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The Reaction of Acylium Salts with Carbodiimides

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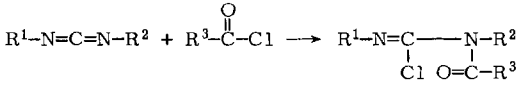
Acylium salts **10** react with aliphatic carbodiimides **1** in the molecular ratio 1 : 3 to give the *s*-triazinium salts **13a – v**. In boiling methanol/dichloromethane compounds **13** loose the alkyl substituents in 1,3-position affording the triazinium salts **15**. At higher temperatures solvolysis of **13** results in loss of the substituents in 2,5-position leading to **16**, while with base at room temperature only the carboxamido substituent on C-2 is split off leading to triazines **18** or **19**, which are transformed into **16** by treatment with dilute hydrochloric acid. The mechanisms of these transformations are discussed. Preparations of the oxadiazinium salts **6a – c** are described.

Die Reaktion von Acyliumsalzen mit Carbodiimiden

Acyliumsalze **10** reagieren mit aliphatischen Carbodiimiden **1** im molekularen Verhältnis 1 : 3 zu den *s*-Triaziniumsalzen **13a – v**. Diese Verbindungen verlieren in siedendem Methanol/Dichlormethan die Alkylsubstituenten in 1,3-Stellung, wobei sich die Triaziniumsalze **15** bilden. Solvolysiert man bei höheren Temperaturen, so erhält man unter Verlust der Substituenten in 2,5-Stellung das Triaziniumsalz **16**. Unter basischen Bedingungen wird bei Raumtemperatur nur die Amidogruppe an C-2 abgespalten. Man isoliert die Triazine **18** bzw. **19**, die mit verd. Salzsäure in **16** übergeführt werden. Die Mechanismen dieser Reaktionen werden diskutiert. Es werden Synthesen der Oxadiaziniumsalze **6a – c** angegeben.

The reaction of aliphatic carbodiimides **1** with acyl chlorides **2** to yield *N*-acyl chloroformamidines **3** has first been described by *Stachel*[1] and *Hartke*[2-4]. This reaction has found applications for the desulfuration of thioamides, and for the preparation of certain heterocycles[5,6].



1 **2** **3**

To our knowledge, reactions of carbodiimides with acylium salts **10** have not been studied till now.

Related with carbodiimides are disubstituted cyanamides, **4**, which are known to form chloroformamidines **5** with acyl chlorides but oxadiazinium salts **6** with acylium salts[7]. For the latter reaction three examples, **6a – c**, are described in the experimental part.

Recently, we studied the reaction of carbodiimides and cyanamides with the heterobutatrienium salts **7**[8]. With two equivalents of carbodiimide the triazinium salts **8** were obtained while cyanamides gave oxadiazinium salts, **9**. Obviously, compounds **7** behave as acylium salts (**7'**) in these reactions.

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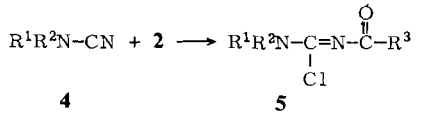
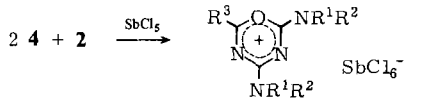
In this connection the question arose on how carbodiimides would react with more conventional unambiguous acylium salts **10** obtained from acyl chlorides in the presence of Lewis acids, MCl_n, like antimony pentachloride, iron trichloride, or zinc dichloride.

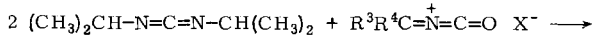


4 **5**

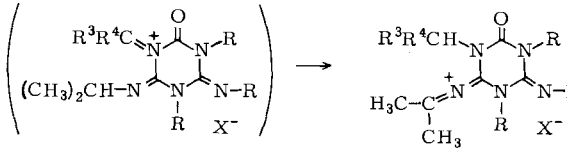


6a-c

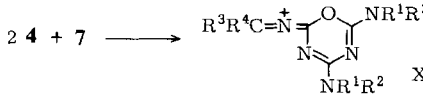
6	R^1	R^2	R^3
a	CH_3	CH_3	C_6H_5
b	$(CH_3)_2CH$	$(CH_3)_2CH$	C_6H_5
c	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_3



7



8 (R = $(CH_3)_2CH$)



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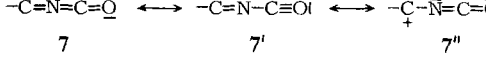


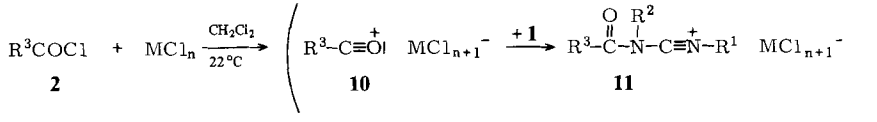
7 **7'** **7''**

Stirring a solution of acetyl chloride and diisopropylcarbodiimide in dichloromethane in the presence of antimony pentachloride at room temperature afforded the triazinium salt **13a** in 73% yield. Similarly, compounds **13b–v** were obtained. Contrary to **7**, which reacts with two equivalents of carbodiimide, the reaction of acylium salts, **10**, requires three equivalents of carbodiimide.

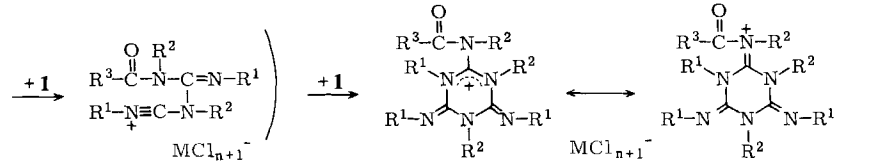
The structures of compounds **13** follow from their NMR spectra and from certain chemical transformations. For instance, in the ^{13}C NMR spectrum of **13a** signals at δ = 173.2, 158.6, and 136.8 are assigned to a carbonyl group and two sorts of C=N carbons (in CD_3CN). At 303 K the six isopropyl groups are anisochronous in the ^1H NMR as well as in the ^{13}C NMR spectrum indicating considerably hindered rotation around the amide nitrogen–C-2 bond. Obviously, the canonical form **13'** is of importance.

We believe that the heterocycles **13** are formed by stepwise polar cycloadditions[9,10] via cyanamidium salts **11** and **12**[11]. The formation of a resonance stabilized guanidinium moiety (**13** ↔ **13'**) must be the driving force for the addition of another molecule of carbodiimide to **12** instead of ring closure to a tetrahydrooxadiazine **14**.

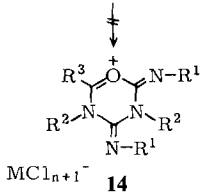
Only aliphatic carbodiimides react with acylium salts to give triazinium compounds **13**. With bis(4-methoxyphenyl)carbodiimide and benzoylium hexachloroantimonate an instable oil was obtained, which might be a derivative of a quinazoline. With cyclohexylisopropylcarbodiimide a mixture of regioisomers (mainly three compounds) was obtained giving an elemental analysis as calculated for **13r**.



2 **10** **11**



12 **13a-v** **13'**



14

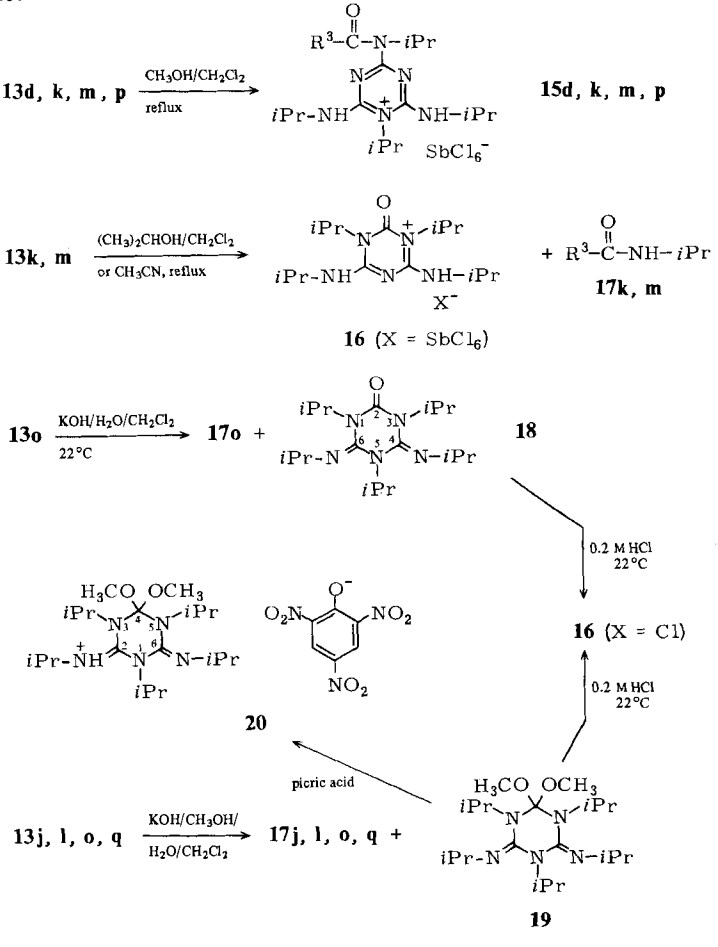
2, 13-16	R^1	R^2	R^3	MCl_{n+1}
a	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_3	$SbCl_6$
b	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_3	$ZnCl_3$
c	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_3	$FeCl_4$
d	$(CH_3)_2CH$	$(CH_3)_2CH$	CH_2Cl	$SbCl_6$
e	$(CH_3)_2CH$	$(CH_3)_2CH$	CCl_3	$SbCl_6$
f	$(CH_3)_2CH$	$(CH_3)_2CH$	CCl_3	$ZnCl_3$
g	$(CH_3)_2CH$	$(CH_3)_2CH$	CCl_3	$FeCl_4$
h	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_2CH$	$SbCl_6$
i	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_2CH$	$ZnCl_3$
j	$(CH_3)_2CH$	$(CH_3)_2CH$	$(CH_3)_2CH$	$FeCl_4$
k	$(CH_3)_2CH$	$(CH_3)_2CH$	C_6H_5	$SbCl_6$
l	$(CH_3)_2CH$	$(CH_3)_2CH$	C_6H_5	$FeCl_4$
m	$(CH_3)_2CH$	$(CH_3)_2CH$	$4\text{-}CH_3C_6H_4$	$SbCl_6$
n	$(CH_3)_2CH$	$(CH_3)_2CH$	$4\text{-}CH_3C_6H_4$	$ZnCl_3$
o	$(CH_3)_2CH$	$(CH_3)_2CH$	$4\text{-}CH_3C_6H_4$	$FeCl_4$
p	$(CH_3)_2CH$	$(CH_3)_2CH$	$4\text{-}FC_6H_4$	$SbCl_6$
q	$(CH_3)_2CH$	$(CH_3)_2CH$	$4\text{-}FC_6H_4$	$FeCl_4$
r	$c\text{-}C_6H_{11}$[a]	$(CH_3)_2CH$[a]	CH_3	$SbCl_6$
s	$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	CH_3	$SbCl_6$
t	$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	CCl_3	$SbCl_6$
u	$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	$(CH_3)_2CH$	$SbCl_6$
v	$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	C_6H_5	$SbCl_6$

[a] A mixture of regioisomers was obtained.

The triazinium salts **13** are rather temperature-sensitive. The product from the reaction of pivaloyl chloride and diisopropylcarbodiimide decomposed on attempts of recrystallization.

Boiling solutions of **13** (R^3 = aryl) in methanol/dichloromethane results in loss of two isopropyl groups and formation of the new triazinium salts **15**. Compound **13a** ($R^3 = CH_3$) proved to be stable under these conditions. With **13d** ($R^3 = CH_2Cl$) the reaction is slow. From boiling dichloromethane alone compounds **13** were recovered unchanged. If solutions of **13k, m** are boiled under reflux in 2-propanol/dichloromethane or acetonitrile, the triazinium salt **16** and the *N*-isopropylarenamides **17** are formed. Shaking **13o** in aqueous potassium hydroxide/dichloromethane at room temperature leads to the triazine **18** and the amide **17o**. Triazine **18** is easily transformed into **16** by treatment with dilute hydrochloric acid.

Stirring the triazinium salts **13j, l, o, q** in a mixture of methanol/water/dichloromethane in the presence of potassium hydroxide yields the orthoester **19** and the carboxamides **17j, l, o, q**. The oily urea acetal[12] **19** was isolated and characterized as its picrate **20**.



The structures of compounds **15** – **20** can be derived from the elemental analyses and the NMR spectra, e. g. in the ^1H NMR spectrum of **15k** signals for two equivalent isopropyl groups linked to NH ($J_{NH,CH}$ = 7 Hz) and two further inequivalent isopropyl groups are observed. The ^{13}C NMR spectrum (CD_2Cl_2) shows signals at δ = 173.7, 161.2, and 154.1 (double intensity), which can be assigned to the carbonyl and the C=N carbons. The high symmetry of **16** is indicated by the NMR spectra, which show signals for only two different isopropyl groups one of which is linked to NH ($J_{NH,CH}$ = 6 Hz). In the ^{13}C NMR spectrum (CD_3CN) the carbonyl resonance is found at 148.1 ppm, and a signal for two equivalent C=N carbons at 154.2. The NMR spectra of **18** show signals for five isopropyl groups the inequivalence of which can be explained assuming different configurations around the two exocyclic C=N double bonds. Considerable line broadening of four of the ^{13}C methyl resonances indicates slow geometrical isomerization at 303 K. Similarly, broad signals for five inequivalent isopropyl and two equivalent OCH_3 groups are observed in the NMR spectra of **20**.

The formation of the products **15** – **20** may be rationalized assuming two competing nucleophilic substitutions in **13**: nucleophilic attack at the isopropyl groups in 1,3-position with the heterocycle as leaving group and solvolytic displacement of the carboxamido group from C-2. Since protonated **18** easily splits off the isopropyl group in 5-position, it seems likely that **16** is formed from **13** via protonated **18**. The formation of **16** + **17** from **13** in boiling acetonitrile or 2-propanol/dichloromethane must be due to small amounts of water in these solvents.

M. A.-T. would like to thank *Deutscher Akademischer Austauschdienst* for a fellowship, and *Yarmouk University, Jordan,* for a study leave.

Experimental Part

IR spectra: Perkin-Elmer IR 299, in dichloromethane. – ^1H and ^{13}C NMR spectra: Jeol JNM-100 and Bruker WM-250 spectrometers, internal reference tetramethylsilane. – The melting points are uncorrected.

2,4-Bis(dimethylamino)-6-phenyl-1,3,5-oxadiazinium Hexachloroantimonate (**6a**): To benzoyl chloride (0.70 g, 5.00 mmol) in absol. dichloromethane (10 ml) was added dropwise at −40 °C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (10 ml) followed by a solution of dimethylcyanamide (0.71 g, 10.10 mmol) in absol. dichloromethane (10 ml). The reaction mixture was slowly warmed to +20 °C and stirred for 3 h at this temperature. With absol. ether (30 ml) a yellow powder was precipitated, which was recrystallized from hot acetone giving yellow prisms (2.41 g, 83%); m. p. 255 – 261 °C (dec.). The compound is nearly insoluble in most organic solvents. – IR: 1700, 1630, 1600 cm^{-1}.

$[C_{13}H_{17}N_4O]SbCl_6$ (579.8) Calcd. C 26.93 H 2.96 N 9.67 Found C 26.69 H 3.09 N 9.71

2,4-Bis(diisopropylamino)-6-phenyl-1,3,5-oxadiazinium Hexachloroantimonate (**6b**): As described for **6a** from diisopropylcarbodiimide (1.28 g, 10.10 mmol). Recrystallization from hot acetonitrile afforded yellow crystals (2.60 g, 75%); m. p. 256 – 257 °C (dec.). – IR: 1680, 1610, 1580, 1560 cm^{-1}. – ^1H NMR (CD_3CN, 348 K): CH_3 δ = 1.40 (d, J = 7 Hz, 12 H), 1.47 (d, J = 7 Hz), 1.51 (d, J = 7 Hz), CH 4.33 (m), 4.57 (m, 2 H), 4.74 (m), *p*-H 7.83 (m), *o*-H 8.22 (d, J = 7 Hz), *m*-H 7.67 (t, J = 8 Hz). – ^{13}C NMR (CD_3CN, 348 K): CH_3 δ = 19.9, 20.1, 20.9, 21.6, CH 49.7, 50.5, 50.8, phenyl 128.5, 130.2, 130.6, 136.8, C=O, C=N 156.1, 158.4, 164.4.

$[C_{21}H_{33}N_4O]SbCl_6$ (692.0) Calcd. C 36.45 H 4.81 N 8.10 Found C 36.56 H 4.73 N 8.21

2,4-Bis(diisopropylamino)-6-methyl-1,3,5-oxadiazinium Hexachloroantimonate (**6c**): As described for **6b** from acetyl chloride (0.40 g, 5.10 mmol). Yield 2.58 g (82%) of yellow crystals; m. p. 195 – 205 °C (dec.). – IR: 1700, 1630, 1570 cm^{-1}. – ^1H NMR (CD_3CN, 348 K): CH_3CO

δ = 2.44. – ^{13}C NMR (CD_3CN, 348 K): CH_3 δ = 19.8, 20.0, 21.0, 21.1, 21.5, CH 49.3, 50.35, 50.42, 50.5, C=O, C=N 169.0, 158.0, 156.3.

$[C_{16}H_{31}N_4O]SbCl_6$ (629.9) Calcd. C 30.50 H 4.96 N 8.90 Found C 30.46 H 5.05 N 8.62

2-(Acetylisopropylamino)-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (**13a**): To acetyl chloride (0.39 g, 5.00 mmol) and diisopropylcarbodiimide (1.92 g, 15.20 mmol) in anhydrous dichloromethane (20 ml) was added dropwise with stirring at −20°C a solution of antimony pentachloride (1.50 g, 5.00 mmol) in absol. dichloromethane (10 ml). Stirring was continued for 4 h at +22°C. Slow addition of absol. ether (60 ml) afforded a colourless powder (2.76 g, 73%); m.p. 143–145°C. – IR: 1700, 1670, 1530 cm^{-1}. – ^{1}H NMR (CD_3CN): CH_3 δ = 1.16 (d, *J* = 6 Hz), 1.21 (d, *J* = 6 Hz), 1.25 (d, *J* = 6 Hz), 1.46 (d, *J* = 7 Hz), 1.51 (d, *J* = 7 Hz), 1.56 (d, *J* = 7 Hz), 2.41, CH 3.41 (sept., *J* = 6 Hz), 4.30 (sept., *J* = 6 Hz, 2H), 4.41 (sept., *J* = 6 Hz), 4.54 (sept., *J* = 7 Hz, 2H). – ^{13}C NMR (CD_3CN): CH_3 δ = 21.0, 21.5, 22.1, 22.3, 23.1, 23.3, 23.6, CH 51.5 (2C), 55.0, 56.0, 58.6 (2C), C=O, C=N 173.2, 158.6, 136.8 (2C).

$[C_{23}H_{45}N_6O]SbCl_6$ (756.1) Calcd. C 36.53 H 6.00 N 11.12 Found C 36.80 H 5.80 N 10.95

2-(Acetylisopropylamino)-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Trichlorozincate (**13b**): As described for **13a** with anhydrous zinc dichloride (0.39 g, 5.00 mmol). The product began to crystallize from the reaction mixture after stirring for 1 h at 22°C. Precipitation with ether (50 ml) yielded colourless crystals (2.49 g, 84%); m.p. 150–151°C. – IR: 1690, 1660, 1520 cm^{-1}. – ^{13}C NMR (CD_3OD, 263 K): CH_3 δ = 20.3 (broad), 21.5, 22.3, 22.6 (broad), 22.8, 23.4, 23.9, CH 51.9, 55.3 (broad), 55.7, 59.1, C=O, C=N 137.4, 158.9, 174.5.

$[C_{23}H_{45}N_6O]ZnCl_3$ (593.4) Calcd. C 46.55 H 7.64 N 14.17 Found C 46.71 H 7.76 N 14.30

2-(Acetylisopropylamino)-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Tetrachloroferrate (**13c**): To a stirred suspension of anhydrous iron trichloride (0.81 g, 5.00 mmol) in absol. dichloromethane (10 ml) first a solution of acetyl chloride (0.39 g, 5.00 mmol) in absol. dichloromethane (10 ml) and than a solution of diisopropylcarbodiimide (1.92 g, 15.20 mmol) was added dropwise at −20°C. Stirring was continued for 4 h at 22°C. Filtration afforded a yellow solution from which the product was precipitated by slow addition of ether (40 ml). Yield 2.66 g (86%) of a yellow powder; m.p. 116–117°C (dec.). – IR: 1680, 1650, 1510 cm^{-1}.

$[C_{23}H_{45}N_6O]FeCl_4$ (619.3) Calcd. C 44.60 H 7.32 N 13.57 Found C 44.52 H 7.27 N 13.37

2-[(Chloroacetyl)isopropylamino]-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (**13d**): As described for **13a** from chloroacetyl chloride (0.56 g, 5.00 mmol). Yield 3.36 g (85%) of a colourless powder; m.p. 133–134°C. – IR: 1690, 1660, 1520 cm^{-1}. – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 20.9, 21.4, 22.5, 22.7, 23.2, 23.5, CH_2 41.3, CH 51.5, 55.3, 58.7, C=O, C=N 135.5, 156.4, 168.1.

$[C_{23}H_{44}ClN_6O]SbCl_6$ (790.6) Calcd. C 34.94 H 5.61 N 10.63 Found C 34.76 H 5.66 N 10.47

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(trichloroacetyl)-amino]-1,3,5-triazinium Hexachloroantimonate (**13e**): As described for **13a** from trichloroacetyl chloride (0.91 g, 5.00 mmol). Yield 3.65 g (85%) of a colourless powder; m.p. 183–188°C (dec.). – IR: 1700, 1660, 1520 cm^{-1}. – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 20.4, 21.4, 21.9, 23.0, 23.1, 23.6, CH 51.8, 55.3, 58.6, 59.3, CCl_3 90.8, C=N 135.3, 154.9, C=O 160.9.

$[C_{23}H_{42}Cl_3N_6O]SbCl_6$ (859.5) Calcd. C 32.14 H 4.93 N 9.78 Found C 31.92 H 5.01 N 9.73

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(trichloroacetyl)amino]-1,3,5-triazinium Trichlorozincate (**13f**): As described for **13e** with anhydrous zinc dichloride

(0.39 g, 5.00 mmol). Yield 2.96 g (85%) of a colourless powder; m.p. 119–120°C. – IR: 1690, 1660, 1510 cm^{-1}.

$[C_{23}H_{42}Cl_3N_6O]ZnCl_3$ (696.7) Calcd. C 39.65 H 6.08 N 12.07 Found C 39.67 H 6.20 N 11.90

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(trichloroacetyl)-amino]-1,3,5-triazinium Tetrachloroferrate (**13g**): As described for **13c** from trichloroacetyl chloride (0.91 g, 5.00 mmol). The product was precipitated with ether (50 ml)/pentane (30 ml). Yield 3.25 g (90%) of a yellow powder; m.p. 128–129°C (dec.). – IR: 1700, 1660, 1520 cm^{-1}.

$[C_{23}H_{42}Cl_3N_6O]FeCl_4$ (722.6) Calcd. C 38.22 H 5.86 N 11.63 Found C 38.04 H 5.81 N 11.46

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(2-methylpropio-nyl)amino]-1,3,5-triazinium Hexachloroantimonate (**13h**): As described for **13a** from isobutyryl chloride (0.53 g, 5.00 mmol). Yield 3.41 g (87%) of a colourless powder; m.p. 135–137°C (dec.). – IR: 1690, 1660, 1530 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 1.18 (d, J = 6 Hz), 1.24 (d, J = 6 Hz), 1.28 (d, J = 6 Hz), 1.29 (d, J = 7 Hz), 1.54 (d, J = 7 Hz), 1.55 (d, J = 7 Hz), 1.61 (d, J = 7 Hz), CH 3.11 (sept., J = 6 Hz), 3.39 (sept., J = 6 Hz), 4.27 (sept., J = 7 Hz, 2H), 4.45 (sept., J = 7 Hz, 2H), 4.54 (sept., J = 6 Hz). – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 19.7, 20.9, 21.4, 22.2, 22.8, 23.2, 23.5, 32.4, CH 51.3, 53.5, 55.2, 58.2, C=N 135.8, 157.9, C=O 179.4.

$[C_{25}H_{49}N_6O]SbCl_6$ (784.2) Calcd. C 38.29 H 6.30 N 10.72 Found C 38.05 H 6.27 N 10.60

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(2-methylpropio-nyl)amino]-1,3,5-triazinium Trichlorozincate (**13i**): In analogy to **13g**. Yield 2.52 g (81%) of a colourless powder; m.p. 133–134°C (dec.). – IR: 1680, 1660, 1520 cm^{-1}.

$[C_{25}H_{49}N_6O]ZnCl_3$ (621.4) Calcd. C 48.32 H 7.95 N 13.53 Found C 48.07 H 8.14 N 13.40

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(2-methylpropio-nyl)amino]-1,3,5-triazinium Tetrachloroferrate (**13j**): In analogy to **13g**. Yield 2.72 g (84%) of yellow leaflets; m.p. 124–125°C (dec.). – IR: 1680, 1660, 1520 cm^{-1}.

$[C_{25}H_{49}N_6O]FeCl_4$ (647.4) Calcd. C 46.38 H 7.63 N 12.99 Found C 46.28 H 7.66 N 12.99

2-(Benzoylisopropylamino)-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (**13k**): As described for **13a** from benzoyl chloride (0.70 g, 5.00 mmol). Yield 3.15 g (77%) of colourless needles; m.p. 126–127°C. – IR: 1660 (shoulder 1700), 1530 cm^{-1}. – ^1H NMR ($CDCl_3$): CH_3 δ = 1.21 (d, J = 6 Hz), 1.27 (d, J = 7 Hz), 1.31 (d, J = 6 Hz), 1.33 (d), 1.69 (d, J = 6 Hz), 1.70 (d, J = 6 Hz), CH 3.42 (m, 1H), 4.29 (m, 2H), 4.73 (m, 3H), phenyl 7.65. – ^{13}C NMR ($CDCl_3$): CH_3 δ = 21.0, 21.2, 22.0, 22.2, 23.2, 23.5, CH 51.1, 55.1, 55.3, 58.3, C=O 171.3, C=N 157.4, 135.4, phenyl: *i,p*-C 132.9, 132.5, *o,m*-C 129.7, 126.6.

$[C_{28}H_{47}N_6O]SbCl_6$ (818.2) Calcd. C 41.10 H 5.79 N 10.27 Found C 40.83 H 5.65 N 10.46

2-(Benzoylisopropylamino)-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Tetrachloroferrate (**13l**): In analogy to **13i**. Yield 2.45 g (72%) of an ochreous powder; m.p. 121–122°C. – IR: 1660 (shoulder 1690), 1620 cm^{-1}.

$[C_{28}H_{47}N_6O]FeCl_4$ (681.4) Calcd. C 49.35 H 6.95 N 12.34 Found C 49.10 H 6.83 N 12.29

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(4-methylbenzoyl)-amino]-1,3,5-triazinium Hexachloroantimonate (**13m**): In analogy to **13i** from 4-methylbenzoyl chloride (0.77 g, 5.00 mmol). Yield 2.95 g (71%) of a colourless powder; m.p. 121–122°C. – IR: 1660 (shoulder 1690), 1610, 1520 cm^{-1}.

$[C_{29}H_{49}N_6O]SbCl_6$ (832.2) Calcd. C 41.85 H 5.94 N 10.10 Found C 41.78 H 6.17 N 10.05

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(4-methylbenzoyl)-amino]-1,3,5-triazinium Trichlorozincate (**13n**): In analogy to **13m**. Yield 2.51 g (75%); m.p. 133 °C (dec.). – IR: 1700, 1660, 1530 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 20.5, 21.3, 21.8, 22.2, 22.3, 23.2, 23.6, CH 51.1, 54.6, 55.3, 58.3, C=O 172.0, C=N 157.4, 136.2, phenyl 143.2, 130.3, 127.1.

$[C_{29}H_{49}N_6O]ZnCl_3$ (669.5) Calcd. C 52.02 H 7.38 N 12.56 Found C 51.89 H 7.39 N 12.51

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-2-[isopropyl(4-methylbenzoyl)-amino]-1,3,5-triazinium Tetrachloroferrate (**13o**): In analogy to **13m**. Yield 2.92 g (84%) of a yellow powder; m.p. 129–130 °C (dec.). – IR: 1660 (shoulder 1690), 1610, 1530 cm^{-1}.

$[C_{29}H_{49}N_6O]FeCl_4$ (695.4) Calcd. C 50.08 H 7.10 N 12.09 Found C 49.86 H 7.45 N 11.94

2-[(4-Fluorobenzoyl)isopropylamino]-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Hexachloroantimonate (**13p**): In analogy to **13i** from 4-fluorobenzoyl chloride (0.79 g, 5.00 mmol). Yield 3.43 g (82%); m.p. 143–145 °C (dec.). – ^{13}C NMR (CD_2Cl_2, 263 K): CH_3 δ = 20.5, 21.3, 22.1, 22.4, 23.2, 23.5, CH 51.4, 54.8, 55.2, 58.5, C=O 170.6, C=N 156.8, 135.6, phenyl: *p*-C 164.9 (d, *J* = 255 Hz), *m*-C 117.2 (d, *J* = 23 Hz), *o,i*-C 129.1 (d, *J* = 4 Hz), 129.5 (d, *J* = 9 Hz).

$[C_{28}H_{46}FN_6O]SbCl_6$ (836.2) Calcd. C 40.22 H 5.55 N 10.05 Found C 40.12 H 5.55 N 9.86

2-[(4-Fluorobenzoyl)isopropylamino]-3,4,5,6-tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazinium Tetrachloroferrate (**13q**): In analogy to **13p**. Yield 2.83 g (81%) of a yellow powder; m.p. 122–124 °C (dec.). – IR: 1660 (shoulder 1690), 1600, 1520 cm^{-1}.

$[C_{28}H_{46}FN_6O]FeCl_4$ (699.4) Calcd. C 48.08 H 6.63 N 12.02 Found C 47.97 H 6.75 N 12.11

Reaction of Cyclohexylisopropylcarbodiimide with Acetylium Hexachloroantimonate: Formation of **13r**: As described for **13a** from cyclohexylisopropylcarbodiimide (2.50 g, 15.05 mmol). Yield 2.32 g (53%) of a colourless powder; m.p. 113–118 °C (dec.). – IR: 1690, 1660, 1520 cm^{-1}. According to the NMR spectra the substance is a mixture of at least three regioisomers, e.g. ^{13}C NMR (CD_3CN, 263 K): CO δ = 173.5, 173.3, C=N 158.1, 158.2, 158.3, 136.8, 136.9.

$[C_{32}H_{57}N_6O]SbCl_6$ (876.3) Calcd. C 43.86 H 6.56 N 9.59 Found C 44.21 H 6.62 N 9.51

2-(Acetylcyclohexylamino)-1,3,5-tricyclohexyl-4,6-bis(cyclohexylimino)-3,4,5,6-tetrahydro-1,3,5-triazinium Hexachloroantimonate (**13s**): As described for **13a** from dicyclohexylcarbodiimide (3.11 g, 15.05 mmol). The product was precipitated from the reaction mixture with absol. ether (80 ml)/pentane (30 ml). Recrystallization from dichloromethane (10 ml)/pentane afforded colourless needles (4.11 g, 76%); m.p. 132–134 °C (dec.). – IR: 1690, 1660, 1520 cm^{-1}. – ^{13}C NMR (CD_2Cl_2): CH_3, CH_2 δ = 22.8, 24.2, 24.3, 25.3, 25.4, 25.6, 25.9, 26.0, 26.1, 26.7, 27.3, 30.6, 31.6, 32.2, 32.3, 32.9, 33.2, 33.4, 33.7, CH 59.2 (2C), 62.5, 62.9, 67.3 (2C), C=N 157.8, 135.8, C=O 172.0.

$[C_{41}H_{69}N_6O]SbCl_6 \cdot CH_2Cl_2$ (1081.4) Calcd. C 46.64 H 6.62 N 7.77
Found C 46.67 H 6.45 N 7.69

1,3,5-Tricyclohexyl-4,6-bis(cyclohexylimino)-2-[cyclohexyl(trichloroacetyl)amino]-3,4,5,6-tetrahydro-1,3,5-triazinium Hexachloroantimonate (**13t**): In analogy to **13s**. Yield 4.84 g (88%) of colourless fine needles; m.p. 176–182 °C (dec.). – IR: 1700, 1660, 1510 cm^{-1}. – ^{13}C NMR (CD_2Cl_2, 263 K): CCl_3 δ = 90.5, C=O 160.7, C=N 154.5, 135.3.

$[C_{41}H_{66}Cl_3N_6O]SbCl_6$ (1099.8) Calcd. C 44.77 H 6.05 N 7.64 Found C 44.37 H 5.97 N 7.40

1,3,5-Tricyclohexyl-4,6-bis(cyclohexylimino)-2-[cyclohexyl(2-methylpropionyl)amino]-3,4,5,6-tetrahydro-1,3,5-triazinium Hexachloroantimonate (**13u**): In analogy to **13s**. Yield 5.13 g (93%)

of colourless fine needles; m.p. 130–131 °C (dec.). – IR: 1680, 1660, 1510 cm^{-1}. – ^{13}C NMR (CD_2Cl_2): C=O δ = 179.4, C=N 158.0, 135.8.

$[C_{43}H_{73}N_6O]SbCl_6 \cdot CH_2Cl_2$ (1109.5) Calcd. C 47.63 H 6.81 N 7.58
Found C 47.95 H 6.83 N 7.60

2-(Benzoylcyclohexylamino)-1,3,5-tricyclohexyl-4,6-bis(cyclohexylimino)-3,4,5,6-tetrahydro-1,3,5-triazinium Hexachloroantimonate (**13v**): In analogy to **13s**. Yield 4.13 g (78%) of colourless fine needles; m.p. 137–139 °C (dec.). – IR: 1660 (shoulder 1690), 1510 cm^{-1}.

$[C_{46}H_{71}N_6O]SbCl_6$ (1058.6) Calcd. C 52.19 H 6.76 N 7.94 Found C 52.05 H 6.72 N 7.80

4-[(Chloroacetyl)isopropylamino]-1-isopropyl-2,6-bis(isopropylamino)-1,3,5-triazinium Hexachloroantimonate (**15d**): A solution of **13d** (3.95 g, 5.00 mmol) in absol. methanol (20 ml)/dichloromethane (30 ml) was boiled under reflux for 5 h. Addition of ether (60 ml)/pentane (30 ml) afforded a precipitate (1.22 g, 31%), which proved to be starting material (IR, NMR). The filtrate was evaporated under reduced pressure. The residue was dissolved in dichloromethane (5 ml). Addition of ether (30 ml)/pentane (20 ml) gave pale yellow fine needles (0.71 g, 20%); m.p. 190–193 °C (dec.). – IR: 1730, 1640, 1580 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 1.41 (d, *J* = 7 Hz, 12H), 1.43 (d, *J* = 7 Hz, 6H), 1.76 (d, *J* = 7 Hz, 6H), CH_2 4.62, CH 4.35 (m, 2H), 4.79 (sept., *J* = 7 Hz), 4.97 (sept., *J* = 7 Hz), NH 5.80 (d, *J* = 7 Hz, 2H). – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 20.5, 20.9, 22.5 (2C), CH_2, CH 47.1, 47.3, 51.2, 51.7, C=O, C=N 154.6, 161.9, 171.7.

$[C_{17}H_{32}ClN_6O]SbCl_6$ (706.4) Calcd. C 28.90 H 4.57 N 11.90 Found C 28.99 H 4.71 N 11.74

4-(Benzoylisopropylamino)-1-isopropyl-2,6-bis(isopropylamino)-1,3,5-triazinium Hexachloroantimonate (**15k**): A solution of **13k** (4.09 g, 5.00 mmol) in absol. methanol (20 ml)/dichloromethane (10 ml) was boiled under reflux for 4 h. Slow addition of ether (50 ml)/pentane (30 ml) afforded pale yellow fine needles (2.20 g, 60%); m.p. 215–217 °C (dec.). – IR: 1710, 1630, 1560 cm^{-1}. – ^1H NMR (CD_2Cl_2): CH_3 δ = 1.14 (d, *J* = 7 Hz, 12H), 1.47 (d, *J* = 7 Hz), 1.65 (d, *J* = 7 Hz), CH 3.84 (m, 2H), 4.62 (sept., *J* = 7 Hz), 4.96 (sept., *J* = 7 Hz), NH 5.44 (d, *J* = 7 Hz, 2H). – ^{13}C NMR (CD_2Cl_2): CH_3 δ = 20.87, 20.90, 22.1, CH 46.6 (2C), 50.5, 50.9, C=O, C=N 173.7, 161.2, 154.1, phenyl 136.5, 133.5, 129.3, 129.2.

$[C_{22}H_{35}N_6O]SbCl_6$ (734.0) Calcd. C 36.00 H 4.81 N 11.45 Found C 35.93 H 5.01 N 11.28

1-Isopropyl-2,6-bis(isopropylamino)-4-[isopropyl(4-methylbenzoyl)amino]-1,3,5-triazinium Hexachloroantimonate (**15m**): From **13m** (4.16 g, 5.00 mmol) as described for **15k**. Yield 2.73 g (73%) of pale yellow fine needles; m.p. 210–214 °C (dec.). – ^1H NMR (CD_3CN, 263 K): CH_3 δ = 1.05 (d, *J* = 7 Hz, 12H), 1.42 (d, *J* = 7 Hz), 1.48 (d, *J* = 7 Hz), CH 3.82 (m, 2H), 4.38 (sept., *J* = 7 Hz), 4.97 (d, *J* = 7 Hz), NH 6.10 (d, *J* = 7 Hz, 2H), phenyl 7.27 (d, *J* = 8 Hz), 7.61 (d, *J* = 8 Hz).

$[C_{23}H_{37}N_6O]SbCl_6$ (748.1) Calcd. C 36.93 H 4.99 N 11.24 Found C 36.75 H 5.02 N 11.27

4-[(4-Fluorobenzoyl)isopropylamino]-1-isopropyl-2,6-bis(isopropylamino)-1,3,5-triazinium Hexachloroantimonate (**15p**): From **13p** (4.18 g, 5.00 mmol) as described for **15d**. The refluxing time was 10 h. Yield 2.97 g (79%) of pale yellow fine needles; m.p. 215–220 °C (dec.). – IR: 1710, 1630, 1560 (shoulder 1600, 1580) cm^{-1}. – ^{13}C NMR (CD_3CN): CH_3 δ = 19.7, 20.9, 21.8 (4C), CH 46.7 (2C), 50.8, 51.1, C=O, C=N 173.6, 162.4, 155.3, phenyl: *p*-C 166.1 (d, *J* = 252 Hz), *m*-C 116.6 (d, *J* = 23 Hz), *o*-C 132.4 (d, *J* = 10 Hz), *i*-C 134.3 (d, *J* = 3 Hz).

$[C_{22}H_{34}FN_6O]SbCl_6$ (752.0) Calcd. C 35.13 H 4.56 N 11.18 Found C 35.37 H 4.63 N 11.09

2,3-Dihydro-1,3-diisopropyl-4,6-bis(isopropylamino)-2-oxo-1,3,5-triazinium Hexachloroantimonate (**16**, X = $SbCl_6$)

a) A solution of **13m** (4.16 g, 5.00 mmol) in 2-propanol (20 ml)/dichloromethane (15 ml) was boiled under reflux for 14 h. Slow addition of ether (50 ml)/pentane (50 ml) afforded a colourless

precipitate (2.33 g, 74%); m.p. 250–255 °C (dec.). – IR: 1740, 1600, 1580, 1540 cm^{-1}. – ^1H NMR (CD_3CN): CH_3 δ = 1.29 (d, *J* = 6 Hz, 12H), 1.47 (d, *J* = 6 Hz, 12H), CH 4.34 (m, 4H), NH 6.58 (d, *J* = 6 Hz, 2H). – ^{13}C NMR (CD_3CN): CH_3 δ = 19.6, 22.1, CH 46.8, 50.6, C=N 154.2, C=O 148.1.

$[C_{15}H_{30}N_5O]SbCl_6$ (630.9) Calcd. C 28.55 H 4.79 N 11.10 Found C 28.43 H 4.88 N 10.85

The filtrate was evaporated. The residue partly crystallized from dichloromethane (3 ml)/pentane (30 ml) at –78 °C affording colourless needles of *N*-isopropyl-4-methylbenzamide (0.21 g, 24%); m.p. 133–135 °C (Lit.[13] 131–133 °C).

b) A solution of **13k** (4.09 g, 5.00 mmol) in acetonitrile (20 ml) was boiled under reflux for 2 h. Addition of ether (30 ml)/pentane (50 ml) afforded a colourless precipitate (1.67 g, 53%); m.p. 250–255 °C (dec.). According to the NMR spectra, the filtrate contained further **16** (X = $SbCl_6$) and *N*-isopropylbenzamide.

2,3-Dihydro-1,3-diisopropyl-4,6-bis(isopropylamino)-2-oxo-1,3,5-triazinium Chloride (**16**, X = Cl)

a) To **13o** (3.48 g, 5.00 mmol) in methanol (30 ml)/dichloromethane (30 ml) was added at 22 °C a solution of potassium hydroxide (2.81 g, 50.0 mmol) in water (20 ml). The mixture was shaken for 5 min and stirred for additional 10 h at 22 °C. The organic layer was separated, washed with water (5 × 25 ml), dried over sodium sulfate, and evaporated under reduced pressure (A, see **20**). The residue was taken up in pentane (30 ml). Filtration yielded *N*-isopropyl-4-methylbenzamide (0.63 g, 71%); m.p. 133–135 °C. The filtrate was evaporated and the remaining oil dissolved in 0.2 M HCl (30 ml)/dichloromethane (20 ml). The precipitating hydrochloride was filtered off and washed with ether and pentane. Yield 1.49 g (90%) of a colourless powder; m.p. 281–282 °C. – IR: 1730, 1590, 1570 (shoulder 1530) cm^{-1}. – ^1H NMR (CD_3OD): CH_3 δ = 1.31 (d, *J* = 7 Hz), 1.51 (d, *J* = 7 Hz), CH 4.44 (m), NH 8.00 (d, *J* = 7 Hz). – ^{13}C NMR (CD_3OD): CH_3 δ = 19.6, 22.0, CH 47.0, 51.3, C=O, C=N 154.6, 148.5.

$[C_{15}H_{30}N_5O]Cl$ (331.9) Calcd. C 54.28 H 9.11 N 21.11 Found C 53.96 H 9.31 N 21.35

When the same procedure was applied to **13l** (3.41 g, 5.00 mmol) *N*-isopropylbenzamide (0.64 g, 78%) was isolated; m.p. 100–101 °C (Lit.[14] 104–105 °C). From **13q** (3.50 g, 5.00 mmol) 4-fluoro-*N*-isopropylbenzamide (0.69 g, 76%) was obtained; m.p. 117–118 °C (Lit.[13] 118–119 °C). Before treatment with hydrochloric acid the NMR spectra of the reaction mixtures showed the presence of **19**.

b) To a solution of **18** (1.01 g, 3.00 mmol) in dichloromethane (20 ml) was added 0.2 M HCl (10 ml). After shaking for 15 min at 22 °C the organic layer was separated and the aqueous layer extracted with dichloromethane (2 × 10 ml). The combined organic solutions were dried over sodium sulfate and evaporated under reduced pressure. The residue was taken up in dichloromethane (5 ml)/ether (30 ml) affording a colourless powder (0.78 g, 78%); m.p. 280–282 °C.

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-4,6-bis(isopropylimino)-1,3,5-triazin-2(1H)-one (**18**): A mixture of **13o** (3.48 g, 5.00 mmol) in dichloromethane (50 ml) and potassium hydroxide (2.81 g, 5.00 mmol) in water (50 ml) was shaken for 10 h at 22 °C. The organic layer was separated, washed with water (5 × 50 ml), dried over sodium sulfate, and evaporated. The residue was taken up in pentane (50 ml). Filtration yielded *N*-isopropyl-4-methylbenzamide (0.82 g, 92%); m.p. 134–135 °C. The filtrate was evaporated leaving a colourless oil, which soon crystallized (1.62 g, 92%). The compound was purified by sublimation; m.p. 65–66 °C. – IR: 1650 cm^{-1}. – ^1H NMR ($CDCl_3$): CH_3 δ = 1.03 (d, *J* = 6 Hz), 1.11 (d, *J* = 7 Hz), 1.14 (d, *J* = 7 Hz), 1.38 (d, *J* = 6 Hz), 1.40 (d, *J* = 6 Hz), CH 3.25 (sept., *J* = 6 Hz, 1H), 4.20 (sept., *J* = 6 Hz, 2H), 4.87 (sept.,

J = 7 Hz, 2H). – ^{13}C NMR ($CDCl_3$): CH_3 δ = 19.0 (broad), 20.6 (broad), 20.7, 23.9 (broad), 24.5 (broad), CH 47.4, 48.2, 54.9, C=O 152.4, C=N 141.7.

$C_{18}H_{35}N_5O$ (337.5) Calcd. C 64.05 H 10.45 N 20.76 Found C 64.12 H 10.60 N 21.01

3,4,5,6-Tetrahydro-1,3,5-triisopropyl-2-(isopropylamino)-6-(isopropylimino)-4,4-dimethoxy-1,3,5-triazinium Picrate (**20**): From **13j** (3.24 g, 5.00 mmol) as described for **16** (X = Cl) till A. The oily product was dissolved in dichloromethane (20 ml). The solution was shaken for 3 h with a solution of picric acid (1.00 g) in methanol (10 ml)/water (10 ml). The organic layer was separated and washed with water (3 × 20 ml), dried over sodium sulfate, and evaporated. The residue was washed with pentane (15 ml). Yield 2.11 g (69%) of an yellow powder; m.p. 112–113 °C. – ^{1}H NMR ($CDCl_3$): CH_3 δ = 1.17 (d, J = 6 Hz, 12H), 1.36 (d, J = 6 Hz, 6H), 1.41 (d, J = 7 Hz, 6H), 1.61 (broad, 6H), 3.38 (broad), CH 3.49 (m, broad), 3.68 (m, broad), 4.01 (m, broad), 4.12 (sept., J = 7 Hz), 5.00 (m, broad), NH 8.65, phenyl 8.84. – ^{13}C NMR ($CDCl_3$): OCH_3 δ = 58.4, OCO 112.3, C=N, aryl 161.8, 158.0 (C6 ?), 142.0, 140.0 (C2 ?), 126.8, 126.1.

$[C_{20}H_{42}N_5O_2][C_6H_2N_3O_7]$ (612.7) Calcd. C 50.97 H 7.24 N 18.29
Found C 50.88 H 7.33 N 18.11

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[102/84]