31G**//HF/6-31G* + ZPVE level. The most striking contrast between this and the corresponding representations at HF/6-13G*//HF/6-31G* + ZPVE is that the higher level of theory favors bridged cations **11**, **13**, and **15**. Thus, the calculated activation energy for the conversion of **3** to **4** is lowered from 19.0 kcal/mol at HF/6-31G*//HF/6-31G* + ZPVE to only 6.1 kcal/mol at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE. This process corresponds to the 1,2-fluorine shift from the 3,3,3-trifluoro-2-propenyl cation (**3**) to the 1,1,2-trifluoroallyl cation (**4**).

Similarly, the barrier to 1,2-hydrogen migration from **3** to **14** is reduced to a mere 0.3 kcal/mol when electron-correlation effects are accounted for. Interestingly, structure **13** is still predicted to be a saddle point. This is in contrast to the studies on smaller systems where the bridging nonclassical cation was found to be a local minimum and not a transition state, after inclusion of electron correlation.[11]

It is striking that the *primary* and *secondary* vinyl cations **3** and **14** are predicted to be of very similar stability. This illustrates a strong destabilizing effect of CF_3 relative to hydrogen both α and β to a vinylic carbocation center.

1,3-Fluorine migration from **14** via the four-membered transition state **15** leads to **16**, the global minimum. Results at HF/6-31G**//HF/6-31G* + ZPVE predict the barrier for such a conversion to be 10.8 kcal/mol. However, at MP4(SDQ)/6-31G**//HF/6-31G* + ZPVE this barrier all but disappears. It is also remarkable that **3**, **13**, **14**, and **15** are so close in energy as to be not energetically distinguishable. As noted by a referee "formation of **3** would lead to a species that is just a point on a potential energy hypersurface that immediately collapses to **16**". Since the isomerization of **3** to **16** is exothermic by 40–50 kcal/mol, with little or no barrier, one would conclude that reaction of the 3,3,3-trifluoro-2-propenyl cation **3** in the gas phase should lead mainly to formation of the 1,1,3-trifluoroallyl cation **16**, with competing formation of the less stable isomer **4**. Solvation effects might result in a somewhat different pattern in solution.

Conclusions

Based on these calculations, the $C_3H_2F_3^+$ system should be ideal for observing fluorine migrations. It is predicted that the relatively unstable 3,3,3-trifluoro-2-propenyl cation **3** can readily rearrange to either the 1,1,2-trifluoroallyl cation **4** or the 1,1,3-trifluoroallyl cation **16**. By analogy, rearrangement via 1,2- or 1,3-fluorine shifts to allyl cations should be favorable in the system $CF_3CH{=}C^+CF_3$ as well. Efforts to observe these reactions experimentally are underway.

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Supplementary Material Available: Z-Matrices for **3–16** and tables of bond lengths, bond angles, and IR frequencies (23 pages). Ordering information is given on any current masthead page.

Regiochemistry of the Coupling of Aryl Radicals with Nucleophiles Derived from the Naphthyl System. Experimental and Theoretical Studies

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We here report the photostimulated reaction of unactivated aromatic halides with ambident nucleophiles derived from the naphthyl system such as 1- and 2-naphthylamide, 2-naphthoxide, 2-naphthalenethiolate, and 2-naphthaleneselenate ions, by the $S_{RN}1$ mechanism of nucleophilic substitution. According to our experimental results, C-arylation in position 1 of the naphthyl moiety is the only reaction observed with 2-naphthoxide ions and it is favored over N-arylation with 1- and 2-naphthylamide ions. Heteroatom arylation is preferred over C-arylation with 2-naphthalenethiolate ions while it is the only observed reaction with 2-naphthaleneselenate ions. A theoretical study was carried out to explain the regiochemistry of the system. In competition experiments, 2-naphthalenethiolate ions proved to be 1.8 ± 0.2 times more reactive than 2-naphthoxide ions for C-substitution toward *p*-anisyl radicals in liquid ammonia.

The radical mechanism of aromatic nucleophilic substitution, or $S_{RN}1$, is a well-known process by which a substitution is produced on a nonactivated adequately substituted substrate.[1] This nucleophilic substitution mechanism is a chain process that involves radicals and radical anions as intermediates. The main steps of this mechanism are sketched in Scheme I.

Scheme I

$$(RX)^{\bullet-} \rightarrow R^{\bullet} + X^{-} \qquad (1)$$

$$R^{\bullet} + Nu^{-} \rightarrow (RNu)^{\bullet-} \qquad (2)$$

$$(RNu)^{\bullet-} + RX \rightarrow RNu + (RX)^{\bullet-} \qquad (3)$$

Ambident behavior of anions in aromatic $S_{RN}1$ reactions is very rare. However, it has been found that aryl radicals

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[1] For reviews, see: (a) Rossi, R. A.; de Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism*; ACS Monograph 178; American Chemical Society: Washington, DC, 1983. (b) Bowman, W. R. *Chem. Soc. Rev.* **1988**, *17*, 283.

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Table I. Reactions of 1- and 2-Naphthylamide Ions with Aryl Halides in Liquid Ammonia[a]

expt.	nucleophile	substrate[b] (M × 10^3)	% X^- [c]	ArH	substitution products (%)[d]
1	2-$C_{10}H_7NH^-$	PhI (8.9)	48	*e*	**3a** (47), **4a** (<1)
2[f]	2-$C_{10}H_7NH^-$	PhI (8.9)	≤3		
3	2-$C_{10}H_7NH^-$	*p*-IAn (7.5)	79	14	**3b** (62), **4b** (6)
4[f]	2-$C_{10}H_7NH^-$	*p*-IAn (7.5)	≤3		
5[g]	2-$C_{10}H_7NH^-$	*p*-IAn (7.5)	32	5	**3b** (29), **4b** (3)
6[h]	2-$C_{10}H_7NH^-$	*p*-IAn (7.5)	12	2	**3b** (6)
7	2-$C_{10}H_7NH^-$	*p*-BrAn (7.9)	14	*e*	**3b** (12)
8	2-$C_{10}H_7NH^-$	1-INaph (7.9)	50	8	**3c** (44)
9	2-$C_{10}H_7NH^-$	1-INaph (3.7)	82	15	**3c** (65)
10[f]	2-$C_{10}H_7NH^-$	1-INaph (7.9)	≤3		
11[i]	2-$C_{10}H_7NH^-$	1-INaph (8.9)	73	44	**3c** (5)
12[j]	2-$C_{10}H_7NH^-$	1-INaph (7.9)	73	41	**3c** (17)
13	2-$C_{10}H_7NH^-$	1-BrNaph (7.2)	33	6	**3c** (25)
14	1-$C_{10}H_7NH^-$	*p*-IAn (8.2)	85	8	**6** (46), **7** (43)
15[f]	1-$C_{10}H_7NH^-$	*p*-IAn (8.2)	≤3		

[a] Irradiation time, 180 min; concentration of the nucleophile potassium salt, 0.015 M. [b] *p*-IAn = *p*-iodoanisole; 1-INaph = 1-iodonaphthalene. [c] Quantified potentiometrically on the basis of the substrate concentration. [d] Quantified by GLC using the internal standard method. [e] Not quantified. [f] Dark reaction. [g] *p*-Dinitrobenzene (20 mol %). [h] *t*-ButOLi. [i] DMSO as solvent. [j] *tert*-Butylamine/NH_3 (30:70) as solvent.

couple with some nucleophiles in more than one position. This behavior has been observed, for instance, in the phenylation of (*p*-anisyl)propenide ion, where the reaction occurred at C-1 and C-3 to almost the same extent.[2]

Also, it has been observed that the phenylacetonitrile anion reacts with 4-bromopyridine by the $S_{RN}1$ mechanism giving the straightforward substitution product (4-pyridyl)phenylacetonitrile as well as a small amount of coupling at C-2 and C-4 of the phenyl ring of the nucleophile.[3] With respect to the phenylamide ion, it has been reported that the solvated electron stimulated reaction of its potassium salt with iodobenzene in liquid ammonia gave diphenylamine (19%) and *o*- and *p*-phenylaniline in 11% yield each.[4]

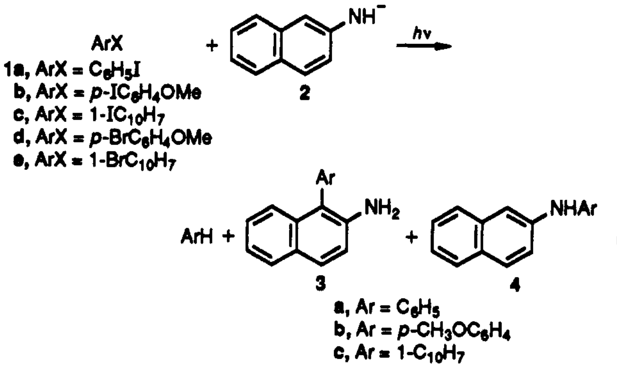
For aromatic alkoxide ions, it has been recently reported that the reaction of phenoxide ions with *o*-, *m*-, or *p*-chlorobenzonitriles, *p*-bromobenzophenone, or 2-chloroquinoline catalyzed with electrons from a cathode gave arylation at C-2 and C-4 of the phenoxide ring. When one of these positions was blocked with a *tert*-butyl group, only one product was formed.[5,6] A similar behavior has been reported for the photostimulated reactions.[7] It has also been reported that in photostimulated reactions with haloarenes, 2-naphthoxide ions gave only C-arylation at C-1.[7,8]

Benzenethiolate[9] and benzeneselenate[10] ions react with aryl radicals by the $S_{RN}1$ mechanism, and coupling on the heteroatom was the only observed reaction. As O, S, and Se belong to the same row of elements of the periodic table and considering the regiospecificity of the 2-naphthoxide ion reaction, we studied the photostimulated reactions of 2-naphthoxide, 2-naphthalenethiolate, and 2-naphthaleneselenate ions toward aryl halides in order to determine the regioselectivity pattern of the system. The 1- and 2-naphthylamide ions were included for comparison. Also we determined the relative reactivity of 2-naphthoxide vs 2-naphthalenethiolate ions toward *p*-anisyl radicals.

A theoretical study was performed in order to determine the factors that control the regiochemistry experimentally observed.

Results

1- and 2-Naphthylamide Ions. The photostimulated reaction of iodobenzene, bromobenzene, and *p*-iodoanisole with phenylamide ions or *p*-tolylamide gave a low yield of substitution products. The highest percentage with both nucleophiles corresponds to the ortho-substituted compounds.[11] These results led us to investigate the reactions of haloaromatic compounds **1a–e** with the anion 2-naphthylamide (**2**) (eq 4).[12]



(4)

The photostimulated reaction of iodobenzene (**1a**) with **2** occurs in a 48% yield (as determined by the halide ion liberated) with formation of 1-phenyl-2-naphthylamine (**3a**) in 47% yield. Traces of the N-substitution product **4a** were observed (Table I, experiment 1).

In the reactions carried out with *p*-iodoanisole (**1b**) and 1-iodonaphthalene (**1c**), the 1-substituted compounds **3b** and **3c** were the main products formed, in 62% and 65% yields, respectively (Table I, experiments 3 and 9). When the reaction was carried out with the lithium instead of

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(9) (a) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173, 3611; **1975**, *40*, 3740. (b) Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 1506.

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Table II. Reactions of 2-Naphthoxide and Phenoxide Ions with Aryl Halides in Liquid Ammonia[a]

expt	nucleophile	substrate[b] ($M \times 10^3$)	% X^{-}[c]	ArH	substitution products (%)[d]
1	$2\text{-}C_{10}H_7O^-$	*p*-IAn (7.5)	61	13	**9b** (42)
2[e]	$2\text{-}C_{10}H_7O^-$	*p*-IAn (7.5)	≤3		
3[f]	$2\text{-}C_{10}H_7O^-$	*p*-IAn (7.5)	17	2	**9b** (12)
4	$2\text{-}C_{10}H_7O^-$	*p*-BrAn (7.5)	13		
5	$2\text{-}C_{10}H_7O^-$	1-INaph (7.0)	76	20	**9c** (53)
6[e]	$2\text{-}C_{10}H_7O^-$	1-INaph (7.0)	≤3		
7[g]	$2\text{-}C_{10}H_7O^-$	1-INaph (7.0)	78	36	**9c** (20)
8	$C_6H_5O^-$	*p*-IAn (7.5)	27	23	
9	$C_6H_5O^-$	4-BrBenz (7.5)	44	15	**11** (17), **12** (9)
10[e]	$C_6H_5O^-$	4-BrBenz (8.2)	≤3		

[a] Irradiation time, 180 min; concentration of the nucleophile potassium salt, 0.015 M. [b] *p*-IAn = *p*-iodoanisole; 4-BrBenz = 4-bromobenzophenone; 1-INaph = 1-iodonaphthalene. [c] Quantified potentiometrically on the basis of the substrate concentration. [d] Quantified by GLC using the internal standard method. [e] Dark reaction. [f] *p*-Dinitrobenzene (20 mol %). [g] Ammonium ion as counterion.

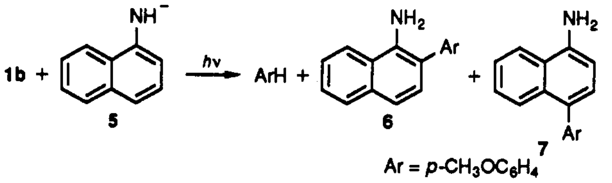
the potassium salt of the nucleophile, a low yield of substitution was determined (Table I, experiment 6). This could be ascribed to the known lower solubility of the lithium salt compared with the potassium salt of amides.[1a]

The photostimulated reactions of the bromo-substituted substrates, such as *p*-bromoanisole (**1d**) and 1-bromonaphthalene (**1e**) with **2**, gave much lower yields than those of the iodine derivatives (Table I, experiments 7 and 13). These results are in agreement with the halogen mobility in the photostimulated $S_{RN}1$ reactions (I > Br > Cl).[1]

The reactions were inhibited by *p*-dinitrobenzene (*p*-DNB) (Table I, experiment 5), a well-known inhibitor of $S_{RN}1$ reactions, and they do not occur in the absence of light stimulation (Table I, experiments 2, 4, and 10).

In order to determine the solvent effect on the preferred site of coupling, we performed the photostimulated reaction of anion **2** with **1c** in DMSO or *tert*-butylamine/ammonia as solvent.[13a] With both solvents, we determined an increased yield of reduction as expected from their major H-donor ability,[1a,13a] with substitution mainly at the C-1 position as observed in liquid ammonia (Table I, expeiments 11 and 12).

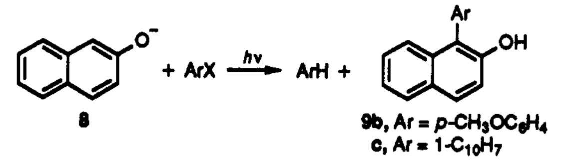
Another nucleophile studied was 1-naphthylamide (**5**), its photostimulated reaction with **1b** being regioselective, with formation of 2-(*p*-anisyl)-1-naphthylamine (**6**) and 4-(*p*-anisyl)-1-naphthylamine (**7**) in 46% and 43% yields, respectively (eq 5) (Table I, experiment 14). This anion failed to react in the absence of photostimulation (Table I, experiment 15).



(5)

Attempts to determine the regiochemistry of the coupling reaction for the 2-anthranylamide ion failed. The low reaction yield observed is probably due to its low solubility in liquid ammonia.

2-Naphthoxide Ions. We studied the photostimulated reactions of the haloaromatic compounds **1b–d** with the 2-naphthoxide anion (**8**) (eq 6). The photostimulated reaction (180 min) of **8** with **1b** in liquid ammonia afforded a 61% yield of iodide ions. The reduction product anisole (13% yield) and the substitution product 1-(*p*-anisyl)-2-naphthol (**9b**) (42% yield) were the only reaction products formed (Table II, experiment 1). The reaction with *p*-bromoanisol (**1d**) is much more sluggish than with **1b** (bromide ions, 13% yield) (Table II, experiment 4).



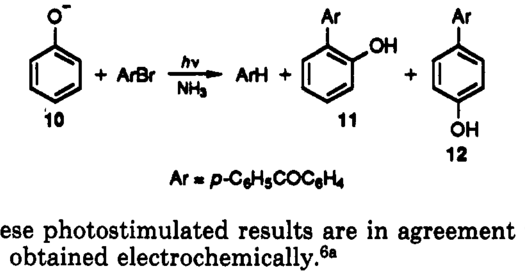
(6)

In the photostimulated reaction of **8** with 1-iodonaphthalene (**1c**) (180 min), we found iodide ion (76% yield), naphthalene (20% yield), and the substitution product 1-naphthyl-2-naphthol (**9c**) in 53% yield (Table II, experiment 5).

The reaction of **8** with either **1b** or **1c** did not occur in the dark while its photostimulated reaction with **1b** was inhibited by *p*-DNB (Table II, experiments 2, 6, and 3, respectively).

We also observed substitution in the photostimulated reaction of 2-naphthol with **1c**. In this case the ammonium salt was probably formed in liquid ammonia. In this reaction there was an increased amount of naphthalene (36%)[13b] together with a 20% yield of the substitution product **9c** (Table II, experiment 7).

On the other hand, the photostimulated reaction of phenoxide ion (**10**) with **1b** (180 min) gave a 27% yield of iodide ion with anisole as the only product detected (23% yield, Table II, experiment 8). The photostimulated reaction of **10** with an electrophilic substrate such as 4-bromobenzophenone gave ortho (**11**) and para substitution products (**12**) in 17% and 9% yield, respectively, together with 15% of benzophenone (Table II, experiment 9) (eq 7). The reaction does not occur in the dark (Table II, experiment 10).



(7)

These photostimulated results are in agreement with those obtained electrochemically.[6a]

2-Naphthalenethiolate Ions. The photostimulated reaction of 2-naphthalenethiolate ions (**13**) with *p*-iodoanisole (**1b**), after quenching with methyl iodide, gave mainly S-coupling of aryl radicals (65%) and a small amount of C-arylation (14%). It is interesting to note that this is the first example in which an arenethiolate ion

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Table III. Reactions of Haloaromatic Compounds with 2-Naphthalenethiolate and 2-Naphthaleneselenate Ions in Liquid Ammonia[a]

expt	nucleophile (M × 10^3)	ArX[b] (M × 10^3)	% I^-[c]	ArH[d]	substitution products (%)[d]
1	2-$C_{10}H_7S^-$ (15.0)	*p*-IAn (7.5)	90	12	**14b** (14), **15b** (65)
2[e]	2-$C_{10}H_7S^-$ (15.0)	*p*-IAn (7.5)	<3		
3[f]	2-$C_{10}H_7S^-$ (15.0)	*p*-IAn (7.5)	10	*g*	**14b** (2), **15b** (6)
4	2-$C_{10}H_7S^-$ (15.0)	1-INaph (7.9)	99	8	**15c** (95)
5[e]	2-$C_{10}H_7S^-$ (15.0)	1-INaph (7.9)	<3		
6	2-$C_{10}H_7Se^-$ (10.0)	*p*-IAn (7.5)	85	7	**17** (85)
7[e]	2-$C_{10}H_7Se^-$ (10.0)	*p*-IAn (7.5)	<5		
8[f]	2-$C_{10}H_7Se^-$ (10.0)	*p*-IAn (7.5)	22	4	**17** (7)

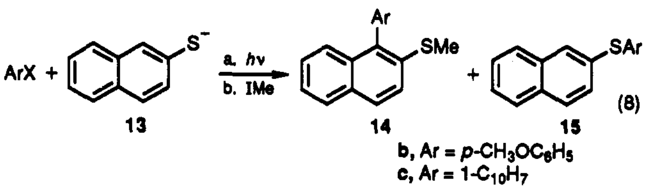
[a] Irradiation time, 180 min; potassium salt of the nucleophiles. [b] *p*-IAn = *p*-iodoanisole; 1-INaph = 1-iodonaphthalene. [c] Quantified potentiometrically on the basis of substrate. [d] Quantified by GLC using the internal standard method. [e] Dark reaction. [f] *p*-Dinitrobenzene (20 mol %). [g] Not quantified.

Table IV. Competition Experiments between 2-Naphthoxide and 2-Naphthalenethiolate Ions toward *p*-Iodoanisole in Liquid Ammonia[a]

2-$C_{10}H_7S^-$ M × 10^3	2-$C_{10}H_7O^-$ M × 10^3	*p*-IAn[b] M × 10^3	% I^-[c]	substitution products (%)[d]		
				15b	**9b**	k_{13}/k_8
7.9	35.2	3.5	90	23	61	1.72
8.0	35.4	3.7	92	23	63	1.65
8.8	17.9	4.3	90	41	43	2.05
					average:	1.8 ± 0.2

[a] Irradiation time, 180 min; potassium salt of the nucleophiles. [b] *p*-IAn = *p*-iodoanisole. [c] Quantified potentiometrically on the basis of substrate. [d] Quantified by GLC using the internal standard method.

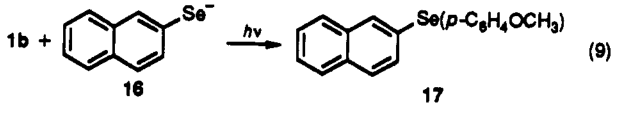
couples at a carbon atom beside the sulfur atom (Table III, experiment 1) (eq 8).



When the reaction of **13** with **1c** was performed, the only product observed was the product of coupling on the sulfur position of the nucleophile (95%) (Table III, experiment 4). The reaction of **13** with either **1b** or **1c** did not occur in the dark, and its photostimulated reaction with **1b** was inhibited by *p*-DNB (Table III, experiments 2, 5, and 3, respectively).

2-Naphthaleneselenate Ions. The photostimulated reaction of *p*-haloanisoles with benzeneselenate ions in liquid ammonia gave a mixture of products due to the reversible coupling of *p*-anisyl radicals with $PhSe^-$ and to the fragmentation of the radical anion intermediates.[14]

In the photostimulated reaction of *p*-iodoanisole (**1b**) with 2-naphthaleneselenate ion (**16**), no scrambling of aryl rings was observed, and the only product obtained was that of coupling on selenium, **17** (85% yield) (Table III, experiment 6).



This reaction does not occur in the dark, and the photostimulated reaction is inhibited by *p*-DNB (Table III, experiments 7 and 8).

Competition Reactions. Once the yields of substitution products **9b** and **15b** were determined in the photostimulated reaction of *p*-iodoanisole with 2-naphthoxide (**8**) and 2-naphthalenethiolate (**13**) ions in excess, it was possible to calculate k_{13}/k_8 by using eq 10.[15] $[NaphS^-]_0$

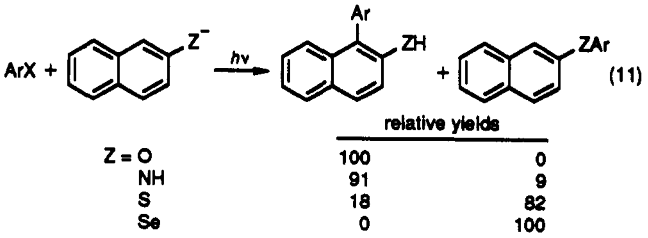
$$\frac{k_{13}}{k_8} = \frac{\ln [NaphS^-]_0/[NaphS^-]_t}{\ln [NaphO^-]_0/[NaphO^-]_t} \tag{10}$$

and $[NaphO^-]_0$ are initial concentrations, and $[NaphS^-]_t$ and $[NaphO^-]_t$ are concentrations at time *t*. This equation is based on a first-order reaction of both nucleophiles with the *p*-anisyl radicals. The k_{13}/k_8 thus determined was 1.8 ± 0.2 (Table IV).

Discussion

From all the results here presented we can conclude that the photostimulated reaction of these nucleophiles with haloaromatic substrates takes place through the $S_{RN}1$ mechanism and that the regiochemistry of the coupling reaction depends on the heteroatom present in the nucleophile. Thus, for the 2-naphthyl system with oxygen as heteroatom, the reaction is regiospecific with C-substitution as the only product observed, while with nitrogen, traces of N-substitution appear. An opposite behavior is observed with the sulfur and selenium derivatives. Coupling on the heteroatom is the main reaction product with sulfur, while it is the only product formed with selenium.

In eq 11 is shown the average product distribution for the photostimulated reactions of these nucleophiles with aryl radicals, considering the substitution products as 100% reaction.



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(15) Bunnett, J. F. In *Investigation of Rates and Mechanisms of Reactions*, 3rd ed.; Lewis, E. S., Ed.; Wiley-Interscience: New York, 1974; Part I, p 159.

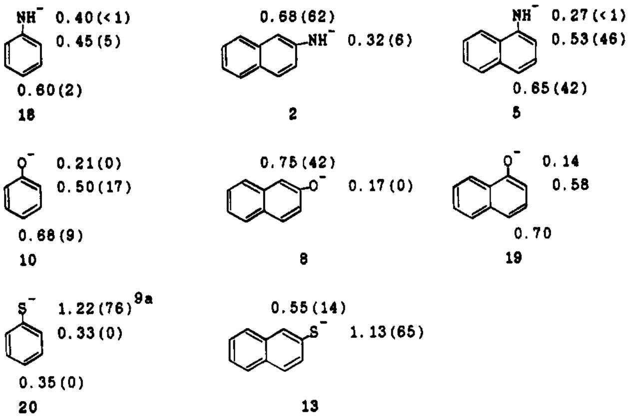


Figure 1. Stabilization energies (eV) for the different coupling positions for nitrogen, oxygen, and sulfur nucleophiles. The experimental values are in parentheses.

From our competition experiments, we could determine that 2-naphthalenethiolate ion is 1.8 times more reactive than 2-naphthoxide ion. On the other hand, it has been found that ketone enolate anions, such as the pinacolone enolate ion, are about 12 times more reactive than benzenethiolate ions.[16] We can estimate that for C-coupling with aryl radicals pinacolone enolate ion is about 22 times more reactive than 2-naphthoxide ion.

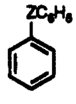
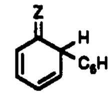
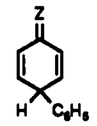
Different approaches can explain the regiochemistry of these reactions. It is usually considered that the regiochemistry of the coupling reaction is governed by thermodynamic control, the product predominantly formed being that generated from the most stable radical anion.[17]

On the other hand, the idea that basicity controls the rates of free-radical addition can also be invoked. In this case we deal with the relative basicities of two or more sites in an ambident anion. Not much attention was paid to this idea because, in the great majority of cases, the thermodynamic stability of radical anions is enough to explain the regiochemistry observed. However, Tolbert et al. have proposed that with ambident carbanions, for which the two approaches give opposite predictions, the product resulting from arylation at the site of highest basicity is the major one.[18]

This problem can also be analyzed through the frontier orbital (FO) theory, which proved to be useful in other cases.[1a] In order to determine the factors governing the regiochemistry of our system, we decided to approach the problem analyzing the expected product distribution from an FO approach as well as considering the thermodynamics of the system.

According to the FO theory, the preferred site of coupling is that corresponding to bond formation at the atom bearing the largest orbital coefficient in the highest occupied molecular orbital (HOMO) of the carbanion.[19] The orbital densities thus serve as a criterion for regioselectivity. In general, the largest HOMO coefficient coincides with the thermodynamic prediction and the two approaches are indistinguishable.

Table V. MNDO Calculated Heats of Formation (kcal/mol) for Nucleophiles and Radical Anions

nucleophile $C_6H_5Z^-$	ΔH_f	ΔH_f radical anions		
				
Z = NH	13.93	39.45	40.36	45.20
Z = O	−42.35	−2.53	−14.08	−8.20
Z = S	−11.54	24.07	29.22	28.45

In order to determine these orbital densities, we proceeded to calculate the equilibrium geometries of the nucleophiles phenylamide (**18**), 2- and 1-naphthylamides (**2** and **5**, respectively), phenoxide ion (**10**), and 2- and 1-naphthoxide ions (**8** and **19**, respectively) as well as benzenethiolate (**20**) and 2-naphthalenethiolate ions (**13**). The calculations were carried out with the semiempirical MNDO method as implemented in AMPACK.[20]

The contributions to the stabilization energy[21] for the reaction of the phenyl radical with different positions of the nucleophiles studied are presented in Figure 1.[22]

In the case of nitrogen nucleophiles, we can see that for the phenylamide ion the coupling at the ortho C position has almost the same stabilization as that at the nitrogen position while coupling at the para C position is slightly more favored than coupling at the previous two. Experimentally, we have determined low yields of substitution in the photostimulated reaction of iodobenzene with this nucleophile.[11] The product distribution determined was N-substitution (<1%), ortho C-substitution (ca. 5%), and para C-substitution (ca. 2%). The fact that ortho C-substitution is experimentally preferred over N-substitution and para C-substitution is ascribed to a statistically higher probability for the ortho site.

For nucleophile 2-naphthylamide (**2**), the highest stabilization corresponds to coupling at C-1, while for nucleophile 1-naphthylamide (**5**), couplings at positions C-2 and C-4 have similar probabilities of occurrence. With

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(16) Galli, C.; Bunnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 7140.

(17) Kornblum, N.; Ackermann, P.; Swiger, R. T. *J. Org. Chem.* **1980**, *45*, 5294.

(18) Tolbert, M. L.; Siddiqui, S. *Tetrahedron* **1982**, *38*, 1079. Tolbert, L. M.; Siddiqui, S. *J. Org. Chem.* **1984**, *49*, 1744.

(19) Within FO theory the stabilization energy is calculated according to

$$E = \sum_{i,j} c_{Hi} c_{Sj} \beta_{ij} / (E_a - E_b)$$

where c_{Hi} is the coefficient of the atomic orbital (AO) Φ_i of atom i in the HOMO frontier orbital of the nucleophile and c_{Sj} is that of the AO Φ_j of the radical center of the aromatic radical in the singly occupied molecular orbital (SOMO). β_{ij} is the resonance integral between atoms i and j in the transition state, and the summation is over all pairs of atoms i,j between which new bonds are being formed.

(20) Available from the Quantum Chemistry Program Exchange (QCPE), program 506.

(21) In all the cases here reported, the energies of the π MO of the nucleophiles are higher than the energy of the SOMO of the aromatic radical. For a situation like this, it is necessary to add, to the stabilization energy given by FO theory, an extra stabilization term equal to the energy difference between the frontier orbitals:

$$E = P_{ab} + (E_{SOMO} - E_{HOMO})$$

where P_{ab} is the frontier orbital term of the equation in footnote 19. The inclusion of the last term is due to the three-electron nature of the perturbation; however, as for a particular nucleophile the term ($E_{SOMO} - E_{HOMO}$) is constant, we only considered P_{ab} as a measurement of the energy stabilization for the different coupling sites.

(22) The values reported were calculated with β_{CC} = 5 eV, β_{CN} = 4.35 eV, and β_{CO} = 3.77 eV according to values previously reported[23] and assuming a distance between the reactivity sites of 2 Å in the transition state. β_{MNDO} values calculated for the geometry of minimum energy at an approach distance of 2 Å between the phenyl radical and the anions PhZ⁻ (Z = NH; O, S) were calculated. The values obtained, even though lower than the previous ones, follow the same order, that is, $\beta_{CC} > \beta_{CN} > \beta_{CO}$ with a β_{CS} higher than the β_{CC}. In our calculations, $\beta_{CS} = \beta_{CC}$ was used.

(23) Houk, N. K.; Sims, J.; Duke, R. E.; Strozier, R. W.; George, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7287. Houk, N. K.; Sims, J.; Watts, C. R.; Luskus, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 7301. See also: Bastide, J.; Ghandour, N. E.; Henri-Rousseau, O. *Bull. Soc. Chim. Fr.* **1973**, 2290, 2294.

both nucleophiles, C-coupling is preferred over N-coupling.

A similar trend is predicted by the FO theory for the case of oxygen nucleophiles. The differences in stabilization energy favoring C- vs O-coupling are higher with these ions than with the nitrogen analogues. On the other hand, with sulfur, the tendency is reversed, and coupling on sulfur is predicted as the more favorable reaction.

Independently of the heteroatom present in the system, C-substitution is enhanced in going from the phenyl to the naphthyl moiety, that is, as the π-system gets bigger.

These theoretical FO results are in agreement with our experimental findings as shown in eq 11.

In order to know if for our system the FO predictions follow the same trend as the thermodynamic control, we proceeded to calculate the minimal energy potential surface for the coupling reaction of phenyl radical with the nucleophiles PhZ^-. Naphthyl nucleophiles are not included due to the large size of their calculations. Our results indicate that the coupling reaction between a radical and the nucleophile under consideration takes place to give the intermediate radical anion without activation energy.[24] The difference in exothermicity for the coupling with the different possible positions was taken as a thermodynamic indication of the preferred site of coupling.

In Table V the heats of formation of the $C_6H_5Z^-$ anions with Z = NH, O, and S as well as those of the radical anions formed due to coupling on Z, ortho carbon, and para carbon are presented.

The radical anion formed due to coupling on nitrogen has almost the same stabilization energy as that formed due to coupling on the ortho carbon. The difference in energy favoring *o*-arylation increases when going from the nitrogen to the oxygen system while with both nucleophiles the *p*-arylation is the least favored reaction. For Z = S, the most stable radical anion is the one due to coupling on the heteroatom. These results agree with the FO predictions for the phenyl system.

We can conclude that the replacement of the heteroatom by a more electronegative one within a file of the periodic table increases the chances for C-substitution. C-Substitution is also favored by replacing the aryl moiety of the nucleophile by a more delocalized one. On the other hand, going down within a family of the periodic table leads to an increase in heteroatom substitution. In other words, as the heteratom of the nucleophile gets softer, the rate of its coupling reaction with the soft phenyl radical increases (Se > S > N > O), while with the harder oxygen, only C-substitution takes place.

Experimental Section

General Method. ^1H NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to Me_4Si (δ), with CCl_4 as the solvent. Mass spectra were obtained with a Finnigan 3300 f-100 mass spectrometer. Infrared spectra were recorded on a Nicolet FTIR 5-SXC spectrophotometer. Gas chromatographic analyses were performed on a Shimadzu GC-8A or Konik instrument with a flame-ionization detector and a Shimatzu CR-3A or Spectra Physics SP-2400 data system, using a column packed with 5% OV17 on Chromosorb G (1.5 m × 3 mm). Column chromatography was performed on silica gel (70–270 mesh, ASTM). Irradiation was conducted in a reactor equipped with four 250-W lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Potentiometric titration of halide ions was performed in a pH meter (Seybold Wien) using a Ag/Ag^+ electrode and a $AgNO_3$ standard. Melting points were obtained with a Büchi 510 apparatus and are not corrected. The high-resolution mass spectra were run in the Chemical Instrumentation Center of the Yale University.

Materials. 2-Naphthylamine (Merck), 1-naphthylamine (Merck), phenol (Merck), 2-naphthol (Merck), 2-naphthalenethiol (Aldrich), *tert*-butyl alcohol (Aldrich), iodobenzene (Aldrich), *p*-bromoanisole (Baker), *p*-iodoanisole (Fluka), 1-iodonaphthalene (Fluka), 1-bromonaphthalene (MCB-reagents), 4-bromobenzophenone (Aldrich), and methyl iodide (Fluka) were commercially available and used as received. 2-Naphthyl selenide ions were prepared from di-2-naphthyl diselenide and potassium metal in liquid ammonia. Di-2-naphthyl diselenide was prepared from selenium metal and 2-iodonaphthalene by photostimulated reaction in liquid ammonia.[25]

Photostimulated Reaction of 2-Naphthylamide Ion with *p*-Iodoanisole. The following procedure is representative of these reactions. The equipment used has been previously described.[1a] To 250 mL of distilled ammonia were added *tert*-butyl alcohol (7 mmol), a catalytic amount of $FeCl_3$ (ca. 5 mg), and then potassium metal (6 mmol) in small pieces (**CAUTION**: *This is a violent reaction*!).[1a] Once the *t*-BuOK was formed, 2-naphthylamine (3 mmol) was added. After 15 min, *p*-iodoanisole (1.5 mmol) was added and the reaction mixture was irradiated for 180 min. The reaction was quenched with an excess of ammonium nitrate. The ammonia was allowed to evaporate, water (50 mL) was added to the residue, and the mixture was extracted twice with diethyl ether (50 mL each). The iodide ions in the aqueous solution were determined potentiometrically. The organic extract was quantified by GLC (internal standard method). The solvent was removed under reduced pressure. The residue, after column chromatography on silica gel [eluted with petroleum ether/benzene (50:50)], gave 1-*p*-anisyl-2-naphthylamine, mp 128.5–130 °C (lit.[12] mp 128.5–130 °C), and *N*-*p*-anisyl-2-naphthylamine, mp 98–99.5 °C (lit.[12,26] mp 104 °C).

Reaction of 2-Naphthylamide Ion with *p*-Iodoanisole in the Dark. Following the same procedure as described before, except that the reaction flask was wrapped with aluminum foil, the iodide ion liberated was found in less than 3% yield after 180 min.

1-Phenyl-2-naphthylamine (3a): isolated by column chromatography and eluted with petroleum ether/benzene (60:40). The solid was recrystallized from petroleum ether, mp 91.5–92.5 °C (lit.[12,27] mp 93–94 °C).

1-Naphthyl-2-naphthylamine (3c): isolated by column chromatography and eluted with petroleum ether/benzene (60:40). The solid was recrystallized from petroleum ether, mp 190–191.5 °C (lit.[12,28] mp 189–190 °C).

2-*p*-Anisyl-1-naphthylamine (6): isolated by column chromatography and eluted with petroleum ether/benzene (60:40). The solid was recrystallized from petroleum ether, mp 147–148.5 °C:[11] IR (BrK) 3456, 3379 cm^{-1}; ^1H NMR δ 3.80 (3 H, s), 4.00 (2 H, s), 6.63–7.83 (10 H, m); MS (20 eV) *m*/*e* (relative intensity) 250 (17), 249 (100), 235 (21), 206 (1), 143 (20), 115 (19), 97 (3), 83 (6), 77 (3), 71 (12), 57 (27), 43 (21), 28 (91); MS (high resolution) 249.1149 (M^+, calcd 249.1153).

4-*p*-Anisyl-1-naphthylamine (7): isolated by column chromatography and eluted with benzene:[11] IR (KBr) 3450, 3376 cm^{-1}; ^1H NMR δ 3.57 (3 H, s), 3.95 (2 H, s), 6.40–8.00 (10 H, m); MS (30 eV) *m*/*e* (relative intensity) 250 (18), 249 (100), 235 (14), 234 (79), 204 (21), 189 (27), 167 (6), 149 (9), 125 (7), 109 (3); MS (high resolution) 249.1140 (M^+, calcd 249.1153).

1-*p*-Anisyl-2-naphthol (9b): isolated by column chromatography and eluted with petroleum ether/diethyl ether (95:5). The solid was recrystallized from ethanol/water, mp 98.5–100.5 °C (lit.[8] mp 98.5–100.5 °C).

1-(1-Naphthyl)-2-naphthol (9c): isolated by column chromatography and eluted with benzene/diethyl ether (95:5). The

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[24] The minimal energy potential surface was inspected by means of the reaction coordinate method. The coordinate was the new bond formed. The stationary points were calculated without any kind of assumptions and characterized by means of the corresponding Hessian matrix.

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[28] Akimoto, H.; Yamada, S. *Tetrahedron* **1971**, *27*, 5999.

solid was recrystallized from methanol, mp 90–93 °C (lit.[8,29] mp 93–95 °C).

2-Hydroxy-4′-benzoylbiphenyl (11): isolated by column chromatography and eluted with benzene, mp 114–116 °C: MS (30 eV) *m/e* (relative intensity) 276 (1), 275 (6), 274 (51), 199 (1), 198 (14), 197 (100), 169 (12), 168 (9), 141 (15), 123 (5), 115 (13), 105 (39), 77 (27), similar pattern to that reported.[6a]

4-Hydroxy-4′-benzoylbiphenyl (12): isolated by column chromatography and eluted with benzene, mp 192–194 °C (lit.[30] mp 194–195 °C): MS (30 eV) *m/e* (relative intensity) 276 (1), 275 (9), 274 (55), 199 (1), 198 (14), 197 (100), 169 (12), 168 (10), 141 (11), 123 (3), 115 (13), 105 (38), 77 (23).

1-*p*-Anisyl-2-naphthyl methyl sulfide (14b): isolated by column chromatography and eluted with petroleum ether/benzene (50:50): ^{1}H NMR δ 2.33 (3 H, s), 3.77 (3 H, s), 6.5–7.9 (10 H, m); MS (30 eV) *m/e* (relative intensity) 282 (3), 281 (11), 280 (90), 267 (3), 266 (16), 265 (16), 250 (26), 235 (6), 234 (29), 223 (6), 222 (16), 221 (33), 218 (5), 202 (6); MS (high resolution) 280.0908 (M$^+$, calcd 280.0922).

***p*-Anisyl 2-naphthyl sulfide (15b)**: isolated by column chromatography and eluted with petroleum ether/benzene (50:50), mp 63–64 °C: ^{1}H NMR δ 3.80 (3 H, s), 6.67–7.93 (11 H, m); MS (30 eV) *m/e* (relative intensity) 268 (5), 267 (16), 266 (100), 252 (4), 251 (22), 235 (9), 234 (12), 223 (14), 222 (12), 159 (3), 139 (12), 116 (4), 115 (65); MS (high resolution) 266.0770 (M$^+$, calcd 266.0765).

1-Naphthyl 2-naphthyl sulfide (15c): isolated by column chromatography and eluted with petroleum ether/diethyl ether (95:5), mp 58–59 °C (lit.[31] mp 60–61 °C): MS (30 eV) *m/e* (relative intensity) 288 (15), 286 (100), 284 (24), 252 (33), 127 (12), 126 (7), 115 (18).

Photostimulated Reaction of 2-Naphthaleneselenate Ion with *p*-Iodoanisole. To 250 mL of distilled ammonia was added di-2-naphthyl diselenide (1 mmol), and then potassium metal in excess was added in small pieces. When all the substrate had reacted, *p*-iodoanisole (1.6 mmol) was added and the reaction mixture was irradiated for 180 min. The product *p*-anisyl 2-naphthyl selenide was isolated by column chromatography and eluted with hexane, mp 80–81 °C: ^{1}H NMR δ 3.93 (3 H, s), 6.83–7.90 (11 H, m); MS (30 eV) *m/e* (relative intensity) 318 (1), 317 (2), 316 (13), 315 (13), 314 (57), 313 (12), 312 (29), 311 (14), 310 (12), 309 (1), 308 (1), 236 (3), 235 (17), 243 (100), 219 (27), 202 (2); MS (high resolution) 314.0213 (M$^+$, calcd 314.0210).

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Supplementary Material Available: Eigenvalues and eigenvectors of the frontier orbitals of the nucleophiles of Figure 1 and the phenyl radical (3 pages). Ordering information is given on any current masthead page.

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Aryl Radicals from Electrochemical Reduction of Aryl Halides. Addition on Olefins

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Aryl radicals generated by direct and indirect (by means of an aromatic anion radical mediator) electrochemistry are reacted with olefins in liquid ammonia and in organic solvents (Me_2SO, MeCN, DMF). The arylated product is obtained in good yield in the latter case. In pure liquid NH_3, the yields are extremely poor. They are improved upon addition of a proton donor such as urea or water; further increase of yields is obtained upon addition of 2-propanol. A reaction mechanism is proposed based on these observations and on the results of deuterium incorporation experiments. Cyclic voltammetry is used to determine the rate constant of the key step in the mechanism, viz, the addition of the aryl radical to the olefin, through its competition with its reaction with nucleophiles in the framework of an $S_{RN}1$ substitution process.

Direct or indirect electrochemical reduction of aryl halides in solvents of low proton availability offers a convenient and controlled[2] means for generation of aryl radicals. The method has been previously applied successfully to the addition of aryl radicals on nucleophiles triggering $S_{RN}1$ aromatic substitution reactions[3] and to reactions based on H atom abstraction by aryl radicals.[4] By indirect

Scheme I

$$\begin{array}{clcr}
 & \text{direct electrochemistry} & \text{indirect electrochemistry} & \\
 & & \mathrm{P} + e^- \rightleftharpoons \mathrm{Q} & \\
(1') & \mathrm{ArX} + e^- \rightleftharpoons \mathrm{ArX}^{\bullet -} & \mathrm{ArX} + \mathrm{Q} \rightleftharpoons \mathrm{ArX}^{\bullet -} + \mathrm{P} & (1) \\
 & \multicolumn{2}{c}{\mathrm{ArX}^{\bullet -} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^- \quad (2)} & \\
(3') & \mathrm{Ar}^{\bullet} + e^- \rightleftharpoons \mathrm{Ar}^- & \mathrm{Ar}^{\bullet} + \mathrm{Q} \rightarrow \mathrm{Ar}^- + \mathrm{P} & (3) \\
 & \multicolumn{2}{c}{\mathrm{Ar}^- + \mathrm{H}^+ \rightarrow \mathrm{ArH} \quad (4)} &
\end{array}$$

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[2] As far as the reducing power of the reacting system is concerned.