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).

Acknowledgment. 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 and Antorchas Foundation.

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.

---

[29] Kabuto, K.; Yashumara, F.; Yamaguchi, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1163.

[30] Fieser, L. F.; Bradser, A. *J. Am. Chem. Soc.* **1936**, *58*, 2337.

[31] Krafft, J. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 2368.

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

Zoubida Chami,[1a,b] Monique Gareil,[1a] Jean Pinson,[1a] Jean-Michel Savéant,*[,1a] and
André Thiébault[1b]

Laboratoire d'Electrochimie Moléculaire de l'Université Paris 7, Unité de Recherche Associée au CNRS no. 438, 2, place Jussieu, 75251 Paris Cedex 05, France, and Laboratoire de Chimie et Electrochimie des Matériaux Moléculaires, Unité de Recherche Associée au CNRS no. 429, Ecole Supérieure de Physique et Chimie Industrielles, 10, rue Vauquelin, 75231 Paris Cedex 05, France

Received August 14, 1989 (Revised Manuscript Received May 22, 1990)

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

direct electrochemistry indirect electrochemistry

$$P + e^- \rightleftharpoons Q$$

$$(1')\quad ArX + e^- \rightleftharpoons ArX^{\bullet -} \qquad ArX + Q \rightleftharpoons ArX^{\bullet -} + P \quad (1)$$

$$ArX^{\bullet -} \rightarrow Ar^{\bullet} + X^- \quad (2)$$

$$(3')\quad Ar^{\bullet} + e^- \rightleftharpoons Ar^- \qquad Ar^{\bullet} + Q \rightarrow Ar^- + P \quad (3)$$

$$Ar^- + H^+ \rightarrow ArH \quad (4)$$

---

[1] (a) Université Paris 7. (b) Ecole Supérieure de Physique et Chimie Industrielles.

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

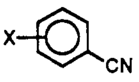
electrochemistry we mean the electrochemical generation of mediators such as aromatic anion radicals which shuttle electrons between the electrode and the aryl halide. The interest of the indirect method as compared to the direct one derives from the fact that aryl radicals are much easier to reduce than the parent aryl halides (Scheme I). Thus, with direct electrochemistry, in the cases where reaction 2 is fast, the aryl radicals are produced close to the electrode surface and will then be reduced there (according to an "ECE" mechanism[5]) before having time to trigger the chemistry of interest in the solution. In indirect electrochemistry, the generation of the aryl radical takes place in the solution, and its reduction mainly occurs by electron transfer from the reduced from of the catalyst, Q (reaction 3). This again competes with the triggering of the chemistry of interest. However, reaction 3 is at maximum at the diffusion limit, and one can decrease the mediator concentration to slow this side reaction. Such a strategy has been applied successfully in several instances in the case of $S_{RN}1$ aromatic substitution reactions.[3k,n]

Whereas the reaction of alkyl radicals with olefins has been the object of many investigations[6] and has been used in the synthesis of numerous natural compounds, there are fewer examples of the reaction of aryl radicals in spite of the current interest in arylation methods.[7] The main reactions involving aryl radicals and olefins are the following. The Meerwein reaction[8] is one of these where an aryl diazonium chloride is reacted with an olefin in the presence of cuprous chloride. It leads either to addition of the aryl group and the chlorine atom or to substitution of one hydrogen of the double bond by the aryl group. The reaction is thought to proceed via a ternary diazonium–Cu(II)–olefin complex. The radicals escaping from this complex undergo side reactions such as dimerization or H atom abstraction. Sandmeyer products are also observed. Yields are average to good in most cases. Starting from aryl diazonium salts, hydroarylation is obtained using trivalent titanium salts as the reducing agents.[9a,b] Ti^{3+} must be used in excess since two electrons are consumed per molecule of olefin and diazonium salt. Good yields are obtained. Intramolecular versions of the same reaction have also been described.[9c–e] Another way to obtain the hydroarylation product is to start from the aryl iodide and to use tributyltin hydride in catalytic amount.[10a] The reaction takes place by a chain process involving the abstraction of the iodine by $Bu_3Sn^{\bullet}$, the addition of $Ar^{\bullet}$ on the double bond, and the abstraction by the ensuing radical of an H atom, thus regenerating the $Bu_3Sn^{\bullet}$ radical. Yields are moderately good. Intramolecular versions of the same reaction starting from an iodo[10b] or a bromo derivative[10c] have again been described.

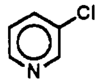
In the following we describe an investigation of the reaction of aryl radicals generated electrochemically, in an indirect manner in most cases, with olefins in organic solvents and in liquid ammonia.[11] Under such conditions, the aryl radical is generated in an outer-sphere manner as the result of an electron transfer from the electrode or from the mediator to the aryl halide, yielding the aryl halide anion radical, which then decomposes into the aryl radical and the halide ion. Among the reactions leading to the addition of an aryl radical to a double bond, the Meerwein and the tributyltin hydride reactions are most likely not outer-sphere processes. The question remains open in the case of the titanium(III) reactions. One interest of the study described below was thus to see what happens when the reducing agents, electrode or aromatic anion–radical mediators, are unambiguously of the outer-sphere type.

Results and Discussion

The following compounds were investigated:



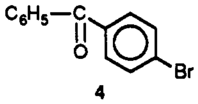
1a: X = *p*-Cl
b: X = *o*-Cl
c: X = *p*-I



2

C_6H_5Br

3



4

$ArCH_2CHRR'$

5a: Ar = 4-CNC_6H_4; R = H; R′ = C_6H_5
b: Ar = 4-CNC_6H_4; R = CH_3; R′ = C_6H_5
c: Ar = 4-CNC_6H_4; R = H; R′ = 4-$CH_3OC_6H_4$
d: Ar = 4-CNC_6H_4; R = H; R′ = 4-ClC_6H_4
e: Ar = 4-CNC_6H_4; R = H; R′ = CN
f: Ar = 4-CNC_6H_4; R = H; R′ = $CH{=}CHCH_3$ and isomers
g: Ar = 2-CNC_6H_4; R = H; R′ = C_6H_5
h: Ar = 3-C_5H_4N; R = H; R′ = C_6H_5
i: Ar = 4-CNC_6H_4; R = H; R′ = OBu
j: Ar = C_6H_5; R = H; R′ = C_6H_5
k: Ar = $C_6H_5COC_6H_4$; R = H; R′ = C_6H_5
l: Ar = 4-CNC_6H_4; R = H; R′ = SC_6H_5

Preparative-Scale Electrolyses. These were carried out in acetonitrile (MeCN), *N*,*N*-dimethylformamide

---

(3) (a) For general papers on the $S_{RN}1$ aromatic nucleophilic substitution see refs 3b–d. For direct or indirect electrochemical induction of $S_{RN}1$ aromatic nucleophilic substitution reactions see refs 3c–s. (b) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413. (c) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (d) Rossi, R. A.; Rossi, R. H. *Aromatic Substitution by the $S_{RN}1$ Mechanism, ACS Monograph 178*; American Chemical Society: Washington, D.C., 1983. (e) Pinson, J.; Savéant, J.-M. *J. Chem. Soc., Chem. Commun.* **1974**, 933. (f) Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1978**, *100*, 1506. (g) Amatore, C.; Chaussard, J.; Pinson, J.; Savéant, J.-M. *J. Am. Chem. Soc.* **1979**, *101*, 6012. (h) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1981**, *103*, 6930. (i) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 817. (j) Lexa, D.; Savéant, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 3503. (k) Swartz, J. E.; Stenzel, T. T. *J. Am. Chem. Soc.* **1984**, *106*, 2520. (l) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1984**, *106*, 6318. (m) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 3451. (n) Amatore, C.; Combellas, C.; Pinson, J.; Oturan, M. A.; Robveille, S.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1985**, *107*, 4846. (o) Amatore, C.; Combellas, C.; Robveille, S.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1986**, *108*, 4754. (p) Amatore, C.; Gareil, M.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Org. Chem.* **1986**, *51*, 3757. (q) Amatore, C.; Combellas, C.; Pinson, J.; Savéant, J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 7. (r) Alam, N.; Amatore, C.; Combellas, C.; Pinson, J.; Savéant, J.-M.; Thiébault, A.; Verpeaux, J. N. *J. Am. Chem. Soc.* **1982**, *53*, 1496. (s) Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiébault, A. *Tetrahedron Lett.* **1989**, *30*, 1373.

(4) (a) Amatore, C.; Badoz-Lambling, J.; Bonnel-Huyghes, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 1979. (b) Andrieux, C. P.; Badoz-Lambling, J.; Combellas, C.; Lacombe, D.; Savéant, J. M.; Thiébault, A.; Zann, D. *J. Am. Chem. Soc.* **1987**, *109*, 1518.

(5) (a) See refs 5b and 3d and references cited therein. (b) Amatore, C.; Gareil, M.; Savéant, J. M. *J. Electroanal. Chem.* **1984**, *176*, 377. (c) Savéant, J. M. *Bull. Soc. Chim. Fr.* **1988**, 225.

(6) (a) Giese, B. *Radicals in Organic Synthesis. Formation of carbon–carbon bonds*; Pergamon Press: New York, 1986. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553. (c) Giese, B. *Ibid.* **1983**, *22*, 753. (d) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (e) Curran, D. P. *Synthesis* **1988**, 417. (f) *Ibid.* **1988**, 489.

(7) Abramovitch, R. A.; Barton, D. H. R.; Finet, J. P. *Tetrahedron* **1988**, *44*, 3039.

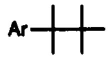
(8) (a) Dombrovski, A. V. *Uspekhii Khimii* **1984**, *53*, 1625; *Russ. Chem. Rev.* **1984**, *53*, 943. (b) Rondestvedt, C. S. *Org. React.* **1960**, *11*, 189. (c) *Ibid.* **1976**, *24*, 225.

(9) (a) Citterio, A.; Vismara, E. *Synthesis* **1980**, 291, (b): Citterio, A. *Org. Synth.* **1984**, *62*, 67. (c) Beckwith, A. L. J.; Gara, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 5689. (d) *Ibid.* **1969**, *91*, 5691. (e) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 593.

(10) (a) Reference 6a, p 246. (b) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 795. (c) Ueno, Y.; Chino, K.; Okawasa, N. *Tetrahedron Lett.* **1982**, *25*, 2575.

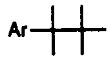
(11) (a) Preliminary results have been described in ref 11b. (b) Chami, Z.; Gareil, M.; Pinson, J.; Savéant, J. M.; Thiébault, A. *Tetrahedron Lett.* **1988**, *29*, 639. (c) A brief account of the reaction of phenyl halides with alkenes in the presence of potassium metal in liquid ammonia has been given recently.[11d] (d) Meijs, G.; Bunnett, J. F. *J. Org. Chem.* **1989**, *54*, 1123.

Table I. Reaction of Electrochemically Generated Aryl Radicals with Olefins in Liquid Ammonia[a]

expt	ArX (concn, mM)	olefin (concn, mM)	additive (concn, mM)	mediator[e] (concn, mM)	% yield ArH	
1	**1a** (25)	styrene (200)	none	none	1	**5a**, 1[b]
2	**1a** (25)	styrene (200)	none	4,4′-bipyridine (19)	1	**5a**, 5[c]
3	**1a** (25)	*α*-methylstyrene (200)	none	4,4′-bipyridine (19)	2	**5b**, 4[c]
4	**1a** (34)	styrene (220)	urea (260)	4,4′-bipyridine (25)	32	**5a**, 38
5	**1a** (34)	styrene (220)	H_2O (1300)	4,4′-bipyridine (25)	20	**5a**, 40
6	**1a** (25)	styrene (220)	2-propanol (410)	4,4′-bipyridine (19)	4	**5a**, 90
7	**1a** (25)	*p*-methoxystyrene (220)	2-propanol (410)	4,4′-bipyridine (19)	24	**5c**, 70
8	**1a** (25)	*p*-chlorostyrene (220)	2-propanol (410)	4,4′-bipyridine (19)	6	**5d**, 64
9	**1a** (25)	*α*-methylstyrene (220)	2-propanol (410)	4,4′-bipyridine (19)	27	**5b**, 56
10	**1a** (25)	acrylonitrile (220)	2-propanol (410)	4,4′-bipyridine (19)	72	**5e**, 17
11	**1a** (25)	1,3-pentadiene (220)	2-propanol (410)	4,4′-bipyridine (19)	23	**5f**, 65[d]
12	**1b** (25)	styrene (220)	2-propanol (410)	2,2′-bipyridine (19)	17	**5g**, 32
13	**2** (25)	styrene (220)	2-propanol (410)	2,2′-bipyridine (19)	17	**5h**, 49

[a] 0.1 M KBr at −38 °C. [b] Other identified products: *p*-$ClC_6H_4CONH_2$, *p*-$CNC_6H_4C_6H_5$, $C_6H_5(CH_2)_4C_6H_5$, 4,4′-$CNC_6H_4C_6H_4CN$, *p*-$CNC_6H_4NH_2$, and telomers containing the C_6H_4CN group (see the Experimental Section). [c] And 4,4′-$CNC_6H_4C_6H_4CN$ (6%). [d] Obtained as a mixture of three isomers (see the Experimental Section). [e] The electrolyses were performed at constant (20 mA/cm^2) current (see the Experimental Section).

Table II. Reaction of Electrochemically Generated Aryl Radicals in Organic Solvents[a]

expt	ArX[b]	olefin (concn, mM)	solvent	mediator[c] (concn 20 mM)	% yield ArH	
14	**1a**	styrene (100)	Me_2SO	naphthonitrile	–	**5a**, 50
15	**1a**	styrene (10)	DMF	naphthonitrile	–	**5a**, 0
16	**1a**	styrene (100)	DMF	naphthonitrile	–	**5a**, 28
17	**1a**	styrene (1000)	DMF	naphthonitrile	5	**5a**, 80
18	**1a**	styrene (100)	MeCN	naphthonitrile	–	**5a**, 52
19	**1a**	styrene (1000)	MeCN	naphthonitrile	–	**5a**, 80
20	**1a**	styrene (1000)	MeCN + 1% H_2O	naphthonitrile	–	**5a**, 85
21	**1a**	styrene (1000)	MeCN + 2% H_2O	naphthonitrile	–	**5a**, 82
22	**1a**	styrene (1000)	MeCN + 5% H_2O	naphthonitrile	–	**5a**, 80
23	**1a**	*α*-methylstyrene (1000)	MeCN	naphthonitrile	0	**5b**, 74
24	**1a**	butyl vinyl ether (1000)	MeCN	naphthonitrile	27	**5i**, 26
25	**1a**	acrylonitrile (1000)	MeCN	naphthonitrile	6	**5e**, 94
26	**1a**	vinyl phenyl sulfide (400)	DMF	naphthonitrile	26	**5l**, 70
27	**1c**	styrene (1000)	MeCN	naphthonitrile	0	**5a**, 50
28	**1c**	acrylonitrile (1000)	MeCN	naphthonitrile	–	**5e**, 30
29	**1b**	styrene (1000)	DMF	4-cyanopyridine	–	**5g**, 38
30	**3**	styrene (400)	MeCN	methyl benzoate	–	**5j**, 79
31	**4**	styrene (400)	MeCN	none[d]	7	**5k**, 57

[a] 10^{-1} M NBu_4BF_4 at 20 °C. [b] Concentration = 20 mM. [c] The potential was set at −1.8 V/SCE in the case of naphthonitrile and 4′-cyanopyridine, −2.20 V/SCE in the case of methylbenzoate. [d] E = −1.75 V/SCE.

(DMF), dimethyl sulfoxide (Me_2SO), and also in liquid ammonia, a solvent that has proved useful in electrochemically induced $S_{RN}1$ reactions because it is a very poor H atom donor.[3b–e] Aryl radicals are indeed excellent H atom scavengers which makes this reaction one of the main side reactions, in addition to electron-transfer reduction at the electrode or in the solution.[3b–e] The results of the direct or indirect (by means of the anion radical of the mediator[12] indicated) electrolyses are listed in Tables I and II. The reduction potentials of the substrates and catalysts were determined by cyclic voltammetry in liquid ammonia and in organic solvents (see the Experimental Section). The electrolyses were performed at constant current in liquid ammonia and at constant potential in organic solvents (see Tables I and II).

In pure liquid ammonia using the direct electrochemical method (direct electron transfer from the electrode to ArX) the yield of coupling product as well as that of the dehalogenated product, ArH, are extremely low (experiment 1). Numerous side products are formed. Some of them, *p*-$ClC_6H_4CONH_2$ and $CNC_6H_4NH_2$, result from the formation of NH_2^- during electrolysis. The 4,4′-dicyanobiphenyl dimer[13] as well as the styrene dimer is also formed (see the Experimental Section) along with tars. A slight improvement is observed (experiments 2 and 3) when electron transfer is carried out by means of a mediator (4,4′-bipyridine anion radical). The yields, however, remain very low, and a large amount of tars is still obtained.

Titration of the chloride ions after electrolysis indicates that only 55% of the starting chlorine atoms are converted

---

(12) Andrieux, C. P.; Savéant, J. M. *Electrochemical Reactions in Investigation of Rates and Mechanisms of Reactions. Techniques of Chemistry*; Bernasconi, Ed., Wiley: New York, 1986; Vol. VI/4E, Part 2, pp 305–390.

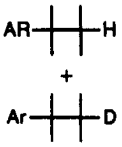
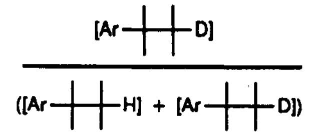
(13) It is the first time that we observe the formation of an Ar–Ar dimer (albeit in low 6% yield) in the course of the electrochemical reduction of an aryl halide ArX.[3c–e] Although, even under redox catalysis conditions, the radical Ar• is certainly in low concentration in the diffusion layer the fact that its rate of dimerization should be close to k_{diff} = 2 × 10^{10} M^{-1} s^{-1} in liquid ammonia, while its rate of reaction with the olefin is about 2.5 × 10^9 M^{-1} s^{-1} (see Table VII) may explain the formation of some Ar–Ar dimer.

(14) Wayner, D. D. M.; McPhee, D. J. M.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

(15) Eastmond, G. C. *Kinetic Data for Homogeneous Free-Radical Polymerizations of Various Monomers in Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1975; Vol. 14, pp 153–473.

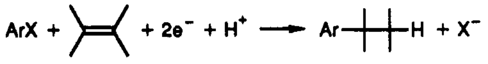
(16) Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1978**, *89*, 335.

Table III. Deuterium-Incorporation Experiments

expt	substrate, olefin, mediator (concn, mM)	solvent		
32	**1a** (10), styrene (1000), naphthonitrile (20)	CD_3CN[a]	82	0.02
33	**1a** (10), styrene (1000), naphthonitrile (20)	$CD_3CN + 5\%\ H_2O$[a]	83	0
34	**1a** (10), styrene (1000), naphthonitrile (20)	$CH_3CN + 5\%\ D_2O$[a]	83	0.66
35	**1a** (10), styrene (200), 4,4′-bipyridine (20)	$NH_3 + CD_3CD(OD)CD_3$ (410 mM)[b]	85	0

[a] $+10^{-1}$ M NBuBF4, temp 20 °C. [b] $+10^{-1}$ M KBr, temp −28 °C.

into chloride ions showing that a substantial part of the aryl halide remains included in the telomers. Addition of a proton donor, urea or water (experiments 4 and 5), significantly improves the yields of the addition product and of ArH, the sum of the two reaching 60–70%. A large amount of a white polymer is, however, obtained, which could be polystyrene or polystyrene with inclusion of benzonitrile groups in the chains. (see the Experimental Section for the mass spectra of oligomers). Addition of 2-propanol (experiments 6–13) leads to a further, substantial increase of the yield of the addition product which reaches 90% in the case of 4-chlorobenzonitrile and styrene. The total yield of the addition product and ArH also increases to 65–94% according to the ArX and the olefin. The number of electrons consumed per molecule of ArX is close to the theoretical value for a reaction leading to the addition product (2 e/molecule) and to ArH (2 e/molecule). It ranges from 1.5 to 2, except in the case of 4-chlorostyrene where it reaches 5. The latter value is related to the reductive cleavage of the C–Cl bond of *p*-chlorostyrene and/or that of the addition product as shown by titration of Cl^- (5.35 mM of Cl^- are found for 2 mM of starting ArCl and 220 mM of 4-chlorostyrene). In all cases, the addition product is the hydroarylation product, the formation of which consumes two electrons and one proton.



The results displayed in Table II show that the reaction can also be successfully carried out in organic solvents. Any of the three most common solvents of organic electrochemistry, Me_2SO, MeCN, and DMF, can be used, although the yields are somewhat lower with DMF than with the two other solvents (compare experiments 14, 16, 18). As expected, the yield of the addition product increases with the concentration of the olefin (experiments 15–17 and 18–19). It is nearly as good, even in the less favorable solvent (DMF), as in liquid ammonia–2-propanol mixtures provided the concentration of olefin is increased by a factor of 5. Addition of water to MeCN (experiments 19–22) does not change the yield to any appreciable extent. It should be noted, in this connection, that the starting acetonitrile already contains ca. 0.3% H_2O. MeCN being a particularly convenient solvent for recovering the products, it was mostly used to further exemplify the reaction with other olefins and aryl halides (experiments 23–31).

Deuterium-Incorporation Experiments. The final product corresponds to the addition of an aryl group and hydrogen on the carbons of the olefin. An important clue to the reaction mechanism is to know whether the hydrogen is transferred as a proton or as hydrogen atom. For this purpose, we carried out electrolyses in CD_3CN, $CD_3CN + 5\%\ H_2O$, and $CH_3CN + 5\%\ D_2O$ and looked for the amount of deuterium incorporation in the addition product. This strategy is based on the fact that water is a better proton donor than acetonitrile whereas, conversely, acetonitrile is a good H atom donor and water a very poor H atom donor.[17,20] It should be noted, however, that in these experiments the cation of the supporting electrolyte is not deuterated and thus may provide protons or H atoms.[20]

In liquid ammonia, an experiment was carried out in the presence of $CD_3CD(OD)CD_3$. NH_3 is a very poor H atom donor[20] whereas 2-propanol is a good H atom donor. The supporting electrolyte, KBr, does not interfere, but residual water (ca. 2 mM) is likely to be the best proton donor present in the medium.

The results of the two series of deuterium incorporation experiments are summarized in Table III. It should be noted that deuteration takes place on the phenyl-substituted carbon of the olefin **5aD** ($CNC_6H_4CH_2CHDC_6H_5$); indeed the percentage of deuteration is the same whether it is measured for the *m*/*e* = 207 peak or for the *m*/*e* = 91 tropylium ion.

Cyclic Voltammetry. In the absence of olefin, the cyclic voltammogram of **1a** in liquid NH_3 shows an irreversible two-electron wave (peak potential at −1.55 V vs Ag/0.01 M Ag^+ at 0.2 V s^{-1}) followed by a one-electron reversible wave (cathodic peak potential at −1.80 V vs Ag/0.01 M Ag^+) representing the reduction of the benzonitrile produced at the first wave:

$$ArX + 2e^- + H^+ \rightarrow ArH + X^-$$

Addition of styrene to the solution does not change the height of the first wave. A small wave appears at the same potential (peak at −1.88 V vs Ag/0.01 M Ag^+ at 0.2 V s^{-1}) as that of a pure sample of the addition product **5a**.

The addition reaction is not expected to compete to a great extent with the reduction of $Ar^\bullet$ when this species is generated by means of direct electron transfer at the electrode; however, one could expect to observe the wave for the addition product when ArCl is reduced by means of a mediator. This was attempted using 4,4′-bipyridine as a mediator (Figure 1a); the addition of the halide **1a** results in an increase of the peak height and a loss of reversibility typical of the occurrence of the catalytic reaction depicted in Scheme I. Addition of the olefin does not change the height of the catalytic wave. As in the case of direct cyclic voltammetry, this is expected even if the addition reaction takes place, since the electron stoichiometry remains two-electrons per molecule with or without the occurrence of the addition reaction. The wave for the addition product could not be observed because of an unfortunate overlapping with the second wave of the

---

(17) (a) M'Halla, F.; Pinson, J.; Savéant, J. M. *Electroanal. Chem.* 1978, *89*, 347. (b) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120.

(18) For the formulation and resolution of such electrochemical kinetics problems see ref 12 and references cited therein.

(19) (a) Kojima, H.; Bard, A. J. *J. Am. Chem. Soc.* **1975**, *97*, 6317.

(20) (a) Bridger, R. F.; Russell, G. A. *J. Am. Chem. Soc.* **1963**, *85*, 3754. (b) Russell, G. A. *Reactivity Selectivity and Polar Effects in Hydrogen Atom Transfer Reactions in Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, p 103.

Table IV. Variations of the Cyclic Voltammetric Peak Height of the Mediator upon Addition of an Aryl Halide, of a Nucleophile, and of an Olefin[a]

mediator (mM)	Arx (mM)	ip_1/ip_0[b]	nucleophile[c] (mM)	ip_2/ip_0[b]	olefin (mM)	ip_3/ip_0[b]
4,4′-bipyridine (2)	**1a** (5.9)	4.9	**6a** (30)	1.8	$C_6H_5CH{=}CH_2$ (100)	3.8
4,4′-bipyridine (1.93)	**1a** (5.3)	4.7	**6b** (30)	1.5	$C_6H_5CH{=}CH_2$ (110)	2.8
4,4′-bipyridine (2.1)	**1b** (4.5)	4.7	**6a** (31)	1.3	$C_6H_5CH{=}CH_2$ (100)	4.0
2,2′-bipyridine (2.1)	**2** (5.2)	3.1	**6a** (31)	1.5	$C_6H_5CH{=}CH_2$ (107)	2.3
4,4′-bipyridine (2.1)	**1a** (4.0)	3.8	**6b** (31)	1.3	$CH_3OC_6H_4CH{=}CH_2$ (107)	1.9
4,4′-bipyridine (2.2)	**1a** (3.7)	3.5	**6a** (31)	1.3	$ClC_6H_4CH{=}CH_2$ (107)	2.2

[a] In liquid NH_3 (+0.1 M KBr), temperature −38 °C. Scan rate 0.2 V s^{-1}. [b] ip_0, cathodic peak height of the mediator without addition of the aryl halide, the nucleophile and the olefin; ip_1, peak height in the presence of the aryl halide; ip_2, in the presence of the aryl halide and the nucleophile; ip_3, in the presence of the aryl halide, the nucleophile and the olefin. [c] ArS^- with Ar = 2-pyridyl (**6a**), Ar = p-$CH_3OC_6H_4$ (**6b**).

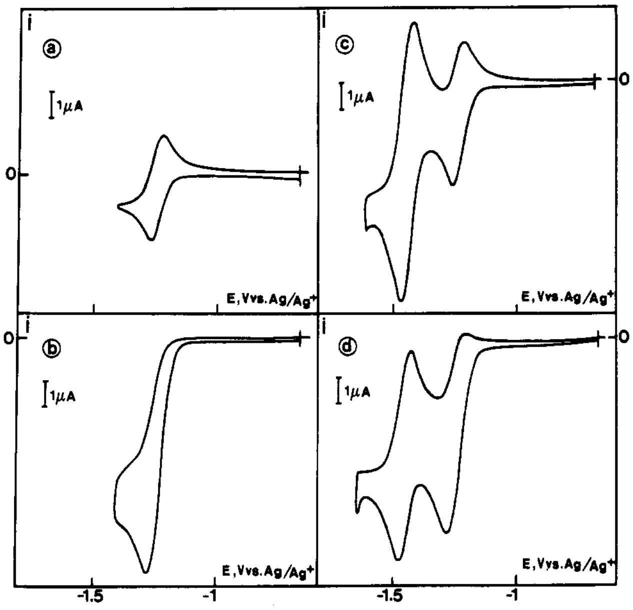


Figure 1. Cyclic voltammetry of 4,4′-bipyridine (2 mM) in liquid NH_3(+0.1 M KBr), alone (a), in the presence of 3.5 mM **1a** (b), with further addition of 30 mM p-$CH_3OC_6H_4S^-$ (c), with further addition of 57 mM styrene (d). Scan rate: 0.2 V s^{-1}. Temperature: −38 °C.

mediator. We had to resort to an indirect method to detect the occurrence of the addition reaction by means of cyclic voltammetry, based on the competition of this reaction with the trapping of the aryl radical by nucleophiles. As found earlier,[3] the latter reaction involves a zero-electron stoichiometry:

$$ArX + e^- \rightleftharpoons ArX^{\bullet -}$$
$$ArX^{\bullet -} \rightarrow Ar^{\bullet} + X^-$$
$$Ar^{\bullet} + Nu^- \rightarrow ArNu^{\bullet -}$$
$$ArNu^{\bullet -} - e \rightleftharpoons ArNu \text{ and/or } ArNu^{\bullet -} + ArX \rightarrow ArNu + ArX^{\bullet -}$$
$$\overline{ArX + Nu^- \rightarrow ArNu + X^-}$$

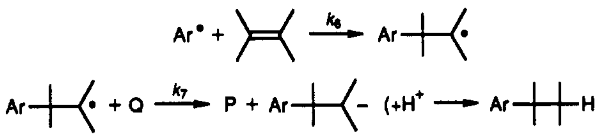
Accordingly, the catalytic wave decreases upon addition of a nucleophile to the solution (Figure 1c), eventually reaching the one-electron reversible cyclic voltammetric behavior of the starting mediator:

$$P + e^- \rightleftharpoons Q \qquad (0)$$
$$Q + ArX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P + ArX^{\bullet -} \qquad (1)$$
$$ArX^{\bullet -} \xrightarrow{k_2} Ar^{\bullet} + X^- \qquad (2)$$
$$Ar^{\bullet} + Nu^- \xrightarrow{k_4} ArNu^{\bullet -} \qquad (4)$$
$$ArNu^{\bullet -} + P \xrightarrow{k_5} ArNu + Q \qquad (5)$$
$$\overline{P + e^- \rightleftharpoons Q}$$

The latter situation is reached when the concentration of the nucleophile is large enough to outrun the competing reduction of the aryl radical

$$Ar^{\bullet} + Q \rightarrow P + Ar^-(+H^+ \rightarrow ArH) \qquad (3)$$

If we now add the olefin to the solution, the mediator wave should increase insofar as the concentration of the olefin is large enough for the addition reaction 6



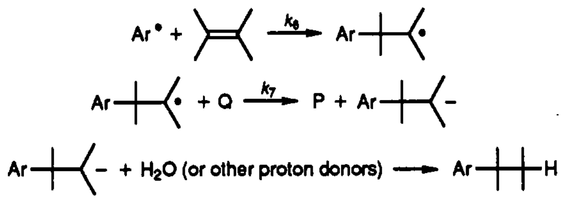
(6)

(7)

to compete with the reaction with the nucleophile (reaction 4). This is what indeed happens as shown in Figure 1d with the example of styrene. More examples are given in Table IV. The analysis of such results will be put on more quantitative grounds, allowing the determination of the rate constant of the addition reaction.

Reaction Mechanism. The preceding observations suggest the following reaction mechanism:

$$P + e^- \rightleftharpoons Q \qquad (0)$$
$$Q + ArX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} P + ArX^{\bullet -} \qquad (1)$$
$$ArX^{\bullet -} \xrightarrow{k_2} Ar^{\bullet} + X^- \qquad (2)$$



(6)

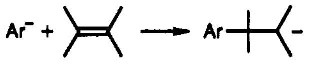
(7)

(8)

In liquid ammonia, the extremely poor yields of addition product and ArH are presumably consequences of both the absence of proton donor and of the poor solubility of the olefin[11d] when no organic cosolvent is added. The strong base (NH_2^-) which is generated by deprotonation of ammonia reacts with the starting aromatic halide and the olefin to give numerous side products. Introduction of a proton donor, water or urea, thus improves the addition product and ArH yields which are further increased by use of 2-propanol as a cosolvent. High yields in addition product are thus obtained. This is also true in the organic solvents where there are no solubility problems.

It appears from the results of competition experiments in which aryl radicals are trapped by nucleophiles that the hydroarylation products derive from the addition of aryl radicals on the double bond. An alternative mechanism would imply an attack of Ar^- on the double bond (instead of $Ar^{\bullet}$ as stated above):

$$Ar^{\bullet} + Q \longrightarrow Ar^- + P \qquad (3)$$



(9)

This possibility can be ruled out as follows by considering the voltammetric experiments. The reversible system of the P/Q catalyst (Figure 1a) is transformed into a large irreversible wave (Figure 1b) by addition of the aromatic halide, the P/Q system becomes reversible again (Figure 1c) by addition of the nucleophile. Such a reversible voltammogram is obtained when the concentration of the nucleophile is large enough to outrun the reduction of the aryl radical (reaction 3). Now, if addition of the olefin renders the wave of P irreversible again (as its height increases), it implies that the attack of the radical on the olefin (reaction 6) outruns the attack on the nucleophile (reaction 4), which, as we have just seen, outruns the reduction of the radical $Ar^\bullet$ (reaction 3). Besides, such a strong base as Ar^- would certainly be protonated by residual water, by the organic solvent used, or by liquid ammonia. In addition, the yields of the reaction (see Tables I and II) are not very sensitive to the electron-donating or electron-withdrawing character of the substituents on the olefin. The deuterium-incorporation experiments show that the hydrogen, in the hydroarylation products, is the result of an electron-transfer reduction of the adduct radical (reaction 7) followed by protonation of the ensuing carbanion (reaction 8) (and deuterium incorporation takes place at this position) rather than from H atom abstraction from 2-propanol (a good H atom donor) in liquid NH_3 or from the organic solvents. Indeed, no deuterium incorporation is observed in the presence of perdeuterated 2-propanol in liquid NH_3 or in perdeuterated acetonitrile (Table III). In liquid ammonia, the proton in reaction 8 comes from residual water rather than from the 2-propanol. In acetonitrile, it comes mostly from water but also partly from another proton source, presumably the tetrabutylammonium cation (experiment 34).

That the transformation of the adduct radical involves a one-electron + one-proton sequence rather than an H atom transfer can be rationalized on the following grounds. In the case of styrene in acetonitrile, the adduct radical is of the benzylic type, close to $PhCH^\bullet\text{-}CH_3$ as far as reducibility is concerned. It thus should have a reduction potential close to −1.6 V vs SCE,[14] i.e., significantly positive of the standard potential of the mediator (−1.8 V vs SCE for naphthonitrile which was used in most cases). The rate constant of reaction 7 should thus be very large, not too far from the diffusion limit. On the other hand, the rate constants for H atom abstraction from the MeCN and 2-propanol can be derived from chain-transfer constants, C_S, C_S = (rate constant of chain transfer)/(rate constant of propagation) in radical polymerization reactions[15] if one assumes, as is usually done, that the rate constant for H atom abstraction of $ArCH_2CRR'[CHArCRR']_nCHAr\dot{C}RR'$ depends little upon the value of n. These rate constants, as well as that of chain propagation (addition of the first adduct radical to an olefin molecule), are summarized in Table V.

It appears from these rate constants that, in the case of styrenes, the reduction of the adduct radical will outrun the H atom abstraction from the solvent by this same radical. With the other olefins, the reduction potential of the radical is not known, but it is certainly more negative in the case of vinyl butyl ether and vinyl phenyl sulfide. However, the rate constants of H atom transfer are so low that reduction is still likely to predominate. The same conclusions are also valid for the competition between the reduction of the first adduct radical and its further addition on another olefin molecule.

As discussed in the introduction, the use of a mediator favors the addition of $Ar^\bullet$ on the double bond at the expense of the reduction of $Ar^\bullet$. This reduction of $Ar^\bullet$ is a particularly serious problem with fast-cleaving halides like **1**, **2**, and **3** since the reduction then takes place at the electrode surface (reaction 3′). This is no longer necessary with **4**, since the cleavage rate constant is so low (2×10^3 s^{-1})[16] that the reduction of $Ar^\bullet$ does not take place at the electrode surface but rather in the solution from the anion radical $ArX^{\bullet -}$[12] and is thus no more efficient than the reduction by the reduced form of the mediator. Another reaction competing with the addition reaction that cannot be avoided in the organic solvents is H atom abstraction from most organic solvents (MeCN, DMSO, DMF):[17]

$$Ar^\bullet + SH \rightarrow ArH + S^\bullet \qquad (10)$$

which has previously been shown to compete with the addition on nucleophiles in the context of electrochemically induced nucleophilic substitution in organic solvents.[2i]

Rate Constant for the Addition Reaction. This was determined by the competition method outlined earlier, in the case of the $p\text{-}CNC_6H_4^\bullet$ radical and styrene in liquid NH_3, in order to get an order of magnitude estimate of the rate constants of such a reaction. The procedure was as follows. Catalytic cyclic voltammetric curves of the type shown in Figure 1b were recorded with 4,4′-bipyridine as the mediator for increasing concentrations of **1a**. The ratio i_p/i_p° (i_p and ip° are peak currents in the absence and presence of **1a**, respectively) was plotted as a function of the excess factor $\gamma = [ArX]/[\text{mediator}]$ for three scan rates (Figure 2a). Then, taking a new solution of **1a**, increasing concentrations of the nucleophile were added (two nucleophiles were used, 2-pyridinethiolate and 4-methoxybenzenethiolate) until (similar to what is shown in Figure 1c) full reversibility was recovered. Styrene was then added in increasing amounts to the solution, resulting in an increase of the peak current (like that shown in Figure 1d). Under these conditions the reduction of $Ar^\bullet$ by the reduced form of the mediator is outrun by its reaction with the nucleophile and with the olefin. In other words, the whole set of reactions taking place in the diffusion layer consists of steps 0–2, 4–5, and 6–8. The current thus flowing at the electrode surface can be obtained by solution of the following set of partial differential equations and initial and boundary conditions:[18]

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \frac{2k_6[\mathrm{Ol}]}{k_4[\mathrm{Nu}^-] + k_6[\mathrm{Ol}]}\lambda_1\, aq$$

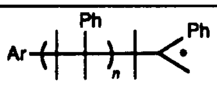
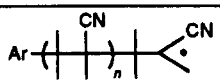
$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda_1\, aq$$

$$\tau = 0,\ y \geq 0 \text{ and } y = \infty,\ \tau \geq 0;\ q = 0,\ a = \gamma$$

$$y = 0,\ \tau \geq 0:\ q = \frac{1}{1 + \exp(-\xi)},\ \frac{\partial a}{\partial y} = 0$$

where the various symbols have the following meaning: $\tau = (F/RT)vt$, and $y = x(FV/RTD)^{1/2}$ are dimensionless expressions of the time (t) and the distance to the electrode (x), v is the scan rate; q and a are the concentrations of the reduced form of mediator and of the aryl halide normalized versus the concentration of the mediator in the bulk of the solution; γ is the excess factor already defined; $\lambda_1 = (RT/F)(k_1/v)$ is the dimensionless expression of the rate constant k, as normalized with respect to the diffusion rate; $\xi = -(F/RT)(E - E^\circ)$ with $E = E_i - vt$ is a dimensionless expression of the electrode potential E (E° is the standard potential of the mediator, E_i is the starting potential of the scan). The above formulation was arrived at taking into account the following condition: reaction 2 is faster than backward reaction 1. This was checked by analysis of the data shown in Figure 2a, which also gave

Table V. Rate Constants of H Atom Abstraction and Chain Propagation

reaction	solvent or additive		
H atom[a,b] abstraction	MeCN	2.8×10^{-3} (5.4×10^{-2})	1.0×10^{-2} (0.19)
	DMF	5.8×10^{-3} (7.5×10^{-2})	1.4×10^{-2} (0.18)
	2-propanol (0.41 M)	2.0×10^{-2} (8.3×10^{-3})	–
chain propagation,[a] 25 °C		66	51

[a] In M^{-1} s^{-1}. [b] Between parentheses: pseudo-first-order rate constants (s^{-1}).

the value of k_1 (1.2×10^4 M^{-1} s^{-1}). Thus the formation of $Ar^{\bullet}$ from the reduction of ArX by Q is kinetically controlled by forward reaction 1. This is the reason for the term $\lambda_1 aq$ in the above two partial differential equations. The second condition is the steady-state assumption applied to $ArX^{\bullet-}$, $Ar^{\bullet}$, and the adduct radical.

The solution of the above system leading to the value of i_p/i_p° (the peak current normalized to its value in the absence of ArX, $ArNu^-$, and the olefin) is given by:

$$\frac{i_p}{i_p^{\circ}} = -\frac{1}{0.446}\left(\frac{\partial q}{\partial y}\right)_{y=0}$$

which can be greatly simplified by transforming a into

$$a^* = \frac{k_6[\mathrm{Ol}]}{k_4[\mathrm{Nu}^-] + k_6[\mathrm{Ol}]}a$$

The system then becomes

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - 2\lambda_1 a^* q$$

$$\frac{\partial a^*}{\partial \tau} = \frac{\partial^2 a^*}{\partial y^2} - \lambda_1 a^* q$$

$$\tau = 0, y \geq 0 \text{ and } y = \infty, \tau \geq 0:\ q = 0, a^* = \gamma^* = \gamma(k_6[\mathrm{Ol}]/k_4[\mathrm{Nu}^-] + k_6[\mathrm{Ol}])$$

$$y = 0, \tau \geq 0:\ q = \frac{1}{1 + \exp(-\xi)},\ \frac{\partial a^*}{\partial y} = 0$$

This is exactly the system which governs the catalytic current in the absence of nucleophile and olefin (reactions 0–3) for which the i_p/i_p° curves have been determined as shown in Figure 2a. The following procedure ensues. The i_p/i_p° ratio obtained after addition of a certain amount of ArX to the mediator, after addition of Nu^- up to the full recovering of the reversibility and after addition of the olefin is entered in the graphs shown in Figure 2a. We then obtain from the corresponding abscissa the corresponding value of γ^* and thus, since we know γ, the value of $k_6[\mathrm{Ol}]/(k_4[\mathrm{Nu}^-] + k_6[\mathrm{Ol}])$ and thus, since we know k_4, the value of k_6. The results are shown in Figure 2b in the form of a plot of γ/γ^* versus the $[\mathrm{Nu}^-]/[\mathrm{Ol}]$ concentration ratio for two nucleophiles, 4-methoxybenzenethiolate and 2-pyridinethiolate. Linear plots are obtained in each case as expected from

$$\frac{\gamma}{\gamma^*} = 1 + \frac{k_4}{k_6}\frac{[\mathrm{Nu}^-]}{[\mathrm{Ol}]}$$

From the slopes, k_6/k_4 is found equal to 0.215 with the first nucleophile and 0.345 with the second nucleophile; k_4 has been determined independently following procedures already described:[3m] 1.2×10^{10} and 9.2×10^9 M^{-1} s^{-1} for the first and second nucleophiles, respectively. Thus k_6 is found to be 2.5×10^9 and 3.2×10^9 M^{-1} s^{-1} from the first and second determination; the average value is 2.8×10^9 M^{-1} s^{-1}.

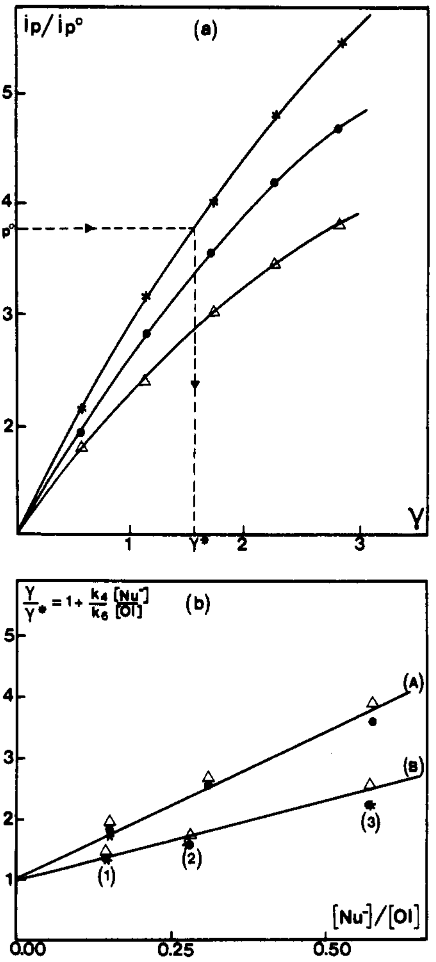
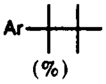


Figure 2. Cyclic voltammetry of 4,4′-bipyridine (2.2 mM) in liquid NH_3 in the presence of 4-chlorobenzonitrile. (a) Peak current ratio as a function of the concentration of ArX (γ = [ArX]/[mediator]) and of the scan rate (△, 0.1; ●, 0.2, *, 0.4 V s^{-1}) in the absence of nucleophile and olefin. The dashed lines show the procedure for determining γ^* (see text): the nucleophile is added until i_p/i_p° becomes unity, then the addition of olefin makes i_p/i_p° increase. Thus at each concentration of olefin, the value of γ is derived from that of i_p/i_p° using the curve corresponding to the scan rate employed. (b) Variation of γ^* thus determined with the $[\mathrm{Nu}^-]/[\mathrm{Ol}]$ concentration ratio for Nu^-:4-methoxybenzenethiolate (A), 2-pyridinethiolate (B); $[\mathrm{Nu}^-]$ = 10 mM in both cases. The group of points (1) corresponds to [styrene] = 133 and 138 mM for A and B, respectively, (2) to 64.5 and 71, (3) to 35 for both A and B. The symbolism for the scan rates is the same as in Figure 2a.

Estimation of the hydroarylation rate constant by competition with the reaction with nucleophiles can also be made at the preparative scale. The results of such experiments with 4-chlorobenzonitrile as substrate, 4,4′-bipyridine as mediator, and 2-pyridinethiolate as nucleophile in liquid NH_3 are given in Table V. The ratio of the yields of the addition product $ArCH_2CHRR'$ and ArNu allows the determination of the ratio of the rate constants

$$\frac{k_6[\mathrm{Ol}]}{k_4[\mathrm{Nu}^-]} = \frac{[\mathrm{ArCH_2CHRR'}]}{[\mathrm{ArNu}]}$$

Table VI. Competition between the Addition of 4-Cyanophenyl Radicals on Olefins and on a Nucleophile[a] (2-Pyridinethiolate)

expt	olefin (concn, mM)	 (%)	ArNu (%)	k_6 (M^{-1} s^{-1})
36	styrene (230)	28	50	1.9×10^9
38	*p*-methoxystyrene (240)	26	33	2.3×10^9
37	*p*-chlorostyrene (260)	21	41	1.6×10^9
39	α-methylstyrene (240)	28	27	3.5×10^9

[a] In liquid NH_3 + 0.41 M 2-isopropanol + 0.1 M KBr. Temperature −38 °C. [b] Nucleophile concentration 8.5 mM; rate constant of the reaction of 4-cyanophenyl radical with 2-pyridinethiolate 9.2×10^9 M^{-1} s^{-1}.

and hence that of k_6 (Table VI). It is seen that there is satisfactory agreement between the cyclic voltammetry and preparative-scale competition methods (with styrene, k_6 is found equal to 2.8×10^9 and 1.9×10^9 M^{-1} s^{-1} by the first and second methods, respectively).

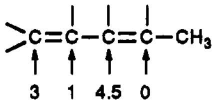
In organic solvents, another method is available for estimating the hydroarylation rate constant from the respective yields of $ArCH_2CHRR'$ and ArH. ArH comes from both reactions 3 and 10. Thus

$$\frac{[ArCH_2CHRR']}{[ArH]} = \frac{k_6[Ol]}{k_{10}[SH] + k_3[Q]}$$

where SH designates the solvent. [Q] is the average concentration of the reduced form of the mediator in the reaction layer corresponding to the catalytic reaction. It is approximately equal to half the bulk concentration of the mediator. On the other hand, as discussed earlier, the rate constant of reaction 3 should be close to the diffusion limit, i.e., 2×10^{10} M^{-1} s^{-1} and 5×10^9 M^{-1} s^{-1} in DMF.[19] The first-order rate constant of H atom transfer from acetonitrile to the 4-cyanophenyl radical, $k_{10}[SH]$, is 4×10^7 s^{-1}.[17b] From other sources,[20] we know that the ratio of the H atom transfer rate constants from DMF and MeCN to the phenyl radical is 7.1 and thus, assuming that the ratio is approximately the same for the 4-cyanophenyl radical, $k_{10}[SH] = 2.8 \times 10^8$ s^{-1} in DMF. Rate constants estimated in this way are listed in Table VII together with others that have been determined by means of the other methods described earlier.

Conclusions

Generation of aryl radicals from the parent halides by means of an outer-sphere one-electron transfer reagent in the presence of olefins gives the hydroarylation product in fair to very good yields, comparable with other methods such as reduction by titanium(III) salts and trialkyltin hydrides, Meerwein, or Pd^0 reactions. The reaction can be carried out in organic solvents such as DMF, MeCN, and Me_2SO and in liquid ammonia. In the latter case, an organic additive, such as 2-propanol, has to be introduced to ensure solubility and proton donors, such as water, must be present. As regards the regioselectivity of the reaction, steric hindrance plays, as expected[6a,21] a major role; in the case of styrenes, acrylonitrile, butyl vinyl ether, and vinyl phenyl sulfide, the aryl radicals add at the less hindered carbon on the olefin. In the case of 1,3-pentadiene the four carbons are attacked in the following ratios:



Steric hindrance at the aryl radical also plays a role (compare experiments 17 and 29 in Table II). The main reactions competing with the hydroarylation reaction are reduction of the aryl radical by the reduced form of the mediator in liquid ammonia and in the organic solvents and H atom abstraction in the organic solvents. The rate constant for the addition of the aryl radicals to the olefins is very large, close to the diffusion-limited value and larger, by 3–4 orders of magnitude, than those of alkyl radicals.[6a] These very large values are in fact required for the indirect electrochemical induction from the parent halides to work since both the electron-transfer reduction and H atom transfer abstraction by aryl radicals are themselves quite fast reactions. The reaction is not very sensitive to polar effects. The radicals that we have used evidence a clear electrophilic character; they can participate in $S_{RN}1$ reactions, but the rate constants with electron-donating or electron-withdrawing substituted olefins are not very different (see, for example, the last two lines of Table VII); this could be expected[21] for a highly exergonic reaction (a value of $\Delta G° = -100$ kJ/mol in the gas phase can be calculated[22] for the reaction of a phenyl radical on styrene).

Experimental Section

The experimental set up, electrochemical cell, and procedures for purifying ammonia and organic solvents have been described previously.[3g,23,24] The potentiostat used for cyclic voltammetry was equipped with a positive-feedback ohmic-drop compensation device.[25] The working electrodes were a mercury drop hanging from a 1 mm diameter gold disk in the organic solvents and in liquid ammonia a 1 mm diameter gold disk polished on alumina. In the preparative experiments the working electrodes were a 15-cm² platinum grid in liquid ammonia and a 27-cm² mercury pool in organic solvents. The reference electrodes were a saturated calomel electrode (SCE) separated from the solution by a bridge in the organic solvents and an Ag/Ag^+ (0.01M) in liquid ammonia $E^{R/0}_{Ag/Ag^+} = E^{R/0}_{SCE} - 0.28$ V. The supporting electrolytes were NBu_4BF_4 (0.1 M) in organic solvents and anhydrous KBr (0.1 M) in liquid ammonia. ACN was distilled at atmospheric pressure in a 1-m column filled with Raschig rings after refluxing for 5 h over calcium hydride, DMF and DMSO were distilled under reduced (10 mmHg) pressure in a 30-cm column filled as above. The reduction potentials of the substrates and catalysts were measured by cyclic voltammetry:

1a	$E_p = -1.55$ $V/Ag.Ag^+$ in liquid ammonia
1b	$E_p = -1.43$ $V/Ag/Ag^+$ in liquid ammonia
2	$E_p = -1.80$ $V/Ag/Ag^+$ in liquid ammonia
4,4′-bipyridine	$E_p = -1.36$ $V/Ag/Ag^+$ in liquid ammonia
2,2′-bipyridine	$E_p = -1.66$ $V/Ag/Ag^+$ in liquid ammonia
1a	$E_p = -2.06$ V/SCE in MeCN
1b	$E_p = -1.94$ V/SCE in MeCN
3	$E_p = -2.68$ V/SCE in DMF
4	$E_p = -1.57$ V/SCE in MeCN
naphthonitrile	$E_p = -1.83$ V/SCE in MeCN
4-cyanopyridine	$E_p = -1.79$ V/SCE in DMF
methyl benzoate	$E_p = -2.22$ V/SCE in DMF

The electrolysis solutions were analyzed by gas chromatography (1.5-m OV-17 column on Chromosorb W 100/120) and HPLC (5 μm silica column eluted with heptane–CH_2Cl_2 or ethyl ether–CH_2Cl_2 mixtures). Some of the final products were synthesized by independent methods for identification by GC, HPLC, TLC, NMR, or mass spectrometry.

4-(2-Phenylethyl)benzonitrile (5a)[26] was prepared in liquid ammonia containing 25 mM NH_2^- (prepared by adding sodium

---

(21) (a) Walling, C. *Free Radical in Solution*; Wiley: New York, 1957. (b) Rüchardt, C. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830. (c) Tedder, J. M.; Walton, J. C. *Acc. Chem. Res.* **1976**, *9*, 183.

(22) Benson, S. W., Ed. *Thermochemical Kinetics*, 2nd ed.; J. Wiley: New York, 1976.

(23) Herlem, M. *Bull. Soc. Chim. Fr.* **1967**, 1685.

(24) Herlem, M.; Minet, J. J.; Thiébault, A. *J. Electroanal. Chem.* 1971, *30*, 203.

(25) Garreau, D.; Savéant, J. M. *J. Electroanal. Chem.* **1972**, *35*, 309.

(26) Rash, F. H.; Boatman, S.; Hauser, C. R. *J. Org. Chem.* **1966**, *32*, 372.

(27) Kayser, E. M.; Petty, J. D. *Synthesis* **1975**, 705.

Table VII. Rate Constants of the Addition of Aromatic Radical on Olefins

solvent, temp (°C)	radical	olefin	k_6 (M^{-1} s^{-1})
liquid NH_3, − 38	2-cyanophenyl	styrene	$3.0 \times 10^{9\,a}$
liquid NH_3, − 38	3-pyridyl	styrene	$2.1 \times 10^{9\,a}$
liquid NH_3, − 38	4-cyanophenyl	styrene	$2.8 \times 10^{9\,a}$
liquid NH_3, − 38	4-cyanophenyl	styrene	$1.9 \times 10^{9\,b}$
liquid NH_3, −38	4-cyanophenyl	*p*-methoxystyrene	$2.3 \times 10^{9\,b}$
liquid NH_3, −38	4-cyanophenyl	*p*-chlorostyrene	$1.6 \times 10^{9\,b}$
liquid NH_3, −38	4-cyanophenyl	α-methylstyrene	$3.5 \times 10^{9\,b}$
DMF, 20	4-cyanophenyl	styrene	$4.5 \times 10^{9\,c}$
DMF, 20	4-cyanophenyl	vinyl phenyl sulfide	$2.2 \times 10^{9\,c}$
MeCN, 20	4-cyanophenyl	butyl vinyl ether	$9.5 \times 10^8 < k_6 < 2.9 \times 10^{9\,c,d}$
MeCN, 20	4-cyanophenyl	acrylonitrile	$1.5 \times 10^{10\,c}$

[a] Competition with $Ar^{\bullet}$ P Nu^- in cyclic voltammetry. [b] Competition with $Ar^{\bullet} + Nu^-$ in preparative-scale electrolysis. [c] Competition with $Ar^{\bullet}$ + SH and $Ar^{\bullet} + Q$. [d] There is some uncertainty on this value as in experiment 24 the overall yield amounts to only 50%.

in the presence of small pieces of iron) by adding 0.02 mol of tolunitrile and then an equivalent amount of benzyl chloride, both dissolved in ethyl ether. After half an hour, ammonium chloride was added to neutralize the excess of base, and ammonia was evaporated. The product was recrystallized (CH_2Cl_2–pentane) as white crystals: mp 41 °C (lit.[26] mp 40–42.5 °C); NMR ($CDCl_3$, TMS) δ 2.9 (s, 4 H, 2 CH_2), 7–7.9 (m, 9 H aromatics); mass (EI), *m/e* 207 (M) (9), 116 (9), 91 (100), 65 (18). Anal. Calcd: C, 86.95; H, 6.28; N, 6.76. Found: C, 86.63; H, 6.34; N, 6.96.

2-(2-Phenylethyl)benzonitrile, 5g,[26] was prepared in the same way as **5a**: colorless oil; NMR ($CDCl_3$, TMS) δ 2.9–3.2 (m, 4 H, 2 CH_2), 7.0–7.9 (m, 8 H, aromatics); mass (EI) *m/e* 207 (M) (55), 116 (25), 91 (100), 65 (98). Anal. Calcd: C, 86.95; H, 6.28; N, 6.75. Found: C, 86.65; H, 6.47; N, 6.81.

4-(2-(4′-Chlorophenyl)ethyl)benzonitrile (5d) was prepared as for **5a**: white crystals; mp 110 °C (lit.[26] mp 111–112 °C); NMR ($CDCl_3$, TMS) δ 2.9 (s, 4 H, 2 CH_2), 7.0–7.7 (m, 8 H, aromatics); mass (EI), *m/e* 241 (M) (5), 125 (100), 116 (5), 89 (17). Anal. Calcd: C, 74.68; H, 4.97; N, 5.8. Found: C, 74.87; H, 4.93; N, 6.03.

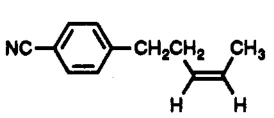
4-(2-(4′-Methoxyphenyl)ethyl)benzonitrile (5c) is prepared as for **5a**: white crystals; mp 95 °C; NMR ($CDCl_3$, TMS) δ 2.93 (s, 4 H, 2 CH_2), 6.7–7.8 (m, 8 H); mass, *m/e* 237 (M) (95), 121 (100), 116 (9), 91 (19), 77 (35). Anal. Calcd: C, 81.01; H, 6.32; N, 5.91. Found: C, 79.97; H, 6.33; N, 5.97.

3-(2-Phenylethyl)pyridine (5h) is prepared according to ref 27 from 3-picoline and benzyl bromide ($CDCl_3$, TMS) δ 2.95 (s, 4 H, 2 CH_2), 7.0–7.6 (m, 7 H, aromatics); mass (EI), *m/e* 183 (M) (39), 91 (100), 77 (5). Anal. Calcd: C, 85.24; H, 7.10; N, 7.65. Found: C, 85.03; H, 7.18; N, 7.07.

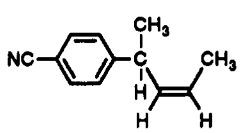
Other products were prepared by electrolysis in liquid ammonia (80 mL, 0.1 M KBr). Typically, 2 g of aryl halides were used in the presence of the olefin (1 M), and currents of 20 mA/cm^2 were passed until the theoretical number of F/mol had been consumed. The solution was then neutralized with ammonium chloride, ammonia was evaporated and the residue was taken up with methylene chloride, the excess of olefin was evaporated under vacuum, and the final product was purified by chromatography on 5-μm silica.

4-(2-Phenyl-2-methylethyl)benzonitrile (5b): white crystals; mp 68 °C; NMR ($CDCl_3$, TMS) δ 2.9 (m, 3 H, CH, CH_2), 1.2, 1.5 (d, 3 H, CH_3), 7.0–7.7 (m, 9 H, aromatics); mass (EI), *m/e* 221 (M) (2), 116 (7), 105 (100), 89 (8), 77 (18). Anal. Calcd: C, 86.87; H, 6.78; N, 6.33. Found: C, 86.88; H, 6.76; N, 6.25.

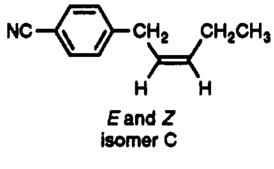
The reaction of 4-chlorobenzonitrile with 1,3-pentadiene leads to **5f**, a mixture of isomers



E and *Z*
isomer A



E and *Z*
isomer B



E and *Z*
isomer C

which can be characterized by NMR ($CDCl_3$, TMS). Isomer A: δ 1.6 (m, *J* = 7.5 Hz, CH_3), 2.37 (m, $CH_2C{=}$), 2.70 (m, $C_6H_5CH_2$). Isomer B: δ 1.25 and 1.50 (2 d, *J* = 6.75 Hz, CH_3CH), 1.68 (m, $CH_3C{=}$), 3.42 (m, $HCCH_3$). Isomer C: δ 0.98 (t, *J* = 7.5 Hz, CH_3), 2.02 (m, CH_2CH_3), 3.18 (d, *J* = 6 Hz, CH_2Ar), and for the three isomers δ 5.3–5.7 (m, ethylenics) and 7.1–7.5 (m, aromatics).

4-(2-Pyridylthio)benzonitrile (8). It is obtained by reduction of 4-chlorobenzonitrile (4 mmol) in the presence of 2-pyridinethiolate (7 mmol) ($S_{RN}1$ reaction) with 4,4′-bipyridine as a catalyst (1 mmol): white solid; mp 50 °C; NMR ($CDCl_3$, TMS) δ 7.1–7.8, 8.4–8.6 (m, 8 H, aromatics); mass spectrum, *m/e* 212 (M) (32), 211 (100), 106 (3), 78 (21). Anal. Calcd: C, 67.92; H, 3.77; N, 13.20. Found: C, 67.76; H, 3.72; N, 13.02.

Other products were synthesized by electrolysis in organic solvents.

2-(4-Cyanophenyl)propanenitrile (5e). In 100 mL of MeCN containing 10^{-1} M NBu_4BF_4, naphthonitrile (10^{-2} M), and 4-chlorobenzonitrile (10^{-2} M) was added an excess (1 M) of acrylonitrile. The anolyte contained MeCN and the supporting electrolyte at the same concentration. The cathode was a mercury pool and the anode a platinum grid. The solution was kept under argon. The potential was set at −1.8 V/SCE (on the voltammetric wave of naphthonitrile). The electrolysis was stopped after 2 F/mol were passed. The solution was evaporated, and the residue was taken up in CH_2Cl_2 and purified by chromatography on silica: white crystals; mp 76 °C (lit.[28] mp 76.5–77 °C); NMR ($CDCl_3$, TMS) δ 2.6–3.2 (m, 4 H, CH_2), 7.3–7.7 (m, 4 H, aromatics); mass (CI, NH_3), *m/e* 174 (M + 18) (100), 156 (M) (3), 116 (66), 102 (3), 74 (17). Anal. Calcd: C, 76.92; H, 5.12; N, 17.94. Found: C, 76.60; H, 5.16; N, 17.83. The following compounds were obtained in the same way.

1-(4-Benzoylphenyl)-2-phenylethane (5k): white crystals; mp 78 °C; NMR ($CDCl_3$, TMS) δ 3.0 (s, 4 H, CH_2), 7.5–8.0 (m, 16 H, aromatics); mass (EI), *m/e* 286 (M) (25), 195 (6), 167 (15), 105 (33), 91 (100), 77 (57). Anal. Calcd: C, 88.11; H, 6.29. Found: C, 87.77; H, 6.31.

1-(4-Cyanophenyl)-2-butoxyethane (5i): Pale yellow oil; NMR ($CDCl_3$, TMS) δ 0.8 (t, 3 H, CH_3), 1.3 (m, 4 H, CH_2), 3.2 (m, 6 H, CH_2), 7.1–7.5 (m, 4 H, aromatics); mass (EI), *m/e* 202 (12), 146 (32), 116 (12).

1-(4-Cyanophenyl)-2-(phenylthio)ethane (5l) obtained in DMF; white solid; mp 50 °C; NMR ($CDCl_3$, TMS) δ 2.8–3.3 (m, 4 H, CH_2), 7.2–7.8 (m, 9 H, aromatics); mass (EI), *m/e* 239 (M) (8), 130 (3), 123 (100), 116 (7), 109 (9), 77 (29). Anal. Calcd: C, 75.31; H, 5.44; N, 5.86. Found: C, 74.93; H, 5.66; N, 5.90.

Direct Electrolysis (without Catalyst) of 4-Chlorobenzonitrile in Liquid Ammonia (Experiment 1). In 80 mL of distilled ammonia containing 4-chlorobenzonitrile (2.5×10^{-2} M), styrene (0.2 M), and KBr (10^{-1} M) was passed a current of 50 mA until 2 F/mol had been consumed. Ammonia was evaporated, and the residue was taken up in CH_2Cl_2. The mixture was then purified by chromatography on silica. The following products were identified in the different fractions.

4-Chlorobenzamide: white solid; mp 172 °C (lit. mp 172–176 °C); NMR ($CDCl_3$, TMS) δ 6 (2 H, displaced by D_2O, NH_2), 7.11, 7.21, 7.45, 7.55 (AA′BB′, 4 H, aromatics); mass (EI), *m/e* 157 (17), 155 (55), 141 (32), 139 (100), 113 (20), 111 (58), 75 (56).

---

(28) Inaba, S.; Reuben, S. D. *Synthesis* **1984**, 842.

4-Cyanobiphenyl: identified by GC–MS; mass (EI), *m/e* 180 (20), 179 (100), 178 (25), 151 (20), 121 (11), 76 (19); (CI, NH_3) 197 (M + 18) (100), 179 (M) 32.

1,4-Diphenylbutane (which is the dimer of styrene): NMR ($CDCl_3$, TMS) δ 1.60 (m, 4 H, CH_2), 2.6 (m, 4 H, CH_2), 7.0–7.7 (m, 10 H, aromatics).

4-(2-Phenylethyl)benzonitrile (5a).

4,4′-Dicyanobiphenyl: identical (HPLC, GC) with an commercial sample (Lancaster Synthesis); mass (EI), *m/e* 205 (20), 204 (100), 178 (5), 150 (7), 102 (8).

4-Aminobenzonitrile: NMR ($CDCl_3$, TMS) δ 4.25 (s, 2 H, displaced by D_2O, NH_2), 6.55, 6.67, 7.34, 7.46 (AA′BB′, 4 H, aromatics); mass (EI) *m/e* 118 (M) (100), 91 (33), 64 (25); (CI, NH_3) 136 (M + 18) (100), 119 (M + 1) (22), 118 (M) (10).

An isomer of $C_6H_5CH_2CH_2CH_2CH(C_6H_4CN)C_6H_5$: mass (CI, NH_3), *m/e* 329 (M + 18), 311 (M).

An isomer of $C_6H_5CH_2CH_2CH(C_6H_5)CH_2CH(C_6H_5)CH_6H_4CN$: mass (CI, NH_3) 433 (M + 18) (20), 415 M (15).

Other unidentified products.

Electrolysis of 4-Chlorobenzonitrile in Liquid Ammonia in the Presence of Catalyst (4,4′-Bipyridine, 10^{-2} M) (Experiment 2). The procedure was the same as above. Beyond the products described in Table I, the following product was indentified in one of the chromatographic fractions from its mass spectrum. $C_6H_5CH_2CH_2CH(C_6H_5)CHOHC_6H_4CN$: *m/e* 327 (56), 222 (24), 130 (100), 105 (97), 102 (85).

Acknowledgment. We are grateful to N. Morin (Ecole Normale Supérieure) for her help in mass spectroscopy analysis.

Surface-Catalyzed Hydrochlorination of Alkenes.[1] The Reaction of the Gases Hydrogen Chloride and 1,3-Butadiene

Linda M. Mascavage, Hongji Chi,[2] Sangmoo La,[3] and David R. Dalton*[,4]

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received June 12, 1990

Mixtures of gaseous hydrogen chloride and gaseous 1,3-butadiene at total pressures less than 1 atm and at temperatures between 294 and 334 K yield mixtures of 3-chloro-1-butene and (*E*)- and (*Z*)-1-chloro-2-butene. The ratio of the product of putative 1,2-addition to those of 1,4-addition is approximately unity with only the amount of (*Z*)-1-chloro-2-butene increasing from ca. 2% of the total reaction product mixture at the lower temperature to ca. 4% at the higher temperature. Kinetic measurements have been made by observing the reaction throughout its course utilizing FT-IR spectroscopy. It is concluded that surface catalysis is required for product formation and that the reaction, which occurs at the walls, is most probably between multilayer adsorbed hydrogen chloride and gaseous or weakly adsorbed 1,3-butadiene.

Introduction

More than five decades ago, Kharasch, Kritchevsky, and Mayo[5] reported on the successful addition of hydrogen chloride to 1,3-butadiene in the absence of solvent at −80 °C and in glacial acetic acid at room temperature; the addition failed to occur in ether. Their analysis, by index of refraction (and distillation), demonstrated that, under the specified conditions for the reaction to occur and *at both temperatures*, the addition yielded 75–80% 3-chloro-1-butene (1) [called "secondary chloride"] and 20–25% 1-chloro-2-butene [called "crotyl chloride"]. Subsequent observation revealed "...that the equilibrium at room temperature in the presence of a trace of ferric chloride is a mixture *containing 50% of each of the chlorides* [emphasis added] ..." but "...in the presence of one mole of hydrogen chloride, the equilibrium mixture contains 70–75% of crotyl and 25–30% of secondary chloride, irrespective of the presence or absence of a trace of ferric chloride (although the ferric chloride has a great influence on the rate of isomerization)".

With greater or lesser fidelity to the original work[5] the passage of time has seen the information incorporated into the paradigm of "kinetic versus thermodynamic control" of organic reactions and inserted as such into recent texts.[6] The interesting questions concerning the geometry of the crotyl chloride (*E* and/or *Z*) initially formed and/or after equilibration, the identity of the "kinetic" product ratio at −80 °C and room temperature, and the failure of the addition reaction when attempted in ether as the solvent have apparently not been addressed.

The apparent gas-phase addition of hydrogen chloride to alkenes has been a subject of interest for many years.[7] Recently, the process, at modest pressures, has been shown to involve surface catalysis,[8] and surface-catalyzed reactions of hydrogen chloride are now thought to be integral to an understanding of aspects of the chemistry of the earth's atmosphere.[9]

---

(1) Presented, in part, at the 196th ACS National Meeting, Los Angeles, CA, September 1988, ORGN 0313.

(2) Taken, in part, from Chi, Hongji, MA Dissertation, Temple University, 1989.

(3) Present address: Ajou University, Suweon 170 Korea.

(4) Author to whom inquiries should be addressed at Temple University.

(5) Kharasch, M. S.; Kritchevsky, J.; Mayo, F. R. *J. Org. Chem.* **1937**, *2*, 489.

(6) The following list, while incomplete, is provided as representative and inclusion of, or failure to list, a work should not be taken as significant. (a) Ingold, C. K. *Structure and Mechanism in Organic Chemistry*; Cornell: Ithaca, 1953; p 657. (b) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 683. (c) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*, 2nd ed.; Benjamin: Menlo Park, 1977; pp 490 and 542. (d) Pine, S. H.; Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry*, 4th ed.; McGraw-Hill: New York, 1980; p 567. (e) Louden, G. M. *Organic Chemistry*; Addison-Wesley: Reading, 1983; p 535. (f) Vollhard, K. P. C. *Organic Chemistry*; Freeman: New York, 1987; p 579. (g) Solomons, T. W. G. *Organic Chemistry*, 4th ed.; Wiley: New York, 1988; p 467.

(7) For some early work, see: (a) Maass, O.; Wright, C. H. *J. Am. Chem. Soc.* **1924**, *46*, 2664. (b) Maass, O. Sivertz, D. *J. Am. Chem. Soc.* **1925**, *47*, 2883. (c) Kistiakowsky, G. B.; Stauffer, C. H. *J. Am. Chem. Soc.* **1937**, *59*, 165. (d) Brearley, D.; Kistiakowsky, G. B.; Stauffer, C. H. *J. Am. Chem. Soc.* **1936**, *59*, 43. (e) Andreu, P.; Noller, H.; Paiz, M. *An. Quim.* **1969**, *65*, 130.

(8) (a) Haugh, M. J.; Dalton, D. R. *J. Am. Chem. Soc.* **1975**, *97*, 5674. (b) Costello, F.; Dalton, D. R.; Poole, J. A. *J. Phys. Chem.* **1986**, *90*, 5352. (c) Tierney, J.; Costello, F.; Dalton, D. R. *J. Org. Chem.* **1986**, *51*, 5191.

(9) See, e.g.: (a) Seinfeld, J. H. *Science* **1989**, *243*, 745 and references therein. (b) McElroy, M. B. *Science* **1989**, *243*, 763 and references therein.

0022-3263/91/1956-0595$02.50/0 © 1991 American Chemical Society