TRIAZOLIUM SALTS, II[1]: DERIVATIVES OF 4,5-DIHYDRO-5,5-DIMETHYL-1,2,4-TRIAZOL-3-ONE

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Abstract - The title compound **1a** was converted into novel N-4-substituted derivatives. Catalytic hydrogenation of **1a** yielded the triazolidin-3-one **3**, the cyclotautomer of acetone semicarbazone **4**. Meerwein salts alkylated the diazene function of **1a** at N-2 affording the triazolium salts **5**.

In the literature, the heterocyclic system of 5,5-disubstituted 4,5-dihydro-1,2,4-triazol-3-ones is mainly represented by 4-aryl substituted derivatives like **1b** which have been made accessible by oxidative ring closure of 4-arylsemicarbazones of ketones.[2-4] By analogy, the oxidative cyclization of 4-arylthiosemicarbazones furnishes 5,5-disubstituted 4-aryl-4,5-dihydro-1,2,4-triazol-3-thiones,[2,4] which in turn upon desulfurization are converted into the corresponding 1,2,4-triazolin-3-ones.[2,4] Recently, an entirely different approach has been described: The treatment of 1,2-bis(isocyanatoalkyl)diazenes with acid provides an efficient method for the preparation of 5,5-dialkyl-4,5-dihydro-1,2,4-triazol-3-ones.[5,6]

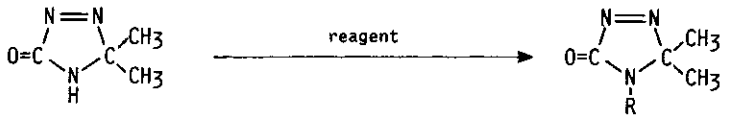
As exemplified by 4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**1a**), all ring nitrogen atoms may participate in chemical reactions: The unsubstituted position at N-4 of **1a** offers the opportunity of introducing substituents not accessible by the aforementioned procedure of oxidative ring closure of semicarbazones,[2-4] thus complementing that method. Furthermore, the diazene function of **1a** is susceptible to chemical derivatization.

Substitution at N-4 of **1a** *(Scheme 1):*

Benzoylation of **1a** (and of homologous 5,5-dialkyl substituted derivatives) has been described to proceed smoothly with benzoyl chloride under Einhorn conditions[6] to yield **1c**. Similarly, the acylation of **1a** with chloroacetyl chloride in the presence of 2,6-lutidine furnished **1d**.

Dedicated to Professor Fritz Sauter, Vienna, on the occasion of his sixtieth birthday.

Scheme 1:



1a **1c-1f, 1h-1j**

Reagent	1	R
	[**1b**	C_6H_5 (lit.[2-4])]
C_6H_5COCl; pyridine	**1c**	C_6H_5CO (lit.[6])
$ClCH_2COCl$; 2,6-lutidine	**1d**	$ClCH_2CO$
4-$CH_3C_6H_4SO_2Cl$; pyridine	**1e**	4-$CH_3C_6H_4SO_2$
4-$CH_3CONHC_6H_4SO_2Cl$; pyridine	**1f**	4-$CH_3CONHC_6H_4SO_2$
	[**1g**	H_2NCO (lit.[6])]
$C_6H_5N{=}C{=}O$	**1h**	C_6H_5NHCO
CH_3I; DBU	**1i**	CH_3
$C_6H_5CH_2Br$; DBU	**1j**	$C_6H_5CH_2$

Analogously, arenesulfonylation at N-4 of **1a** was accomplished by the reaction with 4-methyl- and 4-acetamidobenzenesulfonyl chloride in the presence of pyridine affording the derivatives **1e** and **1f**.

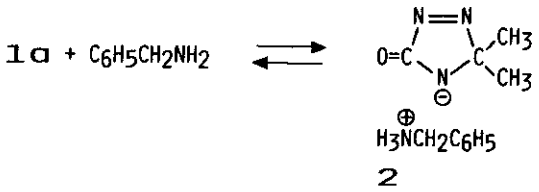
In the course of the acid induced conversion of 1,2-bis(isocyanatoalkyl)diazenes into 1,2,4-triazolin-3-ones (*e.g.* **1a**), 4-aminocarbonyl-1,2,4-triazolin-3-ones have been obtained as by-products.[6] As has been shown for the formation of 4-aminocarbonyl-4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**1g**), this compound does not arise from the reaction of **1a** with isocyanic acid, it is formed in a competing reaction of the common precursor 1,2-bis(isocyanatoalkyl)diazene with acid.[6] On the contrary, **1a** reacted with phenyl isocyanate in refluxing petroleum ether (bp 50-70°C) yielding the 4-carbanilide derivative **1h**. The carbonyl absorptions of **1g**[6] and **1h** differ slightly, both ring- and exocyclic C=O-frequencies of **1h** are lowered owing to the effect of the phenyl group.

Alkylation of **1a** at position N-4 required special reaction conditions: In order to produce the 4-alkyl derivatives **1i** and **1j**, the reaction of **1a** with the alkyl halide (excess of alkyl halide proved useful in raising the yields) had to be carried out in the presence of a nonnucleophilic base like 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU). Upon addition of the base some gas evolution occurred indicating the partial decomposition of **1a**, presumably due to deprotonation[7] and formation of the relatively unstable anion of **1a**.

Combining equivalent quantities of **1a** and benzylamine dissolved in dry ether caused the precipitation of the low melting salt **2** (Scheme 2). The ir spectrum of solid **2** (KBr pellet) shows a drastically lowered carbonyl frequency at 1650 cm^{-1} (as compared to 1815 cm^{-1} of **1a** in KBr[8]); in addition, the typical NH_3^+-absorption is displayed in the range of 3200-2200 cm^{-1}. Remarkably, the ir spectrum of **2** taken in chloroform solution is lacking these frequencies, and the carbonyl frequency of **1a** is observed (at 1760 cm^{-1} in $CHCl_3$[8]) indicating the

dissociation of the salt **2** in solution. Similarly, the uv spectrum of **2** (in $CHCl_3$) matches with that of **1a**.[8] The instability of the crystalline salt **2** prevented a satisfactory elemental analysis.

Scheme 2:



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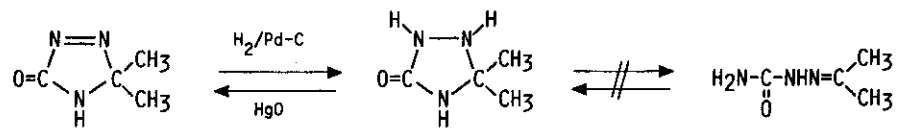
Reactions at the diazene function of **1a**:

In general, alkyl- and aryl-substituted diazenes are poor dienophiles in [4+2] cycloaddition reactions; however, attachment of electron withdrawing substituents like carbonyl groups to both nitrogen atoms of the diazene function results in a drastically enhanced reactivity toward dienes.[9] 4-Aryl-1,2,4-triazolin-3-ones, like **1b**, with both activating and deactivating substituents linked to the diazene function have been found to be unreactive dienophiles;[2] likewise, **1a** did not undergo [4+2] cycloaddition reactions with nucleophilic 1,3-dienes,[10] *e.g.* 2-methyl-1,3-butadiene and (*E*)-1-methoxy-3-trimethylsiloxy-1,3-butadiene.[11,12]

Calytic hydrogenation of **1a** furnished the crystalline 5,5-dimethyl-1,2,4-triazolidin-3-one (**3**) in almost quantitative yield (Scheme 3). In this reduction, the heterocyclic structure is preserved as evidenced by ^1H nmr: The four singlets displayed (ratio 6:1:1:1) are assigned to the equivalent methyl protons and the three NH-groups (exchangeable with D_2O).

Scheme 3:



1a 3 4

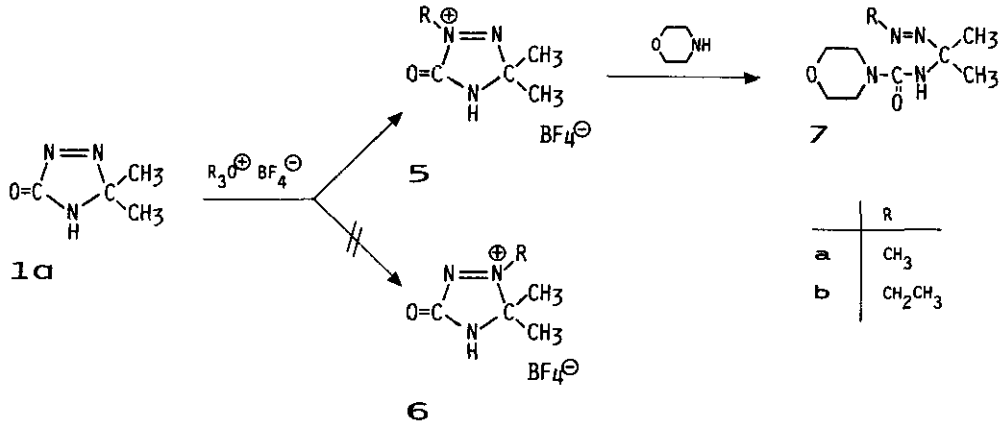
This result contrasts with the ring-cleavage encountered in the course of the reduction of the diazene group of 4-substituted derivatives of **1a**: The reaction of 4-aryl-1,2,4-triazolin-3-ones (e.g. **1b**) with sodium borohydride has been reported to occur with concomitant ring-opening yielding 4-arylsemicarbazones of ketones.[4] Similarly, catalytic hydrogenation of the 4-benzoyl and 4-aminocarbonyl derivatives **1c** and **1g** was found to provide the corresponding open-chain acetone 4-benzoylsemicarbazone and 4-aminocarbonylsemicarbazone[6].

Owing to the hydrazine moiety, the 1,2,4-triazolidin-3-one **3** undergoes facile dehydrogenation: The compound is air sensitive, and mercuric oxide converted **3** into **1a** within a few minutes.

Notably, compound **3** represents the hitherto unknown cyclotautomer of acetone semicarbazone **4**. Attempts to convert acetone semicarbazone **4** into **1a** by employing the oxidative ring-closure method as applied to acetone 4-arylsemicarbazones (*vide supra*),[2-4] *e.g.* by using $FeCl_3$, failed.[10] This is good evidence that the semicarbazone **4** and its cyclotautomer **3** do not equilibrate under the conditions applied.

As mentioned above, alkylation of **1a** at N-4 with alkyl halides in the presence of a base is not easily accomplished. On the other hand, the alkylation of **1a** with Meerwein reagents (R_3O^+ BF_4^-, R = Me, Et) furnished salts (Scheme 4): The attachment of an alkyl substituent at one of the diazene N-atoms of **1a** was confirmed by ^1H nmr, as this goes along with a considerable deshielding of all alkyl protons. The ir spectra display an exceptionally high C=O-frequency at 1855 cm^{-1} which similarly has been encountered in 1-aryl-4,5-dihydro-3,3-dimethyl-5-oxo-3*H*-1,2,4-triazolium salts.[13] Thus, the analogous structure of 1-alkyl-4,5-dihydro-3,3-dimethyl-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborates (**5**) is most likely; the alkylation of **1a** at N-2 may be anticipated from the fact that in the solid state of **1a** an intermolecular hydrogen bond is extended from the protic amide nitrogen atom N-4 to the diazene nitrogen atom N-2,[8] indicating that the latter position is the site of highest electron density.

Scheme 4:



In order to confirm structures **5**, these salts were subjected to the reaction with morpholine. The resultant 1-(1-alkylazo-1-methylethyl)urea derivatives **7** provide the unambiguous structure proof (R connected to N-1 of **5**)[14] ruling out the isomeric structure of the triazolium salts **6** (Scheme 4).

EXPERIMENTAL

Melting points (mp) were determined with a Kofler hot stage microscope (Reichert). Solvents were evaporated using a rotatory evaporator Vapsilator (Chemophor) at ca. 20 mbar. The spectroscopic data were recorded on the following instruments: Beckman AccuLab 4 (ir); JEOL JNM-PMX-60 (^1H nmr; 60 MHz); Gilford 250 (uv);

Varian MAT 44S (ms). Elemental analyses were performed by Dr. J. Zak, Institut für Physikalische Chemie, University of Vienna.

4.5-Dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**1a**) is available as reported.[6]

4-(Chloroacetyl)-4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**1d**): To a stirred solution of **1a** (2.26 g, 20 mmol) and 2,6-dimethylpyridine (2.16 g, 20.2 mmol) in ether (100 ml) was added dropwise within 10 min at 0°C a solution of chloroacetylchloride (2.28 g, 20.2 mmol) in ether (10 ml). After 30 min, the precipitate formed was dissolved upon addition of water (100 ml), and the two layers were separated; the aqueous layer was saturated with sodium chloride and extracted with ether (3 x 30 ml). The combined ether extracts were dried ($MgSO_4$), the solvent was evaporated to yield the pure (by ^1H nmr) crystalline product **1d** (3.56 g, 94%); mp 82.5-85°C (purification by sublimation, 30°C, 0.01 mbar). ^1H Nmr ($CDCl_3$): δ 1.77 [s, 6H, $(CH_3)_2C$]; 4.68 (s, 2H, CH_2). Ir (KBr): 1790, 1730 cm^{-1} (C=O). Uv-vis (methanol): λ_{max} [nm] (log ϵ) 386 (2.32); 247 (3.56). Ms (CI, i-butane): m/z (%) 246 (100) $[M + 57]^+$; 170 (51) $[M + 57 - ClCH=C=O]^+$; 114 (37) $[C_4H_8N_3O^+ = \mathbf{1a}.H^+]$. Anal. Calcd for $C_6H_8ClN_3O_2$: C, 38,01; H, 4.25; Cl, 18.70; N, 22.16. Found: C, 37.73; H, 4.23; Cl, 18.54; N, 22.42.

4,5-Dihydro-5,5-dimethyl-4-(4-methylbenzenesulfonyl)-1,2,4-triazol-3-one (**1e**): A mixture of **1a** (1.13 g, 10 mmol), *p*-toluenesulfonyl chloride (1.91 g, 10 mmol), and pyridine (2.5 ml) was stirred for 6 h; then it was distributed between dichloromethane and water (50 ml each). The organic layer was separated, washed with water, and dried ($MgSO_4$). After evaporation of the solvent, the crystalline residue was dissolved in dichloromethane and chromatographed on silica gel (50 g, deactivated with 10% water; eluent ether) to give pure (by tlc) crystals **1e** (1.08 g, 40 %); mp (decomp.) 150-154°C (ethanol). ^1H Nmr ($CDCl_3$): δ 1.83 [s, 6H, $(CH_3)_2C$)]; 2.43 (s, 3H, CH_3-C_6H_4); 7.18-7.45, 7.78-8.05 (AA'BB', C_6H_4). Ir (KBr): 1780 cm^{-1} (C=O). Uv-vis (ethanol): λ_{max} [nm] (log ϵ) 383 (2.40); 230 (4.20) 255 (sh). Ms (CI, *i*-butane): m/z (%) 268 (100) $[M + 1]^+$; 252 (18); 170 (21); 139 (34); 129 (29); 127 (22); 113 (36). Anal. Calcd for $C_{11}H_{13}N_3O_3S$: C, 49.43; H, 4.90; N, 15,72. Found: C, 49.37; H, 4.81; N, 15,89.

4-(4-Acetamidobenzenesulfonyl)-4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**1f**): Following the procedure described in the preceding experiment, **1a** (1.13 g, 10 mmol), 4-acetamidobenzenesulfonyl chloride (2.33 g, 10 mmol) and pyridine (2.5 ml) were converted into **1f** (1.30 g, 42%); mp (decomp.) 182-184°C (ethanol). ^1H Nmr (DMSO-d_6): δ 1.79 [s, 6H, $(CH_3)_2C$]; 2.08 (s 3H, CH_3CO); 7.60-8.05 (AA'BB', C_6H_4); 10.33 (broad s, 1H, NH exchangeable with D_2O). Ir (KBr): 3330, 3290 (NH); 1760, 1700 cm^{-1} (C=O). Uv-vis (ethanol): λ_{max} [nm] (log ϵ) 383 (2.40); 268 (4.28); 274 (sh). Anal. Calcd for $C_{12}H_{14}N_4O_4S$: C, 46.44; H, 4,55; N, 18,05. Found: C, 46.39; H, 4.53; N, 18.03.

4,5-Dihydro-5,5-dimethyl-4-phenylcarbamoyl-1,2,4-triazol-3-one (**1h**): To a solution of **1a** (2.26 g, 20 mmol) in petroleum ether (boiling range 50-70°C; 200 ml) was added phenyl isocyanate (2.62 g, 22 mmol). The mixture was heated to reflux for 7 h, the residue after evaporation of the solvent was dissolved in dichloromethane and

chromatographed on silica gel (80 g, deactivated by addition of 10% water; eluent ether): The first fractions eluted were collected and yielded crystals of **1h** (3.66 g, 79%); mp (decomp.) 115-117°C (ethanol). ^{1}H Nmr ($CDCl_3$): δ 1.83 [s, 6H, $(CH_3)_2C$]; 7.03-7.63 (m 5H, C_6H_5); 9.73 (s broad, 1H, NH exchangeable with D_2O). Ir (KBr) 3290 (NH); 1760, 1715 cm^{-1} (C=O). Uv-vis (methanol): λ_{max} [nm] (log ϵ) 234 (4.16); 256 (sh); 356 (sh). Ms (CI, *i*-butane): m/z (%) 233 (100) $[M + 1]^+$; 170 (92); 114 (11). Anal. Calcd for $C_{11}H_{12}N_4O_2$: C, 56.89; H, 5.21; N, 24.12. Found: C, 56.73; H, 5.23; N, 24.33.

4,5-Dihydro-4,5,5-trimethyl-1,2,4-triazol-3-one (**1i**): To a stirred solution of **1a** (1.13 g, 10 mmol) and methyl iodide (3.55 g, 25 mmol) in dichloromethane (20 ml) was added dropwise at 0°C a solution of 1,8-diazabicyclo[5.4.0]undecomp.-7-ene (DBU, 1.67 g, 11 mmol) in dichloromethane (5 ml) (toward the end of the addition gas evolution was observed). After 12 h, the solution was concentrated to 10 ml and chromatographed on basic alumina (45 g, activity I; eluent ether); evaporation of the solvent furnished the pure (by tlc) crystals **1i** (1.06 g, 84%); mp 41-41.5°C (purification by sublimation, 20°C, 0.01 mbar). ^{1}H Nmr ($CDCl_3$): δ 1.51 [s, 6H, $(CH_3)_2C$]; 2.97 (s, 3H, CH_3-N). Ir ($CHCl_3$): 1765 cm^{-1} (C=O). Uv-vis (methanol): λ_{max} [nm] (log ϵ) 373 (2.49); 379 (sh). Ms (CI, *i*-butane): m/z (%) 184 (20) $[M + 57]^+$; 128 (59) $[M + 1]^+$; 113 (12) $[C_4H_7N_3O$ = **1a**$^{\cdot+}]$; 73 (57); 72 (100) $[(CH_3)_2C{=}NH\text{-}CH_3]^+$. Anal. Calcd for $C_5H_9N_3O$: C, 47.23; H, 7.13; N, 33.05. Found: C, 47.11; H, 7.14; N, 33.42.

4-Benzyl-4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**1j**): As described in the preceding experiment, **1a** (2.26 g, 20 mmol), benzyl bromide (3.76 g, 22 mmol), and DBU (3.35 g, 22 mmol) in dichloromethane (35 + 5 ml) were converted into crystalline **1j** (2.01 g, 50%); mp 62-64°C (ether). ^{1}H Nmr ($CDCl_3$): δ 1.35 [s, 6H, $(CH_2)_3C$]; 4.52 (s; 2H, CH_2); 7.22 (s, 5H, C_6H_5). Ir ($CHCl_3$): 1760 cm^{-1} (C=O). Uv-vis (methanol): λ_{max} [nm] (log ϵ) 374 (2.48); 383 (sh); 268 (3.34). Ms (CI, *i*-butane): m/z (%) 206 (100) $[M + 3]^+$; 204 (90) $[M + H]^+$; 190 (20); 158 (42); 156 (50); 133 (26) $[C_6H_5CH_2NCO]^{\cdot+}$. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.45; N, 20.68. Found: C, 65.02; H, 6,60; N, 20.99.

Salt **2** (= **1a** benzylamine): To a stirred solution of **1a** (0.57 g, 5 mmol) in dry ether (30 ml) was added dropwise at 0°C within 2 min a solution of benzylamine (0.54 g, 5 mmol) in dry ether (5 ml). The precipitate formed was filtered off, washed with ether and dried (0.01 mbar, 20°C) to give the salt **2**; mp (decomp.) 67-68°C. ^{1}H Nmr ($CDCl_3$): δ 1.53 [s, 6H, $(CH_3)_2C$]; 3.84 (s, 2H, CH_2); 4.11 (s, 3H, NH_3^+, exchangeable with D_2O); 7.22 (broad s, 5H, C_6H_5). Ir (KBr): 3200-2200 (NH_3^+); 1650 cm^{-1} (C=O); ir ($CHCl_3$): 1770 cm^{-1} (C=O). Uv-vis ($CHCl_3$): λ_{max} [nm] (log ϵ) 377 (2.57), 384 (sh); 254 (3.42).

5,5-Dimethyl-1,2,4-triazolidin-3-one (**3**): The solution of **1a** (2.26 g, 20 mmol) in ethanol (60 ml), after addition of Pd-C (10%, 0.22 g), was hydrogenated in a Parr apparatus (2 bar) for 16 h. Filtration through Celite and evaporation of the solvent gave the pure (by tlc) product **3**; mp (decomp.) 114.5-116.5°C (acetone). ^{1}H Nmr (DMSO-d_6): δ 1.20 [s, 6H, $(CH_3)_2C$]; 4.80, 6.67, 7.28 (3 broad ss, 3H, 3 NH, exchangeable with D_2O). Ir (KBr):

3180 (broad, NH); 1680 cm^{-1} (C=O). Ms (CI, *i*-butane): m/z (%) 231 (21); 116 (100) $[M + 1]^+$; 72 (7) $[M - HNCO]^{\cdot +}$. Anal. Calcd for $C_4H_9N_3O$: C, 41.73; H, 7.88; N, 36,50. Found: C, 40.55; H, 7.38; N, 36.06; (contains 2% H_2O).

Oxidation of **3**: Mercuric oxide (1.30 g, 6 mmol) was added to a stirred solution of **3** (0.34 g, 3 mmol) in ethanol (10 ml) at room temperature. After 5 min, elemental mercury was removed by filtration, and the filtrate was evaporated to dryness. To the residue were added ether (30 ml), saturated sodium chloride solution (10 ml), and 2 *N* hydrochloric acid (1 ml). The separated aqueous layer was extracted with ether (3 x 15 ml), the combined ether extracts were washed with saturated sodium chloride solution until neutral, dried ($MgSO_4$), and evaporated to give crystalline **1a** (0.26 g, 77%), identical (by ir and ^1H nmr) with an authentic sample.[6]

4,5-Dihydro-1,3,3-trimethyl-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborate (**5a**): To the stirred slurry of trimethyloxonium tetrafluoroborate (1.53 g, 10.3 mmol) in dichloromethane (35 ml) under nitrogen was added at room temperature within 10 min a solution of **1a** (1.18 g, 10.4 mmol) in dichloromethane (35 ml). After continued stirring for 12 h, addition of ether (40 ml) brought about precipitation of colorless crystals which were filtered off, washed with ether, and dried (0.01 mbar, 30 °C) to give analytically pure **5a** (2.04 g, 92%); mp (decomp.) starting at 95°C. ^1H Nmr (CD_3CN): δ 1.84 [s, 6H, $(CH_3)_2C$)]; 4.40 (s, 3H, CH_3); 7.0-10.1 (broad s, 1H, NH). Ir (KBr): 1855 cm^{-1} (C=O). Uv (acetonitrile): λ_{max} [nm] (log ϵ) 294 (3.11); Anal. Calcd for $C_5H_{10}BF_4N_3O$: C, 27.94; H, 4.69; N, 19.55. Found: C, 27.33; H, 4.58; N, 19.35.

1-Ethyl-4,5-dihydro-3,3-dimethyl-5-oxo-3*H*-1,2,4-triazolium tetrafluoroborate (**5b**): To the stirred solution of triethyloxonium tetrafluoroborate (2.25 g, 118 mmol) in dichloromethane (25 ml) under nitrogen was added at room temperature within 10 min a solution of **1a** (1.35 g, 11.9 mmol) in dichloromethane (10 ml). After continued stirring for 12 h, addition of ether (40 ml) brought about precipitation of colorless crystals which were filtered off, washed with ether, and dried (0.01 mbar, 30 °C) to give analytically pure **5b** (2.36 g, 87%); mp (decomp.) starting at 77°C. ^1H Nmr (CD_3CN): δ 1.60 (t, J = 7 Hz, 3H, CH_3-CH_2); 1.84 [s, 6H, $(CH_3)_3C$]; 4.73 (q, J = 7 Hz, 2H, CH_2); 9.38 (broad s, 1H, NH). Ir (KBr) 1850 cm^{-1} (C=O). Uv (acetonitrile): λ_{max} [nm] (log ϵ) 279 (3.08). Anal. Calcd for $C_6H_{12}BF_4N_3O$: C, 31.47; H, 5.28; N, 18.35. Found: C, 31.32; H, 5.66; N, 18.78.

N-(1-Methylazo-1-methylethyl)-4-morpholinecarboxamide (**7a**): To a stirred slurry of **5a** (1.50 g, 7 mmol) in dry ether (50 ml) at 0°C was added dropwise within 5 min a solution of morpholine (1.22 g, 14 mmol) in dry ether (30 ml). The mixture was stirred for 4 h while warming up to room temperature, and after addition of water (80 ml) the two layers were separated; the aqueous layer was saturated with sodium chloride and extracted with ether (3 x 20 ml). The combined ether extracts were washed with saturated sodium chloride solution until neutral and dried ($MgSO_4$). Evaporation of the solvent yielded the pure (by tlc) crystals **7a** (1.31 g, 87%); mp (decomp.) 115-118°C (*n*-hexane). ^1H Nmr ($CDCl_3$): δ 1.62 [s, 6H, $(CH_3)_2C$]; 3.20-3.47 and 3.57-3.84 (AA'BB', CH_2-CH_2); 3.80 (s, 3H, CH_3); 6.23 (s, 1H, NH, exchangeable with D_2O). Ir ($CHCl_3$): 3380 (NH); 1650 cm^{-1}

(C=O). Uv-vis (acetonitrile): λ_{max} [nm] (log ϵ) 353 (1.20). Ms (CI, *i*-butane): m/z (%) 215 (100) $[M + 1]^+$; 171 (29) $[(CH_3)_2C{=}NH\text{-}CO\text{-}N(CH_2\text{-}CH_2)_2O]^+$. Anal. Calcd for $C_9H_{18}N_4O_2$: C, 50.45; H, 8,47; N, 26,15. Found: C, 50,40; H, 8.43; N, 25.99.

N-(1-Ethylazo-1-methylethyl)-4-morpholinecarboxamide (**7b**): As described before, **5b** (1.60 g, 7 mmol) and morpholine (1.22 g, 14 mmol) were converted into pure (by tlc) **7b** (1.48 g, 93%); mp (decomp.) 81-83°C (purification by sublimation, 30°C, 0.01 mbar). ^{1}H Nmr ($CDCl_3$): δ 1.31 (t, J = 7 Hz, 3H, CH_3-CH_2); 1.62 [s, 6H, $(CH_3)_2C$]; 3.18-3.42, 3.55-3.81 (AA'BB', CH_2-CH_2); 3.88 (q, J = 7 Hz, 2H, CH_2); 6.27 (broad s, 1H, NH, exchangeable with D_2O). Ir ($CHCl_3$): 3370 (NH); 1650 cm^{-1} (C=O); Uv-vis (acetonitrile): λ_{max} [nm] (log ϵ) 354 (1.23). Ms (CI, *i*-butane): m/z (%) 229 (67) $[M + 1]^+$; 188 (15); 171 (100) $[(CH_3)_2C{=}NH\text{-}CO\text{-}N(CH_2\text{-}CH_2)_2O]^+$; 114 (14). Anal. Calcd for $C_{10}H_{20}N_4O_2$ (228.30): C, 52.61; H, 8.83; N, 24.54. Found: C, 52.55; H, 8.78; N, 24.57.

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