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SYNTHESES AND ^{13}C NMR SPECTRA OF FLUORINATED ADAMANTANE DERIVATIVES

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SUMMARY

The syntheses of a variety of fluorine-containing adamantane derivatives are described. The ^{13}C NMR spectra of those compounds with different configurations are interpreted in terms of through-bond and through-space substituent interactions.

INTRODUCTION

In the course of our ^{13}C NMR spectroscopic investigations of aliphatic cage compounds [1] we synthesized a number of fluorinated adamantane derivatives. It was known in the literature that treatment of brominated precursors with silver fluoride provided a suitable procedure by which the two epimeric 4-fluoroadamantanones 2 and 3 had been prepared [2]. Similarly, 2-fluoroadamantane (1) had been obtained [3]. Therefore, we decided to use this method for the synthesis of a number of 2,4-disubstituted adamantanes with at least one fluorine atom.

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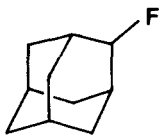
RESULTS AND DISCUSSION



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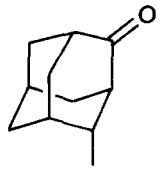

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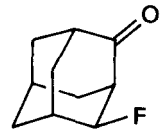

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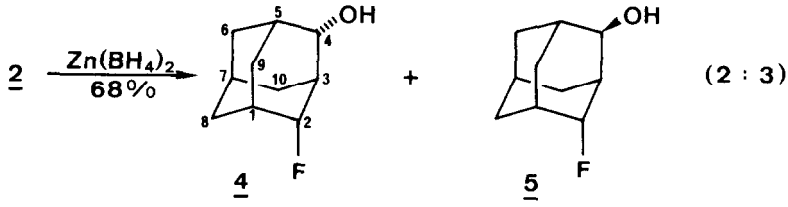
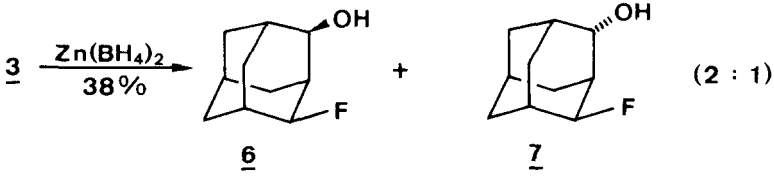
The key compounds in this study were the fluoroadamantanones 2 (equatorial fluorine with respect to the fluorocyclohexanone substructure) and 3 (axial F) [2]. Reductions with zinc borohydride [4,5] afforded the corresponding alcohols 4 - 7; the

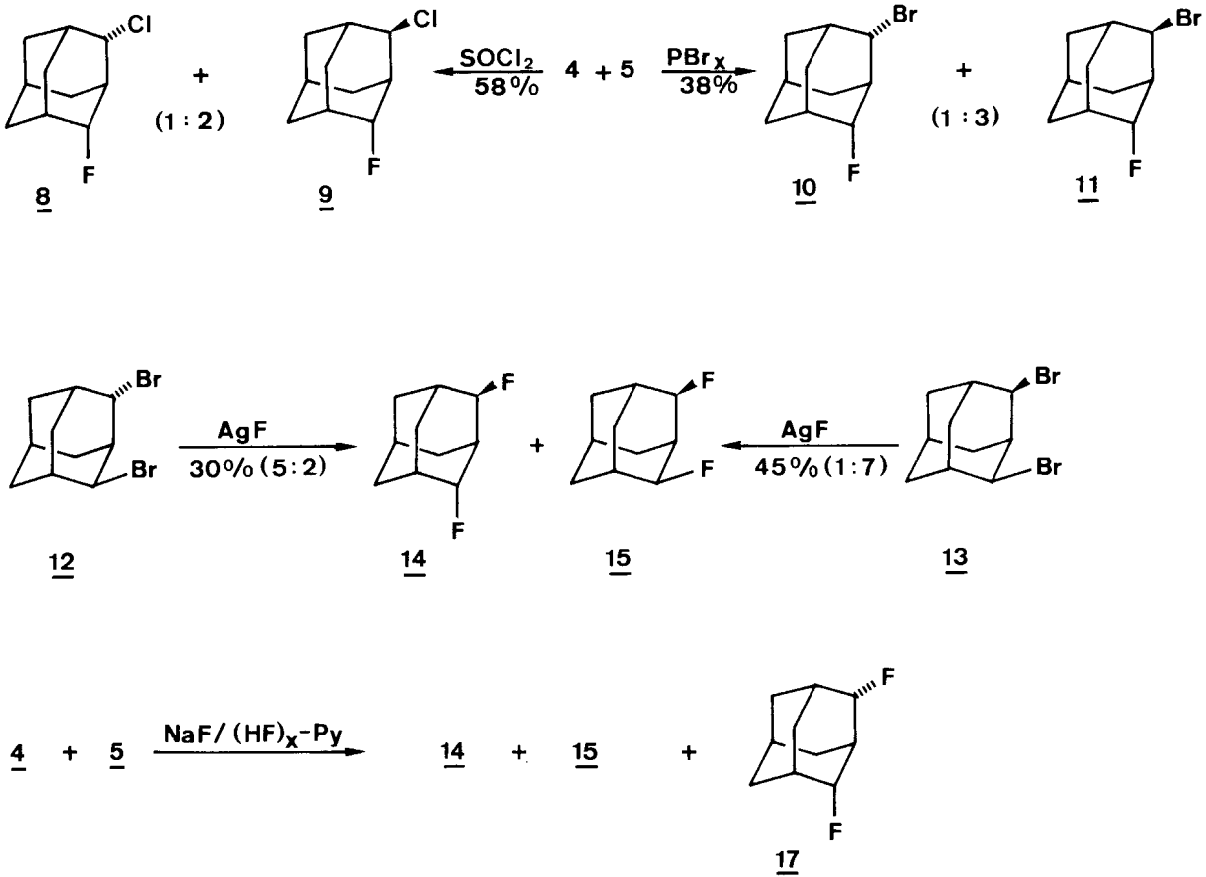


4 5



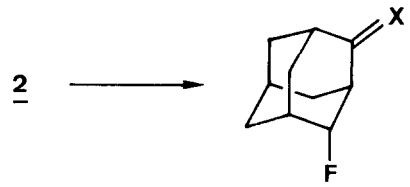
6 7

mixture of 4 and 5 could not be separated into the components chromatographically. When subjected to thionyl chloride it gave the two epimeric 4-chloro-2^{eq}-fluoroadamantanes 8 and 9; treatment with phosphorus bromides (PBr_3/PBr_5) led to the corresponding bromo derivatives 10 and 11.

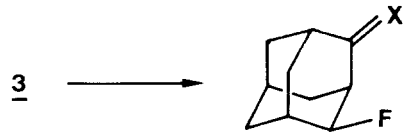

Cl
F
8
+
(1 : 2)
Cl
F
9
SOCl2
58%
4 + 5
PBrx
38%
Br
F
10
+
(1 : 3)
Br
F
11
Br
Br
12
AgF
30% (5:2)
F
F
14
+
F
F
15
AgF
45% (1:7)
Br
Br
13
4 + 5
NaF/ (HF)x-Py
14 + 15 +
F
F
17

Scheme

The difluoroadamantanes were prepared by different procedures: The two epimeric 2,4-dibromoadamantanes 12 and 13 [5,6] were reacted with silver fluoride to give different mixtures of the two difluoro derivatives 14 and 15. In a side reaction traces of fluoroadamantanols were obtained. Interestingly, the products of the same reaction with the diequatorial dibromide 16 [5] afforded only 1 and (4 + 5) but no difluorides. The remaining diequatorial difluoride 17 was obtained along with 14 and 15 by treating the mixture of 4 and 5 with sodium fluoride in hydrofluoric acid - pyridine complex solution [7].

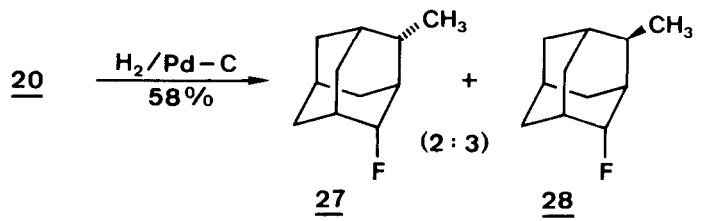


X = S: 18
X = CH_2: 20
X = $C(CN)_2$: 22
X = E − $NOCH_3$: 24
X = Z − $NOCH_3$: 25

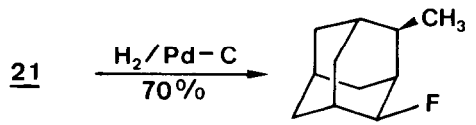


X = S: 19
X = CH_2: 21
X = $C(CN)_2$: 23
X = E − $NOCH_3$: 26

The carbonyl groups in 2 and 3 were converted to the corresponding thiones (18 and 19, respectively), ethenes (20 and 21, respectively) and dicyanoethenes (22 and 23, respectively) by conventional methods [8 - 10]. Reaction of 2 with O-methylhydroxylamine [11] gave a mixture of the two E- and Z-oximes 24 and 25 whereas 3 afforded only the E-oxime 26.



27 28



29

The three 4-methyl-2-fluoroadamantanes 27 - 29 were prepared by hydrogenation of the exomethylene derivatives 20 and 21 over palladium charcoal catalyst.

The ^{13}C NMR data of some of the synthesized fluoroadamantanes have been published by us previously [12,13]. Thus, Table 1 contains only those of the remaining ones.

We have shown that intramolecular through-bond substituent interaction is reflected in non-additivities of individual substituent effects on ^{13}C chemical shifts (SCS)[1]. In the case of 4^{eq}-substituted adamantanones [1] and $2^{eq},4^{eq}$-disubstituted adamantanes [5] we assumed an $n\sigma^*$ orbital interaction. Recently, we found that the direct carbon-fluorine coupling constant $^1J(^{13}C,^{19}F)$ in the compounds 1, 2, 4, 8, 10, 17, 18, 20, 22 and 27 correlate excellently ($r = 0.983$) with the deviation Δ ($= \delta_{exp} - \delta_{calc}$) between the experimental ^{13}C chemical shifts (δ_{exp}) of the fluorine-bearing carbon atoms and their δ_{calc} values, calculated assuming additivity of their SCS [12]; those Δ-values were taken as a measure for the interaction of fluorine with the other substituent [12](Fig. 1). As expected, the corresponding data points of the oximes 24 and 25 fit that correlation nicely.

This interpretation of the ^1J variation [12] was recently questioned by Adcock and Abeywickrema [14] who concluded from their work that $^1J(^{13}C,^{19}F)$ cannot be used as a probe for through-bond effects. In their series of compounds [14] they had found a linear correlation of ^{19}F chemical shifts and $^1J(^{13}C,^{19}F)$ values, the ranges being 1.3 ppm and 1.4 Hz, respectively.

TABLE 1

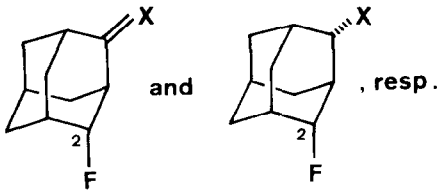
^{13}C chemical shifts (in ppm) and carbon-fluorine coupling constants (in Hz) of various adamantane derivatives[a]

	6	15	24	25	26	29
C-1	31.7	32.4	32.2	-[b]	32.8	33.0
C-2	98.6	94.9	93.6	92.2	95.7	97.3
C-3	35.4	37.1	41.1	34.3	41.3	38.3
C-4	75.3	94.9	162.1	-[b]	162.3	39.0
C-5	34.6	32.4	28.2	34.1	29.0	33.2
C-6	36.3	35.4	36.9	38.4	37.1	39.1
C-7	25.7	25.7	26.9	26.9	26.6	26.8
C-8	38.4	35.4	30.4	30.4	35.6	36.5
C-9	25.2	25.5	32.7	32.4	31.5	25.9
C-10	35.4	33.9	32.9	31.7	-[b]	37.2
CH_3	-	-	61.2	61.1	61.2	19.8
^1J	174.3	185.6	185.3	185.6	183.1	179.8
^2J : C-1	17.7	-[b]	18.3	-[b]	17.2	17.9
C-3	19.6	16.2	21.7	24.1	19.1	15.4
^3J : C-4	< 1	< 1	-[b]	-[b]	< 1	< 1
C-9	< 1	< 1	9.8	19.1	< 1	< 1
C-8	13.4	4.7	< 1	< 1	12[c]	9.7
C-10	8.5	8.6	< 1	< 1	-[b]	10.6

[a] In $CDCl_3$ solution; ^{13}C chemical shifts are referred to internal TMS; coupling constants are accurate to ± 0.2 - 0.3 Hz.

[b] Could not be identified safely.

[c] Inaccurate value due to signal overlap.



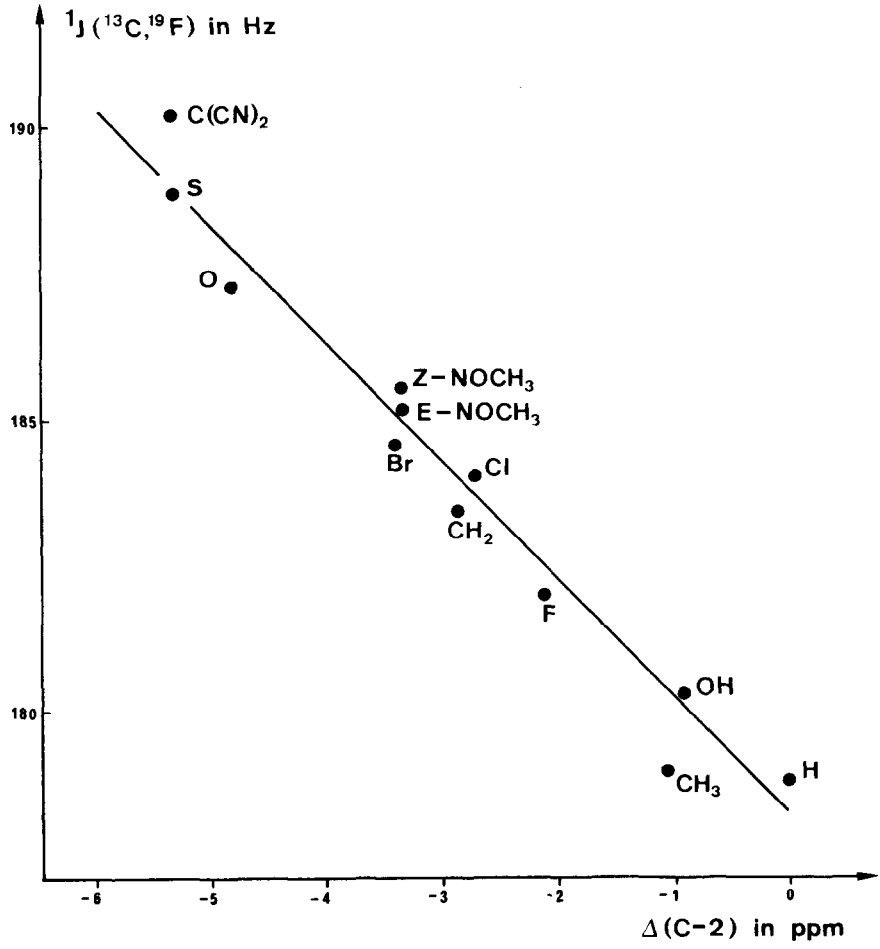


Fig. 1. Correlation of one-bond carbon-fluorine coupling constants $^1J(^{13}C,^{19}F)$ with non-additivity effects (Δ, for explanation see text) of fluorinated adamantane derivatives, cf. ref. [12].

In our case the coupling constants vary for about 12 Hz; this may be explained by the closer proximity of the interfering groups. The range of ^{19}F chemical shifts, however, is very small; we measured a difference of only 0.3 ppm between 1 and 22 which represent the extrema in $^{1}J(^{13}C,^{19}F)$. Thus, we conclude that the interaction mechanisms acting in Adcock's [14] and our compounds cannot be the same.

The ^{13}C NMR data of the diaxial adamantanes 6, 15 and 29 meet our expectations [5] in that we found positive non-additivity effects Δ (+9.6 and +6.9 for 6; +5.6 and +5.6 for 15 and +8.1 and +6.2 for 29) for the signals of the substituted atoms C-2 and C-4, respectively. These Δ-values indicate that the non-additivity effects in such diaxial configurations originate not only in the removal of the 1,3-diaxial hydrogen atom, i.e. a missing γ-gauche interaction effects [5,15], but there seems to be a considerable contribution from electronic through-space interaction between the substituent themselves. The slight deviations Δ for the signals of C-10 in 6 and 15 (6: -1.0; 15: +1.7; 29: -0.4) confirm this latter interpretation since these atoms are in antiperiplanar position to both substituents, and it is well-known that γ-anti SCS react very sensitively to changes in the electronic environment of the perturbing substituent [16].

EXPERIMENTAL

Melting points were determined by using a Büchi-Tottoli melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer, ^{1}H NMR spectra were obtained on Varian T-60 and Bruker WP-80 and ^{13}C NMR spectra on Bruker WH-90 and WM-250 spectrometers. For the NMR spectra the solvent was deuterated chloroform, and the chemical shifts are referenced to internal tetramethylsilane. Mass spectra were recorded on Varian CH-5 and 731 spectrometers. All compounds or mixtures of epimers were purified by column chromatography with silica gel and various ligroin/acetone mixtures as eluants and were >98% pure. Reported yields refer to isolated samples after purification. They are not optimized and are sometimes low due to the high volatility of many of the compounds.

2-Fluoroadamantane (1)

2-Bromoadamantane [17] (1.3 g) was dissolved in 20 ml chlorobenzene and treated with silver fluoride (5.3 g). The mixture was stirred vigorously at 120°C for 2.5 hrs. The whole reaction should be conducted in the dark. After cooling, the reaction mixture was diluted with chloroform, filtered and evaporated. Chromatographic purification afforded 0.45 g (48% yield) of 1 as a white solid. Physical and spectroscopic data correspond to literature values [3,7].

Mixture of epimeric 2^{eq}-fluoroadamantan-4-ols 4 and 5

A 300 mg sample of 2 was reduced by zinc borohydride as described in refs. [4] and [5]. Work-up afforded 205 mg (68% yield) of a 2 : 3 mixture of 4 and 5 which could not be separated chromatographically; ir ($CHCl_3$) 3610, 3465 - 3450 (OH), 1040; ^1H NMR δ 4.53 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 4.51 (1H, d, $J(^1H,^{19}F)$ = 52.0 Hz), 3.77 (1H, m), 3.72 (1H, m), 2.33 (2H, s, OH), 2.22 - 1.4 (24H, m); m/e (relative intensity) 170 (3, M^+), 152 (100), 132 (5), 110 (25), 79 (39). Analysis: Found: C, 70.15; H, 8.80%. $C_{10}H_{15}FO$ requires C, 70.55; H, 8.88%.

2^{ax}-Fluoroadamantan-4^{ax}-ol (6) and -4^{eq}-ol (7)

A 375 mg sample of 3 was reduced by zinc borohydride [4,5]. Work-up and chromatographic separation gave 100 mg (26%) 6 and 44 mg (12%) 7.

1 Fraction (6)

M.p. 119 - 120°C; ir ($CHCl_3$) 3600, 3400 (OH), 1060; ^1H NMR δ 4.83 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 3.83 (1H, m), 2.83 (1H, s, OH), 2.43 - 1.43 (12H, m); m/e (relative intensity) 170 (5, M^+), 152 (7), 150 (100), 91 (41), 80 (59), 79 (88). Analysis: Found: C, 71.00; H, 8.80%. $C_{10}H_{15}FO$ requires C, 70.55; H, 8.88%.

2 Fraction (7)

M.p. 156 - 158°C; ir ($CHCl_3$) 3650, 3450 (OH), 1020; ^1H NMR δ 4.77 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 4.15 (1H, m), 1.93 (1H, s, OH), 2.23 - 1.57 (12H, m); m/e (relative intensity) 170 (11, M^+), 152 (72), 150 (42), 80 (47), 79 (100). Analysis: Found: C, 70.50; H, 8.80%. $C_{10}H_{15}FO$ requires C, 70.55; H. 8.88%.

2^{eq}-Fluoro-4^{eq}-chloroadamantane (8) and -4^{ax}-chloroadamantane (9)

A 300 mg mixture of 4 and 5 was dissolved in 30 ml benzene and refluxed with 3 ml thionyl chloride overnight. Usual work-up and chromatographic separation yielded 64 mg 8 (19%) and 128 mg 9 (39%) as colorless oils.

1 Fraction (9)

Ir ($CHCl_3$) 1005; ^1H NMR δ 5.20 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 4.50 (1H, m), 2.47 - 1.48 (12H, m); m/e (relative intensity) 190/188 (36/12, M^+), 152 (100), 133 (6), 110 (26), 79 (26).

2 Fraction (8)

Ir ($CHCl_3$) 1000; ^1H NMR δ 4.73 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 4.22 (1H, m), 2.45 - 1.73 (12H, m); m/e (relative intensity) 190/188 (18/6, M^+), 152 (100), 132 (8), 91 (39), 79 (39).

2^{eq}-Fluoro-4^{eq}-bromoadamantane (10) and -4^{ax}-bromoadamantane (11)

A 300 mg mixture of 4 and 5 was dissolved in 15 ml ice-cooled phosphorus tribromide and 1.5 g phosphorus pentabromide was added under vigorous stirring at 0°C. The reaction mixture was stirred for further 6 hrs. at the same temperature under moisture exclusion. Then it was poured onto ice-water and extracted with ether several times. The combined organic layers were washed with sodium bicarbonate and water, dried over magnesium sulfate, filtered and evaporated. Chromatographic separation of the crude product afforded 44 mg (11%) 10 and 110 mg (27%) 11.

1 Fraction (11)

M.p. 109 - 110°C; ir 1010; ^{1}H NMR δ 5.03 (1H, d, J(^{1}H,^{19}F) = 50.0 Hz), 4.57 (1H, m), 2.38 - 1.65 (12H, m); m/e (relative intensity) 234/232 (1/1, M^+), 153 (100), 133 (49), 91 (60), 79 (31). Analysis: Found: C, 52.5; H, 5.85%. $C_{10}H_{14}BrF$ requires C, 51.50; H, 6.05%.

2 Fraction (10)

M.p. 145 - 147°C; ir ($CHCl_3$) 1005; ^{1}H NMR δ 5.13 (1H, d, J(^{1}H,^{19}F) = 51.0 Hz), 4.37 (1H, m), 2.47 - 1.50 (12H, m); m/e (relative intensity) 234/232 (1/1, M^+), 153 (100), 133 (37), 91 (51), 79 (28). Analysis: Found C, 52.50; H, 6.20%. $C_{10}H_{14}BrF$ requires C, 51.50; H, 6.05%.

$2^{eq},4^{ax}$- (14) and $2^{ax},4^{ax}$-Difluoroadamantane (15)

A 240 mg sample of the dibromide 12 [5] was reacted with silver fluoride as described above. After work-up and separation 30 mg (21%) 14 and 12 mg (9%) 15 were obtained. With 300 mg of the dibromide 13 [6] the same procedure gave 10 mg (6%) 14 and 69 mg (39%) 15.

1 Fraction (14)

M.p. 136 - 138°C; ir ($CHCl_3$) 970; ^{1}H NMR δ 4.88 (1H, d, J(^{1}H,^{19}F) = 49.0 Hz), 4.53 (1H, d, J(^{1}H,^{19}F) = 50.0 Hz), 2.50 - 1.41 (12H, m); m/e (relative intensity) 172 (78, M^+), 152 (100), 93 (32), 79 (70). Analysis: Found: C, 70.3; H, 9.3%. $C_{10}H_{14}F_2$ requires C, 69.74; H, 8.19%.

2 Fraction (15)

M.p. 125 - 126°C; ir ($CHCl_3$) 1015; ^{1}H NMR δ 4.69 (2H, d, J(^{1}H,^{19}F) = 50.0 Hz), 2.52 - 1.56 (12H, m); m/e (relative intensity) 172 (73, M^+), 152 (100), 91 (34), 79 (77). Analysis: Found: C, 69.70; H, 8.30%. $C_{10}H_{14}F_2$ requires C, 69.74; H, 8.19%.

$2^{eq},4^{eq}$-Difluoroadamantane (17)

A 302 mg mixture of 4 and 5 was treated with 350 mg sodium fluoride and 15 ml 70% hydrogen fluoride - pyridine solution as described by Olah et al. [7]. Chromatographic separation of the crude product yielded 80 mg (26%) 14 and a 96 mg mixture of 15 and 17 in a ratio of approximately 1 : 1 (according to the ^{13}C NMR signal intensities). Since 17 could not be isolated pure, the identification was performed only from the evaluation of the ^{13}C NMR spectrum.

2^{eq}-Fluoroadamantane-4-thione (18)

A 300 mg sample of 2 was treated with phosphorus pentasulfide as described by Greidanus [8] and 220 mg (67%) of 18 was obtained as red-orange oil crystallizing by cooling. Ir ($CHCl_3$) 1135 (C=S), 990; ^1H NMR δ 4.60 (1H, d, $J(^1H,^{19}F)$ = 51.0 Hz), 3.70 (1H, m), 3.40 (1H, m), 2.55 - 1.27 (10H, m); m/e (relative intensity) 184 (52, M^+), 151 (10), 131 (6), 85 (64), 83 (100). Analysis: Found: C, 63.1; H, 7.40%. $C_{10}H_{13}FS$ requires C, 65.18; H, 7.11%.

2^{ax}-Fluoroadamantane-4-thione (19)

A 200 mg sample of 3 was treated with phosphorus pentasulfide as described by Greidanus [8]. However, reaction temperature and time were raised to 100°C and 45 hrs., respectively, to achieve optimal yield. Usual work-up afforded 155 mg (51%) 19 as red-orange oil crystallizing by cooling. Ir ($CHCl_3$) 1140 (C=S), 1000; ^1H NMR δ 4.90 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 3.72 (1H, m), 3.42 (1H, m), 2.50 - 1.85 (10H, m); m/e (relative intensity) 184 (22, M^+), 151 (4), 131 (3), 85 (65), 83 (100). Analysis: Found: C, 65.00; H, 7.40%. $C_{10}H_{13}FS$ requires C, 65.18; H, 7.11%.

2^{eq}-Fluoro-4-exomethylene-adamantane (20)

A 300 mg sample of 2 in 20 ml tetrahydrofuran (THF) was added dropwise under argon to a THF-solution of an ylide prepared from $(C_6H_5)_3PCH_3I$ and n-butyllithium. The mixture was stirred for 2 hrs. at room temperature, poured onto ice-water and extracted with methylene chloride several times. Work-up gave 122 mg (41%) of 20 as a highly volatile solid. Ir ($CHCl_3$) 1660 (C=C), 980; ^{1}H NMR δ 4.60 (2H, s, $=CH_2$), 4.44 (1H, d, $J(^1H,^{19}F)$ = 51.0 Hz), 2.66 (1H, m), 2.33 - 1.27 (11H, m); m/e relative intensity) 166 (100, M^+), 151 (10), 146 (8), 91 (57), 79 (32).

2^{ax}-Fluoro-4-exomethylene-adamantane (21)

As described for the preparation of 20 a 470 mg sample of 3 was reacted with the same ylide yielding 146 mg (31%) of 21 after work-up. Ir ($CHCl_3$) 1670 (C=C), 1095; ^{1}H NMR δ 4.66 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 4.59 (2H, d, $J(^1H,^1H)$ = 7.0 Hz, $=CH_2$), 2.73 - 1.38 (12H, m); m/e (relative intensity) 166 (100, M^+), 151 (7), 146 (4), 91 (42), 79 (35).

2^{eq}-Fluoro-4-dicyanomethylene-adamantane (22)

A 210 mg sample of 2 was treated with malodinitrile as described in the literature [10]. After purification 253 mg (94%) of 22 were obtained as white crystals. M.p. 116 - 117.5°C; ir ($CHCl_3$) 2225 (C≡N), 1595 (C=C), 1030, 1010; ^{1}H NMR δ 4.56 (1H, d, $J(^1H^{19}F)$ = 48.0 Hz), 3.51 (1H, m), 3.25 - 2.21 (4H, m), 2.05 - 1.56 (7H, m); m/e (relative intensity) 216 (100, M^+), 196 (50), 169 (13), 154 (36), 142 (67). Analysis: Found: C, 72.45; H, 6.10; N, 13.10%. $C_{13}H_{13}FN_2$ requires C, 72.20; 6.06; N, 12.95%.

2^{ax}-Fluoro-4-dicyanomethylene-adamantane (23)

As described for 22 a 215 mg sample of 3 was reacted to form 194 mg (71%) 23 as white crystals. M.p. 192 - 193°C; ir ($CHCl_3$) 2220 (C≡N), 1575 (C=C), 1020, 1000; ^{1}H NMR δ 4.85

(1H, d, $J(^1H,^{19}F)$ = 49.0 Hz), 3.53 (1H, m), 3.22 - 2.27 (3H, m), 2.03 - 1.57 (8H, m); m/e (relative intensity) 216 (4, M^+), 196 (4), 174 (25), 148 (37), 79 (100), 78 (69). Analysis: Found: C, 71.90; H, 6.25; N, 13.20%. $C_{13}H_{13}FN_2$ requires C, 72.20; H, 6.06; N, 12.95%.

2^{eq}-Fluoro-4-E-methoximino-adamantane (24) and its Z-isomer (25)

A 300 mg sample of 2 was suspended in 20 ml water with an excess of methoxylamine hydrochloride [11] and sodium acetate. The stirred mixture was heated to 60°C for 4 hrs., and after cooling extracted with methylene chloride. Usual work-up and chromatographic separation gave 98 mg (28%) of 24, 108 mg of a mixture of 24 and 25 and 55 mg (16%) of 25 contaminated with a trace of 24.

1 Fraction (24)

M.p. 72 - 73°C; ir ($CHCl_3$) 2825 (OCH_3), 1640 (C=N), 1030, 990; ^1H NMR δ 4.55 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz, 3.78 (3H, s, OCH_3), 3.43 (1H, m), 2.80 (1H, m), 2.45 - 1.35 (10H, m); m/e (relative intensity) 197 (70, M^+), 166 (28), 146 (32), 91 (41), 81 (48), 79 (100). Analysis: Found: C, 66.90; H, 8.20; N, 7.25%. $C_{11}H_{16}FNO$ requires C, 66.98; H, 8.18; N, 7.10%.

3 Fraction (25)

M.p. 52 - 53°C; ir ($CHCl_3$) 2825 (OCH_3), 1640 (C=N), 1030, 995; ^1H NMR δ 5.15 (1H, d, $J(^1H,^{19}F)$ = 49.0 Hz), 3.80 (3H, s, OCH_3), 3.40 (1H, m), 2.80 (1H, m), 2.32 - 1.32 (10H, m); m/e (relative intensity) 197 (92, M^+), 166 (32), 146 (45), 91 (41), 79 (100). Analysis: Found: C, 67.10; H, 8.30; N, 8.10%. $C_{11}H_{16}FNO$ requires C, 66.98; H, 8.18; N, 7.10%.

2^{ax}-Fluoro-4-E-methoximino-adamantane (26)

By the reaction described above a 300 mg sample of 3 gave 297 mg (84%) of 26. M.p. 103 - 104°C; ir ($CHCl_3$) 2800 (OCH_3), 1635 (C=N), 1020, 975; ^1H NMR δ 4.78 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 3.80 (3H, s, OCH_3), 3.43 (1H, m), 2.80 (1H, m), 2.54 - 1.63

(10H, m); m/e (relative intensity) 197 (100, M^+), 166 (55), 146 (41), 119 (35), 104 (41), 98 (46), 79 (88). Analysis: Found: C, 67.40; H, 8.20; N, 8.15%. $C_{11}H_{16}FNO$ requires C, 66.98; H, 8.18; N, 7.10%.

2^{eq}-Fluoro-4^{eq}-methyl- (27) and -4^{ax}-methyladamantane (28)

A 270 mg sample of 20 was dissolved in 50 ml abs. THF, and after addition of a small amount of palladium-charcoal and two drops of perchloric acid the mixture was hydrogenated at atmospheric pressure and ambient temperature overnight. Work-up gave a 2 : 3 mixture of 27 and 28 as a white, highly volatile solid which could not be separated chromatographically into the components. The yield was 154 mg (56%). Ir ($CHCl_3$) 1090, 980; ^1H NMR δ 4.83 (1H, d, $J(^1H,^{19}F)$ = 50.0 Hz), 4.66 (1H, d, $J(^1H, ^{19}F)$ = 51.0 Hz), 2.97 (2H, m), 2.66 - 1.40 (24H, m), 1.08 and 1.05 (6H, 2d, CH_3); m/e (relative intensity) 168 (100, M^+), 153 (56), 133 (37), 91 (50), 79 (56).

2^{ax}-Fluoro-4^{ax}-methyladamantane (29)

A 146 mg sample of 21 was hydrogenated as described above yielding 104 mg (70%) of 29 as a white, highly volatile solid. Ir ($CHCl_3$) 1080, 970; ^1H NMR δ 4.61 (1H, d, $J(^1H,^{19}F)$ = 51.0 Hz), 2.71 - 1.36 (13H, m), 1.10 (3H, d, CH_3); m/e (relative intensity) 168 (39, M^+), 153 (54), 133 (37), 91 (50), 79 (56).

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