Cascade rearrangement in the reaction of methyl trifluoropyruvate sulfonylimines with terminal alkynes

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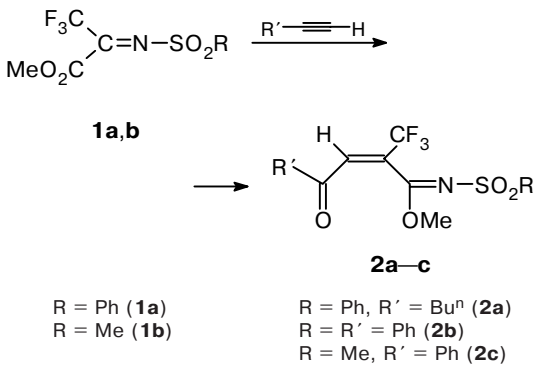
Methyl trifluoropyruvate benzene- and methanesulfonylimines react with hex-1-yne and phenylacetylene to give methyl *N*-sulfonyl-4-oxo-2-trifluoromethyl-4-R-but-2*E*-enimidates. The reaction mechanism includes the formation of a six-centered bipolar ion followed by its cascade rearrangement.

Key words: methyl trifluoropyruvate sulfonylimines, terminal alkynes, cascade rearrangement, methyl *N*-sulfonyl-4-oxo-2-trifluoromethyl-4-R-but-2*E*-enimidates.

Methyl trifluoropyruvate benzene- and methanesulfonylimines (**1a**,**b**)[1,2] regiospecifically react under mild conditions (−50—20 °C) with aromatic and heteroaromatic π-donors (*N*,*N*-dialkylanilines, *N*-alkylanilines, indoles, pyrazol-2-ones, *etc.*) to give *C*-amidoalkylation products in high yields.[3] It has recently been shown[4] that sulfonylimines **1a**,**b** react under the same conditions with 2-methylpropene, 2-phenylpropene, methylidenecycloalkanes, and other π-donor components of ene reactions to yield imino-ene reaction products.

In this communication, we present the results of studies on the reactions of sulfonylimines **1a**,**b** with hex-1-yne and phenylacetylene.

Scheme 1



Results and Discussion

Hex-1-yne and phenylacetylene manifest moderate π-withdrawing properties with the electrophilic center at the C(1) atom. They react with imines **1a**,**b** in an anomalous way both at elevated (80—100 °C) and room temperatures. In both cases, the only reaction products are *N*-sulfonyl-4-oxo-2-trifluoromethyloct-2*E*-enimidate (**2a**) and *N*-sulfonyl-4-oxo-4-phenyl-2-trifluoromethylbut-2*E*-enimidates (**2b**,**c**) (Scheme 1).

Compounds **2a**—**c** are colorless crystalline substances with clearly defined melting points; they slowly decompose by atmospheric moisture. Their compositions and structures were confirmed by elemental analysis and by ^{1}H, ^{19}F, and ^{13}C NMR data. The $^4J_{H,F}$ value in the ^{1}H NMR spectra of compounds **2a**—**c** is very low (0.6 Hz) suggesting the *cis*-arrangement of the H atom and the CF_3 group. For compound **2a**, this was confirmed by X-ray diffraction analysis (Fig. 1).

The formation of imidates **2a**—**c** can be explained by the fact that in the reactions with alkynes imines **1a**,**b** behave like highly electrophilic O=C—C=N— heterodiene systems. The (2+4) interaction is a non-concerted process with an early electron transfer, proceeding *via* an intermediate six-centered bipolar ion **3**. Specific

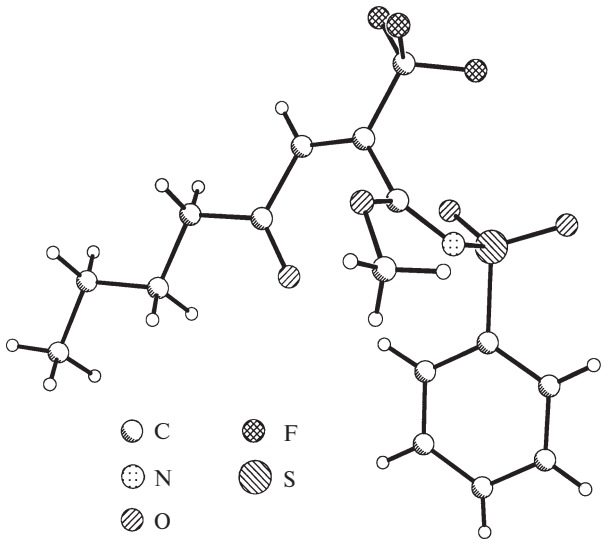


Fig. 1. Structure **2a** according to X-ray diffraction data.

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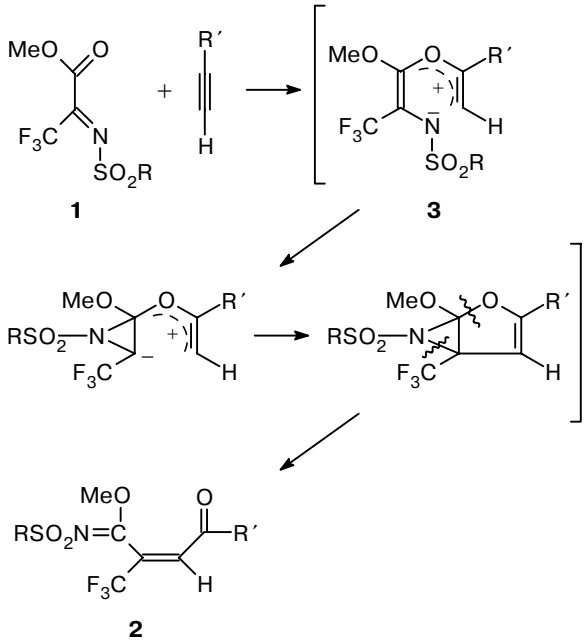
effects of the CF_3 group favor a spontaneous 1,2-shift of the *N*-sulfonylimino group and a 2,3-shift of the alkenyloxy groups, which results in the stereospecific formation of the *E*-double bond (Scheme 2).

Scheme 2



This reaction mechanism suggests that terminal alkynes, unlike typical π-donors, do not enter into charge-controlled concerted reactions with the C=N bond of methyl trifluoropyruvate sulfonylimines. In this case, (2π+4π) interaction followed by an unusual cascade rearrangement proved to be more favorable.

Experimental

Freshly distilled starting reagents and anhydrous CH_2Cl_2 and hexane were used. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 spectrometer (400 and 100 MHz, respectively). ^{19}F NMR spectra were recorded on a Bruker WR-200-SY instrument (188 MHz). The chemical shifts were referenced to HMDS as the internal standard and to trifluoroacetic acid as the external standard.

Synthesis of compounds 2a—c with heating (general procedure). A solution of sulfonylimine **1** (3 mmol) and an alkyne (6 mmol) in 2 mL of anhydrous CH_2Cl_2 was heated in a sealed tube at 100 °C for 3.5 h. The solvent and the excess of the alkyne were removed *in vacuo*, and the residue was recrystallized from hexane.

Methyl *N*-phenylsulfonyl-4-oxo-2-trifluoromethyloct-2*E*-enimidate (2a). Yield 92%, m.p. 79—80 °C. Found (%): C, 51.03; H, 4.62; N, 3.73. $C_{16}H_{18}F_3NO_4S$. Calculated (%): C, 50.92; H, 4.77; N, 3.71. ^1H NMR ($CDCl_3$), δ: 0.91 (t, 3 H, Me, J = 7.2 Hz); 1.35, 1.60 (both m, 2 H each, CH_2); 2.66 (t, 2 H, CH_2, J = 7.2 Hz); 3.92 (s, 3 H, OMe); 6.87 (q, 1 H, =CH, J = 0.6 Hz); 7.49, 7.57, 7.88 (all m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 13.53 (Me); 21.78, 24.89, 43.38 (all CH_2); 56.73 (OMe); 120.39 (q, CF_3, J = 131.0 Hz); 132.04 (q, =CH, J = 2.0 Hz); 133.08 (q, =C—CF_3, J = 18.6 Hz); 126.74, 128.59, 132.74, 140.48 (C arom.); 163.37 (C=N); 197.03 (C=O). ^{19}F NMR ($CDCl_3$), δ: −14.38 (s, CF_3).

Methyl *N*-phenylsulfonyl-4-oxo-4-phenyl-2-trifluoromethylbut-2*E*-enimidate (2b). Yield 86%, m.p. 103—105 °C. Found (%): C, 54.23; H, 3.67; N, 3.49. $C_{18}H_{14}F_3NO_4S$. Calculated (%): C, 54.41; H, 3.53; N, 3.53. ^1H NMR ($CDCl_3$), δ: 3.97 (s, 3 H, OMe); 7.51 (q, 1 H, =CH, J = 0.6 Hz); 7.33, 7.53, 7.65, 7.85, 7.95 (all m, 10 H, 2 Ph). ^{13}C NMR ($CDCl_3$), δ: 56.85 (OMe); 120.02 (q, CF_3, J = 145.0 Hz); 129.52 (q, =CH, J = 2.2 Hz); 135.50 (q, =C—CF_3, J = 18.1 Hz); 126.83, 128.53, 128.65, 128.86, 132.71, 134.37, 135.63, 140.23 (C arom.); 163.51 (C=N); 186.47 (C=O). ^{19}F NMR ($CDCl_3$), δ: −14.47 (s, CF_3).

Methyl *N*-methylsulfonyl-4-oxo-4-phenyl-2-trifluoromethylbut-2*E*-enimidate (2c). Yield 83%, m.p. 88—90 °C. Found (%): C, 46.50; H, 3.48; N, 4.23. $C_{13}H_{12}F_3NO_4S$. Calculated (%): C, 46.57; H, 3.58; N, 4.18. ^1H NMR ($CDCl_3$), δ: 3.05 (s, 3 H, Me); 4.02 (s, 3 H, OMe); 7.60 (q, 1 H, =CH, J = 0.6 Hz); 7.52, 7.65, 7.95 (all m, 5 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 41.67 (Me); 56.73 (OMe); 120.37 (q, CF_3, J = 135.1 Hz); 129.61 (q, =CH, J = 2.2 Hz); 135.29 (q, =C—CF_3, J = 18.3 Hz); 125.68, 128.64, 128.87, 134.40 (C arom.); 164.05 (C=N); 186.83 (C=O). ^{19}F NMR ($CDCl_3$), δ: −14.36 (s, CF_3).

Synthesis of compounds 2a,b under mild conditions. A mixture of sulfonylimine **1** (3 mmol) and an alkyne (6 mmol) was kept with exclusion of moisture at ~20 °C for 40 days. The crystals that formed were filtered off and washed with hexane (3×2 mL). The filtrate was concentrated *in vacuo*, and the residual solid mass was recrystallized from hexane to give an additional amount of the product. The yield of **2a** was 0.42 g (46%), m.p. 80—81 °C. ^{19}F NMR ($CDCl_3$), δ: −14.37 (s, CF_3). A mixture of **2a** with an authentic sample did not depress the melting point. The yield of **2b** was 0.69 g (58%), m.p. 104—105 °C. ^{19}F NMR ($CDCl_3$), δ: −14.48 (s, CF_3). A mixture of **2b** with an authentic sample did not depress the melting point.

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