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# Carbonyl Diisocyanate: A New Preparation and Some Reactions

*Bernhard Akteries* and *Johannes C. Jochims**

Fakultät für Chemie der Universität Konstanz,
Postfach 5560, D-7750 Konstanz

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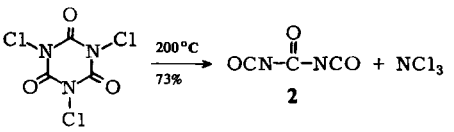
A preparation of carbonyl diisocyanate (**2**) from tri-*n*-butyltin isocyanate (**4**) and phosgene is reported. Correspondingly, the acyl isocyanates **6** were obtained from **4** with acyl chlorides. On standing, carbonyl diisocyanate trimerizes reversibly to the triazine **9**, which could also be prepared by independent syntheses from the triazines **3** or **12**. Reported are reactions of carbonyl diisocyanate with water, hydrogen sulfide, alcohols, phenol, phenol + carbodiimides, thiols, amines, primary ammonium salts, and *N*-unsubstituted imines leading to compounds **14**–**24**.

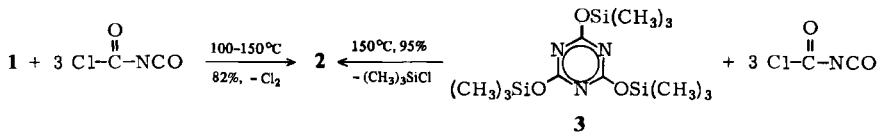
**Carbonyl-diisocyanat: Eine neue Darstellung und einige Reaktionen**

Carbonyl-diisocyanat (**2**) kann durch Umsetzung von Tri-*n*-butylzinn-isocyanat (**4**) mit Phosgen erhalten werden. Entsprechend lassen sich die Acylisocyanate **6** durch Reaktionen von **4** mit Acylchloriden darstellen. Carbonyl-diisocyanat trimerisiert reversibel zum Triazin **9**, das unabhängig auch aus den Triazinen **3** bzw. **12** hergestellt werden konnte. Es werden Reaktionen von Carbonyl-diisocyanat mit Wasser, Schwefelwasserstoff, Alkoholen, Phenol, Phenol + Carbodiimiden, Thiolen, Aminen, primären Ammoniumsalzen und *N*-unsubstituierten Iminen zu den Produkten **14**–**24** beschrieben.

Carbonyl diisocyanate (**2**) belongs to the less thoroughly investigated carbonyl pseudohalides. The compound was first prepared by *Nachbaur*[1] who pyrolyzed isocyanuric trichloride (**1**) to obtain **2** together with the explosive nitrogen trichloride.




**1** **2**




**3**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The corresponding thermal decomposition of isocyanuric triiodide requires higher temperatures[2]. Carbonyl diisocyanate (**2**) can be obtained without formation of explosive side products by treatment of **1**[3] or tris(trimethylsilyl)isocyanuric acid[4] (**3**) with carbonyl chloride isocyanate.

The most direct way to prepare **2** from phosgene or carbonyl difluoride and potassium cyanate was realized by *Sundermeyer* et al.[5,6] using sophisticated techniques in molten salts as solvent, e.g.:

$$2\ KNCO + Cl{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow[76\%,\ -KCl]{LiCl/KCl,\ 450\,^{\circ}C} \mathbf{2} \xleftarrow[-SiCl_4]{heat} Si(NCO)_4 + 2\ Cl{-}\overset{\overset{O}{\|}}{C}{-}Cl$$

Also, these authors[5] mention the preparation of **2** from silicon(IV) tetraisocyanate and phosgene.

The most economical way for the preparation of **2** has been patented by *Hagemann*[7]. The sodium salt of isocyanuric dichloride or **1** are treated with phosgene in high boiling inert solvents to give **2** in good yields, e.g.:

$$2\ \mathbf{1} + 3\ Cl{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow[C_6H_4Cl_2\text{-}(1,2)]{160\text{-}190\,^{\circ}C} 3\ \mathbf{2}\ (80\%)$$

Our attempts to reproduce this method on a laboratory scale led to the experience that reasonable yields of **2** can only be obtained for certain concentrations of **1** in nitrobenzenes, e.g. 1-chloro-2-nitrobenzene as solvent. When **1** was treated with oxalyl chloride instead of phosgene, **2** was obtained in low yields.

Tri-*n*-butyltin isocyanate (**4**) is readily available from urea and bis(tri-*n*-butyltin) oxide[8]. We found that **4** reacts with phosgene to give **2** in reasonable yields.

$$\underset{\mathbf{4}}{2\ (n\text{-}C_4H_9)_3Sn{-}NCO} + Cl{-}\overset{\overset{O}{\|}}{C}{-}Cl \xrightarrow[60\%]{160\,^{\circ}C} \mathbf{2} + \underset{\mathbf{5}}{2\ (n\text{-}C_4H_9)_3Sn{-}Cl}$$

Since tri-*n*-butyltin chloride (**5**) gives bis(tri-*n*-butyltin) oxide on treatment with aqueous potassium hydroxide[9], the reaction sequence can be regarded as a preparation of **2** from urea and phosgene with bis(tri-*n*-butyltin) oxide or **5** as catalyst. The direct reaction of urea with phosgene leads to triuret[10].

Up to 200°C, with or without added catalytic amounts of $SnCl_4$, no reaction occurred between phosgene and trimethylsilyl isocyanate.

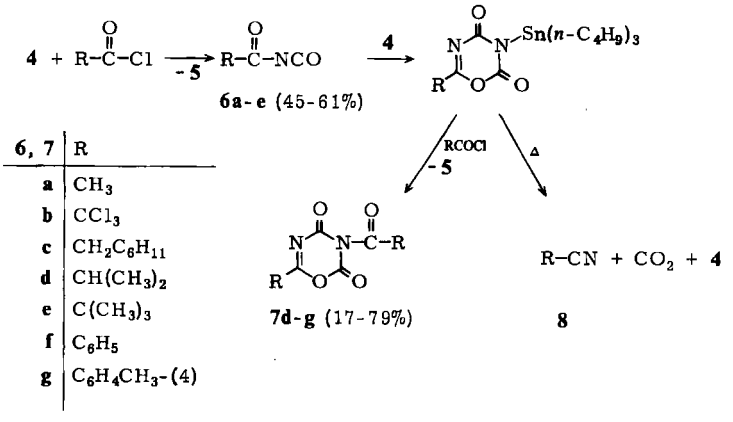
The reaction of **4** with acyl chlorides can be used as a general procedure for the preparation of aliphatic acyl isocyanates[11–13].

Apparently, only the reaction of triethyltin isocyanate with acetyl bromide has been reported in the literature[14]. The formation of acyl isocyanates from trimethylsilyl isocyanate in the presence of $SnCl_4$ may proceed *via* tin isocyanates[15].

From aliphatic acyl chlorides and **4** the acyl isocyanates **6a–e** were obtained in moderate yields, together with the dimers **7** and nitriles **8**, which are sometimes hard to separate from **6**. From aryl chlorides only the dimers **7** were isolated.

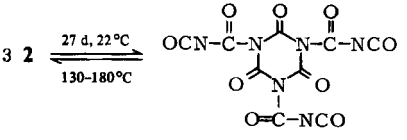
In the presence of **4** acyl isocyanates **6** lose $CO_2$ to give nitriles **8**, as was observed by NMR spectroscopy. A similar decarboxylation was observed during the reaction of acyl chlorides with trimethylsilyl isocyanate[16]. A mechanism explaining the formation of **7** and **8** is proposed in Scheme 1. Direct dimerization of **6** to **7** is known to require catalysts such as triethylamine[17,18] or $SnCl_4$[19]. According to a differential thermoanalysis, the dimerization of **6a** is reversible. Therefore, it seems unlikely that **8** might arise from **7**. No reaction was observed between ethyl chloroformate or 4-nitrobenzoyl chloride and **4**.

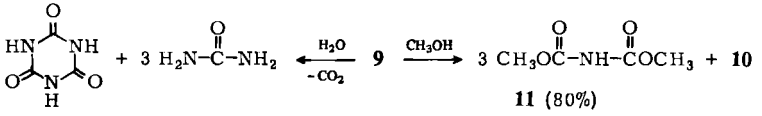
*Scheme 1*




| 6, 7 | R |
|---|---|
| a | $CH_3$ |
| b | $CCl_3$ |
| c | $CH_2C_6H_{11}$ |
| d | $CH(CH_3)_2$ |
| e | $C(CH_3)_3$ |
| f | $C_6H_5$ |
| g | $C_6H_4CH_3$-(4) |

Carbonyl diisocyanate (**2**) is an extremely moisture-sensitive liquid, b.p. 102–104°C, which on standing trimerizes to the triazine **9**, a colourless solid sparingly soluble in most organic solvents. Above 130°C the trimer **9** is depolymerized back to the monomer **2**.




**10** (89%)

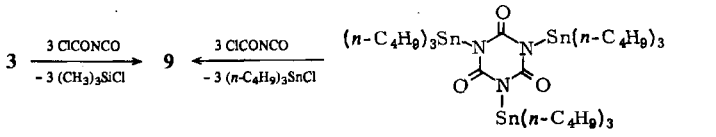
The change of **2** to a solid of unknown structure has been described by several authors[1,3,4,6,7,20].

The IR spectrum of **9** shows a strong NCO band at 2250 $cm^{-1}$ (sulfolane). In the $^{13}C$ NMR spectrum in acetonitrile (263 K) only three resonances are observed (NCO $\delta$ = 129.9,

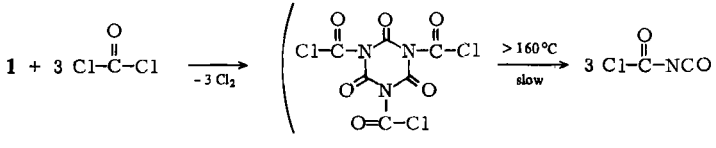
CO 141.7 and 143.9 ppm). Hydrolysis of the very moisture-sensitive compound yielded mainly isocyanuric acid (**10**) together with some urea, while methanolysis gave **10** and dimethyl imidodicarboxylate (**11**).

Finally, a compound obtained at low temperature from **3**[4] or **12** with carbonyl chloride isocyanate proved to be identical with **9**.

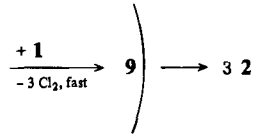
These reactions suggest that the formation of **2** from **1** and phosgene proceeds via intermediates **13** and **9**.

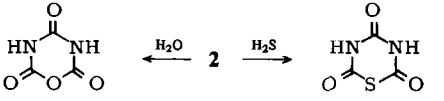



**12**




**13**



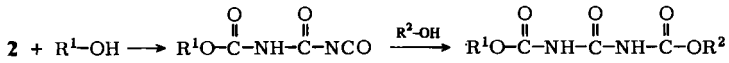

**14** **15**

The analogous transformation of trichloroacetyl chloride with **1** to trichloroacetyl isocyanate has been described[21]. On the other hand, triacylisocyanuric acids with less electron deficient acyl substituents, e.g. 1,3,5-triacetylisocyanuric acid, cannot be thermally depolymerized to acyl isocyanates but decompose on heating.

Carbonyl diisocyanate shows high reactivity against nucleophiles with active hydrogen[1,22]. Water[1] and $H_2S$ react to give the anhydrides **14** and **15**[23], respectively.

Contrary to the corresponding reaction of carbonyl diisothiocyanate[24], **2** does not give cyclic 1:1 addition products with alcohols[1]. With one equivalent of phenol compound **16d** could be isolated, which shows a strong NCO band (2240 $cm^{-1}$, $CH_2Cl_2$) in its IR spectrum. With methanol the mixed ester **17d** was obtained, while with carbodiimides the cycloadducts **18a,b** were formed.

With two equivalents of thiols the esters **19**, apparently an unknown class of compounds, were formed almost quantitatively[22].

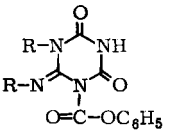


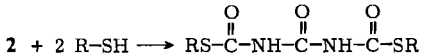
**16** **17a-e**

| 16, 17 | $R^1$ | $R^2$ |
|---|---|---|
| **a** | $CH_3$ | $CH_3$ |
| **b** | $(CH_3)_3C$ | $(CH_3)_3C$ |
| **c** | $C_6H_5CH_2$ | $C_6H_5CH_2$ |
| **d** | $C_6H_5$ | $CH_3$ |
| **e** | $C_6H_5$ | $C_6H_5$ |

**16d** + R–N=C=N–R ⟶

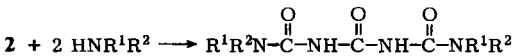
| 18 | R |
|---|---|
| **a** | $C_6H_{11}$ |
| **b** | $(CH_3)_2CH$ |



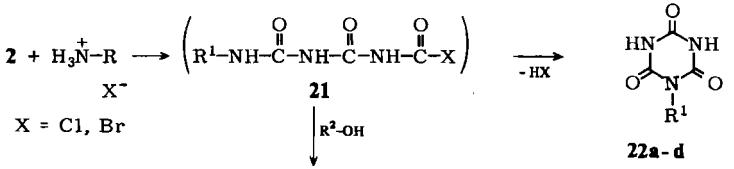


| 19 | R |
|---|---|
| **a** | $C_2H_5$ |
| **b** | $(CH_3)_2CH$ |
| **c** | $C_6H_5$ |

Similarly, with two equivalents of a primary or secondary amine the triurets **20** were obtained. Cyclic 1:1 adducts could not be observed. But with primary ammonium chlorides instead of the free amines the monosubstituted isocyanuric acids **22** were isolated in good yields.



**20a-e**



**21** **22a-d** **23a-c**

| 20 | $R^1$ | $R^2$ |
|---|---|---|
| **a** | $(CH_3)_2CH$ | H |
| **b** | $(CH_3)_3C$ | H |
| **c** | $C_6H_5CH_2$ | $C_6H_5CH_2$ |
| **d** | $C_6H_4Cl$-(4) | H |
| **e** | $C_6H_4CH_3$-(2) | H |

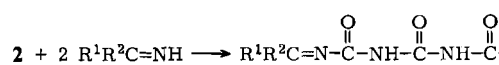
| 22 | $R^1$ |
|---|---|
| **a** | $CH_3$ |
| **b** | $C_2H_5$ |
| **c** | $C_6H_5CH_2$ |
| **d** | $C_6H_4Br$-(4) |

| 23 | $R^1$ | $R^2$ |
|---|---|---|
| **a** | $C_6H_5$ | $CH_3$ |
| **b** | $C_6H_4CH_3$-(4) | $C_2H_5$ |
| **c** | $C_6H_5$ | $[CH_2]_4Br$ |

This reaction passes over intermediates **21**, which for X = Br could be trapped as biuretcarboxylates **23** by addition of alcohols. With anilinium bromide in boiling tetrahydrofuran **2** reacts to give **23c**, the formation of which can be explained by ether cleavage of tetrahydrofuran with HBr and reaction of the forming 4-bromobutanol with **21**.

Alternatively, monoalkylated isocyanuric acids can be prepared, for instance, by condensation of biurets with ethyl carbonate[25].

With *N*-unsubstituted imines **2** reacts to give the novel bisalkylidenetriurets **24a,b**.



| **24** | $R^1$ | $R^2$ |
|---|---|---|
| **a** | $C_6H_5$ | $C_6H_5$ |
| **b** | $C_6H_5$ | $(CH_3)_3C$ |

We would like to thank Mr. *G. Wildermuth* and Prof. Dr. *J. Felsche* for carrying out the differential thermoanalyses, and Mr. *S. Herzberger* for technical assistance.

## Experimental Part

IR spectra: Perkin-Elmer IR 299 spectrometer. – NMR spectra: Bruker WM-250 and JEOL FX 90Q instruments; δ-scale; internal reference tetramethylsilane. – Mass spectroscopy: Varian MAT-312 and MAT-112S spectrometers. – Differential thermoanalyses: Netsch STA 429 instrument. – All solvents had to be carefully dried. All reactions were carried out with exclusion of moisture. Petroleum ether: b.p. 50–70°C. Melting points: uncorrected. In order to be free of **9** the carbonyl diisocyanate had to be distilled directly before use.

*Carbonyl Diisocyanate* (**2**)

a) At 100°C phosgene, dried by passing through concentrated sulfuric acid, was led into a suspension of **1** (23.24 g, 100 mmol) in 1-chloro-2-nitrobenzene (75 g) placed in a 100-ml 2-neck round flask connected to a short distillation apparatus with cooled bridge (+7°C) and recipient (−10°C). The apparatus had to be carefully dried before use. Within 30 min the bath temperature was raised to 160°C. A yellow liquid slowly distilled off. After 90 min the bath temperature was raised to 190°C. After additional 60 min the reaction was finished. Distillation of the condensate in a micro distillation apparatus gave besides a large amount of phosgene 13.45 g (80%) of a colourless moisture-sensitive liquid; b.p. 102–104°C (lit.[1] 103.4°C/705 Torr). – $^{13}C$ NMR ($CDCl_3$, 263 K): CO δ = 144.9, NCO 130.6. – IR (film): NCO 2220, CO 1740, CN 1420, C–N 1060 $cm^{-1}$. – MS: *m/z* = 112 ($M^+$), 70 ($OCNCO^+$), 42 ($NCO^+$), 28 ($CO^+$).

b) At 100°C dry phosgene was passed through tri-*n*-butyltin isocyanate (**4**)[8] (33.21 g, 100 mmol) in an apparatus as described for a). Within 20 min the temperature was raised to 160°C. Nearly colourless **2** distilled off. After 2 h the reaction was finished. Redistillation yielded 3.35 g (60%) of a colourless liquid; b.p. 102–104°C.

*Acetyl Isocyanate* (**6a**): To **4**[8] (16.60 g, 50 mmol) acetyl chloride (3.93 g, 50 mmol) was added dropwise. After stirring for 12 h at +22°C the product was distilled at 22°C/0.1 Torr into a recipient cooled to −78°C. Fractionated distillation gave a colourless liquid (2.53 g,

60%); b.p. 76–78°C (lit.[14] 79–80°C). – IR (film): 2220, 1730 $cm^{-1}$. – $^{13}C$ NMR ($CDCl_3$): $CH_3$ δ = 27.3, NCO 129.8, C=O 168.7.

*Trichloroacetyl Isocyanate* (**6b**): Trichloroacetyl chloride (9.09 g, 50 mmol) and **4** (16.60 g, 50 mmol) were stirred together for 12 h at 60°C. Work-up as described for **6a** yielded a colourless liquid (4.28 g, 45%); b.p. 36–39°C/12 Torr (lit.[12] 80–85°C/20 Torr). – IR (film): 2240, 1755 $cm^{-1}$. – $^{13}C$ NMR ($CDCl_3$): $CCl_3$ δ = 92.4, NCO 130.2, C=O 158.6.

*Cyclohexylacetyl Isocyanate* (**6c**): Cyclohexylacetyl chloride (8.03 g, 50 mmol) and **4** (16.60 g, 50 mmol) were stirred together for 18 h at 22°C. Work-up as described for **6a** gave a colourless liquid; b.p. 36–38°C/0.1 Torr. – IR (film): 2220, 1725 $cm^{-1}$. – $^{13}C$ NMR ($CDCl_3$): $CH_2$, CH δ = 26.0, 26.1, 32.8, 34.7, 48.1, NCO 129.6, C=O 170.8.

$C_9H_{13}NO_2$ (167.2) Calcd. C 64.65 H 7.84 N 8.38 Found C 64.84 H 7.94 N 8.25

*Isobutyryl Isocyanate* (**6d**): From isobutyryl chloride (10.66 g, 100 mmol) as described for **6a**. Yield 6.89 g (61%) of a colourless liquid; b.p. 106–108°C (lit.[26] 50–52°C/100 Torr). – IR (film): 2220, 1720 $cm^{-1}$. – $^{13}C$ NMR ($CDCl_3$, 263 K): $CH_3$ δ = 18.4, CH 39.4, NCO 130.2, C=O 175.9.

*Pivaloyl Isocyanate* (**6e**): From pivaloyl chloride (16.29 g, 50 mmol) as described for **6a**. Yield 3.69 g (58%) of a colourless liquid; b.p. 108–110°C (lit.[13] 110°C). – IR (film): 2220, 1720 $cm^{-1}$. – $^{13}C$ NMR ($CDCl_3$, 263 K): $CH_3$ δ = 26.3, C 42.5, NCO 130.9, C=O 177.9.

*3-Isobutyryl-6-isopropyl-2H-1,3,5-oxadiazine-2,4(3H)-dione* (**7d**): The residue of the distillation of **6d** was dissolved in petroleum ether (300 ml). The product precipitated within 12 h at –80°C. Crystallization from ether (40 ml)/petroleum ether (200 ml) at –80°C afforded a moisture-sensitive colourless powder (3.30 g, 29%); m.p. 58–60°C (dec.). – IR ($CH_2Cl_2$): 1815, 1765, 1720, 1645 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$, 263 K): $CH_3$ δ = 1.33 (d, *J* = 7 Hz), 1.35 (d, *J* = 7 Hz), CH 2.90 (sept, *J* = 7 Hz), 3.15 (sept, *J* = 7 Hz). – $^{13}C$ NMR ($CDCl_3$, 263 K): $CH_3$ δ = 17.8, 18.8, CH 33.9, 39.2, C=O, C=N 144.0, 151.0, 176.5, 176.8.

$C_{10}H_{14}N_2O_4$ (226.2) Calcd. C 53.09 H 6.24 N 12.39 Found C 52.79 H 6.50 N 12.35

*6-tert-Butyl-3-pivaloyl-2H-1,3,5-oxadiazine-2,4(3H)-dione* (**7e**): As described for **7d**. Recrystallization from ether (100 ml) at –20°C afforded colourless needles (1.15 g, 18%); m.p. 141–143°C (dec.). – IR ($CH_2Cl_2$): 1805, 1755, 1720, 1630 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$, 263 K): $CH_3$ δ = 1.37, 1.39. – $^{13}C$ NMR ($CDCl_3$, 263 K): $CH_3$ δ = 26.8, 26.9, C 38.5, 44.5, C=O, C=N 144.2, 151.5, 178.4, 179.5.

$C_{12}H_{18}N_2O_4$ (254.3) Calcd. C 56.68 H 7.14 N 11.02 Found C 56.83 H 7.40 N 11.01

*3-Benzoyl-6-phenyl-2H-1,3,5-oxadiazine-2,4(3H)-dione* (**7f**): A mixture of benzoyl chloride (7.03 g, 50 mmol) and **4** (16.60 g, 50 mmol) was stirred for 12 h at 22°C. After addition of ether (60 ml) the mixture was kept at 22°C for 7 d. Filtration and crystallization of the residue from acetonitrile (30 ml) afforded colourless prisms (5.78 g, 79%); m.p. 162–163°C (lit.[17] 164°C). – IR (KBr): 1805, 1705, 1620 $cm^{-1}$. – $^{13}C$ NMR ([$D_6$]DMSO): C=O, C=N δ = 144.5, 152.0, 165.0, 166.7.

*3-(4-Methylbenzoyl)-6-(4-methylphenyl)-2H-1,3,5-oxadiazine-2,4(3H)-dione* (**7g**): A mixture of 4-methylbenzoyl chloride (7.73 g, 50 mmol) and **4** (16.60 g, 50 mmol) was stirred at 22°C for 60 h. Filtration and crystallization of the residue from acetonitrile (50 ml) yielded colourless platelets (1.89 g, 23%); m.p. 176–178°C. – IR (KBr): 1790, 1710, 1615 $cm^{-1}$. – $^1H$ NMR ([$D_6$]DMSO): $CH_3$ δ = 3.30.

$C_{18}H_{14}N_2O_4$ (322.3) Calcd. C 67.07 H 4.38 N 8.69 Found C 67.06 H 4.35 N 8.76

*1,3,5-Tris(isocyanatocarbonyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione* (**9**)

a) A fused ampulla containing **2** (5.60 g, 50 mmol) was left for 27 d at 22°C. The solid product was freed from traces of **2** by pumping for 10 h at 22°C/$10^{-1}$ Torr. Yield 5.45 g (98%) of a colourless powder; dec. above 130°C to **2** (differential thermoanalysis). – IR (sulfolane): 2250, 1835, 1785, 1750 $cm^{-1}$. – $^{13}C$ NMR ($CD_3CN$, 263 K): NCO δ = 129.9, C=O 141.7, 143.9. For the product being extremely moisture-sensitive, a satisfactory elemental analysis could not be obtained.

$C_9N_6O_9$ (336.2) Calcd. C 32.16 N 25.00 Found C 31.30 N 24.67

b) Carbonyl chloride isocyanate (7.38 g, 70 mmol) in ether (20 ml) was added with stirring to a solution of **3**[27] (6.91 g, 20 mmol) in ether (140 ml)[4]. After 30 min hexane (100 ml) was added dropwise. The reaction mixture was shaken for 30 min and the precipitate was filtered off with exclusion of moisture. Yield 5.65 g (92%) of a colourless powder.

c) As described for b) from **12**[8] (9.96 g, 10 mmol). After addition of hexane (100 ml) the reaction mixture was shaken for 12 h and cooled to −80°C. The precipitate (2.00 g) was isolated with exclusion of moisture. After evaporation of the mother liquor to a volume of 100 ml and addition of hexane (100 ml) further **9** (1.87 g) fell out within 2 d. Recrystallization from ether (100 ml)/hexane (100 ml) afforded a colourless powder (2.57 g, 76%). The products from procedures a)–c) showed identical IR and $^{13}C$ NMR spectra.

*Hydrolysis of* **9**: Water (2 ml) was added dropwise to a solution of **9** (2.02 g, 6 mmol) in acetonitrile (25 ml). After 12 h the solvent was evaporated under reduced pressure. The residue was recrystallized from water (40 ml) to give **10** (1.15 g, 89%). – $^{13}C$ NMR ([$D_6$]DMSO): C=O δ = 149.8.

*Methanolysis of* **9**: Methanol (5 ml) was added dropwise to a solution of **9** (2.02 g, 6 mmol) in acetonitrile (25 ml). After 12 h the solvent was evaporated under reduced pressure. The residue was extracted in a Soxhlet apparatus with ether (200 ml) for 24 h. Compound **10** remained undissolved. Evaporation of the ether gave **11** as a colourless powder (1.91 g, 80%), which was dissolved in dichloromethane (50 ml). Evaporation of the solvent gave a colourless powder; m.p. 128–130°C (lit.[28] 127–129°C). – $^1H$ NMR ($CDCl_3$): $CH_3$ δ = 3.79, NH 7.35. – $^{13}C$ NMR ($CDCl_3$): $CH_3$ δ = 53.0, C=O 151.9.

*2H-1,3,5-Oxadiazine-2,4,6(3H,5H)-trione* (**14**)[1]: Water (0.36 g, 20 mmol) in ether (10 ml) was added dropwise at 0°C to a solution of **2** (2.24 g, 20 mmol) in ether (50 ml). After 1 h at 0°C the precipitate was isolated. Yield 2.30 g (88%) of a colourless powder; m.p. 250°C. – $^{13}C$ NMR ([$D_6$]acetone): NCN δ = 148.3, OCN 145.4.

*2H-1,3,5-Thiadiazine-2,4,6(3H,5H)-trione* (**15**)[23]: At −196°C liquid hydrogen sulfide (6.82 g, 200 mmol) was added to **2** (2.24 g, 20 mmol) placed into an autoclave with teflon lining. The closed autoclave was left for 24 h at 22°C. Evaporation of excess $H_2S$ and crystallization of the residue from dioxane (30 ml) afforded a colourless powder (1.88 g, 66%); m.p. 160°C (dec.) (lit.[23] 160°C (dec.)).

*Phenyl (Isocyanatocarbonyl)carbamate* (**16d**): Phenol (1.88 g, 20 mmol) in cyclohexane (20 ml) was added dropwise to a solution of **2** (2.24 g, 20 mmol) in cyclohexane (25 ml). After 12 h precipitation of the product was completed by slow addition of petroleum ether (50 ml). Yield 4.00 g (97%) of a moisture-sensitive labile colourless powder. – IR ($CH_2Cl_2$): 3390, 2240, 1815, 1730 $cm^{-1}$. – $^1H$ NMR ($CDCl_3$, 263 K): NH δ = 8.61. – $^{13}C$ NMR ($CDCl_3$, 263 K): C=O δ = 149.1, 149.0.

*Dimethyl N,N'-Carbonylbis(carbamate)* (**17a**)[29]: Methanol (1.28 g, 40 mmol) in ether (10 ml) was added dropwise to a solution of **2** (2.24 g, 20 ml) in ether (50 ml) at 0°C. After

12 h at 22°C the mixture was filtrated. The residue was sublimated at 120°C/$10^{-2}$ Torr. Yield 2.96 g (84%) of colourless crystals; m.p. 146–149°C (lit.[29] 154–155°C). – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 3.84, NH 9.35. – $^{13}$C NMR ([$D_6$]acetone): $CH_3$ δ = 53.4, NCN 148.4, NCO 153.7.

*Di-tert-butyl N,N'-Carbonylbis(carbamate)* (**17b**): As described for **17a** from *tert*-butyl alcohol (2.97 g, 40 mmol). The reaction mixture was evaporated under reduced pressure. The residue was dissolved in chloroform (30 ml). After filtration and evaporation of the solvent the remaining oil crystallized at 5°C affording a colourless powder (2.45 g, 94%); m.p. 119–122°C. – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 1.51, NH 8.99. – $^{13}$C NMR ($CDCl_3$): $CH_3$ δ = 28.1, C 83.2, OCN 150.9, NCN 148.9.

$C_{11}H_{20}N_2O_5$ (260.3) Calcd. C 50.76 H 7.75 N 10.77 Found C 50.39 H 7.96 N 10.75

*Dibenzyl N,N'-Carbonylbis(carbamate)* (**17c**): As described for **17a** from benzyl alcohol (2.16 g, 20 mmol). The product crystallized from the reaction mixture. Yield after washing with ether (3 × 5 ml) 2.61 g (79%) of a colourless powder; m.p. 153–154°C. – $^1$H NMR ($CDCl_3$): $CH_2$ δ = 5.18, NH 9.11. – $^{13}$C NMR ($CDCl_3$): $CH_2$ δ = 68.2, C=O 148.4, 152.0.

$C_{17}H_{16}N_2O_5$ (328.2) Calcd. C 62.19 H 4.91 N 8.53 Found C 62.42 H 5.12 N 8.49

*Methyl Phenyl N,N'-Carbonylbis(carbamate)* (**17d**): To a solution of **16d** (4.12 g, 20 mmol) in dichloromethane (50 ml) methanol (1 ml) was added dropwise. The product crystallized within 12 h at 22°C. Yield 3.50 g (74%) of a colourless powder; m.p. 138–140°C. – $^1$H NMR ([$D_6$]DMSO): $OCH_3$ δ = 3.71, NH 10.44, 10.79. – $^{13}$C NMR ([$D_6$]DMSO): $OCH_3$ δ = 52.9, C=O 149.8, 150.3, 152.9.

$C_{10}H_{10}N_2O_5$ (238.2) Calcd. C 50.42 H 4.23 N 11.76 Found C 50.27 H 4.28 N 11.77

*Diphenyl N,N'-Carbonylbis(carbamate)* (**17e**): As described for **17c** from phenol (3.76 g, 40 mmol). Yield 4.56 g (76%) of colourless crystals; m.p. 149–151°C. – $^1$H NMR ($CDCl_3$/[$D_6$]acetone): NH δ = 10.28.

$C_{15}H_{12}N_2O_5$ (300.3) Calcd. C 60.00 H 4.03 N 9.33 Found C 59.72 H 4.00 N 9.32

*Phenyl 3-Cyclohexyl-2-(cyclohexylimino)hexahydro-4,6-dioxo-1,3,5-triazine-1-carboxylate* (**18a**): Dicyclohexylcarbodiimide (4.13 g, 20 mmol) in dichloromethane (25 ml) was added dropwise to a cooled (–78°C) solution of **16d** (4.12 g, 20 mmol) in dichloromethane (25 ml). The temperature was raised within 12 h to +22°C. After addition of charcoal the solution was filtered and the solvent was evaporated. The residue was dissolved in boiling dichloromethane (100 ml)/ether (400 ml). After filtration the product crystallized. Yield after work-up of the mother liquor 4.45 g (54%) of moisture-sensitive colourless prisms; m.p. 185–187°C. – IR (KBr): 1750, 1705, 1665, 1605 $cm^{-1}$. – $^1$H NMR ($CDCl_3$, 263 K): CH δ = 4.56 (m), 4.93 (m), NH 11.86. – $^{13}$C NMR ($CDCl_3$, 263 K): $CH_2$ δ = 24.9, 26.0, 28.3, 28.6, CH 55.6, 56.9, $C_6H_5$ 121.5, 125.8, 129.3, 145.8, C=O, C=N 148.3, 150.9, 153.4, 162.0.

$C_{22}H_{28}N_4O_4$ (412.5) Calcd. C 64.06 H 6.84 N 13.59 Found C 64.14 H 7.01 N 13.66

*Phenyl Hexahydro-3-isopropyl-2-(isopropylimino)-4,6-dioxo-1,3,5-triazine-1-carboxylate* (**18b**): As described for **18a** from diisopropylcarbodiimide (2.52 g, 20 mmol). Crystallization from ether (100 ml) at –18°C afforded after work-up of the mother liquor 5.50 g (83%) of moisture-sensitive colourless needles; m.p. 111–113°C. – IR (KBr): 1750, 1700, 1665, 1645, 1605, 1585 $cm^{-1}$. – $^1$H NMR ($CDCl_3$, 263 K): $CH_3$ δ = 1.47 (d, $J$ = 7 Hz), 1.50 (d, $J$ = 7 Hz), CH 4.99 (sept, $J$ = 7 Hz), 5.42 (broad), NH 11.81. – $^{13}$C NMR ($CDCl_3$, 263 K): $CH_3$ δ = 19.2, CH 47.6, 48.9, $C_6H_5$ 121.4, 125.8, 129.3, 145.6, C=O, C=N 147.9, 150.6, 153.3, 162.0.

$C_{16}H_{20}N_4O_4$ (332.4) Calcd. C 57.82 H 6.07 N 16.86 Found C 57.90 H 6.10 N 16.88

*S,S'-Diethyl N,N'-Carbonylbis(thiocarbamate)* (**19a**): A solution of **2** (1.12 g, 10 mmol) in ether (25 ml) was added dropwise to a solution of ethanethiol (1.24 g, 20 mmol) in ether (25 ml). After 12 h at 22°C pentane (50 ml) was added. At −80°C colourless needles crystallized (2.20 g, 93%, after work-up of the mother liquor); m.p. 114−117°C. − IR (KBr): 3220, 3120, 1720, 1650 $cm^{-1}$. − $^1H$ NMR ($CDCl_3$): $CH_3$ δ = 1.33 (t, *J* = 7 Hz), $CH_2$ 2.96 (q, *J* = 7 Hz), NH 10.04. − $^{13}C$ NMR ($CDCl_3$): $CH_3$ δ = 14.5, $CH_2$ 24.6, C=O 149.2, COS 170.0.

$C_7H_{12}N_2O_3S_2$ (236.3) Calcd. C 35.58 H 5.12 N 11.86 Found C 35.48 H 5.01 N 11.69

*S,S'-Diisopropyl N,N'-Carbonylbis(thiocarbamate)* (**19b**): From 2-propanethiol (1.52 g, 20 mmol) as described for **19a**. Yield 2.56 g (97%) of colourless needles; m.p. 125−127°C. − $^1H$ NMR ($CDCl_3$): $CH_3$ δ = 1.37 (d, *J* = 7 Hz), CH 3.70 (sept, *J* = 7 Hz), NH 9.70. − $^{13}C$ NMR ($CDCl_3$): $CH_3$ δ = 22.9, CH 36.3, C=O 148.6, COS 169.6.

$C_9H_{16}N_2O_3S_2$ (264.4) Calcd. C 40.89 H 6.10 N 10.60 Found C 40.71 H 5.97 N 10.46

*S,S'-Diphenyl N,N'-Carbonylbis(thiocarbamate)* (**19c**): From thiophenol (2.20 g, 20 mmol) as described for **19a**. The product was dissolved in dichloromethane (50 ml). After filtration with added charcoal and evaporation of the solvent a colourless powder was obtained (3.10 g, 93%); m.p. 129−131°C (dec.). − $^{13}C$ NMR ($CDCl_3$): $C_6H_5$ δ = 126.0, 129.4, 130.2, 135.3, C=O 148.7, COS 168.5.

$C_{15}H_{12}N_2O_3S_2$ (332.4) Calcd. C 54.20 H 3.64 N 8.43 Found C 54.45 H 3.81 N 8.55

*Diimidotricarbonic Bis(isopropylamide)* (**20a**): Isopropylamine (2.36 g, 40 mmol) in dichloromethane (25 ml) was added dropwise to **2** (2.24 g, 20 mmol) in dichloromethane (25 ml). After 12 h the solvent was evaporated. The residue crystallized from ethanol (50 ml) affording colourless prisms (4.00 g, 87%, after work-up of the mother liquor); m.p. 188−189°C. − IR (KBr): 3330, 3290, 3160, 1725, 1695, 1645 $cm^{-1}$. − $^1H$ NMR ([$D_6$]DMSO): $CH_3$ δ = 1.12 (d, *J* = 6.4 Hz), CH 3.80, NH 7.37, 9.57. − $^{13}C$ NMR ([$D_6$]DMSO): $CH_3$ δ = 22.4, CH 41.3, C=O 152.2 (2C), 152.9.

$C_9H_{18}N_4O_3$ (230.3) Calcd. C 46.94 H 7.88 N 24.24 Found C 46.88 H 7.89 N 24.30

*Diimidotricarbonic Bis(tert-butylamide)* (**20b**): From *tert*-butylamine (2.93 g, 40 mmol) as described for **20a**. The reaction was carried out at 0°C. After evaporation of the solvent the product was dissolved in chloroform (100 ml). Filtration with added charcoal and evaporation of the solvent yielded a colourless powder (4.18 g, 81%); dec. above 194°C. − $^1H$ NMR ($CDCl_3$): $CH_3$ δ = 1.38, NH 7.73, 8.91. − $^{13}C$ NMR ($CDCl_3$): $CH_3$ δ = 29.0, C 51.1, C=O 152.4 (2C), 154.0.

$C_{11}H_{22}N_4O_3$ (258.3) Calcd. C 51.14 H 8.59 N 21.69 Found C 51.18 H 8.70 N 21.71

*Diimidotricarbonic Bis(dibenzylamide)* (**20c**): From dibenzylamine (7.89 g, 40 mmol) as described for **20a**. Crystallization from ethanol (100 ml) afforded colourless prisms (6.00 g, 59%); m.p. 145−146°C. − $^1H$ NMR ($CDCl_3$): $CH_2$ δ = 4.48. − $^{13}C$ NMR ($CDCl_3$): $CH_2$ δ = 49.7, $C_6H_5$ 127.5, 127.6, 128.6, 136.1, C=O 150.9, 153.8 (2C).

$C_{31}H_{30}N_4O_3$ (506.6) Calcd. C 73.49 H 5.97 N 11.06 Found C 73.27 H 5.99 N 11.09

*Diimidotricarbonic Bis[(4-chlorophenyl)amide]* (**20d**): A solution of **2** (1.12 g, 10 mmol) in ether (10 ml) was added dropwise to a solution of 4-chloroaniline (2.55 g, 20 mmol) in ether (30 ml). After 12 h the solvent was evaporated. Recrystallization of the residue from butanol (200 ml) afforded colourless needles (2.57 g, 70%, after work-up of the mother liquor); dec. above 238°C. − $^1H$ NMR ([$D_6$]DMSO): NH δ = 9.79, 9.93. − $^{13}C$ NMR ([$D_6$]DMSO): $C_6H_5$ δ = 121.2, 127.5, 128.6, 136.3, C=O 150.5 (2C), 152.4.

$C_{15}H_{12}Cl_2N_4O_3$ (367.2) Calcd. C 49.06 H 3.29 N 15.26 Found C 48.96 H 3.21 N 15.13

*Diimidotricarbonic Bis[(2-methylphenyl)amide]* (**20e**): From 2-methylaniline (2.14 g, 20 mmol) as described for **20d**. Crystallization from butanol (80 ml) afforded a colourless powder (2.56 g, 78%); m.p. 189–191°C (dec.). – $^1$H NMR ([D$_6$]DMSO): CH$_3$ δ = 2.26, NH 9.49, 10.05. – $^{13}$C NMR ([D$_6$]DMSO): CH$_3$ δ = 17.4, C$_6$H$_5$ 121.6, 124.2, 126.2, 128.4, 130.2, 135.4, C=O 150.7 (2C), 153.2.

$C_{17}H_{18}N_4O_3$ (326.4) Calcd. C 62.56 H 5.56 N 17.17 Found C 62.52 H 5.37 N 17.14

*1-Methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione* (**22a**)[25]: A suspension of methylammonium chloride (1.35 g, 20 mmol) and **2** (2.24 g, 20 mmol) in tetrahydrofuran (100 ml) was boiled under reflux for 12 h. The reaction mixture was filtrated while hot. Evaporation of the solvent and recrystallization of the residue from ethanol (120 ml) afforded colourless prisms (1.69 g, 69%); m.p. 280°C (lit.[25] 275–285°C). – IR (KBr): 3210, 3100, 1805, 1750, 1690, 1665 cm$^{-1}$. – $^1$H NMR ([D$_6$]DMSO): CH$_3$ δ = 3.05, NH 11.39. – $^{13}$C NMR ([D$_6$]DMSO): CH$_3$ δ = 21.1, C=O 148.3, 149.8 (2C).

*1-Ethyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione* (**22b**)[25]: From ethylammonium chloride (1.63 g, 20 mmol) as described for **22a**. Recrystallization from ethanol (50 ml) afforded colourless crystals; m.p. 218–220°C (lit.[25] 230–231°C). – $^1$H NMR ([D$_6$]DMSO): CH$_3$ δ = 1.09 (t, *J* = 7 Hz), CH$_2$ 3.69 (q, *J* = 7 Hz), NH 11.39. – $^{13}$C NMR ([D$_6$]DMSO): CH$_3$ δ = 12.8, CH$_2$ 35.5, C=O 148.3, 149.4 (2C).

*1-Benzyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione* (**22c**)[25]: From benzylammonium chloride (2.87 g, 20 mmol) as described for **22a**. Crystallization from ethanol (120 ml) gave colourless prisms (3.50 g, 80%); m.p. 238–240°C (lit.[25] 244–245°C). – $^1$H NMR ([D$_6$]DMSO): CH$_2$ δ = 4.84, NH 11.52. – $^{13}$C NMR ([D$_6$]DMSO): CH$_2$ δ = 43.5, C$_6$H$_5$ 127.0, 127.2, 128.1, 136.6, C=O 148.3, 149.7 (2C).

*1-(4-Bromophenyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione* (**22d**)[30]: From 4-bromoanilinium chloride (4.17 g, 20 mmol) as described for **22a**. Yield after recrystallization from ethanol and work-up of the mother liquor 3.90 g (69%) of colourless crystals; m.p. 294–297°C (dec.) (lit.[30] 311°C). – $^1$H NMR ([D$_6$]DMSO): NH δ = 11.60. – $^{13}$C NMR ([D$_6$]DMSO): C$_6$H$_5$ δ = 121.4, 131.2, 131.6, 133.4, C=O 148.5, 149.3 (2C).

*Methyl 5-Phenylbiuret-1-carboxylate* (**23a**): A suspension of anilinium bromide (3.48 g, 20 mmol) and **2** (2.24 g, 20 mmol) in dichloromethane (100 ml) was boiled under reflux for 12 h. Methanol (2 ml) was added and the mixture was refluxed for additional 3 h. Evaporation of the solvent and crystallization of the residue from water (400 ml)/dimethyl sulfoxide (300 ml) afforded colourless prisms (1.60 g, 34%); m.p. 175–177°C. – IR (KBr): 3270, 1770, 1710 cm$^{-1}$. – $^1$H NMR ([D$_6$]DMSO): CH$_3$ δ = 3.74, NH 9.81, 10.04, 10.86. – $^{13}$C NMR ([D$_6$]DMSO): CH$_3$ δ = 52.9, C$_6$H$_5$ 119.6, 123.6, 128.7, 137.3, C=O 149.9, 151.2, 153.5.

$C_{10}H_{11}N_3O_4$ (237.2) Calcd. C 50.63 H 4.67 N 17.72 Found C 50.50 H 4.61 N 17.80

*Ethyl 5-(4-Methylphenyl)biuret-1-carboxylate* (**23b**): From 4-methylanilinium bromide (3.76 g, 20 mmol) and ethanol (10 ml) as described for **23a**. Crystallization from water (60 ml)/dimethyl sulfoxide (240 ml) and recrystallization from water (40 ml)/dimethyl sulfoxide (40 ml) afforded colourless prisms (0.70 g, 13%); m.p. 185–187°C. – $^1$H NMR ([D$_6$]DMSO): CH$_3$ δ = 1.25 (t, *J* = 7 Hz), 2.26, CH$_2$ 4.20 (q, *J* = 7 Hz), NH 9.81, 9.97, 10.82. – $^{13}$C NMR ([D$_6$]DMSO): CH$_3$ δ = 14.0, 20.3, CH$_2$ 60.0, C=O 149.8, 151.3, 153.1.

$C_{12}H_{15}N_3O_4$ (265.3) Calcd. C 54.33 H 5.70 N 15.84 Found C 54.22 H 5.71 N 15.77

*4-Bromobutyl 5-Phenylbiuret-1-carboxylate* (**23c**): A suspension of anilinium bromide (3.48 g, 20 mmol) and **2** (2.24 g, 20 mmol) in tetrahydrofuran (100 ml) was boiled under reflux for 2 h. Evaporation of the solvent, crystallization of the oily residue from water

(200 ml)/ethanol (300 ml) and recrystallization from acetone (60 ml) afforded colourless prisms (1.74 g, 24%); m.p. 168°C. – $^1$H NMR ([D$_6$]DMSO): $CH_2$ δ = 1.77 (m), 1.90 (m), 3.59 (t, $J$ = 7 Hz), 4.19 (t, $J$ = 6 Hz), NH 9.80, 10.04, 10.80. – $^{13}$C NMR ([D$_6$]DMSO): $CH_2$ δ = 26.8, 28.8, 34.3, 65.1, $C_6H_5$ 119.6, 123.6, 128.7, 137.3, C=O 149.9, 151.2, 153.0.

$C_{13}H_{16}BrN_3O_4$ (358.2) Calcd. C 43.59 H 4.50 N 11.73 Found C 43.71 H 4.33 N 11.73

*Diimidotricarbonic Bis[(diphenylmethylene)amide]* (**24a**): A solution of **2** (1.12 g, 10 mmol) in ether (20 ml) was added dropwise at −78°C to a solution of (diphenylmethylene)amine (3.62 g, 20 mmol) in ether (30 ml). The solution was warmed to 22°C within 12 h. Evaporation of the solvent and crystallization of the oily residue from dichloromethane (10 ml)/ether (75 ml)/hexane (30 ml) at −80°C afforded a colourless powder (4.00 g, 84%); m.p. 124−126°C (dec.). – IR (KBr): 3400, 3200, 1740, 1650, 1625 cm$^{-1}$. – $^{13}$C NMR ($CDCl_3$): $C_6H_5$ δ = 128.2, 129.1, 131.3, 135.9, C=O, C=N 148.5, 160.3 (broad), 172.0 (broad).

$C_{29}H_{22}N_4O_3$ (474.5) Calcd. C 73.40 H 4.67 N 11.81 Found C 73.16 H 4.79 N 11.76

*Diimidotricarbonic Bis[(2,2-dimethyl-1-phenylpropylidene)amide]* (**24b**): From (2,2-dimethyl-1-phenylpropylidene)amine (3.22 g, 20 mmol) as described for **24a**. After addition of hexane (100 ml) the reaction mixture was shaken for 1 h and the product was filtered off. Yield after work-up of the mother liquor 4.20 g (97%) of a colourless powder; m.p. 155−158°C (dec.). – $^1$H NMR ($CDCl_3$): $CH_3$ δ = 1.18. – $^{13}$C NMR ($CDCl_3$): $CH_3$ δ = 27.7, C 40.6, $C_6H_5$ 126.3, 127.7, 128.6, 135.2, C=O, C=N 148.8, 160.5 (broad), 184.9 (broad).

$C_{25}H_{30}N_4O_3$ (434.5) Calcd. C 69.10 H 6.96 N 12.90 Found C 69.15 H 6.98 N 12.80


[1] *E. Nachbaur*, Monatsh. Chem. **97**, 361 (1966).
[2] *W. Gottardi*, Monatsh. Chem. **101**, 655 (1970).
[3] *Bayer AG* (Erf. *H. Hagemann*), D.O.S. 2408069 (4. Sept. 1975) [Chem. Abstr. **84**, 43358z (1976)].
[4] *V. I. Gorbatenko* and *L. F. Lure*, Zh. Org. Khim. **16**, 464 (1980) [Chem. Abstr. **93**, 25882x (1980)].
[5] *G. Jäckh* and *W. Sundermeyer*, Chem. Ber. **106**, 1752 (1973).
[6] *W. Verbeek* and *W. Sundermeyer*, Angew. Chem. **79**, 860 (1967); Angew. Chem., Int. Ed. Engl. **6**, 871 (1967).
[7] *Bayer AG* (Erf. *H. Hagemann*), D.O.S. 2411674 (2. Oct. 1975) [Chem. Abstr. **84**, 4508d (1976)].
[8] *W. Stamm*, J. Org. Chem. **30**, 693 (1965).
[9] *G. J. M. van der Kerk* and *J. G. A. Luijten*, J. Appl. Chem. **6**, 93 (1956).
[10] *E. Schmidt*, J. Prakt. Chem. **5**, 35 (1872).
[11] *A. J. Speziale* and *L. R. Smith*, J. Org. Chem. **27**, 3742 (1962).
[12] *A. J. Speziale* and *L. R. Smith*, J. Org. Chem. **28**, 1805 (1963).
[13] *A. J. Speziale, L. R. Smith*, and *J. E. Fedder*, J. Org. Chem. **30**, 4306 (1965).
[14] *V. A. Chauzov* and *Yu. I. Baukov*, Zh. Obshch. Khim. **42**, 1868 (1972) [Chem. Abstr. **78**, 3616c (1973)].
[15] *V. D. Sheludyakov, A. S. Tkachev, S. V. Sheludyakova, V. P. Kozyukov*, and *V. F. Mironov*, Zh. Obshch. Khim. **47**, 2259 (1977) [Chem. Abstr. **88**, 23041v (1978)].
[16] *V. D. Sheludyakov, V. V. Shcherbinin, E. S. Rodinov*, and *V. F. Mironov*, Zh. Obshch. Khim. **42**, 1870 (1972) [Chem. Abstr. **78**, 29881j (1973)].
[17] *O. Tsuge* and *K. Mizuguchi*, Kogyo Kagaku Zasshi **69**, 935 (1966) [Chem. Abstr. **66**, 85552s (1967)].
[18] *O. Tsuge* and *K. Mizuguchi*, Nippon Kagaku Zasshi **86**, 325 (1965) [Chem. Abstr. **63**, 4299e (1965)].
[19] *A. Etienne, B. Bonte*, and *B. Druet*, Bull. Soc. Chim. Fr. **1972**, 251.
[20] *H. Salzburg*, in Methoden der organischen Chemie (*Houben-Weyl*), Vol. E/4, p. 1377, Thieme, Stuttgart, New York 1983.
[21] *A. S. Gordetsov, Yu. I. Dergunov, I. A. Vostokov, V. A. Gal'perin*, and *V. I. Zagranichnyi*, Zh. Org. Khim. **8**, 1763 (1977) [Chem. Abstr. **87**, 168149a (1977)].

[22] *H. Hagemann*, GDCh Meeting, Köln 8.–13.9.1975; referred to in Methoden der organischen Chemie (*Houben-Weyl*), Vol. E/4, Thieme, Stuttgart, New York 1983. Our independent research was essentially completed when this book appeared.
[23] *R. Bunnenberg* and *J. C. Jochims*, Chem. Ber. **114**, 2064 (1981).
[24] *R. Bunnenberg* and *J. C. Jochims*, Chem. Ber. **114**, 2075 (1981).
[25] *W. C. Close*, J. Am. Chem. Soc. **75**, 3617 (1953).
[26] *V. P. Kuzyukov, A. E. Feoktistov*, and *V. F. Mironov*, Zh. Obshch. Khim. **53**, 2155 (1983) [Chem. Abstr. **100**, 51682q (1984)].
[27] *J. C. Jochims, H. von Voithenberg*, and *G. Wegner*, Chem. Ber. **111**, 1693 (1978).
[28] *T. C. Thurber* and *L. B. Townsend*, J. Heterocycl. Chem. **14**, 647 (1977).
[29] *H. Najer* and *P. Mabille*, C. R. Acad. Sci. **242**, 2727 (1956).
[30] *G. Rembarz, E. Fischer*, and *P. Neels*, J. Prakt. Chem. **316**, 128 (1974).

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