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Reaction of N-sulfinyltrifluoromethanesulfonamide with carbodiimides: Formation of N-trifluoromethanesulfonyl-2,4-dialkyl-1,2,4-thiadiazetidin-3-imine 1-oxides

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ABSTRACT

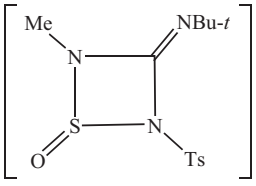
N-sulfinyltrifluoromethanesulfonamide was found to react with diisopropyl- and dicyclohexylcarbodiimides with the formation of N-trifluoromethanesulfonyl-2,4-dialkyl-1,2,4-thiadiazetidin-3-imine 1-oxides. The mechanism includes the [2π + 2π] cycloaddition resulting in 2-trifluoromethanesulfonyl-3-alkylimino-4-alkyl-1,2,4-thiadiazetidine 1-oxides, the ring opening of the latter, rotation about the C–N bond and the ring closure to the final products.

1. Introduction

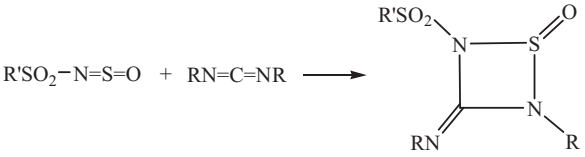
Recently we have developed two new synthetic approaches to N-triflyl guanidines $TfN{=}C(NHR)_2$ (Tf = CF_3SO_2) by the reaction of N-sulfinyltrifluoromethanesulfonamide $CF_3SO_2N{=}S{=}O$ (**1**), with urea or by the addition of trifluoromethanesulfonamide to carbodiimides RN=C=NR (**2**) [1]. It was interesting to investigate the reaction between the two heterocumulenes, **1** and **2**, in order to examine the effect, if any, of the CF_3 group on the known reaction of N-sulfinylarenesulfonamides with carbodiimides [2,3].

2. Results and discussion

The principal question arising in the analysis of the literature data on the reactions of N-sulfinylsulfonamides with carbodiimides is the structure of the cycloadducts formed. In the first work of Ulrich et al., the isolated and proved products of the reaction of MeN=C=NBu-*t* with TsNSO were the products of exchange, MeNSO and TsN=C=NBu-*t* [2]. The intermediacy of the four-membered product of cycloaddition



was only postulated on the basis of similarity with the reactions of carbodiimides with other heterocumulenes like isocyanates and isothiocyanates. More interesting are the results of Minami et al. who have isolated the products of the reaction of $MeSO_2NSO$ and TsNSO with *symmetrical* carbodiimides RN=C=NR and assigned them the structure of the [2π + 2π] cycloadducts [3].



3

Upon heating, compounds **3** were converted into the products of exchange RNSO and $R'SO_2N{=}C{=}NR$, and upon hydrolysis they gave the substituted guanidines $R'SO_2N{=}C(NHR)_2$ [3]. However, as to the structure of the above cycloadducts, it was not proved,

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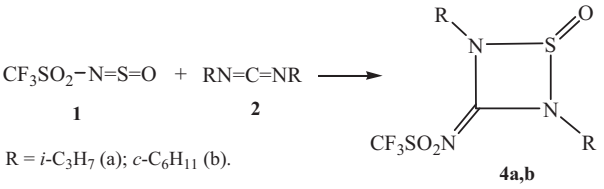
either. Moreover, the ^{1}H NMR spectra of compounds **3** do not support the indicated unsymmetrical structure but rather evidence *against* it [3]. Indeed, compounds **3** have two different NR groups but the proton spectra contain only one NCH (R = *i*-Pr) or NCH_2 (R = *n*-Bu) signal. The ^{13}C NMR spectra were not recorded.

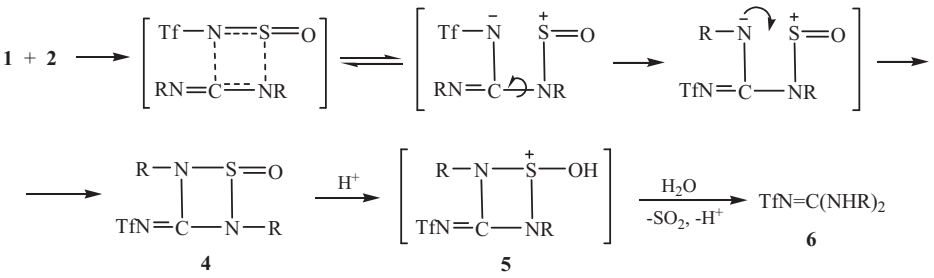
We have performed the reaction of N-sulfinyltrifluoromethanesulfonamide **1** with diisopropylcarbodiimide **2a** and dicyclohexylcarbodiimide **2b** and showed the products to be N-trifluoromethanesulfonyl-2,4-dialkyl-1,2,4-thiadiazetidin-3-imine 1-oxides **4**.



The molecular formulae of compounds **4a**,**b** were established by high-resolution mass spectrometry (HRMS). The symmetrical structure of **4a**,**b** was proved by the absence of different signals of the CH groups attached to the amine and imine nitrogen atoms both in the ^{1}H and ^{13}C NMR spectra. The presence of two slightly different signals of the CH protons in **4a** (see Section 4) is, most probably, due to different location of the two NR groups with respect to the configurationally rigid structure of imine moiety (more close to and more distant from the triflyl group). To exclude accidental coincidence of the signals of R in the alternative structure **3** (highly improbable, especially for ^{13}C NMR, but still possible) we have measured the ^{15}N NMR spectrum of **4a** and found the presence of only one signal at −203.2 ppm, unequivocally indicating the presence of two equivalent NR groups in the molecule (the use of the *hmbcgp* technique does not allow to detect the ^{15}N signal of the CF_3SO_2N group due to the absence of nearby protons).

The measured dipole moment of **4b** was 5.65 D, which is in qualitative agreement with the calculated for the symmetrical structure **4b** (4.81 D) but substantially lower than that calculated for the isomeric structure of the type **3** (7.59 D), which, besides, is 19.3 kcal/mol less stable than structure **4b**.

An additional and independent support came from chemical transformations and UV spectroscopic study of **4b**. The acidic hydrolysis of **4b** in aqueous ethanol with 5–10% triflic acid gave 1,3-dicyclohexyl-2-(trifluoromethylsulfonyl)guanidine **6** (R = *c*-Hex), which is identical to the authentic sample [1].



Note, that a similar symmetrization of the originally formed [2 + 2] cycloadduct via the sequence of the ring opening – ring closure reactions was observed in the reaction of carbodiimides with (dimethylamino)bis(trifluoromethyl)borane, $(CF_3)_2BNMe_2$ [4].

In the UV spectrum of **4b** an absorption band was observed with λ_{max} 216 nm, which practically coincides with the band at λ_{max} 214 nm in the spectrum of the corresponding N-triflylguanidine (**6b**, R = *c*-Hex). This is suggestive of the similarity of the π–π^* transitions responsible for the two bands. However, unlike guanidine **6b**, the addition of 0.1 N HCl to the acetonitrile solution of **4b** led to appearing of a long-wave absorption band with λ_{max} 283 nm corresponding to the transition in its S=O-protonated form **5**.

3. Conclusion

As opposed to the literature data, the reaction of N-sulfinyltrifluoromethanesulfonamide with N,N′-dialkylcarbodiimides gives N-trifluoromethanesulfonyl-2,4-dialkyl-1,2,4-thiadiazetidin-3-imine 1-oxides by the rearrangement of the intermediate [2π + 2π] cycloadducts via the ring opening – ring closure sequence of reactions.

4. Experimental

4.1. General

Melting points are uncorrected. IR spectra were taken on a Bruker Vertex 70 spectrophotometer in KBr. UV spectra were recorded on a Specord UV Vis spectrometer in acetonitrile. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DPX 400 spectrometer at working frequencies 400 (^{1}H), 100 (^{13}C), 40 (^{15}N) and 376 (^{19}F) MHz in chloroform; ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield to TMS, and ^{19}F NMR in parts per million downfield to $CFCl_3$. ^{15}N NMR chemical shifts were obtained from 2D{^{1}H–^{15}N} spectra recorded by the use of a gradient probe working in the *hmbcgp* mode optimized to the long-range coupling constant J_{NH} of 9 Hz, and are reported in parts per million downfield to CH_3NO_2. Electron impact mass spectra were obtained on a GC–MS TRACE DSQ II mass spectrometer (Thermo Fisher Scientific GmbH) at 70 eV. HRMS measurements were performed on a Micromass Q-TOF_{micro} instrument (Waters, Manchester, UK) in the positive electrospray mode. The elemental composition was determined using H_3PO_4 as a standard with deviation < 3 ppm. The dipole moment of **4b** was measured on a Sh2-5 instrument (Angarsk, AO OKBA) at 1 MHz.

Quantum chemical calculations were performed with full geometry optimization using the Gaussian09 package [6] and employing the B3LYP exchange correlation potential in connection with the 6-311G(d,p) basis set.

All solvents were dried and purified before use according to standard procedures. Commercial diisopropylcarbodiimide **2a** of 99% purity (Aldrich) and dicyclohexylcarbodiimide **2b** of 99% purity (Alfa Aesar) were used. N-sulfinyltrifluoromethanesulfonamide [5] was synthesized by the known procedure.

4.2. Synthesis

N-trifluoromethanesulfonyl-2,4-diisopropyl-1,2,4-thiadiazetidin-3-imine 1-oxide 4a. N-sulfinyltrifluoromethanesulfonamide **1** (0.23 g, 1.2 mmol) was added to the solution of

diisopropylcarbodiimide **2a** (0.15 g, 1.2 mmol) in 1 ml of benzene (or chloroform, methylene chloride, or cyclohexane) at vigorous stirring at room temperature, stirred for 4 h, kept overnight, evaporated in vacuum to give **4a** (0.38 g, 98%) as solid with m.p. 60 °C. IR, ν, cm^{-1}: 2986, 2940, 1619, 1465, 1346, 1207, 1129, 795, 746, 621. ^{1}H NMR, δ, ppm: 4.17 sept and 4.18 sept (1H, NCH, 6.5 Hz), 1.35 d and 1.34 d (12H, CH_3, J 6.5 Hz). ^{13}C NMR, δ, ppm: 153.06 (C=NTf), 118.88 q (CF_3, J 318.6 Hz), 50.08 (CH′), 21.05 (CH_3). ^{19}F NMR, δ, ppm: −79.73. Mass spectrum, m/z ($I_{rel.}$, %) ion: 321 (13) [M], 264 (16) [M−NPr], 217 (19) [TfNHCHPr], 201 (48) [$TfNCNCH_2CH_2$], 188 (8) [M–Tf], 175 (15) [TfNHCNH], 147 (47) [TfN], 146 (100) [M−NTf−C_3H_6], 137 (33) [201−SO_2], 105 (41) [PrNSO], 90 (22) [CH_2CH_2NSO], 83 (12) [PrNCN], 69 (40) [CF_3], 58 (19) [PrNH], 43 (17) [Pr]. HRMS: found m/z for $[M]^+$ 321.0438; calcd for $C_8H_{14}F_3N_3O_3S_2$: 321.0429. *Anal.* calcd. for $C_8H_{14}F_3N_3O_3S_2$: C 29.90; H 4.39; N 13.08; found: C, 30.51; H, 4.96; N, 13.32.

N-trifluoromethanesulfonyl-2,4-di(cyclohexyl)-1,2,4-thiadiazetidin-3-imine 1-oxide 4b was prepared in a similar fashion. Yield 0.47 g (97%), solid with m.p. 56 °C. IR, ν, cm^{-1}: 2941, 2863, 1612, 1451, 1348, 1190, 1141, 898, 797, 617. ^{1}H NMR, δ, ppm: 3.92 t.t (2H, CH, J 11.1, 3.7 Hz), 2.18 d (4H, $H_{eq}^{2,6}$, J 11.1 Hz), 1.83 (4H, $H_{ax}^{2,6}$, J 12.4, 2.0 Hz), 1.75–1.10 m (12H, $H^{3,4,5}$). ^{13}C NMR, δ, ppm: 152.76 (C=NTf), 119.06 q (CF_3, J 318.8 Hz), 57.05 (CH), 32.20 and 32.11 ($C^{2,6}$ and $C^{2',6'}$), 24.82 ($C^{3,5}$), 24.64 (C^4). ^{19}F NMR, δ, ppm: −79.25. Mass spectrum, m/z ($I_{rel.}$, %) ion: 401 (20) [M], 352 (9) [M–HSO], 320 (67) [M–C_6H_9], 268 (17) [M−Tf], 238 (64) [M−Tf−C_2H_6], 220 (22) [M−Tf−SO], 219 (17) [M−HSO−Tf], 186 (100) [M−Tf−C_6H_{10}], 145 (59) [$C_6H_{11}NSO$], 138 (33) [$C_6H_{11}NC(N)NH$], 98 (39) [$C_6H_{11}NH$], 83 (100) [C_6H_{11}], 81 (82) [C_3H_5NCN], 69 (28) [CF_3], 55 (64) [C_4H_7], 41 (29) [C_2H_2NH]. HRMS: found m/z for $[M]^+$ 401.1064; calcd for $C_{14}H_{22}F_3N_3O_3S_2$: 401.1055. *Anal.* calcd. for $C_{14}H_{22}F_3N_3O_3S_2$: C 41.88; H 5.52; N 10.47; found: C, 41.86; H, 5.49; N, 10.42.

Hydrolysis of N-trifluoromethanesulfonyl-2,4-di(cyclohexyl)-1,2,4-thiadiazetidin-3-imine 1-oxide 4b. To the solution of **4b** (0.24 g, 0.6 mmol) in 36% ethanol (8 ml) two drops of TfOH was added, stirred for 2 h at room temperature and kept overnight. The product was collected by filtration, washed with water and dried to yield 1,3-dicyclohexyl-2-(trifluoromethylsulfonyl)guanidine **6** (R = *c*-Hex) (0.14 g, 66.7%) as white crystals with m.p. 152 °C (lit. 160 °C [1]). The IR and NMR spectra coincided with those previously reported [1].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2012.04.016.

References

[1] B.A. Shainyan, L.L. Tolstikova, U. Schilde, Journal of Fluorine Chemistry 135 (2012) 261–264.
[2] H. Ulrich, B. Tucker, A.A.R. Sayigh, Journal of the American Chemical Society 94 (1972) 3484–3487.
[3] T. Minami, M. Fukuda, M. Abe, T. Agawa, Bulletin of the Chemical Society 46 (1973) 2156–2159.
[4] D.J. Brauer, S. Buchheim-Spiegel, H. Bürger, R. Gielen, G. Pawelke, J. Rothe, Organometallics 16 (1997) 5321–5330.
[5] H.W. Roesky, G. Holtschneider, H.H. Giere, Zeitschrift fur Naturforschung. Teil B: Chemie, Biochemie, Biophysik, Biologie und Verwandte Gebiete 25 (1970) 252–254.
[6] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A. 01, Gaussian, Inc., Wallingford, CT, 2009.