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SHORT COMMUNICATIONS

Reactions of *N*-Allyl- and *N*-Propargyltriflimides with *N*,*N*′-Disubstituted Carbodiimides

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Abstract—The alkylating activity of *N*-allyl- and *N*-propargyltriflimides toward *N*,*N*′-dicyclohexyl- and *N*,*N*′-diphenylcarbodiimides has been studied. Activation of the nitrogen atom by two electron-withdrawing trifluoromethanesulfonyl groups favors cleavage of the C–N bond in the absence of a catalyst with the formation of *N*-substituted unsaturated ureas.

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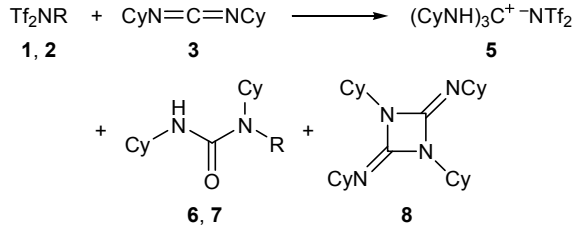
Unsaturated triflimide derivatives of the general formula Tf_2NR (Tf = CF_3SO_2, R = CH=CHR′, $CH_2CH=CH_2$, $CH_2C\equiv CH$) are interesting compounds from the viewpoints of both their synthetic potential and probable tautomeric transformations. Their molecules contain two strong electron-withdrawing trifluoromethanesulfonyl groups on the nitrogen atom, which could considerably extend synthetic potential of unsaturated triflimide derivatives. Prior to our studies in this field [1], only *N*-vinyltriflimides (**I**, $Tf_2NCH=CHAlk$) [2] and *N*-allyltriflimide (**II**, $Tf_2NCH_2CH=CH_2$) [3, 4] have been described. *N*-Vinyltriflimides were formed as minor products in the reactions of triflimide potassium salt with (*E*)-1-alkenyl-(4-trifluoromethylphenyl)-λ^3-bromanes, the major products being the corresponding *O*-vinyl isomers $TfN=S(O)(CF_3)OCH=CHAlk$ [2]. Crude *N*-allyltriflimide was isolated as a brown oily material in the reaction of allylamine with trifluoromethanesulfonic anhydride [3, 4]; the pure compound obtained after distillation was a colorless liquid [1].

In continuation of our studies on unsaturated triflimide derivatives [1, 5], herein we report the reactions of *N*-propargyl- and *N*-allyltriflimides **1** and **2** with *N*,*N*′-dicyclohexyl- and *N*,*N*′-diphenylcarbodiimides **3** and **4**.

In the reaction of pure compounds **1** and **3** at a ratio of 1:1 at room temperature, the conversion was 20% after 5 days; the conversion increased to 55% when 2 equiv of **3** was used. We failed to increase the conversion by carrying out the reaction in a solvent (methylene chloride or chloroform), adding $Y(OTf)_3$ as catalyst, or heating to 50–60°C. NMR analysis of the reaction mixture showed the presence of three compounds. *N*,*N*′,*N*″-Tricyclohexylguanidinium bis(trifluoromethanesulfonyl)imide (**5**) was identified by the signal at δ_F –78.54 ppm in the ^{19}F NMR spectrum of the product mixture, which coincided with that of a sample of **5** prepared by us previously [6]. By column chromatography we also isolated *N*,*N*′-dicyclohexyl-*N*-propargylurea **6** and *N*,*N*′-(1,3-dicyclohexyl-1,3-diazetidine-2,4-diylidene)dimethanamine **8**; the ratio **5**:**6**:**8** was 3:1:5 (Scheme 1). Compound **8** is a dimer of **3** which is likely to be formed under catalysis by triflimide present in the reaction mixture, by analogy with the dimerization of **3** catalyzed by tetrafluoroboric acid [7, 8].

The NMR spectral data and melting point of **8** coincided with those reported for *N*,*N*′-dicyclohexylcarbodiimide dimer obtained by treatment of the solid

Scheme 1.



1, **6**, R = $CH\equiv CCH_2$; **2**, **7**, $CH_2=CHCH_2$.

monomer with SO_2 [9], as well as for the minor product in the peptide synthesis with 1-hydroxybenzotriazole [10] or by-product in the esterification with carbodiimide **3** as dehydrating agent [11].

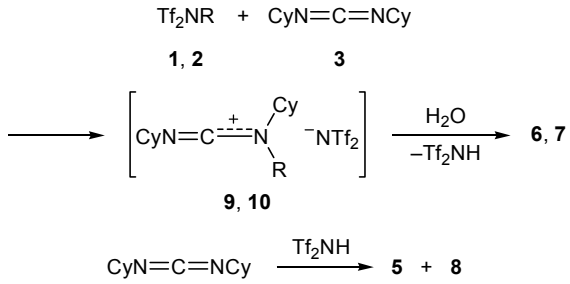
The reaction of *N*-allyltriflimide **2** with carbodiimide **3** at a ratio of 1:2 at room temperature was characterized by a conversion of higher than 95%, and the products were *N*-allyl-*N*,*N*′-dicyclohexylurea **7** and compounds **5** and **8** at a ratio of 1:1:1.

The structure of the products was proved by IR and ^{1}H, ^{13}C, and ^{19}F NMR spectra and elemental analyses. The IR spectra of ureas **6** and **7** contained a carbonyl stretching band at 1626 and 1622 cm^{-1}, respectively, which almost coincided with the $\nu_{C=O}$ band of *N*,*N*′-dicyclohexylurea (1626 cm^{-1}). The IR spectrum of **6** also contained $\nu_{C\equiv C}$ (2111 cm^{-1}) and ν_{C-H} bands (3309 cm^{-1}) typical of terminal alkynes. The asymmetric structure of **6** and **7** followed from the presence in their ^{1}H NMR spectra of two NCH signals belonging to two nonequivalent cyclohexyl groups; these signals appeared ~0.5 and 0.7 ppm downfield relative to the corresponding signal of initial carbodiimide **3**. In the spectrum of **6**, the CH_2 and ≡CH signals were located in a stronger field (Δδ = ~0.8 and 0.3 ppm, respectively) relative to those of *N*-propargyltriflimide. The direction of the double bond polarization in **7** was the same as in **2**. The allyl protons in **7** resonated in a stronger field (by ~0.95, 0.15, and 0.2 ppm for CH_2, CH=, and $=CH_2$, respectively) relative to the corresponding protons of *N*-allyltriflimide. In the ^{13}C NMR spectrum of **6**, signals of carbon atoms of the propargyl group were located at δ_C 34, 72, and 81 ppm, and the allyl carbon nuclei in **7** gave rise to signals at δ_C 49, 116, and 136 ppm. The carbonyl carbon nucleus of both compounds **6** and **7** resonated at δ_C 157 ppm.

Our results suggest a reaction mechanism involving nucleophilic substitution of nucleofugal triflimide residue in molecule **1** or **2** by the action of *N*,*N*′-dicyclohexylcarbodiimide with intermediate formation of salt **9** or **10**. Hydrolysis of the latter in the presence of atmospheric moisture yields *N*-substituted *N*,*N*′-dicyclohexylurea **6** or **7** and triflimide molecule. Nucleophilic substitution in triflimides with saturated substituents on the nitrogen atom has been reported [12–15]. Triflimide reacts with *N*,*N*′-dicyclohexylcarbodiimide according to the mechanism proposed in [6] to give salt **5** and, by analogy with [7, 8], catalyzes dimerization of *N*,*N*′-dicyclohexylcarbodiimide with the formation of compound **8** (Scheme 2).

Unsaturated triflimide derivatives **1** and **2** did not react with *N*,*N*′-dicyclohexylurea under analogous conditions. Compound **1** failed to react with *N*,*N*′-diphenylcarbodiimide (**4**). The low reactivity of *N*,*N*′-diarylcarbodiimides compared to their *N*,*N*′-dialkyl analogs was noted in some publications; in particular, this was observed in the reactions with triflamide leading to guanidines, catalyzed by CuCl and under mechanical activation (liquid-assisted grinding) [16]. The alkylation of *N*,*N*′-diphenylcarbodiimide (**4**) with *N*-allyltriflimide (**2**) follows Scheme 1; however, we failed to isolate analytically pure *N*-allyl-*N*,*N*′-diphenylurea (**11**), and it was characterized only by ^{1}H NMR. Compound **11** underwent hydrolysis to *N*,*N*′-diphenylurea and allyl alcohol during attempted isolation by column chromatography. No diphenylcarbodiimide dimer was formed in this reaction.

Scheme 2.



1, **6**, **9**, R = CH≡CCH$_2$; **2**, **7**, **10**, CH$_2$=CHCH$_2$.

Thus, the reaction of *N*-allyl- and *N*-propargyltriflimides with *N*,*N*′-dicyclohexyl- and *N*,*N*′-diphenylcarbodiimides provides a new method of synthesis of unsaturated *N*-substituted ureas which can be subjected to further modification through the multiple bonds.

Reactions of *N*,*N*′-dicyclohexylcarbodiimide with *N*-propargyl- and *N*-allyltriflimides (*general procedure***).** A mixture of *N*,*N*′-dicyclohexylcarbodiimide and compound **1** or **2** at a ratio of 2:1 was stirred for 5 days at room temperature. Unreacted *N*-substituted triflimide was removed under reduced pressure (0.2 mm) at 40°C, and the residue (~0.5 g) was dissolved in a small amount of chloroform. Compound **8** and *N*-substituted urea **6** or **7** were isolated by column chromatography on silica gel (0.125–0.200 mm) using hexane–ethyl acetate (4:1 for **6** or 5:3 for **7**) as eluent.

***N*,*N*′-(1,3-Dicyclohexyl-1,3-diazetidine-2,4-diylidene)dimethanamine (8).** Yield ~10%, colorless crystals, mp 115–120°C; published data [9]: mp 115–118°C.

***N*,*N*′-Dicyclohexyl-*N*-(prop-2-yn-1-yl)urea (6).** Yield 55%, white crystals, mp 93°C. IR spectrum

(film), ν, cm^{-1}: 3309 (C≡CH), 3221, 2929, 2855, 2111 (C≡C), 1626, 1529, 1451, 1236. ^{1}H NMR spectrum, δ, ppm: 1.10–1.21 m (4H, CH_2), 1.36 t (6H, CH_2, J = 10.1 Hz), 1.63 s (2H, CH_2), 1.67–1.71 m (2H, CH_2), 1.78–1.80 m (4H, CH_2), 1.93–1.96 m (2H, CH_2), 2.26 t (1H, CH, J = 2.4 Hz), 3.67–3.71 m (1H, NCH), 3.86 d (2H, CH_2, J = 2.2 Hz), 4.00–4.05 m (1H, NCH), 4.53 d (1H, NH, J = 6.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.83, 25.54, 25.69, 25.84, 31.08, 31.24, 33.74, 49.36, 54.27, 71.81 (≡CH), 80.92 (C≡), 156.85 (C=O). Found, %: C 72.99; H 10.04; N 10.46. $C_{16}H_{26}N_2O$. Calculated, %: C 73.24; H 9.99; N 10.68.

***N*,*N*′-Dicyclohexyl-*N*-(prop-2-en-1-yl)urea (7).** Yield 65%, white crystals, mp 69–70°C. IR spectrum (film), ν, cm^{-1}: 3349, 2928, 2854, 1622, 1527, 1233. ^{1}H NMR spectrum, δ, ppm: 1.02–1.37 m (10H, CH_2), 1.54–1.65 m (4H, CH_2), 1.73 t (4H, CH_2, J = 14.5 Hz), 1.86–1.90 m (2H, CH_2), 3.61–3.64 m (1H, NCH), 3.68 d.d (2H, CH_2, J = 4.5, 1.8 Hz), 4.17 t.t (1H, NCH, J = 11.8, 3.4 Hz), 4.29 d (1H, NH, J = 6.7 Hz), 5.19 d.d (1H, =CH_2, J = 10.4, 1.04 Hz), 5.24 d.d (1H, =CH_2, J = 17.5, 0.9 Hz), 5.79 d.d.t (1H, CH=, J = 11.9, 10.4, 5.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.81, 25.63, 25.72, 25.88, 31.13, 33.76, 44.79, 49.07, 53.66, 116.08, 136.54, 157.58 (C=O). Found, %: C 72.26; H 10.67; N 10.30. $C_{16}H_{28}N_2O$. Calculated, %: C 72.68; H 10.67; N 10.59.

***N*,*N*′-Diphenyl-*N*-(prop-2-en-1-yl)urea (11).** A mixture of *N*,*N*′-diphenylcarbodiimide (**4**) and *N*-allyltriflimide (**2**) at a ratio of 2:1 was stirred for 5 days at room temperature. Unreacted compound **2** was removed under reduced pressure (0.2 mm) at 40°C, and the residue (~0.5 g) was analyzed by NMR. ^{1}H NMR spectrum, δ, ppm: 4.34 d (2H, CH_2, J = 6.2 Hz), 5.10 d (1H, =CH_2, *cis*, J = 10.1 Hz), 5.13 d (1H, =CH_2, *trans*, J = 17.0 Hz), 6.06 d.d.t (1H, CH=, J = 17.0, 10.3, 6.2 Hz), 6.60–7.10 m (10H, Ph). In the ^{13}C NMR spectrum of **11** we identified only a singlet at δ_C 56.8 ppm (CH_2); aromatic and carbonyl carbon signals were overlapped by signals of *N*,*N*′-diphenylurea and other impurities. By column chromatography (methylene chloride–hexane, 3:1) we isolated a fraction containing mainly urea **11**, whereas elution with hexane–ethyl acetate (5:2) gave a fraction containing mainly *N*,*N*′-diphenylurea. The latter was also present in the first fraction (according to the TLC data). Repeated chromatographic separation gave the same result, i.e., compound **11** undergoes partial hydrolysis during silica gel chromatography.

The IR spectra were recorded on a Bruker Vertex 70 spectrometer. The NMR spectra were measured on a Bruker DPX-400 instrument at 400 (^{1}H), 100 (^{13}C), and 376 MHz (^{19}F) using $CDCl_3$ as solvent and reference; the chemical shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) or CCl_3F (^{19}F). The progress of reactions was monitored by TLC on Silufol UV-254 plates.

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REFERENCES

1. Shainyan, B.A. and Danilevich, Yu.S., *Russ. J. Org. Chem*., 2017, vol. 53, p. 828.
2. Ochiai, M., Okubo, T., and Miyamoto, K., *J. Am. Chem. Soc*., 2011, vol. 133, p. 3342.
3. Müller, P. and Phuong, N.T.M., *Tetrahedron Lett*., 1978, vol. 19, no. 47, p. 4727.
4. Arvai, R., Toulgoat, F., Langlois, B.R., Sanchez, J.-Y., and Médebielle, M., *Tetrahedron*, 2009, vol. 65, p. 5361.
5. Kuzmin, A.V. and Shainyan, B.A., *Russ. J. Org. Chem*., 2017, vol. 53, p. 1505.
6. Shainyan, B.A. and Tolstikova, L.L., *J. Fluorine Chem*., 2014, vol. 168, p. 40.
7. Ulrich, H., *Chemistry and Technology of Carbodiimides*, Chichester: Wiley, 2007.
8. Hartke, K. and Rossbach, F., *Angew. Chem., Int. Ed. Engl*., 1968, vol. 7, p. 72.
9. Kaupp, G., Luebben, D., and Sauerland, O., *Phosphorus, Sulfur Silicon Relat. Elem*., 1990, vol. 53, p. 109.
10. Jakubke, H.-D. an Klessen, C., *J. Prakt. Chem*., 1977, vol. 319, p. 159.
11. Goj, O., Haufe, G., and Fröhlich, R., *Acta Crystallogr., Sect. C*, 1996, vol. 52, p. 1554.
12. Glass, R.S. and Swedo, R.J., *J. Org. Chem*., 1978, vol. 43, p. 2291.
13. Glass, R.S., *Chem. Commun*., 1971, p. 1546.
14. Zhang, J., Martin, G.R., and DesMarteau, D.D., *Chem. Commun*., 2003, p. 2334.
15. Tolstikova, L.L., Bel'skikh, A.V., and Shainyan, B.A., *Russ. J. Org. Chem*., 2010, vol. 46, p. 383.
16. Tan, D., Mottillo, C., Katsenis, A.D., Štrukil, V., and Friščić, T., *Angew. Chem., Int. Ed*., 2014, vol. 53, p. 9321.