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Action of Potassium Fluoride and DBU on β-Fluoro-γ,δ-unsaturated p-Toluenesulfonates: a Convenient Route to Conjugated 2-Fluoroalkadienes

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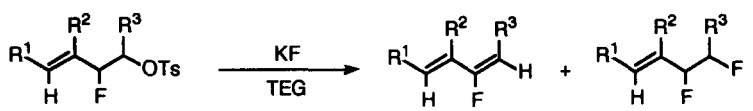
Abstract: *Potassium fluoride reacts in triethyleneglycol (TEG) on β-fluoro-γ,δ-unsaturated p-toluenesulfonates to give 2-fluoroalka-1,3-dienes (HOTs elimination) and the corresponding difluoroolefins (substitution of O-tosyl group by fluorine). S_N/E competition may be related to the structure of the starting tosylate. However, the exclusive formation of conjugated 2-fluoroalkadienes may be realized by using DBU at room temperature instead of KF.*

The action of KF on simple 2-fluoroalkyl- and 1-*F*-alkyl-2-fluoroethyl p-toluenesulfonates has been studied previously.[1-3] A substitution of the *O*-tosyl group by fluorine is observed with monofluorinated tosylates whereas hydrofluoride elimination, giving unsaturated *F*-alkyl tosylates, takes place from *F*-alkylated tosylates.

In the present study, the same reaction is carried out on β-fluoro-γ,δ-unsaturated p-toluenesulfonates.[4] As with monofluorinated and *F*-alkylated tosylates, KF is used in a polar solvent such as TEG in order to increase its basic character.[5] However, as shown in scheme 1 and table 1, the substitution products may be formed next to those resulting from elimination.



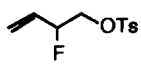
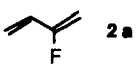
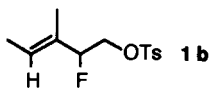
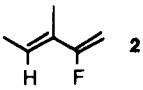
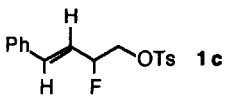
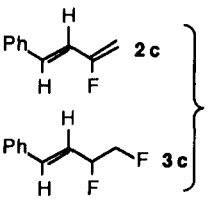
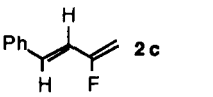
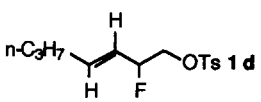
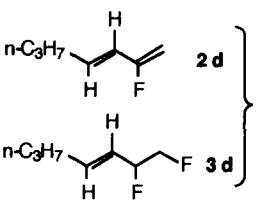
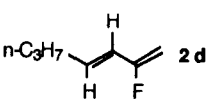
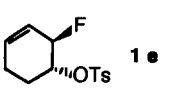
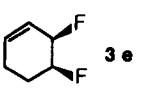
1 **2** **3**

1-3	a	b	c	d	e
R^1	H	CH_3	Ph	n-C_3H_7	-CH_2-
R^2	H	CH_3	H	H	H
R^3	H	H	H	H	-CH_2-

Scheme 1

The S_N/E competition seems to be dependent on the structure of the starting tosylate, since attempts realized in DMSO[6] gave the same results in lower yields.

Table 1. KF and DBU action on β-fluoro-γ,δ-unsaturated p-toluenesulfonates

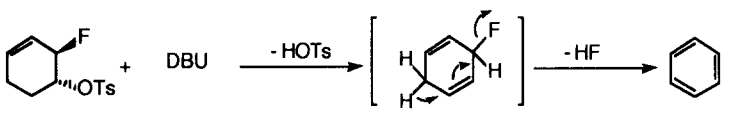
Tosylate	Reagent	Product	E:S_N[a]	bp (°C/Torr)	Yield[b](%)
 **1a**	KF	 **2a**	100:0	11/760	90
 **1b**	KF	 **2b**	100:0	88/760	76
 **1c**	KF	 **2c** **3c**	15:85	103/15	65[b]
	DBU	 **2c**	100:0	45/0.6	94
 **1d**	KF	 **2d** **3d**	7:93	65/100	61[b]
	DBU	 **2d**	100:0	52/100	90
 **1e**	KF	 **3e**	0:100	40/100	33
	DBU	C_6H_6	100:0	81/760	45

[a]Elimination:substitution ratio given by ^{19}F NMR; [b]overall yield.

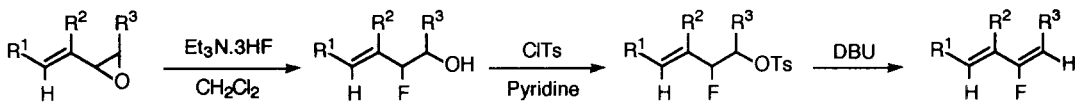
If we consider the non-cyclic compounds of table 1, for which the group -CHF-CH_2-OTs is the same, we notice that the elimination reaction takes place only when the remaining vinyl group is not substituted (**1a**) or is symmetrically substituted on both ethylenic carbon atoms (**1b**). On the contrary, when the vinyl group is monosubstituted on the terminal carbon atom (**1c,d**), the substitution products are predominant. In this case, the donor effect of the substituent increases the electronic density on the second ethylenic carbon and as a consequence decreases the mobility of the hydrogen atom directly linked to the fluorinated carbon atom. Thus, the elimination products become the minor ones.

For the single trans cyclic compound **1e** of table 1, the action of KF gives cis difluorolefin **3e** following an S_N2 mechanism, as was observed for other cyclohexane derivatives.[1,7]

Difluoroolefins **3c-e** are described for the first time. Some conjugated 2-fluoroalkadienes, different from those described here, were prepared following two procedures: the first preparation was realized from 1-chloro-1-fluorocyclopropane derivatives by pyrolysis[8], by the action of Zn[9] or tetrabutylammonium fluoride.[10] The second corresponds to the phosphonium ylide condensation on unsaturated fluoroaldehydes.[11] As the formation of these conjugated 2-fluoroalkadienes may prove useful in the synthesis of other monofluorinated compounds, we looked for another way allowing their preparation in pure form. This was done by the action of DBU[12,13] at room temperature on β-fluoro-γ,δ-unsaturated p-toluenesulfonates. Under these conditions and as shown in table 1, only the elimination of HOTs is observed for compounds **1c** and **1d**, in very good yields (≥90 %), whereas for compound **1e**, the formation of benzene is the result of two elimination reactions as suggested below:



According to scheme 2, this method constitutes a simple route to conjugated 2-fluoroalkadienes from vinyloxiranes[14] as starting materials.



Scheme 2

In conclusion, the action of KF on β-fluoro-γ,δ-unsaturated p-toluenesulfonates allows the preparation of the corresponding conjugated 2-fluoroalkadienes and difluoroolefins.[15] Except in the case of cyclic compound **1e**, when DBU is used as a reagent[15], only conjugated 2-fluoroalkadienes are formed. All new compounds were characterised[16] by IR, ^1H, ^{19}F NMR and MS.

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14. Vinyloxiranes were prepared by treatment of α,β-unsaturated bromhydrins with NaOH under phase-transfer conditions (**1a,e**) or by condensation of α,β-unsaturated aldehydes with dimethylsulfonium methylide (**1b-d**): Baklouti, A. and Hedhli, A. *J. Soc. Chim. Tunisie* **1993**, *III*, 283-291.
15. New compounds were prepared according to the following procedure:
Method using KF: a mixture of tosylate **1** (15 mmol), KF (4.35 g) and TEG (15 mL) was stirred and heated for 4 h to 120 °C. During this period, a slow current of N_2 was allowed to stream through the reaction vessel and then through a trap cooled at -10 °C. Compounds **2** and **3** were distilled and collected in the cold trap. The heavier compounds **2c** and **3c** were separated from the reaction mixture by extraction with ether. The organic phase was washed with water and dried (Na_2SO_4). The solvent was evaporated and the oil obtained was distilled under vacuum.
Method using DBU: equimolar amounts (10 mmol) of tosylate **1c-e** and DBU were mixed and stirred during 5 h at room temperature (50 °C for **1e**). The fluoroalkadiene was then separated from the reaction mixture as described above.
16. Spectral data: ^1H NMR spectra were recorded in $CDCl_3$/TMS on a 250 MHz apparatus and ^{19}F NMR in $CDCl_3/CFCl_3$ on a 235.3 MHz instrument. *2-Fluorobuta-1,3-diene* ***2a***: IR (CCl_4): 1670, 1600, 1140-1050 cm^{-1}. ^1H NMR δ 3.83-6.33 (m, 5 H) ppm. ^{19}F NMR δ -120.00 (ddd, 1 F, J = 50, 26, 16 Hz) ppm. MS (*m/z*, AR): 72 ($M^{+\cdot}$, 100.00), 71 (M-1, 54.38), 52 (12.01). *(E)-2-Fluoro-3-methylpenta-1,3-diene* ***2b***: IR (CCl_4): 1670, 1626, 1120-1070 cm^{-1}. ^1H NMR δ 6.13 (q, 1 H, CH_3-C<u>H</u>=C, J = 6 Hz), 5.01 (m, 2 H, CH_2=C), 1.71 (m, 6 H, 2 CH_3) ppm. ^{19}F NMR δ -114.0 (dd, 1 F, J = 51, 19 Hz) ppm. MS (*m/z*, AR): 101 (M+1, 7.03), 100 ($M^{+\cdot}$, 95.31), 85 (M-CH_3, 100.00), 79 (27.34), 65 (30.46). *(E)-3-Fluoro-1-phenylbuta-1,3-diene* ***2c***: IR ($CHCl_3$): 1650, 1610,1490,1100-1050 cm^{-1}. ^1H NMR δ 7.30 (m, 5 H, H_{arom}), 6.83-6.13 (m, 2 H, CH=CH), 4.93-4.10 (m, 2 H, C=CH_2) ppm. ^{19}F NMR δ -113.3 (ddd, 1 F, J = 48, 27, 19 Hz) ppm. MS (*m/z*, AR): 149 (M+1,10.56), 148 ($M^{+\cdot}$, 100.00), 147 (M-1, 91.86), 133 (40.92), 128 (19.21), 127 (30.69), 77 (12.73). *(E)-3,4-Difluoro-1-phenylbut-1-ene* ***3c***: IR ($CHCl_3$): 1605, 1150-1050 cm^{-1}. ^1H NMR δ 7.30 (m, 5 H, H_{arom}), 7.00-6.00 (m, 2 H, CH=CH), 5,39 (m, 1 H, CHF), 4.53 (ddd, 2 H, CH_2F, J = 48, 24, 5 Hz) ppm. ^{19}F NMR δ -184.2 (m, 1 F, CHF), -228.4 (tt, 1 F, CH_2F, J = 46, 15 Hz) ppm. MS (*m/z*, AR): 169 (M+1, 4.02), 168 ($M^{+\cdot}$, 32.47), 148 (M-HF, 2.06), 135 (M-CH_2F, 100.00), 115 (67.47), 51 (11.65). *(E)-2-Fluorohepta-1,3-diene* ***2d***: IR ($CHCl_3$): 1670, 1600, 1100-1050 cm^{-1}. ^1H NMR δ 6.15-5.35 (m, 4 H, CH=CH-CF=CH_2), 2.10 (m, 2 H, C<u>H</u>$_2$-CH_2-CH_3), 1.50 (m, 2 H, CH_2-C<u>H</u>$_2$-CH_3), 1.00 (t, 3 H, CH_3, J = 6 Hz) ppm. ^{19}F NMR δ -112.8 (ddd, 1 F, J = 48, 22, 17 Hz) ppm. MS (*m/z*, AR): 114 ($M^{+\cdot}$, 100.00), 113 (M-1, 86.34), 94 (13.15), 42 (58.32). *(E)-1,2-Difluorohept-3-ene* ***3d***: IR ($CHCl_3$): 1600, 1150-1040 cm^{-1}. ^1H NMR δ 6.15-5.35 (m, 2 H, CH=CH), 5.10 (m, 1 H, CHF), 4.43 (ddd, 2 H, CH_2F, J = 47, 23, 5 Hz), 2.10 (m, 2 H, C<u>H</u>$_2$-CH_2-CH_3), 1.50 (m, 2 H, CH_2-C<u>H</u>$_2$-CH_3), 1.00 (t, 3 H, CH_3, J = 6 Hz) ppm. ^{19}F NMR δ -182.3 (m, 1 F, CHF), - 228.6 (tt, 1 F, CH_2F, J = 47, 17 Hz) ppm. MS (*m/z*, AR): 135 (M+1, 1.39), 134 ($M^{+\cdot}$, 15.98), 114 (M-HF, 17.82), 101 (M-CH_2F, 13.32), 81 (45.48). *(Cis)-3,4-Difluorocyclohex-1-ene* ***3e***: IR ($CHCl_3$): 1610, 1150-1030 cm^{-1}. ^1H NMR δ 6.00 (m, 2 H, CH=CH), 5.00 (m, 2 H, CHF-CHF), 2.10 (m, 4 H, CH_2-CH_2) ppm. ^{19}F NMR δ -173.5 (m, 1 F, C=C-CF), -174.0 (m, 1 F, CH_2-CF) ppm. MS (*m/z*, AR): 99 (M-F, 7.59), 98 (M-HF, 7.59), 70 (100.00), 57 (36.71).

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