

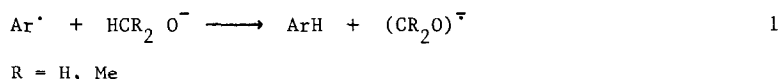
PHOTOSTIMULATED REACTION OF ARYL IODIDES WITH 2-NAPHTHOXIDE IONS BY
THE $S_{RN}1$ MECHANISM

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Summary: The photostimulated reactions of p-iodoanisole (2) and 1-iodonaphthalene (7) with 2-naphthoxide ions in liquid ammonia gave the corresponding 1-aryl-2-naphthols as the only substitution product. These reactions are proposed to proceed via the $S_{RN}1$ mechanism for nucleophilic aromatic substitution.

Since the discovery of the reaction of unactivated aryl halides with nucleophiles by the $S_{RN}1$ mechanism,¹ various nucleophiles have been reported to react with aryl radicals. Among these are carbanions, and also nucleophiles derived from N, P, As, Sb, S, Se, Te, etc.² On the other hand, alkoxide ions have shown to be unable to couple with aryl radicals. Alkoxide anions derived from primary or secondary alkyl alcohols do not react as nucleophiles with aryl radicals. Instead it has been shown that methoxide³ and isopropoxide⁴ anions promote hydrogen atom abstraction. (eq. 1).



Although t-butoxide is widely used as a base in $S_{RN}1$ reactions, it has never been found to react with aryl radicals. t-Butoxide is also a poor hydrogen atom donor since it has only hydrogens bonded to primary carbon atoms.

Phenoxide anions and other aromatic alkoxide anions were found to be unreactive towards aryl radicals under various conditions. The lack of reactivity of p-cresolate anions toward iodobenzene was observed even under unusually intense irradiation in liquid ammonia; and in this case only the dehalogenation of iodobenzene was observed.⁵ Similarly, phenoxide did not react with aryl radicals formed from the reaction of aryl halides with sodium amalgam in t-BuOH/water,⁶ or from aryl radicals generated in DMSO/t-BuO⁻.⁷

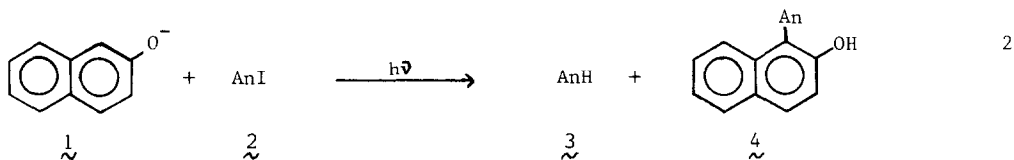
Recently, it was reported that the reaction of o-, m- and p-chlorobenzonitriles with phenoxide anion catalyzed with electrons from a cathode (electrochemical system) gave arylation in positions 2- and 4- of the phenoxide. When one of these positions has a t-butyl group substituent only one product is formed.⁸

The solvated electron stimulated reaction of iodobenzene with phenylamide ions in liquid ammonia gave diphenylamine (N-arylation) and 2- and 4- aminobiphenyls (C-arylation).¹

We reported that the 2-naphthylamide anion reacted under photostimulation with aryl halides in liquid ammonia by the $S_{RN}1$ mechanism, and the main substitution product was formed by the attack of aryl radicals at the one position on the naphthalene ring to give good yields of 1-aryl-2-naphthylamines with small amounts of N-aryl-2-naphthylamines.⁹ We found that the 2-naphthylamide anion is much more reactive than the phenylamide anion under the same experimental conditions.

Since the 2-naphthylamide anion is much more reactive than the phenylamide anion, we thought it of interest to see if the 2-naphthoxide ion shows an enhanced reactivity, compared with phenoxide toward aryl iodides under photostimulation.

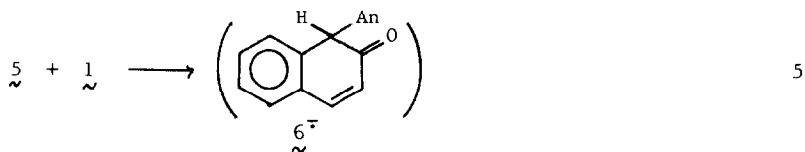
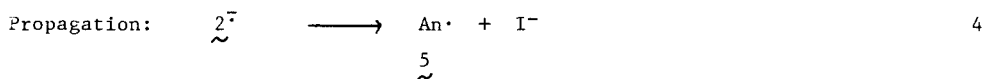
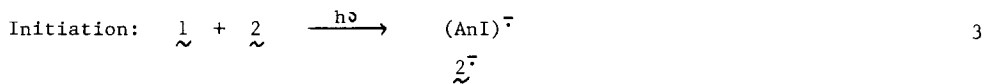
In the photostimulated reaction (180 min.) of 2-naphthoxide ion 1 with p-iodoanisole 2 in liquid ammonia we found a 61% yield of iodide ions, the reduction product anisole 3 (14% yield) and the substitution product 1-p-anisyl-2-naphthol 4¹⁰ (48% yield) as the only reaction products (eq. 2).

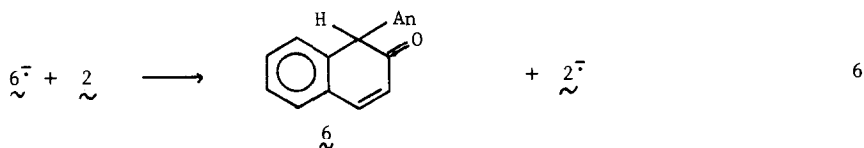


An = p-anisyl

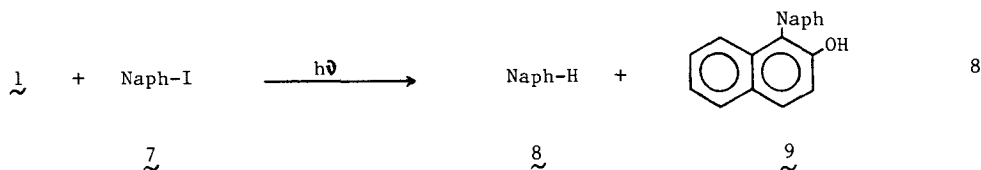
This reaction does not occur in the dark (iodide ion less than 3% in 180 min), and the photostimulated reaction (180 min) was inhibited by p-dinitrobenzene, a well known inhibitor in $S_{RN}1$ reactions² (iodide ion 17%, 3: 2% and 4 with 12% yield). The reaction with p-bromoanisole is much slower than with 2 (bromide ions 13% yield). From all these results we suggest that 1 reacts with 2 by the $S_{RN}1$ mechanism for nucleophilic substitution (Scheme I).^{1,2}

SCHEME I





In the photostimulated reaction of $\tilde{1}$ with 1-iodonaphthalene $\tilde{7}$ (180 min) we found iodide ion (76% yield), naphthalene $\tilde{8}$ (20% yield) and the substitution product 1-naphthyl-2-naphthol $\tilde{9}^{11}$ in 53% yield (eq. 8).



Naph = 1-naphthyl

The photostimulated reaction of phenoxide ion with $\tilde{2}$ (180 min) gave 27% yield of iodide ion, and $\tilde{3}$ was the only product detected (23% yield). No substitution products were found in this reaction. Phenoxide ion also was unreactive toward 2-chloroquinoline under electrochemical stimulation.¹³ The fact that cyanophenyl radicals are able to couple with phenoxide ion under the same conditions, may be due to the more electrophilic character of this radical compared with the phenyl radical.

The fact that 2-naphthoxide ion $\tilde{1}$ reacts under photostimulation with aryl iodides $\tilde{2}$ and $\tilde{7}$ by the $S_{RN}1$ mechanism with enhanced reactivity compared with phenoxide ion to give C-substitution products in position one of the naphthalene ring opens an interesting synthetic route to the arylation of aromatic alkoxide ions. Theoretical work is under way together with a study of the synthetic application of this novel reaction.

Acknowledgements: M.T.B. gratefully acknowledges receipt of a fellowship from the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET). INFIQC is jointly sponsored by the CONICET and the Universidad Nacional de Córdoba. This work is partially supported by the Consejo de Investigaciones de la Provincia de Córdoba (CONICOR).

TABLE: Photostimulated Reaction of Aryl Iodides with 2-Naphthoxide Ions I^- in Liquid Ammonia.^a

Run	Substrate Mx10 ⁻³	Yields, %		
		I ⁻ ^b	ArH ^c	Substitution ^c
				Product
1	2, 7.0	54	14	4, 32
2	2, 7.5	61	13	4, 42
3 ^e	2, 7.5	3	---	-----
4 ^f	2, 7.5	17	2	4, 13
5 ^g	2, 7.0	27	23	-----
6	2, 7.5 ^h	13 ⁱ	j	j
7	7, 7.0	76	20	9, 53
8	7, 7.0	78	35	9, 44 ^d
9 ^e	7, 7.0	3	--	-----

^aReactions were carried out in ca. 200 ml of distilled liquid ammonia with 0.015 M of I^- under nitrogen with 180 minutes of reaction times. Irradiation was performed with four UV-lamps (Philips HPT) emitting maximally at 350 nm. ^bPotentiometrically determined. ^cDetermined by GLC by the internal standard method, unless otherwise stated. ^dIsolated by column chromatography. ^eDark reaction. ^fp-Dinitrobenzene was added (20 mole %). ^gPhenoxide ions. ^hBromobenzene. ⁱBromide ions. ^jNot quantified.

References and notes.

- Kim, J. K.; Bunnett, J. F. *J. Am. Chem. Soc.*, 1970, **92**, 7463, 7464.
- For a review see Rossi, R. A.; de Rossi, R. H., *Aromatic Substitution by the $\text{S}_{\text{RN}}1$ Mechanism* ACS Monograph N° 178, 1983.
- a) Bunnett, J. F.; Wamser, C. C. *J. Am. Chem. Soc.*, 1967, **89**, 6712. b) Bunnett, J. F.; Takayama, H. *J. Am. Chem. Soc.*, 1968, **90**, 5173.
- Rossi, R. A.; Bunnett, J. F.; *J. Org. Chem.*, 1973, **38**, 1407.
- Semmelhack, M. F.; Bargar, R. T. *J. Am. Chem. Soc.*, 1980, **102**, 7765.
- Rossi, R. A.; Pierini, A. B. *J. Org. Chem.*, 1980, **45**, 2914.
- Ciminali, F.; Bruno, G.; Testaferri, C.; Tiecco, M. *J. Org. Chem.*, 1978, **43**, 4509.
- Alam, N.; Amatore, C.; Combellas, C.; Thiebault, A.; Verpeaux, J. N. *Tetrahedron Lett.*, 1987, **28**, 6171.
- Pierini, A. B.; Baumgartner, M. T.; Rossi, R. A. *Tetrahedron Lett.*, 1987, **28**, 4653.
- m.p. = 98.5–100.5°C IR (KBr) 3520, 3438, 1608, 1572, 1488, 1387, 1244, 1175 cm^{-1} . ^1H NMR (60 MHz), Cl_4C (TMS) 3.83 (s, 3H), 5.05 (s, OH), 6.87–7.83 (m, 10H). MS (30 eV) m/e (relative intensity): 252 (2), 251 (18), 250 (M^+ , 100), 236 (5), 235 (26), 218 (11), 208 (3), 207 (18), 189 (15), 179 (27), 178 (37), 165 (10), 144 (15), 126 (11), 115 (9).
- m.p. = 90 – 93°C (lit.¹² 93–5°C). IR (KBr) 3522, 3054, 1620, 1595, 1382, 1195 cm^{-1} . ^1H NMR (60 MHz), Cl_4C (TMS) 4.68 (s, OH), 6.83–8.10 (m). MS (25 eV, relative intensity) m/e: 272, (2), 271 (16), 270 (M^+ , 100), 269 (39), 253 (27), 252 (26), 251 (16), 242 (3), 241 (10), 140 (7), 239 (14), 215 (2).
- Kabuto, K.; Yashumara, F.; Yamaguchi, S. *Bull. Chem. Soc. Japan.*, 1983, **56** 1163.
- Amatore, C.; Chausard, J.; Pinson, J.; Saveant, J. M.; Thiebault, A. *J. Am. Chem. Soc.*, 1979, **101**, 6012.

(Received in USA 28 March 1988)