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Reactions of Carbonyl Diisocyanate with Amides and Acids

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Carbonyl diisocyanate (**1**) reacts with primary amides to give 1-acylated isocyanuric acids (**5**,**6**). With secondary amides, **1** affords the rather instable oxadiazinediones **4**, which for certain substituents rearrange to give triazines (**5**,**10**). With nucleophiles, compounds **4** give oligourets, *e.g.* with ureas pentaurets (**11**,**12**) were obtained. Carbonyl diisocyanate reacts with hydrogen halides to afford the crystalline urea-1,3-dicarbonyl halides **13a–c**. Diverse products (**16**, **17**, **24**, **26**) were obtained with carboxylic acids. In most cases oxadiazinediones (**26**) were isolated, which can be transformed with nucleophiles into acyl ureas **30**, **31**, biurets **32**, and triurets **33**. Acetylation of **26** leads to the reactive heterocycles **34**.

Reaktionen von Carbonyldiisocyanat mit Amiden und Säuren

Carbonyldiisocyanat (**1**) reagiert mit primären Amiden zu 1-acylierten Isocyanursäuren (**5**,**6**). Mit sekundären Amiden werden die recht instabilen Oxadiazine **4** erhalten, die sich, je nach Substitution, zu Triazinen (**5**,**10**) umlagern. Mit Nucleophilen reagieren die Oxadiazine **4** zu Oligoureten, mit Harnstoffen z. B. zu Pentaureten (**11**,**12**). Carbonyldiisocyanat setzt sich mit Halogenwasserstoffen zu den kristallinen Harnstoff-1,3-dicarbonsäurehalogeniden **13a–c** um. Mit Carbonsäuren konnten verschiedene Produkte erhalten werden (**16**, **17**, **24**, **26**). In den meisten Fällen wurden Oxadiazine **26** isoliert, die mit Nucleophilen weiter zu Acylharnstoffen **30**, **31**, Biureten **32** und Triureten **33** umgesetzt werden können. Acetylierung von **26** ergibt die reaktiven Heterocyclen **34**.

In spite of the economical and scientific importance of phosgene, comparatively little efforts have been undertaken to elucidate the chemistry of other carbonyl halides and pseudohalides[1]. The very reactive carbonyl diisocyanate (**1**) was first prepared by *Nachbaur*[2]. Other syntheses, in part patented, have been published[3–10], but hitherto only a few reactions of **1** with simple nucleophiles such as water, alcohols, and amines[1] and a cycloaddition with cyclohexanone[11] have been reported in the literature, although more may be known[12]. In a preceeding paper[10] we reported a new synthesis of **1** and some of its transformations. In this communication reactions of **1** with amides, hydrohalogenic acids[12], and carboxylic acids will be described.

Carbonyl diisocyanate (**1**) reacts with carboxamides **2** according to Scheme 1. With primary amides including 3,3-unsubstituted ureas the monoacylated isocyanuric acids **5a–e** were obtained. Correspondingly, sulfonamides react to give the triazines **6**[12]. The formation of **5** proceeds *via* intermediates **3** and **4**. An isocyanate of type **3** was isolated from the reaction of **1** with phenol[10]. For $R^2 = H$ oxadiazines **4** undergo *Dimroth* rearrangement[13,14] to give **5**.

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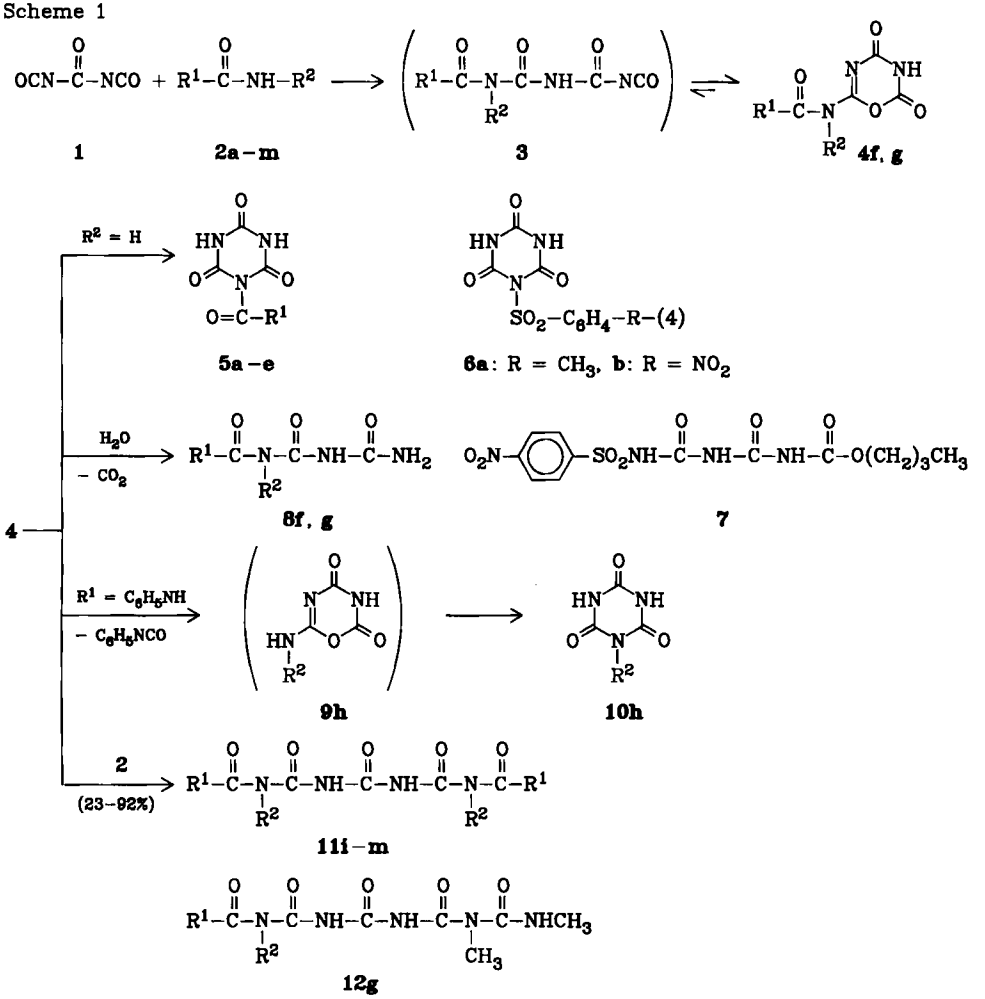
Scheme 1



2–5, 8–12	R^1	R^2		R^1	R^2
a	CH_3	H	**h**	C_6H_5NH	$(CH_3)_2CH$
b	C_2H_5	H	**i**	CH_3NH	H
c	C_6H_5	H	**j**	C_2H_5NH	H
d	$C_6H_4C(CH_3)_3$–(4)	H	**k**	$(CH_3)_3CNH$	H
e	$(C_6H_5)_2N$	H	**l**	C_6H_5NH	H
f	$(CH_3)_2N$	CH_3	**m**	CH_3NH	CH_3
g	$[(CH_3)_2CH]_2N$	CH_3			

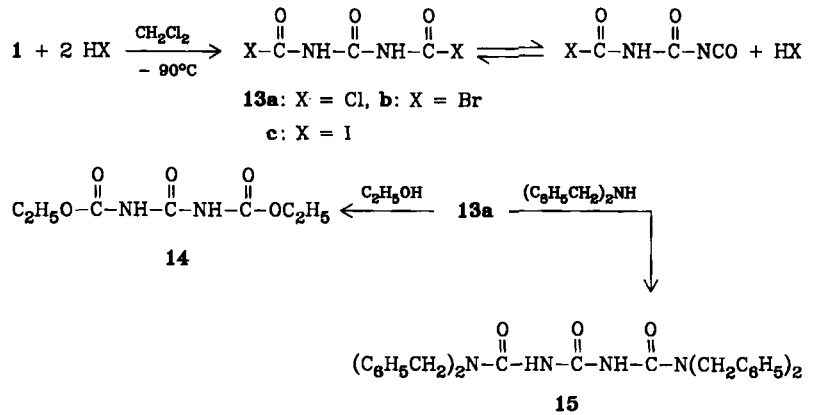
With pivalamide or 4-nitrobenzamide no pure products could be obtained. To our knowledge, 1-acylisocyanuric acids **5** are not known[15]. These compounds react as activated amides. With water **5a** is quickly hydrolyzed to give cyanuric acid and acetic acid. With 4-nitro-

benzenesulfonamide impure **6b** was obtained in moderate yields. Attempts to recrystallize the compound from 1-butanol resulted in ring opening and formation of **7**.

With secondary amides ($R^2 \neq H$), *e.g.*, 1,1,3-trisubstituted ureas **2f,g**, the rather instable oxadiazines **4f,g** could be isolated. The NMR spectra of **4g** show doubling of all signals (263 K, CD_2Cl_2), which must arise from hindered rotation around one of the $C-NR^2$ bonds. With water, **4f,g** are hydrolyzed affording the triurets **8f,g**. The reaction of **1** with the secondary amide 1-isopropyl-3-phenylurea (**2h**) takes a different course. In this case the oxadiazine **4h** loses phenyl isocyanate to give **9h**, which rearranges to give **10h**. Furthermore, the oxadiazines **4** react with amides giving 1,7-diacylated triurets **11,12**. Thus, carbonyl diisocyanate (**1**) and two equivalents of an urea (**2i–m**) afforded the pentaurets **11i–m**.

The extension of this reaction to the preparation of higher oligourets is obvious. As far as we are aware little[16–20], if any[21,22] is known about oligourets higher than triurets. The constitutions of the pentaurets **11i–m** follow from the symmetries of their NMR spectra and the elemental analyses. The compounds are stable high-melting solids.

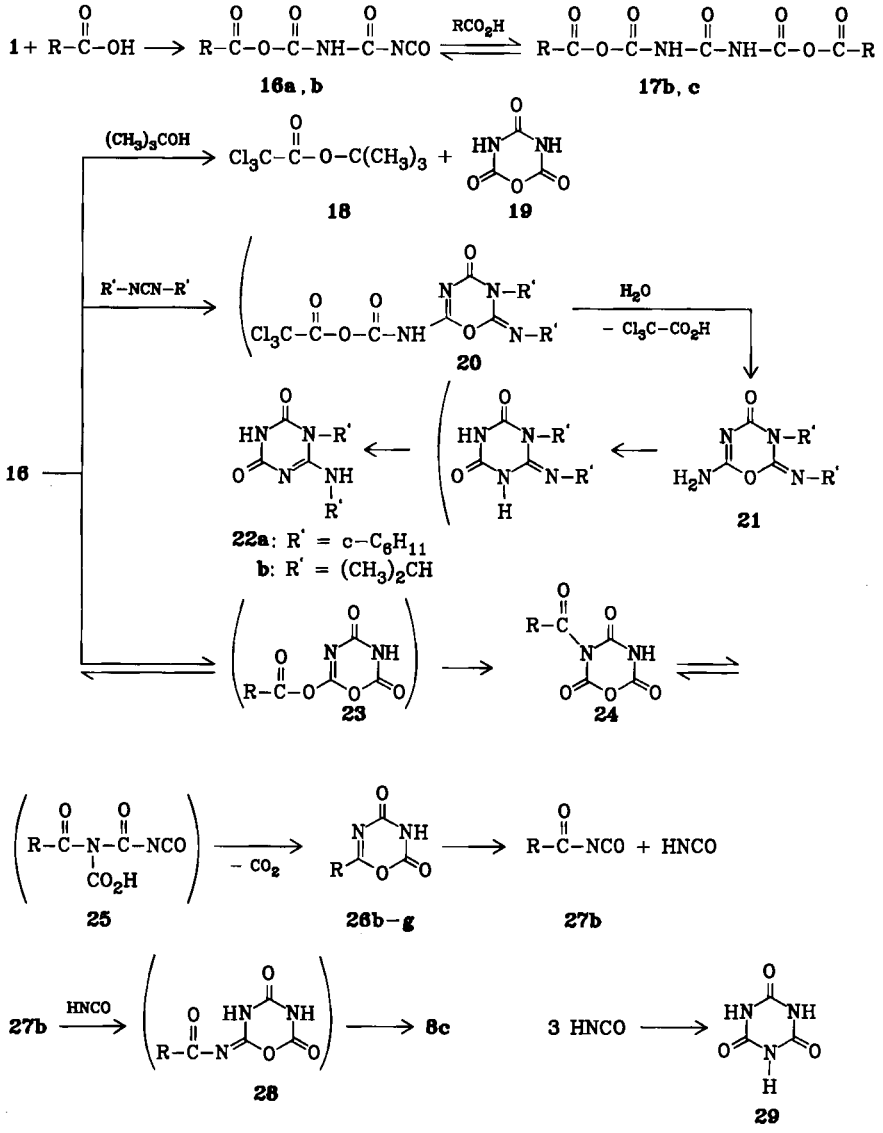
Carbonyl diisocyanate (**1**) adds two equivalents of a hydrogen halide to afford the crystalline urea-1,3-dicarbonyl halides **13a–c** almost quantitatively[12]. At room temperature these compounds slowly lose hydrogen halide. Thus, the IR spectra of **13a** in dichloromethane show a weak isocyanate band at 2215 cm^{-1}, which gradually increases in intensity. At −10°C in the ^{13}C NMR spectra of **13a–c** only two signals with intensity ratios of ca. 1:2 are observed. With ethanol or dibenzylamine **13a** reacts to give **14** or **15**[2,10], respectively.



In Scheme 2 a proposal is shown explaining the diverse products obtained from the reactions of carboxylic acids with **1**.

At room temperature carbonyl diisocyanate reacts with trichloroacetic acid to give the monoadduct **16a**, which was too instable to be isolated. In solution (ether) **16a** shows a strong IR absorption at 2220 cm^{-1} (NCO), and in the ^{13}C NMR

Scheme 2



16, 17, 23–28	R		R
a	CCl_3	e	C_2H_5
b	C_6H_5	f	$(CH_3)_2CH$
c	$(CH_3)_3C$	g	$C_6H_5CH_2$
d	CH_3	h	$C_6H_5(C_2H_5)CH$

spectrum four resonances with chemical shifts in agreement with the proposed constitution. Addition of *tert*-butyl alcohol to the solution of **16a** resulted in the formation of *tert*-butyl trichloroacetate (**18**) together with the anhydride **19**[2]. This can be explained assuming attack of the alcohol on the anhydride function of **16a** in preference to the NCO group. But other mechanisms cannot be excluded at present.

With carbodiimides **16a** reacts to give the triazines **22**, which must arise from a cycloaddition of the carbodiimide to the acyl isocyanate function of **16a**[23–25]. The hypothetic intermediate **20** is probably hydrolyzed by traces of moisture to give **21**, which undergoes *Dimroth* rearrangement[16,17] and tautomerization affording **22** (J_{NHCH} ca. 7 Hz).

At −80°C carbonyl diisocyanate reacts with two equivalents of benzoic acid to afford the anhydride **17b**[12]. This surprisingly stable compound eliminates CO_2 above 130°C. In solution at room temperature an equilibrium **16b** ⇌ **17b** is established [IR: 2230 cm^{-1} (NCO) in CH_2Cl_2]. Elimination of CO_2 from **16b** leads to the formation of the oxadiazine **26b**[26]. This compound can be obtained directly from the reaction of **1** with one equivalent of benzoic acid at room temperature.

The production of **26b** can be envisaged assuming a tautomeric equilibrium between **16b** and **23b**. *Chapman* rearrangement[27] affords **24b**. Elimination of CO_2, probably from **25b**, and ring closure would give **26b**.

According to a differential thermoanalysis **26b** decomposes above 135°C to give CO_2, HNCO, CO, benzoyl isocyanate, **27b**, and benzonitrile. Benzoyl isocyanate and HNCO react to give **8c** *via* **28**. Furthermore, HNCO trimerizes to yield cyanuric acid (**29**). When a sample of **26b** was dried under reduced pressure at 150°C a mixture of **8c** and **29** was isolated.

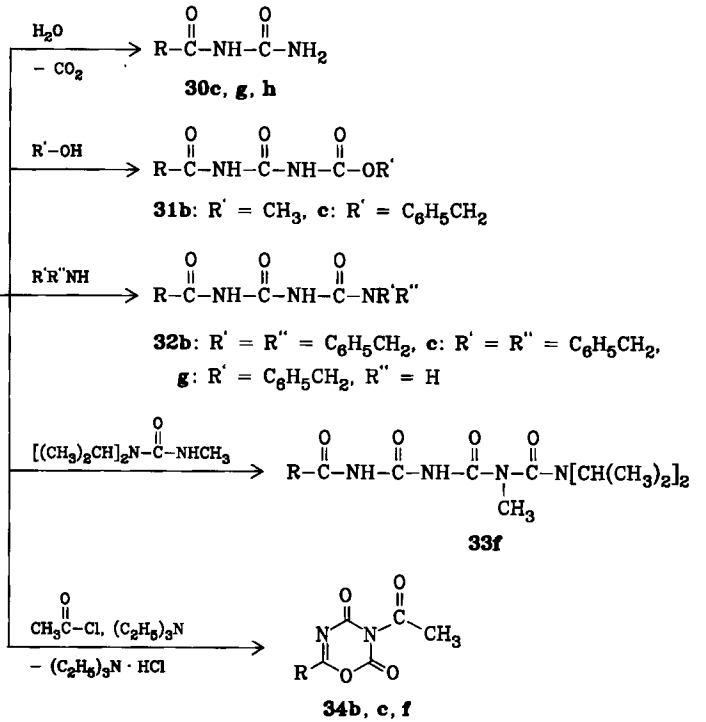
The proposed mechanism for the formation of **26b** was further substantiated by isolation of the rather thermolabile and moisture-sensitive anhydride **24c** from the reaction of **1** with pivalic acid in ether at 0°C. At room temperature in the solid state and faster in solution **24c** eliminates CO_2 to give **26c**. A differential thermoanalysis of **24c** shows a maximum of the CO_2 elimination at 72°C and a melting point (with decomposition) of the resulting **26c** at 118°C.

The constitution of **24c** can be derived from the NMR spectra by comparison with those of **19** and **6**. According to the ^{13}C-NMR spectrum pivalic acid reacts with **1** at −50°C to give the instable diadduct **17c**, which could not be isolated.

Other aromatic carboxylic acids, *e.g.*, 4-nitrobenzoic acid or 4-*tert*-butylbenzoic acid, react with **1** to give complex mixtures of compounds containing according to the NMR spectra **29**, **5** and carboxylic anhydrides. On the other hand, aliphatic carboxylic acids react smoothly to afford the oxadiazines **26c–g** in good yields.

Similar to **5** the heterocycles **26** themselves are preparative usefull although in some cases instable compounds, which rapidly react with nucleophiles. With water the monoacylated ureas **30** were obtained. These compounds can be prepared in a one-pot reaction without isolation of **26**. Alcohols give acylated allophanic acids **31**, amines acylated biurets **32**, and ureas correspondingly triurets **33**. Finally, **26** can be *N*-acetylated in the presence of triethylamine giving **34** (Scheme 3).

Scheme 3



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 90 instruments; δ-scale; internal reference tetramethylsilane. – Mass spectrometry: Varian MAT-312 and MAT-112S spectrometers. – Differential thermoanalyses: Netsch STA 429 instruments. – All reactions were carried out with exclusion of moisture in absolutely dry solvents. Petroleum ether: b.p. 50–70°C. – Melting points: uncorrected.

6-(1,3,3-Trimethylureido)-2H-1,3,5-oxadiazine-2,4(3H)-dione (**4f**): A solution of **2f** (2.04 g, 20 mmol) in ether (100 ml) was added dropwise to a mixture of **1** (2.24 g, 20 mmol) in ether (25 ml). After 12 h at 22°C the product was isolated by filtration affording an instable colourless powder (4.20 g, 98%); dec. above 115°C. – IR (CH_2Cl_2): 3370, 1820, 1730, 1710, 1610 cm^{-1}.

$C_7H_{10}N_4O_4$ (214.2) Calc. C 39.25 H 4.71 N 26.16 Found C 38.98 H 4.72 N 25.90

6-(3,3-Diisopropyl-1-methylureido)-2H-1,3,5-oxadiazine-2,4(3H)-dione (**4g**): From **2g** (3.17 g, 20 mmol) in ether (25 ml) as described for **4f**; yield 5.40 g (100%) of a colourless in solution instable powder; dec. above 105°C. – ^1H NMR (CD_2Cl_2, 263 K): CH_3 δ = 1.22 (d, J = 6 Hz), 1.23 (d, J = 7 Hz), 1.42 (d, J = 7 Hz), 1.46 (d, J = 7 Hz); 3.23, CH 3.52 (m), 3.93 (m); NH 10.40, 10.50. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 19.3, 19.7, 20.3, 21.2, 33.5, 34.4; CH 47.0, 51.8; C=O, C=N 144.6, 145.0, 150.3, 150.9, 154.8, 155.0, 156.8, 157.3.

$C_{11}H_{18}N_4O_4$ (270.3) Calc. C 48.88 H 6.71 N 20.73 Found C 49.05 H 6.80 N 20.61

1-Acetyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**5a**): A solution of **2a** (1.18 g, 20 mmol) in warm tetrahydrofuran (THF) (100 ml) was added dropwise to a solution of **1** (2.24 g, 20 mmol) in THF (30 ml). After 12 h the mixture was filtered. Evaporation of the solvent and crystallization of the residue from dioxane (40 ml)/petroleum ether (50 ml) afforded a colourless powder (2.70 g, 79%); dec. above 186°C. – ^{1}H NMR ([D$_6$]acetone): CH$_3$ δ = 2.55; NH 11.02. – ^{13}C NMR ([D$_6$]DMSO/[D$_6$]acetone (1:2)): CH$_3$ δ = 27.5; C=O 148.6 (2C), 149.3, 172.2.

$C_5H_5N_3O_4$ (171.1) Calc. C 35.09 H 2.95 N 24.56 Found C 34.87 H 3.20 N 24.75

1-Propionyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**5b**): A solution of **1** (1.12 g, 10 mmol) in dichloromethane (25 ml) was added dropwise to a suspension of **2b** (0.73 g, 10 mmol) in dichloromethane (25 ml). After 12 h at 22°C the mixture was filtered. The residue was crystallized from dioxane (30 ml)/petroleum ether (30 ml) affording a colourless powder (1.45 g, 78%); dec. above 300°C. – ^{1}H NMR ([D$_6$]DMSO): CH$_3$ δ = 1.08 (t, J = 7 Hz); CH$_2$ 2.84 (q, J = 7 Hz); NH 11.72. – ^{13}C NMR ([D$_6$]DMSO): CH$_3$ δ = 7.8; CH$_2$ 33.3; C=O 147.8 (2C), 148.4, 175.6.

$C_6H_7N_3O_4$ (185.1) Calc. C 38.92 H 3.81 N 22.70 Found C 38.84 H 3.99 N 22.47

1-Benzoyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**5c**): From **2c** (1.21 g, 10 mmol) as described for **5a** (50 ml THF). Recrystallization from butanol (45 ml) gave a colourless powder (1.80 g, 77%); dec. above 300°C. – ^{1}H NMR ([D$_6$]DMSO): NH δ = 11.88. – ^{13}C NMR ([D$_6$]DMSO): phenyl δ = 129.1, 130.5, 131.3; C=O 148.2 (2C), 148.6, 167.2.

$C_{10}H_7N_3O_4$ (233.2) Calc. C 51.50 H 3.03 N 18.02 Found C 51.65 H 3.14 N 17.83

1-(4-tert-Butylbenzoyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**5d**): From **2d** (1.77 g, 10 mmol) in dichloromethane (30 ml) and **1** (1.12 g, 10 mmol) in ether (20 ml) as described for **5b**; yield (without recrystallization) 2.73 g (94%) of a colourless powder; dec. above 300°C. – ^{1}H NMR ([D$_6$]DMSO): CH$_3$ δ = 1.32; NH 11.80. – ^{13}C NMR ([D$_6$]DMSO): CH$_3$ δ = 30.5; C 35.0, *m*-C 126.0, *i*-C 128.7, *o*-C 130.5, *p*-C 158.9; C=O 148.2 (2C), 148.5, 166.7.

$C_{14}H_{15}N_3O_4$ (289.3) Calc. C 58.12 H 5.23 N 14.53 Found C 58.13 H 5.33 N 14.57

1-(Diphenylcarbamoyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**5e**): From **2e** (2.12 g, 10 mmol) in warm dichloromethane (75 ml) as described for **5b**; yield (without recrystallization) 3.00 g (93%) of a colourless powder; m.p. 240–242°C (dec.). – ^{13}C NMR ([D$_6$]DMSO): phenyl δ = 125.6, 126.6, 127.2, 128.8, 129.2, 129.4, 140.2, 141.0; C=O 146.7, 147.1 (2C), 147.8.

$C_{16}H_{12}N_4O_4$ (324.3) Calc. C 59.26 H 3.73 N 17.28 Found C 59.45 H 3.86 N 17.39

1-(4-Methylphenylsulfonyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**6a**): A solution of 4-toluenesulfonamide (1.71 g, 10 mmol) in dioxane (25 ml) was added dropwise to a solution of **1** (1.12 g, 10 mmol) in dioxane (25 ml). After 12 h the product was precipitated with pentane (50 ml) at 5°C; yield 2.40 g (85%) of a colourless powder; dec. above 228°C. – ^{1}H NMR ([D$_6$]DMSO): CH$_3$ δ = 2.43; NH 11.73. – ^{13}C NMR ([D$_6$]DMSO): CH$_3$ δ = 21.1; phenyl, C=O 128.2, 129.4, 135.4, 145.4, 146.0, 147.5.

$C_{10}H_9N_3O_5S$ (283.3) Calc. C 42.40 H 3.20 N 14.84 Found C 42.65 H 3.30 N 14.74

Butyl 5-(4-Nitrophenylsulfonyl)biuret-1-carboxylate (**7**): A suspension of 4-nitrobenzenesulfonamide (4.04 g, 20 mmol) in THF (50 ml) was added slowly to **1** (2.24 g, 20 mmol) in THF (30 ml). After 12 h at 22°C the solvent was evaporated. Crystallization of the residue from THF (10 ml)/petroleum ether (40 ml) afforded impure **6b** (2.59 g, 42%). – ^{13}C NMR

([D$_6$]DMSO): phenyl, C=O δ = 124.2, 129.8, 143.3, 146.0, 147.5, 150.7. – Recrystallization from boiling butanol (30 ml) gave yellow crystals of **7** (1.94 g, 25%); m.p. 175–177°C. – ^{1}H NMR ([D$_6$]acetone): CH_3 δ = 0.91 (t, J = 7 Hz); OCH_2 4.22 (t, J = 6 Hz); NH 10.07, 10.33, 11.19. – ^{13}C NMR ([D$_6$]acetone): CH_3 δ = 13.8; CH_2 19.4, 31.2, 67.7; phenyl, C=O 124.9, 130.8, 145.0, 148.3, 151.9, 153.2, 155.0.

$C_{13}H_{16}N_4O_8S$ (388.4) Calc. C 40.20 H 4.15 N 14.43 Found C 40.43 H 4.21 N 14.20

1,1,3-Trimethyltriuret (**8f**): To a suspension of **4f** (1.07 g, 5 mmol) in acetonitrile (10 ml) water (2 ml) was added dropwise (CO_2 evolution!). After 2 h at 22°C the solvent was evaporated. The residue crystallized from ethanol (5 ml) yielding colourless prisms (0.77 g, 82%, after work-up of the mother liquor); m.p. 128–130°C. – ^{1}H NMR ($CDCl_3$): CH_3 δ = 2.98, 3.12; NH 5.85, 8.00, 9.11. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 34.2, 37.8; C=O 153.9, 154.3, 158.7.

$C_6H_{12}N_4O_3$ (188.2) Calc. C 38.29 H 6.43 N 29.78 Found C 38.50 H 6.31 N 30.00

1,1-Diisopropyl-3-methyltriuret (**8g**): From **4g** (1.35 g, 5 mmol) as described for **8f**; yield after work-up of the mother liquor 1.09 g (89%) of colourless crystals; m.p. 133–136°C. – ^{1}H NMR ($CDCl_3$): CH_3 δ = 1.33 (d, J = 6 Hz), 3.07; CH 3.70 (sept, J = 7 Hz); NH 5.88, 8.05, 8.44. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 20.7, 33.8; CH 48.7; C=O 153.8, 154.4, 156.1.

$C_{10}H_{20}N_4O_3$ (244.3) Calc. C 49.16 H 8.25 N 22.94 Found C 49.02 H 8.23 N 23.12

1-Isopropyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**10h**): A solution of **2h** (3.56 g, 20 mmol) in dichloromethane (70 ml) was added dropwise at 0°C to **1** (2.24 g, 20 mmol) in ether (25 ml). After 12 h at 15°C the mixture was filtered*). Recrystallization of the residue from boiling ethanol (50 ml) afforded colourless leaflets (1.85 g, 54%, after work-up of the mother liquor); m.p. 256–258°C. – ^{1}H NMR ([D$_6$]DMSO): CH_3 δ = 1.34 (d, J = 7 Hz); CH 4.77 (sept. J = 7 Hz); NH 11.28. – ^{13}C NMR ([D$_6$]DMSO): CH_3 δ = 19.2; CH 44.9; C=O 148.4, 149.4 (2C).

$C_6H_9N_3O_3$ (171.2) Calc. C 42.10 H 5.30 N 24.56 Found C 42.15 H 5.29 N 24.58

1,11-Dimethylpentauret (**11i**): A solution of **1** (1.12 g, 10 mmol) in THF (25 ml) was added dropwise to **2i** (1.48 g, 20 mmol) in THF (25 ml). After 2 h at 22°C the mixture was filtered. The residue (2.53 g, 97%) was dissolved in hot formic acid (30 ml). Addition of water (50 ml) afforded a colourless powder (0.60 g, 23%); m.p. 224–226°C. – IR (KBr): 3330, 1755 (shoulder), 1690 cm^{-1}. – ^{1}H NMR ([D$_6$]DMSO): CH_3 δ = 2.71 (d, J = 4 Hz); NH 7.43 (q, J = 4 Hz), 9.82, 10.47. – ^{13}C NMR ([D$_6$]DMSO): CH_3 δ = 26.1; C=O 150.8, 151.1 (2C), 152.8 (2C).

$C_7H_{12}N_6O_5$ (260.2) Calc. C 32.31 H 4.65 N 32.30 Found C 32.51 H 4.58 N 32.00

1,11-Diethylpentauret (**11j**): From **2j** (1.76 g, 20 mmol) as described for **11i**. Recrystallization from hot acetic acid (100 ml) afforded a colourless powder (1.80 g, 62%); dec. above 209°C. – ^{1}H NMR ([D$_6$]DMSO): CH_3 δ = 1.08 (t, J = 7 Hz); CH_2 3.18 (m); NH 7.53 (t, J = 6 Hz), 9.70, 10.57. – ^{13}C NMR ([D$_6$]DMSO): CH_3 δ = 14.7; CH_2 34.2; C=O 150.8, 151.2 (2C), 152.2 (2C).

$C_9H_{16}N_6O_5$ (288.3) Calc. C 37.50 H 5.60 N 29.16 Found C 37.48 H 5.84 N 29.12

1,11-Di-tert-butylpentauret (**11k**): From **2k** (2.32 g, 20 mmol) as described for **11i**. After 12 h at 22°C the product was filtered off. Recrystallization from ethanol (100 ml) afforded

*) The IR spectrum of the filtrate showed a band at 2230 cm^{-1} (NCO). Addition of methanol (5 ml) afforded an oil (1.80 g, 60%) showing NMR spectra identical to those of authentic methyl *N*-phenylcarbamate.

colourless prisms (2.00 g, 58%); m.p. 210°C (dec.). – ^{1}H NMR ([D$_6$]DMSO/CDCl$_3$): CH$_3$ δ = 1.34; NH 7.46, 9.52, 10.54. – ^{13}C NMR ([D$_6$]DMSO): CH$_3$ δ = 28.4; C 50.3; C=O 150.8, 151.1, 151.5.

$C_{13}H_{24}N_6O_5$ (344.4) Calc. C 45.34 H 7.02 N 24.41 Found C 45.16 H 7.21 N 23.99

1,11-Diphenylpentauret (**11l**): From **2l** (2.72 g, 20 mmol) as described for **11i**. The solvent was evaporated under reduced pressure. Crystallization of the residue from boiling butanol (600 ml) afforded a colourless powder (2.68 g, 70%); dec. above 214°C. – ^{1}H NMR ([D$_6$]DMSO): NH δ = 9.65, 9.86, 10.65. – ^{13}C NMR ([D$_6$]DMSO): phenyl δ = 119.6; *i*-C 123.7, 128.8, *p*-C 137.2; C=O 150.2 (3C), 151.0 (2C).

$C_{17}H_{16}N_6O_5$ (384.4) Calc. C 53.12 H 4.20 N 21.87 Found C 53.13 H 3.98 N 21.60

1,3,9,11-Tetramethylpentauret (**11m**): From **2m** (1.76 g, 20 mmol) as described for **11i**, but in dichloromethane as solvent. After 12 h at 22°C the pure product was filtered off; yield 2.64 g (92%) of a colourless powder; m.p. 170–172°C. – ^{1}H NMR ([D$_6$]DMSO): CH$_3$ δ = 2.68 (d, *J* = 4 Hz), 3.12; NH 7.72 (q, *J* = 4 Hz), 12.21. – ^{13}C NMR ([D$_6$]DMSO): CH$_3$ δ = 27.2, 30.5; C=O 147.9, 151.6 (2C), 156.5 (2C).

$C_9H_{16}N_6O_5$ (288.3) Calc. C 37.50 H 5.60 N 29.16 Found C 37.48 H 5.84 N 29.12

1,1-Diisopropyl-3,9,11-trimethylpentauret (**12g**): A solution of **2g** (3.17 g, 20 mmol) in ether (25 ml) was added dropwise to **1** (2.24 g, 20 mmol) in ether (25 ml). After 6 h at 22°C a solution of **2m** (1.76 g, 20 mmol) in dichloromethane (25 ml) was added dropwise. The suspension was stirred for 12 h at 22°C and filtered. The residue was treated with boiling ethanol (225 ml). After filtration the product crystallized affording colourless needles (4.47 g, 62%); m.p. 161–162°C. – ^{1}H NMR (CDCl$_3$): CH$_3$ δ = 1.34 (d, *J* = 7 Hz), 2.87 (d, *J* = 5 Hz), 3.08, 3.32; NH 7.54, 9.72, 11.66. – ^{13}C NMR (CDCl$_3$): CH$_3$ δ = 20.6 (4C), 27.5, 30.4, 33.9; CH 48.7; C=O 148.3, 152.6, 153.1, 155.5, 155.8.

$C_{14}H_{26}N_6O_5$ (358.4) Calc. C 46.91 H 7.31 N 23.45 Found C 47.07 H 7.10 N 23.47

Carbonylbis(carbamoylchloride) (**13a**): Dry hydrogen chloride was passed (90 min) through a solution of **1** (11.21 g, 100 mmol) in dichloromethane (100 ml) cooled to –92°C. After 12 h at –92°C the suspension was warmed to 0°C. The solvent was evaporated under reduced pressure at 0°C leaving back a colourless moisture-sensitive powder (17.31 g, 94%), which gradually lost HCl at room temperature: dec. 85–88°C. – IR (CH$_2$Cl$_2$): 3350, 3290, 1825, 1755 cm^{-1}. – ^{1}H NMR (CD$_3$CN, 263 K): NH δ = 9.82. – ^{13}C NMR (CD$_3$CN, 263 K): NCN δ = 145.1; CCl 146.4. – MS: *m/z* = 184, 186.

Carbonylbis(carbamoylbromide) (**13b**): From hydrogen bromide as described for **13a**. The crude material was quickly dissolved in warm acetonitrile (12 ml). The solution was immediately cooled to –18°C. At this temperature large colourless prisms (16.56 g, 61%) crystallized; m.p. 115–116°C (dec.). At 22°C the crystals lost HBr. – IR (CH$_2$Cl$_2$): 3370, 3290, 1825, 1740 cm^{-1}. – ^{1}H NMR (CD$_3$CN, 263 K): NH δ = 9.75. – ^{13}C NMR (CD$_3$CN, 263 K): CBr δ = 136.4; NCN 143.7.

Carbonylbis(carbamoyliodide) (**13c**): From hydrogen iodide[28] as described for **13a**; yield 35.70 g (97%) of a very instable brown powder. – ^{1}H NMR (CD$_3$CN, 263 K): NH δ = 9.63. – ^{13}C NMR (CD$_3$CN, 263 K): CI δ = 115.7; NCN 142.4.

Diethyl Urea-1,3-dicarboxylate[29] (**14**): Ethanol (0.92 g, 20 mmol) in ether (25 ml) was added to a solution of **13a** (1.85 g, 10 mmol) in ether (25 ml). After 12 h the solvent was evaporated. The colourless residue (2.03 g, 99%) was identified as **14** by comparison of the IR and NMR spectra with those of authentic material[29].

1,1,7,7-Tetrabenzyltriuret[10] (**15**): A mixture of dibenzylamine (7.89 g, 40 mmol) and triethylamine (4.04 g, 40 mmol) in THF (50 ml) was added dropwise to a cold (0°C) solution of **13a** (3.70 g, 20 mmol) in THF (50 ml). After 3 h at 0°C the reaction mixture was filtered. The filtrate was evaporated under reduced pressure. The residue crystallized from boiling ethanol (50 ml) affording colourless prisms (5.25 g, 52%); m.p. 140–142°C (lit.[10] 145–146°C).

(Isocyanatocarbonyl)carbamic Trichloroacetic Anhydride (**16a**): A solution of trichloroacetic acid (1.63 g, 10 mmol) in ether (15 ml) was added dropwise to **1** (1.12 g, 10 mmol) in ether (10 ml). After 15 h at 22°C the spectra of the solution were recorded. – IR (ether): 2220 cm^{-1}. – ^{13}C NMR (ether, [D_6]acetone/TMS external): CCl_3 δ = 88.2; NCO 130.6; C=O 144.3, 147.6, 154.3. On attempts to remove the solvent the compound decomposed to give a colourless powder of unknown constitution. Addition of *tert*-butyl alcohol (0.74 g, 10 mmol) in ether (10 ml) to the solution of **16a** afforded after 12 h at 22°C a colourless precipitate (1.00 g, 77%) of **19**[30] (IR, NMR spectra). Distillation of the filtrate gave a colourless liquid (1.00 g, 46%), which by spectral comparison with authentic material[30] proved to be **18**; b.p. 60–62°C/12 torr.

N,N'-Carbonylbis(benzoic carbamic anhydride) (**17b**): A solution of **1** (1.12 g, 10 mmol) in dichloromethane (25 ml) was added dropwise at –80°C to a mixture of benzoic acid (2.44 g, 20 mmol) in dichloromethane (50 ml). After 6 h at –80°C and further 12 h at 22°C the precipitate was filtered off; yield 2.90 g (81%) of a colourless moisture-sensitive powder; dec. above 130°C. – ^{13}C NMR ([D_6]acetone/dioxane): CO δ = 150.0; 162.8 (2C), 167.5 (2C).

$C_{17}H_{12}N_2O_7$ (356.3) Calc. C 57.31 H 3.40 N 7.86 Found C 57.18 H 3.42 N 7.97

5-Cyclohexyl-6-cyclohexylamino-1,3,5-triazine-2,4(3H,5H)-dione (**22a**): A solution of trichloroacetic acid (4.09 g, 25 mmol) in ether (25 ml) was added dropwise to **1** (2.80 g, 25 mmol) in ether (25 ml). After 12 h at 22°C the mixture was filtered. At –78°C a solution of dicyclohexylcarbodiimide (5.16 g, 25 mmol) in ether (25 ml) was added dropwise to the filtrate. Within 12 h the reaction mixture was warmed up to 22°C. After evaporation of the solvent the residue was extracted with boiling acetonitrile (70 ml)/water (5 ml) for 30 min. Filtration of the extract, evaporation of the solvent, crystallization of the residue from ethanol (60 ml), and recrystallization from ethanol (40 ml) afforded a colourless powder (3.95 g, 54%); m.p. 248–251°C (dec.). – ^1H NMR ([D_6]DMSO): CH δ = 3.93 (m); NH 7.23 (d, J = 8 Hz), 10.53. – ^{13}C NMR ([D_6]DMSO): CH_2 δ = 24.6, 25.0, 25.2, 25.4, 28.6, 31.7; CH 51.0, 55.1; C=O, C=N 150.6, 154.3, 154.6.

$C_{15}H_{24}N_4O_2$ (292.4) Calc. C 61.62 H 8.27 N 19.17 Found C 61.33 H 8.54 N 19.09

5-Isopropyl-6-isopropylamino-1,3,5-triazine-2,4(3H,5H)-dione (**22b**): From diisopropylcarbodiimide (3.16 g, 25 mmol) as described for **22a**. Crystallization from acetonitrile (50 ml) at –18°C afforded colourless prisms (2.98 g, 56%); m.p. 274–277°C (dec.). – ^1H NMR ([D_6]DMSO): CH_3 δ = 1.18 (d, J = 7 Hz), 1.41 (d, J = 7 Hz); CH 4.21 (m), 4.45 (sept, J = 7 Hz); NH 7.27 (d, J = 7 Hz), 10.55. – ^{13}C NMR ([D_6]DMSO): CH_3 δ = 19.6, 21.7; CH 43.7, 47.0; C=O, C=N 150.5, 154.4, 154.5.

$C_9H_{16}N_4O_2$ (212.3) Calc. C 50.92 H 7.60 N 26.40 Found C 50.98 H 7.86 N 26.60

3-Pivaloyl-2H-1,3,5-oxadiazine-2,4,6(3H,5H)-trione (**24c**): At 0°C a solution of pivalic acid (5.11 g, 50 mmol) in ether (15 ml) was added dropwise to **1** (5.60 g, 50 mmol) in ether (15 ml). After 12 h at 0°C and 24 h at –80°C colourless prisms (2.18 g, 20%) were filtered off at 0°C. Work-up of the filtrate afforded further **24c** (7.73 g, 72%). At 22°C the compound lost

CO_2 giving **26c**. – ^{1}H NMR ([D$_8$]THF, 253 K): CH_3 δ = 1.30; NH 11.72. – ^{13}C NMR ([D$_8$]THF, 253 K): CH_3 δ = 26.9; 45.3; C=O 144.5, 144.6, 148.0, 179.3.

$C_8H_{10}N_2O_5$ (214.2) Calc. C 44.86 H 4.71 N 13.08 Found C 43.26 H 4.76 N 13.13

6-Phenyl-2H-1,3,5-oxadiazine-2,4(3H)-dione[26] (**26b**): A solution of **1** (1.12 g, 10 mmol) in dioxane (25 ml) was added dropwise to benzoic acid (2.44 g, 20 mmol) in dioxane (100 ml). After 12 h at 22°C the solution was evaporated to a volume of 30 ml. Petroleum ether (200 ml) was added. Within 4 d at 5°C a colourless powder (1.28 g, 67%) precipitated; dec. above 135°C. – ^{13}C NMR (dioxane/[D$_6$]acetone, TMS external): phenyl δ = 128.8, 129.2, 129.9, 134.9; OC=O 146.3; C=O 153.3; C=N 165.6.

$C_9H_6N_2O_3$ (190.2) Calc. C 56.85 H 3.18 N 14.73 Found C 56.67 H 3.13 N 14.77

6-tert-Butyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**26c**): Pivalic acid (5.11 g, 50 mmol) in ether (25 ml) was added dropwise to **1** (5.60 g, 50 mmol) in ether (25 ml). The mixture was boiled under reflux for 6 h. Evaporation of the solvent and crystallization of the residue from ether (10 ml) at −80°C (30 d) afforded colourless prisms (5.16 g, 61%); m.p. 108−110°C (dec.). – IR (CH_2Cl_2): 3345, 1795, 1735, 1630 cm^{-1}. – ^{1}H NMR (CD_3CN, 263 K): CH_3 δ = 1.29; NH 9.57. – ^{13}C NMR (CD_3CN, 263 K): CH_3 δ = 27.1; C 38.8; C=O 147.0, 154.3; C=N 179.2.

$C_7H_{10}N_2O_3$ (170.2) Calc. C 49.40 H 5.92 N 16.47 Found C 49.60 H 6.00 N 16.48

6-Methyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**26d**): A solution of **1** (3.36 g, 30 mmol) in ether (20 ml) was added dropwise to acetic acid (1.80 g, 30 mmol) in ether (20 ml). After 12 h at 22°C a colourless powder (2.10 g, 55%) was filtered off; dec. above 148°C. – ^{1}H NMR (CD_3CN): CH_3 δ = 2.30; NH 9.31. – ^{13}C NMR (CD_3CN): CH_3 δ = 21.4; OC=O 146.8; C=O 153.8; C=N 172.2.

$C_4H_4N_2O_3$ (128.1) Calc. C 37.50 H 3.15 N 21.87 Found C 37.15 H 3.08 N 21.82

6-Ethyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**26e**): From propanoic acid (1.85 g, 25 mmol) as described for **26d**; yield 3.21 g (90%) of a colourless powder; dec. above 118°C. – ^{1}H NMR (CD_3CN, 263 K): CH_3 δ = 1.19 (t, J = 7 Hz); CH_2 2.62 (q, J = 7 Hz); NH 9.57. – ^{13}C NMR (CD_3CN, 263 K): CH_3 δ = 9.4; CH_2 28.2; OC=O 146.9; C=O 154.1; C=N 175.4.

$C_5H_6N_2O_3$ (142.1) Calc. C 42.25 H 4.26 N 19.72 Found C 42.11 H 4.20 N 19.80

6-Isopropyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**26f**): From 2-methylpropanoic acid (4.41 g, 50 mmol) as described for **26d**; yield 5.12 g (66%) of colourless moisture-sensitive crystals; dec. above 95°C. – ^{1}H NMR (CD_3CN): CH_3 δ = 19.1; CH 34.5; OC=O 146.7; C=O 154.1; C=N 178.0.

$C_6H_8N_2O_3$ (156.1) Calc. C 46.15 H 5.16 N 17.95 Found C 45.57 H 5.19 N 18.03

6-Benzyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**26g**): From phenylacetic acid (3.40 g, 25 mmol) as described for **26d**; yield 3.83 g (75%) of a colourless moisture-sensitive powder; dec. above 123°C. – ^{1}H NMR (CD_3CN, 263 K): CH_2 δ = 3.91; NH 9.59. – ^{13}C NMR (CD_3CN, 263 K): CH_2 δ = 41.0; phenyl 128.5, 129.6, 130.7, 133.6; OC=O 146.7; C=O 153.8; C=N 172.8.

$C_{10}H_8N_2O_3$ (204.2) Calc. C 58.82 H 3.95 N 13.72 Found C 58.87 H 3.93 N 13.76

N-Pivaloylurea[31] (**30c**): A solution of **26c** (1.70 g, 10 mmol) in acetonitrile (10 ml) and water (2 ml) was stirred for 12 h. Evaporation of the solvent and crystallization of the residue from water (17 ml) afforded colourless crystals (1.05 g, 73%); m.p. 145−147°C (lit.[31] 147−148°C). – ^{13}C NMR ([D$_5$]pyridine): CH_3 δ = 26.8; C 40.1; C=O 156.1, 180.6.

N-(Phenylacetyl)urea (**30g**): From **26g** (2.04 g, 10 mmol) as described for **30c**; yield 1.43 g (80%) of colourless crystals; m.p. 210–212°C. – ^{13}C NMR ([D$_6$]DMSO): CH_2 δ = 42.5; C=O 153.6, 172.4.

$C_9H_{10}N_2O_2$ (178.2) Calc. C 60.66 H 5.66 N 15.72 Found C 60.41 H 5.52 N 15.60

N-(2-Phenylbutyryl)urea (**30h**): A solution of 2-phenylbutanoic acid (1.64 g, 10 mmol) in ether (10 ml) was added dropwise to **1** (1.12 g, 10 mmol) in ether (25 ml). After 24 h at 22°C water (2 ml) was added. After 1 h at 22°C the solvent was evaporated. Crystallization of the residue from ethanol (20 ml) afforded colourless prisms (1.33 g, 64%); m.p. 146–148°C (lit.[32] 147°C). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 12.0; CH_2 26.1; CH 55.2; C=O 155.4, 175.3.

Methyl 4-Benzoylallophanate[33] (**31b**): A mixture of **26b** (1.90 g, 10 mmol) in methanol (50 ml) was boiled under reflux for 15 min. From the filtered solution colourless prisms (1.93 g, 87%, after work-up of the mother liquor) crystallized; m.p. 170–172°C (lit.[33] 169–172°C). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 53.3; C=O 149.5, 152.1, 167.1.

Benzyl 4-Pivaloylallophanate (**31c**): A mixture of **26c** (2.55 g, 15 mmol) and benzyl alcohol (1.62 g, 15 mmol) in ether (50 ml) was stirred for 12 h at 22°C. Evaporation of the solvent and crystallization of the residue from ethanol (10 ml)/water (10 ml) afforded colourless prisms (2.68 g, 64%); m.p. 98–99°C (dec.). – ^{1}H NMR ($CDCl_3$): CH_3 δ = 1.23; CH_2 5.20; NH 9.27, 10.58. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 26.8; C 40.4; CH_2 67.9; C=O 149.3, 151.1, 179.7.

$C_{14}H_{18}N_2O_4$ (278.3) Calc. C 60.42 H 6.52 N 10.07 Found C 60.41 H 6.61 N 9.88

1,1-Dibenzyl-5-benzoylbiuret (**32b**): A mixture of **26b** (4.75 g, 25 mmol) and dibenzylamine (4.93 g, 25 mmol) in THF (150 ml) was stirred for 5 h at 22°C and then refluxed for 1 h. The solvent was evaporated. The residue was dissolved in boiling ethanol (110 ml). After filtration the product crystallized at –20°C affording colourless prisms (8.75 g, 90%); m.p. 148–150°C. – ^{1}H NMR ($CDCl_3$): CH_2 δ = 4.60; NH 9.80, 11.60. – ^{13}C NMR ($CDCl_3$): CH_2 δ = 49.9; C=O 150.4, 153.9, 166.2.

$C_{23}H_{21}N_3O_3$ (387.4) Calc. C 71.30 H 5.46 N 10.85 Found C 71.43 H 5.27 N 10.84

1,1-Dibenzyl-5-pivaloylbiuret (**32c**): A mixture of **26c** (5.11 g, 30 mmol) and dibenzylamine (5.92 g, 30 mmol) in ether (50 ml) was stirred for 12 h at 22°C. Evaporation of the solvent and crystallization of the residue from ethanol (100 ml) afforded a colourless powder (5.60 g, 51%, after work-up of the mother liquor); m.p. 162–164°C (dec.). – ^{1}H NMR ([D$_6$]DMSO): CH_3 δ = 1.15; CH_2 4.54; NH 10.41, 11.26. – ^{13}C NMR ([D$_6$]DMSO): CH_3 δ = 26.4; CH_2 39.8; C 49.5; C=O 149.5, 153.8, 178.3.

$C_{21}H_{25}N_3O_3$ (367.4) Calc. C 68.64 H 6.86 N 11.44 Found C 68.61 H 7.02 N 11.54

1-Benzyl-5-phenacetylbiuret (**32g**): A mixture of **26g** (2.04 g, 10 mmol) and benzylamine (1.07 g, 10 mmol) in acetonitrile (50 ml) was stirred for 12 h at 22°C. Evaporation of the solvent and crystallization of the residue from ethanol (180 ml) afforded a colourless powder (1.83 g, 59%, after work-up of the mother liquor); m.p. 198–200°C (dec.). – ^{1}H NMR ([D$_6$]DMSO): CH_2 δ = 3.76, 4.40 (d, J = 6 Hz); NH 8.43 (t, J = 6 Hz), 10.25, 11.22. – ^{13}C NMR ([D$_6$]DMSO): CH_2 δ = 42.6, 42.9; C=O 151.9, 152.1, 173.7.

$C_{17}H_{17}N_3O_3$ (311.3) Calc. C 65.58 H 5.50 N 13.50 Found C 65.42 H 5.38 N 13.49

7-Isobutyryl-1,1-diisopropyl-3-methyltriuret (**33f**): A mixture of **26f** (3.12 g, 20 mmol) and **2g** (3.17 g, 20 mmol) in ether (50 ml) was boiled under reflux for 5 h. The solvent was evaporated. The oily residue crystallized on rubbing in ether (25 ml) affording a colourless powder (4.61 g, 73%); m.p. 125–126°C (dec.). – ^{1}H NMR ($CDCl_3$): CH_3 δ = 1.20 (d, J = 7 Hz), 1.34 (d, J = 7 Hz), 3.08; CH 2.76 (sept, J = 7 Hz), 3.71 (sept, J = 7 Hz, 2H); NH

9.97 (2H). – ^{13}C NMR ($CDCl_3$): CH_3, CH δ = 18.7, 20.6, 33.7, 36.2, 48.7; C=O 149.2, 152.1, 155.3, 177.5.

$C_{14}H_{26}N_4O_4$ (314.4) Calc. C 53.48 H 8.34 N 17.83 Found C 53.77 H 8.50 N 17.95

3-Acetyl-6-phenyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**34b**): To a mixture of **26b** (3.80 g, 20 mmol) and acetyl chloride (1.97 g, 25 mmol) in dioxane (50 ml) was added dropwise a solution of triethylamine (2.02 g, 20 mmol) in dioxane (10 ml). After 2 h at 22°C the mixture was filtered and the filtrate was evaporated under reduced pressure. The residue crystallized from acetonitrile (30 ml) affording pale yellow moisture-sensitive crystals (2.35 g, 51%, after work-up of the mother liquor); m.p. 147–149°C (dec.). – ^{1}H NMR ([D_6]acetone): CH_3 δ = 2.64. – ^{13}C NMR ([D_6]acetone): CH_3 δ = 26.7; C=O 144.8, 152.0, 171.3; C=N 165.7.

$C_{11}H_8N_2O_4$ (232.2) Calc. C 56.90 H 3.47 N 12.07 Found C 56.67 H 3.73 N 11.96

3-Acetyl-6-tert-butyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**34c**): To a mixture of **26c** (3.40 g, 20 mmol) and acetyl chloride (1.57 g, 20 mmol) in THF (25 ml) was added dropwise at −78°C a solution of triethylamine (2.02 g, 20 mmol) in THF (25 ml). The mixture was warmed up to 10°C within 10 h. Evaporation of the solvent (below 20°C), crystallization of the residue from ether (50 ml)/pentane (100 ml) at −80°C, and recrystallization from ether (60 ml) at −80°C afforded colourless prisms (2.40 g, 57%); m.p. 71–73°C (dec.). – ^{1}H NMR ($CDCl_3$, 263 K): CH_3 δ = 1.38, 2.65. – ^{13}C NMR ($CDCl_3$, 263 K): CH_3 δ = 26.8 (3C), 27.0; C 38.5; C=O 143.6, 150.7, 169.7; C=N 178.2.

$C_9H_{12}N_2O_4$ (212.2) Calc. C 50.94 H 5.70 N 13.20 Found C 50.74 H 5.45 N 13.45

3-Acetyl-6-isopropyl-2H-1,3,5-oxadiazine-2,4(3H)-dione (**34f**): From **26f** (3.12 g, 20 mmol) as described for **34c**. The crude product was dissolved in ether (75 ml). The solution was filtered after addition of charcoal. Evaporation of the solvent and crystallization of the residue from ether (10 ml) at −18°C afforded colourless temperature-sensitive needles (2.30 g, 58%); m.p. 53–55°C. – ^{1}H NMR ($CDCl_3$, 263 K): CH_3 δ = 1.36 (d, J = 7 Hz), 2.66; CH 2.90 (sept, J = 7 Hz). – ^{13}C NMR ($CDCl_3$, 263 K): CH_3 δ = 18.8 (2C), 27.0; C 33.9; C=O 143.5, 150.6, 169.5; C=N 176.6.

$C_8H_{10}N_2O_4$ (198.2) Calc. C 48.48 H 5.09 N 14.14 Found C 48.24 H 4.84 N 14.22

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