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Homo and Hetero Glaser Coupling Involving Acetylene Derivatives of Trifluoromethanesulfonamide

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Abstract—Glaser homocoupling of *N*,*N*-bispropargyltriflamide led to the formation of *N*,*N*'-hexa-2,4-diyne-1,6-diylbis(*N*-prop-2-yne-1-triflamide). Further condensation into a 14-membered heterocycle, 1,8-bis-(triflyl)-1,8-diazacyclotetradeca-3,5,10,12-tetrayne did not occur evidently because of rigid steric requirements to the cyclization. In the Glaser heterocoupling of *N*-propargyltriflamide with arylacetylenes ArC≡CH (Ar = Ph, *p*-CNC_6H_4) the condensation products formed in 20–30% yields.

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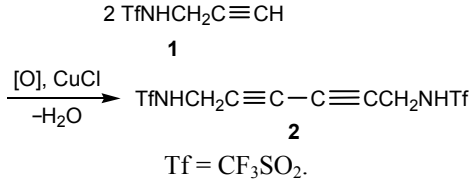
Highly unsaturated trifluoromethanesulfonamide (triflamide $TfNH_2$) are interesting both due to their electronic structure and from the viewpoint of their synthetic potential as building blocks in the organic synthesis. In particular, the derivatives possessing terminal acetylene groups are able to undergo the oxidative dimerization into the corresponding diacetylenes that may be further used in cyclocondensation reactions for the preparation of diverse adducts and functionalized heterocycles. We formerly demonstrated that *N*-propargyltriflamide **1** [1] cleanly dimerized in oxidative conditions at room temperature in water giving *N*,*N*'-hexa-2,4-diyne-1,6-diylbis(triflamide) **2** [2] (Scheme 1).

Scheme 1.

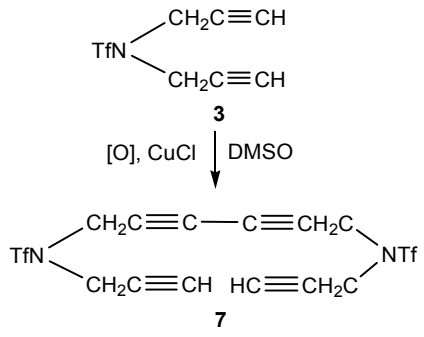


Tf = CF_3SO_2.

In continuation of these studies and in order to expand the family of triflamide diacetylene derivatives in the present work we have studied the oxidative dimerization of *N*,*N*-bispropargyltriflamide **3** (Glaser homo-coupling) and the possibility of cross dimerization of *N*-propargyltriflamide **1** with acetylenes ArC≡CH [Ar = Ph (**4**), *p*-CNC_6H_4 (**5**), *p*-$NO_2C_6H_4$ (**6**)] (Glaser heterocoupling).

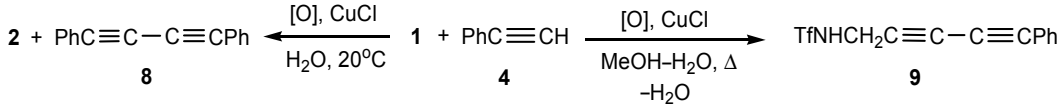
Although the oxidative acetylene dimerization is well known [3], the successive achievement of both mentioned reactions required the selection of special conditions. For instance, unlike the easily dimerized *N*-propargyltriflamide **1** [2], *N*,*N*-bispropargyltriflamide **3** [4] does not afford the product of condensation at room temperature even at 4–5-fold longer reaction time (up to 10 h). The reaction was achieved only after prolonged heating to 70°C in the presence of 20 mol % CuCl with a low preparative yield of *N*,*N*'-hexa-2,4-diyne-1,6-diylbis(*N*-prop-2-yne-1-triflamide) **7** (20%) isolated by column chromatography (Scheme 2).

Scheme 2.



The reaction was accompanied with strong resinification apparently due to the presence of terminal

Scheme 3.



acetylene groups in compounds **3** and **7** that reduced the yield of the target product. Unlike dimer **2** [2] compound **7** is a liquid readily soluble in chloroform. Its structure and composition are proved by IR and NMR spectra and the data of elemental analysis, in particular, by the presence in the ^{1}H NMR spectrum of characteristic doublet and triplet signals of the terminal propargyl group $CH_2C{\equiv}CH$ and of a singlet of the methylene protons of the internal propargyl group $CH_2C{\equiv}C–$, and the appearance in the ^{13}C NMR spectrum of two signals of the methylene groups and four signals of nonequivalent acetylene carbon atoms in the region 70–76 ppm, as well as of a quartet of the CF_3 group. The IR spectrum contains the absorption bands of vibrations ν(≡CH) at 3301 cm^{-1} and ν(C≡C) at 2131 cm^{-1} of weak intensity caused by the symmetric structure of the linear fragment C–C≡C–C≡C–C in the molecule.

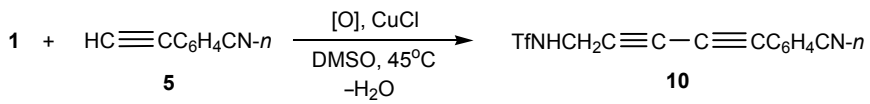
Reaction (2) (Scheme 2) proceeds in homogeneous conditions and does not require the use of the complex CuCl–NH_4Cl, which was necessary in the heterogeneous reaction (1) (Scheme 1). Variation of CuCl concentration did not affect the yield of compound **7**. Its further oxidative condensation by the corresponding 14-membered heterocycle, 1,8-bis(triflyl)-1,8-diazacyclotetradeca-3,5,10,12-tetrayne was not observed apparently because the conformation of compound **7** "prepared" to this condensation and shown in Eq. (2) (Scheme 2) was less sterically favorable than the conformation with the terminal acetylene group turned away for each other. The distinction of reaction (2) occurring in the presence of 20 mol % of CuCl from reaction (1), requiring a double excess of CuCl [2] is probably due to the presence of an acidic NH proton in molecule **1** and its absence in molecule **3**. As a result in the former case the formation of a copper complex with elimination of the acetylene proton is possible only in the presence of excess CuCl, after binding of equimolar amount of CuCl and elimination of more acidic NH proton.

N-Propargyltriflamide **1**, which practically quantitatively dimerizes under heterophase conditions at room temperature as shown in reaction (1) does not enter cross-coupling with phenylacetylene **4** under the same conditions. Only homocondensation products were isolated: diphenyldiacetylene PhC≡CC≡CPh **8** and dimer **2**. It is presumably due to the impeding by the strong acceptor *N*-triflyl group the interaction of the copper complex both with *N*-propargyltriflamide and phenylacetylene, and therefore the cross-coupling requires more stringent conditions. Cross-coupling **3** + **4** with the formation of *N*-(5-phenylpenta-2,4-diyn-1-yl)-triflamide **9** in 30% yield was successfully carried out in the presence of double excess of CuCl in aqueous methanol at heating to 40°C no longer than 4 h (Scheme 3).

In the reaction of *N*-propargyltriflamide **1** with 4-ethynylbenzonitrile **5** at 50°C in aqueous methanol only dimer **2** and products of resinification of 4-ethynylbenzonitrile **5** were obtained. Cross-coupling **1** + **5** with the formation of *N*-[5-(4-cyanophenyl)penta-2,4-diyne-1-yl]triflamide **10** in 20% yield was achieved in DMSO at heating to 45°C for 8 h in the presence of 30% excess of CuCl (Scheme 4). The increase of the CuCl concentration does not affect the yield of the coupling product **10**. At room temperature the reaction does not occur, at raising the temperature to 55°C, same as in aqueous methanol, only dimer **2** and products of resinification of 4-ethynylbenzonitrile **5** were formed. At yet higher temperature (up to 70°C) resinification occurs both with *N*-propargyltriflamide **1** and 4-ethynylbenzonitrile **5**.

Cross-coupling product **10** was isolated by column chromatography; it was a solid substance, well soluble in chloroform, its structure and composition were proved by IR and NMR spectra and by elemental analysis data. In the ^{13}C NMR spectrum of compound **10**, like in that of compound **9**, four signals appeared of nonequivalent acetylene carbon atoms, but three of

Scheme 4.



them in the region 76.6–77.3 ppm overlapped with the solvent (chloroform) signal, therefore the structure **10** was unambiguously proved by registering the ^{13}C NMR spectrum in methanol-d_4.

In reaction of *N*-propargyltriflamide **1** with 4-ethynylnitrobenzene **6** it was impossible to isolate neither the reaction products nor initial compounds due to strong resinification in any applied conditions.

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker DPX 400 at operating frequencies 400 (^1H), 100 (^{13}C), 386 (^{19}F) MHz in $CDCl_3$. The chemical shifts are reported with respect to TMS (^1H, ^{13}C) and CCl_3F (^{19}F).

***N*,*N*′-Hexa-2,4-diyne-1,6-diylbis(*N*-prop-2-yne-1-trifluoromethanesulfonamide) (7).** To a solution of 1 g (4 mmol) of *N*,*N*-bispropargyltriflamide **3**, synthesized by procedure [4], in 10 mL of DMSO was added 80 mg (8 mmol) of CuCl. The reaction mixture was stirred for 8 h at 70°C, poured in water, filtered, the filtrate was extracted with chloroform, the precipitate was washed with a small quantity of chloroform, the combined extracts were washed with water, dried with $MgSO_4$, evaporated, the residue was purified by column chromatography on silica gel (70 mesh), eluent hexane–chloroform, 1 : 3. Yield 0.35 g (20%), yellowish oily liquid. IR spectrum (film), ν, cm^{-1}: 3301 (≡C–H), 2985, 2926, 2854, 2131 (C≡C), 1396, 1340, 1230, 1197, 1147, 1078, 955, 905, 781, 607, 521. ^1H NMR spectrum, δ, ppm: 2.48 t (1H, ≡CH, *J* 2.0 Hz), 4.33 d (2H, HC≡CC$\underline{H}_2$, *J* 2.0 Hz), 4.44 s (2H, C≡CCH_2). ^{13}C NMR spectrum, δ, ppm: 37.62 (C≡C$\underline{C}H_2$), 37.81 (HC≡C$\underline{C}H_2$), 70.00 (C≡$\underline{C}CH_2$), 71.38 (HC≡$\underline{C}CH_2$), 74.86 (C≡$\underline{C}$–$\underline{C}$≡C), 75.61 (C≡$\underline{C}$H), 119.62 q (CF_3, J_{CF} 322.3 Hz). ^{19}F NMR spectrum: δ –75.55 ppm. Found, %: C 37.12; H 2.42; F 25.53; N 6.65; S 14.24. $C_{14}H_{10}F_6N_2O_4S_2$. Calculated, %: C 37.50; H 2.25; F 25.42; N 6.25; S 14.30.

Reaction of *N*-propargyltrifluoromethanesulfonamide (1) with phenylacetylene (4) in water solution. To a solution of 0.33 g (25 mmol) of NH_4Cl and 0.98 g (10 mmol) of CuCl in 10 mL of water was added dropwise 1 g (5 mmol) of *N*-propargyltriflamide **1** [1] and 0.51 g (5 mmol) of phenylacetylene. The reaction mixture was stirred for 4 h at room temperature, filtered, the filtrate was extracted with ethyl ether, the formed precipitate was washed with, a small amount of ether. The combined ether extracts were dried with $MgSO_4$ and evaporated, the solid residue was chromatographed on a column packed with silica gel (70 mesh), eluent dichloromethane–hexane, 1 : 3, separating the homodimerization products, *N*,*N*′-hexa-2,4-diyne-1,6-diylbis(trifluoromethanesulfonamide) **2** and diphenyldiacetylene **8**. Their composition and spectral characteristics are consistent with the data previously published in [4] (**2**) and [5] (**8**).

***N*-(5-Phenylpenta-2,4-diyn-1-yl)trifluoromethanesulfonamide (9).** To a solution of 0.54 g (10 mmol) of NH_4Cl and 0.98 g (10 mmol) of CuCl in 10 mL of water was added dropwise a solution of 1 g (5 mmol) of *N*-propargyltriflamide **1** [1] and 0.51 g (5 mmol) of phenylacetylene in 5 mL of methanol. The reaction mixture was stirred for 4 h at 40°C, filtered, the filtrate was extracted with chloroform, the precipitate was washed with a small amount of chloroform. The combined extracts were dried with $MgSO_4$ and evaporated, the residue was chromatographed on a column packed with silica gel (70 mesh), eluent ethyl acetate–hexane, 1 : 3. Yield 0.42 g (30%), mp 63°C. IR spectrum (KBr), ν, cm^{-1}: 3322 (NH), 3084, 3065, 2973, 2893, 2251 (C≡C), 2216 (C≡C), 1490, 1377, 1233, 1198, 1145, 1056, 990, 849, 757, 690, 609, 526, 514. ^1H NMR spectrum, δ, ppm: 4.27 d (2H, CH_2, *J* 5.6 Hz), 5.40 br.s (1H, NH), 7.32–7.43 m (3H^{m+p}), 7.52 d (2H^o, *J* 7.1 Hz). ^{13}C NMR spectrum, δ, ppm: 34.97 (CH_2), 70.74 (NC$\underline{C}$), 72.70 (CH_2C≡$\underline{C}$), 74.89 (Ph$\underline{C}$≡C), 79.16 (PhC≡$\underline{C}$), 119.57 q (CF_3, J_{CF} 320.8 Hz), 120.99 (C^i), 128.60 (C^m), 129.81 (C^p), 132.82 (C^o). ^{19}F NMR spectrum: δ –76.91 ppm Found, %: C 50.43; H 2.70; F 20.48; N 4.54; S 11.32. $C_{12}H_8F_3NO_2S$. Calculated, %: C 50.17; H 2.81; F 19.84; N 4.88; S 11.16.

Trifluoro-*N*-[5-(4-cyanophenyl)penta-2,4-diyn-1-yl]methanesulfonamide (10). To a solution of 1 g (5 mmol) of *N*-propargyltriflamide **1** [1] and 0.63 g (5 mmol) of 4-ethynylbenzonitrile **5** in 10 mL of DMSO was added 0.64 g (6.5 mmol) of CuCl. The reaction mixture was stirred for 8 h at 45°C, poured in water, filtered, the filtrate was extracted with chloroform, the precipitate was washed with a small amount of chloroform. The combined extracts were washed with water, dried with $MgSO_4$, and evaporated, the residue was chromatographed on a column packed with silica gel (70 mesh), eluent hexane–chloroform, 1 : 1. Yield 0.31 g (20%), mp 98–99°C. IR spectrum (film), ν, cm^{-1}: 3309, 2963, 2925, 2855, 2233, 2172, 2145, 2077, 1603, 1440, 1379, 1232, 1198, 1059, 840, 612, 556. ^1H NMR spectrum, δ,

ppm: 4.29 d (2H, CH_2, *J* 5.8 Hz), 5.36 br.s (1H, NH), 7.59 d (2H, $H^{3,5}$, *J* 8.3 Hz), 7.65 d (2H, $H^{2,6}$, *J* 8.3 Hz). ^{13}C NMR spectrum, δ, ppm: 34.79 (CH_2), 69.76 (NC≡C), 76.64 (CH_2C≡C), 76.68 (PhC≡C), 77.30 (PhC≡C), 112.92 (C^4), 118.18 (C≡N), 125.96 (C^1), 132.25 ($C^{3,5}$), 133.22 ($C^{2,6}$). Since in $CDCl_3$ the CF_3 quartet was not observed and the signals of the acetylene carbon atoms were overlapped with the peak of the solvent, the spectrum of compound was registered in CD_3OD solution. ^{13}C NMR spectrum (CD_3OD), δ, ppm: 34.57 (CH_2), 68.76 (NC≡C), 76.83 (CH_2C≡C), 77.33 (PhC≡C), 80.40 (PhC≡C), 114.00 (C^4), 119.01 (C≡N), 121.19 q (CF_3, J_{CF} 320.1 Hz), 127.31 (C^1), 133.46 ($C^{3,5}$), 134.33 ($C^{2,6}$). ^{19}F NMR spectrum: δ −78.56 ppm. Found, %: C 49.61; H 2.46; F 24.98; N 8.92; S 10.04. $C_{13}H_7F_3N_2O_2S$. Calculated, %: C 50.00; H 2.26; F 25.42; N 8.97; S 10.27.

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