciably from CN in dipole orientations and delocalizing abilities. We will use Taft  $\sigma_1$  values as estimates of polar effects and  $\sigma_p^-$  values obtained from equilibrium acidity data in Me<sub>2</sub>SO<sup>18</sup> as estimates of delocalizing effects. These estimates show that the maximum acidifying effect of CN is due to a

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(18) The  $\sigma_p^-$  values are derived from acidity data for meta- and para-substituted anilines (Algrim, D. J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1983), phenylacetonitriles,<sup>10</sup> and arylidiphenylmethanes.<sup>15</sup>

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combination of a strong dipolar effect ( $\sigma_1 = 0.56$ ) and a strong conjugative effect ( $\sigma_p^- = 0.95$ ).

The PhS function has a much smaller acidifying effect ( $\Delta\Delta pK_a = 9.7$  for  $GCH_2CN$ ) because both its dipolar effect ( $\sigma_1 \approx 0.3$ ) and conjugative effect ( $\sigma_p^- \approx 0.4$ ) are much smaller. The  $\Delta\Delta pK_a$  values for PhS are fairly constant (7.7–9.7 units, Table II), indicating the absence of stereoelectronic effects.

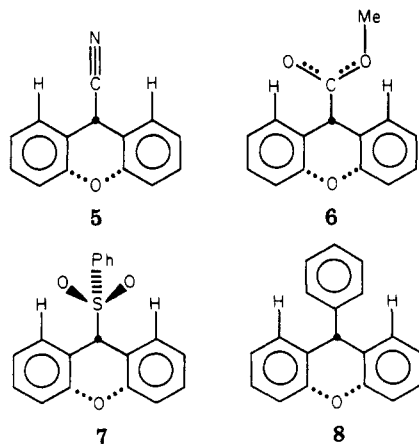
The Ph function also has a much smaller acidifying effect than CN ( $\Delta\Delta pK_a = 10.8$  for  $GCH_2CN$ ) because it too has a much smaller polar effect ( $\sigma_1 \approx 0.2$ ) and conjugative effect ( $\sigma_p^- \approx 0.2$ ). The  $\Delta\Delta pK_a$  values for Ph of 10.8, 14.3, 9.6, and 12.9 for the  $GCH_2CN$ , 9-G-XnH, 9-G-FIH, and  $Ph_2CHG$  substrates, respectively, show, however, that steric inhibition of resonance is large in the 9-Ph-Xn<sup>-</sup> and  $PhCPh_2^-$  ions.

The flat  $CO_2Me$  function has nearly as large an acidifying effect as does the cylindrical CN function in the  $GCH_2CN$  system ( $\Delta\Delta pK_a = 1.7$ ) but depends much more on a conjugative interaction ( $\sigma_p^- = 0.82$  vs.  $\sigma_1 = 0.30$ ). Its effect is not attenuated appreciably in the 9- $CO_2Me$ -FIH ion ( $\Delta\Delta pK_a = 2.1$ ), but attenuation becomes large in 9- $CO_2Me$ -Xn<sup>-</sup> and  $Ph_2CCO_2Me^-$  ions ( $\Delta\Delta pK_a = 4.8$  and 4.4, respectively).

The  $SO_2Ph$  function is similar to the CN function in its conjugative and polar effects ( $\sigma_p^-/\sigma_1 = 1.7$  in both instances), and  $\Delta\Delta pK_a = 0.9$  in the unhindered  $GCH_2CN$  system. The tetrahedral  $SO_2Ph$  function is far more sterically demanding than the flat  $CO_2Me$  function, however. There is evidently severe steric inhibition of resonance in the 9- $PhSO_2$ -Xn<sup>-</sup> and  $Ph_2CSO_2Ph^-$  ions, judging from the  $\Delta\Delta pK_a$  values of 7.7 and 4.8, respectively.

The  $\Delta\Delta pK_a$  values for the  $CO_2Me$  and Ph functions in the 9-G-FIH system are surprisingly close to those in the  $GCH_2CN$  system (2.1 vs. 1.7 and 9.6 vs. 10.8, respectively). This suggests that in the 9- $CO_2Me$ -FIH and 9- $Ph$ -FIH ions the peri hydrogen atoms can bend away to allow effective conjugation of these flat functions. The larger, tetrahedral  $SO_2Ph$  function in the 9- $PhSO_2$ -FIH ion is evidently not so easily accommodated ( $\Delta\Delta pK_a = 3.3$  vs. 0.9).

Idealized geometries, which permit maximum conjugation of the CN,  $CO_2Me$ ,  $SO_2Ph$ , and Ph functions with the carbanion p orbital in a flattened xanthenone ion framework (to allow conjugation also with the benzene rings in the xanthenone), are shown in formulas 5–8.

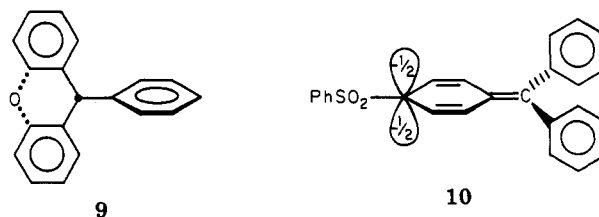


The darkened circle in formulas 5–8 represents the lobes of the carbon p orbital which are orthogonal to the benzene rings. The atoms in the CN,  $CO_2Me$ ,  $SO_2Ph$ , and Ph functions attached to the carbanion center are in the plane of the coplanar benzene rings. The CN function is unhindered, but examination of scalar molecular models shows that the flat  $CO_2Me$  function cannot be sandwiched

in between the peri hydrogen atoms without bending of the C–H bonds. This is true also for the larger  $SO_2Ph$  function. There is evidence that flanking of the carbanion p orbital by the oxygen atoms in the  $SO_2Ph$  function will lead to optimal stabilization.<sup>19</sup> Puckering in the anion will relieve the steric interactions with the peri hydrogens. In the puckered, boat conformation the  $CO_2Me$ ,  $SO_2Ph$ , and Ph functions still exert their full conjugative effect on the carbanion, but the benzene rings in the xanthenone framework do not.

It is not possible for all three functions in  $Ph_2CG^-$  ions to adopt conformations with maximum overlap with the carbanion p orbital when G = Ar,  $CO_2Me$ , or  $SO_2Ph$ . Twisting toward a propeller-type conformation causes steric inhibition of resonance in at least one of the three functions. The result is an appreciable increase in  $\Delta\Delta pK_a$  (12.9, 4.4, and 4.8, respectively).

**Evidence for Conformational Changes in 9-Arylxanthenyl and Aryldiphenylmethyl Ions.** We have seen that the acidifying effect of Ph is smaller in 9-Ph-XnH compared to that in 9-Ph-FIH. Evidently the 9-Ph-Xn<sup>-</sup> carbanion exists primarily in a conformation where the xanthenone framework is flattened and the phenyl ring is in a nearly orthogonal plane (9; the darkened circle represents



the lobes of the carbanion p orbital which project forward and back from the plane of the paper). Substitution of a *m*-Cl group into the phenyl ring of 9-PhXnH causes an increase in acidity of 1.3  $pK_a$  units, which points to a Hammett  $\rho$  for 9-Ar-XnH of about 3.5. A  $\Delta pK_a$  of 2.5 is expected for substitution of *p*- $PhSO_2$  into the Ph ring of 9-PhXnH, assuming a normal  $\sigma(p-PhSO_2)$  of 0.72. The acidifying effect of the *p*- $PhSO_2$  function in 9-(*p*- $PhSO_2C_6H_4$ )XnH is, however, 4.8 units (Table I), corresponding to an apparent  $\sigma^-(p-PhSO_2) = 1.4$ . The acidifying effect of introducing a *p*- $PhSO_2$  group in the phenyl ring of  $PhCH_2CN$  is somewhat larger (6.1 units; Table I), but here,  $\rho_m = 5.7$  and the  $\sigma^-(p-PhSO_2) = 1.0$ . Apparently introduction of a *p*- $PhSO_2$  group into the Ph group of the 9-Ph-Xn<sup>-</sup> ion causes the central ring to pucker in order to allow maximum overlap with the 9-Ph ring so that advantage can be taken of through conjugation involving the *p*- $PhSO_2$  group.<sup>11</sup> A comparable effect is observed for 9-(*p*- $MeSO_2C_6H_4$ )XnH ( $\Delta pK_a = 3.7$ ). A similar conformational change accompanying *p*- $PhSO_2$  substitution has been observed previously for  $Ph_3C^-$ . Here, X-ray data and theory<sup>20</sup> indicate a propeller conformation; substitution of Ph for H in  $Ph_2CH_2$  causes only a 1.8  $pK_a$  unit acidifying effect, indicating minimal conjugative effect, which is consistent with the propeller structure. On the other hand, introduction of *p*- $PhSO_2$  groups into one of the Ph rings of  $Ph_3CH$  increases the acidity of 7 units (Table I), indicating that the conformation has changed from propeller shaped to that shown in 10, where the ring bearing the  $PhSO_2$  substituent is orthogonal to the carbanion p orbital and the other two phenyl rings are twisted.<sup>15</sup> In this in-

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Table III. Rates of Reaction of 9-Substituted Xanthenyl Ions, 9-G-Xn<sup>-</sup>, with Benzyl Chloride at 25 °C<sup>g</sup>

9-G-Xn <sup>-</sup>	pK <sub>a</sub> (9-G-XnH)	k, <sup>a</sup> M <sup>-1</sup> s <sup>-1</sup>	r <sup>e,g</sup>	r <sup>f</sup>
(9-MeFl <sup>-</sup> )	(22.34)	(49.4)	(0.0)	(0.0)
9-CN-Xn <sup>-</sup>	13.59	6.06	1.7	0.45
2,7-Br-9-CO <sub>2</sub> MeXn <sup>-</sup>	14.46	0.175	-0.09	
9-CO <sub>2</sub> MeXn <sup>-</sup>	18.15	2.09	-0.12	0.45
9-(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> )Xn <sup>-</sup>	21.05	4.46	-0.66	-0.25
9-(m-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> S)Xn <sup>-</sup>	22.19	170	0.58	
9-(C <sub>6</sub> H <sub>4</sub> S)Xn <sup>-</sup>	22.8 <sup>b</sup>	365	0.73	-0.15
9-(p-PhSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )Xn <sup>-</sup>	23.1 <sup>c</sup>	0.97	-1.9	
9-(p-MeSO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> )Xn <sup>-</sup>	24.15 <sup>c</sup>	3.47	-2.1	
2-Cl-9-(m-ClC <sub>6</sub> H <sub>4</sub> )Xn <sup>-</sup>	24.8	40.75	-0.82	
9-(m-ClC <sub>6</sub> H <sub>4</sub> )Xn <sup>-</sup>	26.6 <sup>d</sup>	135	-0.84	-0.58

<sup>a</sup> The average of two or more runs with standard deviations of ±5% or less. <sup>b</sup> Reference 8. <sup>c</sup> Reference 11. <sup>d</sup> Reference 12. <sup>e</sup> Calculated from eq 2. It should be noted that the size of these *r* values will change appreciably depending on the value of β that is chosen. They should be looked on as estimates reliable to no more than one significant figure. <sup>f</sup> Values for corresponding 9-G-Fl<sup>-</sup> ions taken from ref 1. <sup>g</sup> The reactivity values (*r*) for 9-G-Xn<sup>-</sup> ions are relative to 9-MeFl<sup>-</sup> ions.

stance ρ<sub>m</sub> = 5.47 and (the apparent) σ<sup>-</sup>(p-PhSO<sub>2</sub>) = 1.26, which is to be compared with a normal σ<sub>p</sub> of 0.72 and a normal σ<sup>-</sup>(p-PhSO<sub>2</sub>) of 1.02.

**Rates of Reactions of 9-Substituted Xanthenyl Carbanions with Benzyl Chloride.** Reactions with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO have been carried out with the conjugate bases of a number of 9-substituted xanthenes, 9-G-XnH, for which equilibrium acidity data are presented in Table I. For the 9-CO<sub>2</sub>Me-Xn<sup>-</sup> and 9-(m-ClC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> ion families a two-point Brønsted β value of 0.29 was obtained. This β value is close enough to the β value of 0.31 for the 9-MeFl<sup>-</sup> ion family to allow us to estimate reactivity values for 9-G-Xn<sup>-</sup> ions by using eq 2, a modified form of eq 1 used for 9-G-Fl<sup>-</sup> ions.

$$r = \beta(\Delta pK_a) - \log(k_{\text{Fl-Me}}/k_{\text{Xn-G}}) \quad (2)$$

Equation 2 gives the reactivity (*r*) in logarithm units for any 9-G-Xn<sup>-</sup> ion, relative to that of a 9-MeFl<sup>-</sup> ion of the same basicity. In eq 2, *k*<sub>Fl-Me</sub> and *k*<sub>Xn-G</sub> are the second-order rate constants for reactions with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO at 25 °C of 9-MeFl<sup>-</sup> and 9-G-Xn<sup>-</sup> ions, respectively. The Brønsted slope, β, is taken as 0.30; ΔpK<sub>a</sub> = pK<sub>a</sub>(9-MeFlH) - pK<sub>a</sub>(9-G-XnH). The value *r* represents the vertical displacement in logarithm units of points for 9-G-Xn<sup>-</sup> ions from the extended 9-MeFl<sup>-</sup> ion family line in Figure 1. Negative *r* values represent retarding effects, and positive *r* values represent accelerating effects. The rate data and *r* values are summarized in Table III.

In calculating the *r* values in Table III (and Table IV) we have made the tacit assumption that the β values for families associated with these ions will be near 0.3. This appears to be a reasonable assumption since it holds true for all the carbanion families examined to date [seven 9-G-Fl<sup>-</sup> ion families,<sup>21</sup> one ArC(R)CN<sup>-</sup> ion family,<sup>22</sup> and three two-point βs in 9-G-Xn<sup>-</sup> ion families (see Figure 1)].

Comparison shows that the *r* values for 9-G-Xn<sup>-</sup> ions in Table III are, for the most part, similar in size to those for 9-G-Fl<sup>-</sup> ions.<sup>1</sup> The *r* value for 9-CN-Xn<sup>-</sup> is, however, not only positive (1.7), indicating a rate acceleration relative to a 9-MeFl<sup>-</sup> ion of comparable basicity, but is more positive than that for 9-CN-Fl<sup>-</sup> by 1.3 log units. This

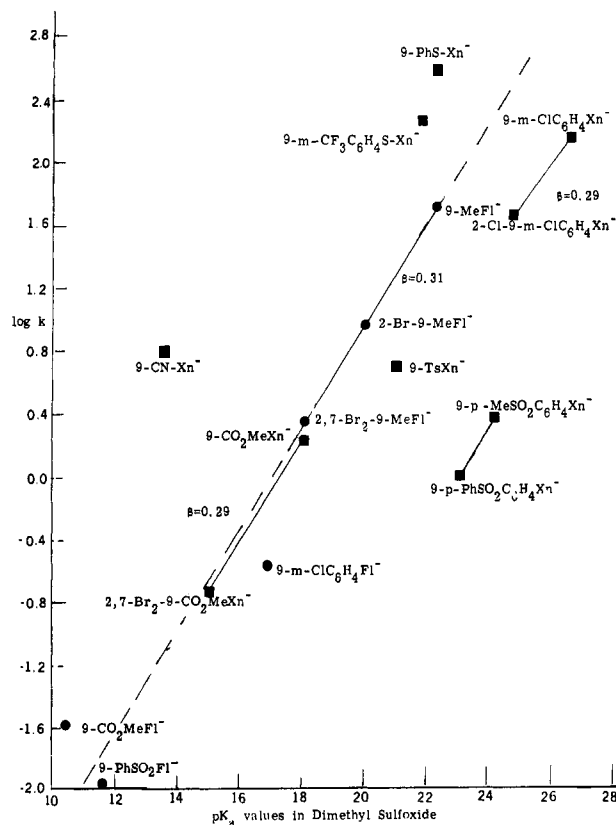
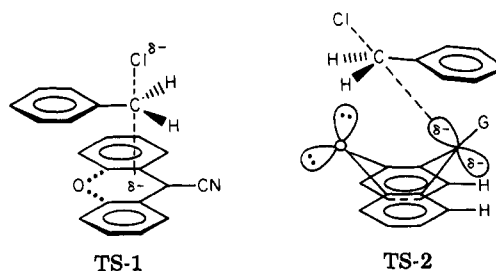


Figure 1. Brønsted plots of log *k* vs. pK<sub>a</sub> for reactions of 9-substituted xanthenes with benzyl chloride in dimethyl sulfoxide solution (data from Table III). The 9-methylfluorenyl ion family line is given as a reference.

suggests that the 9-CN-Xn<sup>-</sup> is reacting in a flattened conformation in the transition state and that the electronic effect of the CN function is being augmented by the effect of the C-O dipole in the xanthenes ring (TS-1 below). The accelerating effect observed for 9-PhS-Xn<sup>-</sup> (2.5-fold relative to the 9-MeFl<sup>-</sup> ion line and 3.6-fold relative to the 9-PhS-Fl<sup>-</sup> ion) is consistent with this interpretation. The CO<sub>2</sub>Me function is not accelerating for xanthenes ions, however, as it is for fluorene ions but instead is mildly retarding (*r* = -0.12). The 9-CO<sub>2</sub>MeXn<sup>-</sup> ion family line nearly coincides with the 9-MeFl<sup>-</sup> ion family line (Figure 1). Evidently a retarding steric effect in the 9-CO<sub>2</sub>MeXn<sup>-</sup> ion is balancing the rate-accelerating electronic effects of CO<sub>2</sub>Me and the C-O dipole. Steric effects in 9-(p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)Xn<sup>-</sup> (9-TsXn<sup>-</sup>) and 9-(m-ClC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> (*r* = -0.66 and -0.84, respectively) are slightly less than for the corresponding fluorenyl ions (Figure 1). These relatively small differences in *r* values for xanthenyl vs. fluorenyl ions indicate that 9-ArS-Xn<sup>-</sup>, 9-CO<sub>2</sub>MeXn<sup>-</sup>, 9-ArSO<sub>2</sub>Xn<sup>-</sup>, and 9-ArXn<sup>-</sup> ions are also flattened in the transition state for S<sub>N</sub>2 reactions with PhCH<sub>2</sub>Cl, as in TS-1.



Introduction of a PhSO<sub>2</sub> or MeSO<sub>2</sub> group into the para position of the Ph group in 9-PhXn<sup>-</sup> causes a sharp decrease in rate (139-fold for 9-(p-PhSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> vs. 9-(m-

(21) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* 1980, 45, 3314-3320.  
(22) Cripe, T. A., unpublished results.

Table IV. Rates of Reaction of Cyano, Ethoxycarbonyl, Phenylsulfonyl, [*p*-(Phenylthio)phenyl]diphenylmethyl, 9-Methyl-10-(ethoxycarbonyl)-9,10-dihydrophenanthryl, 1,2,3-Triphenylindenyl, and Related Acyclic Carbanions with Benzyl Chloride in Dimethyl Sulfoxide Solution at 25 °C

carbon acid	$pK_a$	$k,^a M^{-1} s^{-1}$	$r^g$
(9-MeFlH)	(22.34)	(49.4)	(0.0)
1,2,3-triphenylindene	15.2 <sup>b</sup>	0.014	-1.4
Ph <sub>2</sub> CHCN	17.5 <sup>c</sup>	1.13	-0.19
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> CH(Me)CN	21.7 <sup>d</sup>	124	1.0
Ph <sub>2</sub> CHCO <sub>2</sub> Et	21.88 <sup>e</sup>	0.46	-1.9
9-cyano-9,10-dihydrophenanthrene	21.92 <sup>d</sup>	160	0.6
Ph <sub>2</sub> CHSO <sub>2</sub> Ph	22.3 <sup>c</sup>	0.130	-2.6
9-methyl-10-ethoxycarbonyl-9,10-dihydrophenanthrene	22.65 <sup>c</sup>	29.2	-0.32
Ph <sub>2</sub> CHSO <sub>2</sub> Me	24.05	0.778	-2.3
PhCH(Me)SO <sub>2</sub> Ph	25.7	125	-0.60
Ph <sub>2</sub> C=CHCHPh <sub>2</sub>	25.8	1.66	-2.5
Ph <sub>2</sub> C=NCHPh <sub>2</sub>	26.5	0.854	-3.0
( <i>p</i> -PhSC <sub>6</sub> H <sub>4</sub> )CHPh <sub>2</sub>	28.25 <sup>f</sup>	16.8	-2.2

<sup>a</sup> Average of three runs with standard deviations of  $\pm 5\%$  or less. <sup>b</sup> Measured by G. E. Drucker. <sup>c</sup> Reference 6. <sup>d</sup> Reference 1. <sup>e</sup> Measured by R. D. Press. <sup>f</sup> Reference 15. <sup>g</sup> Calculated by using an equation comparable to eq 2 that relates reactivities in logarithm units relative to those of a 9-MeFl<sup>-</sup> ion of the same basicity.

CiC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup>; Table III). A decrease in rate is expected since the  $pK_a$  has been decreased by 3.5 units, but calculation of  $r$  shows that the rate constant is 1.1 log units smaller than expected relative to the 9-MeFl<sup>-</sup> line. Figure 1 shows this graphically; note that the point for the 9-(*m*-ClC<sub>6</sub>H<sub>4</sub>)Fl<sup>-</sup> ion would fall slightly above an extension of the line drawn between the points for the 9-(*m*-ClC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> and 2-Cl-9-(*m*-ClC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> ions whereas the line drawn between the 9-(*p*-MeSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> and 9-(*p*-PhSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> ion points would be much below this line. The markedly more negative  $r$  values for the 9-(*p*-RSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> ions indicate that the xanthene ring must be puckered rather than flat in the S<sub>N</sub>2 transition state. This is consistent with the conclusion drawn in the preceding section that a puckered conformation is favored by these ions in the initial state. Examination of scalar molecular models shows that approach of the electrophile to the lobes of the *p* orbital of the carbanion in the boat conformation may indeed be hindered. Approach from one side is blocked by the xanthene framework and from the other by the lone pairs of the oxygen atoms (TS-2).

**Reactions of Substituted Diphenylmethyl, 9-Methyl-10-(ethoxycarbonyl)phenanthryl, 1,2,3-Triphenylindenyl, and Related Acyclic Carbanions with Benzyl Chloride.** In this section we examine the rates of reaction with benzyl chloride of substituted diphenylmethyl ions (Ph<sub>2</sub>CG<sup>-</sup>, where G = CN, CO<sub>2</sub>Et, PhSO<sub>2</sub>, and *p*-PhSC<sub>6</sub>H<sub>4</sub>) and some related tri- and tetraphenyl carbanions. The rates of these reactions and the reactivity values,  $r$ , relative to 9-MeFl<sup>-</sup> ions of the same basicity, as calculated from an equation similar to eq 2, are summarized in Table IV and shown graphically in Figure 2.

In calculating these  $r$  values, we have once again assumed that if the basicity of an ion were to be changed over the range where the extrapolations are made by introducing remote substituents, an ion family would be obtained for which the reactivity relative to basicity changes would parallel the 9-MeFl<sup>-</sup> ion family line used as a reference. We know this to be true for one ArC(R)CN<sup>-</sup> family.<sup>22</sup> The family derived by replacing Me in the ArC(Me)CN<sup>-</sup> ion by Ph would presumably give a line very close to that of the 9-MeFl<sup>-</sup> ion family since the Ph<sub>2</sub>CCN<sup>-</sup> ion

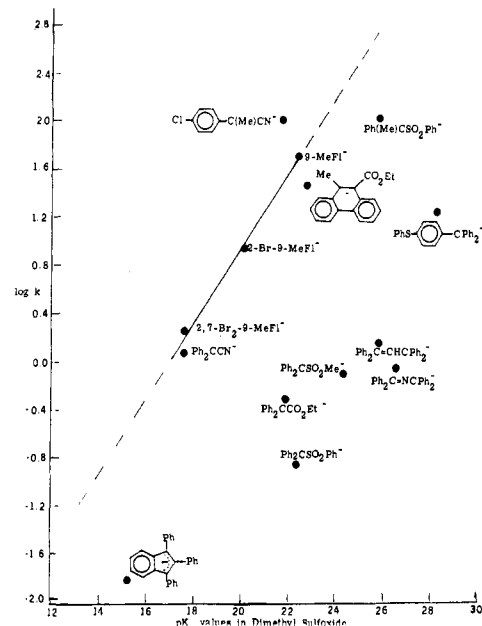
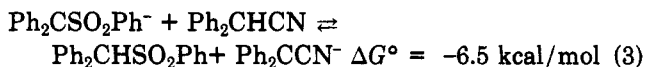


Figure 2. Points for  $\log k$  vs.  $pK_a$  for reactions of substituted diphenylmethyl ions (Ph<sub>2</sub>CG<sup>-</sup>) and related carbanions reacting with benzyl chloride (data from Table IV) placed on a Brønsted plot for the 9-methylfluorenyl ions.

point fits close to this line ( $r = -0.19$ ). The  $r$  values for the Ph<sub>2</sub>CCO<sub>2</sub>Et<sup>-</sup>, Ph<sub>2</sub>CAr<sup>-</sup>, Ph<sub>2</sub>CSO<sub>2</sub>Me<sup>-</sup>, and Ph<sub>2</sub>CSO<sub>2</sub>Ph<sup>-</sup> ions are -1.9, -2.2, 2.3, and -2.6, respectively (Table IV). These values are comparable to that for the 9-*t*-BuFl<sup>-</sup> ion ( $r = -2.6$ ) and that for the 9-(2',4',6'-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)Fl<sup>-</sup> ion (estimated  $r = -3.1$ ) where protrusion of part of the 9-substituent from both sides of the fluorene ring greatly increases the steric effect for approach of the electrophile in the S<sub>N</sub>2 transition state.<sup>1</sup> The propeller-like Ph<sub>2</sub>CCO<sub>2</sub>R<sup>-</sup>, Ph<sub>2</sub>CAr<sup>-</sup>, and Ph<sub>2</sub>CSO<sub>2</sub>R<sup>-</sup> ions present similar difficulties to the approach of the electrophile. Flattening of the anion, as is possible in the Ph<sub>2</sub>CCN<sup>-</sup> ion ( $r = -0.19$ ) or the 9-methyl-10-(ethoxycarbonyl)-9,10-dihydrophenanthryl ion ( $r = -0.32$ ), greatly decreases the steric effect.

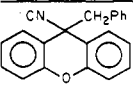
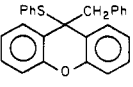
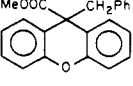
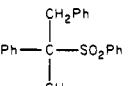
The retarding effects observed for the reactions of these Ph<sub>2</sub>CG<sup>-</sup> ions when G is large are in accord with the destabilizing effects of these groups on the anions revealed by the equilibrium studies described in an earlier section. For example, note that, although the SO<sub>2</sub>Ph group is slightly more acidifying than the CN group, judging from the  $pK_a$  values of 29.0 for CH<sub>3</sub>SO<sub>2</sub>Ph vs. 31.3 for CH<sub>3</sub>CN, Ph<sub>2</sub>CHCN is more acidic than Ph<sub>2</sub>CHSO<sub>2</sub>Ph by 4.8  $pK_a$  units. The greater basicity of the Ph<sub>2</sub>CSO<sub>2</sub>Ph<sup>-</sup> ion than the Ph<sub>2</sub>CCN<sup>-</sup> ion, as defined by eq 3, can be looked on as



the relative degree of destabilization in the two ions caused by steric inhibition of resonance. The less stable, more basic Ph<sub>2</sub>CSO<sub>2</sub>Ph<sup>-</sup> ion might have been expected to react faster with PhCH<sub>2</sub>Cl than does the Ph<sub>2</sub>CCN<sup>-</sup> ion, but the rate is actually 9 times slower (Table VI) because of its greater steric effect.

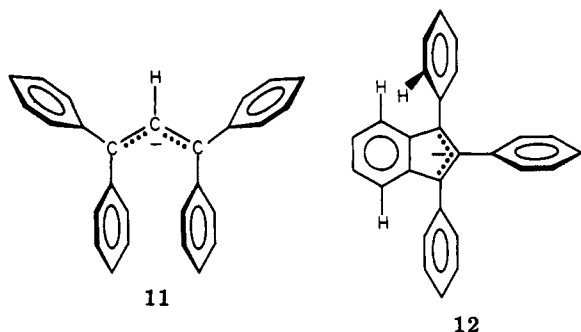
From the results of these investigations of the reactions of carbanions with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO we expect flat carbanions like PhCH=CHCHCN<sup>-</sup> or PhCH=CHCHPh<sup>-</sup> to react with PhCH<sub>2</sub>Cl as fast as or faster than does a 9-MeFl<sup>-</sup> ion of comparable basicity. The presence of the two additional Ph groups in 1,1,3,3-tetraphenylpropene (Ph<sub>2</sub>C=CHCHPh<sub>2</sub>) causes severe twisting in the anion. Now two Ph rings at C-1 and C-3 can become coplanar

Table V. Physical and Spectral Properties of the Products of Carbanions Reacting with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO Solution

product	reaction time, <sup>a</sup> min	yield, %	mp, °C	MS, m/e (relative intensity, assignment)	NMR (CDCl <sub>3</sub> ), δ
	5	98	106.5-107.5	297 (3.7, M <sup>+</sup> ), 206 (100, 9-CN-Xn <sup>-</sup> )	3.15 (2 H, s, CH <sub>2</sub> Ph), 6.2-6.5 (2 H, m, aromatic H), 6.7-7.4 (11 H, m, aromatic H)
	2	93	148-149	380 (8, M <sup>+</sup> ), 379 (18, M <sup>+</sup> - 1), 289 (100, 9-PhS-Xn <sup>-</sup> )	3.65 (2 H, s, CH <sub>2</sub> Ph), 6.3-7.3 (16 H, m, aromatic H), 7.7-8.0 (2 H, m, aromatic H)
	10	93	95-96	330 (1.2, M <sup>+</sup> ), 239 (100, 9-COOMe-Xn <sup>-</sup> )	3.4 (2 H, s, PhCH <sub>2</sub> ), 3.6 (3 H, s, COOCH <sub>3</sub> ), 6.0-6.3 (2 H, m, aromatic H), 6.6-7.3 (11 H, m, aromatic H)
	3	97	136-137	336 (5, M <sup>+</sup> ), 195 (100, PhC(CH <sub>3</sub> )CH <sub>2</sub> Ph)	1.5 (3 H, s, CH <sub>3</sub> ), 3.7 (2 H, AB q, CH <sub>2</sub> ), 6.6-7.6 (15 H, m, aromatic H)

<sup>a</sup> Both reactants approximately 0.1 M.

with the carbon atoms of the allylic ion only if the other two Ph rings come face to face (11). The destabilizing



effect of twisting in the anion is made clear by a comparison of the acidities of Ph<sub>2</sub>C=CHCH<sub>2</sub>Ph vs. Ph<sub>2</sub>C=CHCHPh<sub>2</sub>, which shows that the presence of the fourth Ph provides no additional stabilization for the anion since it causes the acidity to decrease by 0.2 pK<sub>a</sub> unit. The *r* value for reaction of Ph<sub>2</sub>C=CHCPh<sub>2</sub><sup>-</sup> ion with PhCH<sub>2</sub>Cl is -2.5, indicating strong retardation relative to a 9-MeFl<sup>-</sup> ion of equal basicity. Replacement of the =CH moiety at C-2 in Ph<sub>2</sub>C=CHCHPh<sub>2</sub> by =N causes the acidity to decrease by 0.7 pK<sub>a</sub> unit despite the greater electronegativity of sp<sup>2</sup> nitrogen than the sp<sup>2</sup> carbon. The shorter C=N bond should lead to greater crowding of the Ph groups, an interpretation borne out further by the observation of a 1.8 pK<sub>a</sub> unit lower acidity for 1,1,3,3-tetraphenyl-2-azapropene than for 1,1,3,3-tetraphenyl-2-azapropene. Despite its greater basicity the Ph<sub>2</sub>C=NPh<sub>2</sub><sup>-</sup> ion reacts at a rate only about half the rate for the Ph<sub>2</sub>C=CHCPh<sub>2</sub><sup>-</sup> ion (*r* = -3.0 vs. -2.5; Table IV). This result is consistent with the greater twisting of the Ph rings predicted from the acidity data.

The three Ph rings in 1,2,3-triphenylindene are twisted and protrude on both sides of the indenyl framework (12). The steric effect in the reaction of the 1,2,3-triphenylindene ion with PhCH<sub>2</sub>Cl is substantially less than that with the 1,1,3,3-tetraphenylpropenyl ion, however, as shown by the size of the *r* values, -1.4 and -2.5, respectively.

**Summary and Conclusions.** Rate constants for S<sub>N</sub>2 reactions with PhCH<sub>2</sub>Cl of flat, rigid 9-methylfluorenyl ions (9-MeFl<sup>-</sup>) are used as a model for reactions with xanthenyl, diphenylmethyl, 1,1,3,3-tetraphenylpropenyl and like carbanions, which can adopt various conformations. Brønsted correlations allow reactivities (*r* in logarithm units) to be calculated relative to a 9-MeFl<sup>-</sup> ion (*r*

= 0.0) of the same basicity. These *r* values, which depend to some extent on electronic factors but primarily on steric factors, can be related to the conformation of the carbanion in the transition state. The similar sizes of *r* values for xanthenyl ions, 9-G-Xn<sup>-</sup>, where G = CN, CO<sub>2</sub>Me, SO<sub>2</sub>R, and Ph (*r* = 1.7 to -0.84), to those of the corresponding 9-G-Fl<sup>-</sup> ions (*R* = 0.45 to -0.58) indicate that they are nearly flat. However, 9-(*p*-RSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup> ions have large negative *r* values (ca. -2), indicating that they are puckered. The small *r* of -0.19 for Ph<sub>2</sub>CCN<sup>-</sup> indicates that it is nearly flat, while the large negative *r* values for the 1,2,3-triphenylindene, 1,1,3,3-tetraphenylpropenyl, and 1,1,3,3-tetraphenyl-2-azapropenyl ions (-1.4, -2.5, and -3.0, respectively) are consistent with the severe twisting of the phenyl groups expected in these ions.

## Experimental Section

**Acidities** were measured as described in ref 12. Rates were measured as described in ref 21.

**Compounds.** Diphenylacetone, ethyl diphenylacetate, benzhydryl phenyl sulfone, and benzhydryl methyl sulfone were commercially available and recrystallized before use. 9-Methyl-10-(ethoxycarbonyl)-9,10-dihydrophenanthrene was a gift from Professor F. D. Lewis. Preparations of 9-(phenylthio)xanthene and 9-(*m*-chlorophenyl)xanthene have been described previously.<sup>8,12</sup> 9-[*p*-(Phenylsulfonyl)phenyl]xanthene and 9-[*p*-(methylsulfonyl)phenyl]xanthene were prepared by J. C. Branca;<sup>11</sup> 1,1,2,2-tetraphenylpropene was prepared by F. J. Cornforth;<sup>23</sup> 1,2,3-triphenylindene was prepared by G. E. Drucker; [*p*-(phenylthio)phenyl]diphenylmethane was prepared by C. L. Twyman.<sup>15</sup>

**9-Carboxoxanthene.** 9-Carboxamidoxanthene was prepared from the carboxylic acid by conversion to the acid chloride and then reaction with aqueous ammonia as outlined by Durst and Gokel.<sup>24</sup> The amide (3 g) was refluxed 5 h with 30 mL of POCl<sub>3</sub>. The mixture was then poured slowly into 300 mL of cold 5% aqueous NH<sub>3</sub> and stirred. More NH<sub>3</sub> was added to keep the solution alkaline. The resulting solid was recrystallized twice from hexane to give white needles, mp 99-100 °C (lit.<sup>25</sup> mp 99-101 °C).

**2-Chloro-9-(3-chlorophenyl)xanthene.** 2-Chloroxanthone was prepared by heating 4-chlorophenoxide and 2-chlorobenzoic acid together with a catalytic amount of copper, as described by Dhar.<sup>27</sup> Recrystallization from EtOH gave brown needles: mp

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(24) Durst, H. D.; Gokel, G. W. "Experimental Organic Chemistry"; McGraw-Hill: New York, 1980; p 520.

(25) Kasztreiner, E.; Vargha, L. *Acta Chim. Acad. Sci. Hung.* 1962, 32, 473-476.

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166–168 °C (lit.<sup>27</sup> mp 165 °C); 22% yield.

*m*-Chlorophenylmagnesium bromide (0.015 mole) was prepared by the usual Grignard procedure in 20 mL of ether. 2-Chloroxanthone (1.0 g, 0.0043 mol) dissolved in 30 mL of THF was slowly added to the Grignard reagent, and the solution was refluxed for 1 h. The reaction mixture was poured into aqueous NH<sub>4</sub>Cl and extracted with ether. The ether layer was washed with water and brine, dried with MgSO<sub>4</sub>, and rotary evaporated to give a brown oil, 2-chloro-9-(*m*-chlorophenyl)-9-hydroxyxanthone. Crystallization of the oil could not be induced, and it was used without purification since it showed only one spot on TLC (silica, hexane–ether).

The reduction of the xanthidrol was carried out according to the directions of McCollum by using HI generated in situ from I<sub>2</sub> and HOAc.<sup>26</sup> Two recrystallizations from ethanol afforded white, cubic crystals of 2-chloro-9-(3-chlorophenyl)xanthone; mp 120–122 °C; NMR (CDCl<sub>3</sub>) δ 5.1 (1 H, s, 9-H proton), 6.8–7.3 (11 H, m, aromatic protons); mass spectrum, *m/e* (relative intensity) 326, 328, 330 (parent peaks); 9.1, 6.2, and 1.1, respectively, corresponding to <sup>36</sup>Cl<sup>36</sup>Cl, <sup>36</sup>Cl<sup>37</sup>Cl, and <sup>37</sup>Cl<sup>37</sup>Cl, 215, 217 (2-chloroxanthenyl nucleus; 100 and 35.9, respectively, corresponding to <sup>36</sup>Cl and <sup>37</sup>Cl).

9-[*p*-(Methylphenyl)sulfonyl]xanthone was prepared from xanthidrol and sodium *p*-toluenesulfinate in acetic acid as described by Balfe, Kenyon, and Thain.<sup>28</sup> Recrystallization gave white needles: mp 214–215 °C (lit.<sup>28</sup> mp 215–216 °C); TLC on silica (50% hexane–ethyl acetate) showed one spot; NMR (CDCl<sub>3</sub>) δ 2.3 (3 H, s, CH<sub>3</sub>), 5.3 (1 H, s, 9-H proton), 6.6–7.5 (12 H, m, aryl protons).

9-(Methoxycarbonyl)xanthone was synthesized from xanthene-9-carboxylic acid by the general procedure of Anet and Bavin.<sup>29</sup> Recrystallization from methanol gave white needles, mp 84–85 °C (lit.<sup>30</sup> mp 85–86 °C).

2,7-Dibromo-9-(methoxycarbonyl)xanthone. 9-(Methoxycarbonyl)xanthone (0.51 g, 2.1 mmol) was dissolved in 5 mL of CHCl<sub>3</sub>, and bromine (0.80 g, 5 mmoles) in 5 mL of CHCl<sub>3</sub> was added dropwise over a 10-min period. The reaction mixture was stirred 12 h, and then the solvent was removed in vacuo, leaving a brown solid. Two recrystallizations from MeOH/CHCl<sub>3</sub> afforded transparent cubes, mp 161–162 °C. HPLC analysis (30% water/CH<sub>3</sub>CN on a C<sub>18</sub> column, 2.0 mL/min flow rate) showed 1–2% impurity which was not starting material but probably monobrominated product: mass spectrum, *m/e* (relative intensity) 396, 398, 400 (4.6, 9.0, and 4.4, respectively, parent peaks), 337, 339, 341, (49.6, 100, and 45.5, respectively, 2,7-dibromoxanthenyl nucleus).

9-[[*m*-(Trifluoromethyl)phenyl]thio]xanthone was prepared by the general procedure of Sawicki and Oliverio<sup>31</sup> from 9-xanthidrol and *m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SH in AcOH/EtOH. Recrystallizations from MeOH and hexane afforded white crystals: mp 49–50 °C; NMR (CDCl<sub>3</sub>) δ 5.5 (1 H, s, 9-H proton), 6.6–7.5 (12 H, m, aryl protons); Mass spectrum, *m/e* (relative intensity) 339 (16.3;

parent minus one fluorine atom), 181 (xanthenyl nucleus).

**1,1,2-Tetraphenyl-2-azapropene.** Benzhydramine (1.0 g, 5.5 mM), benzophenone (1 g, 5.5 mM), and 0.15 g of ZnCl<sub>2</sub> were mixed and heated to 150 °C with stirring for 20 min. After the mixture cooled to about 100 °C, 20 mL of hot toluene was added and the solution filtered hot. The filtrate was evaporated in vacuo to produce a yellow solid. Two recrystallizations from ethanol afforded white plates, mp 152–152.5 °C (lit.<sup>32</sup> mp 152–153 °C).

**2,4-Diphenyl-3-azapent-2-ene** was prepared by the procedure of Kyba.<sup>33</sup> The oil was bulb-to-bulb distilled two times: oven temp 145 °C, (0.25 mmHg) (lit.<sup>33</sup> bp 102–104, 15 μmHg); NMR (CDCl<sub>3</sub>) δ 1.5 (3 H, d, HCCH<sub>3</sub>), 2.1 (3 H, s, CH<sub>3</sub>C(Ph)=N), 4.6 (1 H, q, HCCH<sub>3</sub>), 6.9–7.8 (10 H, m, aryl protons).

**Product studies** were carried out as described before<sup>21</sup> with 9-CN-Xn<sup>-</sup>, 9-COOMe-Xn<sup>-</sup>, 9-PhS-Xn<sup>-</sup>, and [PhSO<sub>2</sub>C(Me)Ph]<sup>-</sup> reacting with PhCH<sub>2</sub>Cl in Me<sub>2</sub>SO solution. The physical and spectral characteristics of the products are shown in Table V.

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

**Registry No.** 1 (G = H), 92-83-1; 1 (G = CN), 85554-24-1; 1 (G = SPh), 35595-00-7; 1 (G = SO<sub>2</sub>Ph), 85565-53-3; 1 (G = CO<sub>2</sub>Me), 39497-06-8; (G = *m*-ClC<sub>6</sub>H<sub>4</sub>), 58208-48-3; 1 (G = *p*-PhSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 85554-25-2; 1 (G = *p*-MeSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 42503-30-0; 1 (G = OH), 90-46-0; 1 (G = CO<sub>2</sub>H), 82-07-5; 2 (G = H), 101-81-5; 2 (G = CO<sub>2</sub>Me), 3469-00-9; 2 (G = *m*-ClC<sub>6</sub>H<sub>4</sub>), 85554-26-3; 2 (G = *p*-PhSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 85554-27-4; 3 (G = H), 75-05-8; 3 (G = *m*-ClC<sub>6</sub>H<sub>4</sub>), 1529-41-5; 3 (G = *p*-HSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), 85554-28-5; 4 (G = H), 86-73-7; 9-CN-Xn<sup>-</sup>, 85554-29-6; 2,7-Br-9-CO<sub>2</sub>MeXn<sup>-</sup>, 85554-30-9; 9-CO<sub>2</sub>MeXn<sup>-</sup>, 85554-31-0; 9-(*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>)Xn<sup>-</sup>, 85554-32-1; 9-(*m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>S)Xn<sup>-</sup>, 85554-33-2; 9-(C<sub>6</sub>H<sub>5</sub>S)Xn<sup>-</sup>, 85554-34-3; 9-(*p*-PhSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup>, 85554-35-4; 9-(*p*-MeSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup>, 85554-36-5; 2-Cl-9-(*m*-ClC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup>, 85554-37-6; 9-(*m*-ClC<sub>6</sub>H<sub>4</sub>)Xn<sup>-</sup>, 85554-38-7; Ph<sub>2</sub>CHCO<sub>2</sub>Et, 3468-99-3; Ph<sub>2</sub>CHSO<sub>2</sub>Me, 25195-40-8; PhCH(Me)SO<sub>2</sub>Ph, 24422-78-4; Ph<sub>2</sub>C=CHCHPh<sub>2</sub>, 4960-55-8; Ph<sub>2</sub>C=NCHPh<sub>2</sub>, 5350-59-4; (*p*-PhSC<sub>6</sub>H<sub>4</sub>)CHPh<sub>2</sub>, 85554-39-8; Ph<sub>2</sub>CHCN anion, 18802-83-0; *p*-ClC<sub>6</sub>H<sub>4</sub>CH(Me)CN anion, 85535-18-8; Ph<sub>2</sub>CHCO<sub>2</sub>Et anion, 70677-38-2; Ph<sub>2</sub>CHSO<sub>2</sub>Ph anion, 85554-40-1; Ph<sub>2</sub>CHSO<sub>2</sub>Me anion, 22513-78-6; PhCH(Me)SO<sub>2</sub>Ph anion, 85554-41-2; Ph<sub>2</sub>C=CHCHH<sub>2</sub> anion, 67131-61-7; Ph<sub>2</sub>C=NCHPh<sub>2</sub> anion, 85565-54-4; (*p*-PhSC<sub>6</sub>H<sub>4</sub>)CHPh<sub>2</sub> anion, 85554-42-3; *m*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SH, 937-00-8; benzyl chloride, 100-44-7; 1,2,3-triphenylindene, 38274-35-0; 9-methyl-10-ethoxycarbonyl-9,10-dihydrophenanthrene, 85554-43-4; 1,2,3-triphenylindene anion, 85554-44-5; 9-cyano-9,10-dihydrophenanthrene anion, 85535-19-9; 9-methyl-10-ethoxycarbonyl-9,10-dihydrophenanthrene anion, 85554-45-6; 2-chloroxanthone, 13210-15-6; 4-chlorophenoxide, 24573-38-4; 2-chlorobenzoic acid, 118-91-2; *m*-bromochlorobenzene, 108-37-2; 2-chloro-9-(*m*-chlorophenyl)-9-hydroxyxanthene, 85554-46-7; benzhydramine, 91-00-9; sodium *p*-toluenesulfinate, 824-79-3; 9-cyano-9-(phenylmethyl)xanthene, 85554-47-8; 9-(phenylmethyl)-9-(phenylthio)xanthene, 85554-48-9; 9-(methoxycarbonyl)-9-(phenylmethyl)xanthene, 85554-49-0; 1,2-diphenyl-2-(phenylsulfonyl)propane, 85554-50-3; benzophenone, 119-61-9.

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