Chem. Ber. **119**, 1133–1143 (1986)

Cycloadditions of Carbonyl Diisocyanate

Bernhard Akteries and *Johannes C. Jochims**

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

Received September 2, 1985

Carbonyl diisocyanate (**1**) undergoes twofold Diels-Alder type cycloadditions with many compounds containing multiple bonds to give heteronaphthalenes **2**. Cycloadditions of **1** with azomethines (affording **4**), isocyanates (giving **6**), dimethylcyanamide (leading to **9**), and aliphatic carbodiimides (formation of **12**) are described. With aromatic carbodiimides 1:1 cycloadducts are obtained, for which constitutions **15** may be proposed considering the structures of several degradation products (**16**–**19**). A cycloaddition of carbonyl chloride isocyanate to the carbodiimide **18** with formation of triazinetrione **17b** is described.

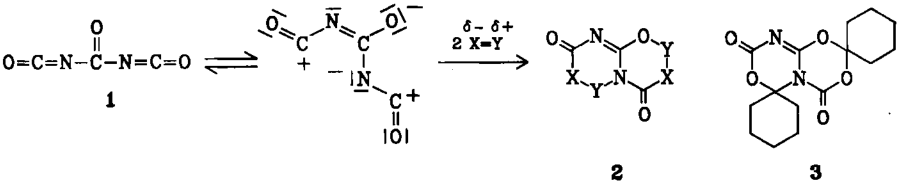
Cycloadditionen von Carbonyldiisocyanat

Carbonyldiisocyanat (**1**) geht mit vielen Verbindungen, die Mehrfachbindungen enthalten, zweifache Cycloaddition vom Diels-Alder-Typ ein, wobei Heteronaphthaline **2** gebildet werden. Cycloadditionen von **1** mit Azomethinen (zu **4**), Isocyanaten (zu **6**), Dimethylcyanamid (zu **9**) und aliphatischen Carbodiimiden (Bildung von **12**) werden beschrieben. Mit aromatischen Carbodiimiden erhält man 1:1-Addukte, für die auf Grund der Strukturen mehrerer Abbauprodukte (**16**–**19**) die Konstitutionen **15** vorgeschlagen werden. Es wird eine Cycloaddition von Carbonylchloridisocyanat mit dem Carbodiimid **18** unter Bildung des Triazintrions **17b** beschrieben.

Only a few reports on the chemistry of the carbonyl pseudohalide carbonyl diisocyanate (**1**) can be found in the literature[1]. The compound has first been prepared by *Nachbaur*[2] who also described reactions of **1** with water, ammonia, and ethanol. Other syntheses of **1**[3–10], its cycloaddition to cyclohexanone[11] and a redistribution reaction with phosgene[7] are known. Further reactions are mentioned in a book[12]. In connection with our interest in the chemistry of carbonyl pseudohalides[13–17] we recently reported on additions of nucleophiles to the extremely reactive **1**[10,18]. In this communication certain cycloadditions of **1** will be described.

Similar to other acyl isocyanates[19–23] carbonyl diisocyanate (**1**) undergoes Diels-Alder type cycloadditions with many compounds containing multiple bonds X=Y according to Scheme 1.

Scheme 1



0009–2940/86/0404–1133 $ 02.50/0

Table 1. Selected ^{13}C NMR data for compounds **3**–**19**

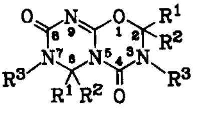
Comp.	Chemical Shifts[a] C=O and Ring Carbons	Other Carbons
3[11]	142.7, 150.6, 155.3, 95.8, 107.3	
4a[b]	147.9/149.6, 153.2/153.9, 155.7/156.1, 69.1/69.3, 87.5/87.6	CH_3 31.3, 32.8, 33.2, 33.6
4b[c]	148.1, 152.9, 156.2, 64.3, 84.5	CH_3 28.4, 29.0, C 57.5, 59.0
4c[c]	148.2, 152.9, 155.4, 64.3, 83.3	CH_3 19.8, 20.4, 20.7, 21.3, CH 47.7, 48.3
4d[b]	148.1, 152.7, 155.7, 63.7, 83.1	CH 54.8, 55.2
4e[c]	147.2, 153.1, 154.7, 70.1, 88.5	
5[d]	73.9, C=O 150.2, 150.4, 151.7	CH_3 20.8, 21.6, 25.0, CH 42.4, 46.3
6a[b]	140.5, 141.5, 143.7, 150.8, 151.9	CH_3 18.7, 18.8, CH 49.0, 50.9
6b[c]	140.7, 141.5, 143.9, 150.7, 151.9	CH_2 29.9, 25.2, 26.1, 26.2, 28.4, 28.6, CH 57.3, 59.0
6c[e]	143.3, 144.1, 145.9, 151.6, 153.3	CH_3 28.1, 28.4, CH_2 34.3, 34.5, C 53.4, 55.6
6d[f]	142.4, 143.1, 145.0, 151.6, 152.1, C=O 166.6, 167.4	CH_3 14.3, 14.4, CH_2 44.2, 45.5, 62.3, 62.7
6e[f]	142.9, 143.6, 145.3, 152.2 (2C)	CH_2 46.7, 48.5
7b[c]	151.1[g], 155.5[g], 158.6	CH_3 14.1, CH_2 25.3, 26.3 (2C), 28.7 (2C), OCH_2 65.7, CH 55.0
7f[d]	153.0[g] (2C), 159.6	CH_3 13.8, 27.4, CH_2 64.5
7g[d]	152.5[g] (2C), 159.9	CH_3 13.9, CH_2 64.7, *i,p*-C 127.8, 135.2, *o,m*-C 128.5, 128.6
9[h]	145.2, 148.9, 153.5, 156.8, 161.0	CH_3 36.9, 37.3, 37.4, 38.2
10[d]	153.2[g] (2C), 155.7	CH_3 37.1
11[c]	160.0, 163.7[g], 164.2[g]	CH_3 14.2, 37.2, CH_2 64.1
12a[c]	123.0, 131.0, 145.1, 150.6, 154.3	CH_3 29.6 (3C), 30.2 (3C), 31.4, 32.4, C 54.8, 56.5
12b[c]	127.1, 131.9, 143.3, 150.6, 153.4	CH_3 19.2, 23.4, 23.7, CH 47.6, 49.5, 50.6, 51.2
12c[c]	127.0, 131.9, 143.5, 150.6, 153.6	CH 54.9, 57.9, 58.1, 59.1
12d[c]	129.5, 133.1, 143.0, 150.0, 153.2	
14[c]	154.1, 155.9, 157.3, 161.3, 168.5	CH_3 14.1, 19.5, 20.8, 21.0, 22.8, CH_2 64.7, CH 42.8, 51.9, 52.4, 53.8
16a[d]	148.3, 148.2, 147.6	*i,p*-C 134.2, 129.2, *o,m*-C 129.7, 129.5, CH_3 19.0, CH 46.8
16c[e]	C=O, C=N, *p*-C 149.3, 150.8, 150.9	CH_3 24.2, CH 34.6, *o,m*-C 128.5, 130.3, *i*-C 134.0
17a[d]	148.4, 148.5, 149.4	CH_3 19.2, CH 46.1, *i,p*-C 134.5, 128.2, *o,m*-C 128.3, 134.5
17b[d]	148.7 (2C), 149.9	CH_3 55.3, *p*-CO 158.9, *i*-C 127.0, *m*-C 113.9, *o*-C 129.8
19a[c]	139.6, 147.7, 148.1, 156.2	CH_3 13.8, 19.3, CH 49.9, OCH_2 61.8, *i,p*-C 129.6, 132.9, *o,m*-C 128.8, 130.2
19b[d]	141.1, 148.4 (2C), 155.4	CH_3 13.4, 55.3, CH_2 18.5, 29.7, 64.6, *p*-CO 159.1, *m*-C 113.7, *i*-C 127.2, *o*-C 130.8

[a] Internal standard TMS; δ-scale. – [b] In $CDCl_3$ at 263 K. – [c] In $CDCl_3$ at 300 K. – [d] In CD_3SOCD_3 at 300 K. – [e] In CD_3CN at 300 K. – [f] In CD_3COCD_3 at 323 K. – [g] Signal broad. – [h] In CD_2Cl_2 at 300 K. – [i] In CD_3CN/CF_3COOD at 300 K.

Thus, cycloaddition of **1** to cyclohexanone gives the dispiro heterocycle **3**[11].

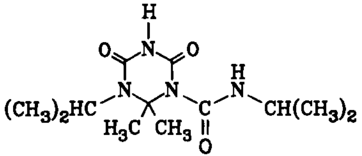
While we were able to reproduce this reaction we obtained only mixtures of compounds with a number of other aldehydes and ketones.

Azomethines $R^1R^2C=NR^3$ add to **1** to give the heterocycles **4**. No reaction was observed with *N*-(diphenylmethylene)aniline ($R^1 = R^2 = R^3 = C_6H_5$).



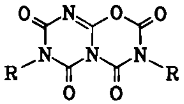
4a – e

4	R^1	R^2	R^3
a	H	C_6H_5	CH_3
b	H	C_6H_5	$C(CH_3)_3$
c	H	C_6H_5	$CH(CH_3)_2$
d	H	C_6H_5	$c-C_6H_{11}$
e	H	C_6H_5	C_6H_5
f	CH_3	CH_3	$CH(CH_3)_2$

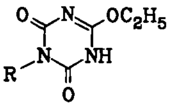


5

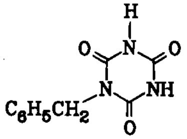
The constitutions of **4** were mainly derived from the ^{13}C NMR spectra (Table 1), which show three signals for $C=O$ and $C=N$ carbons, thus excluding symmetrical structures. For **4a** an almost equimolecular mixture of the diastereomers was obtained. For **4b – e** single stereoisomers of unknown configurations were isolated in each case. Compounds **4a, e** slowly



6a – e

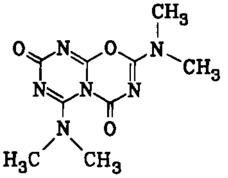


7b, f, g

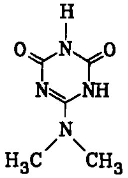


8

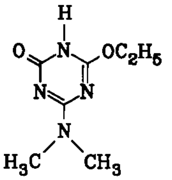
6, 7	R
a	$CH(CH_3)_2$
b	$c-C_6H_{11}$
c	$CH_2C(CH_3)_3$
d	$CH_2CO_2C_2H_5$
e	$CH_2C_6H_5$
f	CH_3
g	C_6H_5



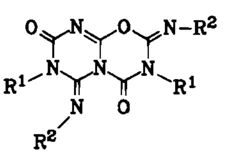
9



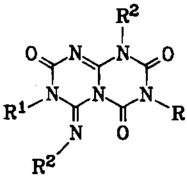
10



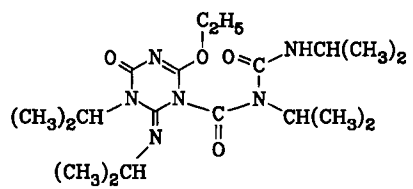
11



12a – d



13



14

12	R^1	R^2
a	CH_3	$C(CH_3)_3$
b	$CH(CH_3)_2$	$CH(CH_3)_2$
c	$c-C_6H_{11}$	$c-C_6H_{11}$
d	$CH(C_6H_5)_2$	$CH(C_6H_5)_2$

decompose in solution. No ^{13}C NMR spectra could be obtained from the rather unstable **4f**. With water **4f** was hydrolyzed to **5**.

In boiling toluene carbonyl diisocyanate (**1**) adds aliphatic and aromatic isocyanates to give the heterocycles **6**[12]. No reaction occurred with *tert*-butyl isocyanate. Solvolysis of **6** in boiling ethanol afforded the triaza heterocycles **7**, while stirring a solution of **6e** in acetone/water gave compound **8**[10] together with 1,3-dibenzylurea.

Table 2. Selected ^1H NMR data of compounds **4**−**19**

Comp.	Chemical Shifts[a]
4a[b]	CH_3 2.66, 2.87, 3.00, 3.21, NCH 6.07, 6.23, 6.52, 6.72
4b[c]	CH_3 1.38, 1.59, CH 6.47
4c[c]	CH_3 0.85 (d, J = 7 Hz), 1.17 (d, J = 7 Hz), 1.25 (d, J = 7 Hz), 1.39 (d, J = 7 Hz), CH 4.50 (sept, J = 7 Hz), 4.64 (sept, J = 7 Hz), 6.23, 6.68
4d[b]	CH 4.25 (m), 4.30 (m), 6.28, 6.72
4e[c]	NCH 6.65
5[d]	CH_3 1.07 (d, J = 7 Hz), 1.34 (d, J = 7 Hz), 1.58, CH 3.74 (sept, J = 7 Hz), 3.78[g]
6a[b]	CH_3 1.44 (d, J = 7 Hz), 1.51 (d, J = 7 Hz), CH 4.93[g] (2H)
6b[c]	CH 4.53[g] (2H)
6c[b]	CH_3 0.94, 0.98, CH_2 3.78, 3.80
6d[f]	CH_3 1.26 (t, J = 7 Hz), 1.27 (t, J = 7 Hz), CH_2 4.21 (q, J = 7 Hz), 4.25 (q, J = 7 Hz), 4.62, 4.70
6e[f]	CH_2 5.04, 5.08
7b[c]	CH_3 1.39 (t, J = 7 Hz), CH_2 4.50 (q, J = 7 Hz), CH 4.61 (m), NH ca. 9.9
7f[d]	CH_3 1.30 (t, J = 7 Hz), 3.10, CH_2 4.36 (q, J = 7 Hz), NH 12.40
7g[d]	CH_3 1.32 (t, J = 7 Hz), CH_2 4.41 (q, J = 7 Hz), NH 12.55
9[h]	CH_3 3.17, 3.18, 3.19, 3.20
10[d]	CH_3 3.03, NH 10.49, 10.87
11[c]	CH_3 1.38 (t, J = 7 Hz), 3.20, CH_2 4.43 (q, J = 7 Hz)
12a[c]	CH_3 1.29 (9H), 1.35 (9H), 3.24, 3.33
12b[c]	CH_3 1.18 (d, J = 7 Hz, 12H), 1.47 (d, J = 7 Hz), 1.48 (d, J = 7 Hz), CH 3.34 (sept, J = 7 Hz), 4.08 (sept, J = 7 Hz), 4.78 (sept, J = 7 Hz), 4.81 (sept, J = 7 Hz)
12d[c]	CH 5.12, 5.90
14[c]	CH_3 1.20 (d, J = 7 Hz), 1.33 (d, J = 7 Hz), 1.40 (d, J = 7 Hz), 1.40 (t?), 1.56 (d, J = 7 Hz), CH_2 4.43 (q, J = 7 Hz), CH 3.96 (m), 4.11 (sept, J = 7 Hz), 4.25 (sept, J = 7 Hz), 4.67 (sept, J = 7 Hz), NH 6.44 (d, J = 7 Hz)
15c[i]	CH_3 1.30 (d, J = 7 Hz), CH 3.07 (sept, J = 7 Hz), Ph 7.43 (d, J = 8 Hz), 7.56 (d, J = 8 Hz)
16a[d]	CH_3 1.42 (d, J = 7 Hz), CH 5.16[g], NH 5.67, 11.26
16c[e]	CH_3 1.26 (d, J = 7 Hz), 3.01 (sept, J = 7 Hz)
17a[d]	CH_3 1.38 (d, J = 7 Hz), CH 4.84 (sept, J = 7 Hz), NH 11.72
17b[d]	CH_3 3.77, NH 11.91
19a[c]	CH_3 1.02 (t, J = 7 Hz), 1.49 (d, J = 7 Hz), CH_2 3.39 (q, J = 7 Hz), CH 5.12 (sept, J = 7 Hz), NH 9.61
19b[d]	CH_3 0.79 (t, J = 6.5 Hz), 3.77, CH_2 1.15 (m, 4H), 3.13 (t, J = 6.5 Hz), NH 11.89

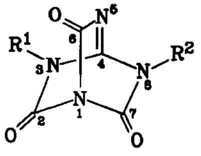
a)−i) see Table 1.

Carbonyl diisocyanate reacts with dimethylcyanamide to give **9**. With other dialkylcyanamides mixtures of compounds were obtained. In agreement with the proposed structure hydrolysis of **9** leads to **10** and ethanolysis to **11**. In the NMR spectra of **9** four signals for the methyl groups are observed indicating hindered rotation around the sp^3-C−N bonds.

Even at −80°C vigorous reactions take place between **1** and enamines yielding mixtures of strongly smelling compounds.

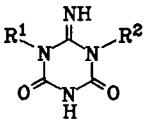
Finally, the reactions of **1** with carbodiimides were studied. With aliphatic carbodiimides stable double cycloaddition products were obtained, for which constitutions **12** or **13** may be discussed. With the unsymmetrical *tert*-butylmethylcarbodiimide only one compound **12a** (or **13a**) was obtained, the ^{13}C NMR shifts (Table 1) of which are similar to those of **12** (or **13**) **b**−**d**. This fact, together with the experience that *N*-*tert*-butyl-substituted *s*-triazines are not formed easily seem to speak against constitutions **13**. Under comparable conditions di-*tert*-butylcarbodiimide does not react with **1**. The oxadiazine ring of **12b** is quickly opened by ethanol affording **14**.

The reaction of **1** with aromatic or aliphatic-aromatic carbodiimides takes a different course. Here 1:1 adducts **15a**−**c** were obtained. These products are of low solubility in most organic solvents. Attempted recrystallizations of the moisture sensitive powders led to decomposition. Therefore, correct elemental analyses

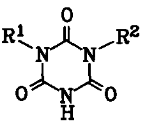


15a−c

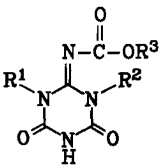
15−19	R^1	R^2
a	$CH(CH_3)_2$	C_6H_5
b	$C_6H_4OCH_3$−(4)	$C_6H_4OCH_3$−(4)
c	$C_6H_4CH(CH_3)_2$−(4)	$C_6H_4CH(CH_3)_2$−(4)



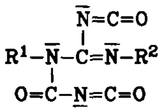
16a, c



17a, b

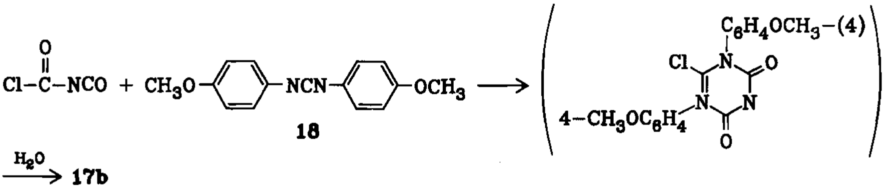


19a: R^3 = C_2H_5
b: R^3 = n-C_4H_9



$$R^1-\overline{N}-\underset{\underset{O=C-\underline{N}=C=O}{|}}{\overset{\overset{\overline{N}=C=O}{|}}{C}}=\overline{N}-R^2$$

20



could not be obtained. Our structural proposal **15** is based on the symmetry of the ^1H NMR spectrum of **15c** (Table 2) in trifluoroacetic acid/acetonitrile.

In the mass spectra of **15a, b** strong molecular peaks were observed. Other prominent peaks can be assigned to the loss of NCO, R^1NCO, and R^2NCO. Hydrolysis of **15a, c** under mild conditions gave **16a, c**, while in boiling 2 M HCl **17a, b** were obtained from **15a, b**. Compound **17b** was prepared by an independent synthesis from carbonyl chloride isocyanate and the carbodiimide **18**. In boiling alcohols **15a, b** were transformed into the esters **19a, b**.

It seems likely, that the first step of the formation of **15** consists in an addition of **1** to the carbodiimides giving **20**, similar to the reaction of other acyl chlorides with carbodiimides[24]. Further work is in progress to confirm the structures of **15**.

We would like to thank Mr. *S. Herzberger* for technical assistance.

Experimental Part

IR spectra (KBr): Perkin-Elmer IR 299. – NMR spectra: Bruker WM-250, Jeol FX 90; δ-scale; internal reference tetramethylsilane. – Mass spectra: Varian MAT 312 and 112 S. – All reactions were carried out with exclusion of moisture in absolute solvents. – Petroleum ether: b.p. 50–70°C. – Melting points: uncorrected.

2,3,6,7-Tetrahydro-cis,trans-3,7-dimethyl-2,6-diphenyl-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**4a**): A solution of **1** (1.12 g, 10 mmol) in ether (20 ml) was added dropwise at −78°C to a solution of benzylidenemethylamine (2.38 g, 20 mmol) in ether (30 ml). The reaction mixture was warmed up to +22°C within 12 h. Slow addition of pentane (50 ml) and shaking for 30 min afforded a colourless, in solution unstable, moisture sensitive precipitate (2.76 g, 79%); dec. above 103°C. – IR: 1740, 1680, 1610 cm^{-1}.

$C_{19}H_{18}N_4O_3$ (350.4) Calcd. C 65.13 H 5.18 N 15.99 Found C 64.93 H 5.14 N 15.85

3,7-Di-tert-butyl-2,3,6,7-tetrahydro-2,6-diphenyl-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**4b**): From benzylidene-*tert*-butylamine (3.22 g, 20 mmol) as described for **4a**. The product crystallized at −80°C from the ethereal reaction mixture without addition of pentane affording a colourless moisture sensitive powder (3.49 g, 80%); m.p. 149–151°C (dec.).

$C_{25}H_{30}N_4O_3$ (434.5) Calcd. C 69.10 H 6.96 N 12.90 Found C 68.80 H 6.72 N 12.89

2,3,6,7-Tetrahydro-3,7-diisopropyl-2,6-diphenyl-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**4c**): From benzylideneisopropylamine (2.94 g, 20 mmol) as described for **4a**. Yield 2.80 g (69%) of a colourless moisture sensitive, in solution unstable powder; dec. above 108°C.

$C_{23}H_{26}N_4O_3$ (406.5) Calcd. C 67.96 H 6.45 N 13.79 Found C 67.87 H 6.36 N 13.82

3,7-Dicyclohexyl-2,3,6,7-tetrahydro-2,6-diphenyl-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**4d**): From benzylidenecyclohexylamine (3.77 g, 20 mmol) as described for **4b**. Yield 4.11 g (85%) of a moisture sensitive powder; m.p. 163–165°C (dec.).

$C_{29}H_{34}N_4O_3$ (486.6) Calcd. C 71.58 H 7.04 N 11.52 Found C 71.38 H 7.09 N 11.54

2,3,6,7-Tetrahydro-2,3,6,7-tetraphenyl-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**4e**): From benzylideneaniline (3.62 g, 20 mmol) as described for **4a**. Yield 4.52 g (95%) of a colourless moisture sensitive, in solution unstable powder; dec. above 94°C.

$C_{29}H_{22}N_4O_3$ (474.5) Calcd. C 73.40 H 4.67 N 11.81 Found C 72.81 H 4.77 N 11.60

Hexahydro-N,3-diisopropyl-2,2-dimethyl-4,6-dioxo-1,3,5-triazine-1-carboxamide (**5**): From isopropylideneisopropylamine[25] (1.98 g, 20 mmol) as described for **4a**. The very moisture sensitive product (**4f**) was precipitated from the ethereal reaction mixture with hexane (150 ml). Filtration afforded a colourless powder, which was immediately dissolved in acetonitrile (30 ml) containing water (2 ml). After 12 h the solvent was removed under reduced pressure. Crystallization of the residue from ethanol (25 ml) afforded a colourless powder (0.50 g, 19%, after work-up of the mother liquor); m.p. 251 – 253 °C (dec.).

$C_{12}H_{22}N_4O_3$ (270.3) Calcd. C 53.31 H 8.20 N 20.73 Found C 53.31 H 8.37 N 20.44

3,7-Diisopropyl-2H,6H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-2,4,6,8(3H,7H)-tetrone (**6a**): A mixture of isopropyl isocyanate (3.40 g, 40 mmol) and **1** (2.24 g, 20 mmol) in toluene (20 ml) was boiled under reflux for 12 h. To the cooled solution pentane (100 ml) was added. The precipitate was filtered off and dissolved in dichloromethane (50 ml). The solution was filtered after addition of charcoal. Evaporation of the solvent under reduced pressure afforded a colourless moisture sensitive powder (3.45 g, 61%); m.p. 205 – 207 °C (dec.). – IR: 1830 (sh), 1790, 1740, 1700, 1650 cm^{-1}.

$C_{11}H_{14}N_4O_5$ (282.3) Calcd. C 46.80 H 5.00 N 19.85 Found C 46.55 H 4.83 N 19.73

3,7-Dicyclohexyl-2H,6H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-2,4,6,8(3H,7H)-tetrone (**6b**): From cyclohexyl isocyanate (5.00 g, 40 mmol) as described for **6a**. Yield 4.20 g (58%) of a colourless powder; m.p. 208 – 210 °C (dec.).

$C_{17}H_{22}N_4O_5$ (362.4) Calcd. C 56.34 H 6.12 N 15.46 Found C 55.97 H 6.31 N 15.05

3,7-Bis(2,2-dimethylpropyl)-2H,6H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-2,4,6,8(3H,7H)-tetrone (**6c**): From neopentyl isocyanate (4.52 g, 40 mmol) as described for **6a**. The product crystallized from the toluene solution on cooling. The precipitate was dissolved in boiling acetone (80 ml). The solution was filtered after addition of charcoal. From the filtrate colourless moisture sensitive needles (4.84 g, 72%) crystallized at – 80 °C; m.p. 254 – 257 °C (dec.).

$C_{15}H_{22}N_4O_5$ (338.4) Calcd. C 53.24 H 6.55 N 16.56 Found C 53.27 H 6.66 N 16.67

Diethyl 3,4,7,8-Tetrahydro-2,4,6,8-tetraoxo-2H,6H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-3,7-diacetate (**6d**): From ethyl isocyanatoacetate (5.16 g, 40 mmol) as described for **6c**. Yield 5.14 g (69%) of colourless moisture sensitive needles; m.p. 183 – 186 °C (dec.).

$C_{13}H_{14}N_4O_9$ (370.3) Calcd. C 42.17 H 3.81 N 15.13 Found C 42.16 H 3.72 N 15.11

3,7-Dibenzyl-2H,6H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-2,4,6,8(3H,7H)-tetrone (**6e**): From benzyl isocyanate (5.33 g, 40 mmol) as described for **6c**. The precipitate was dissolved in boiling ethyl acetate (400 ml). After addition of charcoal and filtration colourless needles (4.29 g, 57%) crystallized at – 18 °C; m.p. 228 – 230 °C (dec.).

$C_{19}H_{14}N_4O_5$ (378.3) Calcd. C 60.31 H 3.73 N 14.81 Found C 60.19 H 3.76 N 14.73

3-Cyclohexyl-6-ethoxy-1,3,5-triazine-2,4(1H,3H)-dione (**7b**): A solution of **6b** (1.81 g, 5.0 mmol) in ethanol (50 ml) was boiled under reflux for 30 min. Cooling to – 18 °C afforded a colourless precipitate (0.89 g, 74%); m.p. 215 – 218 °C.

$C_{11}H_{17}N_3O_3$ (239.3) Calcd. C 55.21 H 7.16 N 17.57 Found C 55.20 H 7.27 N 17.29

6-Ethoxy-3-methyl-1,3,5-triazine-2,4(1H,3H)-dione (**7f**)[26]: A solution of **1** (2.24 g, 20 mmol) and methyl isocyanate (2.28 g, 40 mmol) in toluene (25 ml) was kept at 120 °C for 12 h in an autoclave (teflon lining). Cooling to 22 °C and filtration afforded a colourless powder, which was boiled under reflux for 1 h in ethanol (50 ml). Evaporation of the solvent and crystallization of the residue from ethanol (30 ml) afforded colourless needles (1.55 g, 58%, after work-up of the mother liquor); m. p. 194–196°C (lit.[26] 215°C). – IR: 1735, 1670, 1625 cm^{-1}.

6-Ethoxy-3-phenyl-1,3,5-triazine-2,4(1H,3H)-dione (**7g**)[27]: From phenyl isocyanate (4.77 g, 40 mmol) as described for **7f**. An autoclave is not required. The product was precipitated with petroleum ether (100 ml) and recrystallized from ethanol affording colourless leaflets (1.35 g, 61%); m. p. 235–237°C (dec.) (lit.[27] 257–258°C).

2,6-Bis(dimethylamino)-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**9**): At 22°C **1** (2.24 g, 20 mmol) was added dropwise (exothermic reaction!) to dimethylcyanamide (2.10 g, 30 mmol) in toluene (10 ml). After 12 h the mixture was filtered. The residue was extracted with boiling acetonitrile (25 ml). From the filtrate a colourless powder (1.54 g, 41%) crystallized at –18°C; m. p. 205–208°C (dec.). – IR: 1780, 1720, 1660, 1620 cm^{-1}. – MS (70 eV): m/z = 252 (0.6%, M^+).

$C_9H_{12}N_6O_3$ (252.2) Calcd. C 42.85 H 4.80 N 33.33 Found C 42.76 H 5.08 N 33.03

6-(Dimethylamino)-1,3,5-triazine-2,4(1H,3H)-dione (**10**): A mixture of dimethylcyanamide (2.80 g, 40 mmol) and **1** (2.24 g, 20 mmol) in toluene (20 ml) was boiled under reflux for 8 h. The precipitate was filtered off and suspended in acetonitrile (25 ml). After addition of water (0.36 g, 20 mmol) the mixture was stirred for 5 h at 22°C and after that heated to 80°C. From the clear solution a precipitate fell out on cooling to 22°C. Recrystallization from dimethyl sulfoxide (2 ml) afforded a colourless powder (0.95 g, 30%), which did not melt below 300°C. – MS (70 eV): m/z = 156 (25%, M^+).

$C_5H_8N_4O_2$ (156.2) Calcd. C 38.46 H 5.16 N 35.88 Found C 38.26 H 5.11 N 35.59

4-(Dimethylamino)-6-ethoxy-1,3,5-triazin-2(1H)-one (**11**)[28]: A mixture of dimethylcyanamide (1.40 g, 20 mmol) and **1** (1.12 g, 10 mmol) in pentane (10 ml) was stirred for 12 h at 22°C. After evaporation of the solvent the residue was boiled under reflux in ethanol (25 ml) for 15 min. From the clear solution a colourless powder (0.83 g, 45%) crystallized on cooling; m. p. 208–210°C (lit.[28] 213–214°C).

2,6-Bis(tert-butylimino)-2,3,6,7-tetrahydro-3,7-dimethyl-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**12a**): A solution of **1** (1.12 g, 10 mmol) in ether (25 ml) was added dropwise at –78°C to a solution of *tert*-butylmethylcarbodiimide (2.24 g, 20 mmol) in ether (25 ml). The reaction mixture was warmed up to 22°C within 15 h. Filtration, dissolution of the residue in ether (150 ml) and crystallization at –80°C afforded a colourless powder (3.00 g, 89%); m. p. 149–151°C (dec.). – IR: 1780, 1730, 1720 (shoulder), 1670, 1630 cm^{-1}. – MS (70 eV): m/z = 336 (0.4%, M^+), 321 (8, M – CH_3), 224 (16, M – $(CH_3)_3CNCNCH_3$), 209 (100, M – $(CH_3)_3CNCNCH_3$, – CH_3), 169 (35, M – $(CH_3)_3CNCNCH_3$, – $(CH_3)_3C$), 57 (95, $(CH_3)_3C$).

$C_{15}H_{24}N_6O_3$ (336.4) Calcd. C 53.56 H 7.19 N 24.98 Found C 53.37 H 7.19 N 25.07

2,3,6,7-Tetrahydro-3,7-diisopropyl-2,6-bis(isopropylimino)-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**12b**): From diisopropylcarbodiimide (2.52 g, 20 mmol) as described for **12a**. Crystallization at –80°C from ether (100 ml) afforded after filtration from a mucous impurity a colourless powder (2.64 g, 72%); m. p. 150–152°C (dec.). – IR: 1780, 1710, 1680, 1630 cm^{-1}. – MS (70 eV): m/z = 364 (1.5%, M^+), 321 (7, M – $(CH_3)_2CH$), 279 (3, M – $(CH_3)_2CHNCO$), 238 (13, M – $(CH_3)_2CHNCNCH(CH_3)_2$), 195 (14, M – $(CH_3)_2CHNCNCH(CH_3)_2$, – $(CH_3)_2CH$), 168 (33, M – $(CH_3)_2CHNCNCH(CH_3)_2$, – OCNCO).

$C_{17}H_{28}N_6O_3$ (364.5) Calcd. C 56.02 H 7.74 N 23.06 Found C 56.39 H 7.78 N 22.88

3,7-Dicyclohexyl-2,6-bis(cyclohexylimino)-2,3,6,7-tetrahydro-4H,8H-[1,3,5]triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**12c**): From dicyclohexylcarbodiimide (4.12 g, 20 mmol) as described for **12a**. Yield 4.00 g (76%) of a colourless powder; dec. above 235 °C. – MS (70 eV): *m*/*z* = 524 (0.2%, M$^+$).

$C_{29}H_{44}N_6O_3$ (524.7) Calcd. C 66.38 H 8.45 N 16.02 Found C 66.47 H 8.57 N 15.92

3,7-Bis(diphenylmethyl)-2,6-bis[(diphenylmethyl)imino]-2,3,6,7-tetrahydro-4H,8H-[1,3,5]-triazino[2,1-b]-1,3,5-oxadiazine-4,8-dione (**12d**): A suspension of bis(diphenylmethyl)-carbodiimide (3.75 g, 10 mmol) in ether (25 ml) was added dropwise to **1** (0.56 g, 5.0 mmol) in ether (25 ml). Stirring for 12 h, evaporation of the solvent, and crystallization of the residue from dichloromethane (10 ml)/ether (100 ml) afforded (at –80 °C) a colourless powder (4.08 g, 95%); m. p. 189 – 191 °C.

$C_{57}H_{44}N_6O_3$ (861.0) Calcd. C 79.51 H 5.15 N 9.76 Found C 79.67 H 5.45 N 9.74

6-Ethoxy-1,2,3,4-tetrahydro-N,3-diisopropyl-N-[(isopropylamino)carbonyl]-2-(isopropylimino)-4-oxo-1,3,5-triazine-1-carboxamide (**14**): A solution of **12b** (1.09 g, 3.0 mmol) in ethanol (10 ml) was kept at 50°C for 2 min. Longer heating resulted in complete decomposition of **12b**. From the cold solution unchanged **12b** (0.54 g, 50%) crystallized. The mother liquor was evaporated to a volume of 2 ml. On cooling colourless prisms of **14** (0.38 g, 31%) crystallized; m. p. 156 – 159 °C. – IR: 3325, 1685, 1655, 1595 cm^{-1}. – MS (70 eV): *m*/*z* = 410 (3%, M$^+$).

$C_{19}H_{34}N_6O_4$ (410.5) Calcd. C 55.59 H 8.35 N 20.48 Found C 55.43 H 8.61 N 20.60

3-Isopropyl-8-phenyl-1,3,5,8-tetraazabicyclo[2.2.2]oct-4-ene-2,6,7-trione (**15a**): A solution of **1** (1.12 g, 10 mmol) in ether (15 ml) was added dropwise to isopropylphenylcarbodiimide (1.60 g, 10 mmol) in ether (15 ml). Stirring for 12 h at 22 °C and filtration yielded a colourless powder (2.63 g, 97%) of low solubility in the usual organic solvents; m. p. 208 – 210°C (dec.). – IR: 1720, 1640, 1430 cm^{-1}. – MS (70 eV): *m*/*z* = 272 (42%, M$^+$), 230 (91, M – NCO), 187 (100, M – $(CH_3)_2CHNCO$), 145 (85, M – NCO, – $(CH_3)_2CHNCO$), 119 (55, C_6H_5NCO).

$C_{13}H_{12}N_4O_3$ (272.3) Calcd. C 57.35 H 4.44 N 20.58 Found C 57.89 H 4.81 N 20.23

3,8-Bis(4-methoxyphenyl)-1,3,5,8-tetraazabicyclo[2.2.2]oct-4-ene-2,6,7-trione (**15b**): A solution of **1** (1.12 g, 10 mmol) in dichloromethane (15 ml) was added dropwise to bis(4-methoxyphenyl)carbodiimide (2.54 g, 10 mmol) in dichloromethane (15 ml). Stirring for 12 h at 25 °C and filtration yielded a pale yellow powder (3.52 g, 96%) of low solubility in the usual organic solvents. A reasonable elemental analysis could not be obtained; dec. above 215°C. – MS (70 eV): *m*/*z* = 366 (100%, M$^+$), 323 (32, M – NCO), 254 (23, $CH_3OC_6H_4NCNC_6H_4OCH_3$), 149 (72, $CH_3OC_6H_4NCO$).

$C_{18}H_{14}N_4O_5$ (366.3) Calcd. C 59.01 H 3.85 N 15.30 Found C 57.21 H 4.13 N 14.91

3,8-Bis(4-isopropylphenyl)-1,3,5,8-tetraazabicyclo[2.2.2]oct-4-ene-2,6,7-trione (**15c**): From bis(4-isopropylphenyl)carbodiimide (2.78 g, 10 mmol) as described for **15a**. Yield 3.16 g (81%) of a yellowish powder, which decomposed on attempts of purification.

6-Imino-1-isopropyl-5,6-dihydro-5-phenyl-1,3,5-triazine-2,4(1H,3H)-dione (**16a**): A suspension of **15a** (1.36 g, 5.0 mmol) in acetonitrile (25 ml)/water (1 ml) was shaken for 12 h. The solvent was removed under reduced pressure. The residue was extracted with boiling ethanol (10 ml). From the extract a precipitate was obtained on cooling. Recrystallization from ethanol afforded a colourless powder; m. p. 202 – 205 °C. – IR: 3300, 1740, 1610, 1430 cm^{-1}. – MS (70 eV): *m*/*z* = 246 (71%, M$^+$), 245 (28, M – H).

$C_{12}H_{14}N_4O_2$ (246.3) Calcd. C 58.52 H 5.73 N 22.76 Found C 58.36 H 5.75 N 22.77

6-Imino-1,5-bis(4-isopropylphenyl)-5,6-dihydro-1,3,5-triazine-2,4(1H,3H)-dione (**16c**): From **15c** (3.91 g, 10 mmol) as described for **16a**. Yield 2.48 g (68%) of a colourless powder; m. p. 235–237°C (dec.). – MS (70 eV): *m/z* = 364 (36%, M^+), 363 (89, M – H).

$C_{21}H_{24}N_4O_2$ (364.5) Calcd. C 69.20 H 6.64 N 15.38 Found C 68.75 H 6.84 N 15.09

1-Isopropyl-3-phenyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**17a**): A suspension of **15a** (2.72 g, 10 mmol) in 2 M HCl (50 ml) was boiled under reflux for 5 h. Evaporation of the solvent and crystallization of the residue from water (15 ml) afforded colourless prisms (0.60 g, 24%); m. p. 164–166°C. – MS (70 eV): *m/z* = 247 (43%, M^+).

$C_{12}H_{13}N_3O_3$ (247.3) Calcd. C 58.29 H 5.30 N 17.00 Found C 58.22 H 5.41 N 17.00

1,4-Bis(4-methoxyphenyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (**17b**)[29]

a) A solution of carbonyl chloride isocyanate (1.06 g, 10 mmol) in dichloromethane (15 ml) was added dropwise to **18** (2.54 g, 10 mmol) in dichloromethane (10 ml). After stirring for 12 h at 22°C water (2 ml) was added and the mixture was stirred for further 30 min. Evaporation of the solvent and crystallization of the oily residue from ethanol afforded colourless prisms (2.20 g, 64%, including work-up of the mother liquor); m. p. 212–215°C (dec.) (lit.[29] 220–223°C). – MS (70 eV): *m/z* = 341 (79%, M^+).

b) A solution of **15b** (3.66 g, 10 mmol) in 2 M HCl (50 ml) was boiled under reflux for 8 h. On cooling a colourless powder precipitated (1.54 g, 42%); m. p. 213–214°C.

Ethyl (Hexahydro-1-isopropyl-4,6-dioxo-3-phenyl-1,3,5-triazin-2-ylidene)carbamate (**19a**): A suspension of **15a** (2.72 g, 10 mmol) in ethanol (15 ml) was boiled under reflux for 15 min. The product crystallized at –18°C affording colourless prisms (1.52 g, 48%); m. p. 222–224°C. – MS (70 eV): *m/z* = 318 (32%, M^+), 277 (74, M – C_3H_5), 231 (44, M – $NCO_2C_2H_5$).

$C_{15}H_{18}N_4O_4$ (318.3) Calcd. C 56.59 H 5.70 N 17.60 Found C 56.56 H 5.92 N 17.60

Butyl [Hexahydro-1,3-bis(4-methoxyphenyl)-4,6-dioxo-1,3,5-triazin-2-ylidene]carbamate (**19b**): A suspension of **15b** (1.83 g, 5.0 mmol) in *n*-butanol (20 ml) was boiled under reflux for 5 min. At –18°C colourless prisms (1.40 g, 64%) were obtained; m. p. 248–250°C. – MS (70 eV): *m/z* = 440 (10%, M^+), 367 (5, M – C_4H_9O), 340 (35, M – C_4H_8OCO).

$C_{22}H_{24}N_4O_6$ (440.5) Calcd. C 59.99 H 5.49 N 12.72 Found C 60.16 H 5.43 N 12.79

---

[1] Methoden der organischen Chemie (*Houben-Weyl*), Vol. E/4, Ed. *H. Hagemann*, Thieme 1983.

[2] *E. Nachbaur*, Monatsh. Chem. **97**, 361 (1966).

[3] *W. Gottardi*, Monatsh. Chem. **101**, 665 (1970).

[4] *Bayer AG* (inventor *H. Hagemann*), D.O.S. 2408069 (4. Sept. 1975) [Chem. Abstr. **84**, 43358z (1976)].

[5] *Bayer AG* (inventor *H. Hagemann*), D.O.S. 2411674 (2. Oct. 1975) [Chem. Abstr. **84**, 4508d (1976)].

[6] *W. Verbeek* and *W. Sundermeyer*, Angew. Chem. **79**, 860 (1967); Angew. Chem., Int. Ed. Engl. **6**, 871 (1967).

[7] *G. Jäckh* and *W. Sundermeyer*, Chem. Ber. **106**, 1752 (1973).

[8] *V. I. Gorbatenko* and *L. F. Lure*, Zh. Org. Khim. **16**, 464 (1980).

[9] *W. Schäfer* in lit.[1], p. 1376.

[10] *B. Akteries* and *J. C. Jochims*, Chem. Ber. **119**, 83 (1986).

[11] *H. Hagemann*, *H. Heitzer*, and *D. Wendisch*, Liebigs Ann. Chem. **1976**, 1634.

[12] *H. Hagemann*, GDCH meeting, Köln 8.–13.9.1975; reference in lit.[1], p. 1377. Our independent research was completed when this book appeared.

[13] *R. Bunnenberg* and *J. C. Jochims*, Chem. Ber. **114**, 1132 (1981).

[14] *R. Bunnenberg* and *J. C. Jochims*, Chem. Ber. **114**, 1746 (1981).
[15] *R. Bunnenberg* and *J. C. Jochims*, Chem. Ber. **114**, 2064 (1981).
[16] *R. Bunnenberg* and *J. C. Jochims*, Chem. Ber. **114**, 2075 (1981).
[17] *R. Bunnenberg, J. C. Jochims*, and *H. Härle*, Chem. Ber. **115**, 3587 (1982).
[18] *B. Akteries* and *J. C. Jochims*, Chem. Ber. **119**, 669 (1986).
[19] *O. Tsuge* in The Chemistry of Cyanates and their Thio Derivatives, p. 445ff., *S. Patai* Ed., Wiley 1977.
[20] *B. A. Arbuzov* and *N. N. Zobova*, Synthesis **1974**, 461.
[21] *B. A. Arbuzov* and *N. N. Zobova*, Synthesis **1982**, 433.
[22] *O. Tsuge*, Heterocycles **12**, 1067 (1979).
[23] *K. A. Nuridzhanyan*, Russ. Chem. Rev. **39**, 130 (1970).
[24] *K. Hartke* and *E. Palou*, Chem. Ber. **99**, 3155 (1966).
[25] Methoden der organischen Chemie (*Houben-Weyl-Müller*), Vol. 7/2b, p. 1949, Thieme, Stuttgart 1976.
[26] *J. Perronnet* and *L. Taliani*, J. Heterocycl. Chem. **17**, 673 (1980).
[27] *M. Ogawa, T. Matsui, K. Oyamada*, and *J. Tobitsuka*, Plant Cell Physiol. **18**, 841 (1977).
[28] *P. R. Atkins, S. E. J. Glue*, and *I. T. Kay*, J. Chem. Soc., Perkin Trans. 1 **1973**, 2644.
[29] *P. A. Argabright* and *B. L. Phillips*, J. Org. Chem. **35**, 2253 (1970).

[198/85]