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# A NOVEL AND VERSATILE ACCESS TO FLUORINATED CARBO- AND HETEROCYCLIC COMPOUNDS EMPLOYING ELECTRON-RICH FLUORODIENES AS CYCLOADDITION COMPONENTS

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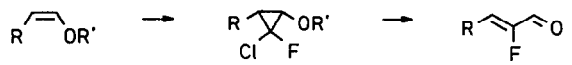
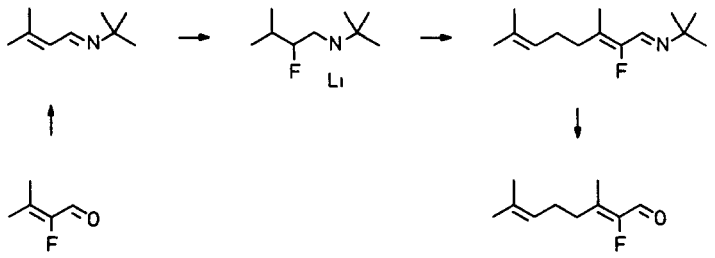
**Summary :** The readily accessible 2-fluoro-1-trimethylsilyloxy-1,3-dienes undergo Diels-Alder type cycloaddition with a variety of dienophiles under mild conditions. In this way, fluoro-2-cyclohexenols, fluoro-2,5-dihydropyranols, fluoro-2,5-dihydro-2-pyridinols, fluoropyridines, fluoro-3,6-dihydro-1,2-oxazines and fluoropyrroles can be efficiently prepared

Chlorofluorocarbene can be conveniently generated from dichlorofluoromethane ("Freon 21") and sodium hydroxide in liquid/liquid or liquid/solid phase systems [1]. It reacts particularly readily with enethers affording alkoxy substituted *gem*-chlorofluorocyclopropanes. When the latter compounds are treated with boiling water, solvolytic ring opening takes place producing α-fluorinated α, β-unsaturated aldehydes or ketones. [1]

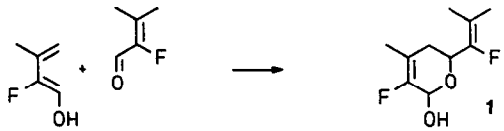


2-Fluoro-2-alkenals are versatile building blocks for the linear assembly of carbon moieties. Phosphorus ylids can be employed to transform them into 2-fluorodienes by means of the Wittig olefination procedure [2]. Schiff bases formed upon condensation with *tert*-butylamine can be deprotonated at the γ-position and subsequently alkylated thus giving rise, after acid hydrolysis and reduction, to chain elongated 2-fluoroalkyl alcohols such as fluoro-geraniol or fluorofarnesol [3].

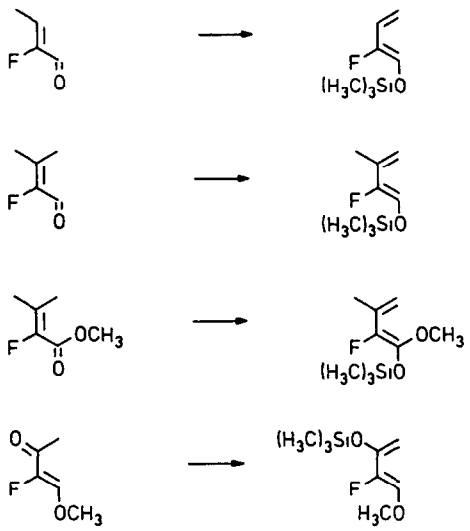


In addition, 2-fluoro-2-alkenals are excellent components for Diels-Alder type cycloaddition reactions as we recognized by chance Upon prolonged standing in a refrigerator, 2-fluoro-3-methyl-2-butenal ("fluoroprenal")

spontaneously dimerized affording 3-fluoro-6-(1-fluoro-2-methyl-1-propenyl)-2-hydroxy-4-methyl-5,6-dihydro-2*H*-pyran (1). [4] Apparently, the carbonyl precursor had produced small concentrations of the corresponding dienol form which was intercepted by cycloaddition with the aldehyde and, as consumed, restituted by the ongoing tautomeric equilibration.




All one had to do now in order to facilitate such [4+2] cycloaddition processes was to convert the 2-fluoro-2-alkenals into permanent dienol derivatives. This was easily accomplished by treating them with chlorotrimethylsilane in the presence of a base such as triethylamine. Similarly an α-fluorinated α,β-unsaturated ester and a related ketone were converted into the corresponding silyloxy bearing fluorodienes.

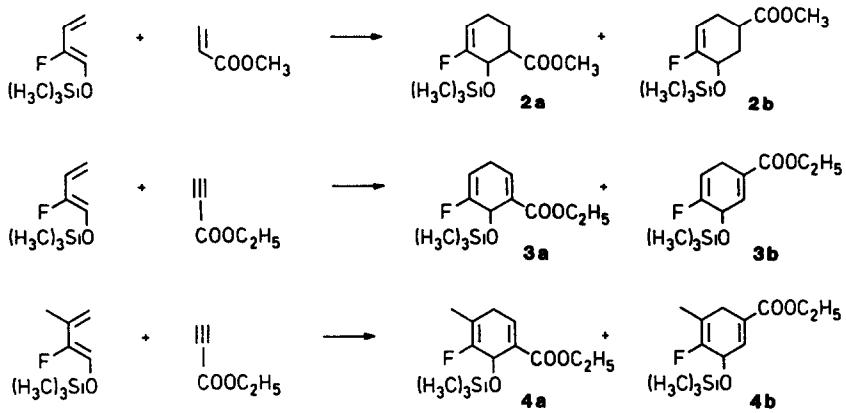



*α,β-Unsaturated esters, anhydrides and ketones as dienophiles*

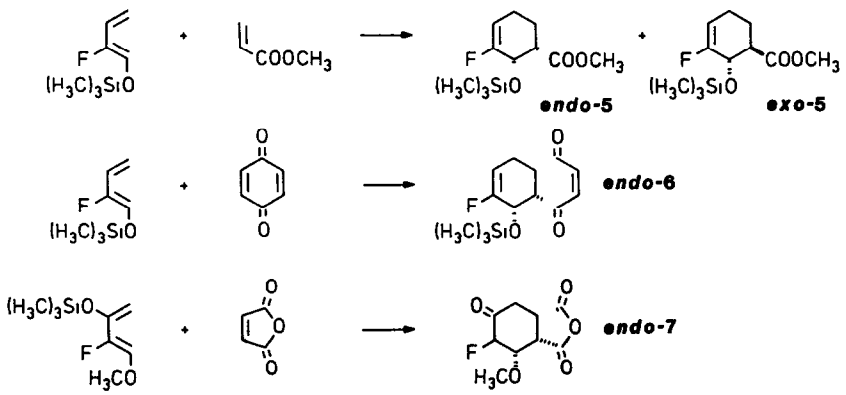
Diels-Alder reactions between 2-fluoro-1-trimethylsilyloxy-1,3-dienes and dimethyl acetylenedicarboxylate have already been reported to give dimethyl fluorophthalates via 3-trimethylsilyloxy-1,4-cyclohexadien-1,2-dicarboxylic acid esters [5]. Ethyl propiolate, methyl acrylate maleic anhydride and 1,4-benzo- as well as 1,4-naphthoquinones were now found to be suitable dienophiles too.

First we wanted to probe the *reactivity* of the fluorinated silyloxydienes in comparison with the halogen-free parent compounds. As competition experiments revealed, the fluorine substituent exerts a small rate retarding effect . $k_F/k_H$ ratios of 0 59 (2-fluoro-1-trimethylsilyloxy-1,3-butadiene plus methyl acrylate), 0.37 (2-fluoro-1-trimethylsilyloxy-1,3-butadiene plus dimethyl acetylenedicarboxylate) and 0.25 (2-fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene plus dimethyl acetylenedicarboxylate) were determined.

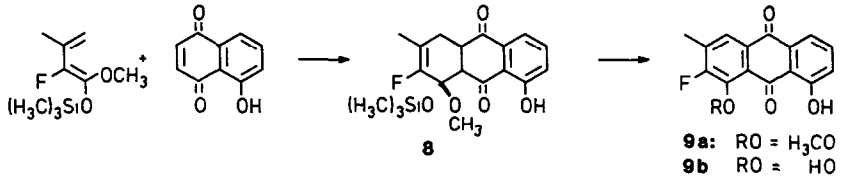
Next we studied the *regioselectivity* of such Diels-Alder reactions. The product having juxtaposed silyloxy and ester functions was exclusively formed in one case (**2a** : **2b** > 98 : 2) and was largely preponderant in two others (**3a** : **3b** = 75 : 25 and **4a** : **4b** = 90 : 10; all being isolated as the corresponding benzoic esters after Lewis acid catalyzed elimination of trimethylsilanol [5]). Remarkably enough, however, the halogen substituent was found to diminish the regioselectivity inherent in the parent diene. For example, while 2-fluoro-1-trimethylsilyloxy-1,3-diene produced the two regioisomers in a 75 : 25 ratio, 1-trimethylsilyloxy-1,3-butadiene itself gave only trace amounts (< 5%) of the minor isomer. This difference in regioselective behavior reflects the dual electronic character of the fluorine substituent. Its inductive electron withdrawing effect slightly impairs the ordinary mode of electron flow.




Finally, we focussed on the *stereoselectivity* of the fluorodiene cycloaddition reactions. With methyl acrylate as the dienophile, both 1-trimethylsilyloxy-1,3-butadiene and 2-fluoro-1-trimethylsilyloxy-1,3-butadiene gave the same 2 : 1 *endo/exo* ratio of cyclohexenecarboxylic esters **5** In contrast, the reactions between 2-fluoro-1-trimethylsilyloxy-1,3-butadiene and *p*-benzoquinone and between 2-fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene and maleic anhydride produced the *endo* isomers **6** and **7** exclusively Oxidative elimination occurs very readily with the cycloadduct **6**, converting it into 6-fluoro-1,4-naphthoquinone.

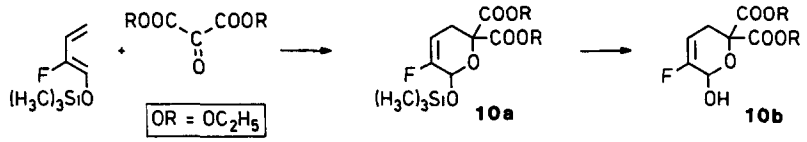


2-Fluoro-1-methoxy-3-methyl-1-trimethylsilyloxy-1,3-butadiene, a ketene acetal derivative obtained by deprotonation and *in situ* silylation of methyl 2-fluoro-3-methyl-2-butenoate, and 5-hydroxy-1,4-naphthoquinone underwent the Diels-Alder reaction with perfect *endo* stereoselectivity and, in addition, under remote function regiocontrol [6]. The dihydroanthraquinone **8** was isolated as the sole product. Upon addition of dilute acid, a mixture of methoxy and hydroxy compounds **9a** and **9b** was obtained. Treatment with acid led ultimately to pure 2-fluoro-1,8-dihydroxy-3-methylanthraquinone (**9b**), a fluorinated analogue of the natural product chrysophanol. [7]

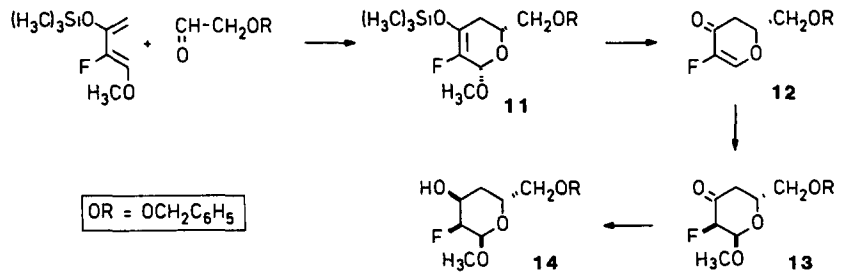



*Saturated Carbonyl Compounds as Dienophiles*

Ketones react with electron-rich dienes only if activated by electron withdrawing substituents. When 2-fluoro-1-trimethylsilyloxy-1,3-butadiene and diethyl 2-oxomalonate were heated 15 h to 150 °C, the cycloadduct **10a** formed which was directly hydrolyzed to the hemiacetal **10b** (in equilibrium with the open-chain tautomeric aldehyde).



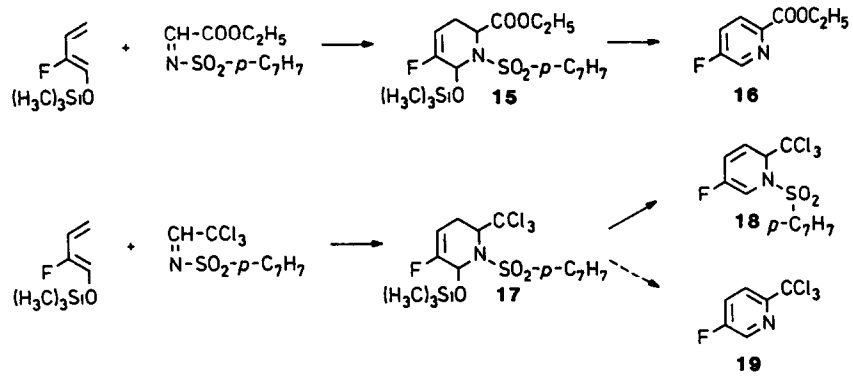

The transient dihydropyran **11** resulting from the cycloaddition between 2-fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene, a fluorine bearing "Danishefsky's diene" [8], and benzyloxyacetaldehyde was transformed into the dihydropyranone **12** upon acid hydrolysis. Acid catalyzed readdition of methanol led to the acetal **13** which finally was stereoselectively reduced to the bisdeoxy glycoside **14**.



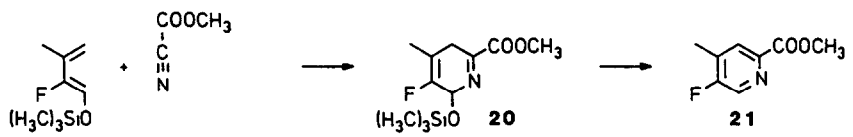

*Imines and Nitriles as Dienophiles*

Again activation of the dienophile by electron-poor substituents is required in order to bring about the cycloaddition between dienes and imines or nitriles. *N*-(Ethoxycarbonylmethylene)-*p*-toluenesulfonamide reacted

smoothly with 2-fluoro-1-trimethylsilyloxy-1,3-butadiene to yield a cycloadduct **15** which upon consecutive treatment with *p*-toluenesulfonic acid and triethylamine lost trimethylsilanol and *p*-toluenesulfinate to give ethyl 5-fluoropyridine-2-carboxylate (**16**). With *N*-(2,2,2-trichloroethylidene)-*p*-toluenesulfonamide a similar heterocycle **17** was obtained which under acidic condition was convertd into 5-fluoro-1-*p*-toluenesulfonyl-2-trichloromethyl-1,2-dihydropyridine (**18**). Despite several attempts to submit it to a base promoted elimination of *p*-toluenesulfinic acid, only trace amounts of 5-fluoropyridine-2-carboxylic acid (**19**) besides a large quantity of dehydrohalogenated by-products were formed.

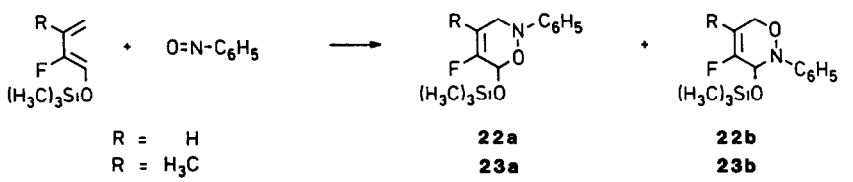


Trichloroacetonitrile did not react with 1-fluoro-3-methyl-1,3-butadiene. Methyl cyanoformate, however, formed readily the expected cycloadduct **20**. The latter intermediate spontaneously aromatized to afford the methyl 5-fluoro-4-methylpyridine-2-carboxylate (**21**).



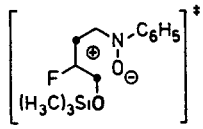
*Nitroso Compounds as Dienophiles*

Nitrosobenzene reacted smoothly with 2-fluoro-1-trimethylsilyloxy-1,3-butadiene to produce a 1 : 3 mixture of 4-fluoro-2-phenyl-3-trimethylsilyloxy-3,6-dihydro-1,2-oxazine (**22a**) and 5-fluoro-2-phenyl-6-trimethylsilyloxy-3,6-dihydro-1,2-oxazine (**22b**) With 2-fluoro-3-methyl-1-trimethylsilyloxy-1,3-butadiene a 3 : 1 mixture of the regioisomers **23a** and **23b** was obtained.

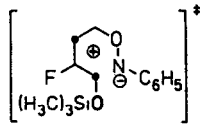


The lack of regioselectivity can be well understood in the framework of the perturbation theory of frontier molecular orbital interactions [9]. One arrives at the same conclusions if one tries to evaluate the relative free enthalpies of the two Diels-Alder transition states on the basis of their partially zwitterionic character (limiting

structures **24a** and **24b**). Due to the charge delocalization offered by the phenyl ring, the basicity of the nitrogen and the oxygen anions should not differ very much. Hence there is little discrimination against one or the other of the regioisomeric channels.

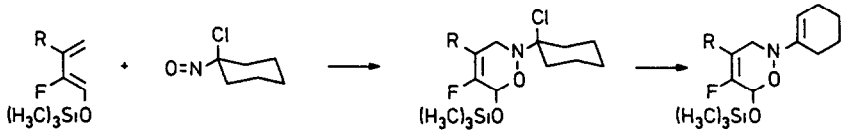


**24a**



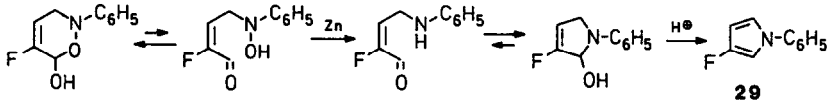
**24b**

An alkyl substituent will, of course, make the nitrogen center more basic. Therefore, 1-chloro-1-nitrosocyclohexane should give the intermediates **25** and **26** or, after spontaneous dehydrochlorination, the stable cycloadducts **27** and **28** as the sole regioisomers. This expectation was indeed confirmed by the experiment.

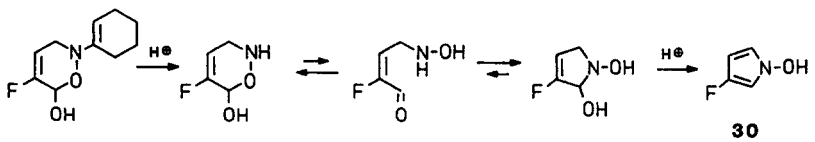


R = H **25** **27**
R = $H_3C$ **26** **28**

Upon acid hydrolysis the 6-trimethylsilyloxy substituted 3,6-dihydrooxazines generate cyclic hemiacetals and a rapid tautomeric equilibrium between the latter species and 4-hydroxyamino-2-butenals is established. In the presence of zinc, the nitrogen attached hydroxy group can be removed and the resulting amine can undergo acid catalyzed recyclization and dehydration. In this way, the 3-fluoro-1-phenylpyrrole (**29**) was formed by ring contraction of the dihydrooxazine **22a** If the reducing agent is omitted, 1-hydroxypyrrols are obtained as exemplified by the conversion of the dihydrooxazine **25** into 3-fluoro-1-hydroxypyrrole (**30**).



**29**



**30**

Monofluoropyrroles are yet virtually unknown. [10] 1-Hydroxypyrrole [11] and a few derivatives thereof [11] have been reported in literature. The suggested methods of preparation are, however, fairly laborious and their practical utility is restricted due to poor yields.

## EXPERIMENTAL PART

### 1. Generalities

The standard equipment and methods used throughout this work have been described in previous related articles [12]. Hints how to carry out competition experiments can be also found there.

### 2. Electron-rich Fluoro-1,3-dienes

The synthesis of 2-fluoro-1-trimethylsilyloxy-1,3-butadiene and 2-fluoro-3-methyl-1-trimethylsilyloxy-1,3-butadiene has been described previously [5]. Analogously the two methoxy and trimethylsilyloxy substituted fluorodiene buildings blocks were obtained from methyl 2-fluoro-3-methyl-2-butenoate and, respectively, 3-fluoro-4-methoxy-3-buten-2-one [the latter being prepared by ring opening solvolysis of 1-chloro-1-fluoro-3-methoxy-2-methyl-2-(trimethylsilyloxy)cyclopropane; bp 75 - 76 °C/10 mmHg; $n_D^{20}$ 1.4762].

**2-Fluoro-1-methoxy-3-methyl-1-trimethylsilyloxy-1,3-butadiene** : Methyl 2-fluoro-3-methyl-2-butenoate [13] (13 g, 0.10 mol) was added dropwise, in the course of 30 min, to a solution of lithium diisopropylamide (0.12 mol) in tetrahydrofuran (0.10 L) and hexane (0.10 L) at -75 °C. After additional 30 min, chlorotrimethylsilane (30 mL, 26 g, 0.24 mol) was added. [14] At 25 °C, the reaction mixture was filtered and the liquid concentrated. A colorless oil distilled at bp 49 - 50 °C/1.5 mmHg; yield 80%; $n_D^{20}$ 1.4504. - $^1$H-NMR : $\delta$ 5.05 (0.84 × 1 H, symm. m), 5.02 (0.16 × 1 H, symm. m), 4.75 (0.84 × 1 H, symm. m), 4.71 (0.16 × 1 H, symm. m), 3.78 (0.84 × 3 H, d, *J* 1.6), 3.57 (0.16 × 3 H, d, *J* 0.8), 1.9 (3 H, m), 0.28 (0.16 × 9 H, d, *J* 1.4), 0.26 (0.84 × 9 H, s). - $^{19}$F-NMR : -90.0 (dt, *J* 21.0, 4.5). - MS : 205 ($M^+$ +1, 6%), 131 (4%) 77 (100%) - Analysis : calc for $C_9H_{17}FO_2Si$ (204.32) C 52.91, H 8.39; found C 52.74, H 8.39%.

**2-Fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene** : Under nitrogen, a mixture of *(Z)*-3-fluoro-4-methoxy-3-buten-2-one (12 g, 0.10 mol; prepared by stirring a solution of *(Z)*- and *(E)*-1-methoxy-2-trimethylsilyloxy-propene [15] and dichlorofluoromethane in pentane, in which potassium *tert*-butoxide was suspended, 3 h at -20 °C; 68%; bp 75 - 76 °C/10 mmHg), triethylamine (24 mL, 17 g, 0.17 mol), a small amount of anhydrous zinc chloride (0.1 g) in benzene (40 mL) was heated 6 h to reflux. It was cooled to 25 °C, diluted with hexane (40 mL), filtered and distilled. A colorless liquid was collected, 83%; bp 70 - 72 °C/8 mmHg; $n_D^{20}$ 1.4450. - $^1$H-NMR : $\delta$ 6.08 (1 H, dt, *J* 21.0, 0.7), 4.58 (1 H, ddd, *J* 4.5, 2.0, 0.7), 4.25 (1 H, ddd, *J* 4.5, 2.0, 0.7), 3.75 (3 H, s), 0.25 (9 H, s). - $^{19}$F-NMR : $\delta$ -90.0 (dt, *J* 21.0, 4.5). - Analysis : calc. for $C_8H_{15}FO_2Si$ (190 29) C 50.50, H 7.95; found C 50.78, H 7.66%.

### 3. Cycloadducts Obtained With α,β-Unsaturated Carbonyl Compounds

**3-Fluoro-6-(1-fluoro-2-methyl-1-propenyl)-2-hydroxy-4-methyl-5,6-dihydro-2*H*-pyran (1)** : 2-Fluoro-3-methyl-2-butenal [16] (1.0 g, 10 mmol) was allowed to stand over Amberlyst-15 resin (0.12 g) in a small screw-cap bottle during 15 days at 25 °C. As evidenced by nmr, two thirds of the aldehyde had dimerized at this point. The material was dissolved in hot dichloromethane (2 mL) and hexane was added until the solution became turbid. At 0 °C, crystals precipitated. They were collected and dried, 38%; mp 231 - 232 °C (dec.). - $^1$H-NMR (360 MHz) : $\delta$ 5.38 (1 H, s, broad), 4.96 (1 H, ddd, *J* 25.1, 11.6, 3.6), 2.70 (1 H, ddd, *J* 16 0, 11.6, 7.1), 1.84 (1 H, *J* 16.0, 3.6), 1.69 (9 H, d, *J* 3.1). - $^{13}$C-NMR (90.5 MHz) : $\delta$ 150.6 (d, *J* 244.3), 149.1 (d, *J* 252.8), 114.5 (d, *J* 16.6), 112.4 (d, *J* 9.8), 89.8 (dd, *J* 167.5, 37.9), 63.5 (dd, *J* 145.6, 27.7), 30.7 (t, *J* 124.4), 16.9 (q, *J* 125.0), 16.1 (q, *J* 127.5), 13.6 (q, *J* 127.5). - $^{19}$F-NMR . -65 (d hept, *J* 25.5, 3.3), -68 (m) - MS : 204 (2%, $M^+$), 203 (7%), 187 (100%), 186 (84%). - Analysis : calc. for $C_{10}H_{14}F_2O_2$ (204.21) C 58.82, H 6.91; found C 58.73, H 7.05%.

Two-dimensional nmr techniques allowed to determine unambiguously all coupling constants. On this basis the *cis* configuration was assigned, both the hydroxy group and the alkenyl side chain preferentially occupying the quasi-equatorial position.

**Methyl 3-fluoro-2-trimethylsilyloxy-3-cyclohexene-1-carboxylate (2a)** : A mixture of 2-fluoro-1-trimethylsilyloxy-1,3-butadiene (3.2 g, 20 mmol), methyl acrylate (5 4 mL, 5 2 g, 60 mmol) and a trace amount of hydroquinone in toluene (20 mL) was refluxed 48 h under a nitrogen atmosphere. Distillation afforded 75% of **2a** with a 2 : 1 *endo/exo* diastereomeric ratio; bp 62 - 64 °C/1.5 mmHg. - $^1$H-NMR : $\delta$ 5.3 (1 H, m), 4.63 (0.33 × 1 H, ddd, *J* 6.0, 3.5, 1.7), 4.53 (0.67 × 1 H, dd, *J* 9.5, 3.7), 3 71 (3 H, s), 2.75 (0.33 × 1 H, symm. m), 2.60 (0.67 × 1 H, symm. m),

2.0 (4 H, m), 0.15 (0.33 × 9 H, d, *J* 0.8), 0.11 (0.67 × 9 H, d, *J* 0.8). - $^{19}$F-NMR : δ -49.3 (0.67 × 1 F, symm. m), 53.2 (0.33 × 1 F, symm. m). - MS : 246 ($M^+$, 3%), 231 (100%), 171 (99%). - Analysis : calc. for $C_{11}H_{19}FO_3Si$ (246.35) C 53.63, H 7.77; found C 54.10, H 7.78%.

**Ethyl 5-fluoro-6-trimethylsilyloxy-1,4-cyclohexadiene-1-carboxylate (3a) and ethyl 4-fluoro-3-trimethylsilyloxy-1,4-cyclohexadiene-1-carboxylate (3b)** : In the same way a 3 : 1 regioisomeric mixture of **3a** and **3b** was obtained when ethyl propiolate was employed as the dienophile; 81%; bp 64 - 68 °C/0.5 mmHg. Upon attempted chromatographic separation using silica gel as the support, the minor component decomposed. - **9a** : $^1$H-NMR : δ 7.05 (1 H, symm. m), 5.43 (1 H, dddd, *J* 15.0, 4.2, 3.0, 1.3), 5.16 (1 H, dd, *J* 10.1, 5.1), 4.30 (1 H, dq, *J* 10.9, 7.0), 4.20 (1 H, dq, *J* 10.9, 7.0), 3.09 (1 H, dm, *J* 24.5), 2.88 (1 H, dm, *J* 24.5), 1.33 (3 H, t, *J* 7.0), 0.20 (9 H, d, *J* 0.8). - **9b** :$^1$H-NMR : δ 6.79 (1 H, symm. m), 5.47 (1 H, dt, *J* 15.5, 3.8), 4.90 (1 H, symm. m), 4.24 (2 H, q *J* 7.0), 3.0 (2 H, m), 1.31 (3 H, t, *J* 7.0), 0.21 (9 H, s).

When the crude reation mixture was heated 1 h to reflux in the presence of aluminum chloride, **3a** and **3b** were converted to ethyl 3-fluorobenzoate [17] and ethyl 4-fluorobenzoate [18], respectively.

**Ethyl 3-fluoro-4-methylbenzoate and ethyl 4-fluoro-3-methylbenzoate** : A similar reaction between 2-fluoro-3-methyl-1-trimethylsilyloxy-1,3-butadiene [5] (3.5 g, 20 mmol) and ethyl propiolate (2.0 mL, 2.0 g, 20 mmol) produced a 9 : 1 mixture of cycloadducts **4a** and **4b**. The latter were immediately aromatized in the presence of a catalytic quantity of aluminum chloride affording ethyl 3-fluoro-4-methylbenzoate [19] and ethyl 4-fluoro-3-methylbenzoate [20] in a 9 : 1 ratio. $^1$H-NMR : δ 7.9 (0.1 × 2 H, m), 7.75 (0.9 × 1 H, dd, *J* 7.9, 1.6), 7.68 (0.9 × 1 H, dd, *J* 10.1, 1.6), 7.26 (0.9 × 1 H, t, *J* 7.9), 7.05 (0.1 × 1 H, t, *J* 8.8), 4.38 (0.9 × 2 H, q, *J* 7.1), 4.37 (0.1 × 2 H, q, *J* 7.1), 2.35 (0.9 × 3 H, d, *J* 2.0), 2.36 (0.1 × 3 H, d, *J* 2.0), 1.40 (3 H, t, *J* 7.1).

**Dimethyl 4-fluoro-5-hydroxyphthalate** : The colorless crystalline product was obtained after 4 h of heating to reflux a solution of 2-fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (3.8 g, 20 mmol) and dimethyl acetylenedicarboxylate (2.8 g, 20 mmol), treatment of the product with a few drops of conc. hydrochloric acid and chromatography on silica gel; 86%; mp 93 - 94 °C. - $^1$H-NMR : δ 7.55 (1 H, d, *J* 10.5), 7.25 (1 H, d, *J* 8.2), 6.55 (1 H, broad, s), 3.89 (3 H, s), 3.91 (3 H, s). - $^{19}$F-NMR : -71.3 (dd, *J* 10.7, 8.1). - MS : 228 ($M^+$, 24%), 197 (100%), 181 (8%), 167 (10%). - Analysis : calc. for $C_{10}H_9FO_5$ (228.17) C 52.64, H 3.98; found C 52.51, H 4.23%.

**(4a*R**,5*R**,8a*R**)-6-Fluoro-5-trimethylsilyloxy-4a,5,8,8a-tetrahydronaphthalene-1,4-dione** (*endo*-**6**) : 2-Fluoro-1-trimethylsilyloxy-1,3-butadiene [5] (3.2 g, 20 mmol) and *p*-benzoquinone (2.2 g, 20 mmol) were dissolved in toluene (50 mL) and kept 15 h at 25 °C. The residue remaining after the evaporation of the solvent was recrystallized to yield colorless prisms, 65%; mp 104 - 106 °C. - $^1$H-NMR : δ 6.88 (1 H, d, *J* 10.2), 6.70 (1 H, dd, *J* 10.2, 1.0), 5.35 (1 H, ddd, *J* 15.5, 5.0, 2.9), 4.42 (1 H, dd, *J* 9.5, 3.9), 3.2 (2 H, m), 3.10 (1 H, dt, *J* 18.3, 5.0), 2.14 (1 H, dm, *J* 18.3), 0.00 (9 H, d, *J* 0.9). - $^{19}$F-NMR : -47.1 (m). - MS : 268 ($M^+$, 6%), 253 (56%), 178 (19%), 75 (100%). - Analysis : calc. for $C_{13}H_{16}FO_3Si$ (268.36) C 58.18, H 6.38; found 57.92, H 6.35%.

**6-Fluoro-1,4-naphthoquinone** : Some conc. hydrochloric acid (0.2 mL) and manganese dioxide (3.5 g, 40 mmol) were added to an ethereal solution (50 mL) of *endo*-**6** (2.7 g, 10 mmol). The suspension was vigorously stirred for 30 min before being filtered and the liqued phase being evaporated to dryness. Sublimation at 75 °C and under reduced pressure (10 mmHg) gave bright yellow crystals; 91%; mp 82 - 83 °C. -$^1$H-NMR : δ 8.15 (1 H, dd, *J* 8.6, 5.2), 7.75 (1 H, dd, *J* 8.6, 2.5), 7.45 (1 H, td, *J* 8.6, 2.5), 7.01 (2 H, *J* 10.0). - $^{19}$F-NMR : -38.6 (td, *J* 8.6, 5.2). - MS : 176 ($M^+$, 92%), 148 (21%), 122 (63%), 94 (100%). - Analysis : calc. for $C_{10}H_5FO_2$ (176,15) C 68.19, H 2.86, found C 68.34, H 2.78%.

***t*-4-Fluoro-*t*-3-methoxy-5-oxocyclohexane-*r*-1-*c*-2-dicarboxylic anhydride** (*endo*-**7**) : A solution containing 2-fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (3.8 g, 20 mmol) and maleic anhydride (2.0 g, 20 mmol) in toluene (10 mL) was allowed to stand 1 h at 25 °C. It was evaporated to dryness and the residue taken up in a 1 : 10 (v/v) mixture (20 mL) of conc. hydrochloric acid and tetrahydrofuran. After 30 min. at 25 °C, water (0.1 L) was added. Extraction with dichloromethane (5 × 30 mL), evaporation of the combined and washed organic layers and recrystallization from 1 : 2 (v/v) acetone/hexane mixture gave the colorless product : 81%; mp 159 - 160 °C. - $^1$H-NMR : δ 5.04 (1 H, ddd, *J* 47.4, 1.8, 0.8), 4.47 (1 H, ddd, *J* 9.8, 3.0, 1.8), 3.60 (1 H, dd, *J* 10.0, 3.0), 3.53 (1 H, td, *J* 10.0, 3.4), 3.30 (1 H, dt, *J* 18.7, 3.4), 2.87 (1 H, dd, *J* 18.7, 10.0). - $^{19}$F-NMR : -138.4 (dddd, *J* 47.6, 10.2, 2.8, 1.4). - MS : 216 ($M^+$, 1%), 144 (100%), 102 (55%). - Analysis : calc. for $C_9H_9F_5$ (216.16) C 50.01, H 4.20; found C 50 08, H 4.31%.

**2-Fluoro-1,8-dihydroxy-3-methylanthracene-9,10-dione ("fluorochrysophanol", 9b)** : 2-Fluoro-1-methoxy-3-methyl-1-trimethylsilyloxy-1,3-butadiene (5.1 g, 25 mmol) and 5-hydroxy-1,4-naphthoquinone ("juglone"; 3.5 g, 20 mmol) were codissolved in toluene (30 mL). After 10 h at 25 °C, some hydrochloric acid (0.2 mL) was added and the mixture was stirred vigoroulsy while a stream of air was bubbled in. After evaporation to dryness a solid consisting of **9b** and its *O*-methyl derivative **9a** was left behind. It was heated with a 1 : 1 (v/v) mixture (80 mL) of 48% hydrobromic acid and glacial acetic acid 2 h to reflux temperature. The suspension was deluted with water (0.1 L). The precipated was collected, washed with water, dried and recrystallized from toluene to afford brown needles: 86%; mp 238 - 240 °C (reprod.). - $^1$H-NMR : $\delta$ 12.02 (1 H, s), 11.98 (1 H, s), 7.83 (1 H, dd, *J* 5.8, 1.0), 7.70 (1 H, dd, *J* 6.1, 5.8), 7.69 (1 H, d, *J* 5.0), 7.30 (1 H, dd, *J* 6.1, 1.0), 2.45 (3 H, d, *J* 2.0). - $^{19}$F-NMR : -66.9 (dq, *J* 5.5, 2.5). - MS : 272 ($M^+$, 100%), 254 (80%), 139 (22%). - Analysis : calc. for $C_{15}H_9FO_4$ (272.23) C 66.18, H 3.33; found C 66.32, H 3.30%.

## 4. Cycloadducts Obtained With Saturated Carbonyl Compounds

**Diethyl 5-fluoro-6-hydroxy-3,6-dihydro-2*H*-pyran-2,2-dicarboxylate (10b)** : 2-Fluoro-1-trimethylsilyloxy-1,3-butadiene (3.2, 20 mmol) and diethyl oxopropandicarboxylate (diethyl mesoxalate; 3.5 g, 20 mmol) was heated 15 h to 150 °C under a nitrogen atmosphere. The reaction product was dissolved in wet ethyl acetate and absorbed on silica gel (25g). The dry powder was poured on top of a column filled with fresh silica gel and hexane. The product was eluted with a 3 : 7 (v/v) mixture of ethyl acetate and hexane; 81%; mp 48 - 50 °C. The nmr spectrum shows the hemiacetal **10b** to be in equilibrium with the ring-opened 5-hydroxyalkenal form [**diethyl *(E)*-2-(3-fluoro-3-formyl-2-propenyl)-2-hydroxypropanedioate**]. - $^1$H-NMR : $\delta$ 9.33 (0.6 × 1 H, d, *J* 16.1), 6.01 (0.6 × 1 H, dt, *J* 17.8, 8.7), 5.80 (0.4 × 1 H, d, broad, *J* 7.0), 5.40 (0.4 × 1 H, d, *J* 7.0), 5.05 (0.4 × 1 H, ddd, *J* 14.0, 5.8, 2.8), 4.02 (0.6 × 1 H, s), 3.82 - 4.02 (0.4 × 4 H, m), 3.82 (0.6 × 4 H, q, *J* 7.1), 2.98 (0.6 × 2 H, dd, *J* 8.7, 1.2), 2.85 (0.4 × 1 H, ddd, *J* 17.0, 5.8, 3.3), 2.46 (0.4 × 1 H, dddd, *J* 17 0, 6 1, 2.8, 1.7), 0.91 (0.4 × 3 H, t, *J* 7.0), 0.86 (0.4 × 3 H, t, *J* 7.0), 0.80 (0.6 × 6 H, t, *J* 7.1). - $^{19}$F-NMR : -58.3 (0.4 × 1 F, ddd, *J* 14.0, 6.1, 3.3), -60.5 (0.6 × 1 F, dd, *J* 17.8, 16.1). - MS · 262 ($M^+$, 1%), 189 (12%), 115 (100%) - Analysis : calc. for $C_{11}H_{15}FO_6$ (262.23) C 50.38, H 5.77; found C 50.39, H 5.85%.

**2-Benzyloxymethyl-5-fluoro-2,3-dihydro-2*H*-pyran-4-one (12)** : Zinc chloride (2.7 g, 20 mmol), some triethylamine (approx. 0.2 mL), benzyloxyacetaldehyde [21] (6.0 g, 40 mmol) and 2-fluoro-1-methoxy-3-trimethylsilyloxy-1,3-butadiene (7.6 g, 40 mmol) were consecutively dissolved in a 1 : 1 (v/v) mixture (20 mL) of tetrahydrofuran and benzene. After 4 h at 25 °C, the solvents were evaporated and the residue taken up in dichloromethane (50 mL) which contained trifluoroacetic acid (2 mL), before 2 h later the organic material was absorbed on silica gel (10 g). The dry powder was placed on top of a column packed with fresh silica gel (100 g). Elution with a 1 : 4 (v/v) mixture of ethyl acetate and hexane followed by distillation afforded **12** as a colorless oil; 86%; bp 135 - 136 °C/0.05 mmHg; $n_D^{20}$ 1.5401. - $^1$H-NMR : $\delta$ 7.59 (1 H, d, *J* 4.4), 7.4 (5 H, m), 4.62 (2 H, *J* 12.0), 4.6 (1 H, m), 3.75 (1 H, dd, *J* 11 0, 3 9), 3 68 (1 H, dd, *J* 11.0, 5.9), 2.90 (1 H, dd, *J* 17.2, 14.5), 2.53 (1 H, ddd, *J* 17.2, 4.2, 3 6). - $^{19}$F-NMR : -56.3 (t, *J* 4.2). - MS : 237 ($M^+$ + 1, 1%), 190 (4%), 115 (8%), 91 (100%).

***t*-6-Benzyloxymethyl-*c*-3-fluoro-*r*-2-methoxy-4-tetrahydropyranone (13)** : The dihydropyranone **12** (4.7 g, 20 mmol) and gaseous hydrogen chloride (50 mmol) were dissolved in methanol (50 mL). After standing 8 h at 25 °C, the mixture neutralized with solid sodium hydrogencarbonate (5 g) and was concentrated. Acetone (50 mL) and a trace of hydrochloric acid were added before, 2 h later, the product was absorbed on silica gel (10 g). Elution with a 3 : 7 (v/v) ethyl acetate/hexane mixture from fresh silica gel (100 g) gave **13** (57%) as on oily substance (bp ~ 130 °C/0.05 mmHg) which was contaminated with an unidentified minor isomer (6%). - $^1$H-NMR : $\delta$ 7.4 (5 H, m), 5.28 (1 H, d, *J* 4.1), 5.00 (1 H, ddd, *J* 47.5, 4.1, 1.0), 4.63 (2 H, d, *J* 12.0), 4.24 (1 H, symm. m), 3.67 (1 H, dd, *J* 10.5, 3.4), 3.58 (1 H, dd, *J* 10.5, 4.6), 3.48 (3 H, s), 2.75 (1 H, ddd, *J* 14.5, 11.2, 1.0), 2.52 (1 H, ddd, *J* 14.5, 4.5, 3.0), . $^{19}$F-NMR : -144.6 (dd, *J* 47.7, 4.6). - MS (c.i.) : 286 ($M$ + $NH_4^+$, 1%), 236 (1%), 142 (6%), 105 (7%), 91 (100%). - Analysis : calc. for $C_{14}H_{17}FO_4$ (268.28) C 62.68, H 6.39; found C 63.11, H 6.25%.

***t*-6-Benzyloxymethyl-*c*-3-fluoro-4-hydroxy-*r*-2-methoxytetrahydropyran (14)** : The tetrahydropyranone **13** (1.3 g, 5.0 mmol) was added to a solution of lithium tri-*sec*-butylborohydride ("L-selectride", 10 mmol) in tetrahydrofuran (20 mL) cooled to -75 °C. After 1 h at this temperature, the reaction mixture was absorbed on silica gel (10 g). The dry powder obtained after evaporation of the solvent was allowed to stand overnight (15 h) in the air

and was then placed in a column filled with fresh silica gel (100 g) and hexane. The syrupy product was eluted with a 2 : 3 (v/v) ethyl acetate/hexane mixture; 87%. - $^1$H-NMR : $\delta$ 7.3 (5 H, m), 5.00 (1 H, d, $J$ 3.5),4.61 (2 H, s), 4.51 (1 H, dt, $J$ 45.7, 3.5), 4.30 (1 H, s, broad), 4.22 (1 H, symm. m), 3.6 (3 H, m), 3.52 (3 H, s), 1.96 (1 H, dm, $J$ 14.3), 1.83 (1 H, ddd, $J$ 14.3, 12.0, 2.5). - $^{19}$F-NMR : -139.1 (dt, $J$ 45.7, 6.0). - MS : 238 ($M^+$ - $CH_3OH$, 2%), 129 (4%), 107 (10%), 91 (100%). - Analysis : calc. for $C_{14}H_{19}FO_4$ (270.30) C 62.21, H 7.08; found C 62.11, H 7.13%.

## 5. Cycloadducts Obtained with Imines or Nitriles

**Ethyl 5-fluoro-6-hydroxy-1-*p*-toluenesulfonyl-1,2,3,6-tetrahydropyridine-2-carboxylate (15)** : 2-Fluoro-1-trimethylsilyloxy-1,3-butadiene [5] (4.8 g, 30 mmol) and ethyl *N*-(*p*-toluenesulfonyl)iminoacetate [22] (7.7 g, 30 mmol) were dissolved in toluene (50 mL) and heated 2 h to 80 °C. Then the solvent was replaced by tetrahydrofuran (50 mL) and 2 N hydrochloric acid (10 mL) was added. After 30 min at 25 °C, the mixture was poured into water (0.10 L) and extracted with diethyl ether (3 × 50 mL). The combined and dried organic layers were evaporated to dryness and the residue was recrystallized from diethyl ether/hexane; 91%; mp 118 - 120 °C (colorless prisms). - $^1$H-NMR : $\delta$ 7.83 (2 H, dm, $J$ 8.3), 7.28 (2 H, dm, $J$ 8.3), 5.81 (1 H, dm, $J$ 11.5), 5.34 (1 H, dddd, $J$ 14.5, 6.5, 2.2, 0.8), 4.99 ( 1 H, d, $J$ 11.5), 4.88 (1 H, dt, $J$ 7.5, 1.2), 4.02 (2 H, q, $J$ 7.1), 2.73 (1 H, dddt, $J$ 17.0, 7.5, 7.0, 2.1), 2.50 (1 H, ddddd, $J$ 17.0, 6.5, 3.0, 1.2, 0.7), 2.43 (3 H, s), 1.18 (3 H, t. $J$ 7.1). - $^{19}$F-NMR : -53.9 (dm, $J$ 14.5). - MS : 343 ($M^+$, 33%), 326 (100%), 270 (58%). - Analysis : calc. for $C_{15}H_{18}FNO_5S$ (343.37) C 52.47, H 5.28; found C 52.74, H 5.21%.

**Ethyl 5-fluoro-2-pyridinecarboxylate (16)** : Tetrahydropyridine 15 (6.9 g, 20 mmol) and a small amount (approx. 0.1 g) of *p*-toluenesulfonic acid were dissolved in toluene (25 mL). After 1 h at 80 °C, triethylamine (3.5 mL, 2.5 g, 25 mmol) was added to the reaction mixture which was allowed to stand 1 h at 25 °C. Chromatography on silica gel (100 g) with a 1 : 4 (v/v) ethylacetate/hexane as the eluent gave 90% of 16; mp 59 - 61 °C. - $^1$H-NMR: $\delta$ 8.6 (1 H, d, $J$ 2.9), 8.20 (1 H, dd, $J$ 8.8, 4.6), 7.54 (1 H, ddd, $J$ 8.8, 7.9, 2.9), 4.48 (2 H, q, $J$ 7.0), 1.45 (3 H, t, $J$ 7.0). - $^{19}$F-NMR : 57.6 (dd, $J$ 7.9, 4.6). - MS : 169 ($M^+$, 6%), 124 (20%), 97 (100%). - Analysis : calc. for $C_8H_8FNO_2$ (169.15) C 56.80, H 4.77; found C 56.74, H 5.03%.

**5-Fluoro-1-*p*-toluenesulfonyl-2-trichloromethyl-1,2-dihydropyridine (18)** : 2-Fluoro-1-trimethylsilyloxy-1,3-butadiene [5] (3.2 g, 20 mmol) and 2,2,2-trichloro-*N*-(*p*-toluenesulfonyl)ethanimine [23] (6.2 g, 20 mmol) in toluene (50 mL) were heated 4 h to reflux. The solvent was removed and replaced by tetrahydrofuran (30 mL) containing some (3 mL) conc. hydrochloric acid. After 30 min at 25 °C, the mixture was evaporated in the presence of silica gel (10 g). The dry powder was transferred into a column filled with fresh silica gel (150 g) and hexane. Elution with ethyl acetate/hexane (3 : 7, v/v) gave colorlesss 19; 85%,; mp 121 - 122 °C. - $^1$H-NMR : $\delta$ 7.65 (2 H, dm, $J$ 8.5), 7.29 (2 H, dm, $J$ 8.5), 6 5 (1 H, m, 1 H), 6.16 (1 H, dddd, $J$ 10.0, 6.2, 1.8, 1.1), 5.90 (1 H, symm. m), 5.32 (1 H, dm, $J$ 6.0), 2.44 (3 H, s). - $^{19}$F-NMR : -78.0 (symm. m). - MS : 252 ($M^+$-$CCl_3$, 7%), 155 (14%), 91 (100%). - Analysis : calc. for $C_{13}H_{11}Cl_3FNO_2S$ (370.66) C 42.13, H 2.99; found C 42.08, H 3.04%.

**Methyl 5-fluoro-4-methyl-2-pyridinecarboxylate (21)** : 2-Fluoro-3-methyl-1-trimethylsilyloxy-1,3-butadiene (7.0 g, 40 mmol) and methyl cyanoformate (3.4 g, 40 mmol) in toluene (20 mL) were heated 5 days to reflux. Chromatography on silica gel (150 g) with ethyl acetate/hexane (3 : 7, v/v) as the eluent afforded colorless crystals; 36%; mp 64 - 65 °C. - $^1$H-NMR : $\delta$ 8 47 (1 H, s), 8.05 (1 H, d, $J$ 6.2), 3.99 (3 H, s), 2.39 (3 H, d, $J$ 1.0). - $^{19}$F-NMR : - 62.6 (dq, $J$ 6.2, 1.2). - MS : 169 ($M^+$, 2%), 139 (9%), 111 (100%). - Analysis : calc. for $C_8H_8FNO_2$ (169.15) C 56.80, H 4.77; found C 56 84, H 4.28%.

## 6. Cycloadducts Obtained With Nitroso Compounds

**5-Fluoro-2-phenyl-6-trimethylsilyloxy-3,6-dihydro-1,2-oxazine (22a)** and **4-fluoro-1-phenyl-6-trimethylsilyloxy-3,6-dihydro-1,2-oxazine (22b)** : 2-Fluoro-1-trimethylsilyl-1,3-butadiene [5] (6.4 g, 40 mmol) and nitrosobenzene (4.2 g, 40 mmol) were dissolved in toluene (50 mL). After about 1 h at 25 °C, the characteristic turquoise-blue color had disappeared. Distillation afforded an oily mass which contained **22a** and **22b** in the approximate ratio of 1 : 3. - $^1$H-NMR : $\delta$ 7.2 (5 H, m), 5.6 (1 H, m), 5.51 (0.25 × 1 H, s, broad), 5.34 (0.75 × 1 H, dd, $J$ 6.7, 1.0), 4.59 ((0 75 × 1 H, dddd, $J$ 14.8, 7.0, 1.5, 1 0), 4.44 (0.75 × 1 H, ddd, $J$ 14.8, 5.1, 4.5), 4.05 (0.25 × 1 H, ddd, $J$ 5.2, 5.5, 3.6), 3.73 (0.25 × 1 H, dddd, $J$ 15.2, 6.5, 1.8, 1.0), 0.26 (0.25 × 9 H, s), -0.07 (0.75 × 9 H, s). - $^{19}$F-NMR : -56.5 (0 75 × 1 F, symm. m), 60 9 (0 25 × 1 F, ddd, $J$ 12.0, 6 5, 3 6).

The regioisomers **22a** and **22b** (0.8 g, 30 mmol) were dissolved in methanol (50 mL) and a small amount (about 0.2 mL) of conc. hydrochloric acid was added. After 30 min at 25 °C, a cyclic hemiacetal and a 3-methoxy substituted oxazine in the ratio of 1 : 3 had formed. The two components could be easily separated by column chromatography using ethyl acetate/hexane (3 : 7 v/v) as the eluent. - **5-Fluoro-6-hydroxy-2-phenyl-3,6-dihydro-1,2-oxazine** : 97% (with respect to **22a**); mp 98 - 99 °C. - $^1$H-NMR : $\delta$ 7.3 (5 H, m), 5.63 (1 H, dddd, $J$ 12.0, 5.7, 1.8, 0.7), 5.39 (1 H, d, broad, $J$ 11.5), 3.99 (1 H, ddd, $J$ 15.5, 5.7, 3.7), 3.82 (1 H, d, $J$ 11.5), 3.78 (1 H, dddd, $J$ 15.5, 7.0, 1.8, 1.0). - $^{19}$F-NMR : -60.0 (symm. m). - MS : 195 ($M^+$, 12%), 108 (47%), 7.7 (100%). - Analysis : calc. for $C_{10}H_{10}FNO_2$ (195.19) C 61.53, H 5.16; found C 61.63. H 5.24%.

**4-Fluoro-3-methoxy-2-phenyl-3,6-dihydro-1,2-oxazine** : 90% (with respect to **22b**); bp 89 - 90 °C/0.2 mmHg. - $^1$H-NMR : $\delta$ 7.2 (5 H, m), 5.73 (1 H, ddd, $J$ 12.8, 4.2, 1.7), 5.31 (1 H, dd, $J$ 6.0, 1.4), 4.58 (1 H, dddd, $J$ 14.9, 7.1, 1.7, 1.4), 4.42 (1 H, ddd, $J$ 14.9, 5.0, 4.2), 3.39 (3 H, s). - $^{19}$F-NMR : -55.8 (symm. m). - MS : 209 ($M^+$, 29%), 178 (9%), 102 (100%). - Analysis : calc. for $C_{11}H_{12}FNO_2$ (209.22) C 63.15, H 5.78; found C 62.90, H 5.74%.

With 2-fluoro-3-methyl-1-trimethylsilyloxy-1,3-butadiene [5] as one of the components, a 3 : 1 mixture of **5-fluoro-4-methyl-2-phenyl-6-trimethylsilyloxy-3,6-dihydro-1,2-oxazine** (**23a**) and **4-fluoro-5-methyl-3-trimethylsilyloxy-3,6-dihydro-1,2-oxazine** (**23b**) was obtained. The main component crystallized upon trituration with hexane. - **23a** : mp 57 - 58 °C. - $^1$H-NMR : $\delta$ 7.2 (5 H, m), 5.49 (1 H, symm. m), 3.87 (1 H, dd, $J$ 14.9, 4.3), 3.66 (1 H, dd, $J$ 14.9, 6.2), 1.79 (3 H, dd, $J$ 2.1, 0.9), 0.25 (9 H, s). - $^{19}$F-NMR : -71.5 (symm. m). - MS : 281 ($M^+$, 21%), 174 (100%), 73 (83%), 77 (56%) - Analysis : calc. for $C_{14}H_{20}FNO_2Si$ (281.40 C 59.77, H 7.16; found C 59.75, H 7.12%. - **23b** : $\delta$ 7.2 (5 H, m), 5.33 (1 H, dm, $J$ 7.1), 4.49 (1 H, ddm, $J$ 14.2, 6.7), 4.23 (1 H, dd, $J$ 14.2, 5.9), 1.70 (3 H, dd, $J$ 1.9, 0.8), -0 07 (9 H, s)

**2-(1-Cyclohexenyl)-5-fluoro-6-trimethylsilyloxy-3,6-dihydro-1,2-oxazine** (**27**) : 2-Fluoro-1-trimethylsilyloxy-1,3-butadiene [5] (4.8 g, 30 mmol), 1-chloro-1-nitrocyclohexane [24] (4,4 g, 30 mmol), triethylamine (5.6 mL, 4.0 g, 40 mmol) in toluene (50 mL) were kept about 2 h until the blue color had dissapeared. After evaporation to dryness, the residue was thoroughly extracted with cyclohexane. The filtrate was concentrated to afford the crude product **27**; 90%. - $^1$H-NMR : $\delta$ 5.50 (1 H, ddd, $J$ 12.5, 5.7, 2.0), 5.34 (1 H, s, broad), 5.13 (1 H, t, $J$ 4.0), 3.67 (1 H, ddd, $J$ 15.2, 5.7, 3.7), 3.50 (1 H, dddd, $J$ 15.2, 6.5, 2.0, 1.0), 2.2 (4 H, m), 1.6 (4 H, m), 0.23 (9 H, s).

**2-(1-Cyclohexenyl)-5-fluoro-4-methyl-6-trimethylsilyloxy-3,6-dihydro-1,2-oxazine** (**28**) : In an analogous reaction with 2-fluoro-3-methyl-1-trimethylsilyloxy-1,3-butadiene [5] (5.2 g, 30 mmol), **28** was obtained; 85%. - $^1$H-NMR : $\delta$ 5.33 (1 H, s, broad), 5.13 (1 H, tt, $J$ 4.0, 1.0), 3.49 (1 H, dd, $J$ 15.0, 4.5), 3.42 (1 H, dd, $J$ 15.0, 5.5), 2.3 (4 H, m), 1.71 (3 H, dd, $J$ 2.5, 1.0), 1.6 (4 H, m), 0.22 (9 H, s).

## 7. Pyrroles

**1-Phenyl-3-fluoropyrrole** (**29**) : 5-Fluoro-6-hydroxy-2-phenyl-3,6-dihydro-1,2-oxazine (2.0 g, 10 mmol; see above) and zinc powder (2.0 g, 30 mmol) in glacial acetic acid (20 mL) were vigorously stirred during 8 h at 25 °C. The mixture was carefully neutralized with a diluted aqueous solution of sodium hydroxide and extracted with hexane (3 × 50 mL). The organic phase was evaporated and the residue purified by chromatography on silica gel (100 g); 57% of **29**; mp 33 - 34 °C. - $^1$H-NMR : $\delta$ 7.3 (5 H, m), 6.8 (2 H, m), 6 05 (1 H, dd, $J$ 3.0, 1.9). - $^{19}$F-NMR : -101.5 (symm. m). - MS . 161 ($M^+$, 100%), 149 (47%), 133 (73%). - Analysis : calc. for $C_{10}H_8FN$ (161.18) C 74.52, H 5.00; found C 74.28, H 5 26%.

**1-Benzoyloxy-3-fluoropyrrole** . Upon addition of 50% aqueous acetic acid (10 mL) to a solution of crude dihydrooxazine **27** (approx. 25 mmol) in diethyl ether (50 mL) a two-phase system was obtained which was vigorously stirred 3 h at 25 °C. The organic layer was washed with water (3 × 25 mL) and treated with benzoyl chloride (4 2 g, 30 mmol) in the presence of excess pyridine (10 mL). After evaporation to dryness a residue was left behind which was submitted to chromatography on silica gel (150 g) using a 1 : 4 (v/v) mixture of ethyl acetate and hexane as the eluent, the product was isolated as colorless crystals; 72% (with respect to the diene precursor of **27**); mp 68 - 69 °C. - $^1$H-NMR : $\delta$ 8.2 (2 H, m), 7.6 (3 H, m), 6.6 (2 H, m), 5.97 (1 H, dd, $J$ 3.5, 2.5). - $^9$F-NMR : -102.6 (t, $J$ 3.5). - MS : 205 ($M^+$, 4%), 105 (100%), 77 (33%). - Analysis : calc. for $C_{11}H_8FNO_2$ (205.19) C 64.39, H 3.93, found C 64.62, H 3.82%.

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