8 (17 mg, 8%), **3a** (46.5 mg, 20%), and polymeric material (45%) were isolated.

5-Phenyl-2-(trifluoromethyl)pent-2-ene (7): MS, *m/e* 214 (M^+), 91; ^1H NMR δ 1.65 (s, 3, CH_3), 2.6 (br m, 4, 2 × CH_2), 6.15 (br m, 1, ethylenic H), 7.2 (s, 5, Ar H); ^{19}F NMR δ −70.3.

5-Phenyl-2-(trifluoromethyl)pent-1-ene (8): MS, *m/e* 214 (M^+), 118, 104, 91; ^1H NMR δ 1.5–2.5 (br m, 4, 2 × CH_2), 2.7 (br t, 2, CH_2), 5.4 (q, J = 1.3 Hz, 1, ethylenic H cis to CF_3), 5.7 (m, 1, ethylenic H trans to CF_3), 7.4 (s, 5, Ar H); ^{19}F NMR δ −69.3; ^{13}C NMR δ 29.2, 35.2 (2 CH_2), 117.6 (q, J = 6 Hz, ethylenic CH_2), 126.1, 128.5 (arom CH), 138.5 (q, J = 29 Hz, ethylenic quatern C), 141.7 (s, arom quatern C).

Procedure D. (Runs 20–22). The solvolysis was carried out with 1.4 g of **3c** (4 mmol) in hexafluoroisopropyl alcohol (10 mL) by using either 1 g of CO_3Na_2 (run 20) or 1 g of CF_3COONa (run 21) as buffer, or no buffer at all (run 22); after being heated for 16 h at 100 °C, the hexafluoroisopropyl alcohol was evaporated and the reaction mixture was extracted with CH_2Cl_2, washed with water, dried, evaporated, and purified by chromatography (SiO_2, pentane and ether).

Run 20. Procedure D afforded 60 mg of **7** (28%), 23 mg of **8** (11%), 49 mg of **3a** (21%), and 38% of polymeric material.

Run 21. Procedure D afforded a mixture of 51 mg of **7** (24%), 30 mg of **8** (14%), 46 mg of **3a** (20%), and 40% of polymeric material.

Run 22. Procedure D afforded a mixture of 43 mg of **8** (20%) and 306 mg of **3e** (80%).

2-(Hexafluoroisopropoxy)-5-phenyl-2-(trifluoromethyl)-pentane (3e): ^1H NMR δ 1.2 (br s, 3, CH_3), 1.7 and 2.7 (br s and br m, 6, 3 × CH_2), 5.8 (m, 1, H *i*-Pr), 7.23 (s, 5, Ar H); ^{19}F NMR δ −74.3 (d, J = 7 Hz, CF_3-*i*-Pr), −83.7 (s, CF_3).

Acknowledgment. We gratefully acknowledge Rhône-Poulenc Recherches for its financial support (Accord de Recherches CNRS-Rhône-Poulenc No. 820-209) and a collaborative research NATO grant which permitted helpful discussions with Prof. T. T. Tidwell from Toronto University, Canada. We are also indebted to Dr. B. Langlois from Rhône-Poulenc and J. P. Bégué (CNRS) for stimulating discussions.

Registry No. **1a**, 112298-06-3; **1b**, 112298-07-4; **1c**, 112298-08-5; **1d**, 112298-09-6; **1e**, 112298-10-9; **1f**, 112298-11-0; **1g**, 112298-12-1; **1h**, 112298-13-2; **1i**, 112298-14-3; **1j**, 112298-15-4; **2a**, 112298-16-5; **2b**, 112319-75-2; **2c**, 112298-17-6; **2d**, 112298-18-7; **2e**, 112298-19-8; **2f**, 112298-20-1; **2g**, 112298-21-2; **2h**, 112298-22-3; **3a**, 112298-23-4; **3b**, 112298-24-5; **3c**, 112298-25-6; **3d**, 112298-26-7; **3e**, 112298-27-8; **4a**, 85674-68-6; **4b**, 112298-28-9; **4c**, 112298-29-0; **4d**, 112298-30-3; **4e**, 112298-31-4; **5c**, 112298-32-5; **5d**, 112319-76-3; **6a**, 112298-33-6; **6b**, 112298-34-7; **6c**, 112298-35-8; **6d**, 112298-36-9; **6e**, 112298-37-0; **6f**, 112298-38-1; **6g**, 112298-39-2; **6h**, 112298-40-5; **7**, 33501-90-5; **8**, 112298-41-6; 1-bromo-3-(*p*-chlorophenyl)propane, 64473-35-4; 1-bromo-3-(*m*-chlorophenyl)propane, 91085-89-1; 3-(*m*-chlorophenyl)propanol, 22991-03-3; 3-(*p*-chlorophenyl)propanol, 6282-88-8; (*m*-chlorophenyl)magnesium bromide, 36229-42-2; (*p*-methoxyphenyl)magnesium bromide, 13139-86-1; 1-bromo-3-phenylpropane, 637-59-2; 1-bromo-3-(*p*-methylphenyl)propane, 54540-53-3; 1-bromo-3-(*p*-methoxyphenyl)propane, 57293-19-3.

Supplementary Material Available: Table V showing the ^{13}C chemical shifts of the CF_3 alcohols **1a,h–j** and **2a–h** (1 page). Ordering information is given on any current masthead page.

Intramolecular Friedel–Crafts Alkylation and Chloroalkylation of 5-Aryl-1,1,1-trifluoropentan-2-ones. A Route to (Trifluoromethyl)dihydronaphthalenes and (Trifluoromethyl)tetrahydronaphthalenes

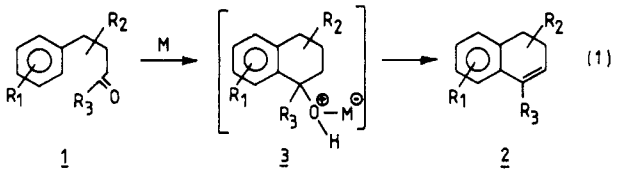
D. Bonnet-Delpon,† M. Charpentier-Morize,*† and R. Jacquot‡

CNRS-CERCOA, 2-8 rue H. Dunant, B.P. 28, 94320 Thiais, France, and Rhône-Poulenc Santé, Centre de Recherches de Vitry, 13, quai Jules Guesde, B.P. 14, 94400 Vitry-sur-Seine, France

Received February 5, 1987

The Friedel–Crafts cyclization of some 5-aryl-1,1,1-trifluoropentan-2-ones yields selectively either 1-(trifluoromethyl)dihydronaphthalenes or 1-chloro-1-(trifluoromethyl)tetrahydronaphthalenes or 1-aryl-1-(trifluoromethyl)tetrahydronaphthalenes, depending on the solvent and the acid.

The Friedel–Crafts cyclization of γ-aryl ketones 1 generally yields 1-substituted 3,4-dihydronaphthalenes **2**,[1] although the product from 5-phenylpentan-2-one (**1a**), (R_1, R_2 = H, R_3 = CH_3) disproportionates under cyclization conditions to a 1:1 mixture of 1-methylnaphthalene and 1-methyl-1,2,3,4-tetrahydronaphthalene[2] (eq 1).



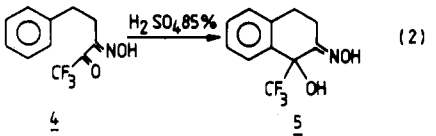
(1)

1 **3** **2**

M = H^+ or Lewis acid

1a, **2a**: R_1 = R_2 = H, R_3 = CH_3

Although it is generally agreed that the intermediate to **2** is the complex **3**, until recently the only reported isolation of the corresponding benzylic alcohol involved the cyclization of the α-trifluoromethyl ketone **4** to give **5**[3] (eq 2).



(2)

4 **5**

In a recent study of the Friedel–Crafts reaction of benzene with 1,1,1-trifluoroacetone, we were able to isolate

† CNRS-CERCOA.

‡ Rhône-Poulenc Santé.

(1) Olah, G. *Friedel-Crafts Relat. React. 1963–1965* **1964**, *2* (Part 2), 659–901.

(2) Quillet, J. P.; Dreux, J. *C. R. Hebd. Seances Acad. Sci.* **1964**, *258*, 1259.

(3) Fung, S.; Abraham, N. A.; Bellini, F.; Sestanj, K. *Can. J. Chem.* **1983**, *61*, 368.

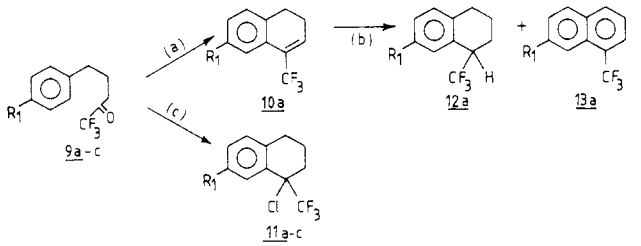
0022-3263/88/1953-0759$01.50/0

Table I. Cyclization of Ketone 9a with Protic Acids or Lewis Acids in CH_2Cl_2

run	acid	temp, °C	rctn time, h	products (% isolated yields) 10a	11a	12	13
1	$ZnCl_2$ or $SnCl_4$	40	16	no reaction			
2	$FeCl_3$	20	3[a] (or more)	90			
3	CF_3CO_2H	70	4[a]	80			
4	TiF_4	0	3[a]	55			
5	H_2SO_4	0	0.5[a]	65[b]		11[b]	11[b]
6	SbF_5	0	3[a]	16[b]		17[b]	16[b]
7	$AlCl_3$	20	1.5[a]		70		
8	$AlCl_3$	20	5		60		
9	$TiCl_4$	0	3[a]		90		
10	$TiCl_4$	20	5	5	80		

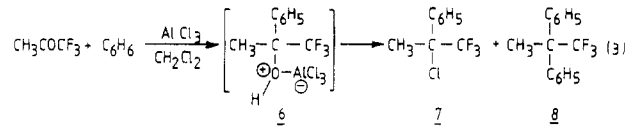
[a] Time necessary for complete disappearance of **9a**. [b] Ratio of areas under ^{19}F NMR peaks related to the total yields of isolated products.

Scheme I[a]

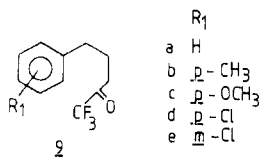


[a] (a) $FeCl_3$, CF_3COOH, TiF_4, or H_2SO_4; (b) SbF_5 or H_2SO_4; (c) $AlCl_3$ or $TiCl_4$.

the tertiary benzylic alcohol corresponding to the intermediate complex **6** at low temperature.[4] However, under acid conditions at higher temperatures, the alcohol was rapidly converted into the chloride **7** and the diphenyl derivative **8** (eq 3).



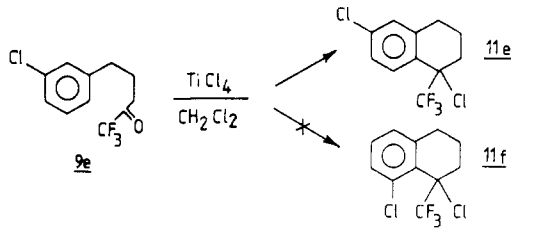
In view of these results, we have undertaken a study of the Friedel–Crafts cyclization of some γ-aryl-α-trifluoromethyl ketones **9**, in search of new methods for the introduction of a trifluoromethyl group on aliphatic carbon.



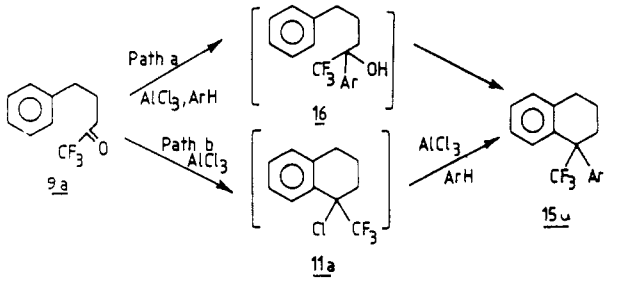
The cyclization of ketones **9**[5] was investigated in protic acids or in methylene chloride with 1 equiv of a Lewis acid. The structures of the products were determined from spectral data; assignments of carbon atoms were made from ^{13}C NMR off resonance, from J_{CF} coupling, and by empirical additively rules.

The principal product from the cyclization of **9a** is either dihydronaphthalene **10a** or chloride **11a**, depending on the nature of the acid (Table I). Excellent yields of **10a** were obtained with CF_3CO_2H or $FeCl_3$; the lower yield in the presence of TiF_4 reflects the formation of some polymeric material. In the presence of H_2SO_4 or SbF_5, **10a** disproportionated to a mixture of tetralin **12a** and naphthalene **13a** (runs 5 and 6 and Scheme I). On the other hand, cyclization with $TiCl_4$ for 3 h gave a high yield of **11a**; continuation of this reaction for a longer period induced formation of a small amount of **10a**. Chloride **11a** is also obtained with $AlCl_3$ but accompanied by some polymeric byproduct. No reaction occurred with $ZnCl_2$ or $SnCl_4$. Treatment of **11a** with $FeCl_3$ in methylene chloride converted it quantitatively into **10a**.

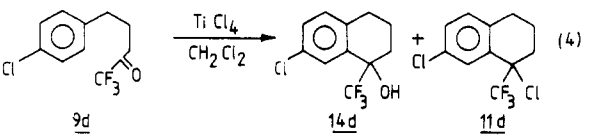
Scheme II



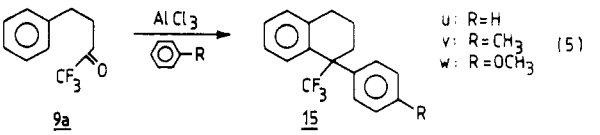
Scheme III



We also explored the cyclization of ketones **9b–e** with $TiCl_4$. Reaction of **9b,c** for 3 h at 0 °C gave good yields (80%) of 1-chloro-1-(trifluoromethyl)-substituted-1,2,3,4-tetrahydronaphthalenes **11b,c**. The cyclization of **9e** was shown, by the ^4J coupling between F and an aromatic CH in the ^{13}C NMR spectrum, to give only 1-chloro-1-(trifluoromethyl)-6-chlorotetrahydronaphthalene (**11e**) with none of the 8-chloro isomer **11f** (Scheme II). A different result was obtained with **9d**, which is deactivated by the meta chlorine.[5] Not only was the reaction slow (starting material still present after 24 h at 20 °C) but also the major product was alcohol **14d** (50%), with a lesser amount (15%) of chloride **11d** (eq 4).



By analogy to eq 3, it was expected that aryl compounds used as solvents for these cyclizations might participate in the reaction. Cyclization of **9a** with $AlCl_3$ in benzene, toluene, or anisole did lead to the aryltetralins **15u–w** in yields of about 60% (eq 5). The para position of the CH_3

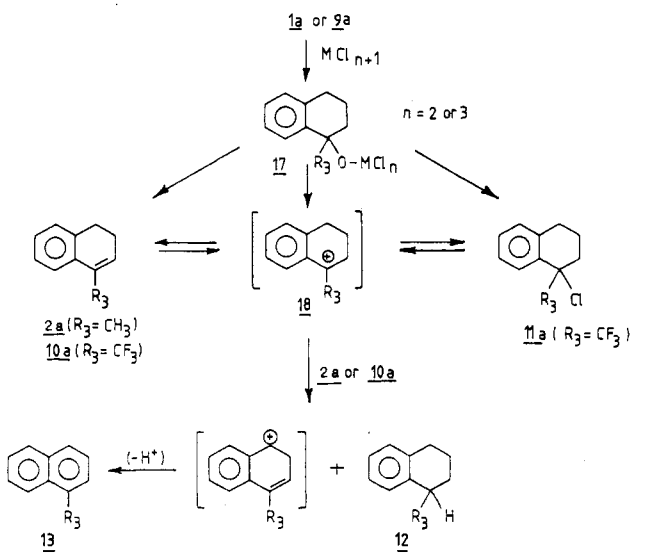


and OCH_3 groups in **15v** and **15w** was shown by the symmetry of the aromatic protons in their NMR spectra.

Compounds **15** might be formed by either path a or path b in Scheme III. We prepared intermediate **16** (Ar = C_6H_5) and showed that both it and **11a** are converted into **15u** on treatment with $AlCl_3$ in benzene. However, we consider that path a is unlikely. First, path a implies that the intermolecular addition of the aryl solvent is faster

(4) Bonnet-Delpon, D.; Charpentier-Morize, M. *Bull. Soc. Chim. Fr. Special Fluor.* **1986**, *6*, 933.
(5) Bonnet-Delpon, D.; Cambillau, C.; Charpentier-Morize, M.; Jacquot, R.; Mesureur, D.; Ourevitch, M. *J. Org. Chem.*, preceding paper in this issue.

Scheme IV



than the intramolecular addition of the phenyl group. If this were so, addition of a second molecule of the aromatic solvent would be expected in analogy to eq 3, but no diaryl product could be detected in any of these reactions. Second, we found that if the reaction of **9a** with $AlCl_3$ in benzene was stopped before complete disappearance of starting material, some chloride **11a** was present in the reaction mixture. Accordingly, we believe that chlorides **11** are the precursors to **15**. However, we note that compounds **15** were formed only in the presence of $AlCl_3$; similar reactions of **9a** in the presence of $TiCl_4$ or $FeCl_3$ gave only **11a** and **10a**, respectively.

Discussion

It appears reasonable that the initial step in the cyclization of **9a** or **1a** is the formation of a complex **17** (Scheme IV). This complex from **1a** ($R_3 = CH_3$) never leads to the corresponding alcohol or chloride even when M = Ti but is readily converted into the stable tertiary benzylic carbocation **18**, which then undergoes elimination to **20**. In contrast, in complex **17** from **9a** ($R_3 = CF_3$), ionization of the C–$OMCl_n$ bond to give **18** would require about 60 kcal mol^{-1} more energy (calculated destabilizing effect of the CF_3 group[6]). Thus this complex should be sufficiently stable to allow isolation of alcohols **14** after hydrolysis, as we demonstrated for **14d** from **9d** (eq 4). Accordingly we performed the following experiments.

First, in the cyclization of **9a** with 1 equiv of $TiCl_4$ in methylene chloride at −50 °C, after 48 h the reaction mixture contained starting material (25%), chloride **11a** (25%), and alcohol **14a** (50%). Second, attempted cyclization of **9a** with a catalytic amount of $TiCl_4$ at 0 °C gave no reaction. Third, in the cyclization of **9a** with 0.25 equiv of $TiCl_4$ at 0 °C, alcohol **14a** was detected at the beginning of the reaction, and after 5 h, **11a** was formed in 85% yield; all of the chlorine in $TiCl_4$ was consumed in this reaction. Thus cyclization of **9a** can stop at the alcohol stage, and chloride **11a** is formed directly from complex **17**. Such a reaction has been observed in nonfluorinated compounds when primary and secondary alcohols[7-9] are treated with halogenated Lewis acids, presumably by an S_Ni mechanism.[7] We conclude that **11a** is formed directly from **17** by an S_Ni mechanism that does not involve the intermediacy of destabilized carbocation **18** ($R_3 = CF_3$). This conclusion is supported by the stability of chloride **11a** (runs 8 and 10).

The formation of **10a** and **15** could occur directly from **11a** or through complex **3** or **17**. However, it is difficult to assess the carbocationic character of either conversion and to explain the selectivity of different Lewis acids. On the other hand, the formation of disproportionation products **12** and **13** would seem to involve the transient existence of carbocation **18** ($R_3 = CF_3$), despite its low stability.

Experimental Section

^1H NMR and ^{19}F NMR spectra were recorded on a Varian EM 360 apparatus (60 MHz) in $CDCl_3$ solution by using Me_4Si and $CFCl_3$ as internal standards. ^{13}C NMR spectra were determined on a CFT 20 instrument (20 MHz), in $CDCl_3$ (Me_4Si as internal standard).[12] Reported signal multiplicities are related to C–F coupling. Mass spectra were obtained in a Nermag R10-10 apparatus coupled to a gas-phase chromatograph (capillary column CPSIL-5, 25 m) and in a Kratos MS50 spectrometer. Gas chromatographic analyses were performed on a Carlo Erba 4130 chromatograph (capillary column SE 30 10 m or 25 m).

Lewis Acid Facilitated Ketone Cyclization Method. Unless otherwise specified, reactions were performed in dry solvents under argon, with reaction volume adjusted to produce a solution about 0.3 M in ketone. Solutions were cooled to the desired temperatures, and 1 equiv of Lewis acid was added dropwise through a septum cap or in small portions. When starting material has disappeared, the mixture was hydrolyzed with an equal volume of water. The organic layer was then washed twice with brine, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The crude product was further purified by column chromatography (on neutral SiO_2, 70–230 mesh) with a pentane/ether eluant.

Cyclization of Ketone 9a: with $FeCl_3$ in CH_2Cl_2 (Run 2). **9a** (500 mg, 2.3 mmol) in 8 mL of CH_2Cl_2 treated at 20 °C with 375 mg (2.3 mmol) of $FeCl_3$ afforded after 3 h or 15 h 410 mg (90%) of **10a**. **10a**: ^1H NMR δ 2.50 (br m, 4 H, 2 × CH_2), 6.60 (m, 1 H, C=CH), 7.13 (m, 4 H, arom); ^{19}F NMR δ −64.3; ^{13}C NMR;[12] high-resolution mass spectrum M^+ 198.0655, calcd for $C_{11}H_9F_3$ 198.0656.

With $FeCl_3$ in Benzene. In the same conditions, 500 mg (2.3 mmol) of **1a** in 8 mL of benzene afforded 365 mg (80%) of **10a**.

With CF_3COOH/H_2SO_4 (Run 3). **9a** (432 mg, 2 mmol) in 7 mL of a solution of H_2SO_4 (2×10^{-2} M) in CF_3COOH was maintained at 70 °C for 4 h. After evaporation of CF_3COOH, the reaction mixture was extracted with CH_2Cl_2, washed with $H_2O/NaHCO_3$ until neutral, and dried on $MgSO_4$. After evaporation and purification, 320 mg (80%) of **10a** was obtained.

With TiF_4 in CH_2Cl_2 (or Benzene) (Run 4). **9a** (432 mg, 2 mmol) in 7 mL of CH_2Cl_2 (or benzene), maintained during 3 h at 5 °C, with 232 mg (2 mmol) of TiF_4, afforded 220 mg (55%) of **10a**.

With Concentrated H_2SO_4 (Run 5). **9a** (432 mg, 2 mmol) was maintained at 0 °C in 8 mL of concentrated H_2SO_4 for 30 min. The solution was neutralized with $NaHCO_3$, extracted with Et_2O, washed with water, dried, and evaporated and afforded 340 mg (87%) of a mixture of **10a**, **12**,[5] and **13**[11] in the ^{19}F NMR proportion of 75/12.5/12.5.

With SbF_5 in CH_2Cl_2 (Run 6). To a solution of 432 mg (2 mmol) of **9a** in 8 mL of CH_2Cl_2 was added 2 mL of a 1 M solution of SbF_5 in CH_2Cl_2 at 0 °C. After 3 h, the solution was neutralized

(6) Paddon-Row, M. N.; Houk, K. N.; Tidwell, T. T. *Tetrahedron Lett.* **1982**, *23*, 383. Bonnet-Delpon, D.; Charpentier-Morize, M.; Loupy, A. *Chem. Phys. Lett.* **1985**, *116*, 478.

(7) Gerrard, W.; Lappert, M. F. *J. Chem. Soc.* **1951**, 1020.

(8) Norris, J. F.; Sturgis, B. J. *Am. Chem. Soc.* **1939**, *61*, 1413. Farah, B. S.; Gilbert, E. *J. Org. Chem.* **1965**, *30*, 1241. Nakamura, E.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 7360.

(9) Among numerous examples of cycloalkylations of γ-aryl ketones, it seems that only one reaction of halogenoalkylation has been reported (the reagent was HBr in CH_3COOH).[10]

(10) Colonge, J.; Collomb, F. *Bull. Soc. Chim. Fr.* **1951**, M.285.

(11) Kunshenko, B. V.; Alekseeva, L. A.; Yagupol'skii, L. M. *Zh. Org. Khim.* **1972**, *8*, 830. Kitching, W.; Bullpitt, M.; Gartshore, D.; Adcock, W.; Khor, T. C.; Doddrell, D.; Rae, I. D. *J. Org. Chem.* **1977**, *42*, 2411.

(12) Bonnet-Delpon, D.; Ourevitch, M. *Magn. Reson. Chem.*, in press.

with $NaHCO_3$, washed with water, dried, and evaporated and afforded 195 mg (50%) of a mixture of **10a**, **12**,[5] and **13**[11] in the ^{19}F NMR proportion of 33/35/32.

With $AlCl_3$ in CH_2Cl_2 (Runs 7 and 8). **9a** (216 mg, 1 mmol) in 3 mL of CH_2Cl_2 treated at 20 °C with 133 mg (1 mmol) of $AlCl_3$ for 1 h 30 min afforded 164 mg (70%) of chloride **11a**. If the reaction is maintained for 5 h, **11a** is obtained but with a 60% yield. **11a**: ^1H NMR δ 2.10 (m, 2 H), 2.50 (m, 2 H), 2.80 (m, 2 H), 7.25 (m, 3 H, arom), 7.80 (m, 1 H, arom); ^{19}F NMR δ −73.0; ^{13}C NMR;[12] MS, *m/e* 234 (M^+), 199 ($M^+ - Cl$), 165 ($M^+ - CF_3$), 159, 130, 129, 128, 127; high-resolution mass spectrum M^+ 234.0422, calcd for $C_{11}H_{10}ClF_3$ 234.0423.

With $AlCl_3$ in Benzene. **9a** (432 mg, 2 mmol) in 7 mL of benzene treated at 5 °C with 266 mg (2 mmol) of $AlCl_3$ afforded, after 2 h, 300 mg (54%) of **15u**. If the reaction is maintained for a shorter time, it leads to a mixture of **11a** and **15u**. **15u**: ^1H NMR δ 1.80 (m, 2 H), 2.35 (m, 2 H), 2.70 (m, 2 H), 7.30 (s, 9 H, arom); ^{19}F NMR δ −65.3; ^{13}C NMR;[12] MS, *m/e* 276 (M^+), 207 ($M^+ - CF_3$), 198, 129, 91. Anal. Calcd for $C_{17}H_{15}F_3$: C, 73.90; H, 5.47; F, 20.63. Found: C, 73.84; H, 5.55; F, 19.57.

With $AlCl_3$ in Toluene. Under the same conditions as in benzene, **9a** and $AlCl_3$ afforded 348 mg (60%) of **15v**. **15v**: ^1H NMR δ 1.67 (m, 2 H), 2.23 (s, 3 H), 2.30 (m, 2 H), 2.73 (m, 2 H), 7.03 (s) and 7.17 (s) (8 H, arom); ^{19}F NMR δ −66.7; ^{13}C NMR.[12]

With $AlCl_3$ in Anisole. Under the same conditions as in benzene, **9a** and $AlCl_3$ afforded 459 mg (75%) of **15w**. **15w**: ^1H NMR δ 1.73 (m, 2 H), 2.33 (m, 2 H), 2.80 (m, 2 H), 3.77 (s, 3 H), 7.03 (m, AB syst 4 H), 7.30 (m, 4 H, arom); ^{19}F NMR δ −66.8; ^{13}C NMR;[12] high-resolution mass spectrum M^+ 306.1230, calcd for $C_{18}H_{17}OF_3$ 306.1231.

With $TiCl_4$ in CH_2Cl_2 (Run 10). **9a** (540 mg, 2.5 mmol) in 7 mL of CH_2Cl_2 treated at 0 °C with 475 mg (0.275 mL, 2.5 mmol) of $TiCl_4$ afforded, after 3 h, 526 mg (90%) of **11a**. The same reaction performed at 20 °C for 5 h afforded 25 mg (5%) of **10a** and 465 mg (80%) of **11a**.

With $TiCl_4$ in Benzene. In the same proportions as in run 10, **9a** and $TiCl_4$ maintained in 7 mL of benzene at 5 °C for 2 h afforded **11a** (55%). When reaction was maintained for a longer time or at higher temperature, the same product **11a** was obtained.

With $TiCl_4$ in CH_2Cl_2 at −50 °C. **9a** (540 mg, 2.5 mmol) in 7 mL of CH_2Cl_2 was treated at −50 °C with 475 mg (0.275 mL, 2.5 mmol) of $TiCl_4$ and afforded, after 48 h, 146 mg (25%) of **11a**, 130 mg (24%) of starting material **9a**, and 248 mg (46%) of alcohol **14a**. **14a**: ^1H NMR δ 1.93 (m, 4 H, 2 × CH_2), 2.70 (m, 2 H), 3.30 (br s, 1 H, OH), 7.10–7.83 (m, 4 H, arom); ^{19}F NMR δ −78.0; ^{13}C NMR;[12] MS, *m/e* 216 (M^+), 198 ($M^+ - H_2O$), 147 ($M^+ - CF_3$), 129, 91; high-resolution mass spectrum M^+ 216.0763, calcd for $C_{11}H_{11}OF_3$ 216.0762.

If temperature was allowed to rise before workup, the only product was chloride **11a**.

With 0.25 equiv of $TiCl_4$ in CH_2Cl_2. **1a** (540 mg, 2.5 mmol) in 7 mL of CH_2Cl_2 was treated at 0 °C with 0.25 equiv of $TiCl_4$ (118 mg = 1 mL from a 10-mL solution of 1.180 g of $TiCl_4$ in CH_2Cl_2). The reaction progress was monitored by GC and indicated, after 1 h, a mixture of **9a** (12%), **11a** (53%), and **14a** (33%) and, after 5 h, only chloride **11a**. Workup and purification afforded 500 mg (85%) of **11a**.

Cyclization of Ketone 9b with $TiCl_4$ in CH_2Cl_2. **9b** (1 g, 4.34 mmol) in 12 mL of CH_2Cl_2, treated at 0 °C with 824 mg (0.477 mL, 4.34 mmol) of $TiCl_4$, afforded, after 3 h, 865 mg (80%) of **11b**. **11b**: ^1H NMR δ 2.0 (m, 2 H), 2.4 (s, 3 H + m, 2 H), 2.8 (br t, 2 H), 7.0–7.6 (m, 3 H, arom); ^{19}F NMR δ −73.3; ^{13}C NMR;[12] high-resolution mass spectrum M^+ 248.0579, calcd for $C_{12}H_{12}ClF_3$ 248.0579.

Cyclization of Ketone 9c with $TiCl_4$ in CH_2Cl_2. Under the same conditions, 1 g (4.06 mmol) of **9c** afforded, after 3 h, 860 mg (80%) of **11c**. **11c**: ^1H NMR δ 2.00 (m, 2 H), 2.40 (m, 2 H), 2.73 (m, 2 H), 3.77 (s, 3 H), 6.67–7.30 (m, 3 H, arom): ^{19}F δ −74.1; ^{13}C NMR;[12] high-resolution mass spectrum M^+ 264.0529, calcd for $C_{12}H_{12}OClF_3$ 264.0528.

Cyclization of 9d with $TiCl_4$ in CH_2Cl_2. Under the same conditions, 1 g (4 mmol) of **9d** afforded, after 12 h, 80% of starting material. Reaction was maintained at 20 °C for 24 h and afforded 160 mg (15%) of **11d**, 400 mg (40%) of **9d**, and 400 mg (40%) of **14d**. **11d**: ^1H NMR δ 2.10 (m, 2 H), 2.43 (m, 2 H), 2.83 (m, 2 H), 6.86–7.26 (m, 2 H, arom H_5 and H_6), 7.67 (s, 1 H, H_8); ^{19}F NMR δ −74.7; ^{13}C NMR;[12] high-resolution mass spectrum M^+ 268.0031, calcd for $C_{11}H_9Cl_2F_3$ 268.0033. **14d**: ^1H NMR δ 2.10 and 2.77 (m, 3 × CH_2), 4.5 (br m, 1 H, OH), 7.13 (m, 2 H, arom H_5 and H_6), 7.78 (s, 1 H, H_8); ^{19}F NMR δ −78.3; ^{13}C NMR.[12]

Cyclization of 9e with $TiCl_4$ in CH_2Cl_2. **9e** (500 mg, 2 mmol) in 6 mL of CH_2Cl_2, treated at 0 °C with 380 mg (0.22 mL, 2 mmol) of $TiCl_4$, afforded, after 3 h, 430 mg (80%) of **11e**. **11e**: ^1H NMR δ 2.03 (m, 2 H), 2.43 (m, 2 H), 2.87 (m, 2 H), 7.13 (m, 1 H, H_5), 7.10 and 7.67 (m, AB syst, H_7 and H_8); ^{19}F NMR δ −74.6; ^{13}C NMR.[12]

Cyclization of 5-Phenyl-2-pentanone[2] with $TiCl_4$ in CH_2Cl_2. Ketone (1.62 g, 10 mmol) in 20 mL of CH_2Cl_2, treated with 1.9 g (1.1 mL, 10 mmol) of $TiCl_4$, afforded, after 6 h, besides oligomers, 290 mg (20%) of 1-methyltetrahydronaphthalene and 280 mg (20%) of 1-methylnaphthalene identical with products already described.[2,11,13] 1-Methyltetrahydronaphthalene: MS, *m/e* 146 (M^+), 131 ($M^+ - 15$); ^{13}C NMR δ 20.5 (C_1), 22.8 (CH_3), 30.0 (C_4), 31.5 (C_2), 32.5 (C_1), 125.6 (C_6, C_7), 128.0 (C_5), 129.0 (C_8), 136.9 (C_{10}), 142.1 (C_9).

Cyclization of Alcohol 16[5] with $AlCl_3$. **16** (588 mg, 2 mmol) in 10 mL of benzene (or CH_2Cl_2) was maintained for 3 h at 20 °C in the presence of 266 mg (2 mmol) of $AlCl_3$. **15u** (348 mg, 63%) was obtained.

Behavior of the Chloride 11a: with $AlCl_3$ in Benzene. **11a** (468 mg, 2 mmol) in 7 mL of benzene was treated at 5 °C during 2 h with 266 mg (2 mmol) of $AlCl_3$. After workup and separation from polymeric material, 250 mg (45%) of **15u** was isolated.

With $FeCl_3$ in CH_2Cl_2. **11a** (468 mg, 2 mmol) in 7 mL of CH_2Cl_2 was treated at 20 °C during 2 h with 325 mg (2 mmol) of $FeCl_3$. After workup and purification, 320 mg (80%) of **10a** was obtained.

Acknowledgment. We thank Rhône-Poulenc Recherches for financial support (Accord de Recherches CNRS-Rhône-Poulenc No. 820-209). Dr. B. Langlois, from Rhône-Poulenc, is gratefully acknowledged for stimulating discussions.

Registry No. **9a**, 85674-68-6; **9b**, 112298-28-9; **9c**, 112298-29-0; **9d**, 112298-30-3; **9e**, 112298-31-4; **10a**, 112481-79-5; **11a**, 112481-80-8; **11b**, 112481-81-9; **11c**, 112481-82-0; **11d**, 112481-83-1; **11e**, 112481-84-2; **12**, 112298-32-5; **13**, 26458-04-8; **14a**, 112481-85-3; **14d**, 112481-86-4; **15u**, 112298-33-6; **15v**, 112481-87-5; **15w**, 112298-38-1; **16**, 112298-16-5; 5-phenyl-2-pentanone, 2235-83-8; 1-methyltetrahydronaphthalene, 1559-81-5; 1-methylnaphthalene, 90-12-0.

(13) Schneider, H. J.; Agrawal, P. K. *Org. Magn. Reson.* **1984**, *22*, 180.