4198 *J. Org. Chem.* **1983**, *48*, 4198–4202

Reaction of Polycyclic Aromatic Hydrocarbons with Ozone. Linear Free-Energy Relationships and Tests of Likely Rate-Determining Steps Using Simple Molecular Orbital Correlations

William A. Pryor,* Gerald J. Gleicher,*[1] and Daniel F. Church

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Received June 7, 1983

Nine unsubstituted, polycyclic aromatic hydrocarbons were allowed to react with ozone at 25 °C, and relative rate constants were obtained by direct competitive techniques. The rate constants show a large variation with substrate structure, with nearly three powers of ten difference between the least reactive (benzene) and most reactive (anthracene, perylene) compounds studied. Linear free-energy relationships between the rate data and calculated molecular orbital parameters have been obtained. The optimum correlations are found for models based on rate-determining π-complex or σ-complex formation rather than simultaneous addition of ozone to two carbon atoms. Electrophilic attack by ozone to yield a σ-complex also appears to be the rate-determining step based on the results obtained for changes in selectivity with variation of solvents.

The reaction of ozone with polycyclic, aromatic hydrocarbons (PAH) has been of interest to several groups of chemists in varied fields. Moriconi and Salce considered the possibility that this reaction could serve as a probe in elucidating models of hydrocarbon carcinogenicity.[2] An equally important body of data has been generated by studies on the use of ozone in waste water purification.[3] More recently, it has been pointed out that the products of ozonation of PAH may themselves show pronounced carcinogenic and mutagenic character.[4]

This extensive field has been thoroughly reviewed by Bailey in his recent monograph on organic ozone chemistry.[5] Although Bailey discusses the chemistry of over twenty unsubstituted PAH in detail, few references are given to papers concerned with evaluating relative reactivities among these compounds. This is surprising in view of the long-standing difficulty of determining the features in a PAH that control the preferred site of attack by ozone. It is recognized that as the structural complexity of a PAH increases, two types of reaction are possible. The PAH may undergo initial 1,2,3-trioxolane formation and ultimate scission of the most reactive bond, and/or it may undergo aromatic substitution by ozone at the most reactive atom(s) to ultimately yield quinone products. This latter process is usually associated with the meso positions of acene structures.

Structure–reactivity data for the ozonation of aromatic substrates are found in the literature. In most cases, however, it is the effect of substituents on the rate of ozonation that has received attention rather than comparison among structurally dissimilar PAH. Several groups of workers have obtained the relative reactivities of substituted benzenes toward ozone,[6-8] and corresponding data for naphthalenes[9] and anthracenes[10] can be calculated from results in the literature. A paper published a decade ago by Razumovskii and Zaikov contains rate constants for the ozonation of five unsubstituted PAH at 20 °C and is unique in supplying the basis for at least some relative rate data.[11] The present paper reports the results of the competitive ozonation of nine PAH at 25 °C. The compounds utilized are shown in Figure 1. This paper also, for the first time, discusses the correlation of experimental relative rate data with calculated measures of reactivity.

Experimental Section

Materials. All PAH utilized were of highest available commercial grade and were used without further purification. No contaminants could be detected by gas chromatography on a capillary column and purities in excess of 99% were probable. The same was true for *p*-diiodobenzene (MCB). Chlorobenzene (Eastman) was distilled before use; its purity was comparable to the other materials employed. Nanograde dichloromethane (Mallinckrodt) was used throughout this study. Ozone–oxygen mixtures were prepared by flowing oxygen through a Welsbach T-23 ozone genertor. The average flow of ozone generated was 0.0021 ± 0.0006 mmol/min.

Analysis. Analyses of reaction mixtures were carried out on a Varian Model 3700 gas chromatograph and CDS 111 electronic integrator. An SE-30 capillary column (15 m, fused silica) was used in all runs.

Results

The present study made use of direct competitive techniques to evaluate relative reactivities. All studies were carried out at 25 °C. Solutions containing pairs of PAH were prepared in dichloromethane. The average total molarity was approximately 0.1 M, although more concentrated solutions (as high as 1.0 M) were sometimes utilized. Aliquots of these solutions were treated directly with ozone in an oxygen stream for varying lengths of time. Because of the ability of ozone to react with most organic substrates, no internal GC standard was added to the reaction mixture until 30 min to 3 h after the direct ozonation was concluded. Calibration factors for all PAH's relative to internal standards were predetermined over a wide range of concentrations. The internal standards utilized in this investigation were chlorobenzene, *p*-diiodobenzene, or phenanthrene, chosen so as to maximize GC separability.

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Table I. Relative Reactivities of PAH toward Ozone at 25 °C in Dichloromethane

system		k_{rel}	av dev	correction factors bond	correction factors atom	Razumovskii and Zaikov
benzene[a]	1	0.028	0.006	6	6	7.5×10^{-4}
triphenylene[b]	8	0.062	0.016	6	6	
naphthalene	2	0.236	0.020	4	4	0.03
phenanthrene	4	1.0		1	2	1.0[d]
chrysene[b]	7	1.72	0.08	2	2	
pyrene	5	1.90	0.12	2	4	1.0[d]
1,2-benzanthracene[e]	6	6.21	0.64	1	1	
perylene[c]	9	10.32	1.28	4	4	
anthracene[c]	3	11.32	1.34	1	2	62.5

[a] Run vs. naphthalene. [b] Average value of direct and indirect runs. See text. [c] Run vs. pyrene. [d] In the text of their article Razumovskii and Zaikov state pyrene is more reactive than phenanthrene. The numerical results presented, however, lead to a relative rate of unity. [e] The total relative rate of this compound is assumed to be evenly partitioned between the two reactions discussed in the text.

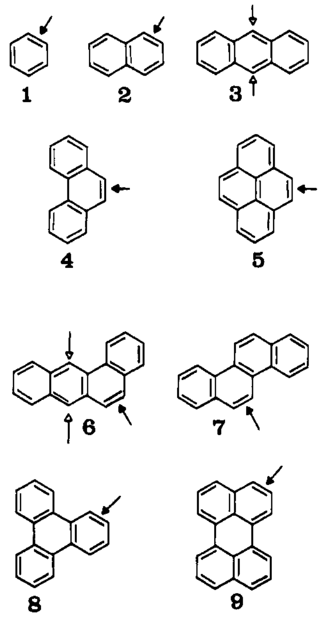


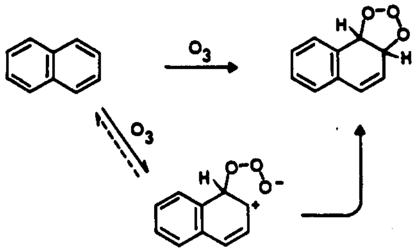
Figure 1. PAH studied. Closed arrows are directed to bonds cleaved. Open arrows directed to reactive meso positions.

In most cases, one member of the PAH pair was phenanthrene 4. This compound was chosen as a suitable reference in view of its expected reactivity in the mid-range among the substrates investigated. When extreme reactivity differences between PAH or GC inseparability precluded the use of phenanthrene, either naphthalene 2 or pyrene 5 was used in its place. Runs on selected systems indicate that no appreciable error is introduced into the results by this approach. Thus, for example, when chrysene 7 was run directly against phenanthrene a relative rate of 1.79 ± 0.11 was obtained. When chrysene was run against pyrene and the relative rate obtained was then multiplied by the pyrene–phenanthrene rate factor, a corresponding value of 1.64 ± 0.15 was found. Acceptable but slightly poorer agreement was found between the triphenylene–phenanthrene direct value of 0.05 ± 0.01 and the composite triphenylene–naphthalene times naphthalene–phenanthrene value of 0.07 ± 0.02. In both of these cases, weighted averages of all relative rates were used.

All reactions were run in replicate. Reaction times varied from 30 min to 4 h. In most runs (85%), PAH disappearance was limited to 25–55%. In some runs, however, up to 73% of PAH loss was observed. Table I summarizes all relative reactivities.

One entry in Table I merits a word of caution. Benzene occupies a unique position among the substrates investigated. It is both the least reactive compound studied and the most volatile at 25 °C. The amount of benzene that would normally evaporate under reaction conditions in the absence of ozone was determined and utilized as a correction factor. Table I shows these corrected results. Because of these uncertainties the benzene value is best regarded as an upper limit of reactivity. Such corrections were unnecessary for the other PAH's studied.

Scheme I



Discussion

The structures in Figure 1 show arrows directed toward specific bonds or atom pairs indicating those sites of preferred reaction as summarized by Bailey.[5] It is usual to observe that each PAH yields one specific product, although prolonged exposure to ozone can lead to subsequent degradation and the formation of a secondary product. Only in the case of one of these PAH, 1,2-benzanthracene 6, is a situation encountered where reaction at different sites occurs with comparable facility.[12,13] This PAH possesses both an extremely reactive bond between atoms 5 and 6 and a pair of reactive meso positions at atoms 7 and 12. The relative importance of reaction at these two sets of positions is not clear. It was originally claimed that 6 is exclusively oxidized to the quinone by ozone.[12] Subsequent workers, however, have reported that ozonolysis also occurs, with reaction at the 5–6 bond predominating.[13] In view of this, we have arbitrarily chosen to assume that the total reactivity of this PAH is due to equal rates of these two reactions; however, only modest changes are found in the correlations given below if either of these alternative pathways is assumed to represent the sole reaction of 1,2-benzanthracene.

Over the past quarter century, workers have attempted to distinguish between attack by ozone at the "bonds" or the "atoms" of aromatic systems. The former possibility may be treated as the aromatic equivalent of the 1,3-dipolar addition of ozone to a double bond to initially form a 1,2,3-trioxolane in the Criegee ozonolysis mechanism.[14]

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Table II. Summary of Linear Least Squares Correlations of Relative Rate Data for the Reaction of PAH with Ozone with Various Molecular Orbital Parameters

nature of correlation		correlation coefficient	stand dev
bislocalization	HMO	0.504	0.983
	PMO	0.841	0.616
σ-complex formation	HMO	0.901	0.460
	PMO	0.937	0.370
π-complex formation	$Ox_{1/2}$	0.896	0.421
	IP	0.897	0.418
SCF-MO	HOMO[a]	0.899	0.413

[a] Calculated using the SCF-MO method.[26]

The latter can be considered as an electrophilic aromatic substitution to initially form a σ-complex that then cyclizes. These two possibilities are illustrated using naphthalene as the PAH in Scheme I. This controversy is discussed in detail by Bailey.[5] In terms of molecular orbital theory, the pathways differ with respect to the number of ring carbon atoms removed from conjugaton in the rate-determining step. Proponents of both views are fond of citing the behavior of specific compounds to buttress their positions. Support for bond attack is obtained from the tendency of pyrene **5** to react at the C_4–C_5 bond[15] even though position 1 has the most favorable atom localization energy. Conversely, anthracene **3** (and larger acenes) undergo very little bond attack, but preferentially yield quinones on reaction with ozone due to attack at reactive meso positions.

Relative rate data are given in Table I. The corresponding results of Razumovskii and Zaikov[11] are also given when available. There is a strong parallelism between their results and those from the present study. A plot of the logarithms of the two sets of relative rate data yield a linear correlation with a coefficient of 0.994. The slope of 1.89 ± 0.07 found for the correlation, however, indicates a much greater sensitivity to PAH identity in the work by the Russians. Our studies were carried out at 25 °C while the Russians utilized a temperature of 20 °C; this small temperature difference cannot explain the difference in selectivity. The earlier workers, however, used a much less polar solvent (carbon tetrachloride), than the dichloromethane utilized here; this difference in solvent could be quite important if the rate-determining step involves charge development and will be discussed below.

In performing correlations of this type, it is necessary to recognize that there are many possible parameters, and that these parameters may be obtained from calculations carried out at varying levels of sophistication. We have not tried to be all-inclusive in our choice of parameters; rather, we have chosen to confine ourselves to parameters that have been suggested in the literature.

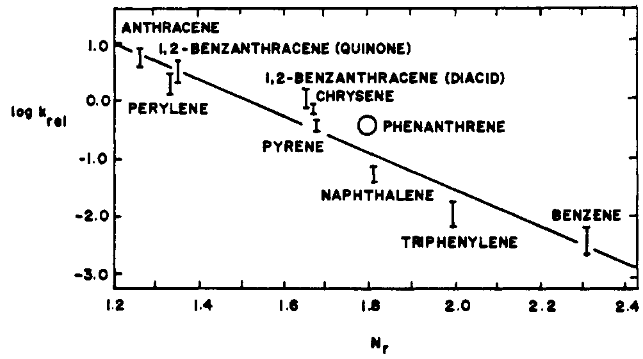
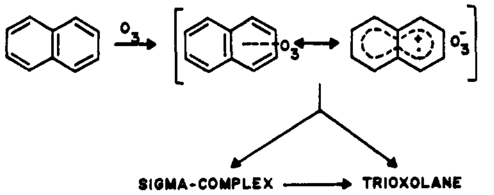


Figure 2. Logarithms of statistically corrected relative rates of the reactions of PAH with ozone vs. PMO reactivity number.

Scheme II



The bond attack pathway can be most readily treated by utilizing bislocalization energies, which may be regarded as the π-energy difference between the starting arene and a system with two fewer atoms in the conjugated system. This approach, which does not require that the two atoms in question be bonded to each other, was originally discussed by Wallenberger.[16] A linear least squares analysis between HMO values of these energies[17] and the logarithms of our statistically corrected rate ratios[18] yielded a very poor correlation with a coefficient of only 0.504. (All correlation data are summarized in Table II.) A somewhat better correlation was obtained if the bislocalization energies were calculated from Dewar's PMO approach;[19] however, the correlation coefficient is still only 0.841. The poor showing of this model may be traced to two experimental points. Firstly, the inherent difference between systems that undergo bond cleavage and those which undergo para quinone formation is great; ortho and para bislocalization energies may, therefore, not be directly comparable. Indeed, in earlier discussions of the preferred position of ozone attack, workers have suggested that "empirical correction factors" be added to the para bislocalization energies to bring them in line with their ortho counterparts.[17a] The same incompatability of terms appears to hold in the present case, thus invalidating attempts to utilize both within the same correlation. While this may, in part, be correct, it should be noted that poor correlations are still found for this model even when compounds that lead to formation of quinones are *not* included among the data. The most serious discrepancy concerns the reactivity of perylene **9**. Based on bislocalization energies, this PAH should be no more reactive than naphthalene **2**. It has even been suggested that its reactivity might be slightly less than that of the latter PAH.[20] We find, however, that **9** is over 40 times as reactive as **2**. The failure of this model thus appears to be real and not due to an artifact of the calculations.

The model involving rate-determining attack at a single ring carbon has been similarly evaluated.[21] Utilization of HMO localization energies[17] gives a linear correlation with a coefficient of 0.901. The corresponding PMO "reactivity number"[19] again provides a better value of 0.937; this op-

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(21) The parameters employed correspond to those for the positions that are actually attacked. Thus, in pyrene atom 4 rather than atom 1 is considered. Calculations all show atoms 5 and 6 in 1,2-benzanthracene to be virtually equivalent. An average of the localization energies for these two sites was used.

Table III. Solvent Effect on Anthracene-Pyrene Relative Reactivity at 25 °C

solvent	e_{25}	k_{rel}
carbon tetrachloride	2.23	15.6 ± 1.5
benzene	2.27	5.32 ± 0.59
dichloromethane	8.90	5.96 ± 0.33
acetone	20.7	2.92 ± 0.54
acetonitrile	37.4	3.04 ± 0.22

timum correlation is illustrated in Figure 2. These results suggest that atom attack is a better model for ozone–PAH reactivity than is bond attack.

An additional pathway for PAH–ozone reactions also might exist. Ozone has long been known to be capable of forming charge-transfer complexes with aromatic systems.[22] Originally these π-complexes were prepared and investigated at high dilution in glasses at −195 °C, but recent work in our laboratory indicates that an ozone–cumene complex can be detected in concentrated solution even at −40 °C.[23] The possiblity that the formation of such complexes lies on the pathway of ozonation, and might even affect the rate-determining step, has received less support in the literature than the two pathways previously discussed. Scheme II shows the relationship of a charge-transfer complex to the previously discussed intermediates using naphthalene as a representative system. Formation of such a complex represents a situation in which no atoms of the PAH are removed from conjugation; instead, an electron has been transferred to ozone from a delocalized molecular orbital of the PAH. This suggests that correlation with experimental ionization potentials, half-wave oxidation potentials and/or charge-transfer bands of the PAH's are all appropriate. Calculated energies of the corresponding HOMO's would also be a suitable parameter. Since the PAH are acting as units in all these cases, no statistical correction need be applied to the experimentally obtained relative rates.

As might be expected, all the above parameters are closely interrelated and give essentially equivalent correlations. Use of half-wave oxidation potentials[24] yields a linear relationship with a correlation coefficient of 0.896. Use of a typical set of ionization potentials,[25] produces a corresponding correlation coefficient of 0.897. Finally, HOMO energies, as calculated by an SCF MO approach,[26] give a coefficient of 0.899. While all these correlation coefficients are only modest, they are comparable to those found for the σ-complex model.

Further support for those pathways in which ions and/or radical–ions are intermediates is obtained from a consideration of the solvent effects upon ozone–PAH selectivity. As has already been mentioned, Razumovskii and Zaikov[11] observed a much greater selectivity in carbon tetrachloride than we obtained in dichloromethane. We have examined a specific PAH pair (anthracene–pyrene) undergoing competitive ozonation at 25 °C in five solvents to ascertain whether overall trends can be determined. (It was not possible to use a wider range of solvents because the solvents must have low reactivity toward ozone, have GC separability, and have the ability to dissolve the large, non-polar PAH. The results are given in Table III. The selectivity in carbon tetrachloride is appreciably greater than that found in dichloromethane, in agreement with the findings of the Russian workers, and selectivity generally decreases with increasing solvent polarity. This would, in terms of a traditional reactivity–selectivity relationship, imply greater reactivity for PAH undergoing ozonation in solvents of higher dielectric constant, presumably because of stabilization of charged intermediates.

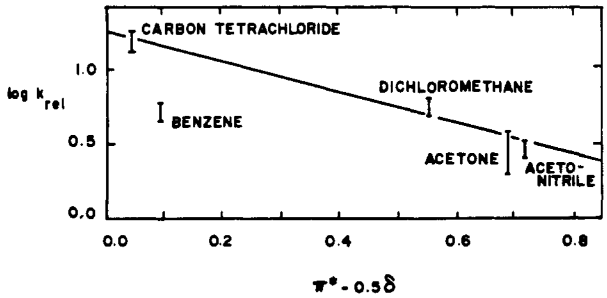

Figure 3. Logarithm of relative reactivity for reaction of anthracene/pyrene with ozone vs. the polarity–polarizability parameters of the solvents employed.

Taft, Kamlet, and their co-worker have developed various linear solvation energy relationships.[27] If benzene is excluded, a good linear relationship can be obtained between the logarithms of our anthracene–pyrene relative rate factors and their solvent polarity parameter, π*, when corrected for differences in polarizability, δ, between "normal" and polyhalogenated solvents.[28] For this correlation, a coefficient of 0.977 is found. The correlation is shown in Figure 3. The extremely large deviation of the data obtained in benzene from the overall correlation is most likely due to the ability of this solvent to stabilize an intermediate ion by complexation, a factor that is not taken into account in the Taft–Kamlet approach. The results obtained in benzene are more supportive of a rate-determining σ-complex formation since, if rate-determining ozone–PAH π-complexation were taking place, greater rather than less selectivity would be expected in this solvent. One must be cautious, however, in utilizing the results obtained in a single solvent in so conclusive a manner. There exists such a plethora of solvent parameters that a set may be chosen in which benzene exhibits no special behavior. The little used E_K scale developed by Walther is one such example.[29]

Conclusions

We feel that the results of these studies favor a mechanism for the PAH–ozone reaction involving a rate-determining electrophilic substitution by ozone. Not only do the calculated parameters obtained from this model best correlate the rate data, but the large dependence of selectivity on solvent polarity also favors a reaction involving formation of a charge-separated species. Previous doubt concerning this mechanism has centered on the behavior of pyrene **5**, where the products isolated correspond to attack at a less favorable position than predicted. This dilemma can be resolved if σ-complex formation is regarded as a reversible process and if loss of ozone and re-aromatization of the σ-complex compete with cyclization. This would be equally true whether the cyclization occurs at an atom adjacent to that originally attacked to form a 1,2,3-trioxolane or in a transannular fashion to yield a bicyclic ozonide which would give rise to quinone prod-

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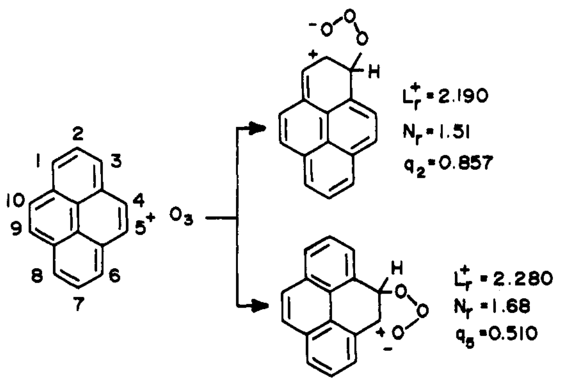
Scheme III



ucts. Steric or electronic factors which militate against cyclization will favor the reverse reaction; this reversal will then lead to other σ-complexes that can cyclize more readily, thus resulting in formation of products not consistent with attack by ozone at the "most favorable" atom. This is diagramatically represented for pyrene in Scheme III. Both the HMO atom localization and PMO reactivity number parameters slightly favor attack at position 1 relative to position 4. Subsequent 1,2,3-trioxolane formation would occur via bonding between the negatively charged terminal oxygen and an accessible positively charged carbon. When initial ozone attack is at position 4, position 5 maintains a large amount of positive charge (low charge density, q) and cyclization would be expected to be rapid. However, if the initial attack occurs at position 1, position 2 has less positive character, cyclization would be slower, and more reversal could occur. Thus the observed products found would be those expected from attack at the C_4–C_5 bond.

Acknowledgment. This work was supported in part by grants from the National Science Foundation, the National Institutes of Health (HL-16029), and the National Foundation for Cancer Research.

Registry No. Benzene, 71-43-2; triphenylene, 817-59-4; naphthalene, 91-20-3; phenanthrene, 85-01-8; chrysene, 218-01-9; pyrene, 129-00-0; 1,2-benzanthracene, 56-55-3; perylene, 198-55-0; anthracene, 120-12-7.

Substitution Reactions of Nitrothiophenes. 6. Disparate Mechanisms for Substitution Reactions at Neopentyl Carbons Bearing 4- and 5-Nitrothienyl Groups[1,2]

Felicity I. Flower, Peter J. Newcombe, and Robert K. Norris*

Department of Organic Chemistry, The University of Sydney, N.S.W., 2006 Australia

Received April 22, 1983

The reaction of the (5-nitro-2-thienyl)- and (4-nitro-2-thienyl)neopentyl chlorides (**9** and **10**) with *p*-toluenesulfinate, azide, and *p*-toluenethiolate ions proceeds smoothly and in high yield (70–95%) under mild conditions (20 °C, Me_2SO) to give the sulfones **14** and **15**, the azides **16** and **17**, and the sulfides **18** and **19**, respectively. The mechanisms of these substitutions are quite different, however. The substitutions in the 5-nitro series take place by the $S_{RN}1$ mechanism, whereas those in the 4-nitro series take place by the ionic S_N(AEAE) process, which involves initial attack of a nucleophile at the 5-position of the thiophene ring.

Nucleophilic substitution at a neopentylic carbon is a notoriously difficult process and is strongly sterically hindered under conditions which favor the S_N2 mechanism.[3] We have found that the benzylic substrate **1**, under S_N2 conditions, e.g., sodium benzenethiolate in Me_2SO, is extremely resistant to nucleophilic attack.[4] The *p*-nitrobenzylic analogue **2**, on the other hand, reacts very smoothly and gives a near quantitative yield of the sulfide **3**. Both **1** and **2** are sterically hindered because the benzylic carbon is also part of a neopentyl group. In similar fashion the lithium salt **4** of 2-nitropropane readily reacts with **2** to give the ketone **5**, whereas the chloride **1** is completely unreactive.[5] The substitution reactions of **2** have been shown[4,5] to be examples of the $S_{RN}1$ reaction,[6] which, for benzylic substrates, is given in Scheme I. More

ArCH(X)Bu^t

	Ar	X
1	Ph	Cl
2	p-$O_2NC_6H_4$	Cl
3	p-$O_2NC_6H_4$	PhS
6	m-$O_2NC_6H_4$	Cl
7	p-$O_2NC_6H_4$	p-$MeC_6H_4SO_2$
8	m-$O_2NC_6H_4$	p-$MeC_6H_4SO_2$

Scheme I

$$\mathrm{ArCR^1R^2X} + \mathrm{A^-} \longrightarrow [\mathrm{ArCR^1R^2X}]^{-\cdot} + \mathrm{A^\cdot} \qquad (1)$$

$$[\mathrm{ArCR^1R^2X}]^{-\cdot} \longrightarrow \mathrm{Ar\dot{C}R^1R^2} + \mathrm{X^-} \qquad (2)$$

$$\mathrm{Ar\dot{C}R^1R^2} + \mathrm{A^-} \longrightarrow [\mathrm{ArCR^1R^2A}]^{-\cdot} \qquad (3)$$

$$[\mathrm{ArCR^1R^2A}]^{-\cdot} + \mathrm{ArCR^1R^2X} \longrightarrow \mathrm{ArCR^1R^2A} + [\mathrm{ArCR^1R^2X}]^{-\cdot} \qquad (4)$$

$\mathrm{Li^+\ {}^-CMe_2NO_2}$ **4**

p-$\mathrm{O_2NC_6H_4COBu^t}$ **5**

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[1] (a) Supported by Grants C73-15098 and C79-15554 from The Australian Research Grants Scheme. (b) Abstracted, in part, from the Ph.D. Thesis of Peter J. Newcombe, The University of Sydney, Sept 1980. (c) For the previous paper in this series see ref 2.

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