189. Synthesis of *N,N*-Disubstituted Lactone Hydrazones *via* (Sulfonylimino)-ethers

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The dihydropyran **3** reacts with sulfonyl azides to give the known (sulfonylimino)-ethers (= lactone sulfonylimines) **4** and **18**. Reaction of **4** with $NH_2NH_2 \cdot H_2O$ leads to the aminotriazole-dibutanol **5**, characterized as its tetraacetate **8**, and not, as previously claimed, to **6** or **7**. Similarly, the dihydrofuran-derived (tosylimino)-ether **10** yields **11**. The structure of **5** was established by X-ray analysis, and a mechanism for its formation is proposed. Reaction of **4** with NH_2NMe_2 afforded the lactone hydrazone **16** and the hydrazidine **17**. Catalysis by imidazole suppressed the formation of **17**. Similarly, the [(trifluoromethyl)sulfonyl]imine **18** yielded **16**, and, by reaction with $NH_2N(Me)Ph$ or 4-amino-4*H*-1,2,4-triazole, the lactone hydrazone **19** and the adduct **20**, respectively. The 1,4-lactone hydrazone **21** was obtained from **10** or from **22**. The structure of **20** was established by X-ray analysis. Treatment of **16** with BuLi followed by BnBr yielded the α-alkylated lactone hydrazone **23**.

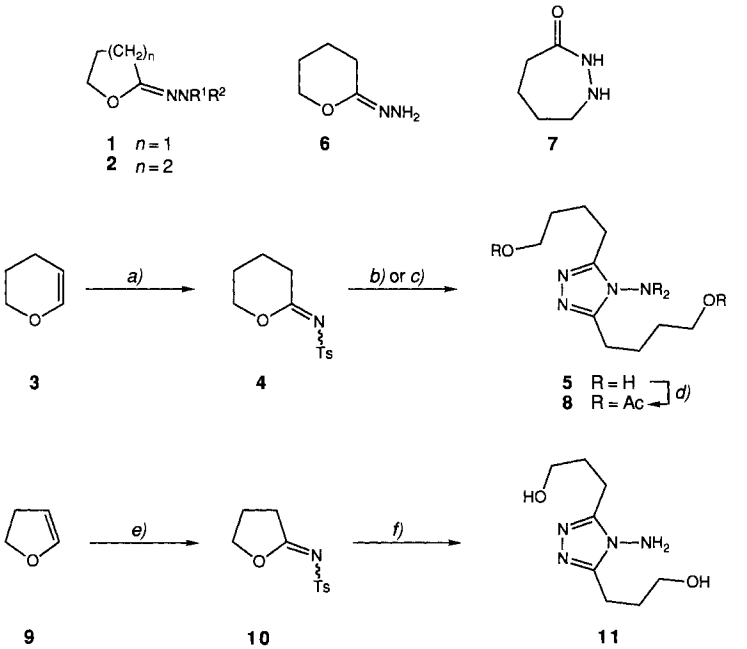
Carbanionic derivatives of *N,N*-dialkylated hydrazones are important intermediates for the regio-, diastereo-, and enantioselective formation of C,C bonds [1–4]. Carbanionic derivatives of *N,N*-disubstituted lactone hydrazones of the type **1** and **2** (R^1,R^2 = alkyl, *Scheme 1*), however, have so far not been used for C,C-bond formations, presumably because they are less easily available and less stable. The only method for the synthesis of *N,N*-disubstituted lactone hydrazones[2]) is the one of *Enders* and coworkers [8] who cyclized *N,N*-dialkyl-ω-chlorohydrazides by treatment with $AgBF_4$.

We wished to find new methods for the preparation of lactone *N,N*-dialkylhydrazones derived from valero- and from butyrolactone. These lactone hydrazones may be useful for the preparation of alkylated lactones; they are also models for 2-deoxyglycono-1,5- and -1,4-lactone hydrazones. We are currently investigating the preparation and use of such glyconolactone hydrazones [9–11]. In this context, we noted a report by *Huisgen* and coworkers [12] that the dihydropyran **3** reacts with tosyl azide (TsN_3) to give the lactone tosylimine **4**, and that **4** reacts with hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) in 75% yield to a crystalline product to which *Huisgen* and coworkers assigned the structure **6** or **7**, based upon an elemental analysis and an IR spectrum. Following their procedure, we obtained **4** and from the latter and $NH_2NH_2 \cdot H_2O$ a product (79%) with the same melting point and IR bands as the one reported (*Scheme 1*). However, we observed that the reaction mixture developed a pink-to-red colour, and based on the spectral data of the

[1]) Taken from the Diploma Work of *S. Fritschi*, Zürich, 1989.

[2]) Lactone imines react with 4-toluenesulfonohydrazides (= tosylhydrazines) to yield lactone tosylhydrazones [5–7], but the analogous reaction with *N,N*-dialkylhydrazines did not lead to lactone *N,N*-dialkylhydrazones [8].

Scheme 1



a) 1 Equiv. of TsN_3, 3 equiv. of **3**, 80°, 2.5 h; 95%. *b*) $NH_2NH_2 \cdot H_2O$, reflux; 79%. *c*) 1.5 Equiv. of $NH_2NH_2 \cdot H_2O$, toluene, reflux, 2 h; 84%. *d*) Ac_2O, r.t., 93 h; 95%. *e*) 1 Equiv. of TsN_3, 4 equiv. of **9**, 30°, 3 h; 88%. *f*) 1.5 Equiv. of $NH_2NH_2 \cdot H_2O$, toluene, reflux, 2 h; 88%.

product, its X-ray analysis (see below), and its conversion to a tetraacetate **8** (see *Exper. Part*), we assigned structure **5** to this product.

The combustion analysis of **5** is in agreement with a molecular formula $(C_5H_{10}N_2O)_n$. The ^{13}C-NMR spectrum (1 *s* and and 4 *t*) suggests the presence of a monomer or of a symmetric di- or oligomer. The IR spectrum ($CHCl_3$) is characterized by bands at 3440 and 3340 cm^{-1}. In the ^{1}H-NMR spectrum ((D$_6$)DMSO), a *s* at 5.70 ppm and a *t* at 4.43 ppm disappear upon addition of D_2O, whereas a *q* at 3.41 ppm changes into a *t*. The chemical shift of this *q* agrees better with a CH_2OH than with a CH_2NH_2 or a $RCONHCH_2$ group. A *t* at 60.6 ppm in the ^{13}C-NMR spectrum clearly evidences the presence of a CH_2—O group. That **5** is a 4-substituted butanol and not a monomeric cyclic compound like **6** or **7** is shown in the ^{1}H-NMR spectrum by the *t* at 2.64 ppm and the 2 *m* at 1.75–1.60 and 1.60–1.44 ppm and in the ^{13}C-NMR spectrum by the 3 *t* at 32.2, 23.7, and 23.3 ppm. The EI-MS shows signals at *m/z* 228, 211, 197, and 184 for M^+, $[M - OH]^+$, $[M - CH_2OH]^+$, and $[M - (CH_2)_2OH]^+$, suggesting a dimeric structure for **5**. This is confirmed by the ^{15}N-NMR spectrum which exhibits a *s* at −80.3 (2 N-atoms), a *s* at −202.9, and a *t* (J = 72.3 Hz) at −320.8 ppm for an NH_2 group. The INEPT spectrum shows additional small long-range couplings of the signals at −80.3 and −202.9 ppm. Thus, two $(CH_2)_4OH$ residues and one NH_2 group must be attached to a triazole nucleus. The chemical shifts of the aromatic C-atoms (154.6 ppm; *cf.* the chemical shift of 1,2,4-triazole (147.6 ppm) with the one of 1,2,3-triazole (130.4 ppm) [13]) and of the N-atoms [14] are in favour of a 1,2,4-triazole structure.

The signal for the Ac_2N group in the ^{1}H-NMR spectrum of **8** resonates at 2.35 ppm and the one for the two AcO groups at 2.04 ppm. These groups give rise to a broad band at 1740 cm^{-1} in the IR spectrum.

Similarly, treatment of the dihydrofuran **9** with TsN_3 according to *Huisgen* and coworkers [12] gave the lactone tosylimine **10** and hence, by treatment with $NH_2NH_2 \cdot H_2O$, the triazole-dipropanol **11** (88%). The triazole-dialkanols **5** and **11** were

prepared before by condensation of the corresponding hydroxyalkanohydrazide with hydrazine hydrate at elevated temperatures (> 170°) [15][3]).

The X-ray structure analysis of dibutanol **5** (see *Fig. 1*) reveals that one hydroxybutyl group lies in the plane of the triazole ring, whereas the hydroxyethyl part of the other group is turned out of the plane. Several intermolecular H-bonds between the OH group and N(1) or N(2) and between the NH_2 group and the O-atoms are observed. There are no intramolecular H-bonds. The dihedral angles C(3)–N(4)–N(11)–H(26) of −136.1° and C(3)–N(4)–N(11)–H(27) of 99.0° indicate that the plane H(26)–N(11)–H(27) is eclipsed to the plane of the triazole ring.

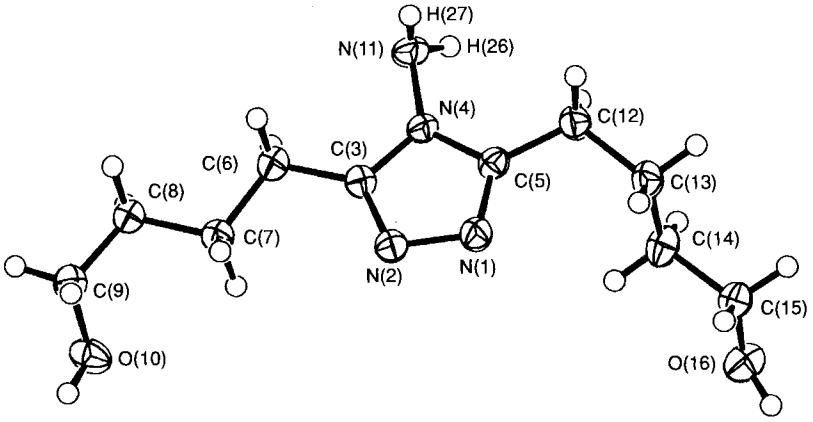


Fig. 1. *X-Ray structure of* **5**. Arbitrary numbering.

Data Collection, Structure Determination, and Refinement for Compound **5**: Crystals were obtained from MeCN $C_{10}H_{20}N_4O_2$ (228.29). Monoclinic $P2_1/c$ (# 14); $a = 7.940(1)$, $b = 14.629(1)$, $c = 11.822(1)$ Å; $\beta = 121.21(1)°$; $V = 1174.5(2)$ Å^3; $D_x = 1.29$ Mg/m^3; $Z = 4$. Intensities were measured in the ω-scan mode on a *Nicolet-R3* diffractometer at 21° using MoK_α graphite-monochromated ($\mu = 0.86$ cm^{-1}) radiation (no absorption correction, but extinction correction applied), scan speed 2°/min, and subjected to the usual corrections. For the refinement of the cell dimensions, 64 reflections were used in the range of $34° < 2\Theta < 42°$. Of the 4227 total reflections collected, 3157 were observed ($I > \sigma(I)$). $2\Theta_{max} = 63°$; $R = 0.078$; $R_w = 0.063$; $w = 1/\sigma^2(F)$; $\langle\sigma(d(C,C))\rangle = 0.002$ Å. The structure was solved with the direct-methods routine of SHELXS-86, [19] and the refinement performed with SHELXTL, version 5.1 [20].

The formation of the aminotriazole-dibutanol **5** from the lactone sulfonylimine **4** may be rationalized by assuming that the reaction of **4** with $NH_2NH_2 \cdot H_2O$ leads to the lactone hydrazone **6** (*Scheme 2*) which is not stable under the reaction conditions. It is attacked by the NH_2 group of a second molecule of **6**, leading by addition-elimination to **12**. Intramolecular, nucleophilic addition of the NH group in **12** leads to the intermediate **13** and hence, by elimination, to **5**. A similar addition of the NH_2 group in **12**, followed by elimination, leads to the dihydrotetrazine **14**. Dihydrotetrazines are known to be easily

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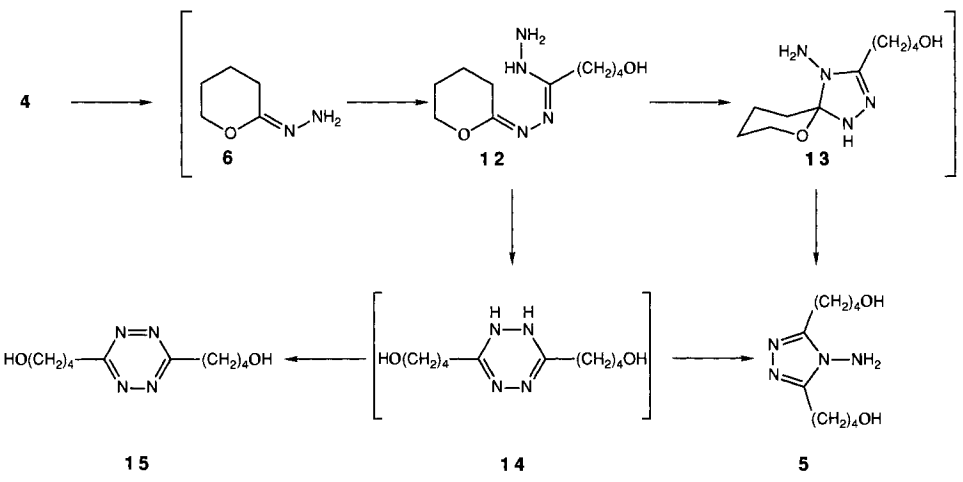
[3]) In a similar way, 4-amino-4*H*-1,2,4-triazole-3,5-diethanol and -3,5-dimethanol were prepared [16]. Acetylation of these compounds (with Ac_2O at 120–130°) yielded the corresponding amino-di-*O*-acetates. Acetylation of 17,17′-(4-amino-4*H*-1,2,4-triazole-3,5-diyl)bi(heptadecan-7-ol) (at 140°) gave the triacetylated derivative [17]. These results were rationalized by the weakly basic character of the amino group [16] (pK_{HA}(**5**) = 8.53; pK_{HA}(**11**) = 8.50) and by assuming intramolecular H-bonds [18].

Scheme 2



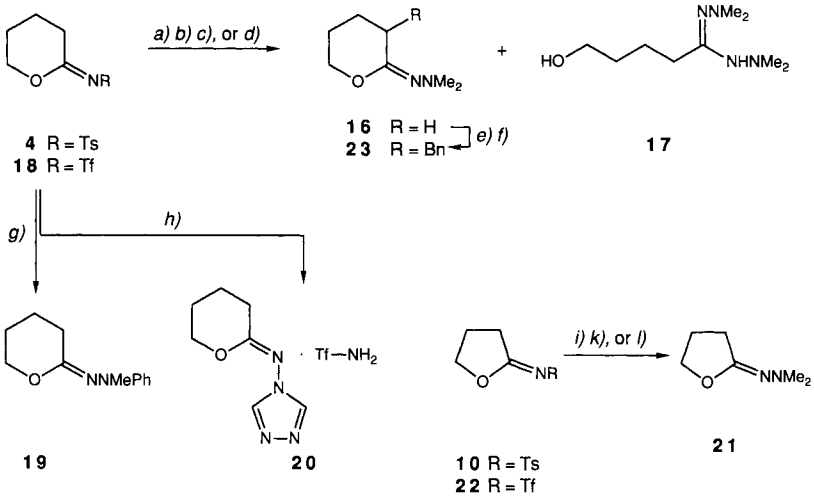
oxidized to (red) tetrazines [21] or to rearrange to 4-amino-4*H*-1,2,4-triazoles [21–23]. Formation of the tetrazine **15** explaines the red colour which we observed on reaction of **4** with $NH_2NH_2 \cdot H_2O$ and which was also reported by *Adamek* [16]. According to this mechanism, **4** should react with *N,N*-dialkylhydrazines to form the desired lactone *N,N*-dialkylhydrazones.

Treatment of lactone tosylimine **4** with a small excess of *N,N*-dimethylhydrazine (NH_2NMe_2; 3 h, 25°) gave the lactone hydrazone **16** in only 14% [8] yield (*Scheme 3*). The main product was the crystalline hydrazidine **17** (28%). Addition of a catalytic amount of imidazole reduced the reaction time, suppressed the formation of **17**, and raised the yield of **16** to 61% (50 min at 0°). Nevertheless, **4** and larger excesses of NH_2NMe_2 reacted to **17** (69%), even in presence of imidazole. The lactone [(trifluoromethyl)sulfonyl]imine **18** (prepared from **3** and trifluoromethanesulfonyl azide (TfN_3) [24] (67%)) reacted with NH_2NMe_2 to yield 60% of **16**, even in the absence of imidazole; but addition of imidazole, 2-chloropyridin-6-ol, quinolin-8-ol, camphorsulfonic acid, AcOH, or 2,4-dinitrophenol did not raise the yield of **16.** Similarly, **18** reacted with *N*-methyl-*N*-phenylhydrazine to **19** (37%), which decomposed upon storage at 5°, and with 4-amino-4*H*-1,2,4-triazole in the presence of a catalytic amount of quinolin-8-ol to the corresponding lactone hydrazone, which was isolated as the crystalline adduct **20** containing 1 equiv. of trifluoromethanesulfonamide ($TfNH_2$). Several recrystallizations in Et_2O/hexane yielded 53% of hygroscopic crystals of **20**, suitable for X-ray analysis (see below) which established its structure.

The five-membered lactone tosylimine **10** [12] reacted with NH_2NMe_2, in the absence of a catalyst (1 h, 70–75°) to yield 43% of the lactone hydrazone **21** [8]. The [(trifluoromethyl)sulfonyl]imine **22**, generated *in situ* from the dihydrofuran **9** and TfN_3, reacted much faster then **10**, but gave only 26% of **21**. The yield dropped to 6% when the reaction was run at 0° for 1 h.

The IR spectrum of **17** is characterized by OH bands at 3600–3040 cm^{-1}. The NMR spectra agree well with a structure of a butan-1-ol, substituted at C(4). The presence of only two MeN signals (^{13}C-NMR: 48.9 and 46.4

Scheme 3



a) **4**, 1.08 equiv. of NH_2NMe_2, toluene, 24°, 3 h; 14% of **16** and 28% of **17**. *b*) **4**, 1.0 equiv. of NH_2NMe_2, 10% of imidazole, toluene, 0°, 50 min; 61% of **16**. *c*) **4**, 4 equiv. of NH_2NMe_2, 10% of imidazole, toluene, reflux, 18 min; 69% of **17**. *d*) **18**, 1.0 equiv. of NH_2NMe_2, THF, 0°, 50 min; 60% of **16**. *e*) 0.99 Equiv. of BuLi, THF, −78° to −30°. *f*) 0.97 Equiv. of BnBr, −78° to 19°, 17 h; 63%. *g*) 1.0 Equiv. of NH_2NMePh, THF, −18°, 10 min; 37%. *h*) 1.0 Equiv. of 4-amino-4*H*-1,2,4-triazole, 1,4-dioxane, 26°, 1 h; 53%. *i*) **10**, 1.02 equiv. of NH_2NMe_2, toluene, 75°, 1 h; 47%. *k*) **10**, 1.0 equiv. of NH_2NMe_2, toluene, 0°, 1 h; 6%. *l*) **22**, 0.9 equiv. of NH_2NMe_2, CH_2Cl_2, 0°, 6 min; 26%.

ppm; ^{1}H-NMR: 2.49 and 2.33 ppm) indicates a fast equilibrium of the diastereoisomers at room temperature. The [(trifluoromethyl)sulfonyl]imines **18** and **22** show characteristic IR bands for the C=N bond at 1610 and 1640 cm^{-1}, respectively, with the absorption of the five-membered isomer shifted to higher wave numbers. Similar differences for the C=N absorption of five- and six-membered derivatives were reported for the corresponding lactone tosylimines [12] and for hydroximo-lactones [25]; they are also observed for the lactone hydrazones **16**, **19**, and **20** *vs.* **21**. In the ^{13}C-NMR spectra, the characteristic signals for C(2) of **18** and **22** occur at 176.5 and 184.1 ppm, respectively, and between 156.7 and 161.7 ppm for the lactone hydrazones **16**, **19**, **21**, and **20**. The CF_3 groups of **18** and **22** give rise to a characteristic *q* at 118.7 ppm (J(C,F) = 319.4 Hz) at 22°; at 118.0 ppm (J(C,F) = 318.1 Hz) at −80°, and at 118.8 ppm (J(C,F) = 319.3 Hz) at 25°; 118.3 ppm (J(C,F) = 318.3 Hz) at −40°, respectively. For a discussion of the configuration of the lactone sulfonylimines and the lactone hydrazones, see below. IR bands of 3430 and 3360 cm^{-1} confirm the presence of $TfNH_2$ in the adduct **20**. In the CI-MS, **20** gives rise to peaks at m/z 333 (69, $[2M + 1]^+$) and 167 (100, $[M + 1]^+$); the peak at 150 (2, $[M + 1]^+$) originates from $TfNH_2$.

The X-ray structure analysis of adduct **20** (see *Fig. 2*) shows that an intermolecular bond is formed between NH_2 of $TfNH_2$ and N(4) (d(N,H) = 0.84 Å, d(N(4),H) = 2.05 Å, angle N–H–N(4) = 165°). The imine C=N bond of the imino-ether moiety is (*Z*)-configurated (d(C(1),N(1)) = 1.26 Å, d(N(1),N(2)) = 1.41 Å, angle O(1)–C(1)–N(1)–N(2) = 3.4°). The tetrahydropyran ring adopts a flattened $^5C_2$ conformation, and the triazole ring is turned out of conjugation with the imino-ether moiety by *ca.* 30°, avoiding steric interaction between H–C(6), the O-atom, and H–C(*endo*) (d(H,O) = 2.3 Å).

Data Collection, Structure Determination, and Refinement for Compound **20**. Crystals were obtained from Et_2O/hexane. $C_7H_{10}N_4O \cdot CH_2F_3NO_2S$ (315.28). Triclinic, centrosymmetric $P\bar{1}$ ($\neq 2$); a = 12.382(3), b = 13.789(4), c = 9.151(3) Å; α = 109.07(3), β = 91.65(2), γ = 71.03(2)°; V = 1391.3(8) Å^3; D_x = 1.505 Mg/m^3;

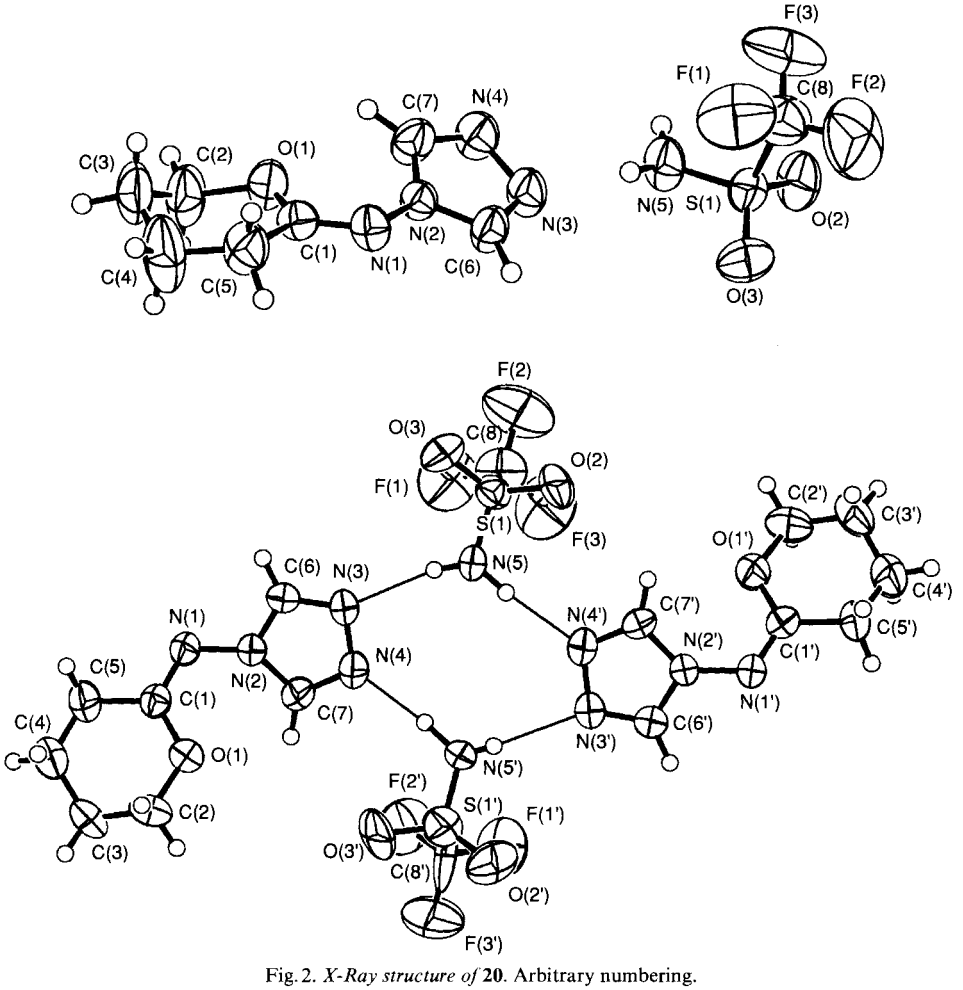


Fig. 2. *X-Ray structure of* **20**. Arbitrary numbering.

$Z = 4$. Intensities were measured in the ω-scan mode on a *Nicolet-R3* diffractometer at 21° using MoK_α graphite-monochromated ($\mu = 2.70\ cm^{-1}$) radiation (no absorption correction, but extinction correction applied), variable scan speed (3–29.3°/min), and subjected to the usual corrections. For the refinement of the cell dimensions, 25 reflections were used in the range of $15° < 2\Theta < 24°$. Of the 4501 total reflections collected, 2257 were observed ($I > 2.5\sigma(I)$). Unique total reflections = 3866 (Rmerg = 0.048). $2\Theta_{max} = 46°$; $R = 0.067$; $R_w = 0.066$; $w = 1/(\sigma^2(F) + 0.00036 \cdot F^2)$; $\langle\sigma(d(C,C)\rangle = 0.008$–$0.010$ Å. The structure was solved with the direct-methods routine of SHELXS-86 [19], and the refinement was performed with SHELXTL, version 5.1 [20]. All non-H-atoms were located in the inital E-map. The identity of the co-crystallizing species ($TfNH_2$) was confirmed with the location of the two NH_2 H-atoms in a difference map. All other H-atoms were also located. Only the NH_2 H-atoms were allowed to refine freely; a riding model was used for the others, with only the isotropic temperature factors being refined. The CF_3 groups show some indication of disorder which is probably a small vibration about the S–C bond. Only one set of positions could be determined, but large thermal displacement parameters are associated with the F-atoms.

Esters, (sulfonylimino)-ethers, lactone hydrazones, and similar derivatives [25] can form (*Z*)- and (*E*)-diastereoisomers. In the solid state of esters and lactone hydrazones,

both (*Z*) [9] [26–28] and (*E*)-isomers [29] [30] were observed. No X-ray analysis of a (sulfonylimino)-ether is known. As reported by *Enders* and coworkers [8], the γ-lactone hydrazone **21** is a 9:1 mixture of the (*Z*)- and (*E*)-isomers. The assignment is based upon the ^{13}C-NMR spectrum, where the C(3) signal of the (*E*)-isomer is shifted upfield by 3.3 ppm, due to a γ-effect, and upon the ^{1}H-NMR spectrum, where CH_2(3) of the major isomer resonates at higher fields ($\Delta\delta = 0.17$ ppm), similarly to what was observed for hydroximo-lactones [25] [31]. Similar $\Delta\delta$ values for C(3) (3.2 and 3.3 ppm, resp.) are found for the δ-lactone hydrazones **16** and **19** (see *Table*). Both show an even stronger preference for the (*Z*)-isomer ((*Z*)/(*E*) = 19:1). The presence of only one MeN signal indicates fast rotation around the N–N bond which may be favoured by the fact that the MeN groups are twisted out of the plane of the imino-ether moiety (as in the solid state of **20**). At room temperature, the ^{13}C-NMR spectra of the lactone sulfonylimines **4**, **18**, and **22** show signals for one isomer, whereas the broad signal of **10** points towards an (*E*)/(*Z*) equilibrium. Indeed, sharp signals for the isomers of **4**, **10**, **18**, and **22** are observed at temperatures $\leq -40°$. For the δ-lactone imines, one isomer is strongly preferred, while the isomeric γ-lactone imines are present in about equal amounts. The C(2) signals of the major isomers of the δ-lactone imines **4** and **18** occur distinctly at higher fields ($\Delta\delta = 5.1$ and 7.8 ppm) than those of the minor isomers and, by analogy, are tentatively assigned to the (*Z*)-conformers.

To illustrate that α-lithiation and alkylation of 1,5-lactone *N*,*N*-dialkylhydrazones is possible, regardless of their (*Z*)-configuration, we treated **16** with BuLi (−78 to −30°) and then with benzyl bromide at −78° and isolated the benzylation product **23** in 63% yield (*Scheme 3*).

The ^{1}H-NMR spectrum of **23** shows two complicated *m* at 3.30–3.18 ppm (H–C(3)) and signals for 3 H at 1.93–1.83 ppm (H–C(4), 2 H–C(5)) which change by irradiation at 1.4 ppm (1.50–1.39 (*m*, H–C(4))). Irradiation at 3.2 ppm (H–C(3)) modifies the shape of the *m* at 2.70–2.58 ppm (PhCH_2). In the ^{13}C-NMR spectrum, C(3) resonates as a *d* at 38.2 ppm. The presence of only one signal for C(3) and a comparison with the chemical shifts for the corresponding signals of the other lactone hydrazones (see *Table*) suggests that only the (*Z*)-isomer is formed.

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Experimental Part

General. All solvents were dried and distilled before use: 1,4-dioxane, hexane, THF, and toluene over Na, CH_2Cl_2 over P_2O_5, and MeOH over Mg. TLC: 0.255 mm precoated silica-gel plates (*Merck*, silica gel *60* F_{254}) with the solvent systems indicated; detection by UV (254 nm) and/or dipping the TLC plates into a 10% ethanolic phosphormolybdic acid soln. followed by heating to 200°. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). M.p.: uncorrected. pK_{HA} Values: determined by potentiometry. UV spectra (λ_{max} in nm (ε)): 1-cm quartz cell. IR spectra: 3% $CHCl_3$ soln. or KBr. ^{1}H- and ^{13}C-NMR spectra: chemical shifts in ppm rel. to TMS as internal standard; ^{15}N-NMR spectra: chemical shifts in ppm rel. to $MeNO_2$ as external standard. MS: *Varian-112S* or *Mat 90* apparatus (EI, 70 eV; CI, isobutane).

Trifluoromethanesulfonyl Azide (TfN_3). According to a modified procedure [24], trifluoromethanesulfonic anhydride (9.4 ml, 156.1 mmol) in hexane or CH_2Cl_2 (50 ml) was added to a soln. of NaN_3 (21.83 g, 335.5 mmol) and $Bu_4N(HSO_4)$ (1.12 g, 3.6 mmol) in H_2O (55 ml) at 0°. After stirring for 1 h, extraction with hexane, drying the org. layer (NaOH), and filtration gave a soln. of TfN_3, which was stable at 4° for several days. IR (hexane): 2150*s*, 1405*m*, 1210*s*, 1150*s*, 1120*s*; [24]: 2151, 1408, 1250–1111 (3 peaks).

N-*(Tetrahydro-2*H*-pyran-2-ylidene)trifluoromethanesulfonamide* (**18**). The soln. of TfN_3, prepared as described above, was treated with 3,4-dihydro-2*H*-pyran (8.4 ml, 92.6 mmol) and stirred at 40° for 7.5 h. After 12 h at −20°, the precipitate was filtered off and dried in vacuum, yielding **18** (8.8 g, 67%). M.p. 73.5–74.5°. IR ($CHCl_3$):

Table. ^{13}C-*NMR* (50.6 MHz, $CDCl_3$) *Chemical Shifts* [ppm] *of Lactone Hydrazones and Related Compounds*

	Temperature [°C]	(*Z*)/(*E*) Ratio	Configuration	C(2)	C(3)	C(4)	C(5)	C(6)	Other
4	25°			170.8	28.8	17.4	21.5	70.8	Ts: 143.1, 138.9, 129.1, 127.1, 21.5
	−40°	14:1	*Z*	171.4	28.6	16.7	21.3	71.3	Ts: 143.1, 137.2, 128.9, 126.8, 20.9
			E	176.5	27.5		21.0	70.2	Ts: 143.1, 137.4, 129.0, 126.1
10	55°[a])					22.6	72.2	–	Ts: 143.3, 138.7, 129.3, 127.1, 21.4
	−50°	47:53	*Z*	175.6	31.7	21.6	75.8	–	Ts: 143.3, 137.3, 129.0, 126.9, 21.3
			E	182.2	29.5	22.5	71.6	–	Ts: 143.3, 137.4, 129.2, 126.4, 31.3
18	22°			176.5	29.0	17.0	21.3	72.6	CF_3: 118.7 (J(C,F) = 319.4 Hz)
	−80°[b])	14:1	*Z*	177.0	28.9	16.6	20.8	73.8	CF_3: 118.0 (J(C,F) = 318.1 Hz)
			E	184.8	29.7	18.7	21.7	70.2	
22	25°			184.1	31.8	22.0	75.6	–	CF_3: 118.8 (J(C,F) = 319.3 Hz)
	−40°	11:9	*Z*	181.0	32.1	21.8	77.6	–	CF_3: 118.3 (J(C,F) = 318.3 Hz)
			E	187.4	31.6	22.1	74.4	–	CF_3: 118.5 (J(C,F) = 319.4 Hz)
16	24°	19:1	*Z*	156.7	26.5	19.0	22.9	67.8	Me: 47.0
			E		23.3	19.3	22.6	68.1	Me: 47.3
23	23°		*Z* (> 98%)	157.6	38.2	24.3	21.6	67.8	$PhCH_2$: 139.5, 129.0, 128.0, 125.9, 38.3; Me: 47.2
21	25°	9:1	*Z*	161.5	27.8	23.1	71.5	–	Me: 47.2
			E		24.5	22.9	69.3	–	Me: 48.0
19	23°	19:1	*Z*[c])	158.8	26.6	19.1	23.0	68.2	Ph: 128.5, 119.3, 114.9; Me 41.5
			E		23.3	19.2	22.9	68.6	Ph: 128.7; Me: 42.8
20	23°		*Z*	161.7	26.1	17.9	22.3	69.9	Triazole: 141.3; CF_3: 119.6 (J(C,F) = 319.8 Hz)

[a]) The signals of C(3) and C(5) are broad. At 25°, broad signals for C(3), C(4), and C(5) of both isomers are observed. [b]) In CD_2Cl_2. [c]) In the ^{1}H-NMR spectrum, the signals of MeN show a (*Z*)/(*E*) ratio of 85:15.

2970*w*, 1610*s*, 1480*w*, 1460*w*, 1450*w*, 1405*m*, 1355*s*, 1285*s*, 1180*m*, 1130*s*, 1070*m*, 1065*m*, 985*m*, 900*s*. ^{1}H-NMR (200 MHz, $CDCl_3$, 295 K): 4.58 (*t*, $J = 6.1$, $CH_2(6)$); 2.75 ('*t*', $J \approx 7.0$, $CH_2(3)$); 2.02–1.92 (*m*, 4 H). CI-MS: 232 (100, $[M + 1]^+$). Anal. calc. for $C_6H_8F_3NO_3S$ (231.19): C 31.17, H 3.49, F 24.65, N 6.06, S 13.87; found: C 31.10, H 3.62, F 24.40, N 6.10, S 13.62.

*4-Amino-4*H-*1,2,4-triazole-3,5-dibutanol* (**5**). A mixture of **4** (1.7 g, 6.8 mmol) [12] and 80% $NH_2NH_2 \cdot H_2O$ (0.4 ml, 10.3 mmol) in toluene (10 ml) was boiled under reflux for 2 h. Evaporation of the solvent at 30°/15 Torr and FC (AcOEt/MeOH 8:2) of the red residue gave **5** (0.651 g, 84%, white crystals) and tosylamide (1.31 g, 88%). By following *Huisgen*'s procedure ([12]: 75%), we obtained 79% of **5**. M.p. 117.2–117.5° ([12]: 116–118°; [15]: 118–120°). R_f (AcOEt/MeOH 7:3) 0.36. $pK_{HA} = 8.30$. IR (KBr): 3700–3000*s* (with maxima at 3340, 3300, and 3160), 2970*s*, 2940*s*, 2920*s*, 2860*s*, 1625–1620*m*, 1535*s*, 1480*m*, 1465*s*, 1425*s*, 1370*m*, 1360*m*, 1335*m*, 1315*m*, 1280*w*, 1090*s*, 1080*s*, 1055*s*, 1050*s*, 1025*w*, 980*w*, 945*m*, 915*s*, 885*m*, 855*m*, 825*m*, 765*s*, 750*m* ([12]: IR (KBr): 3345, 1625). IR ($CHCl_3$), *ca.* 1% sat. soln.): 3440*w*, 3340*w*, 3050–2830 (*several weak bands*), 1600*w*, 1345*m*, 1160*s*, 1095*m*. ^{1}H-NMR (200 MHz, (D_6)DMSO): 5.70 (*s*, exchange with D_2O, NH_2); 4.43 (*t*, $J = 5.2$, irrad. at 3.4→*s*, exchange with D_2O, 2 OH); 3.41 ('*q*', $J \approx 6.0$, irrad. at 4.43→*t* ($J = 6.5$), addition of D_2O→*t* ($J = 6.5$), 2 $CH_2(1)$); 2.64 ('*t*', $J \approx 7.4$, 2 $CH_2(4)$); 1.75–1.60 (*m*, irrad. at 3.41→1.72–1.64, *m*, 2 $CH_2(2)$); 1.60–1.44 (*m*, 2 $CH_2(3)$). ^{13}C-NMR (50 MHz, (D_6)DMSO): 154.6 (*s*, C(3), C(5) of triazole); 60.6 (*t*, 2 C(1)); 32.3 (*t*, 2 C(4)); 23.7 (*t*); 23.3 (*t*). ^{15}N-NMR (40 MHz, (D_6)DMSO): −80.3 (*s*, N(1), N(2); INEPT: *t*, $J = 2.2$); −202.9 (*s*, N(4); INEPT: *t*, $J = 1.6$); −320.3 (*t*, NH_2; INEPT: *t*, $J = 73.4$). EI-MS: 228 (3, $M^{+\cdot}$), 197 (12), 184 (10), 183 (69), 170 (100), 157 (13), 153 (25), 140 (22), 139 (31), 126 (57), 125 (12), 114 (19). Anal. calc. for $C_{10}H_{20}N_4O_2$ (228.3): C 52.63, H 8.83, N 24.55; found: C 52.66, H 8.63, N 24.62.

*4-(Diacetylamino)-4*H-*1,2,4-triazole-3,5-dibutyl Diacetate* (**8**). A soln. of **5** (100 mg, 0.7 mmol) in Ac_2O (7 g, 0.069 mol) was stirred at 23° for 93 h. Addition of MeOH and H_2O, extraction with CH_2Cl_2, and FC (AcOEt/MeOH 95:5) gave oily **8** (165 mg, 95%). R_f (AcOEt/MeOH 95:5) 0.35. IR (KBr): 2960*w*, 1830*w* (sh), 1740*s*, 1550*w*, 1420*w*, 1390*w*, 1370*m*, 1095*w*, 935*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.09 (*t*, $J = 6.2$, $CH_2(1)$); 2.51 ('*t*', $J \approx 7.4$, $CH_2(4)$); 2.35 (*s*, 2 AcO); 2.04 (*s*, 2 AcNH); 1.93–1.67 (*m*, 8 H). ^{13}C-NMR (50 MHz, (D_6)DMSO): 170.4 (*s*, 2 C=O); 169.6 (*s*, 2 C=O); 153.1 (*s*, C(3), C(5)); 63.3 (*t*, 2 C(1)); 27.5 (*t*, 2 C(4)); 24.5 (*q*, 2 Me); 22.3 (*t*), 22.2 (*t*, 2 C(2), 2 C(3)); 20.7 (*q*, 2 Me). MS: 397 (6, $[M + 1]^+$), 356 (23), 355 (100), 313 (18), 295 (31).

Treatment of **4** *and of* **18** *with* NH_2NMe_2: A) Treatment of **4** (304 mg, 1.2 mmol) [12] with NH_2NMe_2 (0.1 ml, 1.3 mmol) in toluene (2 ml) for 3 h at 24°, evaporation of the solvent, and dissolution of the residue in MeCN and hexane gave, after filtration, the crude solid $TsNH_2$ (0.229 g). FC (AcOEt/MeOH 7:3) of the combined residue of the filtrate and crude $TsNH_2$ gave $TsNH_2$ (172 mg, 84%), **16** (23 mg, 14%), and **17** (68 mg, 28%).

B) A soln. of **4** (500 mg, 2 mmol), NH_2NMe_2 (0.15 ml, 2 mmol) and imidazole (14.1 mg, 0.2 mmol) in toluene (3 ml) was stirred for 50 min at 0° and then poured into ice-cooled 1N NaOH (15 ml). The mixture was extracted with hexane and then with CH_2Cl_2. Drying the CH_2Cl_2 layer (NaOH), evaporation, and bulb-to-bulb distillation of the residue (40°/0.06 Torr) gave **16** (174 mg, 61%).

C) The reaction of **4** (1 g, 4 mmol) with NH_2NMe_2 (1.21 ml, 16 mmol) and imidazole (27 mg, 0.4 mmol) in toluene (5 ml) for 18 min under reflux followed by evaporation of the solvent and crystallisation of the residue gave crude **17** (0.586 g, 72%) which was purified by FC (AcOEt/MeOH 7:3, 0.556 g, 69%) and by sublimation (75°/0.5 Torr; 0.452 g, 57%).

D) A mixture of **18** (500 mg, 2.16 mmol) and NH_2NMe_2 (0.16 ml, 2.16 mmol) in THF (5 ml) was stirred for 50 min at 0° and then poured into ice-cooled 1N NaOH (15 ml). Extraction of the mixture with hexane and CH_2Cl_2, drying the CH_2Cl_2 layer (NaOH), evaporation of the solvent, and bulb-to-bulb distillation of the residue gave **16** (0.185 g, 60%).

*Tetrahydro-2*H-*pyran-2-one* N,N-*Dimethylhydrazone* (**16**): R_f (AcOEt/MeOH/H_2O 7:3:2) 0.16. UV (Et_2O): 250 (2714). IR ($CHCl_3$): 2950*s*, 2860*s*, 2820*m*, 2780*w*, 1640*s*, 1470*m*, 1445*w*, 1390*w*, 1345*m*, 1155*m*, 1080*s*, 1055*s*, 1020*m*, 1005*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.21 (*t*, $J = 5.9$, $CH_2(6)$); 2.51 (*s*, 2 Me); 2.39 ('*dd*', $J \approx 6.5$, 7.7, $CH_2(3)$); 1.86–1.79 (*m*, 4 H). EI-MS: 142 (100, $M^{+\cdot}$), 100 (18), 99 (21), 86 (21), 85 (17), 60 (20), 59 (54), 58 (21). Anal. calc. for $C_7H_{14}N_2O$ (142.2): C 59.13, H 9.92, N 19.70; found: C 59.01, H 9.66, N 19.50.

*5-Hydroxy-*N,N,N′,N′-*tetramethylpentanohydrazide Hydrazone* (**17**): R_f (AcOEt/MeOH 7:3) 0.05. M.p. 55.5–56.5°. B.p. 75°/0.1–0.5 Torr. IR ($CHCl_3$): 3600–3040*m*, 2980*s*, 2950*s*, 2860*s*, 2820*m*, 2780*m*, 1620*s*, 1465*m* (sh), 1455*m*, 1435*m*, 1405*m* (sh), 1155*m*, 1090*m*, 1075*m* (sh), 1050*m*, 1015*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.60 (br. *s*, exchanged with MeOD, NH); 3.64 (*t*, $J = 5.9$, addition of MeOD→3.62, *t* ($J = 6.0$), $CH_2(5)$); 3.11 (br. *s*, exchange with MeOD, OH); 2.49 (*s*, 2 Me); 2.35 (*t*, $J = 7.1$, addition of MeOD→2.29, *t* ($J = 7.5$), $CH_2(2)$); 2.33 (*s*, 2 Me); 1.84–1.52 (*m*, $CH_2(3)$, $CH_2(4)$). ^{13}C-NMR (50 MHz, $CDCl_3$): 162.0 (*s*, C(1)); 61.1 (*t*, C(5)); 48.9 (*q*, 2 Me); 46.4 (*q*, 2 Me); 31.9 (*t*, C(2)); 29.9, 23.2 (2*t*, C(3), C(4)). EI-MS: 202 (27, $M^{+\cdot}$), 143 (58), 100 (14), 60 (35), 59 (36), 58 (24), 44 (100). Anal. calc. for $C_9H_{22}N_4O$ (202.3): C 53.43, H 10.96, N 27.69; found: C 53.26, H 10.84, N 27.90.

*3-Benzyltetrahydro-2*H*-pyran-2-one* N,N-*Dimethylhydrazone* (**23**). BuLi (0.47 ml, 0.7 mmol; 1.5M in hexane) was added to a cooled (−78°) soln. of **16** (101 mg, 0.71 mmol) in THF (3 ml). The soln. was allowed to warm to −30°, kept at −30° for 2 min, and cooled to −78°. After addition of benzyl bromide (8 µl, 0.68 mmol), the mixture was left at 19° for 17 h, then poured onto ice-cooled 1N NaOH (15 ml) and extracted with CH_2Cl_2. The org. layer was dried (NaOH) and evaporated. FC (AcOEt/MeOH 9:1) of the residue gave **23** (99 mg, 63%). R_f (AcOEt/MeOH/H_2O 7:2:1) 0.50. IR ($CHCl_3$): 3090*w*, 3070*w*, 3000*m* (sh), 2960*s*, 2910*m*, 2870*s*, 2830*s*, 2790*w*, 1660*m* (sh), 1640*s*, 1610*w*, 1495*w*, 1470*m*, 1455*m*, 1390*w*, 1175*s* (sh), 1160*s*, 1095*s*, 1080*s*, 1065*s* (sh), 1025*w*, 985*s*, 910*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.27 ('*td*', $J \approx 1.8$, 7.3, 2 arom. H); 7.20–7.16 (*m*, 3 arom. H); 4.25–4.10 (*m*, 2 H–C(6)); 3.30–3.18 (*m*, irrad. at 1.4→change of the *m*, H–C(3)); 2.70–2.58 (*m*, irrad. at 3.2→change of the *m*, 2 PhC*H*); 2.52 (*s* 2 Me); 1.93–1.83 (*m*, irrad. at 1.4→change of the *m*, H–C(4), 2 H–C(5)); 1.50–1.39 (*m*, H–C(4)). CI-MS: 233 (100, $[M + 1]^+$).

*Tetrahydro-2*H*-pyran-2-one* N-*Methyl*-N-*phenylhydrazone* (**19**). A soln. of $NH_2N(Me)Ph$ (0.1 ml, 0.87 mmol) in THF (4 ml) was added dropwise to a cooled (−18°) soln. of **18** (0.2 g, 0.87 mmol) in THF (1 ml). This mixture was stirred for 10 min, poured onto ice-cooled 1N NaOH (25 ml), and extracted with hexane. Drying of the org. layer with NaOH, evaporation of hexane, and removal of unreacted $NH_2N(Me)Ph$ by distillation at 60°/0.05 Torr left **19** (65 mg, 37%) which decomposed upon storage at 5°. R_f (AcOEt/hexane 1:1) 0 to 0.23 (tailing). UV (Et_2O): 223 (701), 271 (1272), 291 (1196). IR ($CHCl_3$): 3100*w*, 3060*w* (sh), 2960*s*, 2880*m*, 2800*w*, 1640*s*, 1600*s*, 1490*s*, 1460*m*, 1445*m*, (sh), 1400*w*, 1345*m*, 1280*s*, 1100*s*, 1080*s*, 1060*s*, 1030*m*, 995*m*, 940*m*, 920*m*. ^{1}H-NMR (200 MHz, $CDCl_3$; (*Z*)/(*E*) ≈ 85:15): 7.34–7.14, 7.06–6.92, 6.92–6.76 (3*m*, 5 arom. H); 4.22 (*t*, $J = 5.9$, CH_2(6)); 3.08 (*s*, 2.55 H); 3.00 (*s*, 0.45 H, Me); 2.58 ('*t*', $J \approx 7.1$, CH_2(3)); 2.00–1.72 (*m*, 4 H).

Tetrahydro-N-*(4*H*-1,2,4-triazol-4-yl)-2*H*-pyran-2-imine–Trifluoromethanesulfonamide (1/1)* (**20**). A soln. of **18** (0.25 g, 1.08 mmol), quinolin-8-ol (24 mg, 0.16 mmol) and 4-amino-4*H*-1,2,4-triazole (91 mg, 1.08 mmol) in 1,4-dioxane (2 ml) was stirred at 26° for 1 h. Evaporation and drying of the residue at 0.05 Torr gave an oily residue which crystallized upon trituration with hexane. Several recrystallizations in Et_2O/hexane gave **20** (0.179 g, 53%) as deliquescent crystals. R_f (AcOEt/MeOH/H_2O 7:2:1) 0.35. IR ($CHCl_3$): 3430*w*, 3360*w*, 3150*w*, 3000*w*, 1650*m*, 1510*m*, 1390*m*, 1280*m*, 1260*s* (sh), 1200*s*, 1150*m*, 1070*m*, 1050*s*, 930*m*, 850*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.45 (*s*, 2 arom. H); 4.39 (*t*, $J = 6.0$, CH_2(6)); 2.65 (*t*, $J = 7.1$, CH_2(3)); 2.08–1.86 (*m*, 4 H). CI-MS: 333 (69, $[2M + 1]^+$ of the pyran), 167 (100, $[M + 1]^+$ of the pyran), 150 (2, $[M + 1]^+$ of $TfNH_2$). Anal. calc. for $C_7H_{10}N_4O \cdot CH_2F_3NO_2S$ (315.3): C 30.48, H 3.84, F 18.10, N 22.21; found: C 30.52, H 3.69, F 18.41, N 22.23.

N-*(Tetrahydrofuran-2-ylidene)trifluoromethanesulfonamide* (**22**). A soln. of TfN_3 (13.4 mmol, prepared as described above) was treated with 2,3-dihydrofuran (1.5 ml, 19.9 mmol) and stirred for 160 min at 27°. Evaporation at 30°/200 Torr gave oily **22** (2.269, 78%). A sample was distilled at 80°/0.05 Torr. $n_D^{20} = 1.432$. IR ($CHCl_3$): 3020*w*, 2960*w*, 2930*w*, 1640*s* (sh), 1630*s*, 1460*w*, 1395*m*, 1360*s*, 1190*m*, 1135*s*, 1055*w*, 1040*w*, 1005*w*, 945*w*, 910*m*, 835*m*. ^{1}H-NMR (200 MHz, $CDCl_3$, 295 K): 4.72 (*t*, $J = 7.2$, CH_2(5)); 3.12 ('*t*', $J \approx 8.1$, CH_2(3)); 2.48–2.33 (*m*, CH_2(4)). EI-MS: 217 (< 1, $M^{+\cdot}$), 148 (100), 106 (11), 69 (47), 68 (28), 56 (52). Anal. calc. for $C_5H_6F_3NO_3S$ (217.17): C 27.65, H 2.78, F 26.24, N 6.45, S 14.76; found: C 27.41, H 2.90, F 26.49, N 6.65, S 14.91.

*4-Amino-4*H*-2,4-triazole-3,5-dipropanol* (**11**). As described for **5**, **10** (1.7 g, 7.1 mmol) [12] and 80% $NH_2NH_2 \cdot H_2O$ (0.41 ml, 10.7 mmol) in toluene (10 ml) were stirred under reflux for 2 h yielding **11** (0.629 g, 88%). M.p. 152° ([15]: 152–154°). $pK_{HA} = 8.53$. IR (KBr): 3290*s*, 3200*s*, 2960*s*, 2940*s*, 2880*s*, 2840*s*, 2770*s*, 2610*w*, 2500*w*, 1650*m*, 1540*s*, 1530*s*, 1465*m*, 1445*s*, 1430*s*, 1360*s*, 1350*s*, 1070*s*, 1050*s*, 925*m*, 910*s*. ^{1}H-NMR (200 MHz, (D$_6$)DMSO): 5.71 (*s*, exchange with D_2O, NH_2); 4.58 (*t*, $J = 5.2$, exchange with D_2O, 2 OH); 3.47 (*q*, $J = 6.0$, addition of $D_2O \rightarrow t$ ($J = 6.4$), 2 CH_2(1)); 2.67 (*dd*, $J = 5.2$, 10.2, addition of $D_2O \rightarrow 2.71$, '*t*' ($J \approx 7.7$), 2 CH_2(3)); 1.9–1.7 (*m*, 2 CH_2(2)). ^{13}C-NMR (50 MHz, (D$_6$)DMSO): 154.7 (*s*, C(3), C(5) of triazole); 60.4 (*t*, 2 C(1)); 30.0 (*t*, 2 C(3)); 20.7 (*t*, 2 C(2)). EI-MS: 156 (100), 155 (15), 141 (21), 139 (16). Anal. calc. for $C_8H_{12}N_4O_2$ (200.2): C 47.99, H 8.05, N 27.98; found: C 48.08, H 7.93, N 28.19.

Tetrahydrofuran-2-one N,N-*Dimethylhydrazone* (**21**). A) At 30°, NH_2NMe_2 (0.32 ml, 4.3 mmol) was added dropwise to a soln. of **10** [12] (1 g, 4.2 mmol) in toluene (6 ml) and stirred at 75° for 1 h. Evaporation and FC (AcOEt/MeOH 7:3 → MeOH/H_2O 3:4) of the residue gave **21** (258 mg, 47%).

B) At 0°, NH_2NMe_2 (1.6 ml, 21 mmol) was added dropwise to a soln. of **10** (5.018 g, 21 mmol) in toluene (30 ml) and stirred at 0° for 1 h. After 12 h at −18°, $TsNH_2$ (27%) precipitated. Filtration and distillation of the residue of the filtrate at 120°/15 Torr gave **21** (0.165 g, 6%). The residue (4.679 g) consisted of a brown polymerisate.

C) At 0°, 2,3-dihydrofuran (0.76 ml, 10 mmol) was added to a soln. of TfN_3 (prepared from Tf_2O (6.72 mmol) and NaN_3 (14.4 mmol)) in CH_2Cl_2 and stirred for 90 min at 0° and for 60 min at 23°. The mixture was cooled to 0° and treated with NH_2NMe_2 (0.46 ml, 6.0 mmol). After stirring for 6 min, the mixture was poured onto ice-cooled 1N NaOH and extracted with hexane and CH_2Cl_2. The CH_2Cl_2 layer was dried (NaOH), concentrated, and distilled (140°/15 Torr), affording **21** (0.203 g, 26%). R_f (AcOEt/MeOH/H_2O 7:2:1) 0.19. UV (Et_2O): 242 (1258), IR

($CHCl_3$): 2990*s* (sh), 2960*s*, 2910*s*, 2870*s*, 2830*m*, 2790*m*, 1680*s*, 1470*m*, 1455*m*, 1435*m*, 1375*m*, 1185*s*, 1095*m*, 1040*s*, 1020*m*, 995*s*, 985*m*. ^{1}H-NMR (200 MHz, $CDCl_3$, (*Z*)/(*E*) ≈ 7:3): (*Z*)-isomer: 4.35 (*t*, *J* = 6.8, CH_2(5)); 2.59 (*t*, *J* = 8.0, CH_2(3)); 2.53 (*s*, 2 Me); 2.12 ('*dt*', *J* ≈ 1.5, 7.5, CH_2(4)); (*E*)-isomer: 4.22 (*t*, *J* = 7.0, CH_2(5)); 2.76 ('*t*', *J* ≈ 7.9, CH_2(3)); 2.42 (*s*, 2 Me). EI-MS: 128 (100, $M^{+\cdot}$), 127 (27), 86 (28), 85 (11), 72 (10), 43 (45).

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