55. Thermolysis of Carbamoyl Azides.
II. A Novel Reduction of Azides with Elemental Copper[1]

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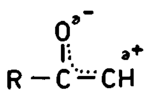
Summary

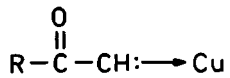
Copper(0) does not catalyze the decomposition of dialkylcarbamoyl azides **5a–e** but instead it is oxidized to copper(II) while the azides **5** are reduced by uptaking one electron per molecule and eliminating nitrogen. A probable explanation for the formation of the resulting copper(II) diisocyanate diamine complexes **8a,b** (see *Scheme 2*) as well as the other reaction products is given. A mechanism involving a carbamoyl nitrene as well as a *Curtius* rearrangement can be excluded.

Introduction. – The thermal decomposition of α-diazo ketones catalysed by silver salts [1] proceeds *via* 1,2-rearrangement (or the *Wolff* rearrangement [2]) to an intermediate ketene which then reacts further. If elemental copper powder instead of the silver salt is used, the yield of rearranged products diminishes strongly in favour of formal carbene-type insertion products [3] [4]. *Yates* [5] investigated the copper-catalysed decomposition of several diazoketones in protic solvents and did not find any rearranged product at all. He has interpreted the observed results as analogous to an electrophilic substitution in which the reactant is either a resonance-stabilized carbonyl carbene **1** or a copper-complexed carbenoid **2**.



$$R-\overset{\overset{O^{\delta-}}{\vdots}}{C}\cdots CH^{\delta+}$$

1



$$R-\overset{\overset{O}{\|}}{C}-CH\!:\!\longrightarrow Cu$$

2

The *Wolff* rearrangement parallels electronically the *Curtius* rearrangement of the so called 'nonrigid' [6–8] carbonyl azides which results in the formation of isocyanates, the latters being isoelectronic with the ketenes. The similarities between these two reaction systems prompted us to extend the copper-catalysed decomposition study on to such types of carbonyl azides which are thus far not known to behave as 'rigid' azides, *i.e.* they do not usually form a nitrene intermediate[2]).

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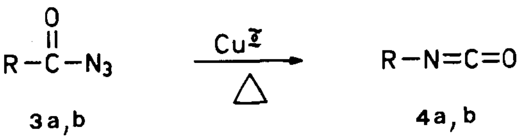
[1]) Part I: see [17].

[2]) Copper-catalysed decomposition of benzenesulfonyl azide has already been reported [9] and it is known that certain tetrazoles (or their open-chained tautomers, the imidazides) eliminate nitrogen more easily in the presence of copper or copper compounds [10] [11]. Furthermore, copper influences the reaction course.

Results. – Thermolysis of aliphatic and aromatic acyl azides, *e.g.* **3a, b** in non-polar solvents are known to yield the corresponding isocyanates **4a, b** in high yields [12] [13]. Addition of copper powder – catalytic amounts or excess – does not change the reaction course. No products derived from a nitrene intermediate have been observed, even though such intermediates are known to be formed under photolytic conditions [14] [15].

Scheme 1

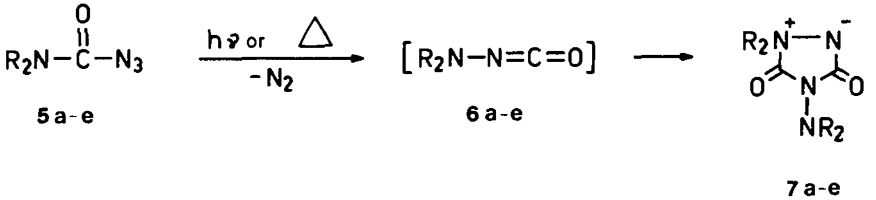


a) R = $C_{13}H_{27}$

b) R = C_6H_5

Dialkylcarbamoyl azides **5a–e** have been reported to undergo the *Curtius* rearrangement by photolysis (**5c, d**) [16] and by high vacuum thermolysis (**5a–e**) [17] leading to intermediate isocyanato-dialkylamines **6a–e** which then dimerize to 5,5-dialkyl-3-dialkylamino-2,4-dioxo-5-azonia-imidazolidides[3]) **7a–e**, yields being nearly quantitative in the latter case (*Scheme 2*).

Scheme 2



a) R_2 = $(CH_2)_5$

b) R_2 = CH_2CH_2-O-CH_2CH_2

c) R = CH_3

d) R = C_2H_5

e) R = $CH(CH_3)_2$

When piperidino-(**5a**) or morpholinoformyl azide (**5b**) was heated in a high-boiling non-polar solvent such as mesitylene or tetralene in presence of an excess of finely divided copper powder, smooth decomposition began at 135° as the colorless solution turned greenish-brown. Hot filtration of the mixture after ~90% of the theoretical amount of nitrogen have been liberated and diluting with ether/methylene

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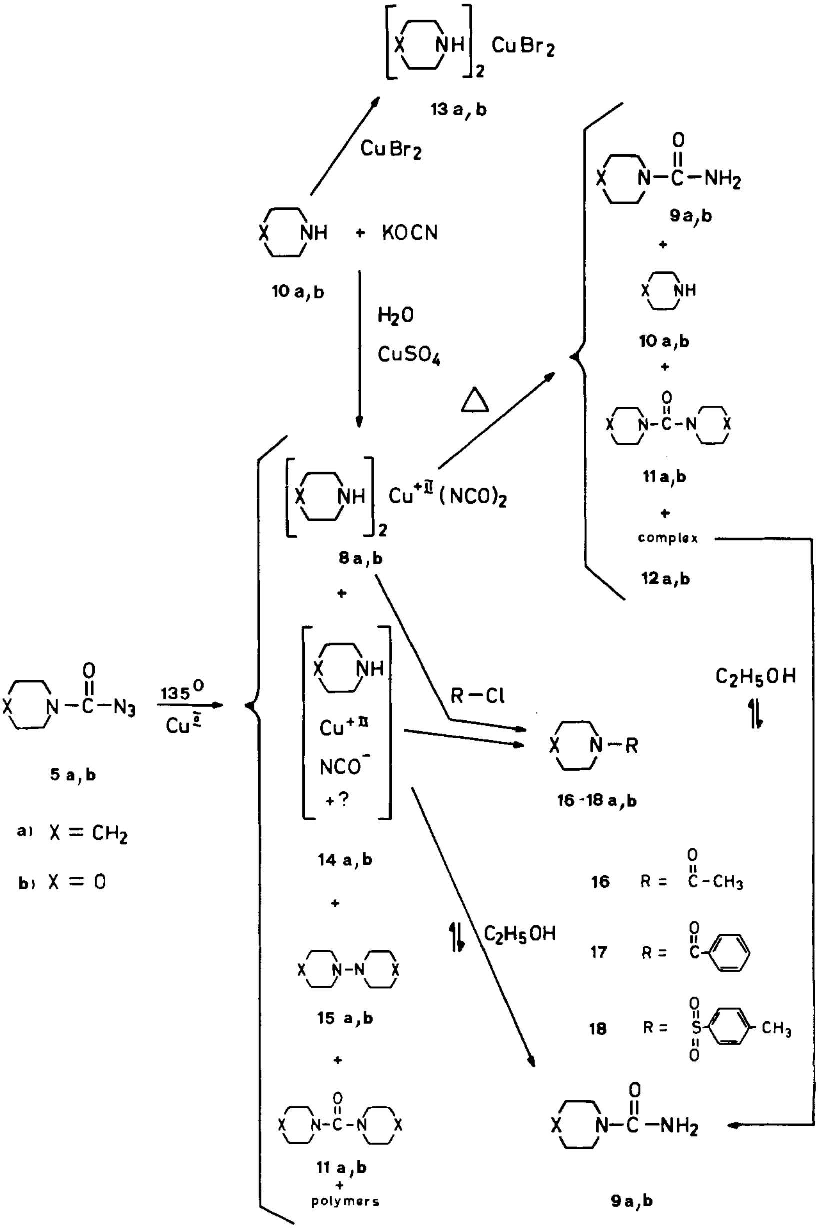
[3]) In previous papers imidazolidides of this type have been referred to as imidazolidin-1-ides [17], 1,2-betaines (Helv. *56*, 2061 (1973)), 1,2-aminimides (Tetrahedron Letters *1974*, 2621, 3249, 4263) and triazolidiniumhydroxide inner salts (C.A.).

chloride 1 : 1 let to the isolation of a mixture of a deep blue (**8a, b**) and a green compound (**9a, b**) of which the blue component could be extracted with boiling acetone. A very strong absorption in the IR.-spectrum of **8a** at 2245 cm^{-1} (**8b**: 2215 cm^{-1}) suggests the presence of an isocyanate function while the sharp absorption at 3280 cm^{-1} (**8b**:

Scheme 3



3230 cm^{-1}) can be attributed to a hydrogen-bonded N–H. Upon warming of the complexes **8a, b** in a closed high vacuum system to 80° mainly 1-pentamethylene urea (**9a**) and 1-(4-oxapentamethylene) urea (**9b**), respectively, along with traces of the secondary amines **10a, b** and the symmetrical ureas **11a, b** (ratio 20:1:1) were eliminated. The IR. spectrum of the greenish residue **12a, b** did still contain a very broad isocyanate absorption at 2200 cm^{-1}. Elemental analyses were not reproducible, however, since after treating **12a, b** with boiling ethanol ureas **9a, b**, again, have been isolated; the corresponding amines **10a, b** seem still to be part of the complexes.

Measurements of the magnetic susceptibility of **8a** showed that it obeys the *Curie-Weiss* law with $\vartheta = -6°K$. A $\mu_{eff}(295.2°K) = 1.66$ *Bohr* magnetons (BM) corresponds to a low value for isolated paramagnetic copper(II) ions (normal values being in the region of 1.9 BM [18]), however, substantial number of organic derivatives of copper(II) salts show somewhat subnormal moments due to exchange effects between adjacent copper ions [19] [20].

These results and elemental analysis of **8a, b** are in agreement with the proposed structure as diamine copper(II) isocyanate. They, both, could be prepared independently by treating an aqueous solution of excess potassium cyanate and the amine with a solution of copper sulfate[4]).

The green products **14a, b**[5]) which were left after washing out **8a, b** were insoluble in any solvent without immediate decomposition. Electron paramagnetic resonance (EPR.) measurements showed again the presence of copper(II). IR. spectral characteristics (**14a**: 2230 cm^{-1}, **14b**: 2170 cm^{-1} for the isocyanate function and 3260 cm^{-1} and a broad band at 3400 cm^{-1} for N–H, as well as analogies in the fingerprint region) suggest the presence of mainly the same components as in **8a, b**. However, since elemental analyses of **14a, b** obtained in different runs were not reproducible within the limits of error, they seem to be polymorphous complexes containing most likely various amounts of the thermolysis products of **8a, b**, *i.e.*: **9a, b**, **11a, b** and/or **12a, b** (see *Scheme 3*)[6]).

In addition to **8a, b** and **14a, b** small amounts of the tetrasubstituted symmetrical hydrazines **15a, b** and the ureas **11a, b** along with tar-like polymers have been isolated from the mother liquor.

In contrast to **8a, b** none of the ureas **9a, b** has been eliminated from complexes **14a, b** by just heating. After treatment with boiling ethanol, however, they could be isolated in high yields. Reaction of both, **8a, b** and **14a, b** with acetyl-, benzoyl- or tosylchloride yielded the corresponding amides **16–18a, b**.

In order to check which ones (if any) of the isolated compounds not containing copper(II), *i.e.*: **11a, b** and **15a, b**, have been formed in thermal side reactions not

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[4]) Complexes of the general structure $L_2Cu(NCO)_2$ are known for L = dibenzylamine [21], pyridine [22] or picoline [21]. Furthermore, similar types of copper(II) complexes containing a copper(II) halide moiety have precedence in the literature [23] [24], thus we were able to prepare analogous compounds **13a, b** by adding the appropriate secondary amines **10a, b** to anhydrous copper(II) bromide (see *Scheme 3*).

[5]) Thermolysis of **5c, d** in presence of copper only gave the green complexes of type **14**.

[6]) Complex **14a** also follows the *Curie-Weiss* law with $\vartheta \approx 10°K$ but the very low magnetic moment $\mu_{eff}(295.2°K) \approx 1{,}3$ BM hints to a bi- or polynuclear complex with a strong Cu(II)–Cu(II)-interaction [20].

involving participation of the metal in the decomposition step, we performed a thermolysis of **5a** in tetralene without copper[7]).

Smooth decomposition took place at 175–185° and stopped after about 85% of the theoretical amount of nitrogen has been evolved. Working up of the reaction mixture gave 5-pentamethylene-3-piperidino-2,4-dioxo-5-azonia-imidazolid-1-id (**7a**) (5.5%), pentamethylene urea (**9a**) (7.7%), 1,4-bis(pentamethylene)-semicarbazide (**23**) (13.7%), bis(pentamethylene)-hydrazine (**15a**) (3.5%), 1,3-dipiperidino-1,3,5-triazidine-trione (**25**) (11.2%) along with traces of several unidentified compounds and a considerable amount of polymers.

Formation of all isolated products can be best explained by assuming the *Curtius* rearrangement as the first step. As in photolysis [16] and high vacuum thermolysis [17] of **5a** the intermediate N-isocyanato-piperidine (**6a**) which is unstable as monomer dimerizes to the 5-pentamethylene-3-piperidino-2,4-dioxo-5-azonia-imidazolid-1-id (**7a**). At high temperature, however, one might assume that most of **6a** fragments homolytically into a piperidino- (**20**) and an isocyanato radical **21**. Recombination of the former leads to N,N′-bis(pentamethylene)-hydrazine (**15a**). Piperidino radical (**20**), even though being a feeble dehydrogenating agent [26] and **21** might pick up each a hydrogen atom to form piperidine (**10a**) and isocyanic acid (**22**). Reaction of **10a** and **22** explains the formation of pentamethylene-urea (**9a**). Piperidine (**10a**) acts also as a trapping agent for the newly formed isocyanato-dialkylamine **6a** and produces 1,4-bis(pentamethylene)-semicarbazide (**23**). Isocyanic acid (**22**) seems to react with **6a** to a carbazoyl isocyanate **24** which then adds another molecule **6a** to give 1,3-dipiperidino-1,3,5-triazidine-trione (**25**). There are, of course, several other reaction paths possible yielding **25**. A considerable amount of the products polymerized (40%).

Discussion. – The overall reaction which takes place can be described by the following equations:

$$\mathrm{Cu(0)} + 2\,\mathrm{R_2N{-}CO{-}N_3} \longrightarrow \mathrm{Cu^{+2}} + 2\,\mathrm{R_2N^{\cdot}} + 2\,\mathrm{NCO^-} \qquad (1)$$

$$2\,\mathrm{R_2N^{\cdot}} + 2\,\mathrm{H^{\cdot}} \longrightarrow 2\,\mathrm{R_2NH} \qquad (2)$$

$$\mathrm{Cu(II)(NCO)_2} + 2\,\mathrm{R_2NH} \longrightarrow \mathrm{(R_2NH)_2Cu(II)(NCO)_2} \qquad (3)$$

Equations (2) and (3) are known processes, *i.e.*, hydrogen abstraction of amino radicals and complexation of copper(II) salts with amines (see above). A conclusive explanation of what goes on in process (1) is not evident, although, there are a few facts which point out possible reaction paths.

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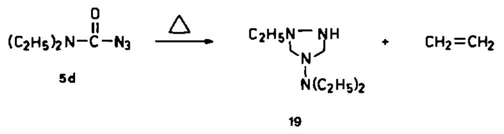
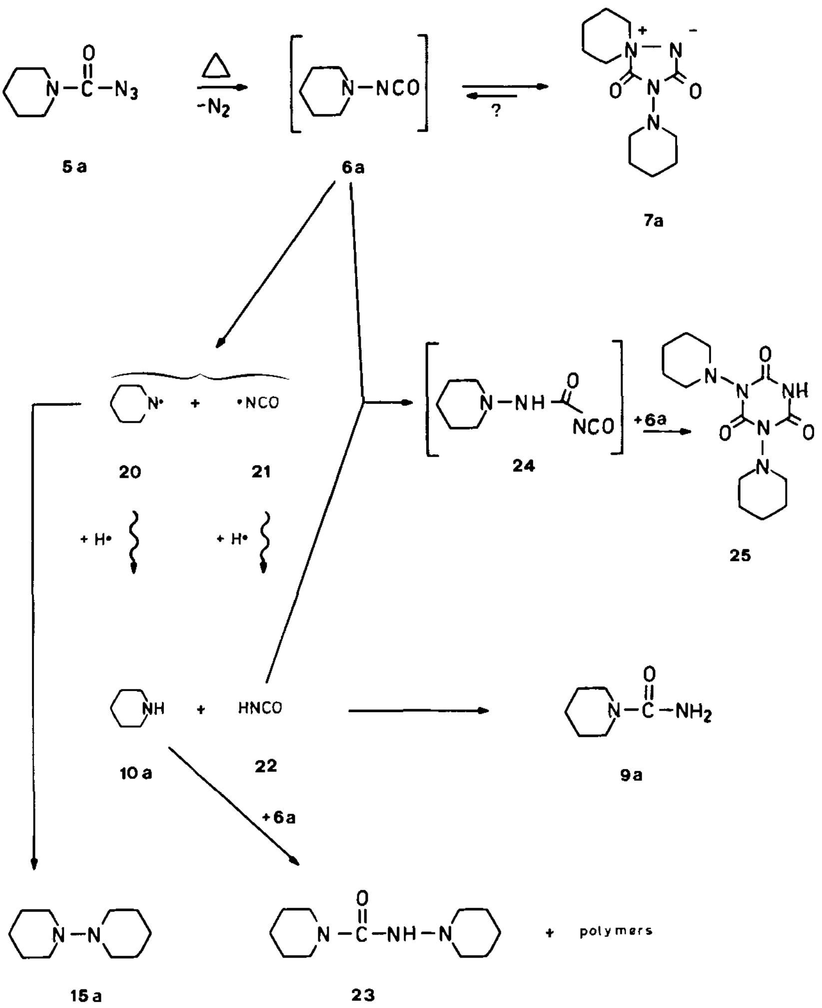
[7]) Thermolysis of neat N,N-diethylcarbamoyl azide (**5d**) has been recently mentioned [25]. The only isolated product (in 17% yield) was 1-ethyl-4-diethylamino-1,2,4-triazolidine-2,5-dione (**19**). Its formation has been explained by an attack of the negatively charged N(1) atom of the thermally unstable azonia-imidazolid-1-ide **7d** at a hydrogen atom of the terminal carbon atom in one of the alkyl groups at N(5). Subsequent elimination of ethylene leads to **19**. A similar reaction occurs with **5e** [17].



Scheme 4



1. Since in presence of copper only the decomposition of carbamoyl azides **5** seem to proceed by the scission of the isocyanato moiety from the rest of the molecule it is likely that the first step involves a close interaction of the starting azide with the surface of copper involving the amino-nitrogen. A one electron transfer with concerted amine-carbonyl-bond breaking might then induce the splitting off of nitrogen which takes place at a considerably lower temperature than without copper. The resulting amino radical **20** might recombine and account for the formation of the hydrazine-type products **15a, b**. Copper(I), as intermediate, could then reduce the second azide molecule, again, by previous complexation.

2. A reaction path involving an intermediate carbamoyl nitrene can be ruled out – no products derived from a nitrene whatsoever have been found, besides, a reduction

at this step does not occur in cases where copper-nitrene complexes have been postulated as intermediates [4] [9].

3. The azide decomposition does not proceed *via Curtius* rearrangement. If this were the case, copper(0) had to reduce two isocyanato-amine molecules. When we generated **6c** by thermolysing 5,5-dimethyl-3-*t*-butyl-2,4-dioxo-5-azonia imidazolidid [37] [38] in tetraline in the presence of copper powder no oxidation of copper(0) was observed neither did **6c** deviate from its well known reactional behaviour [37].

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Experimental part

General remarks. Melting points were determined on a *Tottoli* apparatus and are not corrected. Elemental analysis were carried out by Dr. *Thommen* (Mikrochemisches Laboratorium, Universität Basel), copper has been titrated with 'Komplexon III' according to *Schwarzenbach* [19]. All products for which analytical data are not cited, are known from literature and have been prepared independently for comparison. IR. spectra (cm^{-1}) have been recorded on a *Beckmann* IR-20A apparatus. – ^{1}H-NMR. spectra: *Varian* A-60-A, chemical shifts in ppm (internal standard: tetramethylsilane, $\delta=0$ ppm). Abbreviations: s = singlet, m = multiplet, br. = broad (number of H). – MS. spectra: *Bell-Howell* CEC 21-490, mass numbers in m/e (relative intensities in %), M^+ = parent peak.

1a. *Thermolysis of pentamethylenecarbamoyl azide* **5a** *in the presence of copper(0).* 3.15 g (50 mmol) of copper powder (thoroughly washed with acetone and oven-dried) were added to a solution of 1.54 g (10 mmol) of pentamethylenecarbamoyl azide (**5a**) in 5 ml tetralene. The mixture was degassed and warmed up under nitrogen to 135° at which temperature evolution of nitrogen started. At the end of the decomposition (after *ca.* 4 h) the mixture was filtered while hot and diluted with 20 ml methylene chloride/ether 1:1 which caused precipitation of a greenish-blue material. This was filtered off again, and washed with methylene chloride/ether 1:1. Thorough extraction with hot acetone and evaporation gave 301.7 mg (1.4 mmol, 28%) of **8a**. – IR. (Kbr): 3530, 3272, 2957, 2883, 2245, 1464, 1385, 1351, 1335, 1325, 1282, 1204, 1129, 1093, 1058, 1038, 1015, 956, 888, 628, 614.

$C_{12}H_{20}CuN_4O_2$	Calc.	C 45.34	H 6.97	N 17.62	Cu 19.99%
(317.8)	Found	„ 45.34	„ 6.97	„ 17.24	„ 20.0%

Complex **14a** remained undissolved and was dried i.HV. (978 mg). – IR. (Kbr): 3400 (br.), 3260, 2941, 2865, 2230, 1630 (br.), 1455, 1343, 1195, 1085, 1050, 1030, 1007, 948, 882, 630, 618. – Results of elemental analysis: C 38.4 ± 1.1 H 5.78 ± 0.6 N 14,55 ± 0.8 Cu 27 ± 1.5.

The low-boiling sovents were distilled off from the mother liquor and fractional recondensation of the tetralene solution at 10^{-4} Torr gave 85 mg (0.5 mmol, 5%) of the hydrazine **15a** which was precipitated as its picrate (m.p.: 153°, lit.: [20]) and 36 mg (0.18 mmol, 1,8%) of the urea **11a** (m.p.: 42°, lit.: 43° [21]).

1b. *Thermolysis of (4-oxa-pentamethylene)carbamoyl azide* (**5b**) *in the presence of copper(0)* (see 1a). Yields: copper(II) diisocyanate dimorpholine: 385 mg (1.19 mmol, 24%). – IR. (KBr): 3460, 3230, 2965, 2860, 2215, 1442, 1420, 1330, 1310, 1251, 1180, 1106, 1087, 1049, 1022, 873, 596.

$C_{10}H_{16}CuN_4O_4$	Calc.	C 37.56	H 5.04	N 17.52	Cu 19.86%
(319.8)	Found	„ 37.39	„ 4.98	„ 17.77	„ 20.0%

Complex **14b**: 780 mg. – IR. (KBr): 3420 (b), 3240, 2910 (b), 2170, 1630, 1572 (b), 1432 (b), 1105, 1020, 980, 870, 640, 595.

All solvents were distilled off from the mother liquor and the residual solid fractionnally sublimed (10^{-2} Torr) yielding: 111 mg (0.65 mmol, 6.5%) of **11b** (m.p.: 101°, lit.: 103° [22]) and 65 mg (0.32 mmol, 3.2%) of **15b** (m.p.: 143°, see [23]).

2. *Thermolysis of* **8a** resp. **8b**. 5 mmol of **8a** resp. **8b** were filled in one branch of a reversed U-shaped glass tube with a tap on top of it. The system was evacuated to 10^{-3} Torr and the product heated up to 80° while the other section of the tube was cooled with liquid nitrogen. After 2 h the weight of the thermolysed product was constant. The obtained products were separated by GC. or fractional sublimation and gave:

		mg	mmol	m.p.(°)	Lit.
Pentamethylene urea	**9a**	257	2	102	[24]
(4′-Oxapentamethylene) urea	**9b**	198	1.52	112	[24]
Piperidine	**10a**	75	0.89	[a]	
Morpholine	**10b**	48	0.56	[a]	
Bis(pentamethylene) urea	**11a**	80	0.51	43	[22]
Bis(4′-oxapentamethylene) urea	**11b**	105	0.66	102	[23]

[a]) Identified by GC.

3. *Reaction of* **14a,b** *with acid chlorides*. In a 1:3 weight ratio, **14a,b** and the acid chloride (*viz.* acetyl chloride, benzoyl chloride or tosyl chloride) were heated up under reflux for 15 min. Excess acid chloride was distilled off and the resulting products sublimed (distilled) from the reaction mixture and further purified by short path distillation (**16a,b**) or recrystallisation (**17a,b**: methylene chloride/hexane, **18a**: ether/hexane, **18b**: ethanol/water), and resublimation. Yields are indicated as % of the reacting starting material, *i.e.*: they show approximatively the content of amine in complexes **14a,b**.

		Yield(%)	m.p. (b.p.)	Authentic sample	Lit.
N-Acetyl-piperidine	**16a**	44	(229°)		[25]
N-Acetyl-morpholine	**16b**	38	(242°)		[26]
N-Benzoyl-piperidine	**17a**	41	47°	48°	[26]
N-Benzoyl-morpholine	**17b**	45	75°	75°	[27]
N-Tosyl-piperidine	**18a**	32	101°	103°	[28]
N-Tosyl-morpholine	**18b**	40	146°	147°	[29]

4a. *Pentamethylene urea* **9a** *from* **14a**. A solution of 114 mg of **14a** in 3 ml ethanol was heated for 3 h under reflux and under nitrogen. After standing at RT. overnight the mixture was centrifuged and the residue washed with 2 ml ethanol. Evaporation of the solvent and sublimation of the residue yielded 51 mg (0.39 mmol) of **9a**, m.p.: 105° [24].

4b. *4′-Oxapentamethylene urea* **9b** *from* **14b** (see 4a). Yield: 45 mg (0,35 mmol) of **9b**, m.p.: 111° [24].

5. *Copper(II) diisocyanate diamine (general procedure)*. To a solution of 0.2 mol potassium cyanate and 0.1 mol of the secondary amine in water was added a solution of 0.02 mol of copper(II) sulfate under vigorous stirring at RT. The resulting blue precipitate was rapidly filtered off and washed with cold ethanol, methylene chloride and pentane and dried i. HV. Yields were quantitative based on copper(II) sulfate. Slight changes in the ratio of potassium cyanate to amine caused formation of several other complexes. Prolonged standing of the complex in water resulted in decomposition.

6. *Thermolysis of pentamethylenecarbamoyl azide* **5a** *in tetralene without copper*. A mixture of 1.54 g (10 mmol) of **5a** in 4 ml tetralene was degassed and heated to 180°. When the evolution of nitrogen ceased, the solution was cooled to RT. and diluted with 50 ml of ether. The precipitate formed was filtered off. Recrystallisation from methylene chloride/ether gave 70 mg (0.28 mmol, 5.5%) of 5-pentamethylene-3-piperidino-2,4-dioxo-5-azonia-imidazolid-1-id **7a**, m.p.: 268° [17]. Ether was evaporated from the mother liquor and hexane (40 ml) added. The viscous precipitate was heated in hexane under reflux and chloroform was added dropwise until the oily products were dissolved. Filtration and repeated fractional sublimation gave 98 mg (0.77 mmol, 7.7%) of pentamethylene

urea **9a**, [24], 145 mg (0.69 mmol, 13.7%) of 1,4-bis-pentamethylene semicarbazide **23** [24], and 110 mg (0.37 mmol, 11.2%) of 1,3-dipiperidino-1,3,5-triazidine-trione **25**, m.p.: 228°. – IR. (KBr): 3420, 3200, 3070, 2938, 2855, 1743, 1690, 1440, 1403, 1372, 1346, 1295, 1032, 748. – NMR. ($CDCl_3$): 1,67 (*m*, br., 12H); 3,3 (*m*, br., 8H); 9,5 (br., 1H). – MS. 213 (M^+, 33), 169 (2), 126 (19), 99 (4), 84 (100), 83 (74).

$C_{13}H_{21}N_5O_3$ (295.3) Calc. C 52.86 H 7.17 N 23.71% Found C 52.74 H 7.19 N 23.12%

The solvents were evaporated from the filtrate after adding 1 g of activated silica gel. The resulting powder was subjected to recondensation i.HV. (10^{-5} Torr) and yielded 29 mg (0.17 mmol, 3.5%) of bis-pentamethylene hydrazine (**15a**), isolated as its picrate (m.p.: 154°, [20]). The left over products were mainly polymers.

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