

TRIAZOLIUM SALTS, III¹:1-(1,1-DIMETHYLETHYL)-4,5-DIHYDRO-3,3-DIMETHYL-5-OXO-3*H*-1,2,4-TRIAZOLIUM
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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.

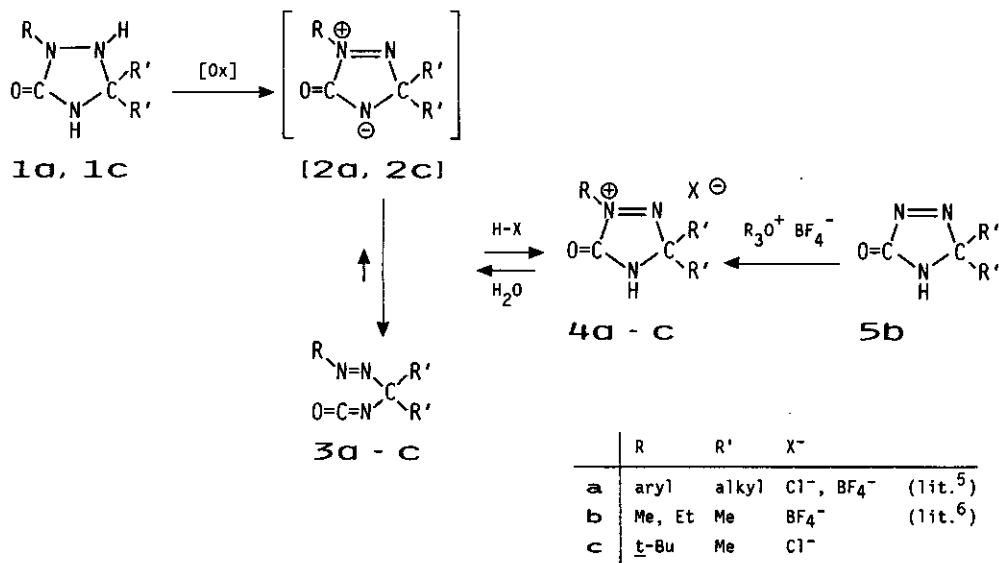
The oxidative ring-opening of 2-aryl-1,2,4-triazolidin-3-ones **1a** has been found to provide an efficient access to the geminal arylazoalkyl isocyanates **3a**² (Scheme 1), which in turn have been noted for their unusual chemical reactivity.^{3,4} Notably, the treatment of **3a** with aqueous acids 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):

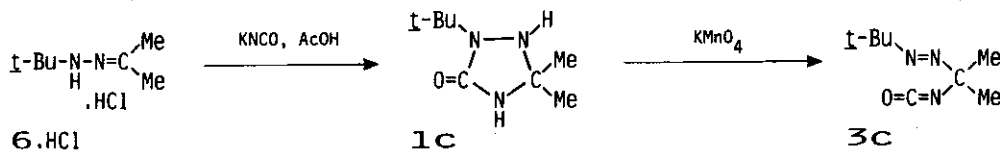
In a patent,⁸ a two step synthesis of compound **3c** has been described: The conversion of 2-propanone (1,1-dimethylethyl)hydrazone (**6**) with chlorine into 1-(1-chloro-1-methylethyl)-2-(1,1-dimethylethyl)diazene is followed by the displacement of chloride with potassium cyanate. On the other hand, 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:



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):

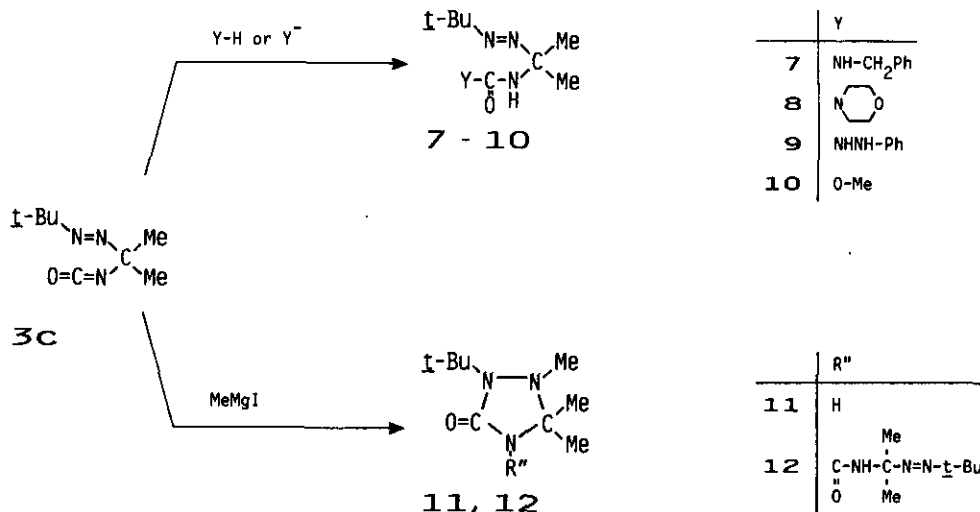
Similar to other geminal azoalkyl isocyanates,³ the reaction of **3c** with various nucleophilic reagents takes place in different ways: N-Nucleophiles like amines, phenylhydrazine, and the anion derived from the amide **11** (*vide infra*) gave rise to the formation of the usual addition products to 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 compounds⁴ and others⁹) 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:



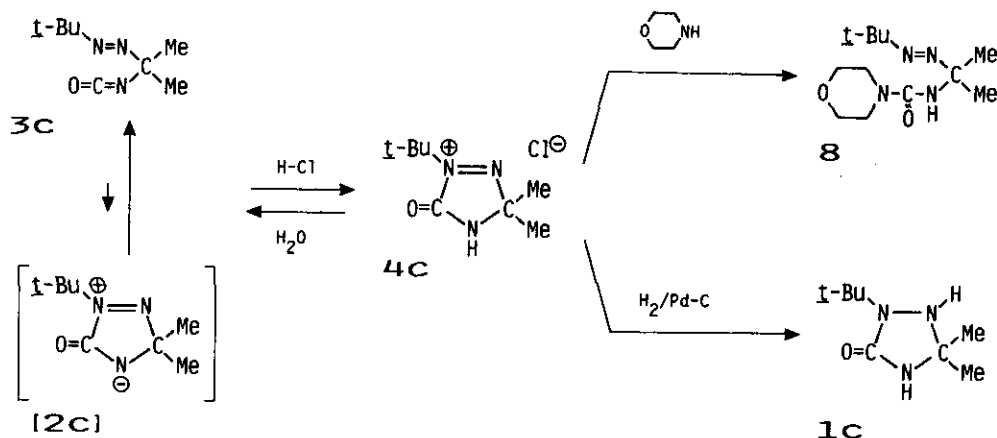
1-(1,1-Dimethylethyl)-4,5-dihydro-3,3-dimethyl-5-oxo-3H-1,2,4-triazolium chloride (4c). Preparation, Structure, and Reactions (Scheme 4):

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 4a⁵ 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 function¹⁰ (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 reversion 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 (¹H 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). $^1\text{H Nmr}$ (DMSO- d_6): δ 1.33 [s, 9H, $(\text{H}_3\text{C})_3\text{C}$]; 2.07, 2.22 [2s, 6H, $(\text{H}_3\text{C})_2\text{C}=\text{C}$]; 10.93 (broad s, 2H, 2 NH). Anal. Calcd for $\text{C}_7\text{H}_{17}\text{ClN}_2$: 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). $^1\text{H Nmr}$ (CDCl_3): δ 1.36 [broad s, 15 H, $(\text{CH}_3)_3\text{C}$ and $(\text{CH}_3)_2\text{C}$]; 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 (Cl, *i*-butane): m/z (%) 171 (5); 115 (19) [$\text{M}-\text{C}_4\text{H}_8$] $^+$; 100 (100) [$\text{C}_3\text{H}_6\text{N}_3\text{O}$] $^+$. Anal. Calcd for $\text{C}_8\text{H}_{17}\text{N}_3\text{O}$: 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%); $n_D^{20} = 1.4222$. $^1\text{H Nmr}$ (CDCl_3): δ 1.28 [s, 9H, $(\text{CH}_3)_3\text{C}$]; 1.43 [s, 6H, $(\text{CH}_3)_2\text{C}$]. Ir (neat) 2225, 2180, 2140 cm^{-1} (N=C=O). Uv (*n*-hexane): λ_{max} [nm] ($\log \epsilon$) 348 (1.42). Anal. Calcd for $\text{C}_8\text{H}_{15}\text{N}_3\text{O}$: 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). $^1\text{H Nmr}$ (CDCl_3): δ 1.13 [s, 9H, $(\text{CH}_3)_3\text{C}$]; 1.50 [s, 6H, $(\text{CH}_3)_2\text{C}$]; 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] ($\log \epsilon$) 359 (1.26); 218 (3.46); 237 (sh). Ms (Cl, *i*-butane): m/z (%) 277 (100) [$M + H$]⁺; 191 (15) [$(CH_3)_2C=NHCONH-CH_2C_6H_5$]⁺. 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-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] ($\log \epsilon$) 356 (1.20). Ms (Cl, *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] ($\log \epsilon$) 357 (1.26); 282 (3.20); 235 (4.07). Ms (Cl, *i*-butane): m/z (%) 192 (6) [$(CH_3)_2C=NHCO-NHNHC_6H_5$]⁺; 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. 1H 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 $[M]^+$ (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. 1H 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) [$(CH_3)_2C=NH-CO-C_9H_{18}N_3O]^+$; 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-3H-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. ¹H Nmr (CDCl₃): δ 1.53 [s, 9H, (CH₃)₃C]; 1.66 [s, 6H, (CH₃)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 C₈H₁₆ClN₃O: 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.

REFERENCES AND NOTES

1. Part II: lit.⁶ - Geminal Azo- and Heteroelement Functions; Part 9. Part 8: lit.⁶ Taken in part from lit.⁷
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9. The addition of *p*-toluenesulfonic acid to the diazene group of compounds **3** gives rise to the formation of 1-(4-methylbenzenesulfonyl)-1,2,4-triazolidin-3-ones. Unpublished results.
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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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