

PHOTOSTIMULATED REACTIONS OF HALOARENES WITH 2-NAPHTHYLAMIDE IONS.

A FACILE SYNTHESIS OF 1-ARYL-2-NAPHTHYLAMINES.

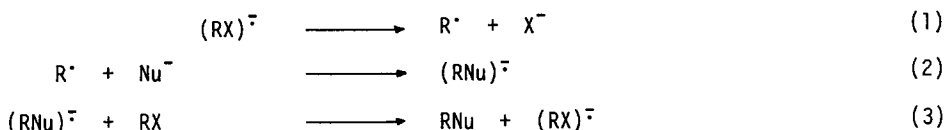
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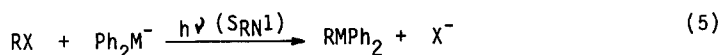
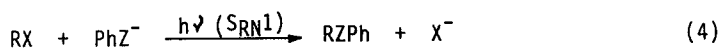
Abstract: The photostimulated reactions of aryl iodides with 2-naphthylamide ions in liquid ammonia gave 1-aryl-2-naphthylamines as the major substitution product. This reaction is proposed to occur by the  $S_{RN}1$  mechanism of nucleophilic substitution

The  $S_{RN}1$  mechanism is a well known process by which a nucleophilic substitution is produced on a non-activated adequately substituted substrate. This nucleophilic substitution mechanism is a chain process which involves radicals and radical anions as intermediates. The main steps of this mechanism are sketched in Scheme I.<sup>1</sup>

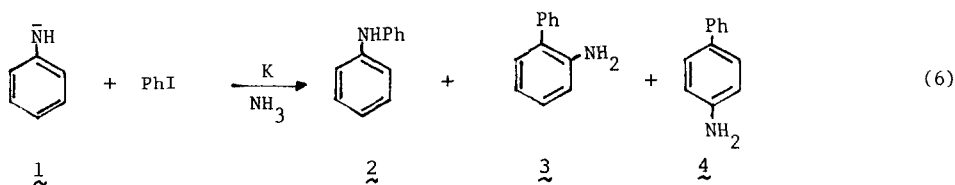
SCHEME I



The scope of the mechanism has been investigated through the reaction of several substrates and nucleophiles. The common feature of the process is that the substitution is produced in the substrate at the position bearing the leaving group and in nucleophiles such as  $PhZ^{-}$  ( $Z = S, Se, Te$ )<sup>2</sup> or  $Ph_2M^{-}$  ( $M = P, As, Sb$ )<sup>3</sup> at the center bearing the negative charge (eq. 4, 5).



An exception to this behaviour has been observed with the nucleophile phenylamide 1. It has been reported that in the solvated electron stimulated reaction of iodobenzene with the potassium salt of 1 in liquid ammonia the products formed were diphenylamine 2 (19%), ortho-3 and para-phenylaniline 4 in 11% yield each (eq. 6).<sup>4</sup>



The behavior of nucleophile 1 could be ascribed to an important delocalization of the negative charge on the ortho and para positions of the aromatic ring. This distribution of the negative charge could be modified through adequate substituents on the aromatic moiety of the nucleophile thus leading to variations of the product distribution for this type of reaction.

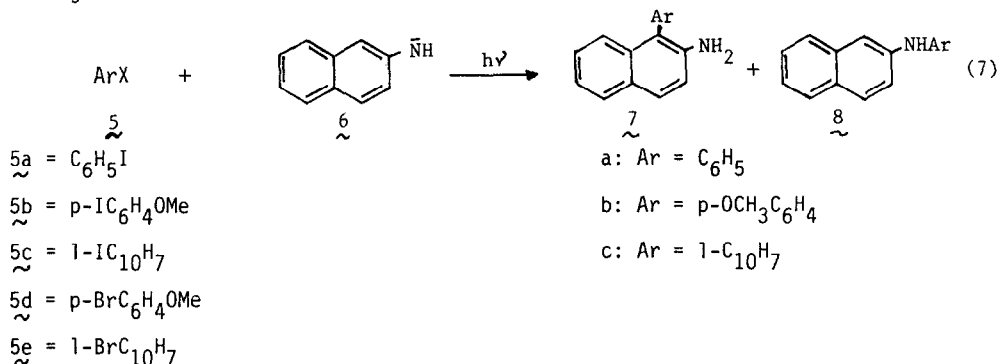
For this reason we decide to investigate the photostimulated reaction of type 1 nucleophiles with different haloaromatic substrates.

Instead of stimulating reaction by means of solvated electrons, we chose photo-stimulative in order to assure a homogeneous reaction medium. It has been reported that amide ions react under photostimulation with haloarenes by the  $S_{RN}1$  mechanism.<sup>5</sup>

The nucleophiles were generated by acid-base reaction of the corresponding amine with an equivalent amount of either sodium amide<sup>4</sup> or potassium tert-butoxide<sup>6</sup> in liquid ammonia.

The photostimulated reaction of iodobenzene, p-iodoanisole, p-iodobenzonitrile or their bromo derivatives with 1 or p-tolylamide gave a low yield of substitution products ( $\approx 8\%$ ) but with both nucleophiles the highest percentage corresponds to the ortho-substituted compound.<sup>7</sup>

These results lead us to investigate the reactions of haloaromatic compounds 5a-5e with the anion 2-naphthylamide 6 (eq. 7), on the believe that this anion would have a lower ionization potential to initiate the photostimulated reaction than anion 1, thus increasing the percentage of substitution reaction.<sup>1</sup>



The photostimulated reaction of iodobenzene (5a) with 6 occurs in a 48% yield (as determined by the halide ion liberated) with the formation of 1-phenyl-2-naphthylamine 7a<sup>8</sup> in 47% yield. Trace of the N-substitution product 8a was observed (Table, entry 1).

In the reactions carried out with p-iodoanisole (5b) and 1-iodonaphthalene (5c) the 1-substituted compounds 7b<sup>9</sup> and 7c<sup>10</sup> were the main reaction products formed in 63% and 45% yield respectively (Table, entry 3, 4, 7).

Reduction products were formed in both of these reactions in an average yield of 9%. The highest percentage of N-substitution was determined for reaction of compound 5b with a

7% yield of 8b.<sup>11</sup> The photostimulated reaction of the bromo derivatives, such as p-bromoanisole (5d) and 1-bromonaphthalene (5e) with 6 gave much less reaction than the iodo derivative. These results are in agreement with the halogen mobility in the photostimulated  $S_{RN}1$  reactions ( $I > Br > Cl$ ).<sup>1,12</sup>

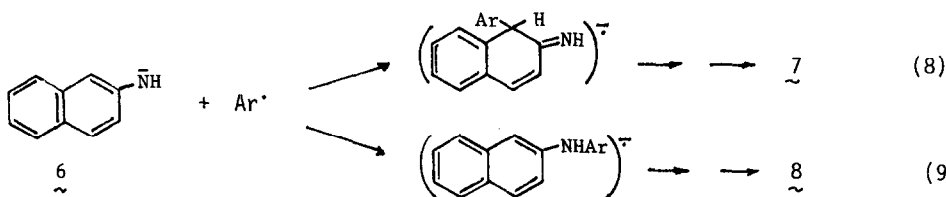
These reactions were inhibited by p-dinitrobenzene (Table, entry 6), a well known inhibitor of  $S_{RN}1$  reactions and they do not occur in absence of light (Table, entry 2, 5, 8). All these results let us to propose a  $S_{RN}1$  mechanism in play for the above reactions (Scheme I).

TABLE: Photostimulated Reaction of Haloaromatic Compounds with 2-Naphthlamide Ions in Liquid Ammonia<sup>a</sup>

Run	Substrate $M \times 10^3$	<u>6</u> $M \times 10^3$	$X^-$	ArH	Products, Yield % <sup>b</sup>	
					<u>7</u>	<u>8</u>
1	<u>5a</u> , 8.9	15.0	48	---	47.0	1.0
2 <sup>c</sup>	<u>5a</u> , 8.9	15.0	3	---	--	--
3	<u>5b</u> , 7.5	15.0	77	6.2	46.2 <sup>d</sup>	7.7 <sup>d</sup>
4	<u>5b</u> , 7.5	15.0	79	11.1	63.2	6.3
5 <sup>c</sup>	<u>5b</u> , 7.5	15.0	3	--	--	--
6 <sup>e</sup>	<u>5b</u> , 7.5	15.0	32	5.1	28.8	2.9
7	<u>5c</u> , 7.9	15.0	60	9.0	45.0	1.2
8 <sup>c</sup>	<u>5c</u> , 7.9	15.0	3	--	--	--
9	<u>5d</u> , 7.9	15.0	14	--	12.0	--
10	<u>5e</u> , 7.2	15.0	33	5.9	25.1	--

<sup>a</sup>Reactions were carried out in ca. 200 mL of distilled liquid ammonia under nitrogen with reactions times of 180 minutes. Irradiation was performed with four uv-lamps (Philips HPT) emitting maximally at 350 nm. <sup>b</sup>Determined by GLC by the internal standard method, unless otherwise stated. <sup>c</sup>Dark reaction. <sup>d</sup>Isolated by column chromatography. <sup>e</sup>p-Dinitrobenzene was added (20 mole %).

Formation of the C- and N-substitution products could be ascribed to the competitive coupling reactions of aryl radicals with the anion 6 (eq 8, 9).



These results show that the attack to the position 1 of the naphthalene ring (C arylation) is 5-8 times faster than the attack to the nitrogen (N arylation). The fact that C-substitution is the main reaction path opens a new synthetic route to these type of compounds. Variations in the ratio of C/N-substitution is being study through the reactions of homo and hetero-substituted nucleophiles, as well as their scope as synthetic approach to arylation of aromatic amide ions.

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#### Notes and References

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- m.p. = 91.5-92.5 °C (Lit<sup>13</sup>93-94 °C). IR (KBr) 3470, 3400  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (60MHz,  $\text{C}_4\text{H}_9\text{TMS}$ )  $\delta$  3.5 (s,2H); 6.67-7.83 (m,11H); MS (70eV), m/e (relative intensity): 219 ( $\text{M}^+$ , 100), 218 (81), 217 (60), 201 (11), 189 (11), 141 (4), 109 (22), 94 (19), 91 (6), 83 (10), 77 (7), 57 (24), 43 (17), 29 (5).
- m.p. = 128.5-130 °C. IR (KBr) 3570, 3450  $\text{cm}^{-1}$ .  $^1\text{HNMR}$  ( $\text{C}_4\text{H}_9\text{TMS}$ )  $\delta$  3.69 (s,2H), 3.84 (s,3H), 6.96-7.73 (m,10H);  $^{13}\text{C-NMR}$  (20,15 MHz,  $\text{C}_3\text{DC}$ ) 55.21, 114.65, 117.90, 119.50, 121.90, 124.20, 126.07, 127.80, 127.90, 128.44, 129.01, 131.90, 134.06, 141.25, 158.95, MS (30eV) M/e (relative intensity): 249 ( $\text{M}^+$ ,60), 234 (33), 206 (30), 204 (30), 189 (27), 178 (30), 152 (22), 142 (14), 125 (48), 119 (53), 105 (86), 91 (41), 83 (33), 77 (46), 57 (91), 43 (100), 41 (52), 28 (19).
- m.p = 190-191.5 °C (Lit. <sup>14</sup>189-190°C). IR (KBr) 3570, 3435  $\text{cm}^{-1}$ ;  $^1\text{HNMR}$  ( $\text{C}_4\text{H}_9\text{TMS}$ )  $\delta$  3.33 (s,2H), 6.50-8.00 (m,13H); MS (70 eV) m/e (relative intensity): 269 ( $\text{M}^+$ , 100), 267 (36), 252 (21), 239 (7), 149 (1), 133 (28), 126 (9), 106 (6), 78 (68) 63 (3), 51 (9), 39 (6), 27 (2).
- m.p. = 98-99.5°C (lit. <sup>15</sup> 104°C). IR(KBr): 3450  $\text{cm}^{-1}$ . MS (30eV) (relative intensity): 249 ( $\text{M}^+$ , 94), 236 (15), 234 (100), 206 (18), 204 (35), 180 (13), 178 (31), 142 (3), 140 (31), 127 (60), 115 (32), 106 (32), 91 (20), 89 (9), 77 (38), 65 (9), 51 (12), 39 (14), 27 (12).
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