TRIAZOLIUM SALTS, III[1]: 1-(1,1-DIMETHYLETHYL)-4,5-DIHYDRO-3,3-DIMETHYL-5-OXO-3*H*-1,2,4-TRIAZOLIUM CHLORIDE

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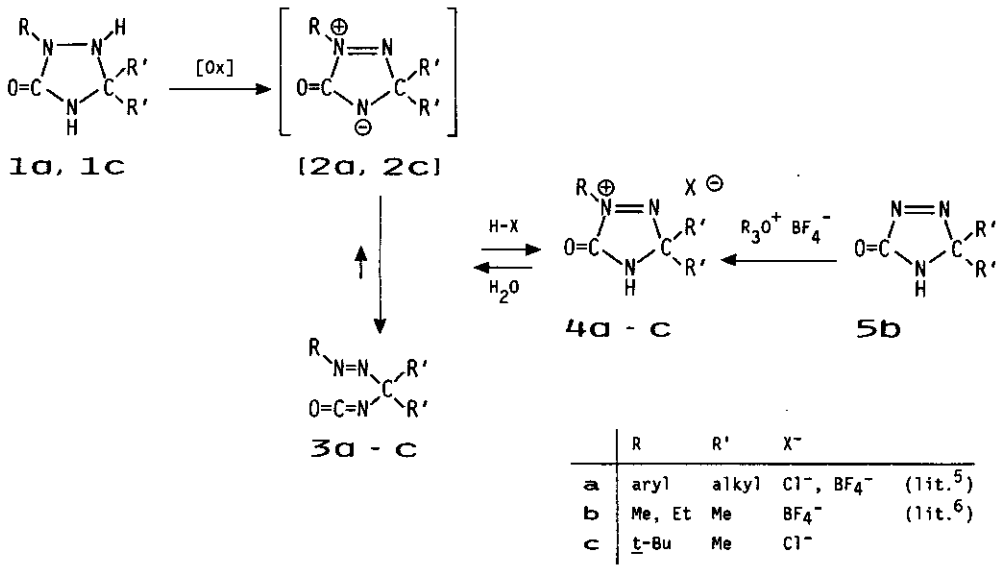
Abstract - The cycloaddition reaction of acetone *t*-butylhydrazone (**6**) with cyanic acid yielded the 1,2,4-triazolidin-3-one **1c**, subsequent oxidative ring-opening afforded the *t*-butylazoalkyl isocyanate **3c**. Derivatization of the isocyanate function of **3c** furnished the carbamic acid derivatives **7** - **10**. Reactions involving both geminal functional groups of **3c** led to the heterocycles **11**, **12**, and the title compound **4c**; some properties and reactions of the triazolium salt **4c** are described.

The oxidative ring-opening of 2-aryl-1,2,4-triazolidin-3-ones **1a** has been found to provide an efficient access to the geminal arylazoalkyl isocyanates **3a**[2] (Scheme 1), which in turn have been noted for their unusual chemical reactivity.[3,4] Notably, the treatment of **3a** with aqueous acids affords 1-aryl-1,2,4-triazolium salts **4a**.[5]
1-Alkyl-1,2,4-triazolium salts **4b** have been first obtained from the reaction of 4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (**5b**) with trialkyloxonium tetrafluoroborates.[6,7] The scope of this latter approach to 1-alkyl-1,2,4-triazolium salts **4** (Scheme 1, R = alkyl) appears to be limited by the availability of the appropriate alkylating reagent. Therefore, the procedure which has been proved successful to prepare 1-aryl-1,2,4-triazolium salts **4a** from **3a**[5] has been applied for the synthesis of the 1-(*t*-butyl)-1,2,4-triazolium salt **4c**.

Synthesis of 1-(1,1-dimethylethyl)-2-(1-isocyanato-1-methylethyl)diazene (**3c**) (Scheme 2):
In a patent,[8] a two step synthesis of compound **3c** has been described: The conversion of 2-propanone (1,1-dimethylethyl)hydrazone (**6**) with chlorine into 1-(1-chloro-1-methylethyl)-2-(1,1-dimethylethyl)diazene is followed by the displacement of chloride with potassium cyanate. On the other hand, arylazoalkyl isocyanates **3a** are accessible by an efficient reaction sequence from arylhydrazones of aliphatic and araliphatic ketones.[2,3] Thus, it was at hand to extend this procedure to the preparation of the alkylazoalkyl isocyanate **3c** (Scheme 2).

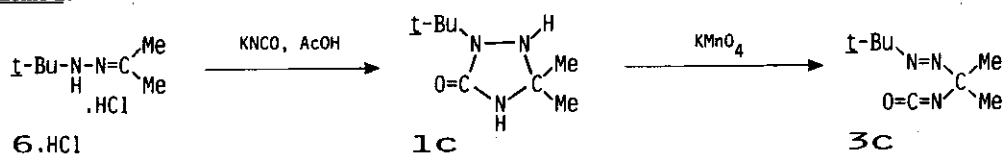
Scheme 1:



	R	R'	X⁻	
a	aryl	alkyl	Cl^-, BF_4^-	(lit.[5])
b	Me, Et	Me	BF_4^-	(lit.[6])
c	t-Bu	Me	Cl^-	

Mixing of *t*-butylhydrazine hydrochloride and acetone gave 2-propanone *t*-butylhydrazone hydrochloride (**6** hydrochloride); this salt was treated with potassium cyanate in acetic acid. The apparent [3 + 2] cycloaddition reaction of **6** with isocyanic acid (generated *in situ*) afforded 2-(1,1-dimethylethyl)-5,5-dimethyl-1,2,4-triazolidin-3-one (**1c**). Subsequent treatment of **1c** with an aqueous solution of potassium permanganate brought about oxidative ring-opening and provided 1-(1,1-dimethylethyl)-2-(1-isocyanato-1-methylethyl)diazene (**3c**).

Scheme 2:



Reaction of **3c** with nucleophiles (Scheme 3):

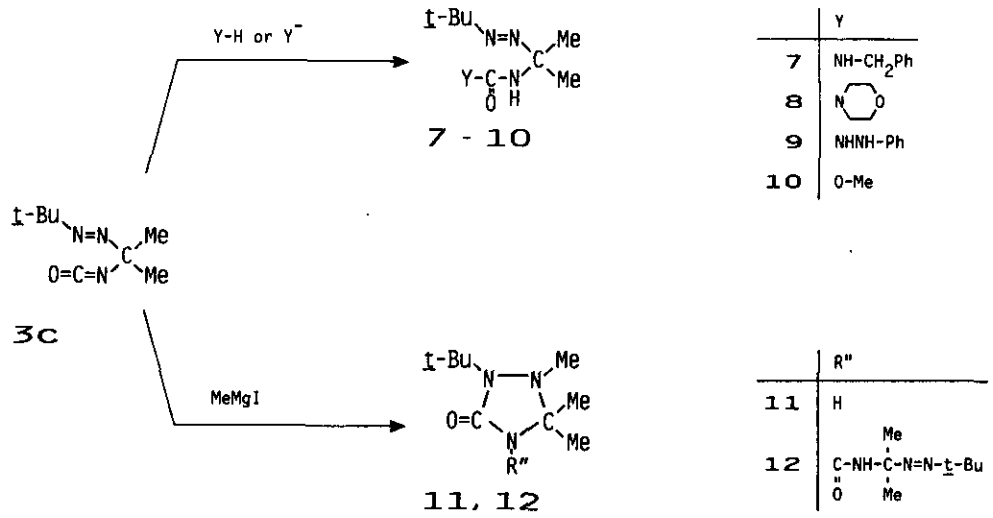
Similar to other geminal azoalkyl isocyanates,[3] the reaction of **3c** with various nucleophilic reagents takes place in different ways: N-Nucleophiles like amines, phenylhydrazine, and the anion derived from the amide **11** (*vide infra*) gave rise to the formation of the usual addition products to the heterocumulene function of **3c** yielding the respective urea derivatives **7** - **9**, and **12**.

By contrast, **3c** proved reluctant to react with neutral O-nucleophiles like water (*cf* the preparation of **3c**) and alcohols at room temperature. The reaction with methanol under reflux was sluggish and incomplete; methoxide catalysis was necessary to accomplish the conversion of **3c** into the methyl carbamate **10**.

Certain nucleophilic reagents (Grignard compounds[4] and others[9]) are notorious in attacking the diazene group rather than the isocyanate function of geminal arylazoalkyl isocyanates **3a**; involving the latter functional group

in a concomitant ring-closure reaction, 1,2,4-triazolidin-3-one derivatives (with the nucleophilic group attached to N-1) are formed.[4] Similarly, the reaction of **3c** with methylmagnesium iodide yielded 2-(1,1-dimethylethyl)-1,5,5-trimethyl-1,2,4-triazolidin-3-one **11**. In addition, small amounts of **12** were isolated, the product of the nucleophilic addition of the first-formed anion of **11** to the isocyanate function of another molecule **3c**; this reaction path was proved in a separate experiment.

Scheme 3:



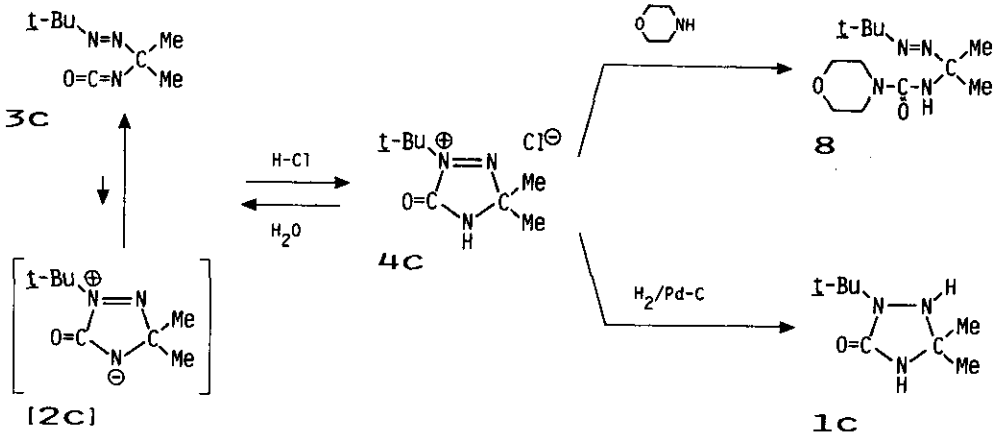
1-(1,1-Dimethylethyl)-4,5-dihydro-3,3-dimethyl-5-oxo-3*H*-1,2,4-triazolium chloride (**4c**), Preparation, Structure, and Reactions (Scheme 4):

Acids have been found to induce ring-closure of arylazoalkyl isocyanates **3a** leading to the formation of 1-aryl-triazolium salts **4a**, the structure of which has been proved by X-ray analysis.[5] By analogy, the reaction of **3c** with hydrogen chloride in ether induced a high yield conversion into the colorless, crystalline 1-(t-butyl)triazolium salt **4c**.

Spectral and chemical properties of **4c** are paralleling those of the related triazolium salts **4**,[5,6] and substantiate the structure: The uv spectrum of **4c** compares well with that of 1-alkyltriazolium salts **4b**;[6] the transformation of the diazene group of **3c** to the diazenium moiety of **4c** is accompanied by a drastic change of the uv absorption. Similarly to the related triazolium salts **4a**[5] and **4b**,[6] the ir spectrum of **4c** exhibits an exceptionally high carbonyl frequency at 1855 cm^{-1}; this is incompatible with a conceivable carbamoyl chloride function[10] (resulting from the addition of hydrogen chloride to the isocyanate group) but provides good evidence of a carbonyl group attached to a strong electron acceptor, *i.e.* the diazenium moiety of **4c**.

The azoalkyl isocyanate **3c** is insoluble in water, but it readily dissolves in 2 *N* hydrochloric acid; the uv spectrum of this solution matches with that of **4c**. On the other hand, dissolving the triazolium salt **4c** in water brought about the reconversion into the azoalkyl isocyanate **3c**.

Scheme 4:



The heterocyclic compound **4c** may be regarded as derivative of **2c**, the cyclic valence tautomer of **3c**. However, the zwitterionic species **2c** has not been substantiated by any spectral evidence. Despite the strongly electrophilic carbonyl group, as indicated by the high carbonyl frequency, **4c** does not appear to be attacked at this position by nucleophilic reagents; **4c** rather reacts as an acid, and upon deprotonation at N-4 (*e.g.* by water), the conceivably first-formed zwitterionic heterocyclic intermediate **2c** undergoes valence isomerization affording the azoalkyl isocyanate **3c**.

On the other hand, the reaction of **4c** with morpholine furnished the azoalkylurea derivative **8**, which may be viewed to result from the nucleophilic attack of the amine at the carbonyl function of **3c**; more likely, and in keeping with both the apparent acidity of **4c** and the normal electrophilicity of the isocyanate group in **3c** toward amines (*vide supra*), the formation of the urea **8** is envisaged to emerge from the deprotonation of **4c** and its reconversion into **3c** (possibly *via* **2c**) followed by the reaction with morpholine as described above.

The triazolium salt **4c** was readily reduced: Catalytical hydrogenation furnished the triazolidin-3-one **1c**.[11] The oxidizing potency of **4c** became apparent also towards other compounds.[12]

EXPERIMENTAL

Solvents were evaporated using a rotatory evaporator Vapsilator (Chemophor) at ca. 20 mbar. Melting points (mp) were determined with a Kofler hot stage microscope (Reichert). The spectroscopic data were recorded on the following instruments: JEOL JNM-PMX-60 (^{1}H nmr; 60 MHz); Beckman AccuLab 4 (ir); Gilford 250 (uv); Varian MAT 44S (ms). Elemental analyses were performed by Dr. J. Zak, Institut für Physikalische Chemie, University of Vienna.

2-Propanone (1,1-dimethylethyl)hydrazone hydrochloride (**6** hydrochloride): The slurry obtained by mixing (1,1-dimethylethyl)hydrazine hydrochloride (24.92 g, 0.2 mol) and acetone (240 ml) was stirred at room temperature.

After 20 h the crystals were filtered off, washed with acetone, and dried (0.01 mbar, 30°C) to give the pure salt **6** hydrochloride (29.9 g, 88%): mp (decomp.) 175-178°C (acetone). ^{1}H Nmr (DMSO-d_6): δ 1.33 [s, 9H, $(H_3C)_3C$]; 2.07, 2.22 [2s, 6H, $(H_3C)_2C=$]; 10.93 (broad s, 2H, 2 NH). Anal. Calcd for $C_7H_{17}ClN_2$: C, 51.05; H, 10.41; Cl, 21.53; N, 17.01. Found: C, 51.19; H, 10,38; Cl, 21.25; N, 17,27.

2-(1,1-Dimethylethyl)-5,5-dimethyl-1,2,4-triazolidin-3-one (**1c**):

(a) From **6** hydrochloride: The mixture of **6** hydrochloride (16.5 g, 0.1 mol) and acetic acid (12.0 g) was diluted with water (15 ml). The resultant solution was stirred and chilled to 0°C, and a solution of potassium cyanate (16.2 g, 0.2 mol) in water (30 ml) was added dropwise within 10 min. The precipitated crystals were filtered off, washed with little water, and dried *in vacuo*: **1c** (10.44 g, 61%); mp 111.5-112.5°C (purification by sublimation, *60°C, 0.01 mbar*). ^{1}H Nmr ($CDCl_3$): δ *1.36 [broad s, 15 H, $(CH_3)_3C$ and $(CH_3)_2C$]; 4.10 (broad s, 1H, NH,* exchangeable with D_2O); 5.66 (broad s, 1H, NH, exchangeable with D_2O). Ir (KBr): 3200 (NH); 1680 cm^{-1} (C=O). Ms (CI, *i*-butane): m/z (%) 171 (5); 115 (19) $[M-C_4H_8]^{\cdot+}$; 100 (100) $[C_3H_6N_3O]^+$. Anal. Calcd for $C_8H_{17}N_3O$: C, 56.11; H, 10.01; N, 24.54. Found: C, 56.30; H 9.78; N, 24.93.

(b) Hydrogenation of **4c**: A solution of **4c** (1.03 g, 5 mmol; *vide infra*) in acetic acid (100 ml) supplied with Pd-C (10%; 0.1 g) was hydrogenated in a Parr apparatus (22°C, 2 bar, 4 h). The catalyst was removed by filtration through Celite, and the solvent was evaporated. The residue, after neutralization with a few drops of 2 *N* NaOH, was extracted with dichloromethane (30 ml); the extract was washed with water until neutral and dried ($MgSO_4$). Evaporation of the solvent yielded the crystalline product **1c** (0.76 g, 89%), identical (by ir) with the sample prepared as described above.

1-(1,1-Dimethylethyl)-2-(1-isocyanato-1-methylethyl)diazene (**3c**): To the vigorously stirred mixture of finely powdered **1c** (8.56 g, 50 mmol) and ether (300 ml) was added portionwise the solution of potassium permanganate (10.0 g, 63 mmol) in water (300 ml); 15 min after completion, the precipitated manganese dioxide was filtered off, and the two layers of the filtrate were separated: The aqueous layer was washed with ether, and the combined ether solution was washed with water until neutral, and dried ($MgSO_4$). After evaporation of ether the residual oil was distilled under reduced pressure, the fraction boiling at 54-55°C (20 mbar) was collected: **3c** (6.29 g, 74%); n_D^{20} = 1.4222. ^{1}H Nmr ($CDCl_3$): δ 1.28 [s, 9H, $(CH_3)_3C$]; 1.43 [s, 6H, $(CH_3)_2C$]. Ir (neat) 2225, 2180, 2140 cm^{-1} (N=C=O). Uv (*n*-hexane): λ_{max} [nm] (log ϵ) 348 (1.42). Anal. Calcd for $C_8H_{15}N_3O$: C, 56.78; H 8.93; N 24.83. Found: C, 56.63; H, 8.94; N, 25.10.

1-Benzyl-3-[1-[(1,1-dimethylethyl)azo]-1-methylethyl]urea (**7**): To the stirred solution of benzylamine (1.07 g, 10 mmol) in ether (10 ml) was added dropwise within 5 min a solution of **3c** (1.69 g, 10 mmol) in ether (5 ml). After 15 min the solvent was evaporated, and the solid residue was recrystallized from *n*-hexane to give colorless crystals **7** (2.49 g, 90%); mp (decomp.) 117.5-118.5°C (*n*-hexane). ^{1}H Nmr ($CDCl_3$): δ 1.13 [s, 9H, $(CH_3)_3C$]; 1.50 [s, 6H, $(CH_3)_3C$]; 4.28 (d, J = 5.5 Hz, 2H, CH_2; the coupling collapses upon addition of D_2O); 5.12 (broad t,

J = 7 Hz, 1H, $C_6H_5CH_2NH$, exchangeable with D_2O); 5.78 (broad s, 1H, NH, exchangeable with D_2O); 7.12-7.30 (m, 5H, C_6H_5). Ir (KBr): 3305 (NH); 1630 cm^{-1} (C=O). Uv (acetonitrile): λ_{max} [nm] (log ϵ) 359 (1.26); 218 (3.46); 237 (sh). Ms (CI, *i*-butane): m/z (%) 277 (100) $[M + H]^+$; 191 (15) $[(CH_3)_2C{=}NHCONH\text{-}CH_2C_6H_5]^+$. Anal. Calcd for $C_{15}H_{24}N_4O$: C, 65.19; H, 8.75; N 20.27. Found: C, 65.38; H, 8.91; N, 20.54.

N-[1-[(1,1-Dimethylethyl)azo]-1-methylethyl]-4-morpholinecarboxamide (**8**):

(a) From **3c**: Following the procedure as described in the preceding experiment, **3c** (1.69 g, 10 mmol) and morpholine (0.87 g, 10 mmol) gave **8** (2.28 g, 89%); mp 84.5-86.5°C (*n*-hexane). ^1H Nmr ($CDCl_3$): δ 1.22 [s, 9H, $(CH_3)_3C$]; 1.59 [s, 6H, $(CH_3)_2C$]; 3.17-3.43 and 3.54-3.80 [2 AA'BB', 2 $(CH_2\text{-}CH_2)$]; 6.50 (broad s, 1H, NH, exchangeable with D_2O). Ir (KBr): 3350, 3300 (NH); 1650, 1630 cm^{-1} (C=O); ir ($CHCl_3$): 3360 (NH); 1635 cm^{-1} (C=O). Uv (acetonitrile): λ_{max} [nm] (log ϵ) 356 (1.20). Ms (CI, *i*-butane): m/z (%) 171 (27); 114 (100). Anal. Calcd for $C_{12}H_{24}N_4O_2$: C, 56.23; H, 9.44; N, 21.86. Found: C, 56.33; H, 9.42; N, 21.73.

(b) From **4c** (*vide infra*): To the stirred slurry of **4c** (0.82 g, 4 mmol) in ether (20 ml) at 0°C was added within 5 min a solution of morpholine (0.70 g, 8 mmol) in ether (5 ml). After continued stirring for 4 h at room temperature, water (20 ml) was added, and the two layers were separated; the aqueous layer was repeatedly extracted with ether, and the combined ether extracts were dried ($MgSO_4$). Evaporation of the solvent left behind a crystalline residue **8** (0.92 g, 90%), pure (by tlc) and identical (by ir and ^1H nmr) with the sample obtained above.

4-[1-[(1,1-Dimethylethyl)azo]-1-methylethyl]-1-phenylsemicarbazide (**9**): As described in the preceding experiment under (a), **3c** (1.69 g, 10 mmol) and phenylhydrazine (1.08 g, 10 mmol) produced the colorless, crystalline precipitate **9** (2.41 g, 87%); mp 127.5-128.5°C (acetonitrile). ^1H Nmr ($CDCl_3$): δ 1.10 [s, 9H, $(CH_3)_3C$]; 1.53 [s, 6H, $(CH_3)_2C$]; 5.78 (broad s, 1H, NH, exchangeable with D_2O); 6.23 (broad s, 1H, NH, exchangeable with D_2O); 6.63-7.33 (m, 6H, C_6H_5 and NH). Ir (KBr): 3360, 3295, 3220 (NH); 1670 cm^{-1} (C=O). Uv (acetonitrile): λ_{max} [nm] (log ϵ) 357 (1.26); 282 (3.20); 235 (4.07). Ms (CI, *i*-butane): m/z (%) 192 (6) $[(CH_3)_2C{=}NHCO\text{-}NHNHC_6H_5]^+$; 92 (9); 65 (8); 58 (100). Anal. Calcd for $C_{14}H_{23}N_5O$: C, 60.62; H, 8.36; N, 25.25. Found: C, 60.52; H, 8.42; N, 25.22.

Methyl N-[1-[(1,1-dimethylethyl)azo]-1-methylethyl]carbamate (**10**): To a stirred solution of sodium (0.23g, 10 mmol) in methanol (15 ml) at 0°C was added dropwise within 10 min a solution of **3c** (1.69 g, 10 mmol) in methanol (10 ml). After 10 h the reaction mixture was distributed between ether and water (100 ml each). The aqueous layer was saturated with sodium chloride and extracted with ether (3x 30 ml); the combined ether layers were washed repeatedly with saturated sodium chloride solution until neutral, and dried ($MgSO_4$). After evaporation of ether, the residual liquid was distilled in a Kugelrohr apparatus (60°C, 0.01 mbar) to yield a colorless liquid **10** (1.90 g, 95%); n_D^{20} = 1.4337. ^1H Nmr ($CDCl_3$): δ 1.19 [s, 9H, $(CH_3)_3C$]; 1.53 [s, 6H, $(CH_3)_2C$]; 3.63 (s, 3H, CH_3O); 6.30 (broad s, 1H, NH, exchangeable with D_2O). Ir ($CHCl_3$): 3360 (NH); 1720 cm^{-1} (C=O). Uv

(acetonitrile): λ_{max} [nm] (log ϵ) 357 (1.18). Anal. Calcd for $C_9H_{19}N_3O_2$: C, 53.71; H, 9.52; N, 20.88. Found: C, 53.06; H, 9.49; N, 20.88.

2-(1,1-Dimethylethyl)-1,5,5-trimethyl-1,2,4-triazolidin-3-one (11): To a solution of methylmagnesium iodide, prepared from methyl iodide (2.13 g, 15 mmol) and magnesium (0.36 g, 15 mmol) in dry ether (15 ml), was added dropwise within 30 min at 0°C a solution of **3c** (2.54 g, 15 mmol) in dry ether (20 ml). After 1 h stirring at room temperature, a saturated aqueous solution of ammonium chloride (50 ml) was added, the aqueous layer was separated and repeatedly extracted with ether. The combined ether extracts were dried ($MgSO_4$), the solvent was evaporated, and the solid residue was recrystallized from *n*-pentane to give pure (by tlc), colorless crystals **11** (1.92 g, 69%); mp 123-125°C. ^{1}H Nmr ($CDCl_3$): δ 1.32 [s, 9H, $(CH_3)_3C$]; 1.41 [s, 6H, $(CH_3)_2C$]; 2.51 (s, 3H, CH_3-N); 4.96 (broad s, 1H, NH, exchangeable with D_2O). Ir (KBr): 3200 (broad, NH); 1695 cm^{-1} (C=O). Ms (CI, *i*-butane): m/z (%) 371 (25); 257 (11); 224 (11); 186 (100); 72 (18). Ms (EI, 75 eV): m/e (%) 185 $[M]^{\cdot+}$ (100); 171 (7). Anal. Calcd for $C_9H_{19}N_3O$: C, 58.35; H, 10.34; N, 22,68. Found: C, 58.61; H, 10.26; N, 23.07.

2-(1,1-Dimethylethyl)-4-[1-[(1,1-dimethylethyl)azo]-1-methylethyl]aminocarbonyl-1,5,5-trimethyl-1,2,4-triazolidin-3-one (12): The mother liquor from the recrystallization of **11** was concentrated and chromatographed on silica gel (30 g, deactivated with 10% water; eluent ether): The solvent of the first fractions collected was evaporated, and the viscous residue, after storing in the refrigerator for several days, turned crystalline: **12** (0.04 g, 1.5%); mp 59-62°C. ^{1}H Nmr ($CDCl_3$): δ 1.20 [s, 9H, $(CH_3)_3C$]; 1.33-1.80 [m, 21H, $(CH_3)_3C$, 2 $(CH_3)_2C$]; 2.48 (s, 3H, CH_3-N); 8.90 (broad s, 1H, NH, exchangeable with D_2O). Ir (KBr): 3230 (broad NH); 1710, 1670 cm^{-1} (2 C=O). Uv (*n*-hexane): λ_{max} [nm] (log ϵ) 359 (1.26). Ms (CI, *i*-butane): m/z (%) 269 (6) $[(CH_3)_2C{=}NH\text{-}CO\text{-}C_9H_{18}N_3O]^+$; 212 (56); 156 (95); 114 (100). Anal. Calcd for $C_{17}H_{34}N_6O_2$: C, 57.60; H, 9.67; N, 23.71. Found: C, 57.50; H, 9.71; N, 23.64.

Preparation of **12** from **11**: To a solution of methylmagnesium iodide, prepared from methyl iodide (1.07 g, 7.5 mmol) and magnesium (0.18 g, 7.5 mmol) in ether (10 ml), was added at 0°C within 15 min a solution of **11** (1.40 g, 7.5 mmol) in ether (35 ml). The mixture was stirred at room temperature for 30 min, and then a solution of **3c** (1.28 g, 7.5 mmol) in ether (10 ml) was added dropwise within 15 min. After continued stirring for 4 h, a saturated aqueous ammonium chloride solution (80 ml) was added, and the residue obtained after work-up as described above was subjected to column chromatography on silica gel [50 g, deactivated with 10% water; eluents: petroleum ether/ether (2:1), and starting from fraction 26, ether; fractions of 20 ml were collected]: Fractions 1-2 contained **12** (0.68 g, 37% with respect to **11** consumed); an unidentified product (0.02 g) was eluted in fractions 4-5; unchanged **11** (0.43 g) was recovered from fractions 30-31.

1-(1,1-Dimethylethyl)-4,5-dihydro-3,3-dimethyl-5-oxo-3*H*-1,2,4-triazolium chloride (4c): To a stirred solution of **3c** (1.69 g, 10 mmol) in dry ether (5 ml) at 0°C was added dropwise within 3 min a saturated solution of hydrogen chloride in dry ether (10 ml). After 10 min the precipitated crystals were filtered off, washed with dry ether, and

purified by sublimation (30°C, 0.01 mbar): **4c** (1.91 g, 93%); mp (decomp. and sublim.) beginning at 118°C. ^{1}H Nmr ($CDCl_3$): δ 1.53 [s, 9H, $(CH_3)_3C$]; 1.66 [s, 6H, $(CH_3)_2C$]; 4.46 (broad s, 1H, NH). Ir (KBr): 1855 cm^{-1} (C=O). Uv (2 *N* HCl): λ_{max} [nm] (log ϵ) 296 (3.13). Anal. Calcd for $C_8H_{16}ClN_3O$: C, 46.71; H, 7.84; Cl, 17.24; N, 20.48. Found: C, 46.63; H, 7.61; Cl, 17.31; N, 20.57.

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11. **1c** is formed as a major product in the course of a rather unexpected and complex reaction of 1,2-bis-(1-isocyanato-1-methylethyl)diazene with methylmagnesium iodide.[7]
12. **4c** is also reduced to **1c** by the reaction with benzyl alcohol and with mercaptans; the latter compounds are converted into benzaldehyde and disulfides,[7] respectively.

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