taining spots other than the remaining 3. The mixture was diluted with 20 mL of CH_2Cl_2 and transfered into a separatory funnel, and 20 mL of water was added. After the mixture was shaken, the aqueous layer was further extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over Na_2SO_4 and evaporated, and the residue was treated with 10 mL of ethyl acetate. The insoluble solid was filtered and washed with ethyl acetate (2 × 3 mL). The filtrate was evaporated in vacuo, and after repeated coevaporation with toluene (3 × 5 mL) the residue was chromatographed on silica gel and eluted with CH_2Cl_2–MeOH to give 76 mg (15%) of **5**: NMR ($CDCl_3$) δ 1.20–1.85 (m, 6 H, $(CH_2)_3$), 3.02 (m, 1 H, 5′-H), 3.27 (m, 2 H, CH_2O of THP), 3.51 (m, 1 H, 5′-H), 3.67 (s, 3 H, CH_3O), 4.16 and 4.28 (br s, diastereomeric 4′-H), 4.34 (d, 1 H, J = 7 Hz, CH_2OP of one of diastereomers), 4.56 (dd, 1 H, J = 8 Hz, CH_2OP of the other diastereomer), 4.86 (br s, 1 H, 2′-H), 5.44–5.84 (m, 2 H, CH of THP and 3′-H), 5.92 (m, 1 H, 1′-H), 6.68 and 6.73 (d, 2 H, J = 8.8 Hz, Ar H), 6.98–7.75 (m, 23 H, Ar H and N^1H), 8.67 and 8.92 (s, 1 H, N^2 H). Anal. Calcd for $C_{50}H_{47}Cl_3O_{10}N_5PS$: C, 57.34; H, 4.52; N, 6.69; Cl, 10.16; S, 3.06. Found: C, 57.02; H, 4.79; N, 6.39; Cl, 10.15; S, 3.22.

5′-*O*-(Methoxytrityl)-2′-*O*-(tetrahydropyranyl)-*O*^{6}-(di-*n*-butylthioxophosphoranyl)-*N*^{2}-benzoylguanosine (6). To a solution of 744 mg (1 mmol) of **3** in 20 mL of dry CH_2Cl_2 were added 175 μL (1.25 mmol) of triethylamine, 5 mg (0.04 mmol) of DMAP, and 386 mg (1.5 mmol) of di-*n*-butylthioxophosphoranyl bromide. The mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo, and the residue was chromatographed on silica gel and eluted with CH_2Cl_2–MeOH to give 884 mg (96%) of **6**: NMR ($CDCl_3$) δ 0.96 (t, 6 H, J = 1 Hz, CH_3C), 1.15–2.00 (m, 6 H, $(CH_2)_3$ of THP), 2.40–2.80 (m, 12 H, $(CH_2)_3$), 2.86 (br, 1 H, OH), 3.05–3.58 (m, 2 H, CH_2O of THP), 3.42 (m, 1 H, one of the 5′-Hs), 3.69 (s, 3 H, CH_3O), 3.72 (m, 1 H, one of the 5′-Hs), 4.23 (m, 1 H, 4′-H), 4.68 (m, 2 H, 2′- and 3′-H), 5.24 (t, 1 H, J = 5.5 Hz, CH of THP), 6.14 (d, 1 H, J = 6 Hz, 1′-H), 6.66 (d, 2 H, J = 9.2 Hz, Ar H), 7.00–7.58 (m, 17 H, Ar H), 8.03 (s, 1 H, 8-H), 8.31 (s, 1 H, NH). Anal. Calcd for $C_{50}H_{58}N_5O_8PS$: C, 65.28; H, 6.35; N, 7.61. Found: C, 64.79; H, 6.30; N, 7.37.

2′-*O*-(Methoxytetrahydropyranyl)-*O*^{6}-(di-*n*-butylthioxophosphoranyl)-*N*^{2}-tritylguanosine 5′-(*S*,*S*-Bis(4-methoxyphenyl) Phosphorodithioate) (8). To a solution of 979 mg (0.985 mmol) of **7** in 20 mL of dry CH_2Cl_2 were added 0.233 mL (4.16 mmol) of triethylamine, 387 mg (1.5 mmol) of di-*n*-butylthioxophosphoranyl bromide, and 7.3 mg (0.06 mmol) of DMAP, and the mixture was stirred for 10 min. Then the solvent was removed, and the residue was chromatographed on silica gel to give 706 mg (62%) of **8**: NMR ($CDCl_3$) δ 0.09 (m, 6 H, CH_3C), 1.18–1.90 (m, 12 H, $(CH_2)_2$ and CH_2 of mTHP), 2.04 (m, 4 H, CH_2P), 2.71 (s, 3 H, CH_3O of mTHP), 2.75 (d, 1 H, J = 3 Hz, OH), 3.56 (m, 4 H, CH_2O), 3.80 (s, 6 H, CH_3O), 4.02–4.42 (m, 4 H, 3′-, 4′-, and 5′-H), 4.65 (t, 1 H, J = 6 Hz, 2′-H), 5.68 (d, 1 H, J = 6 Hz, 1′-H), 6.39 (s, 1 H, N^2 H), 6.83 (d, 4 H, J = 9 Hz, Ar H), 7.10–7.52 (m, 19 H, Ar H), 7.71 (s, 1 H, 8-H). Anal. Calcd for $C_{57}H_{67}O_{10}N_5P_2S_3$: C, 60.04; H, 5.92; N, 6.14. Found: C, 60.45; H, 6.34; N, 5.92.

2′-*O*-(Methoxytetrahydropyranyl)-*O*^{6}-(2,4,6-triisopropylbenzenesulfonyl)-*N*^{2}-tritylguanosine 5′-(*S*,*S*-Bis(4-methoxyphenyl) Phosphorodithioate) (9). To a solution of 199 mg (0.2 mmol) of **7** in 2 mL of dry CH_2Cl_2 were added 242 mg (0.8 mmol) of TPS, 0.12 mL (0.88 mmol) of triethylamine, and 8.5 mg (0.07 mmol) of DMAP, and the mixture was stirred for 18 h. The solvent was then removed in vacuo, and the residue was chromatographed on silica gel to give 247 mg (94%) of **9**: NMR ($CDCl_3$) δ 1.22 (d, 18 H, J = 6 Hz, $(CH_3)_2$), 1.50 (m, 4 H, CH_2), 2.56 (s, 3 H, CH_3O), 2.70 (m, 1 H, CH), 3.50 (m, 4 H, CH_2O), 3.72 (s, 3 H, CH_3O), 3.77 (m, 6 H, CH_3O), 3.70–4.55 (m, 5 H, 2′-, 3′-, 4′-, and 5′-H), 5.32 (d, 1 H, J = 6 Hz, 1′-H), 6.07 (s, 1 H, N^2 H), 6.56 (m, 4 H Ar H), 6.92–7.51 (m, 22 H, Ar H), 7.52 (s, 1 H, 8-H). Anal. Calcd for $C_{65}H_{74}N_5O_{13}PS_3 \cdot 3H_2O$: C, 59.39; H, 6.13; N, 5.33. Found: C, 59.35; H, 6.14; N, 5.13.

Synthesis of 10. Typical Procedure. A mixture of 138 mg (0.15 mmol) of **6** and 95 mg (0.23 mmol) of **4** was rendered anhydrous by repeated coevaporation with dry pyridine (3 × 2 mL) and dissolved in 3 mL of dry pyridine. To the solution was added 145 mg (0.45 mmol) of TPS. After being stirred for 12 h, the mixture was poured into 20 mL of CH_2Cl_2, transfered into a separatory funnel, and shaken with 20 mL of water. The CH_2Cl_2 layer was collected, and the aqueous layer was further extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried over Na_2SO_4, evaporated in vacuo, and treated with 10 mL of ethyl acetate. The insoluble solid was filtered and washed with ethyl acetate (2 × 3 mL). The filtrate was evaporated in vacuo and coevaporated with toluene three times. The residue was chromatographed on silica gel and eluted with CH_2Cl_2–MeOH to give 51 mg (33%) of **5** and 92 mg (50%) of **10** as ca. 1:1 diastereomeric mixture. For **10**: NMR ($CDCl_3$) δ 0.95 (m, 6 H, CH_3), 1.10–2.10 (m, 14 H, CH_2), 2.62 (m, 4 H, CH_2P), 3.00–3.54 (m, 4 H, CH_2O of THP and 5′-H), 3.70 (s, 3 H, CH_3O), 4.13 and 4.12 (br s, 1 H, diastereomeric 4′-H), 4.52 (m, 2 H, CH_2OP), 4.77 (br s, 1 H, 2′-H), 5.25–5.70 (m, 2 H, CH of THP and 3′-H), 6.07 (m, 1 H, 1′-H), 6.66 and 6.70 (d, 2 H, J = 9.2 Hz, Ar H), 8.06 (s, 1 H, 8-H), 8.35 and 8.41 (s, 1 H, diastereomeric NH). Anal. Calcd for $C_{58}H_{64}Cl_3N_5O_{10}P_2S_2$: C, 56.93; H, 5.27; N, 5.72. Found: C, 56.70; H, 5.39; N, 5.74.

Registry No. 1, 77001-23-1; 2, 79970-26-6; 3, 79970-27-7; 4, 79970-29-9; 5 (isomer 1), 79970-30-2; 5 (isomer 2), 79970-31-3; 6, 79970-32-4; 7, 79970-33-5; 8, 79970-34-6; 9, 79970-35-7; 10 (isomer 1), 79970-36-8; 10 (isomer 2), 79970-37-9; 2′-*O*-(tetrahydropyranyl)-*N*^{2}-benzoylguanosine, 60324-96-1; *S*,*S*-diphenyl 2,2,2-trichloroethyl phosphorodithioate, 79970-38-0; di-*n*-butylthioxophosphoranyl bromide, 55656-88-7; MMTrCl, 14470-28-1.

Fluorination with Xenon Difluoride. 27. The Effect of Catalyst on Fluorination of 1,3-Diketones and Enol Acetates

Barbara Zajc and Marko Zupan*

"J. Stefan" Institute and Department of Chemistry, "Edvard Kardelj" University of Ljubljana, 61000 Ljubljana, Yugoslavia

Received July 17, 1981

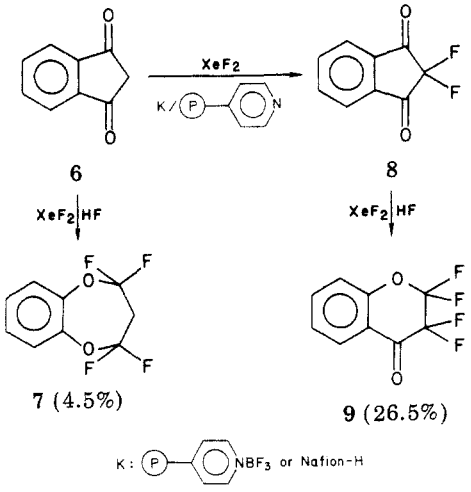
Xenon difluoride is a mild fluorinating agent for fluorination of alkenes, acetylenes, aromatic, and heteroaromatic molecules; this topic has recently been reviewed.[1] It is known that the course of fluorination strongly depends on the following factors: the structure of the organic molecule, the catalyst used, and solvent polarity and temperature. The importance of the correct selection of catalyst for successful fluorination has been shown in fluorination of several alkenes, and so far, the catalysts which have been found to be effective are hydrogen fluoride,[2] hydrogen fluoride–pyridine,[3] boron trifluoride,[4] boron trifluoride etherate,[5] pentafluorothiophenol,[6] trifluoroacetic acid,[7] and bromine.[8]

Fluorination of 1,3-diketones has received much less attention than reactions involving other halogens. Reaction with perchlorylfluoride in the presence of base resulted in the formation of mono-[9] and difluoro[10] products, the

(1) Filler, R. *Isr. J. Chem.* **1978**, *17*, 71.
(2) Zupan, M.; Pollak, A. *J. Chem. Soc., Chem. Commun.* **1973**, 845.
(3) Gregorčič, A.; Zupan, M. *Collect. Czech. Chem. Commun.* **1977**, *42*, 3192.
(4) Stavber, S.; Zupan, M. *J. Chem. Soc., Chem. Commun.* **1978**, 969.
(5) Shackelford, S. A.; McGuire, R. R.; Pflug, J. L. *Tetrahedron Lett.* **1977**, 363.
(6) Gregorčič, A.; Zupan, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1085.
(7) Zupan, M.; Pollak, A. *Tetrahedron Lett.* **1974**, 1015.
(8) Stavber, S.; Zupan, M. *J. Fluorine Chem.* **1977**, *10*, 271.
(9) Machleidt, H.; Hartmann, V. *Justus Liebigs Ann. Chem.* **1964**, *679*, 9.
(10) Inman, C. E.; Oesterling, R. E.; Tyczkowski, E. A. *J. Am. Chem. Soc.* **1958**, *80*, 6533.

0022-3263/82/1947-0573$01.25/0

Scheme I



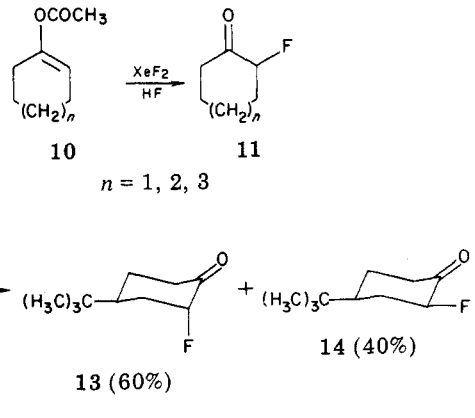
major disadvantage of these reagents being the tendency for violent explosions.[11] Recently the first example of fluorination of β-diketones by xenon hexafluoride intercalate, $C_{19}XeF_6$, resulting in monofluoro products, was published.[12] We now report an investigation to find a new catalyst convenient for fluorination of 1,3-diketones.

Results and Discussion

Xenon difluoride readily reacted at room temperature with acetylacetone (1) in methylene chloride and in the presence of HF as catalyst. A stoichiometric amount of xenon difluoride resulted in the formation of only difluoro product (3), while the use of 2 equiv of xenon difluoride gave 70% (determined by ^{19}F NMR) of 3,3-difluoropentane-2,4-dione (3), which was purified by GLC and identified by IR, NMR, and mass spectroscopy.[10] The formation of monofluoro product (2) was observed on modification of experimental conditions, i.e., higher dilution and a higher ratio of substrate to xenon difluoride (2.3:1).

The hydrogen fluoride catalyzed fluorination of 5,5-dimethylcyclohexane-1,3-dione (4) with 2 mmol of xenon difluoride gave a complex mixture in low yield. We found that the choice of the insoluble cross-linked polystyrene–4-vinylpyridine complex with boron trifluoride[13] as catalyst improved the overall yield, but a mixture of products was still obtained. Finally, we found that under the following conditions only 2,2-difluoro-5,5-dimethylcyclohexane-1,3-dione (5) was formed in high yield: to a solution of diketone (4, 1 mmol) in methylene chloride (20 mL) were added insoluble cross-linked polystyrene–4-vinylpyridine (50% of pyridine rings; 600 mg), xenon difluoride (2.2 mmol), and insoluble cross-linked polystyrene–4-vinylpyridine–boron trifluoride complex (100 mg). The mixture was stirred at room temperature for 20 h, the catalyst was filtered off, the solvent was evaporated under reduced pressure, and 2,2-difluoro-5,5-dimethylcyclohexane-1,3-dione (5) was purified by GLC. A similar result was observed when insoluble cross-linked polystyrene–4-vinylpyridine–boron trifluoride complex was replaced by Nafion-H.[14]

Scheme II



HF-catalyzed room-temperature fluorination of indan-1,3-dione (6, Scheme I) resulted in the formation of insoluble high-melting products, which were filtered off; the solvent was evaporated and from the reaction mixture one product was isolated by GLC in very low yield. Its ^{19}F NMR spectrum showed a triplet signal at −63 ppm (J = 9 Hz) and its proton NMR spectrum showed a quintet signal at 2.96 ppm (J = 9 Hz, 2 H) and a broad singlet at 7.6 ppm (4 H). Besides a molecular peak at m/e 222 (25, $C_9H_6F_4O_2$), the mass spectrum showed a basic fragment at m/e 113 (100, C_3HF_4). On the basis of the spectroscopic data, we established that 1,2-(1,1,3,3-tetrafluorotrimethylenedioxy)benzene (7) was formed. After modification of experimental conditions, as in the case of fluorination of compound 4, only one product was formed, which was isolated by preparative GLC. On the basis of spectroscopic data, we established that 2,2-difluoroindan-1,3-dione (8) was formed in high yield.

Nafion-H catalyzed fluorination of 8 with xenon difluoride was unsuccessful, while hydrogen fluoride fluorination resulted in a product which showed two broad signals at −92.7 and −131.5 ppm in its ^{19}F NMR spectrum. Besides a molecular peak at m/e 220 (67, $C_9H_4F_4O_2$), its mass spectrum showed a basic peak at m/e 120 (100, $M^+ - C_2F_4$). On the basis of the spectroscopic data (IR, $\nu_{C=O}$ = 1735 cm^{-1}), we established that 2,2,3,3-tetrafluorochroman-4-one (9) was formed.

Enol acetates have been fluorinated with ClO_3F[11] and with fluoroxy compounds.[15] HF-catalyzed fluorination of cyclic enol acetates (10) with xenon difluoride at room temperature gave the α-fluorocycloalkanones. The yield and contamination with cycloalkanones depends on exclusion of moisture and the amount of catalyst. All such reactions needed only a catalytic amount of hydrogen fluoride, while larger proportions resulted in increased amounts of impurities. In the presence of only catalytic amounts of hydrogen fluoride, the decomposition of enol acetate is diminished (2–20%, the decomposition of larger rings being more pronounced). Fluorination of enol acetate of 4-*tert*-butylcyclohexanone (12) gave two α-fluoro products 13 and 14 in the ratio 3:2, respectively.

Experimental Section

IR spectra were recorded with a Perkin Elmer 257 spectrometer; ^1H and ^{19}F NMR spectra were recorded by a JEOL JNM PS 100 from $CDCl_3$ solution with Me_4Si or CCl_3F as internal reference. Mass spectra and high-resolution measurements were taken on a CEC 21 110 spectrometer. GLC was carried out on a Varian Aerograph Model 1800 instrument. Methylene chloride was purified and stored over molecular sieves.[16] Xenon difluoride

(11) Sharts, C. M.; Sheppard, W. A. *Org. React.* **1974**, *21*, 125.
(12) Yemul, S. S.; Kagan, H. B. *Tetrahedron Lett.* **1980**, 277.
(13) Insoluble cross-linked polystyrene–4-vinylpyridine complex with boron trifluoride was prepared by passing boron trifluoride through a suspension of polystyrene–4-vinylpyridine containing 2% pyridine rings. The polymeric complex contains 1.04% boron.
(14) Nafion is a registered trademark of the Du Pont Co., whom we thank for a gift of potassium salt of Nafion 501 used in preparing activated Nafion-H resinsulfonic acid.
(15) Hesse, R. H. *Isr. J. Chem.* **1978**, *17*, 60.

was prepared by a photosynthetic method[17] and its purity was better than 99.5%.

3,3-Difluoropentane-2,4-dione (3). One millimole of pentane-2,4-dione (1) was dissolved in 2 mL of methylene chloride, 2.2 mmol of xenon difluoride was added under stirring at 25 °C, and a catalytic amount of hydrogen fluoride (5–8 mg) was introduced. After 1 h, the reaction mixture was diluted by methylene chloride (10 mL), washed with 10 mL of $NaHCO_3$ and water, and dried over anhydrous sodium sulfate. The solvent was partly evaporated under reduced pressure and the reaction mixture was analyzed by ^{19}F NMR spectroscopy and GLC. The product was isolated by preparative GLC (Carbowax 20M 25%, Varaport 30 70/80, T = 110 °C) and 59 mg (42.8%) of colorless liquid, bp 114 °C (T_{bp}[13] = 114 °C) was obtained: exact mass calcd for $C_5H_6F_2O_2$ 136.0336, found 136.0340; mass spectrum, m/e 136 (M^+, 1), 94 (14), 46 (5), 44 (11), 43 (100), 42 (18).

3-Fluoropentane-2,4-dione (2). Five millimoles of pentane-2,4-dione (1) was dissolved in 10 mL of methylene chloride, 2.2 mmol of xenon difluoride was added with stirring at 25 °C, and a catalytic amount of hydrogen fluoride (5–8 mg) was introduced. After 20 h, the reaction mixture was diluted with methylene chloride (10 mL), washed with $NaHCO_3$ and water, and dried over anhydrous sodium sulfate. The solvent was partly evaporated under reduced pressure and the reaction mixture was analyzed by ^{19}F NMR spectroscopy and GLC. The product was isolated by preparative GLC (Carbowax 20M, 25%, Varaport 30 70/80, T = 120 °C) and 41 mg (7%) of very volatile liquid product was isolated: exact mass calcd for $C_5H_7FO_2$ 118.0430, found 118.0433; mass spectrum, m/e 118 (M^+, 11), 103 (15), 76 (8), 49 (9), 43 (100).

2,2-Difluoro-5,5-dimethylcyclohexane-1,3-dione (5). One millimole of 5,5-dimethylcyclohexane-1,3-dione (4) was dissolved in 20 mL of methylene chloride, and 600 mg of insoluble cross-linked polystyrene–4-vinylpyridine, 2.2 mmol of xenon difluoride, and under stirring at room temperature 100 mg of insoluble cross-linked polystyrene–4-vinylpyridine–boron trifluoride complex (or 200 mg of Nafion-H) were added. The reaction mixture was stirred for 20 h and filtered, the polymers were washed with methylene chloride, the solvent was evaporated, and 150 mg of crude product was isolated, which was analyzed by ^{19}F NMR and GLC. The product was purified by preparative GLC (SE-30 10%, Chromosorb A 45/60, T = 120 °C) and 92 mg (52%) of solid product, mp 49–51 °C was obtained: exact mass calcd for $C_8H_{10}F_2O_2$ 176.0649, found 176.0653; mass spectrum, m/e 176 (M^+, 14), 119 (11), 83 (100), 56 (20), 55 (50), 42 (14), 41 (33).

2,2-Difluoroindan-1,3-dione (8). One millimole of indan-1,3-dione (6) was dissolved in 20 mL of methylene chloride, and 600 mg of insoluble cross-linked polystyrene–4-vinylpyridine, 2.2 mmol of xenon difluoride, and under stirring 200 mg of Nafion-H (or 100 mg of insoluble cross-linked polystyrene–4-vinylpyridine–boron trifluoride complex) were added. The reaction mixture was stirred at room temperature for 20 h, the polymers were filtered off and washed with methylene chloride, the solvent was evaporated in vacuo, and 155 mg of crude product was isolated. Purification of the product by preparative GLC (OV-17 10%, Chromosorb A 45/60, T = 185 °C) resulted in 96.5 mg (53%) of crystalline product (mp 117–118 °C): exact mass calcd for $C_9H_4F_2O_2$ 182.0179, found 182.0180; mass spectrum, m/e 182 (M^+, 91), 104 (100), 50 (23).

1,2-(1,1,3,3-Tetrafluorotrimethylenedioxy)benzene (7). Five millimoles of indan-1,3-dione (6) was dissolved in 15 mL of methylene chloride, 12.5 mmol of xenon difluoride was added, and under stirring a catalytic amount of anhydrous hydrogen fluoride (5–8 mg) was introduced. After 20 h, 10 mL of methylene chloride was added, the insolbule product was filtered off, and the filtrate was washed with $NaHCO_3$ and water and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and the crude reaction mixture was analyzed by ^{19}F NMR spectroscopy and GLC and 50 mg (4.5%) of crystalline product, mp 38–39 °C, was isolated: exact mass calcd for $C_9H_6F_4O_2$ 222.0304, found 222.0307; mass spectrum, m/e 222 (M^+, 25), 202 (17), 113 (100), 110 (10), 109 (11), 92 (15), 82 (12), 81 (17), 69 (17), 64 (62), 63 (33), 53 (12), 52 (20), 51 (25), 50 (20), 44 (60), 43 (18).

2,2,3,3-Trifluorochroman-4-one (9). A 0.25-mmol sample of 2,2-difluoroindan-1,3-dione (8) was dissolved in 0.7 mL of methylene chloride, 0.32 mmol of xenon difluoride was added, and under stirring a catalytic amount of anhydrous hydrogen fluoride (5–8 mg) was introduced. After 20 h, 5 mL of methylene chloride was added, the reaction mixture was washed with $NaHCO_3$ and water, and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo and 50 mg of reaction mixture was obtained. Preparative GLC separation (OV-17 10%, Chromosorb A 45/60, T = 135 °C) gave 14.4 mg (26.5%) of colorless oily product: exact mass calcd for $C_9H_4F_4O_2$ 220.0147, found 220.0149, mass spectrum, m/e 220 (M^+, 67), 154 (12.5), 126 (14.5), 120 (100), 95 (13), 92 (72), 66 (16.5), 64 (23), 63 (20), 50 (20).

Fluorination of Enol Acetates (10). One millimole of enol acetate **10** was dissolved in 2 mL of methylene chloride, 1 mmol of xenon difluoride was added, and under stirring a catalytic amount of hydrogen fluoride (5–8 mg) was introduced. The reaction mixture was stirred at room temperature under a dry nitrogen atmosphere, and after 6 h, 10 mL of methylene chloride was added. The reaction mixture was washed with $NaHCO_3$ and water and dried over anhydrous sodium sulfate and the solvent was evaporated in vacuo. The crude reaction mixture was analyzed by ^{19}F NMR and GLC, and pure α-fluorocycloalkanones were isolated by preparative GLC.

2-Fluorocyclohexanone[9] (11, n = 1). A 100-mg sample of crude reaction mixture, containing 93% of α-fluorocyclohexanone, 5% of starting material, and 2% of cyclohexanone (determined by GLC), was separated by preparative GLC (Carbowax 20 M 10%, Varaport 30 80/100, T = 115 °C) and 66.8 mg (57.6%) of liquid product, bp 187 °C dec, was isolated: exact mass calcd for C_6H_9FO 116.0637, found 116.0640; mass spectrum, m/e 116 (M^+, 27), 72 (12), 68 (17), 59 (17), 55 (100), 42 (59), 41 (23).

2-Fluorocycloheptanone[9] (11, n = 2). A 120-mg sample of crude reaction mixture, containing 86% of α-fluorocycloheptanone and 14% of cycloheptanone (determined by GLC), was separated by preparative GLC (Carbowax 20M 10%, Varaport 30 80/100, T = 118 °C) and 80 mg (61.5%) of liquid product, bp 178 °C dec, was isolated: exact mass calcd for $C_7H_{11}FO$ 130.0793, found 130.0790; mass spectrum, m/e 130 (M^+, 14), 84 (42), 69 (13), 68 (36), 59 (16), 56 (32), 55 (100), 42 (32), 41 (54).

2-Fluorocyclooctanone[9] (11, n = 3). A 130-mg sample of crude reaction mixture, containing 80% of α-fluorocyclooctane and 20% of cyclooctanone (determined by GLC), was separated by preparative GLC (SE-30 10%, Chromosorb A 45/60, T = 115 °C) and 53.4 mg (37%) of oily product, decomposing on heating, was isolated: exact mass calcd for $C_8H_{13}FO$ 144.0950, found 144.0949; mass spectrum, m/e 144 (M^+, 10), 101 (11), 100 (77), 98 (91), 83 (11), 70 (16), 69 (13), 67 (10), 59 (17), 56 (16), 55 (100), 42 (74), 41 (49).

***trans*-2-Fluoro-4-*tert*-butylcyclohexanone[18] (13).** A 75-mg sample (22%) of colorless oily product, decomposing on heating, was isolated by preparative GLC (Carbowax 20M 10%, Varaport 30 70/80, T = 130 °C): exact mass calcd for $C_{10}H_{17}FO$ 172.1263, found 172.1264; mass spectrum, m/e 172 (M^+, 8), 116 (21), 96 (23), 95 (10), 83 (10), 57 (100), 55 (23), 41 (60).

***cis*-2-Fluoro-4-*tert*-butylcyclohexanone[18] (14).** A 50-mg sample (15%) of colorless liquid product, decomposing on heating, was isolated by preparative GLC (Carbowax 20M 10%, Varaport 30 70/80, T = 130 °C): exact mass calcd for $C_{10}H_{17}FO$ 172.1263, found 172.1261; mass spectrum, m/e 172 (M^+, 7), 116 (19), 96 (33), 95 (14), 67 (10), 57 (100), 55 (20), 41 (48).

Registry No. 1, 123-54-6; 2, 759-02-4; 3, 1547-51-9; 4, 126-81-8; 5, 76185-12-1; 6, 606-23-5; 7, 79952-90-2; 8, 76185-13-2; 9, 79952-91-3; 10 (n = 1), 1424-22-2; 10 (n = 2), 14477-74-8; 10 (n = 3), 14478-13-8; 11 (n = 1), 694-82-6; 11 (n = 2), 1755-11-9; 11 (n = 3), 1755-14-2; 12, 7360-39-6; 13, 35394-07-1; 14, 35394-08-2; xenon difluoride, 13709-36-9; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8.

Supplementary Material Available: Full NMR data for compounds 2–4, 7–9, 11 (n = 1, 2, 3), 13, and 14 (2 pages). Ordering information is given on any current masthead page.

(16) Weissberger, A., Ed.; "Techniques of Organic Chemistry"; Interscience: New York, 1955; Vol. VII.
(17) Williamson, S. M. *Inorg. Synth.* **1968**, *11*, 147.
(18) Allinger, N. L.; Blatter, H. M. *J. Org. Chem.* **1962**, *27*, 1523.