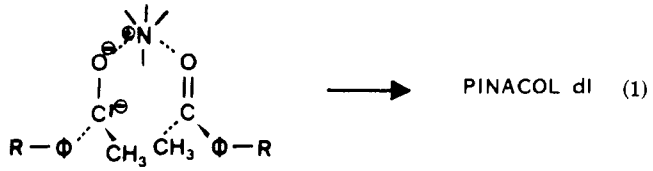
basic medium, to the anion. As a matter of fact, the protonation tends to be favored, and the carbinol percentage increases.

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

Table I. Reactions with the Bromo Ketones 2–4

starting compd	reagent	temp, °C	reactn time, h	transform yield, %[a]	reactn prod, %[a] fluoro	ethylenic	ketol	chloro
$PhC(O)CH_2Br$ (2)	1a	rt[c]	1.5	b	61		33	6
	1b	70	13	96.1	85.2		9.8	4.9
	1c	75	22	93.7	97			3
PhC(O)CHBrMe (3)	1a	60	2	98	79		19.5	1.5
	1b	70	20	91.7	91.9		4.3	3.7
	1c	75	40	95	98			2
$PhC(O)CBrMe_2$ (4)	1a	60	18	100	32.5	47.5	19.5	trace
	1b	70	75	87.3	41.5	43.7	9.4	5.4
	1c	75	70	90	59.7	36.1	2.5	1.7

[a] Transformation yields and relative proportions of the reaction products are determined by ^1H NMR on the crude reaction mixture. [b] Not determined because of the degradation of the bromo ketone 2. [c] rt = room temperature.

of this ion generally remains nonnegligible and may cause the formation of undesired side products from elimination reactions.[2a,b,e,f,i,o]

Recently we have shown that polymer supported dihydrogen trifluoride $P^+H_2F_3^-$ (P^+ = cationic part of a macroreticular basic anion-exchange resin, e.g., Amberlyst A 26 or Amberlite IRA 900) can act as a good source of nucleophilic fluorine, which induces the addition of HF to activated acetylenic bonds without exhibiting any important basic character.[3] This interesting property has led us to compare the nucleophilic power of various [F^-, nHF] anions by testing the reactivities of the polymer-supported reagents $P^+[F^-, n\text{HF}]$ 1 (n = 0, 1a; n = 1, 1b; n = 2, 1c) versus the >C–X moiety (X = Br or sulfonate group), the chemistry of the reagents $P^+HF_2^-$ (1b) and $P^+H_2F_3^-$ (1c) remaining unexplored in this field. The results show significant differences that will be illustrated from reactions with the bromo ketones $PhC(O)CBrR^1R^2$ (R^1 = R^2 = H, 2; R^1 = H, R^2 = Me, 3; R^1 = R^2 = Me, 4) and with secondary nonactivated -CHX- groups in the compounds n-$C_6H_{13}CHOMsCH_3$ (15) (Ms = methylsulfonyl), n-$C_6H_{13}CHBrCH_3$ (16), and 3β-OMs-5α-cholestane (17).

Results

The polymer-supported reagents 1a–c are obtained from the corresponding commercial resins P^+Cl^- as the starting material, which is first transformed into the hydroxide form P^+OH^-.[2e,f] Washing this last form by an excess of aqueous 1 M HF does not lead to P^+F^- (1a) but to $P^+[F^-, 1.5\text{HF}]$ (1d). This result is provided by the acidimetric titration of 1d after drying in benzene (see Experimental Section); the molecular weight of 1 molar equiv of P^+ was determined in previous works.[3b]

The resin $P^+[F^-, 1.5\text{HF}]$ (1d) leads to P^+F^- (1a) after washing with water until neutrality,[2f] and to $P^+H_2F_3^-$ (1c) after stirring in a saturated aqueous solution of an equimolecular mixture $HF–KHF_2$;[3b] then these reagents 1a and 1c are dried as 1d respectively in benzene and in 1,2-dichloroethane (DCE). $P^+HF_2^-$ (1b) is obtained from either dried 1d or dried 1c by neutralizing excess HF with a stoichiometric amount of aqueous 1 M NaOH reduced by ca. 15% since, as we observed, the drying of 1b in benzene by the distillation of the azeotrope water–benzene induces the elimination of a small amount of HF.[4]

In a first series of experiments, the polymer-supported reagents 1a–c were allowed to react with the bromo ketones $PhC(O)CBrR^1R^2$ 2–4 in CCl_4. The results are listed in the Table I.

With $PhC(O)CH_2Br$ (2), the polymer-supported fluoride 1a reacts very quickly at room temperature (95% of 2 is transformed in 1.5 h) but an important degradation of the bromo ketone 2 occurs, ca. 35% as determined from ^1H NMR. The crude reaction mixture consists of unidentified aromatic compounds along with the fluoro ketone $PhC(O)CH_2F$ (5), the ketol $PhC(O)CH_2OH$ (6), and the chloro ketone $PhC(O)CH_2Cl$ (7) in the relative proportions 5/6/7 = 61/33/6 in molar ratio. No degradation appears during the reactions with $P^+HF_2^-$ (1b) and with $P^+H_2F_3^-$ (1c); a very small amount of chloro ketone 7 is still formed in both cases, while the ketol 6 is observed only in the reaction with 1b, and the formation of the fluoro ketone 5 is essentially quantitative by using the reagent 1c.

With PhC(O)CHBrMe (3), the three reagents 1a–c afford mainly the fluoro ketone PhC(O)CHFMe (8) in high yields (77–93%) in the order 1a < 1b < 1c; very small amounts of the chloro ketone PhC(O)CHClMe (10) are also obtained, and the formation of the ketol PhC(O)CHOHMe (9) is important with 1a, unimportant with 1b, and not observed with 1c.

With $PhC(O)CBrMe_2$ (4), four products can be formed: mainly the fluoro ketone $PhC(O)CFMe_2$ (11) and the ethylenic ketone $PhC(O)CMe{=}CH_2$ (12), and to a lesser extent the ketol $PhC(O)C(OH)Me_2$ (13) and the chloro ketone $PhC(O)CClMe_2$ (14). The best yield of fluoro ketone 11 by far is obtained with the reagent 1c, whereas the reagents 1a and 1b provide the ethylenic ketone 12 as the major product, the yield of the ketol 13 still following the sequence 1a > 1b > 1c.

From all these results, which differentiate well the three polymer-supported reagents 1a–c, some characteristics appear. Firstly, despite the drying of the reagents 1a–c by the azeotropic elimination of water in a suitable solvent, the reagents 1a and 1b, unlike 1c, keep a nonnegligible

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(4) $P^+HF_2^-$ (1b) cannot be prepared by washing P^+Cl^- or P^+OH^- with an excess of aqueous solution of 1 M KHF_2 (or NH_4HF_2); in this case the obtained reagent is $P^+[F^-, 1.5\text{HF}]$ (1d).

Table II. Reactions with Compounds 15–17

starting compd	reagent	solvent	temp °C	reactn time, h	reactn prod, % fluoro	reactn prod, % ethylenic	ref
2-OMs-octane (15)	1a	pentane	36	20	70	25	a
	1a	benzene	60	21	55	45	b
	1c	CCl_4 or n-dodecane	80	90	49[d]	18[d,e]	c
2-bromooctane (16)	1a	pentane	36	30	20	73	a
	1b	CCl_4 or n-dodecane	70	120	20[d]	19.5[d,f]	c
	1c		80	120	30[d]	10[d,f]	c
3β-OMs-5α-cholestane (17)	1a	toluene	100	60	32	31	b
	1c	n-octane	120	140	70[g]	30[g]	c

[a] Reference 2e. [b] Reference 2f. [c] This work. [d] Yield determined by GLC and ^1H NMR. [e] The ratio of 2-octene to 1-octene is 95/5. [f] Only 2-octene. [g] Yields determined by ^1H NMR.

amount of water, which leads to undesired hydrolysis by-products for a noticeable part. The formation in a very small extent of the chloro ketones **7**, **10**, and **14**, mainly obtained with **1b**, might result from a side reaction involving CCl_4 and H_2O, as it is known that CCl_4, HF, or an HF donor such as NH_4HF_2 and an hydroxyl group can furnish chloride ions;[5] besides we observed that when the reactions are carried out in benzene, the chloro derivatives are not formed. Secondly, the basicities of **1a** and **1b** appear to be quite close and clearly higher than that of **1c**, as it results from the formation of the ethylenic ketone **12**. Finally, although the overall reactivities can be ranked in the order **1a** > **1b** ~ **1c**, in all cases the best yield of fluoro substitution is provided by the reagent **1c**.

It then appeared interesting to examine if the use of dihydrogen trifluoride (**1c**) could improve the formation of fluoro compounds which are reported to be hardly produced by the reaction of the fluoride **1a** with a -CHX- group (X = Br or (methylsulfonyl)oxy group bonded to a nonactivated carbon atom).[2e,f] Thus were chosen 2-OMs-octane (**15**), 2-bromooctane (**16**), and 3β-OMs-5α-cholestane (**17**), and the results are summarized in Table II.

As was already observed,[2e,f] compound **15** undergoes the substitution reaction most easily; 2-fluorooctane (**18**) is the major reaction product with either reagent **1a** or **1c**, this latter reagent, though less reactive than **1a**, leading to comparable or even slightly better yields of fluoro substitution. However, with 2-bromooctane (**16**), the reagents **1a** and **1c** are again well differentiated; whereas **1a** reacts mainly as a base and leads to octenes as major products,[2e] the reagent **1c** essentially acts as a nucleophile and gives rise to 2-fluorooctane (**18**) for the greater part. Owing to these differences, the reaction of **16** with the hydrogen difluoride **1b** was also investigated; the equal formation of substitution and elimination products confirms that the basicity of **1b** remains high and that its nucleophilic power is clearly weaker than that of **1c**. Finally, the reaction of 3β-OMs-5α-cholestane (**17**), which requires a high temperature, shows the interest to use the reagent **1c** in these conditions, since the fluoro substitution, greatly limited with **1a** at 100 °C,[2f] reaches a 70% yield at 120 °C with **1c**; a clean S_N2 process is deduced from the ^{19}F NMR spectra, which are consistent with the formation of 3α-fluoro-5α-cholestane (**19**) without any appreciable amount (<3%) of its epimer.

Discussion

It has already been noted that the H-bonding ability of the fluoride ion is increased with the size of the counter-cation, hydrates of tetraalkylammonium fluorides being readily formed most likely as a consequence of the relatively weak bond between the onium cation and the fluoride ion.[6] On the other hand, $F^-(H_2O)_2$, issued from $(CH_3)_4NF{\cdot}2H_2O$, was reported to behave in an aprotic medium as both the fluoride ion and the hydroxide ion.[7] Thus it is not surprising that in polymer-supported fluoride **1a** water is still present at some extent and that the overall reactivity of **1a** as nucleophile and base is not quite different from what observed with "anhydrous" tetrabutylammonium fluoride.[2m]

In polymer-supported hydrogen difluoride **1b** the relatively weak interaction between the HF_2^- anion and the large countercation may enhance the affinity of this ion toward water and so account for the small amount of water which is kept by the reagent **1b**. However because of the strong hydrogen bond in HF_2^-, this ion is expected to be less reactive than the F^- ion as both nucleophile and base, as we observed. $Bu_4N^+HF_2^-$ was also reported to act as nucleophile and base.[2o]

The different behavior of polymer-supported dihydrogen trifluoride (**1c**) can be accounted for as follows. It has been shown that in $H_2F_3^-$ the hydrogen bonds are notably weaker than in HF_2^-,[8] that which may increase the possibility of in situ F^- formation from $H_2F_3^-$. Moreover the large size of the $H_2F_3^-$ ion, while reducing its H-bonding ability toward water, is likely to enhance its soft base character and to diminish its protophilicity by comparison with F^-.[9] Thus it seems reasonable to consider the $H_2F_3^-$ ion mainly as a nucleophile, that which appears to be well supported by our results.

Experimental Section

^1H NMR spectra were run on a Varian EM-360 instrument using $CDCl_3$ or CCl_4 as a solvent and Me_4Si as an internal standard; ^{19}F NMR spectra were taken on a JEOL JNM-SX 100 (94.14 MHz) or a Bruker AM-200 SY (188.28 MHz) spectrometer with $CDCl_3$ as a solvent and $CFCl_3$ as an external standard. Chemical shifts are reported in δ units downfield from the references; the coupling constants (*J*) are expressed in hertz (Hz). Gas chromatographic analyses were carried out with a Carlo Erba Fractovap GT chromatograph using a 2 m × 2 mm column packed with 10% Carbowax 20M on Chromosorb W (60–80 mesh). High-resolution mass spectra (HRMS) were obtained on a Varian MAT 311 mass spectrometer at an ionization potential of 70 eV.

The resins Amberlyst A 26 and Amberlite IRA 900 in the chloride form and carbon tetrachloride (spectroscopic grade) are commercial products. Bromo ketones **2–4**,[10] 2-OMs-octane (**15**),[11]

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2-bromooctane (16),[12] and 3β-OMs-5α-cholestane (17)[13] are prepared as described.

Preparation of P⁺[F⁻, 1.5HF] (1d). Wet commercial resin in the chloride form Amberlyst A 26 or Amberlite IRA 900 (50 g, ca. 0.1 molar equiv), packed in a polyethylene column, were washed with an aqueous solution of 2 M NaOH until elimination of chloride ions ($AgNO_3$ test) and then with water until neutrality, and 220 mL of a 1 M HF aqueous solution were passed through the column. The resin was washed with acetone (50 mL) followed by diethyl ether (50 mL) and then poured into 400 mL of benzene, and a further dehydration was achieved by distilling the azeotrope water–benzene. The resin was filtered and dried in the air. Titration by sodium hydroxide gave the acidity of the resin, approximately 6 mequiv g^{-1} as H^+, which corresponds to the formula P⁺[F⁻, 1.5 HF].

Preparation of the Fluoride P⁺F⁻ (1a). The wet form P⁺[F⁻, 1.5HF] (**1d**) obtained as above after the reaction of 1 M HF was washed with water until neutrality. Then the resin was washed with acetone (50 mL) followed by diethyl ether (50 mL), and an additional dehydration performed by distilling the azeotrope water–benzene in the same conditions as with **1d** leads to the dried form P⁺F⁻ (**1a**).

Preparation of the Hydrogen Difluoride $P^+HF_2^-$ (1b). Dried $P^+H_2F_3^-$ (**1c**) (see ref 3b) (5.2 g, ca. 0.02 molar equiv) was stirred in 8 mL of 0.2 M NaOH (0.017 mol) at room temperature for 20 min. Then the resin was filtered and washed with acetone (10 mL) followed by diethyl ether (10 mL), and an additional dehydration was achieved by distilling the azeotrope water–benzene from 80 mL of benzene. The resin was filtered and dried in the air, and the titration with NaOH gave an average acidity of 3.8–4.6 mequiv g^{-1} (H^+), which corresponds respectively to P⁺[F⁻, 0.9HF] and P⁺[F⁻, 1.1HF].

The same procedure can be used from dried **1d** with convenient amounts of sodium hydroxide.

General Procedure for the Reactions of the Reagents 1a–c with the Bromo Ketones 2–4. To 0.01 mol of bromo ketone **2–4** dissolved in CCl_4 (30 mL) was added the reagent **1a** (10 g, ~0.04 mol F⁻), or **1b** (5 g, ~0.02 mol HF_2^-), or **1c** (5.5 g, ~0.02 mol $H_2F_3^-$). The reaction mixture, contained in a 50-mL round-bottomed flask equipped with a reflux condenser and a $CaCl_2$ tube, was heated under stirring (for the temperature and the reaction times, see Table I). After cooling to room temperature, the resin was filtered off and washed with dry diethyl ether (50 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated; then the crude reaction mixture was analyzed by ^1H and ^{19}F NMR. The obtained products were identified unambiguously by comparison with data from literature and if necessary by high-resolution mass spectrometry.

2-Fluoro-1-phenylethanone (5). ^1H NMR: CH_2F 5.53 (d, $^2J_{HF}$ = 47) [lit.[2e] 5.4, $^2J_{HF}$ = 48]. ^{19}F NMR: −230.3 (t, $^2J_{HF}$ = 47) [lit.[14] −231.9, $^2J_{HF}$ = 47].

2-Hydroxy-1-phenylethanone (6). ^1H NMR: CH_2 4.83 (s), OH 3.4 (s) [lit.[15] CH_2 4.85 (s), OH 3.1 (s)].

2-Chloro-1-phenylethanone (7). ^1H NMR: CH_2 4.72 (s) [lit.[16] 4.75 (s)].

2-Fluoro-1-phenylpropanone (8). ^1H NMR: 1.58 (dd, 3 H), 5.6 (dq, 1 H), $^2J_{HF}$ = 48.7, $^3J_{HF}$ = 24, $^3J_{HH}$ = 6.8 [lit.[17] 1.61 (dd, 3 H), 5.48 (dq, 1 H), $^2J_{HF}$ = 48.7, $^3J_{HF}$ = 23.5, $^3J_{HH}$ = 6.7]. ^{19}F NMR: −180.5 (sext), $^2J_{HF}$ = 48.2, $^3J_{HF}$ = 24.1.

2-Hydroxy-1-phenyl-1-propanone (9). ^1H NMR: CH_3 1.35 (d, J = 7), OH 4.9 (s) [lit.[15] CH_3 1.35 (d), CH 4.97 (q, J = 7), OH 4.95 (s)]. Note: the CH signal, centered at ca. δ = 5, is not well resolved as it is mixed with one of the two quadruplets provided by the CHF group in 8 and with the OH signal.

2-Chloro-1-phenyl-1-propanone (10). ^1H NMR: CH_3 1.68 (d, J = 7) [lit.[18] 1.65].

2-Fluoro-2-methyl-1-phenyl-1-propanone (11). ^1H NMR: CH_3 1.68 (d, 6 H), $^3J_{HF}$ = 21.8. ^{19}F NMR: −142.1 (hept), $^3J_{HF}$ = 21.6 [lit.[19] −144, $^3J_{HF}$ = 22].

2-Methyl-1-phenyl-2-propen-1-one (12). ^1H NMR: 2.07 (dd, 3 H, J ~ 1.3), 5.63 (m, 1 H), 5.92 (m, 1 H, J ~ 1.3). HRMS: m/e (M^+) calcd for $C_{10}H_{10}O$: 146.073, found 146.075.

2-Hydroxy-2-methyl-1-phenyl-1-propanone (13). ^1H NMR: 1.53 (s, 6 H), 3.75 (s, 1 H) [lit.[19] 1.5 (s, 6 H), 3.85 (s, 1 H)].

2-Chloro-2-methyl-1-phenyl-1-propanone (14). ^1H NMR: CH_3 1.9 (s) [lit.[20] 1.9 (s)].

General Procedure for the Reactions of the Reagents 1a–c with the Compounds 15–17. **1a** (10 g, ~0.04 mol F⁻), **1b** (5 g, ~0.02 mol HF_2^-), or **1c** (5.5 g, ~0.02 mol $H_2F_3^-$) was added into a 50-mL round-bottomed flask equipped with a reflux condenser and a $CaCl_2$ tube to 0.01 mol of compound **15–17** dissolved in 30 mL of solvent (CCl_4 or n-dodecane for compounds **15** and **16**, n-octane for compound **17**, see below), and the reaction mixture was heated under stirring (for the temperature and the reaction times, see Table II). The analyses of the reaction products were carried out as follows.

The reactions with compounds **15** and **16** were followed by ^1H NMR when CCl_4 was used, that which allows to determine the overall yield of transformation and to estimate the relative yields of 2-fluorooctane (**18**) and octenes. n-Dodecane as a solvent was used for an accurate analysis of the obtained products by GLC (oven temperature 70 °C).

The reaction of compound **17** in n-octane was followed by ^1H NMR. The usual workup after the reaction gave a crude reaction mixture of 3α-fluoro-5α-cholestane (**19**) and 2-cholestene (**20**) which was analyzed by ^1H and ^{19}F NMR.

2-Fluorooctane (18). ^1H NMR: CHF 4.55 (dm, 1 H, $^2J_{HF}$ = 48) [lit.[2e] 4.57, $^2J_{HF}$ = 49]. ^{19}F NMR: −170.8, $^2J_{HF}$ = 49 [lit.[2m] −172.5, $^2J_{HF}$ = 46].

3α-Fluoro-5α-cholestane (19). ^1H NMR: CHF 4.8 (dm, 1 H, $^2J_{HF}$ = 48). ^{19}F NMR: −179.4 (dm, $^2J_{HF}$ = 47) [lit.[2f] ^1H 4.8; ^{19}F −181; $^2J_{HF}$ = 47.9]. The epimer 3β-fluoro-5α-cholestane was detected in the ^{19}F spectrum as a very small doublet with δ = −166 [lit.[2f] −167.6].

2-Cholestene (20). ^1H NMR: CH=CH 5.6 (m) [lit.[21] 5.6 (m)].

Acknowledgment. We are indebted to Professor A. Gorgues for valuable discussions during this work.

Registry No. **2**, 70-11-1; **3**, 2114-00-3; **4**, 10409-54-8; **5**, 450-95-3; **6**, 582-24-1; **7**, 532-27-4; **8**, 21120-36-5; **9**, 5650-40-8; **10**, 6084-17-9; **11**, 71057-10-8; **12**, 769-60-8; **13**, 7473-98-5; **14**, 7473-99-6; **15**, 924-80-1; **16**, 557-35-7; **17**, 3381-51-9; **18**, 407-95-4; **19**, 3856-83-5; [F, 1.5HF], 100830-75-9; F⁻, 16984-48-8; HF_2^-, 18130-74-0; $H_2F_3^-$, 12260-12-7; amberlyst A 26l, 39339-85-0; amerlite IRA 900, 9050-97-9; 2-octene, 111-67-1; 1-octene, 111-66-0.

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Chemistry and Composition of (Trialkylsilyl)cuprates Derived from Cuprous Halides

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Received April 27, 1989

Since the discovery of R_2 CuLi by Gilman[1] in 1952, most organocuprate chemistry has favored alkyl-based reagents which are known to exist as both lower order[2] and higher

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