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SHORT COMMUNICATIONS

Reaction of α*H*,α*H*,ω*H*-Perfluoroalkyl Benzyl Sulfones with Compounds Having an Active Methylene Group

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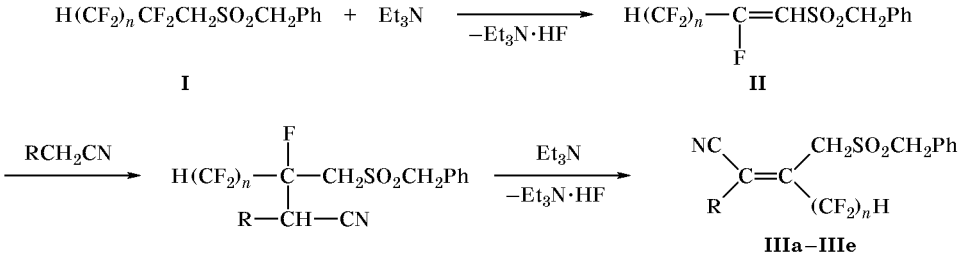
Reaction of electron-deficient olefins with various nucleophilic reagents underlies a well known synthetic route to functionally substituted organic nitrogen, phosphorus, oxygen, and sulfur compounds [1]. Therefore, it is important to search for new methods of synthesis of alkenes having electron-acceptor substituents at the double bond. The present communication reports on a procedure for synthesizing new fluorinated alkenes by reaction of α*H*,α*H*,ω*H*-perfluoroalkyl benzyl sulfones **I** with compounds having an active methylene group. We previsouly described the reaction of sulfones **I** with amines [2–4]. The initial stage in this reaction is dehydrofluorination of sulfone **I** by the action of a base to give vinyl sulfone **II** which then reacts with nucleophiles, following the addition–elimination pattern [3].

We have found that sulfones **I** in the presence of triethylamine react with compounds possessing an active methylene group (such as malononitrile, ethyl cyanoacetate, and 2-cyanomethylbenzothiazole) to give alkenes **IIIa**–**IIIe** (Scheme 1). Compound **IIIb** was isolated as a mixture of isomers with respect to the double bond at a ratio of 3:2, although the reaction mixture (according to the ^{19}F NMR data) contained only one isomer by the end of the process. Presumably, the *Z*,*E* isomerization occurs during recrystallization of the product from boiling carbon tetrachloride. Analogous compound **IIId** with a longer polyfluoroalkyl group was isolated as a single isomer. Only one isomer **IIIe** was also obtained from octafluoropentyl benzyl sulfone and 2-cyanomethylbenzothiazole.

Reaction of polyfluoroalkyl benzyl sulfones I with methylene-active compounds in the presence of triethylamine. To a mixture of 2 mmol of sulfone **I** and 4 mmol (0.56 ml) of triethylamine in 15 ml of benzene we added 2 mmol of malononitrile, ethyl cyanoacetate, or 2-cyanomethylbenzothiazole. The mixture was heated to the boiling point and was kept for 24 h at room temperature. The solvent was distilled off, the residue was treated with water, and the precipitate was filtered off, washed on a filter with 3 ml of diethyl ether, and recrystallized.

[1-(Benzylsulfonylmethyl)-2,2-difluoroethylidene]malononitrile (IIIa). Yield 72%, mp 113–115°C (from $CHCl_3$). ^1H NMR spectrum (acetone-d_6), δ, ppm: 4.69 s (2H, CH_2), 4.82 s (2H, CH_2), 6.99 t (1H, HCF_2, J_{HF} = 53.0 Hz), 7.46 m (3H, H_{arom}),

Scheme 1.



III, *n* = 1, R = CN (**a**), CO_2Et (**b**); *n* = 3, R = CN (**c**), CO_2Et (**d**), 2-benzothiazolyl (**e**).

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7.53 m (2H, H_{arom}). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 54.72 t (=C**C**H_2, $^3J_{CF}$ = 2.9 Hz); 61.70 s (C**H**$_2$Ph); 97.25 t (=**C**CN, $^3J_{CF}$ = 7.0 Hz); 110.30 t (CN, $^4J_{CF}$ = 2.0 Hz); 111.29 t (CN, $^4J_{CF}$ = 1.8 Hz); 111.71 t (HCF_2, J_{CF} = 245.3 Hz); 128.22, 129.71, 130.04, 132.16 s (C_{arom}); 156.89 t (HCF_2**C**=, $^2J_{CF}$ = 23.1 Hz). ^{19}F NMR spectrum (benzene), δ_F, ppm: –118.12 d (2F, HCF_2, $^2J_{HF}$ = 53.0 Hz). Found, %: N 9.48; S 10.74. $C_{13}H_{10}F_2N_2O_2S$. Calculated, %: N 9.45; S 10.82.

Ethyl 3-(benzylsulfonylmethyl)-2-cyano-4,4-difluoro-2-butenoate (IIIb). Yield 56%, mp 120–122°C (from CCl_4). ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.31* t (3H, Me), 1.36 (3H, Me), 4.33* q (2H, CH_2Me), 4.39 q (2H, CH_2Me), 4.55 s (2H, CH_2), 4.64* s (2H, CH_2), 4.70 s (2H, CH_2), 4.87* s (2H, CH_2), 6.94* t (1H, HCF_2, J_{HF} = 53.4 Hz), 7.37 t (1H, HCF_2, J_{HF} = 53.7 Hz), 7.40–7.50 m (5H, H_{arom}). ^{19}F NMR spectrum (benzene), δ_F, ppm: –115.76* d (2F, HCF_2, $^2J_{HF}$ = 53.4 Hz), –116.79 d (2F, HCF_2, $^2J_{HF}$ = 53.7 Hz). Found, %: N 4.14; S 9.27. $C_{15}H_{15}F_2NO_4S$. Calculated, %: N 4.08; S 9.34.

[1-(Benzylsulfonylmethyl)-2,2,3,3,4,4-hexafluorobutylidene]malononitrile (IIIc). Yield 77%, mp 134–136°C (from $CHCl_3$). ^1H NMR spectrum (acetone-d_6), δ, ppm: 4.78 s (2H, CH_2), 4.85 s (2H, CH_2), 6.85 t.t (1H, HCF_2, $^2J_{HF}$ = 51.3 Hz, $^3J_{HF}$ = 5.3 Hz), 7.46 m (3H, H_{arom}), 7.54 m (2H, H_{arom}). ^{13}C NMR spectrum (acetone-d_6), δ, ppm: 55.57 s (=C**C**H_2); 62.61 s (**C**H_2Ph); 101.11 t (=**C**CN, $^3J_{CF}$ = 6.4 Hz); 109.03 t.t (HCF_2, J_{CF} = 252.8 Hz, $^2J_{CF}$ = 30.6 Hz); 110.24 s (CN); 111.31 s (CN); 111.89 t.m (HCF_2**C**F_2, J_{CF} = 262.4 Hz); 112.38 t.t (**C**F_2C=, J_{CF} = 260.5 Hz, $^2J_{CF}$ = 32.6 Hz); 128.12, 129.73, 130.11, 132.17 s (C_{arom}); 150.85 t (HCF_2**C**=, $^2J_{CF}$ = 24.4 Hz). ^{19}F NMR spectrum (benzene), δ_F, ppm: –110.85 m (2F, CF_2), 127.45 m (2F, CF_2), 136.44 d.m (HCF_2, $^2J_{HF}$ = 51.3 Hz). Found, %: N 7.15; S 8.28. $C_{15}H_{10}F_6N_2O_2S$. Calculated, %: N 7.07; S 8.09.

Ethyl 3-benzylsulfonylmethyl-2-cyano-4,4,5,5,-6,6-hexafluoro-2-hexenoate (IIId). Yield 88%, mp 135–137°C (from CCl_4). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 t (3H, Me), 4.39 s (2H, CH_2), 4.40 q (2H, CH_2Me), 4.58 s (2H, CH_2), 6.11 t.t (1H, HCF_2, $^2J_{HF}$ = 51.9 Hz, $^3J_{HF}$ = 5.2 Hz), 7.45 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.88 s (Me); 50.87 s (=C**C**H_2); 63.07 s (CH_2Me); 64.54 s (**C**H_2Ph); 107.66 t.t (HCF_2, J_{CF} = 255.0 Hz, $^2J_{CF}$ = 31.1 Hz); 110.94 t.m (HCF_2**C**F_2, J_{CF} = 263.3 Hz); 111.82 s (CN); 113.88 t.t (**C**F_2C=, J_{CF} = 260.8 Hz, $^2J_{CF}$ = 33.1 Hz); 118.62 t (=**C**CN, $^3J_{CF}$ = 4.3 Hz); 126.92, 129.39, 129.80, 131.02 s (C_{arom}); 143.06 t (HCF_2**C**=, $^2J_{CF}$ = 23.6 Hz). ^{19}F NMR spectrum (benzene), δ_F, ppm: –112.15 m (2F, CF_2), 128.69 m (2F, CF_2), 137.50 d.m (HCF_2, $^2J_{HF}$ = 51.9 Hz). Found, %: N 3.05; S 7.12. $C_{17}H_{15}F_6NO_4S$. Calculated, %: N 3.16; S 7.23.

2-(2-Benzothiazolyl)-3-benzylsulfonylmethyl-4,4,5,5,6,6-hexafluoro-2-hexenenitrile (IIIe). Yield 81%, mp 189–191°C (from CCl_4). ^1H NMR spectrum (acetone-d_6), δ, ppm: 4.79 s (2H, CH_2), 5.43 s (2H, CH_2), 6.89 t.t (1H, HCF_2, $^2J_{HF}$ = 51.0 Hz, $^3J_{HF}$ = 5.4 Hz), 7.40 m (5H, H_{arom}), 7.70 m (2H, H_{arom}), 8.19 d.m (1H, H_{arom}), 8.29 d.m (1H, H_{arom}). ^{19}F NMR spectrum (acetone), δ_F, ppm: –108.26 m (2F, CF_2), 126.74 m (2F, CF_2), 136.92 d.m (HCF_2, $^2J_{HF}$ = 51.0 Hz). Found, %: N 5.52; S 13.08. $C_{21}H_{14}F_6N_2O_2S_2$. Calculated, %: N 5.55; S 12.71.

The NMR spectra were recorded on a Varian VXR-300 spectrometer at 299.9 (^1H), 75.4 (^{13}C), and 282.2 MHz (^{19}F) using acetone (^1H 2.05 ppm, ^{13}C 29.84 ppm), chloroform (^1H 7.26 ppm, ^{13}C 77.16 ppm), and hexafluorobenzene signals (^{19}F –162.9 ppm) as reference.

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* Major isomer.