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A Convenient Synthesis of a New Push-pull Alkenes: β-alkoxyl vinyl trifluoromethyl sulfones

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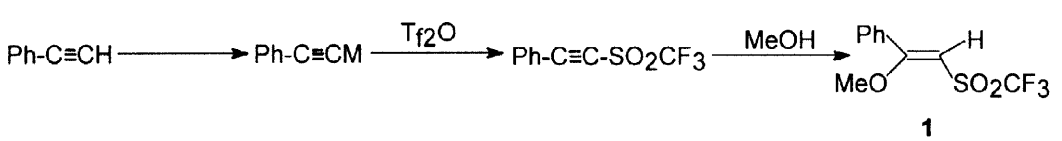
Abstract: A new push-pull alkene, β-ethoxy vinyl trifluoromethyl sulfone EtOCH=CHT$_f$ was prepared from the reaction of trifluoromethanesulfonyl chloride with vinyl ether in the presence of pyridine. Similarly, 4-trifluoro-methyl sulfonyl 2,3-dihydrofuran and 5-trifluoro- methyl sulfonyl 2,3-dihydro-2H-pyran were prepared in moderate yields. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Vinyl sulfones are known to be reactive compounds.[1] Due to its negative inductivity, the sulfonyl group is a strong electron-withdrawing group, resulting in an electron deficiency at the double bond. This effect is even more pronounced in the vinyl perfluoroalkylsulfones.[2-3] The highly activated carbon-carbon double bond is ready for nucleophilic attack and dipolar cycloaddition.[4-5] The preparation and reactions of the vinyl perfluoroalkyl sulfones are of great interest and many results have been reported.[6-8] In this regard, we now report here on the facile synthesis of new push-pull ethylenes i.e. β-alkoxyvinyl trifluoromethyl-sulfones ROCH=CHSO$_2$CF$_3$ from readily available starting materials.

Hanack[9]and Fuchs[10] recently reported respectively that base-catalyzed addition of methanol to 2-phenyltrifluoromethane MeOC(Ph)=CHSO$_2$CF$_3$ **1** to give 2-methoxyl 2-phenyltrifluoromethanesulfone-vinyl, compound **1** was prepared from the reaction of Tf$_2$O with phenyl ethynyl salt; thus:



1

Unfortunately, because unable to prepare HC=CSO$_2$CF$_3$ by above method,[9] compound ROCH=CHSO$_2$CF$_3$ **2** has not been reported till present. We have now succeeded in synthesizing this push-pull vinyl triflone in good yields.

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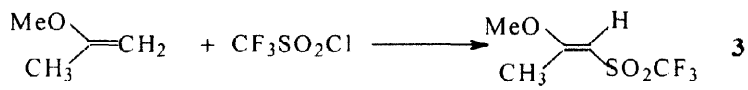
Treatment of trifluoromethanesulfonyl chloride with ethyl vinyl ether in the presence of equal mole pyridine gave the expected β-ethoxyvinyltriflone **2**, thus:

$$EtOCH{=}CH_2 + CF_3SO_2Cl \xrightarrow[CH_2Cl_2]{Py} EtOCH{=}CHSO_2CF_3 \quad (E \text{ and } Z) \qquad \mathbf{2}$$

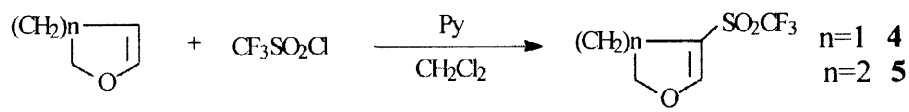
This reaction was easily carried out in CH_2Cl_2 at room temperature. After removal of the solvent, the product can be distilled out under reduced pressure. Compound **2** is a stable and colorless liquid. According to its ^1H NMR and ^{13}C NMR spectra, **2** is a mixture of two isomers with the E/Z ratio about 9:1. In several different scale preparative procedures, the ratio of E/Z isomer is nearly constant . The ^{13}C NMR chemical shifts of the two double bond carbon atoms in the E-isomer are 162.17 ppm and 101.85 ppm, both being down field compared with those of Z-isomer.The ^{1}HNMR shows a similar tendency (see table 1). The two isomers can be separated by column chromatography, the Z-isomer having the longer retention time. Similar treatment of 2-methoxypropene with CF_3SO_2Cl give 2-methoxy-2-methylvinyl triflone **3**.



3

Compared with **2** the β-carbon atom of compound **3** is more positively charged caused by two electron donating groups. Its ^{13}C NMR clearly shows this point (see table 1).

This synthetic method is also applicable to cyclic vinyl ethers, under similar reaction condition 2,3-dihydrofuran or 3,4-dihydro-2H-pyran reacted readily with CF_3SO_2Cl and gave the corresponding triflones **4** and **5** in moderate yields.



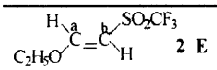
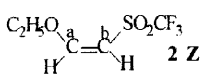
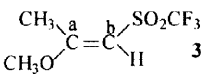
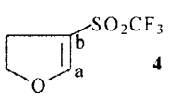
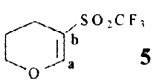
n=1 **4**
n=2 **5**

Similar treatment of R_fSO_2F (R_f: C_4F_9, $ICF_2CF_2OCF_2CF_2$, ClC_4F_8) with vinyl ether gave no reaction occurred. Instead of CF_3SO_2Cl, $(CF_3SO_2)O$ was also used to react with vinyl ether or 3,4-dihydro-2H-pyran: however, no compound **2** or **4** was obtained. Even when this reaction was carried out at -10℃, only a sticky dark oil was obtained.

In contrast to the compound $EtOCH=CHCOCF_3$, which is readily hydrolyzed to CF_3COCH_2CHO in dilute HCl solution at room temperature,[11] compounds **2**, **3**, **4** and **5** did not hydrolyzed under similar condition, even when heated with 30% HCl at 60℃ for 8h, **2** was recovered quantitatively.

In summary, the present work provides a facile and easily scaled up method to prepare new push-pull ethylenes, β-alkoxylvinyltriflones[12]. Their chemical properties now are under investigation .

Table 1 β-alkoxylvinyltriflones **2**, **3**, **4**, and **5** prepared

Product	yield (%)	b.p/m.p (℃)	δ_C (ppm)	δ_H(ppm)	IR (ν_{max}, cm^{-1}): C=C, -SO2
 **2 E**	68%	44-45 /2 torr	C(a) 162.17 C(b) 101.85	H(a) 7.35, J_{HH} = 14 Hz H(b) 5.82	1600(C=C), 1340(SO_2)
 **2 Z**	7.5%	44-45 /2 torr	C(a) 160.14 C(b) 100.85	H(a) 7.05, J_{HH} = 6 Hz H(b) 5.32	1593(C=C) 1380(SO2)
 **3**	77%	42-43 /2 torr	C(a) 172.37 C(b) 97.14	H(b) 5.46	1590(C=C) 1377(SO_2)
 **4**	78%	48-50	C(a) 160.38 C(b) 112.23	H(a)7.30	1600(C=C) 1370(SO_2)
 **5**	76%	55-56 /2 torr	C(a) 161.31 C(b) 112.30	H(a)7.15	1610(C=C) 1380(SO_2)

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12. analysis data for products **2, 3, 4, 5**

2-E: IR(ν_{max}, cm^{-1}): 3056 (s), 2995, 2980(m), 1600(C=C), 1470(C-H), 1340, 1390,1180(s), 1140(C-F); δ_H(ppm):1.10(t,CH_3,$^3J_{HH}$=8Hz),3.93(q,CH_2O),5.82(d,CH=,$^3J_{HH}$=14Hz),7.35(d,CH=); δ_F(ppm):-77.8 (s,CF_3) δ_C(ppm): 13.50(CH_3), 67.62(OCH_2), 101.85(CH=), 124.62(q, CF_3, $^2J_{CF}$=280Hz), 162.17(OCH=); HRMS for $C_5H_7F_3O_3S$: Calcd: 204.0073 ; Found: 204.0078. **2-Z:** IR(ν_{max}, cm^{-1}): 3066(s), 2960, 2920(m), 1593(s,C=C), 1370(s,SO_2),1280(m),1197,1133,1060(s,C-F); δ_H(ppm): 1.06(t,CH_3,$^3J_{HH}$=8Hz), 3.86(q, OCH_2), 5.32(d, CH=, J_{HH}=6Hz), 7.05(d,CH=); MS(m/z, %): 204(M^+,0.11), 203(M^+-H,0.83), 189(M^+-CH_3,100), 172(M^+-2O 6.32), 119(M^+-O-CF_3,56.07), 91(M^+-O-CF_3-C_2H_4,19.37), 69(CF_3^+,10.28), 45(EtO^+,11.74); HRMS for $C_5H_7F_3O_3S$: Calcd: 204.0073; Found: 204.0078. **3:** IR(ν_{max}, cm^{-1}): 2960, 2920, 1590(C=C), 1450, 1460, 1377(m SO_2), 1198, 1061(s,C-F); δ_H(ppm): 5.46(s,CH=), 3.70(s,OCH_3), 2.10(s,CH_3); δ_F(ppm):-79.6(s, CF_3); δ_C(ppm): 18.30(CH_3), 56.21(OCH_3), 97.14(=$CHSO_2CF_3$), 127.18(q, CF_3, $^2J_{CF}$=280Hz), 172.37(^aC=); MS(m/z,%): 206(M^++2,70.91),174(M^+-2CH_3,1.57),171(M^+-H-2O, 15.22), 137(M^+-SO-F,66.48), 105(M^+-SO_2-F-O,37.41), 69(CF_3^+,27.29), 43($C_2H_3O^+$,100.00). **4:** IR(ν_{max}, cm^{-1}): 3075, 2990(C-H), 1600(C=C), 1370(SO_2), 1200, 1170, 1140(C-F); δ_H(ppm): 3.13(t,CH_2,$^3J_{HH}$=8Hz), 4.73(t,OCH_2), 7.30(s,=CHO); δ_F(ppm): -72.3(s,CF_3); δ_C(ppm): 25.48(CH_2), 73.83(OCH_2), 112.23 (CF_3SO_2C=), 125.95(q,CF_3, $^1J_{CF}$=278HZ), 160.38(OCH=); MS(m/z, %): 202(M^+,0.33), 186(M^+-O, 1.67), 170(M^+-2O,1.25), 119(M^+-F-SO_2,6.57), 117(M^+-CF_3-O or CF_3SO^+,100), 101(CF_3S^+,4.19), 69(CF_3^+, 7.40), 68($C_4H_4O^+$,5.87). **5:** IR(ν_{max}, cm^{-1}): 3066(m), 2970, 2960,1610(s,C=C), 1460(m), 1440(m), 1380(m,SO_2), 1340(m), 1223(m), 1240(s, SO_2), 1180-1080(vs, C-F); δ_H(ppm): 3.86(t, OCH_2,J_{HH}=8Hz), 2.36(t,CH_2), 2.05(m, CH_2), 7.15(s,=CH); δ_F(ppm): -72.3(s,CF_3); δ_C(ppm): 18.53(CH_2), 22.50(CH_2), 86.73(OCH_2), 112.30(CF_3SO_2C=), 126.10 (q,CF_3,$^1J_{CF}$=280HZ), 161.31(OCH=); MS(m/z, %): 215(M^+-1,0.64), 199(M^+-H-O,2.60), 133($CF_3SO_2^+$,6.94) 131(M^+-CF_3-O,100.00), 115(M^+-CF_3-2O,17.60), 69(CF_3^+,8.63)