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The Role of Single-Electron Transfer in S_N2-Type Substitution Reactions of Anions with Alkyl Halides

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Rate constants (k_{obsd}) for reactions of electrophiles with: (a) various carbanions, including 9-substituted fluorenide ions (9-GFl$^-$), 9-substituted xanthenide ions, α-cyano carbanions, and β-diketo enolate ions, (b) phenothiazinide (PTZ$^-$) and carbazole (Cb$^-$) nitranions, (c) 4-substituted phenoxide ions, and (d) thiophenoxide ions, have been compared with rate constants for single-electron transfer (k_{SET}) calculated using a Marcus-type equation. For both 9-GFl$^-$ carbanion and 2-GPTZ$^-$ nitranion families reacting with SET acceptors, such as 1,1-dinitrocyclohexane, the k_{obsd}/k_{SET} ratio is near unity. For 9-GFl$^-$ carbanions reacting with Ph_2CHCl the k_{obsd}/k_{SET} ratios range from 2 to 10^5, those for 2-PTZ$^-$ nitranions from 370 to 1.3×10^4, and those for Cb$^-$ nitranions from 10^8 to 10^{10}. For reactions of $4\text{-}GC_6H_4O^-$ oxanions with Ph_2CHCl the ratios range from 10^3 for G = Me_2N to 10^{13} for G = CN; for PhS$^-$ ion reacting with *n*-BuBr the ratio is 10^{17}. The significance of these results with respect to the role of an outer sphere SET mechanism in substitution reactions of anions with alkyl halides is discussed.

Nucleophilic substitutions with alkyl halides and the like are among the most common reactions in all of chemistry. The realization in 1966 that such reactions can occur by a single electron transfer (SET) chain mechanism,[1] and later that the scope of these chain reactions could be broadened to include aryl halides,[2] led to a wealth of new chemistry.[3] A nonchain SET-type mechanism involving radical pair intermediates (eq 1) has long been recognized

$$A^- + RX \rightarrow A^{\bullet}RX^{\bullet -} \rightarrow A^{\bullet}R^{\bullet}X^- \rightarrow A\text{–}R + X^- \quad (1)$$

as a possibility for nucleophilic substitution reactions.[4] Furthermore, the presence of radical species in such reactions, as detected by trapping or spectroscopic methods, has often been offered as evidence for their formation as intermediates.[5] It is difficult to decide whether these radicals are intermediates or artifacts, however, and a recent critical evaluation of mechanistic probes of this type for the detection of SET processes indicated that they are subject to serious complications.[6]

Recently, however, Lund has provided convincing evidence for the presence of SET character in the S_N2-type substitution reactions of *tert*-butyl, neopentyl, and 1-adamantyl bromides with the carbanion derived from 1-*N*-methyl-4-(methoxycarbonyl)-1,4-dihydropyridine. The rate constant for the SET reaction with *t*-BuBr was found to fit the line for a Marcus-type plot of log k_{obsd} vs $E_{ox}(A^-)$ for comparable reactions of *t*-BuBr with a series of aromatic radical anions, $ArH^{\bullet -}$, which are clearly outer sphere SET processes.[7b] It has been suggested by Lund that these substitutions occur by a hybrid SET–S_N2 spectrum of mechanisms.[7a] Also, Pross and Shaik have presented theoretical arguments to support a merging of, or a competition between, SET and S_N2 mechanisms.[8]

Eberson has used a form of the Marcus equation (eq 2) to calculate rates of SET for reactions of anions with 33 different electrophiles and compared the k_{SET} rates with k_{obsd} in order to determine whether or not SET is feasible.[9] In eq 2, k_d is the diffusion controlled rate constant, which

$$\log k_{SET} = \log k_d - \log \{1 + 0.2 \exp[\lambda/4(1 + (\Delta G^\circ/\gamma))^2/RT]\} \quad (2)$$

in Me_2SO is 3×10^9, λ is the intrinsic barrier (chosen from literature values and sometimes modified to give the best fit to the data), and ΔG° is estimated from the redox potentials of the anion and electrophile. Comparison of the k_{obsd}/k_{SET} ratio for the reactions then provides a rough classification into "SET feasible" and "SET not feasible".

In our laboratory a series of sterically hindered 9-(dialkylamino)fluorenide ions has been shown to react with Ph_2CHCl by a SET mechanism to form high yields of S_N2-type substitution products.[10] The ratio of the rate for SET calculated according to eq 2, k_{obsd}/k_{SET}, was near unity. Ratios near unity were also observed for this series of carbanions reacting with F_3CCH_2I, a known SET acceptor giving radical products. These results, which complement those of Lund,[7] prompted questions as to how general SET mechanisms were for substitution reactions of Ph_2CHCl, and other alkyl halides, with other 9-GFl$^-$ carbanions, as well as other anions (nitranions, oxanions,

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Table I. Rate Constants Observed and Calculated for Reactions of 9-Substituted Fluorenide Ions, 9-GFl⁻, with 1,1-Dinitrocyclohexane in Me_2SO at 25 °C

G	pK_{HA}[a]	$E_{ox}(A^-)$[b,c]	$\Delta G°$	k_{obsd}[d]	k_{obsd}/k_{SET}[e]
4-MeOC_6H_4	18.55	−0.344	5.09	214[c]	12
C_6H_5(3-Me)	18.7	−0.338	5.23	195[c]	12
4-MeC_6H_4	18.3	−0.318	5.70	93[c]	9.3
C_6H_5	17.9	−0.278	6.62	18[c]	4.4
Bz(2-Br)	18.9	−0.258	7.08	9.8[d]	3.8
t-Bu(2-Br)	21.7	−0.256	7.13	4.8[d]	1.2
3-ClC_6H_4	16.85	−0.188	8.69	0.76[c]	1.5
Me(2,7-Br_2)	17.7	−0.181	8.86	0.81[d]	1.3
C_6H_5(2-Br)	15.65	−0.144	9.71	0.081[c]	0.46
Bz(2,7-Br_2)	16.9	−0.114	10.40	0.068[d]	0.82
t-Bu(2,7-Br_2)	19.4	−0.100	10.72	0.073[d]	1.2
PhS	15.4	−0.099	10.75	0.012[d]	0.18
$4\text{-MeSO}_2C_6H_4$	15.4	−0.099	10.79	0.010[c]	1.8
C_6H_5(2-SO_2Ph)	13.8	−0.030	12.33	0.081[c]	0.083

[a] Values reported in earlier papers from this laboratory. [b] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE_{aq}. [c] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1985–1988. [d] M^{-1} s^{-1}; Bausch, M. J. Ph. D. Dissertation, Northwestern University, 1985. [e] $E_{rd} = -0.565$ V vs SHE_{aq}; $\lambda = 38$.

Table II. Rate Constants Observed and Calculated for Reactions of 9-Substituted Fluorenide Ions, 9-GFl⁻, with 1-(*p*-Tolylsulfonyl)-1-nitrocyclohexane in Me_2SO at 25 °C

G	pK_{HA}[a]	$E_{ox}(A^-)$[b]	$\Delta G°$	k_{obsd}[a,c]	k_{obsd}/k_{SET}[d]
MeO	22.1	−0.574	+6.99	178	2.5
i-PrO	21.4	−0.567	+7.15	120	2.0
i-Pr_2N	20.5	−0.485	+9.04	15.9	2.0
t-BuO	21.3	−0.483	+9.09	4.15	0.55
Me	22.3	−0.480	+9.15	2.0	0.28
t-$BuCH_2$	20.3	−0.443	+10.00	0.78	0.28
$PhC(Me)_2CH_2$	20.3	−0.433	+10.24	0.74	0.35
t-Bu	24.35	−0.409	+10.79	0.71	0.63
MeS	18.0	−0.261	+14.20	0.058	0.30
t-Bu(2-Br)	21.7	−0.256	+14.32	0.055	0.34
i-PrS	16.9	−0.210	+15.38	0.076	1.2
Me(2,7-Br_2)	17.7	−0.181	+16.05	0.072	0.40
t-Bu(2,7-Br_2)	19.4	−0.100	+17.91	0.053	0.34

[a] Bordwell, F. G.; Bausch, M. J.; Wilson, C. A. *J. Am. Chem. Soc.* **1987**, *109*, 5465–5470. [b] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE_{aq}. [c] M^{-1} s^{-1}. [d] Calculated as described in ref 10; $E_{rd} = -0.877$ vs SHE_{aq}; $\lambda = 30$.

thianions, etc.). In this paper we provide a partial answer to this question.

Results and Discussion

Reactions of 9-Substituted Fluorenide Ions (9-GFl⁻) with Single-Electron Acceptors. Rate data for reactions of a variety of 9-GFl⁻ ions with the single-electron acceptors 1,1-dinitrocyclohexane and 1-nitro-1-(*p*-tolylsulfonyl)cyclohexane, which were used in earlier studies,[11] have now been analyzed according to the method of Eberson[9] (Tables I and II).

The variable parameters in the Marcus equation (eq 2) are (a) $\Delta G°$, which is estimated from the difference in the reduction potentials of the electrophile, *E*, and the oxidation potentials of the anions, i.e., $E_{rd}(E) - E_{ox}(A^-)$, both referenced to the same electrode (e.g., SHE_{aq}), and (b) λ, an estimate of the change in molecular and solvation energies occurring during the reaction. Eberson has provided estimates of the size of λ for reactions with a variety of electrophiles from an average of the self-exchange values of the donor and acceptor pairs, i.e., $\lambda = (\lambda_{A^-} + \lambda_{RX})/2$. His values are used where applicable, and other λ values were assigned by analogy. The log k_{SET} values shown in Tables I and II were obtained by starting with λ values from Eberson's tables and modifying them so as to obtain the best correspondence between k_{SET} and k_{obsd}. For example, Eberson estimates that $\lambda = 48$ for reactions of cyclopentadiene-type carbanions reacting in ROH solvents by SET with nitrobenzene or 1,3-dinitrobenzene.[9a] We find a better fit when $\lambda = 38$ for reactions of 9-GFl⁻ ions with 1,1-dinitrocyclohexane (Table I). However, Eberson[9b] reports that if one assumes that these reactions are 0.2 V more endergonic, a better fit is also obtained. (Since the reduction of $1,1\text{-}(NO_2)_2\text{-c-}C_6H_{10}$ is irreversible, some uncertainty is present in the $\Delta G°$ values.) For another group of 9-GFl⁻ ions reacting with 1-nitro-1-(*p*-tolylsulfonyl)cyclohexane the fit is better with $\lambda = 30$ (Table II).

It should be kept in mind that in all cases the value of λ is an estimate and that the accuracy of the Marcus calculations are limited thereby, but a change of λ of 10 kcal/mol causes a change of only 2.5 kcal/mol in $\Delta G^{\ddagger}$ since $\lambda = 4\Delta G^{\ddagger}$. The effect of the choice of λ on the k_{obsd}/k_{SET} ratio can be illustrated with the following example. In Table I our choice of $\lambda = 38$ for the reaction of the 9-(3-ClC_6H_4)Fl⁻ ion reacting with $1,1\text{-}(NO_2)_2C_6H_{10}$ gives $k_{obsd}/k_{SET} = 1.2$. If λ is taken as 33 the ratio drops to 0.17; for $\lambda = 43$ the ratio increases to 8.9. The uncertainty introduced by the choice of λ restricts the assignment of mechanism, and we suggest that k_{obsd}/k_{SET} within 1 or 2 orders of magnitude of unity be considered as indicating that SET is feasible. We will see that very few reactions of anions with alkyl halides fall within this range.

The 9-GFl⁻ ions in Table I are arranged in order of decreasing negative values for their oxidation potentials, $E_{ox}(A^-)$. The rate constants for reactions with the SET acceptor, 1,1-dinitrocyclohexane, decrease in about the same order, and a Marcus-type plot of log k_{obsd} vs $E_{ox}(A^-)$ is roughly linear (Figure 1). In view of the diversity in size of the substituents, G, at the reaction site (e.g., C_6H_5, $C_6H_5CH_2$, *t*-Bu, *t*-$BuCH_2$, Me), this supports our view that the rates for these SET's are relatively independent of steric effects.[10,12] The inclusion of the points for R_2N, RO, and RS for a similar plot[12] of the data in Table II indicates that the rates are sensitive to $E_{ox}(A^-)$ only, despite a change in the nature of the atom attached at the 9-position.

The k_{obsd}/k_{SET} ratios in Tables I and II are for the most part near unity and all are within the "SET feasible" region, as expected. When combined with the data for reactions of the 9-R_2NFl⁻ ion series with SET acceptors,[10] they cover an $E_{ox}(A^-)$ range of 0.765 V or 15 kcal/mol. These examples indicate that Eberson's method[9] can be

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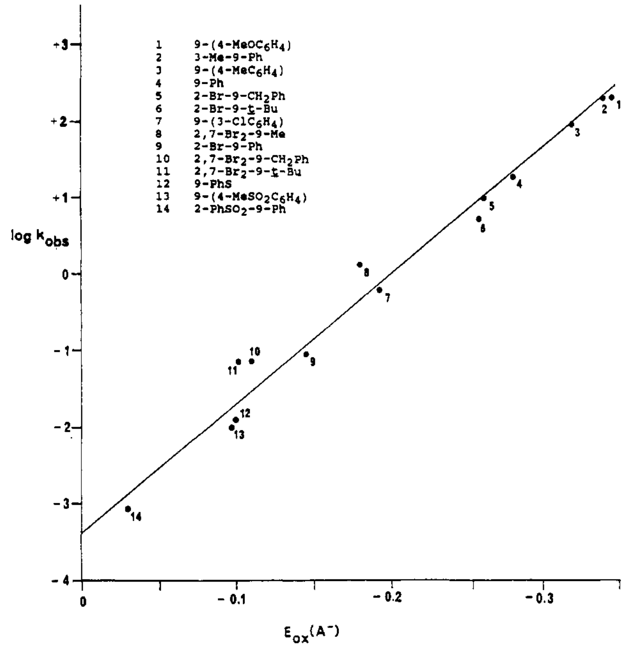


Figure 1. Plot of log k_{obsd} versus oxidation potentials for reactions of fourteen 9-substituted fluorenide ions (9-GFl$^-$) reacting with 1,1-dinitrocyclohexane (Table I). The nature of G and of other substituents is indicated on the figure.

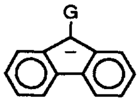
Table III. Rate Constants Observed and Calculated for Reactions of 9-Substituted Fluorenide Ions, 9-GFl$^-$, with Ph$_2$CHCl in Me$_2$SO at 25 °C

G	pK_{HA}	E_{ox}(A$^-$)^a	$\Delta G°$	k_{obsd}^{b}	k_{obsd}/ k_{SET}^{e}
MeO	22.1	−0.574	−2.4	0.28	1.9
Me	22.3	−0.480	−0.23	0.60	25
c-C$_6$H$_{11}$	23.0	−0.434	+0.83	0.10	10
Bz	21.36	−0.402	+1.57	0.30	58
Bz(2-Br)	18.9	−0.296	+4.01	0.088	140
4-MeC$_6$H$_4$	18.33	−0.318	+3.51	0.074^c	77
t-Bu	24.35	−0.284	+4.29	0.041	85
C$_6$H$_5$	17.9	−0.278	+4.43	0.058^{c,d}	140
3-ClC$_6$H$_4$	16.85	−0.188	+6.50	0.038^c	600
Bz(2,7-Br$_2$)	16.9	−0.152	+7.33	0.027	930
t-Bu(2,7-Br$_2$)	19.4	−0.10	+8.53	0.084	900
4-MeSO$_2$Ph	15.2	−0.097	+8.60	0.016^c	1.8 × 10^3
CO$_2$Me	10.35	+0.253	+16.8	(8.1 × 10^{-4})^d	3.1 × 10^5
CO$_2$Me(2-Br)	8.2	+0.376	+19.51	(1.6 × 10^{-6})^d	1.2 × 10^4
CO$_2$Me(2,7-Br$_2$)	6.5	+0.502	+22.41	(8.7 × 10^{-7})^d	1.8 × 10^5

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE$_{aq}$ by adding −0.125. [b] M^{-1} s^{-1}. [c] Hughes, D. L. Ph.D. Dissertation, Northwestern University, 1981. [d] Mrozack, S. R. Ph.D. Dissertation, Northwestern University, 1982. [e] E_{rd} = −0.47 (vs SHE$_{aq}$); λ = 65.

expected to provide a good test for the feasibility of SET in reactions of anions with electrophiles.

In the sections that follow we will apply the Eberson method to test the feasibility of SET in the reactions of a variety of anions, including 9-substituted fluorenide ions, 9-GFl$^-$ (1), 9-substituted xanthenide ions, 9-GXn$^-$ (2), substituted phenothiazinide ions, PTZ$^-$ (3), and substituted carbazolide ions, Cb$^-$ (4), with benzyl, benzhydryl, and other alkyl halides.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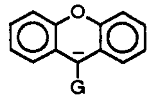
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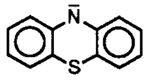
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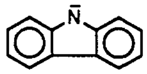
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Table IV. Rate Constants Observed and Calculated for Reactions of 9-Substituted Fluorenide Ions, 9-GFl$^-$, with (p-ClC$_6$H$_4$)$_2$CHCl in Me$_2$SO at 25 °C

G	pK_{HA}^{a}	E_{ox}(A$^-$)	$\Delta G°$	k_{obsd}^{b}	k_{obsd}/k_{SET}^{d}
MeO	22.1	−0.574	−1.64	3.9	50
Me	22.34	−0.480	+0.54	9.8^c	760
c-C$_6$H$_{11}$	23.0	−0.434	+1.59	1.8	350
t-Bu	24.35	−0.409	+2.17	0.34^c	110
Ph	17.9	−0.278	+5.20	0.68^c	3200
PhS	15.4	−0.104	+9.21	0.025^c	5100
CO$_2$Me	10.35	+0.253	+17.43	0.047^c	4.3 × 10^6
CN	8.3	+0.292	+18.35	0.0035^c	8.1 × 10^6

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE$_{aq}$ by adding −0.125. [b] M^{-1} s^{-1}. [c] Mrozack, S. R. Ph.D. Dissertation, Northwestern University, 1982. [d] E_{rd} = 0.4 × (−1.259) = −0.503 V vs SHE$_{aq}$; λ = 65.

Table V. Rate Constants Observed and Calculated for Reactions of 9-Substituted Fluorenide Ions, 9-GFl$^-$, with PhCH$_2$Cl in Me$_2$SO at 25 °C

G	pK_{HA}	E_{ox}(A$^-$)^a	$\Delta G°$	k_{obsd}^{b}	k_{obsd}/k_{SET}^{d}
MeO	22.1	−0.574	+3.4	14.5^c	1.45 × 10^4
Me	22.3	−0.480	+5.5	49.0^c	3.1 × 10^5
Et	22.6	−0.476	+5.6	40.7^c	3.2 × 10^5
i-Pr	23.2	−0.458	+6.0	2.95^c	2.95 × 10^4
Bz	21.36	−0.407	+7.2	19.5	6.2 × 10^5
PhO	19.9	−0.326	+7.7	2.82	1.4 × 10^5
t-Bu	24.35	−0.284	+10.1	0.47	2.4 × 10^5
Ph	17.9	−0.278	+10.2	0.62	3.1 × 10^5
3-ClC$_6$H$_4$	16.85	−0.188	+12.3	0.26	1.0 × 10^6
t-BuS	15.9	−0.134	+13.5	0.32	5.1 × 10^6
t-Bu(2-Br)	21.7	−0.133	+13.5	0.078	1.2 × 10^6
PhS	15.4	−0.099	+14.3	0.25	7.9 × 10^6
4-MeSO$_2$C$_6$H$_4$	15.2	−0.097	+14.4	0.065	2.1 × 10^6
t-Bu(2,7-Br$_2$)	19.4	+0.025	+17.2	0.017	1.1 × 10^7
CO$_2$Me	10.35	+0.025	+22.4	0.027	k.4 × 10^9
CN	8.3	+0.326	+24.1	0.0062	9.8 × 10^9

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE$_{aq}$ by adding −0.125. [b] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314–3320. [c] C. A. Wilson, unpublished results. [d] E_{rd} = −0.72 V vs SHE$_{aq}$; λ = 65.

Reactions of 9-GFl$^-$ Ions with Benzhydryl and Benzyl Chlorides. Applications of the Eberson analysis to 9-GFl$^-$ ions reacting with Ph$_2$CHCl, (p-ClC$_6$H$_4$)$_2$CHCl, and PhCH$_2$Cl are shown in Tables III–V.

Examination of k_{obsd}/k_{SET} in Table III suggests that the radical pair mechanism is feasible only for those anions listed in the upper half of the table. The ratios become progressively larger in the bottom half of the table as the E_{ox}(A$^-$) values become less negative. It is not surprising that 9-MeOFl$^-$ ion gives evidence of reaction by a SET mechanism since its E_{ox}(A$^-$) value is as negative as those of several of the 9-R$_2$NFl$^-$ ions (−0.438 to −0.865) that have been shown to give S$_N$2-type substitution products by a SET mechanism.[10] 9-MeFl$^-$ and 9-c-C$_6$H$_{11}$Fl$^-$ ions also have E_{ox}(A$^-$) values in this region but have higher k_{obsd}/k_{SET} ratios (25 and 10, respectively).

The k_{obsd}/k_{SET} ratio for the reaction of 9-MeOFl$^-$ ion with (p-ClC$_6$H$_4$)$_2$CHCl (Table IV) also places it in the SET feasible region, but the other ratios are too high and all of those for reactions of 9-GFl$^-$ with PhCH$_2$Cl in Table V are much too high to be placed in this category.

Oxidation potentials of carbanions become more negative in an approximately linear manner as their basicities increase.[13] 9-Substituted xanthenide ions with aryl or PhS substituents follow this trend and have E_{ox}(A$^-$) values ranging from −0.511 to −0.724 V (Table VI), but the

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[13] (a) Kern, J. M.; Sauer, J. D.; Federlin, P. *Tetrahedron* **1982**, *38*, 3023–3033. (b) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985. (c) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2872–2877. (d) Bordwell, F. G.; Harrelson, J. A., Jr.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105. (e) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J.; Bares, J. E. *J. Phys. Org. Chem.* **1988**, *1*, 209–223.

Table VI. Rate Constants Observed and Calculated for Reactions of 9-Substituted Xanthenide Ions, 9-GXn⁻, and Ph_2CCN^- with $PhCH_2Cl$ in Me_2SO at 25 °C

anion	pK_{HA}	$E_{ox}(A^-)^a$	$\Delta G°$	$k_{obsd}{}^b$	$k_{obsd}/k_{SET}{}^c$
$3\text{-}ClC_6H_4Xn^-$	26.6	−0.724	+0.10	135	6700
$4\text{-}MeSO_2C_6H_4Xn^-$	24.15	−0.606	+2.6	3.47	1700
$PhSXn^-$	22.8	−0.603	+2.7	355	1.8×10^5
$4\text{-}PhSO_2C_6H_4Xn^-$	23.1	−0.511	+4.8	0.98	3100
CO_2MeXn^-	18.15	−0.270	+10.4	2.09	1.3×10^6
Ph_2CCN^-	17.5	−0.010	+16.4	1.12	3.5×10^8

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE_{aq} by adding −0.125. [b] $M^{-1}\ s^{-1}$; Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2216–2222. [c] $E_{rd} = -0.72$ vs SHE_{aq}; $\lambda = 65$.

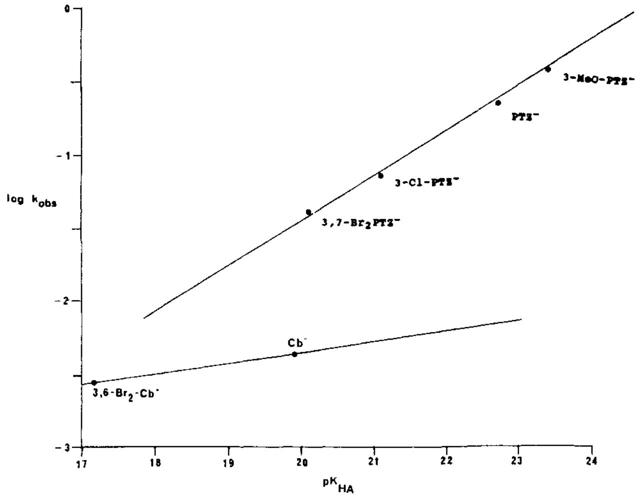

Figure 2. Brønsted plot for reactions of phenothiazinide and carbazolide ions with benzyhydryl chloride (Table VII).

k_{obsd}/k_{SET} ratios for reactions with $PhCH_2Cl$ are nevertheless too high to be SET feasible. It seems likely, however, that 9-GXn⁻ ions will initiate SET reactions with Ph_2CHCl because there is evidence that they have appreciable steric demands[14] in addition to highly negative oxidation potentials. We can anticipate that anions more basic than 9-GXn⁻ ions, such as Ph_3C^-, Ph_2CH^-, and $PhCH_2^-$, which have pK_{HA} values in Me_2SO of 30.6, 32.2, and ~43 (extrapolated),[15] respectively, will also favor SET substitution mechanisms. Indeed, there is evidence to indicate that Ph_2CH^- and Ph_3C^- ions react with benzylic chlorides by radical pair mechanisms.[16]

Reactions of Nitranions with Benzyl and Benzhydryl Chlorides. Brønsted plots of log k_{obsd} vs pK_{HA} for reactions of remotely substituted carbazolide ions (GCb⁻) and phenothiazinide ions (GPTZ⁻) with $PhCH_2Cl$ have been found to be essentially colinear with a slope of about 0.3.[17] In contrast, the Brønsted plots for the reactions of GCb⁻ and GPTZ⁻ ions with Ph_2CHCl are sharply diverging (Figure 2), as are the lines for Marcus-type plots.

Table VII. Rate Constants Observed and Calculated for Reactions of Phenothiazinide (PTZ⁻), Phenoxazinide (POX⁻), and Carbazolide (Cb⁻) Nitranions with Ph_2CHCl in Me_2SO at 25 °C

anion	pK_{HA}	$E_{ox}(A^-)^a$	$\Delta G°$	$k_{obsd}{}^c$	$k_{obsd}/k_{SET}{}^d$
3-MeOPTZ⁻	23.4	-0.318^b	+3.51	0.37	370
POZ⁻	21.7	-0.253^b	+5.00	1.91^d	7600
PTZ⁻	22.7	-0.209^b	+6.02	0.22	2600
3-ClPTZ⁻	21.1	−0.131	+7.82	0.069	3800
$3,7\text{-}Br_2PTZ^-$	20.1	−0.050	+9.69	0.040	13000
Cb⁻	19.9	+0.414	+20.4	0.0043	10^8
$3,6\text{-}Br_2Cb^-$	17.15	+0.610	+24.90	0.0028	10^{10}

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE_{aq} by adding −0.125. [b] Partially reversible; becomes completely reversible at 300 mV/s with no change in E_p. [c] $M^{-1}\ s^{-1}$. [d] Hughes, D. L. Ph.D. Dissertation, Northwestern University, 1981. [e] $E_{rd} = -0.47$ vs SHE_{aq}; $\lambda = 65$.

Table VIII. Rate Constants Observed and Calculated for Reactions of Ring-Substituted Phenothiazinide Nitranions (GPTZ⁻) with 1,1-Dinitrocyclohexane in Me_2SO at 25 °C

subst	pK_{HA}	$E_{ox}(A^-)^{a,b}$	$\Delta G°$	$k_{obsd}{}^c$	$k_{obsd}/k_{SET}{}^e$
$2\text{-}Me_2N$	23.5	−0.315	+5.77	200^d	1.8
2-MeO	22.5	−0.222	+7.91	13.2^b	1.1
H	22.7	−0.209	+8.21	10.5^b	1.2
$3,7\text{-}Br_2$	20.1	−0.050	+10.05	0.14^b	0.11
2-Cl	20.8	−0.035	+10.95	0.17^b	0.37
$2\text{-}CF_3$	20.65	−0.072	+11.36	0.069^b	0.077

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE_{aq} by adding −0.125. [b] Cheng, J.-P. Ph.D. Dissertation, Northwestern University, 1987. [c] $M^{-1}\ s^{-1}$. [d] Clemens, A. H., unpublished results. [e] $E_{rd} = -0.565$ vs SHE_{aq}; $\delta i = 32$.

Table IX. Rate Constants Observed and Calculated for Reactions of Phenothiazinide (PTZ⁻), Phenoxazinide (POX⁻), and Carbazolide (Cb⁻) Ions with $PhCH_2Cl$ in Me_2SO at 25 °C

anion	pK_{HA}	$E_{ox}(A^-)^a$	$\Delta G°$	$k_{obsd}{}^b$	$k_{obsd}/k_{SET}{}^c$
POZ⁻	21.66	−0.253	+10.8	16.7	1.7×10^7
PTZ⁻	22.72	−0.209	+11.8	2.57	6.4×10^6
2-ClPTZ⁻	20.79	−0.090	+14.5	0.60	2.4×10^7
Cb⁻	19.9	+0.414	+26.2	0.34	5.4×10^{12}
3-ClCb⁻	18.50			0.11	
$3,6\text{-}Br_2Cb^-$	17.15	+0.610	+30.7	0.045	1.8×10^{14}

[a] Measured by cyclic voltammetry vs Ag/AgI; Bausch, M. J., Ph.D. Dissertation, Northwestern University, 1985; referenced to SHE_{aq} by adding −0.125. [b] $M^{-1}\ s^{-1}$; Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 3234–3239. [c] $E_{rd} = -0.72$ vs SHE_{aq}; $\lambda = 65$.

Examination of Table VII shows that the oxidation potential of Cb⁻ anion is highly positive, whereas that with the PTZ⁻ anion is substantially negative and the CV is partially reversible. The more negative value (by 0.623 V or 14.4 kcal/mol) and partial CV reversibility for the latter can be associated with the much greater stability of the PTZ• radical, as compared to the Cb• radical. The sharp divergence in the Brønsted and Marcus plots for the reactions of PTZ⁻ and Cb⁻ anion families with Ph_2CHCl points to a change in mechanism. It seems likely that 3-MeOPTZ⁻, PTZ⁻, and 3-ClPTZ⁻ ions are reacting with Ph_2CHCl by competing SET and S_N2 mechanisms. The reactions of $2\text{-}Me_2NPTZ^-$, 2-MeOPTZ⁻, and PTZ⁻ nitranions with the SET acceptor 1,1-dinitrocyclohexane all give k_{obsd}/k_{SET} ratios close to unity according to the Eberson analysis (Table VIII). The k_{obsd}/k_{SET} values for the three remaining PTZ⁻ ions bearing electron-withdrawing substituents are smaller than unity but still in the SET feasible region. The reaction of PTZ⁻ with Ph_2CHCl gave a good yield of substitution product, whereas that with 1,1-dinitrocyclohexane gave a complex mixture of radical-type products.[18]

The k_{obsd}/k_{SET} ratios for PTZ⁻ ions reacting with $PhCH_2Cl$ are of the order of 10^7 and those with Cb⁻ ions are of the order of 10^{13} (Table IX).

Reactions of Oxanions, Enolate Ions, and Thianions with Alkyl Halides. Rates of substitution reactions of

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[14] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2216–2222.

[15] Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 2964–2968.

[16] Zieger, H. E.; Angres, I.; Mathiesen, D. *J. Am. Chem. Soc.* **1976**, *98*, 2580–2585.

[17] Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1984**, *106*, 3234–3239.

[18] Clemens, A. H., unpublished results.

Table X. Rate Constants Observed and Calculated for Reactions of Phenoxide Ions, $GC_6H_4O^-$, with Ph_2CHCl in Me_2SO at 25 °C

G	pK_{HA}	$E_{ox}(A^-)$[a]	$\Delta G°$	k_{obsd}[b]	k_{obsd}/k_{SET}[c]
4-Me_2N	19.8	−0.097	+8.60	10^{-2}	10^3
4-MeO	19.1	+0.132	+13.9	8.3×10^{-3}	1.7×10^5
4-*t*-Bu	19.05	+0.315	+18.1	4×10^{-3}	7.3×10^6
4-Ph	17.1	+0.380	+19.6	4.4×10^{-3}	4.2×10^7
4-CN	13.2	+0.900	+31.6	1.5×10^{-3}	1.9×10^{13}

[a] Measured by cyclic voltammetry vs Ag/AgI; referenced to SHE_{aq} by adding −0.125. [b] $M^{-1}\ s^{-1}$. [c] $E_{rd} = -0.47$ vs SHE_{aq}; $\lambda = 65$.

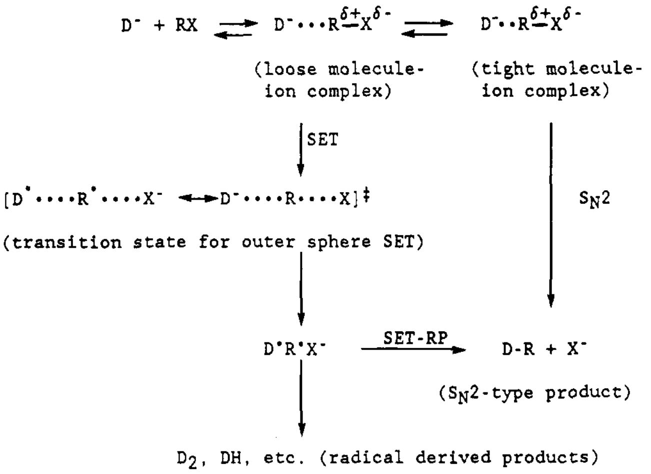
Ph_2CHCl with phenoxide ions, 4-$GC_6H_4O^-$, with basicities varying over a range of 9 kcal/mol and $E_{ox}(A^-)$ values varying over a range of 23 kcal/mol are shown in Table X. The k_{obsd}/k_{SET} ratios are large, and those for substitution reactions with $PhCH_2Cl$ are even larger (Table XI).

Reactions of the enolate ion derived from $MeCH(COCH_3)_2$ with EtI and that derived from $EtCH(COCH_3)_2$ with MeI also have very high k_{obsd}/k_{SET} ratios. The latter two alkylations occur on carbon, although the major portion of the negative charge density on these ambident ions is on oxygen. The enolate ions derived from monoketones are more basic and have more negative oxidation potentials. For example, the enolate ion derived from acetone has pK_{HA} of 26.5 and $E_{ox}(A^-) = +0.076$. This potential is, however, still much too positive to evoke a SET reaction with ordinary alkyl halides.

Thianions are known to be more easily oxidized than oxanions and would at first sight appear to be more likely to undergo reactions by SET mechanisms. Examination of Table XI shows, however, that PhS^- ion, which is ca. 8 pK_{HA} units less basic than PhO^-, has an oxidation potential only 35 mV more negative. The very high k_{obsd}/k_{SET} for the reaction with *n*-BuBr (3×10^{17}) makes it seem unlikely that the PhS^- ion will undergo SET with alkyl halides.

Mechanisms for Substitution Reactions of Anions with Alkyl Halides. The experimental evidence accumulated to date points to three distinct mechanisms by which these substitution reactions occur: (1) Ingold's concerted S_N2 mechanism, (2) the Kornblum–Russell–Bunnett (KRB) radical chain mechanism, and (3) a SET radical pair (SET–RP) mechanism. The overall equation for S_N2 substitutions involving anions, A^-, and alkyl halide electrophiles, RX, indicates that one electron is transferred from A^- to X, and Pross and Shaik have described the mechanism in terms of concerted SET or inner sphere SET.[8] The KRB mechanism depends on a SET between a radical anion and the electrophile being rapid enough to carry the chain and usually requires photoinitiation to start the chain.[3] For ordinary alkyl halides, the SET–RP mechanism requires a combination of an anion with a highly negative oxidation potential (<−0.5 V) and steric constraints in the anion and/or alkyl halide.[7-10] The S_N2 and SET–RP mechanisms are pictured as competing in Scheme I.

Scheme I



In the first step in Scheme I a loose molecule–ion complex is formed. Since the binding of D^- to RX is weak, the lifetime of the complex is very short. It will either revert rapidly to starting material or undergo further solvent loss and reorganization to form a tighter molecule–ion complex. In Scheme I, it is assumed that the critical distance for an S_N2 reaction has been achieved in the latter,[19] giving rise to a concerted S_N2 (inner sphere SET) reaction. The loose molecule–ion complex is relatively free of steric effects. So, if there is a steric barrier to the formation of the tight molecule–ion complex, a long-range outer sphere SET to form a radical pair (SET–RP mechanism) may compete with the concerted S_N2 mechanism if $\Delta G°$ is in the proper range.[8] For 9-R_2NFl^- ions, this range is +0.8 to −9.0 kcal/mol for substitution reactions with Ph_2CHCl or $(p\text{-}ClC_6H_4)_2CHCl$.[10] The results in Tables I and II indicate that for reactions of 9-GFl^- carbanions with good SET acceptors the range can extend as far as 10 kcal/mol into the endergonic region. For substitution reactions of 9-GFl^- ions with Ph_2CHCl and $(p\text{-}ClC_6H_4)_2CHCl$ the results in Tables III and IV indicate, however, that the SET–RP mechanism holds only up to $\Delta G° \simeq +2$ kcal/mol, at best. For 9-GFl^- and 9-GXn^- carbanions reacting with $PhCH_2Cl$ the relatively high k_{obsd}/k_{SET} ratios in Tables V and VI are more consistent with an S_N2 mechanism.

The results with phenothiazinide ion and its 2-substituted derivatives reacting with 1,1-$(NO_2)_2$-c-C_6H_{10} are consistent with the SET mechanism expected. Their reactions with Ph_2CHCl appear to be going by competing S_N2 and SET–RP mechanisms, but those with $PhCH_2Cl$ are clearly in the S_N2 domain (Tables VII–IX). Since carbazolide nitranions have oxidation potentials about 0.5 V more positive than their fluorenide ion counterparts, it would appear that there is little prospect of finding nucleophilic substitution reactions of nitranions or amines with alkyl halides that go by pure SET–RP mechanisms.

Carbanions have the widest range of oxidation potential of any anions, with nitranions coming in second. Oxanions and thianions have a more limited $E_{ox}(A^-)$ range. Oxanions and nitranions have much more positive oxidation potentials than do carbanions of the same basicity, as would be expected from the higher electronegativities of N and O. Note, for example, that $E_{ox}(A^-)$ for PhO^- ion ($pK_{HA} = 18.0$) is +0.425 V in Me_2SO (Table XI) compared to −0.278 V for 9-$PhFl^-$ ion, for which $pK_{HA} = 17.9$ (Table I). Thianions, as expected, appear to have oxidation potentials comparable to those of carbanions at the same basicity as judged by that of +0.390 V for PhS^- ion ($pK_{HA} = 10.3$) and +0.253 V for 9-CO_2MeFl^- ion ($pK_{HA} = 10.35$; Table XI), but they have a much more limited range of basicities and $E_{ox}(A^-)$ values.

In this discussion we have assigned a SET–RP mechanism to a few substitution reactions with Ph_2CHCl where k_{obsd}/k_{SET} ratios are within 1 or 2 orders of magnitude of unity, but the majority of substitutions with Ph_2CHCl or other alkyl halides appear to go by concerted S_N2 mechanisms. There appears to be general agreement that there

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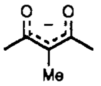
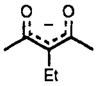
(19) For a recent discussion of the importance of "critical distance" in chemical reactions, see: (a) Menger, F. M. In *Nucleophilicity*; Harris, J. M., McManus, S. F., Eds.; Advances in Chemistry Series No. 215; American Chemical Society: Washington, DC, 1987; Chapter 14. Menger, F. M. *Acc. Chem. Res.* **1985**, *18*, 128–134.

Table XI. Rate Constants Observed and Calculated for Anions of Various Types with Alkyl Halides in Me_2SO at 25 °C

anion	pK_{HA}	$E_{ox}(A^-)^a$	$\Delta G°$	k_{obsd}	k_{obsd}/K_{SET}
$4\text{-}NH_2C_6H_4O^-$	20.75	−0.281	+10.1	4.37^b	1.7×10^6
$4\text{-}MeOC_6H_4O^-$	19.11	−0.097	+14.4	1.15^b	3.6×10^7
$C_6H_5O^-$	18.03	+0.425	+26.4	0.32^b	6.4×10^{12}
$3,4,5\text{-}Cl_3C_6H_2O^-$	12.75	+0.875	+36.8	0.0028^b	2.75×10^{16}
	15.35	+0.396	+30.6	$0.23^{c,d}$	1.8×10^{13}
	15.07	+0.424	+34.7	$4.20^{d,e}$	1.1×10^{17}
PhS^-	10.3	+0.390	+32.3	9.77^f	3×10^{17}
$9\text{-}MeFl^-$	22.3	−0.480	+12.2	15.5^f	6.2×10^7
$9\text{-}PhFl^-$	17.9	−0.278	+16.9	0.17^f	8.5×10^7
$9\text{-}CO_2MeFl^-$	10.35	+0.253	+29.1	0.0083^f	5.2×10^{12}

[a] Vs SHE. [b] Reaction with $PhCH_2Cl$; λ = 65 (present work). [c] Reaction with EtI; λ = 53. [d] Arnett, E. M.; Maroldo, S. G.; Schriver, G. W.; Schilling, S. L.; Troughton, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 2091–2099. [e] Reaction with MeI; λ = 53. [f] Reaction with *n*-BuBr; λ = 65 (D. L. Hughes, Ph.D. Dissertation, Northwestern University, 1981).

will be a region where the two mechanisms will merge or compete.[7-9] It may be that k_{obsd}/k_{SET} ratios in the range of 10^3–10^4 are indicative of this region, but the calculations are too approximate at present to lend much confidence to such an assignment.

Summary and Conclusions

The test for single electron transfer (SET) by comparison of k_{obsd} with k_{SET}, which was devised by Eberson,[9] has been extended to nitranions, oxanions, and thianions, as well as to additional families of carbanions. Earlier work has revealed that k_{obsd}/k_{SET} ratios were near unity for reactions of a series of $9\text{-}R_2NFl^-$ carbanions with the F_3CCH_2I SET acceptor to give radical products, and for reactions with Ph_2CHCl to give substitution products. Similar results have now been found for more endergonic reactions of other $9\text{-}GFl^-$ carbanions with known SET acceptors, $1,1\text{-}(NO_2)_2\text{-}c\text{-}C_6H_{10}$ and $1\text{-}NO_2\text{-}1\text{-}Ts\text{-}C_6H_{10}$, and for phenothiazinide ions with $1,1\text{-}(NO_2)_2\text{-}c\text{-}C_6H_{10}$. Application of the test to reactions with $PhCH_2Cl$ for $9\text{-}GFl^-$ and $9\text{-}GXn^-$ carbanions, phenothiazinide and carbazolide nitranions, $GC_6H_4O^-$ oxanions, PhS^-, thianions, and carbanion–oxanions derived from β-diketones revealed no evidence for SET. It follows that most substitution reactions of anions with alkyl halides do not involve outer sphere SET.

Experimental Section

The methods used for determination of rate constants[20] and cyclic voltammetry measurements[13d] have been described in earlier publications. Instrumentation for NMR, mass spectra, and melting point measurements were described in the previous paper.[10b]

Materials. The sources and purification of the alkyl halides were described in the previous paper.[10b] The references in Tables I–XI provide sources of other electrophiles and nucleophiles presented in this paper.

Product Studies. Details of product studies for reactions whose rates have been previously published can be located in the appropriate references in Tables I–XI. In particular, reaction of $9\text{-}PhFl^-$ and $9\text{-}(p\text{-}CH_3C_6H_4)Fl^-$ ions with $1,1\text{-}(NO_2)_2\text{-}c\text{-}C_6H_{10}$ were found to give $(9\text{-}PhFl)_2$ and $[9\text{-}(p\text{-}CH_3C_6H_4)Fl]_2$ dimers together with $(c\text{-}C_6H_{10}NO_2)_2$ and $c\text{-}C_6H_{10}{=}NO_2^{-}$.[11b] Reaction of $9\text{-}t\text{-}BuFl^-$ ion with $1\text{-}NO_2\text{-}1\text{-}Ts\text{-}c\text{-}C_6H_{10}$ gave $9\text{-}t\text{-}BuFlH$ instead of the dimer plus a mixture of other radical-derived products.[12]

The following reactions were shown to give high yields of S_N2 products: $9\text{-}(p\text{-}CH_3C_6H_4)Fl^-$ ion with Ph_2CHCl,[21] $9\text{-}PhFl^-$ and $9\text{-}PhSFl^-$ ions with $(p\text{-}ClC_6H_4)_2CHCl$,[22] $9\text{-}GFl^-$ ion with $PhCH_2Cl$ (G = Ph, *t*-Bu, CO_2Me),[21,23] $9\text{-}GXn^-$ ions with $PhCH_2Cl$ (G = CN, CO_2Me, PhS),[14] POZ^- and PTZ^- ions with $PhCH_2Cl$,[17] Cb^- ion with $p\text{-}CF_3C_6H_4CH_2Cl$,[21] Ph_2CCN^- ion with $PhCH_2Cl$,[23] and $p\text{-}ClC_6H_4O^-$ with $PhCH_2Cl$.[21] Additional product studies are provided below.

Reaction of PTZ^- with Ph_2CHCl. Phenothiazine (82.1 mg, 4.1×10^{-4} mol) was treated with 1 equiv of potassium dimsyl followed by 1 equiv of benzhydryl chloride and stirred for 30 min. Workup with ether/water gave 129 mg (86%) of crude substitution product: mp 135–137 °C; ^1H NMR ($CDCl_3$) δ 6.6 (s, 1 H), 6.8–7.7 (m, 18 H); MS (*m/e*) 366 (2.1), 365 (molecular ion, 7.4), 199 (20.2), 198 (100).

Reaction of Cb^- Ion with Ph_2CHCl. Carbazole (136.8 mg, 8.2×10^{-4} mol) was reacted as above with potassium dimsyl and benzhydryl chloride for 30 min. Workup gave 210 mg (77%) of crude substitution product: ^1H NMR ($CDCl_3$) δ 5.9 (s, 1 H), 7.1–8.2 (m, 18 H). Recrystallization from ethanol/water gave crystalline material, mp 159–161.5 °C; GLC analysis indicated the presence of 5% of an impurity with a shorter retention time. High-resolution mass spectrometry gave the correct molecular weight for the major product, $C_{25}H_{19}N$. Microanalysis was satisfactory for H and N, but 0.9% low for carbon.

Reaction of $p\text{-}MeOC_6H_4O^-$ with Ph_2CHCl. *p*-Methoxyphenol (88.9 mg, 7.2×10^{-4} mol) was reacted as above with potassium dimsyl and benzhydryl chloride for 48 h. Workup gave 192.8 g (93% of crude substitution product; mp 82–84 °C): ^1H NMR ($CDCl_3$) δ 3.75 (s, 3 H), 6.65–7.5 (m, 14 H); MS (*m/e*) 290 (molecular ion, 2.67), 167 (100), 123 (2.1); mp (EtOH) 85–86 °C. The ^1H NMR ($CDCl_3$) spectrum of the recrystallized material was identical with that of the crude product. Microanalyses were satisfactory for carbon and hydrogen.

Reaction of $p\text{-}CNC_6H_4O^-$ Ion with Ph_2CHCl. *p*-Cyanophenol (86.4 mg, 7.25×10^{-4} mol) was reacted as above with potassium dimsyl and benzhydryl chloride for 48 h. Workup gave 204 mg (99%) of crude substitution product: ^1H NMR ($CDCl_3$) δ 6.25 (s, 1 H), 6.8–7.9 (m, 14 H); MS (*m/e*) 285 (1.2, molecular ion), 167 (6.8), 119 (84.8), 105 (100), 77 (52.4); mp (EtOH) 147–149 °C. The ^1H NMR ($CDCl_3$) spectrum of the crystallized material, mp 147–149 °C, was identical with that of the crude product. Microanalyses were satisfactory for carbon and hydrogen.

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