fractions were combined and further purified by flash silica chromatography and HPLC (55% hexane/ethyl acetate, Dynamax silica) to obtain vallartanone A (**6**, 29.8 mg) and vallartanone B (**7**, 5.6 mg).

Vallartanone A (6): white crystals; mp 69 °C; $[\alpha]_D = -176°$ (*c* 0.68, $CHCl_3$); IR ($CHCl_3$) 1645, 1600 cm^{-1}; UV (MeOH) 215 nm (ϵ 12 296), 264 (28 510); ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) see Table I; HRMS *m/z* 346.2145, $C_{21}H_{30}O_4$ requires 346.2144.

Vallartanone B (7): oil; $[\alpha]_D = -133°$ (*c* 0.59, $CHCl_3$); IR ($CHCl_3$) 1645, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) see Table I; ^{13}C NMR ($CDCl_3$) see Table I; HRMS *m/z* 332.1986, $C_{20}H_{28}O_4$ requires 332.1987.

Hydrogenation of Vallartanone A (6). A solution of vallartanone A (**6**, 10.6 mg) in ethyl acetate (3 mL) containing 5% palladium on carbon (10 mg) was stirred vigorously under 1 atm of hydrogen for 18 h. The catalyst was removed by filtration through Celite, the solvent was evaporated, and the residue was purified by HPLC on Partisil (60% hexane–ethyl acetate) to obtain 6,7-dihydrovallartanone A (**8**, 1.2 mg, 11% yield) and recovered vallartanone A (50%).

6,7-Dihydrovallartanone A (8): oil; IR ($CHCl_3$) 1715, 1655, 1595 cm^{-1}; UV (MeOH) 216 nm (ϵ 10 822), 259 nm (ϵ 10 915); ^1H NMR ($CDCl_3$) δ 0.94 (d, 6 H, *J* = 7.0 Hz, H-20, 21), 1.00 (d, 3 H, *J* = 6.6 Hz, H-1), 1.04 (d, 3 H, *J* = 7.0 Hz, H-19), 1.24 (t, 3 H, *J* = 7.0 Hz, H-15), 1.40 (d, 3 H, *J* = 7.0 Hz, H-18), 1.87 (m, 1 H, H-2), 1.97 (s, 3 H, H-16), 2.00 (s, 3 H, H-17), 2.23 (dq, 1 H, *J* = 10.0, 7.0 Hz, H-6), 2.43 (dq, 1 H, *J* = 10.6, 7.0 Hz, H-4), 2.62 (AB q, 2 H, *J* = 15.0, 7.0 Hz, H-14), 3.00 (dd, 1 H, *J* = 10.6, 2.0 Hz, H-3), 3.27 (dq, 1 H, *J* = 7.0, 4.0 Hz, H-8), 3.34 (dd, 1 H, *J* = 10.0, 4.0 Hz, H-7); LRMS *m/z* = 348.3, $C_{21}H_{32}O_4$ requires 348.2.

Epimerization of Vallartanone A (6). Sodium hydroxide (4 M, 1.5 mL) was added to a solution of vallartanone A (**6**, 18.5 mg) in dry THF (3 mL), and the mixture was stirred vigorously under nitrogen for 18 h. The mixture was partitioned between water and ether, and the organic layer was washed with water (1 mL), dried over sodium sulfate, and evaporated to dryness. The residue was purified on ODS-Partisil (75% methanol–water) to obtain a 4:1 mixture of vallartanone A (**6**, 14.2 mg) and 8-*epi*-vallartanone A (**9**, 4.3 mg).

8-*epi*-Vallartanone A (9): oil; ^1H NMR ($CDCl_3$) δ 0.95 (d, 3 H, *J* = 6.9 Hz), 0.96 (d, 3 H, *J* = 6.9 Hz), 1.07 (d, 3 H, *J* = 6.9 Hz, H-20), 1.23 (t, 3 H, *J* = 7.7 Hz, H-15), 1.49 (d, 3 H, *J* = 7.0 Hz, H-18), 1.73 (s, 3 H, H-19), 1.94 (s, 3 H), 1.95 (s, 3 H), 2.00 (m, 1 H, H-2), 2.45 (dq, 1 H, *J* = 12.8, 6.9 Hz), 2.61 (q, 3 H, *J* = 7.7 Hz, H-14), 2.62 (q, 3 H, *J* = 7.7 Hz, H-14), 3.71 (dd, 1 H, *J* = 12.8, 2.8 Hz, H-3), 4.14 (q, 1 H, *J* = 7.0 Hz, H-8).

Hydrogenation of 8-*epi*-Vallartanone A (9). A solution of 8-*epi*-vallartanone A (**9**, 4.3 mg) in ethyl acetate (3 mL) containing 5% palladium on carbon (5 mg) was stirred vigorously under 1 atm of hydrogen for 18 h. The catalyst was removed by filtration through Celite, the solvent was evaporated, and the residue was purified by HPLC on Partisil (60% hexane–ethyl acetate) to obtain 6,7-dihydro-8-*epi*-vallartanone A (**10**, 0.25 mg, 5.5% yield), the starting material (**9**, 1.0 mg, 24% yield), and several other unidentified products.

6,7-Dihydro-8-*epi*-vallartanone A (10): oil; UV (MeOH) 215 nm (ϵ 9222), 259 nm (ϵ 12 350); ^1H NMR ($CDCl_3$) δ 0.95 (d, 3 H, *J* = 6.5 Hz, H-20), 1.01 (d, 3 H, *J* = 6.9 Hz, H-21), 1.04 (d, 3 H, *J* = 7.2 Hz, H-19), 1.12 (d, 3 H, *J* = 6.9 Hz, H-1), 1.19 (t, 3 H, *J* = 7.6 Hz, H-15), 1.35 (d, 3 H, *J* = 6.9 Hz, H-18), 1.90 (m, 1 H, H-2), 1.94 (s, 3 H, H-17), 2.00 (s, 3 H, H-16), 2.21 (dq, 1 H, *J* = 7.2, 2.0 Hz, H-6), 2.58 (q, 2 H, *J* = 7.6 Hz, H-14), 2.65 (dq, 1 H, *J* = 10.8, 6.5 Hz, H-4), 3.12 (dd, 1 H, *J* = 10.8, 2.2 Hz, H-3), 3.18 (dq, 1 H, *J* = 9.8, 6.9 Hz, H-8), 3.73 (dd, 1 H, *J* = 9.8, 2.0 Hz, H-7); EIMS *m/z* 348.3.

Acknowledgment. We thank Dr. Ellen Barrabee and Mary Kay Harper for assistance with field collections. Dr. Ted Molinski also collected specimens and helped conduct field studies. This research was supported by a grant from the National Science Foundation (Grant CHE86-03091).

Registry No. **6**, 12247-98-2; **7**, 122947-99-3.

Notes

Electrochemistry in Micellar Media. Dimerization of Electroreducible Amphiphilic Aromatic Ketones in Aqueous Media: A Stereochemical Approach

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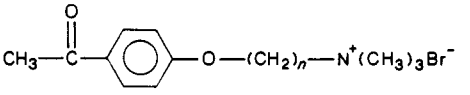
Received February 23, 1989

During the past decade, numerous studies have reported the influence of surfactants on electrochemical mechanisms.[1] Previous papers from our laboratory have described the electrochemical behavior of amphiphilic molecules such as [(4-acetylphenoxy)alkyl]trimethylammonium salts[2-4] **1–5**. The ability of some of them to give micelles or mixed micelles when a second surfactant is added (i.e., cetyltrimethylammonium bromide, CTAB) affects the electrochemical processes.[4] As we reported in the latter work, compounds **1–5** follow two different electrochemical reduction models depending on the hydrocarbon chain length: The first concerns the ketones **1–3**, bearing a short hydrocarbon chain. They are not included within micelles of CTAB, and the reduction occurs, under such conditions, through a surfactant (CTAB) adsorbed layer at the mercury electrode.



1, *n* = 3
2, *n* = 4
3, *n* = 6
4, *n* = 8
5, *n* = 10

The second is observed with compounds **4** and **5**, possessing the two longest hydrocarbon chains. They are able to form micelles themselves, and in the presence of CTAB

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(1) For examples see: (a) Guidelli, R.; Piccardi, G.; Moncelli, M. R. *J. Electroanal. Chem.* **1981**, *129*, 373. (b) McIntire, G. L. *Am. Lab.*, **1986**, 173. (c) Jaeger, D. A.; Bolikal, D.; Nath, B. *J. Org. Chem.* **1987**, *52*, 276, and references therein.

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0022-3263/89/1954-5377$01.50/0

Table I. Electrolysis of $CH_3C(O)C_6H_4O(CH_2)_nN^+(CH_3)_3Br^-$ [1 (n = 3) and 5 (n = 10)]

entry	pH	ketone (amt, mol)	[CTAB], mol L^{-1}	potential of electrolysis, V/SCE	electricity consumption, F mol^{-1}	% pinacol (mol)[a]	% carbinol (mol)[a]	r = dl/meso[a]
1[b]	2.7	1 (3.2×10^{-3})	0	-1.30	0.95	73	27	2.0
2[b]	2.7	1 (3.2×10^{-3})	1×10^{-2}	-1.30	1.0	≃100	c	2.5
3	8	1 (3.2×10^{-3})	0	-1.62	1.4	20	80	1.1
4	8	1 (3.2×10^{-3})	1×10^{-2}	-1.62	1.5	7	93	1.5
5	10.3	1 (3.2×10^{-3})	0	-1.65	1.1	75	25	d
6	10.3	1 (3.2×10^{-3})	1×10^{-2}	-1.65	1.3	26	74	d
7[b]	2.7	5 (2.4×10^{-3})	0	-1.35	1.0	≃100	c	2.0
8[b]	2.7	5 (2.4×10^{-3})	1×10^{-2}	-1.30	1.1	≃100	c	2.0
9	8	5 (2.4×10^{-3})	0	-1.60	1.5	24	76	1.3
10	8	5 (2.4×10^{-3})	1×10^{-2}	-1.55	1.5	26	74	1.8
11	10.3	5 (2.4×10^{-3})	0	-1.65	1.6	26	74	1.4
12	10.3	5 (2.4×10^{-3})	1×10^{-2}	-1.60	1.6	23	77	1.8
13		1 (3.2×10^{-3})	0	NaHg reduction		20	80	1.8

[a] Values given are an average of two runs. [b] In acidic media (entries 1, 2 and 7, 8) the starting material is not totally consumed when the electrolyses are stopped. The amount of the unreduced ketone is estimated by measuring the intensity of the remaining reduction wave and corresponds to 10–15%. [c] Unobserved in the ^{13}C NMR. [d] Meso unobserved in the ^{13}C NMR.

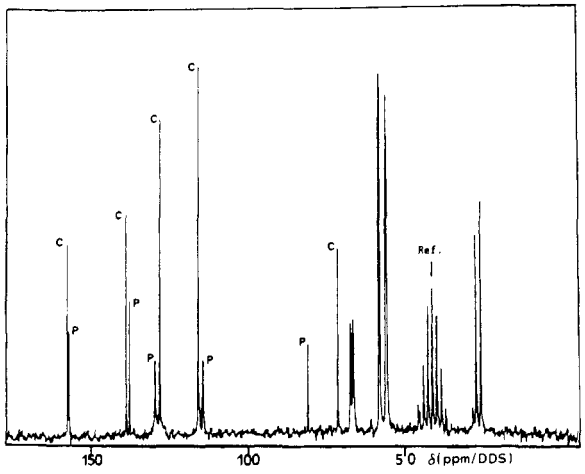


Figure 1. NaHg reduction of $CH_3C(O)C_6H_4O(CH_2)_3N^+(CH_3)_3Br^-$; ^{13}C NMR spectra (solvent D_2O–DMSO).

there are mixed micelles that are the "vehicle" of the substrate to the electrode surface.

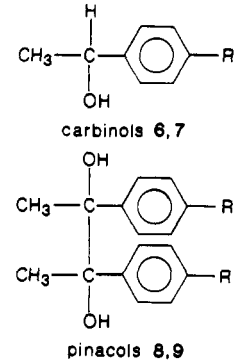
This study has been performed with compounds **1** and **5**, bearing respectively a hydrocarbon chain of 3 and 10 carbon atoms. They are the most representative substrates of the two electrochemical models defined above. We shall report herein the effects of their amphiphilic properties and of those of a foreign surfactant (CTAB) on the partitioning and on the stereochemistry of the reduction products (carbinols and diastereomeric pinacols).

The two main problems we met during our investigations were (a) the extraction, from an aqueous solution, of the reduction products bearing hydroxyl groups and ammonium heads and (b) the characterization of the carbinol–pinacol and diastereomeric ratios. The reduction products are soluble only in water, methanol, or ethanol, so that extraction by organic solvents is impossible. To minimize the solubilization of the buffer components during the extraction, pH and ionic strength were kept constant by using potassium phosphate (pH = 2.7 and 10.4) and carbonate (pH = 8) buffer solutions and KCl as the supporting electrolyte (see the Experimental Section).

Results and Discussion

It is generally accepted that aromatic ketones and in particular (4-acetylphenoxy)alkylammonium bromides are reduced according to the pH of the solution with the formation of carbinol or pinacol in various amount.[5-8]

The electrolysis of compounds **1** (n = 3) and **5** (n = 10) was performed in various media depending on pH values and on other surfactant conditions. The relative quantities of the corresponding carbinols **6** and **7** and pinacols **8** and **9** are summarized in Table I.



6 and **8**, R = —O—$(CH_2)_3$—$N^+(CH_3)_3$

7 and **9**, R = —O—$(CH_2)_{10}$—$N^+(CH_3)_3$

In acidic medium, the electrolysis potential is kept constant at the reduction step that corresponds to a one-electron transfer, leading to the neutral radical. The latter intermediate can dimerize to form diastereomeric pinacols.

Carbinols **6** and **7** and pinacols **8** and **9** give sufficiently separated ^{13}C NMR spectra to allow a quantitative analysis after cancelling of the nuclear Overhauser effect. The relative percentages of pinacol and carbinol have been determined by measuring the intensity of the well-defined ^{13}C NMR signals of –C–OH recorded in D_2O, as demonstrated for the chemical reduction (entry 13, Table I; see Figure 1). ^1H NMR could be used only for carbinol **6** and pinacol **8**, and the results were in agreement with those obtained with ^{13}C NMR. For compounds bearing longer alkyl chains, the $-CH_2-$ and $-CH_3$ signals are superposed and prevent any quantitative analysis of ^1H NMR spectra.

With D_2O as solvent, the two diastereomeric pinacols cannot be distinguished either in ^{13}C or in ^1H NMR spectra (the CH_3–C– signals have the same chemical shift). Our products do not dissolve sufficiently in other solvents ($CDCl_3$, CD_3COCD_3) to allow any study. The characterization of the two diastereoisomers is possible with only one solvent (DMSO-d_6) and only one ^{13}C signal (–C–OH; Figure 2). The assignment of each signal to the *dl* or meso

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Table II. ^{13}C NMR Signals of Ketones 1 and 5, Carbinols 6 and 7, and Pinacols 8 and 9

compound (n)	CH_3	$-(CH_2)_n-$	$-N^+(CH_3)_3$	—C=O	-C-OH	Ar
1 (3)	28.1	24.2, 64.4, 66.8	53.9	198.2		163.7, 132.2 131.8, 116.0
6 (3)	27.5	24.2, 64.6, 66.4	53.8		69.2	158.6, 141.5 128.1, 115.7
8 (3)	27.5	24.2, 64.4, 66.3	53.7		78.9, 78.4	157.8, 140.0 130.0, 113.8
5 (10)	30.1	23.5, 27.3, 29.9, 66.7, 69.3	53.6	197.7		164.1, 131.9 131.3, 115.7
7 (10)	30.3	23.6, 27.3, 30.0, 66.8, 68.8	53.6		69.1	158.9, 140.9 127.9, 115.4
9 (10)	30.2	23.5, 27.2, 29.9, 66.6, 68.7	53.5		78.9, 78.4	158.2, 139.3 129.9, 113.5

[a] Solvent DMSO-d_6. Values given in ppm referenced to DDS.

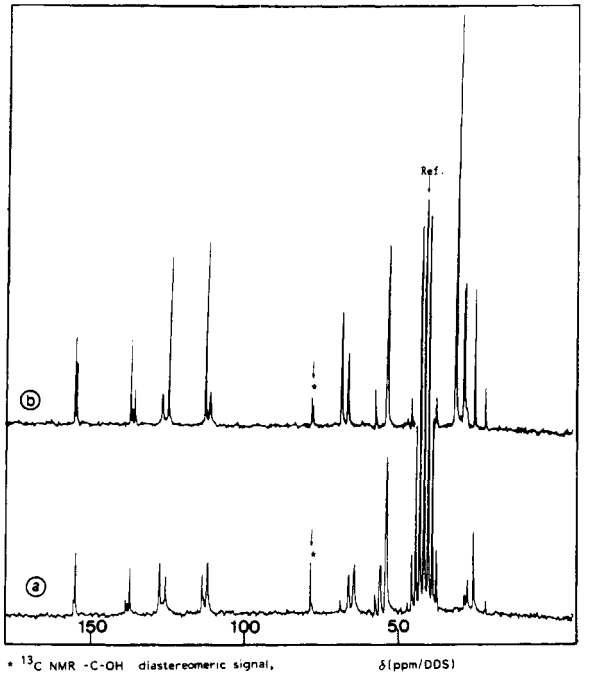

Figure 2. (a) Electroreduction of $CH_3C(O)C_6H_4O(CH_2)_3N^+(CH_3)_3Br^-$ (1). (b) Electroreduction of $CH_3C(O)C_6H_4O(CH_2)_{10}N^+(CH_3)_3Br^-$ (5) at pH = 10.3. ^{13}C NMR spectra (solvent DMSO-d_6).

forms has been based on a comparison with similar signals recorded in the same conditions for pinacols of acetophenone, *p*-methoxyacetophenone (solvent DMSO-d_6), and other diastereomeric alcohols.[9] In all cases, the -C-OH ^{13}C NMR signal of the *dl* form appears at lower field. The ^{13}C NMR chemical shifts (relative to a DDS reference) are given in Table II.

The electrochemical reduction of α,β ethylenic or aryl alkyl ketones in aqueous or organic media has been widely investigated.[5-8] Some papers have reported the study of the ratio $r = dl/meso$ of the diastereomeric pinacols formed in an electrochemical reduction as a function of the medium.[10-15] In the case of (acetylphenoxy)alkylammonium salts, we observe (Table I) that the carbinol and pinacol percentages and the diastereomeric ratios (r) depend, on one hand, on the pH of the solution and, on the other hand, on the ability of the substrate to form micelles or mixed micelles in the presence of a second surfactant (i.e., CTAB). The difference in the behavior of compounds 1 and 5 is particularly important for entries 5, 6 and 11, 12 in Table I (pH = 10.3).

In acidic or weakly basic medium, the presence of CTAB modifies for compound 1 the percentage of the reduction product 6 and the reductive coupling product 8 in a different way. In the acidic medium, the pinacol formation is markedly favored by addition of CTAB. As we have shown previously,[4] under such conditions compound 1 is reduced through an adsorbed layer of CTAB. Therefore, the first one-electron step leading to the neutral radical is better separated from the second one (anion formation), and the carbinol formation is lowered. In a weakly basic solution, on the contrary, the carbinol percentage increases in the presence of CTAB (entry 4). The anion radical resulting from the first electron transfer is more strongly solvated by the CTAB ammonium heads present in the double layer, making easier the second electron transfer.

The reduction of compound 5, which is able to form micelles or mixed micelles, is not affected at any pH by the presence of CTAB. In all cases, the electroreducible moiety is included within an ordered assembly that virtually supresses the modifications due to a medium change.

In such media, the diastereomeric pinacol ratio $r = dl/meso$ does not vary significantly as a function of added CTAB (Table I, entries 1–4 and 7–10). Under these conditions, the dimerization may occur by a fast radical–radical coupling with a lack of stereoselectivity as postulated by Lund and co-workers.[16]

In basic medium, the electroreduction of aromatic ketones leads to the formation of varying amounts of the corresponding carbinols and pinacols. The electropinacolization involving radical–radical, radical–substrate, or ion–substrate coupling is commonly reported.[11,17]

Under strongly basic conditions, the behavior of compounds 1 and 5 is completely different in regard to both the partitioning of the reduction products and the stereochemistry of the pinacols. When the ketone 1 with a short alkyl chain is reduced in the buffer solution (pH = 10.3) without any other surfactant, a high yield of pinacol is obtained, as generally reported for aromatic ketones under similar pH conditions (Table I, entry 5).[12] In the presence of CTAB the percentages of pinacol and carbinol are inverted (Table I, entry 6). The ketone 1 is reduced at the electrode through an adsorbed layer of the surfactant ammonium salt, contributing to a better solvation of the cetyl radical by the ammonium heads and leading, as in weakly

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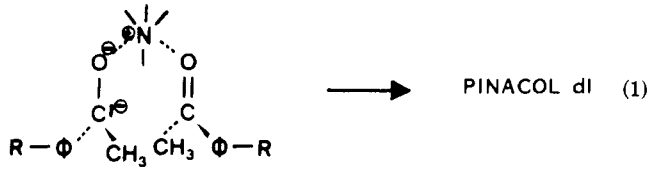
basic medium, to the anion. As a matter of fact, the protonation tends to be favored, and the carbinol percentage increases.

The electroreduction of compound **5** gives nearly the same ratio of carbinol and pinacol with or without the presence of CTAB. The electroreducible moiety is then included within micelles or mixed micelles, which prevent the influence of the basic medium or of the solvation phenomena.

In this pH range (e.g., pH = 10.3), the reduction of ketone **1** alone or in the presence of CTAB yields mostly the formation of the *dl* diastereoisomer (Table I, entries 5, 6; Figure 2). As pointed our previously,[4] the ketone **1** is reduced through an adsorbed layer of CTAB at the mercury electrode. The presence of ammonium heads leads to intimate ion-pair intermediate formation with the cetyl radical or the cetyl anion (also capable of a nucleophilic attack on the substrate).[18] According to the steric interactions pointed out by Stocker and Jenevein[11] for aromatic ketones, the less hindered solvated intermediate would appear to favor the *dl* form (eq 1).



(1)

In the case of the reduction of ketone **5** and under the same conditions of pH, the ratio of the two diastereomeric pinacols is quite similar to that obtained in the weakly basic medium. The carbonyl function is reduced inside the hydrophobic part of an organized assembly, micelle, or mixed micelle in the presence of CTAB, which can minimize the pH effects and the ion-pair formation and can increase via a radical–radical coupling the amount of the meso form.

In summary, the study of electroreducible amphiphilic molecules has confirmed the role played by micellization and adsorption at the electrode in dimerization processes. Pinacols are more likely to be formed by radical–radical coupling when the substrate gives rise to formation of ordered assemblies and by a nucleophilic addition when the reduction occurs through an adsorbed layer. The partitioning of the reduction products as well as the stereochemistry of the pinacols are in agreement with such reduction models.

Experimental Section

Solvents and Materials. The starting materials (ketones) were synthesized and recrystallized as previously described.[2] The cetyltrimethylammonium bromide (CTAB) was purchased from Fluka and recrystallized in a 4/1 v/v acetone–methanol mixture.[19] To minimize the solubilization of inorganic salts in ethanol during the extraction of the reduction products, we used the following buffer solutions[20] for 1 L of solution: (i) pH = 2.7, 0.1 mol of KH_2PO_4, 0.026 mol of H_3PO_4; (ii) pH = 8, 0.1 mol of $KHCO_3$; (iii) pH = 10.4, 0.025 mol of K_2HPO_4, 0.0041 mol of KOH. The ionic strength was adjusted to 0.5 M by adding KCl.

Electrolysis Procedure. A Tacussel PRT 100-1X potentiostat coupled with a Tacussel IG5N integrator was used for controlled-potential electrolyses, which were performed in a three-glass cell joined by two sintered glasses. The cathodic cell contained 150 mL of buffer solution, 1 g of ketone, a SCE reference electrode, a N_2 tube, and a mercury pool of 16 cm^2 at the bottom of the cell as the working electrode. The anode was a glassy carbon electrode. The electrolysis cell was thermostated at 30 °C. Stirring and the N_2 flow were continued throughout the experiment, and the solvent was preelectrolyzed at the adequate potential until the Coulomb level decreased to zero. The termination of the electrolysis was determined by voltammetric checks.

Reduction Products Extraction. When the electrolyses were stopped, the solutions were lyophilized, after neutralization in the case of basic medium. The reduction products were then extracted with 40 mL of absolute ethanol and dried in a vacuum after evaporation of the solvent. In the presence of CTAB, the dry lyophilized residue was first extracted by dichloromethane to remove CTAB and afterward reextracted by ethanol. In acidic medium (pH = 2.7) 1 g of ketone **1** gives after extractions 0.70 g of a mixture of the two diastereomeric pinacols. With ketone **5**, 1 g of the starting material gives 0.85 g of pinacols. Ketones **1** and **5** were also reduced by sodium amalgam[21,22] with formation of a mixture of carbinol and pinacol (Table I).

Analysis. Authentic samples of carbinols were obtained by a chemical reduction of **1** and **5** with sodium borohydride. The pinacols have been identified by their ^{13}C (Table II) or ^1H NMR spectra (solvent DMSO-d_6, δ relative to DDS as internal reference).

Pinacol **8**: ^1H NMR δ 6.90 (4 H AA'BB'), 3.60 (CH_2O), 3.50 (CH_2N^+), 3.25 ($N^+(CH_3)_3$), 2.20 (CH_2), 1.50 (CH_3C).

Pinacol **9**: 6.85 (4 H AA'BB'), 4.00 (CH_2O), 3.35 (CH_2N^+, $N^+(CH_3)_3$), 1.50 (($CH_2)_8$, CH_3C).

The spectra were recorded on a Varian T60 instrument for the proton NMR and on a Bruker WP80 instrument for ^{13}C NMR. Quantitative measurements in ^{13}C NMR were performed on the Bruker MSL300 instrument using the gated resonance technique (gated 2) with a pulse time of 20 s. The solvents used were DMSO-d_6 and a mixture of 75% D_2O/25% DMSO (as a reference) respectively for the determination of the diastereomeric pinacols and carbinol–pinacol ratios. All the reduction products were very hygroscopic, preventing well-defined melting point measurements.

Acknowledgment. Financial assistance from Electricité de France (Convention d'étude B01D36) and the CNRS (U.A. 434, Thermodynamique et Electrochimie en solution) is gratefully acknowledged.

Registry No. 1, 120534-65-8; 2, 112147-86-1; 3, 120534-66-9; 4, 120534-67-0; 5, 120534-68-1; 6, 122489-45-6; 7, 122489-46-7; 8, 122489-47-8; 9, 122519-41-9; CTAB, 57-09-0.

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Nucleophilic Fluorine Displacement Reactions. A Comparison of Reactivities of Polymer-Supported Fluoride and Acid Fluorides P^+F^-, *n* HF (*n* = 0–2)

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Received December 8, 1988

One of the most attractive ways for introducing fluorine into an organic compound consists of reaction of ionic fluorides by nucleophilic substitution. Numerous and recent methods have been developed that may enhance the nucleophilicity of the fluoride ion;[1,2] however the basicity

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0022-3263/89/1954-5380$01.50/0