# Cyclization Reactions of Chloro-Substituted 2-Azoniaallene Salts with Bifunctional Nucleophiles

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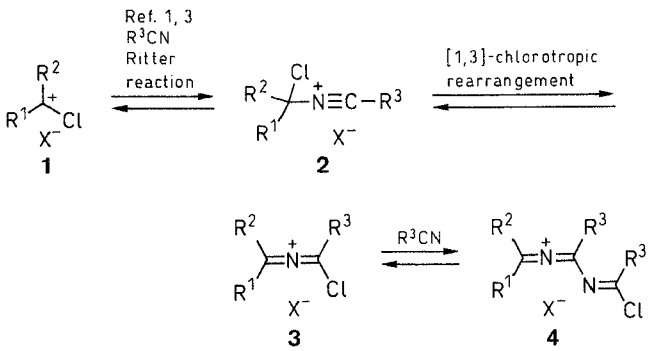
The multifunctional electrophilic chloro-substituted 2-azoniaallene salts **3–5** react with bifunctional nucleophiles under cyclization to furnish heterocycles. Preparations of the 1,2,3,4-tetrahydro-1,3-dimethyl-2,4-dioxopyrimido[4,5-*d*]pyrimidines **7a,b, 10a,b, 14, 17a,b,** and the 5,6,7,8-tetrahydro-6,8-dimethyl-5,7-dioxopyrimido[5,4-*e*]-1,3-oxazin-1-ium salts **9a,b, 15,** first representatives of a new ring system, are reported. Furthermore, the 2,3-dihydro-1,3-dimethyl-4-(methylthio)-2-oxo-1,3,5-triazinium salts **11d,e, 13,** and 3-(dimethylamino)-4,5-dihydro-5-oxo-2-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium hexachloroantimonate **(12)** are obtained.

The Ritter reaction of amino substituted α-chlorocarbenium salts **1** ($R^1 = R^4R^5N$), e.g. of Vilsmeier–Arnold reagents ($R^2$ = H), with nitriles affords nitrilium salts **2**, which rearrange to 1-amino-3-chloro-substituted 2-azoniaallene salts **3**. Preparations and reactions of these salts, which have also been named 3-chloro-2-aza-2-propenimi-nium salts, have been reviewed by Liebscher.[1,2]




**1** **2** **3** **4**

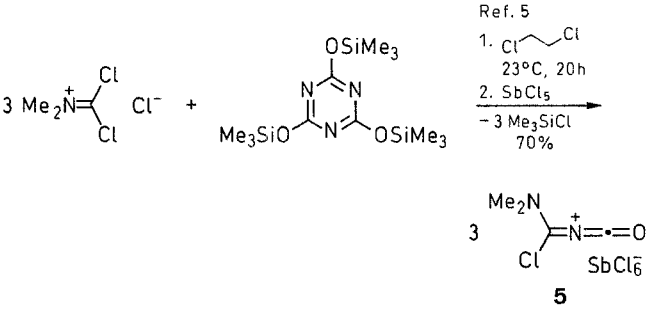
| 3, 4, 7, 9–11 | $R^2$ | $R^3$ | 3, 4, 7, 9–11 | $R^2$ | $R^3$ |
|---|---|---|---|---|---|
| **a** | Ph | Ph | **d** | SMe | 4-$ClC_6H_4$ |
| **b** | 4-$ClC_6H_4$ | 4-$ClC_6H_4$ | **e** | SMe | SMe |
| **c** | 4-$ClC_6H_4$ | SMe | | | |

$R^1$ = Cl; X = $SbCl_6$

**Scheme 1**

We reported that the tandem-Ritter [1,3]-chlorotropic rearrangement sequence of salts **1** can be generalized. Instead of stabilizing cations **1** with an amino group $R^1$, we successfully used other substituents, e.g., aryl.[3] By this method the salts **3a, b** have been prepared. The cations **3**, which are themselves α-chlorocarbenium ions, react with electron-rich nitriles to furnish products **4**.[3,4] Thus, with methyl thiocyanate and the dichlorocarbenium salts **1b** the hexachloroantimonate **4c** is obtained.

Related to compounds **3** is the 1-oxa-3-azoniabutatriene salt **5**, which has been prepared by the following route.[5]




**5**

**Scheme 2**

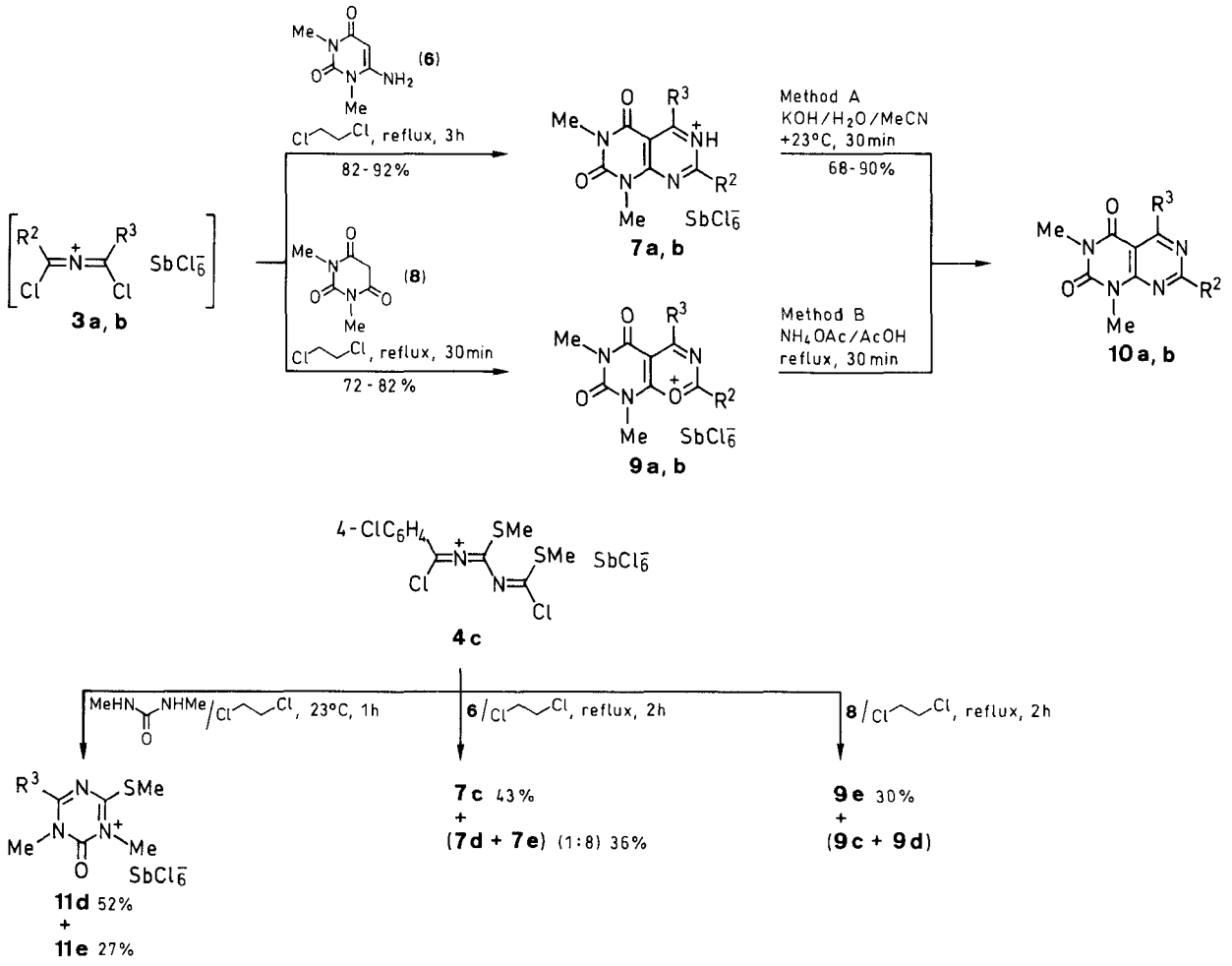
Chloro-substituted 2-azoniaallene salts **3–5** are strong bifunctional (trifunctional in the case of **4**) electrophiles, which should undergo cyclization reactions with molecules with two nucleophilic centers. Here, I report such cyclizations of the salts **3a,b,4c,** and **5**.

Reactions of the cumulenes **3a, b** ($R^2 = R^3$) with 6-amino-1,3-dimethyluracil **(6)** or 1,3-dimethylbarbituric acid **(8)** afford the heterocycles **7a,b** and **9a,b**, respectively.

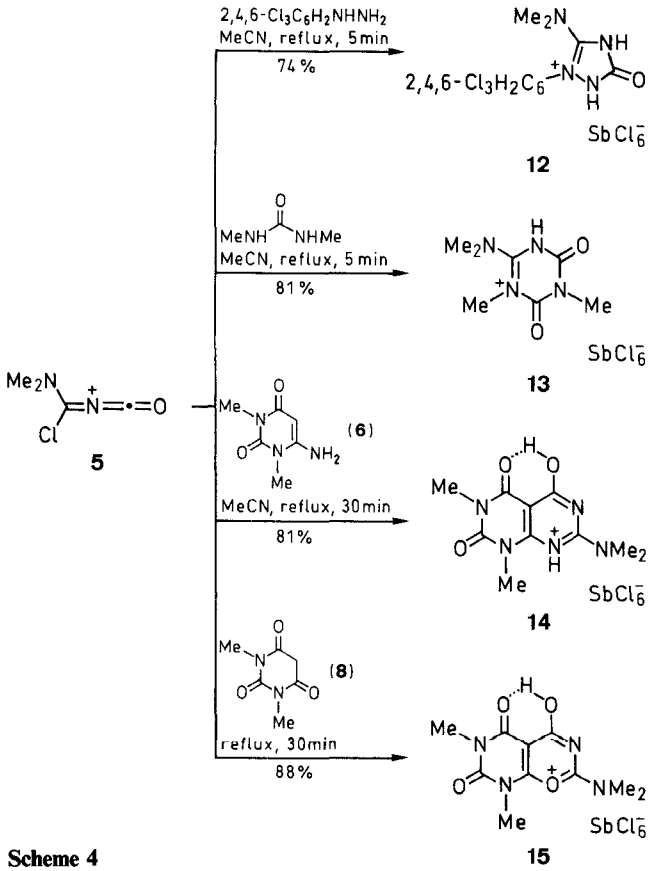
While several syntheses of pyrimido[4,5-*d*]pyrimidines are known[6–23] the ring system **9** is unreported in the literature, to the best of my knowledge. Treatment of **7a,b** with aqueous potassium hydroxide yields the free bases **10a,b**. These compounds are also obtained from the heterocycles **9a,b** on reaction with ammonium acetate in boiling acetic acid.

Reactions of **4c** with uracil derivative **6**, barbituric acid **8**, and 1,3-dimethylurea, respectively, do not give the expected eight-membered rings. Instead, mixtures of six-membered heterocycles **7c–e**, **9c–e**, and **11d,e** are formed. This can be rationalized considering the reversibility of the reaction sequence of Scheme 1, that is, compound **4c** can reversibly lose either 4-chlorobenzonitrile or methyl thiocyanate. The resulting 1,3-dichloro-substituted 2-azoniaallene salts then react with the nucleophile to afford the products mentioned above. Addition–elimination sequences starting with attack of the nucleophile with comparable probability either on the $R^2C$ or the $R^3C$ carbon atoms of **4c** seem less likely because the electrophilicity of the $R^2C$ carbon atom should be much more pronounced than that of the $R^3C$ groups.

The cumulene **5** reacts with 2,4,6-trichlorophenylhydrazine to afford the triazolium salt **12**. With 1,3-dimethylurea the triazinium salt **13** is obtained, while the uracil **6** furnishes the bicyclus **14**. Finally, the barbituric acid **8** is transformed into the bicycle **15**. The structures are substantiated by the $^1H$, $^{13}C$ NMR, the IR spectra (Table), and the elemental analyses. Problematic are the

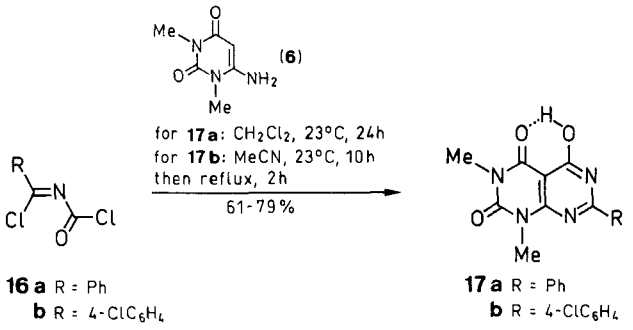


Scheme 3



Scheme 4

assignments to the regioisomers **7c,d** and **9c,d**, which are based on comparison of the $^1$H NMR spectra with those of the bases **17a,b**.[16,19,20] The known compounds **17a,b** are obtained from the reaction of **16a,b**[4] with uracil **6**.



Scheme 5

Compounds **17** show resonances (in DMSO-$d_6$) for the aryl protons between $\delta = 7.4$ and 7.6. This range seems to be specific for an aryl group in 7-position. In agreement herewith the $^1$H NMR spectra of the structurally related salts **7a,b** and **9a,b** show signals for a 7-aryl substituent around $\delta = 7.5$. However, for the aryl group in 5-position a resonance corresponding to two protons is shifted down-field ($\delta = > 8.3$ see Table 1) due to the deshielding effect of the carbonyl group in 4-position. The other

**Table.** Selected NMR and IR Data for the Compounds Prepared[a]

| Product[a] | Molecular Formula | $^1$H NMR ($CD_3CN$/TMS) $\delta$, $J$ (Hz) | $^{13}$C NMR ($CD_3CN$/TMS) | IR (KBr) $\nu$ ($cm^{-1}$) |
|---|---|---|---|---|
| **4c** | $C_{11}H_{10}Cl_9N_2S_2Sb$ (675.2) | 2.80, 2.89 ($CH_3$), 7.66 (m), 8.17 (m) (aryl)[b] | 18.9, 20.6 ($CH_3$), 130.9, 131.0, 133.9, 144.4 (phenyl), 156.6, 170.0, 190.0 (C=N)[b] | 1543, 1589,[c] 1636 |
| **7a** | $C_{20}H_{17}Cl_6N_4O_2Sb$ (679.8) | 3.20, 3.67 ($CH_3$), 7.46–7.63 (8H), 8.44–8.48 (m, 2H) (phenyl)[d] | 28.0, 29.5 ($CH_3$), 104.0 (C4a), 127.1, 128.5, 129.0, 129.1, 131.9, 135.9, 138.5 (phenyl), 150.7, 157.6, 159.0, 163.7, 168.8 (C=O, C=N, C8a)[d, e] | 1570, 1612, 1690, 1736, 3262 |
| **7b** | $C_{20}H_{15}Cl_8N_4O_2Sb$ (748.7) | 3.30, 3.84 ($CH_3$), 7.67–7.76 (6H), 8.27–8.30 (m, 2H) (aryl), 11.95 (NH)[f] | – | 1528, 1563, 1598, 1694, 1752 |
| **7c** | $C_{15}H_{14}Cl_7N_4O_2SSb$ (684.3) | 2.82 ($SCH_3$), 3.25, 3.73n ($NCH_3$), 7.53–7.62 (aryl), 8.29 (NH)[f] | 15.3 ($SCH_3$), 29.3, 31.6 ($NCH_3$), 103.6 (C4a), 129.5, 129.7, 131.8, 138.8 (aryl), 151.0, 158.5, 158.9, 163.0, 171.9 (C=O, C=N, C8a)[f] | 1520, 1582, 1690, 1740 |
| **7d** | $C_{15}H_{14}Cl_7N_4O_2SSb$ (684.3) | 2.63 ($SCH_3$), 3.43, 3.70 ($NCH_3$), 7.41–7.49 (m, 2H), 8.36–8.39 (m, 2H) (aryl)[g] | 14.1 ($SCH_3$), 28.2, 29.7 ($NCH_3$), 102.7 (C4a), 128.8, 130.3, 134.6, 138.6 (aryl), 150.9, 156.4, 160.2, 162.5, 175.0 (C=O, C=N, C8a)[g] | – |
| **7e** | $C_{10}H_{13}Cl_6N_4O_2S_2Sb$ (619.9) | 2.50, 2.58 ($SCH_3$), 3.39, 3.57 ($NCH_3$)[g] | 14.0, 14.4 ($SCH_3$), 28.1, 29.6 ($NCH_3$), 100.6 (C4a), 150.8, 155.4, 160.2, 173.9, 174.8 (C=O, C=N, C8a)[g] | – |
| **9a** | $C_{20}H_{16}Cl_6N_3O_3Sb$ (680.8) | 3.40, 3.91 ($CH_3$), 7.62–8.18 (8H), 8.54–8.58 (m, 2H) (phenyl)[f] | 30.2, 32.3 ($CH_3$), 103.5 (C4a), 126.8, 129.6, 131.2, 132.5, 133.5, 134.2, 137.5, 139.4 (phenyl), 148.4, 157.0, 162.6, 165.2, 176.8 (C=O, C=N, C8a)[f] | 1549, 1589, 1632, 1709, 1760[h] |
| **9b** | $C_{20}H_{14}Cl_8N_3O_3Sb$ (749.7) | 3.41, 3.89 ($CH_3$), 7.65–8.16 (6H), 8.50–8.53 (m, 2H) (aryl)[f] | 30.3, 32.4 ($CH_3$), 103.7 (C4a), 125.5, 130.0, 131.6, 132.6, 134.0, 135.2, 143.8, 145.9 (aryl), 148.4, 157.0, 161.9, 165.2, 175.2 (C=O, C=N, C8a) | 1543, 1582, 1636, 1702, 1756 |
| **9c** | $C_{13}H_{13}Cl_7N_3O_3SSb$[i] (661.3) | 3.15, 3.26, 3.64 ($CH_3$), 7.31–7.45 (aryl)[i] | | |
| **9d** | $C_{13}H_{13}Cl_7N_3O_3SSb$[i] (661.3) | 7.71 (m, 2H), 8.25 (m, 2H) (aryl)[i] | | |
| **9e** | $C_{10}H_{12}Cl_6N_3O_3S_2Sb$ (620.8) | 2.86, 2.92 ($SCH_3$), 3.38, 3.62 ($NCH_3$)[j] | 16.5, 19.2 ($SCH_3$), 29.6, 31.5 ($NCH_3$)[j] | 1531, 1624, 1682, 1748 |
| **10a** | $C_{20}H_{16}N_4O_2$ (344.3) | 3.46, 3.90 ($CH_3$), 7.53–7.72 (8H), 8.61–8.65 (m, 2H) (phenyl)[g] | 28.5, 29.8 ($CH_3$), 103.7 (C4a), 127.6, 128.5, 129.1, 129.2, 129.8, 132.1, 136.2, 138.4 (phenyl), 151.2, 157.9, 159.5, 165.2, 170.4 (C=O, C=N, C8a)[g] | 1675, 1721[h] |
| **10b** | $C_{20}H_{14}Cl_2N_4O_2$ (413.2) | 3.49, 4.00 ($CH_3$), 7.50–7.69 (6H), 8.28–8.32 (m, 2H) (aryl)[k] | 30.3, 32.2 ($CH_3$), 105.4 (C4a), 127.1, 127.2, 130.4, 130.8, 131.6, 131.9, 141.9, 145.6 (aryl), 151.4, 158.8, 160.6, 161.7, 164.9(?) (C=O, C=N, C8a)[k] | 1675, 1721[h] |
| **11d** | $C_{12}H_{13}Cl_7N_3OSSb$ (617.2) | 2.87 ($SCH_3$), 3.67, 3.70 ($NCH_3$), 7.67–7.91 (4H) (aryl)[l] | 17.2 ($SCH_3$), 34.9, 38.6 ($NCH_3$), 129.6, 130.6, 132.7, 141.6 (aryl), 147.9, 167.5, 181.4 (C=O, C=N)[l] | 1520, 1570,[j] 1589,[j] 1756 |
| **11e** | $C_7H_{12}Cl_6N_3OS_2Sb$ (552.8) | 2.87 ($SCH_3$), 3.62 ($NCH_3$)[j] | 16.9 ($SCH_3$), 34.4 ($NCH_3$)[j] | 1520, 1760 |
| **12** | $C_{10}H_{10}Cl_9N_4OSb$ (643.1) | 3.11 ($CH_3$), 7.74 (aryl), 9.7 (NH)[f, n] | 39.6 ($CH_3$), 128.7, 130.7, 138.2, 139.5 (aryl), 150.3, 153.2 (C=O, C=N)[f] | 1709, 1767 |
| **13** | $C_7H_{13}Cl_6N_4O_2Sb$ (519.7) | 3.14, 3.18, 3.21, 3.30 ($CH_3$), 8.30 (NH)[f] | 29.7, 30.4, 37.6, 39.0 ($CH_3$), 147.9, 153.1, 156.7 (C=O, C=N)[f] | 1648, 1698 |
| **14** | $C_{10}H_{14}Cl_6N_5O_3Sb$ (586.7) | 3.20, 3.23, 3.48, 3.55 ($CH_3$), 8.03, 10.73 (NH)[f] | 31.4, 32.0, 37.6, 39.1 ($CH_3$), 83.8 (C4a), 147.7, 154.6, 158.2, 160.7, 165.5 (C=O, C=N, C8a)[f] | 1571, 1667, 1744, ≈3200[n] |
| **15** | $C_{10}H_{13}Cl_6N_4O_4Sb$ (587.7) | 3.34, 3.39, 3.40, 3.58 ($CH_3$), 9.41 (NH)[f] | 29.2, 31.2, 39.2, 40.4 ($CH_3$), 85.0 (C4a), 149.1, 156.5, 162.0, 162.2, 170.8 (C=O, C=N, C8a)[f] | 1698, 1756[h, j] |
| **17a** | $C_{14}H_{12}N_4O_3$ (284.3) | 3.12, 3.47 ($CH_3$), 7.43–7.54 (phenyl), 12.45 (OH)[d] | 27.6, 29.3 ($CH_3$)[d] | 1567, 1598, 1679 |
| **17b** | $C_{14}H_{11}ClN_4O_3$ (318.7) | 3.10, 3.45 ($CH_3$), 7.45–7.54 (aryl), 12.31 (OH)[d, e] | 27.6, 29.3 ($CH_3$)[d, e] | 1563,[j] 1590, 1682 |

[a] Satisfactory microanalyses obtained: C ±0.39, H ±0.24, N ±0.28.
[b] At 50°C.
[c] Shoulder.
[d] In DMSO-$d_6$.
[e] At 70°C.
[f] In $CD_3CN$ at 27°C.
[g] In $CDCl_3$ at 27°C.
[h] In $CH_2Cl_2$.
[i] Compound not isolated. In $CDCl_3/CD_3CN$ (1:1).
[j] In $CD_3CN/CD_3NO_2$ (1:1) at 60°C; the substance is sparingly soluble.
[k] In $CF_3COOD/CDCl_3$ (1:1).
[l] In $CD_3CN$ at 40°C.
[m] At 0°C.
[n] Broad.

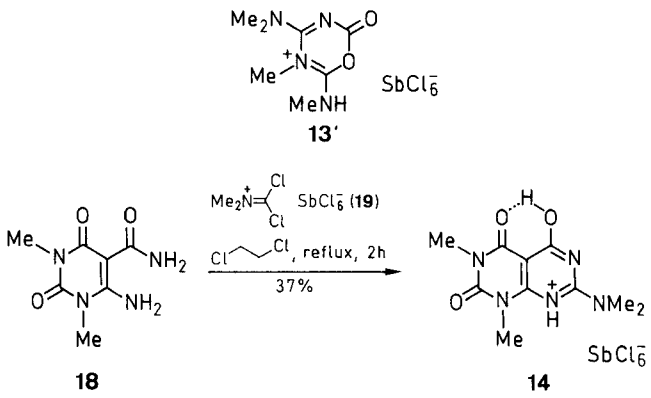
proton resonances for the 5-aryl group again appear in a narrow range around $\delta = 7.5$. Low-field signals around $\delta = 8.3$ corresponding to two protons are also observed for the salts **7d** and **9d**, which accordingly must bear an aryl substituent in 5-position. On the other hand, compounds **7c** and **9c** show only aryl resonances close to $\delta = 7.5$, which are assigned to 7-aryl groups.

For compound **13** an alternative oxadiazinium structure **13'** may be discussed. However, $^1$H-decoupling experi-

ments show the absence of any $HNCH_3$ coupling. It is unlikely that the site of protonation in **13'** should be the amide nitrogen atom in preference to the more basic exocyclic amidine N.

The reaction of **5** with the aminouracil **6** could in principial lead to two regioisomers. However, only a single compound is formed. The structural assignment **14** is based on an independent synthesis from uracil **18** with the phosgene iminium salt **19**, which affords a product in low yield showing NMR and IR spectra identical to those of **14**. In the $^1H$ NMR spectrum ($CD_3CN$) of compound **14** signals at $\delta = 10.73$ and 8.03 are tentatively assigned to OH and NH. It is known that acetic anhydride[24] or isocyanates,[25,26] acylate 6-aminouracil at C5, and not at the amino group. Furthermore, the carbonyl group of **5** is more electrophilic than the amidine carbon atom. Nucleophilic attack occurs exclusively on C=O of **5**.[27-35] The structural assignment of **12** is also based on this argument.

Similarly, the reaction of **5** with the barbituric acid **8** affords a single regioisomer, to which structure **15** is assigned, because it is well known that **8** is attacked by nucleophiles on C5.[36-43]




**Scheme 6**

All solvents were dried by standard methods. All experiments were carried out with exclusion of moisture. The following instruments are used. IR – Mattson Polaris FT-IR spectrophotometer; $^1H$ and $^{13}C$ NMR – Bruker WM-250 and AC-250 spectrometers. The melting points are uncorrected.

**1-Chloro-3-[chloro(methylthio)methyleneamino]-1-(4-chlorophenyl)-3-(methylthio)-2-azoniaallene Hexachloroantimonate (4c):**[4]
A solution of $SbCl_5$ (2.99 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added dropwise with stirring to a cold (−30 °C) solution of trichloro(4-chlorophenyl)methane (2.29 g, 10 mmol) in $ClCH_2CH_2Cl$ (40 mL). An orange precipitate was formed. After stirring at −30 °C for 10 min a solution of methyl thiocyanate (1.46 g, 20 mmol) in $ClCH_2CH_2Cl$ (80 mL) was added. The mixture was warmed to 23 °C within 30 min and then boiled under reflux for 30 min. Evaporation of the solvent and crystallization of the residue at −20 °C from $ClCH_2CH_2Cl$ (20 mL) afforded yellow needles (4.26 g, 63%), which can be recrystallized from $CH_2Cl_2$ (60 mL); mp 164–166 °C.

**1,2,3,4-Tetrahydro-1,3-dimethyl-2,4-dioxo-5,7-diphenylpyrimido[4,5-*d*]pyrimidin-6-ium Hexachloroantimonate (7a):**
A solution of $SbCl_5$ (2.99 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added dropwise at −30 °C to a stirred solution of trichloro(phenyl)methane (1.96 g, 10 mmol) and benzonitrile (1.03 g, 10 mmol) in $ClCH_2CH_2Cl$ (50 mL). After warming to +23 °C the mixture was boiled under reflux for 10 min. After cooling to +23 °C a suspension of **6** (1.55 g, 10 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added to the mixture. Boiling under reflux for 3 h and evaporation of the solvent afforded a pale yellow powder (5.55 g, 82%), which could be recrystallized from hot MeCN to give colorless prisms; mp 249–251 °C.

**5,7-Bis(4-chlorophenyl)-1,2,3,4-tetrahydro-1,3-dimethyl-2,4-dioxopyrimido[4,5-*d*]pyrimidin-6-ium Hexachloroantimonate (7b):**
From trichloro(4-chlorophenyl)methane (2.30 g, 10 mmol) and 4-chlorobenzonitrile (1.38 g, 10 mmol) as described for **7a**. Yield: 6.88 g (92%) of a pale yellow powder; mp 260–263 °C (dec). Crystallization from hot MeCN or DMF affords the base **10b**; mp 284–285 °C.

**7-(4-Chlorophenyl)-1,2,3,4-tetrahydro-1,3-dimethyl-5-(methylthio)-2,4-dioxopyrimido[4,5-*d*]pyrimidin-6-ium Hexachloroantimonate (7c):**
From trichloro(4-chlorophenyl)methane (2.30 g, 10 mmol), methyl thiocyanate (1.46 g, 20 mmol) and **6** (1.55 g, 10 mmol), as described for **7a**. The mixture was boiled under reflux for 2 h. Crystallization of the oily product from MeCN (20 mL) afforded a mixture of **7d** and **7e** (2.24 g, 36%) in ratio 1:8 according to the $^1H$ NMR spectrum. Evaporation of the solvent from the mother liquor and precipitation of the residue from $CH_2Cl_2$ (10 mL)/$Et_2O$ (20 mL) afforded **7c** as a yellow powder (2.92 g, 43%); mp 152–155 °C (dec).

**5,6,7,8-Tetrahydro-6,8-dimethyl-2,4-diphenyl-5,7-dioxopyrimido[5,4-*e*]-1,3-oxazin-1-ium Hexachloroantimonate (9a):**
A suspension of **8** (1.56 g, 10 mmol) and **3a** prepared in situ as described for **7a** in $ClCH_2CH_2Cl$ (50 mL) was boiled under reflux for 30 min. After cooling to 23 °C a pale yellow powder (4.88 g, 72%) was filtered off; mp 240–243 °C (dec). Recrystallization from hot MeCN furnished yellow prisms.

**2,4-Bis(4-chlorophenyl)-5,6,7,8-tetrahydro-6,8-dimethyl-5,7-dioxopyrimido[5,4-*e*]-1,3-oxazin-1-ium Hexachloroantimonate (9b):**
From **3b** (6.67 g, 10 mmol) as described for **9a**. Yield: 6.18 g (82%) of a pale yellow powder, which could be recrystallized from hot MeCN to afford yellow prisms; mp 265–269 °C (dec).

**5,6,7,8-Tetrahydro-6,8-dimethyl-2,4-bis(methylthio)-5,7-dioxopyrimido[5,4-*e*]-1,3-oxazin-1-ium Hexachloroantimonate (9c):**
From **4c** prepared from trichloro(4-chlorophenyl)methane (2.30 g, 10 mmol), methyl thiocyanate (1.46 g, 20 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in situ, and **8** (1.56 g, 10 mmol) as described for **9a**. The mixture was boiled under reflux for 2 h. After cooling to +23 °C a yellow powder (5.36 g) was filtered off. Crystallization from hot MeCN (70 mL) gave yellow prisms (1.86 g, 30%); mp 250–251 °C (dec). Evaporation of the solvent from the mother liquor and addition of $CH_2Cl_2$ (20 mL) to the oily residue afforded a mixture of compounds. According to the $^1H$ NMR spectrum ($CD_3CN$) this mixture consisted of **9c–e** and unidentified products.

**1,2,3,4-Tetrahydro-1,3-dimethyl-5,7-diphenylpyrimido[4,5-*d*]pyrimidine-2,4-dione (10a):**
Method A: A solution of KOH (16.83 g, 300 mmol) in $H_2O$ (50 mL) was added at +23 °C to a stirred suspension of **7a** (6.80 g, 10 mmol) in MeCN (50 mL). After stirring for 30 min the organic compound was extracted with $CH_2Cl_2$ (3 × 100 mL). Drying ($Na_2SO_4$) and evaporation of the solvent afforded a pale yellow powder, which was reprecipitated from $CH_2Cl_2$ (50 mL)/$Et_2O$ (100 mL). Yield: 3.11 g (90%); mp 224–226 °C (ref[23]: 230 °C).

Method B: A mixture of **9a** (6.81 g, 10 mmol) and $NH_4OAc$ (3.85 g, 50 mmol) in AcOH (25 mL) was boiled under reflux for 30 min. After cooling and neutralization with $NaHCO_3$ in $H_2O$ (200 mL) the mixture was extracted with $CH_2Cl_2$ (2 × 100 mL). Work-up furnished a pale yellow powder (1.58 g, 46%); mp 220–225 °C.

**5,7-Bis(4-chlorophenyl)-1,2,3,4-tetrahydro-1,3-dimethylpyrimido[4,5-*d*]pyrimidine-2,4-dione (10b):**
Method A: From **7b** (7.48 g, 10 mmol) as described for **10a**. Yield: 2.79 g (68%) of a pale yellow powder, which can be recrystallized from hot DMF to furnish colorless leaflets; mp 284–285 °C.

Method B: From **9b** (7.50 g, 10 mmol) as described for **10a**. Yield: 2.46 g (60%) of a pale yellow powder; mp 275–280°C.

**4-(4-Chlorophenyl)-2,3-dihydro-1,3-dimethyl-6-(methylthio)-2-oxo-1,3,5-triazin-1-ium Hexachloroantimonate (11d) + 2,3-Dihydro-1,3-dimethyl-4,6-bis(methylthio)-2-oxo-1,3,5-triazin-1-ium Hexachloroantimonate (11e):**
A mixture of **4c** (6.75 g, 10 mmol) and 1,3-dimethylurea (0.88 g, 10 mmol) in $ClCH_2CH_2Cl$ (30 mL) was stirred at +23°C for 1 h. Filtration and washing of the precipitate with MeCN (10 mL)/$ClCH_2CH_2Cl$ (10 mL) gives **11e** as a colorless powder (1.51 g, 27%); mp 255–256°C (dec). Recrystallization from hot MeCN gives colorless needles. The mother liquor of the preparation of **11e** was evaporated under reduced pressure. The residue crystallized on washing with $CH_2Cl_2$ (10 mL). Yield of **11d**: 3.23 g (52%) of a colorless powder. Crystallization from hot MeCN affords colorless prisms; mp 190–192°C (dec).

**3-(Dimethylamino)-4,5-dihydro-5-oxo-2-(2,4,6-trichlorophenyl)-1*H*-1,2,4-triazol-2-ium Hexachloroantimonate (12):**
A solution of **5** (4.68 g, 10 mmol) and 2,4,6-(trichlorophenyl)hydrazine (2.11 g, 10 mmol) in MeCN (30 mL) was boiled under reflux for 5 min. Filtration from an impurity and evaporation of the filtrate left back an oily residue, which crystallized at −20°C from $CH_2Cl_2$ (10 mL)/pentane (2 mL). Yield: 4.76 g (74%) of pale yellow fine crystals; mp 205–207°C (dec).

**6-(Dimethylamino)-2,3,4,5-tetrahydro-1,3-dimethyl-2,4-dioxo-1,3,5-triazin-1-ium Hexachloroantimonate (13):**
From **5** (4.68 g, 10 mmol) and 1,3-dimethylurea (0.88 g, 10 mmol) as described for **12**. Evaporation of the filtrate afforded a colorless powder (4.21 g, 81%); mp 203–207°C (dec). Reprecipitation from MeCN/$Et_2O$ afforded a colorless powder.

**7-(Dimethylamino)-1,2,3,4-tetrahydro-5-hydroxy-1,3-dimethyl-2,4-dioxopyrimido[4,5-*d*]pyrimidin-8-ium Hexachloroantimonate (14):**
a) A solution of **5** (4.68 g, 10 mmol) and **6** (1.55 g, 10 mmol) in MeCN (40 mL) was refluxed for 30 min. After cooling to 23°C and slow addition of $Et_2O$ (100 mL) a buff powder (4.76 g, 81%) was filtered off; mp 210–213°C (dec). Reprecipitation from MeCN/$Et_2O$ afforded a colorless powder.

b) A mixture of **18**[44] (1.98 g, 10 mmol) and **19** (4.61 g, 10 mmol, prepared from the chloride[45] with $SbCl_5$) in $ClCH_2CH_2Cl$ (60 mL) was boiled under reflux for 2 h. After cooling to 23°C a pale yellow powder was filtered off (2.19 g, 37%).

**2-(Dimethylamino)-5,6,7,8-tetrahydro-4-hydroxy-6,8-dimethyl-5,7-dioxopyrimido[5,4-*e*]-1,3-oxazin-1-ium Hexachloroantimonate (15):**
From **6** (1.56 g, 10 mmol) as described for **14**. Yield: 5.22 g (88%) of a buff powder, which could be reprecipitated from MeCN/$Et_2O$; mp 209–211°C (dec).

**1,2,3,4-Tetrahydro-5-hydroxy-1,3-dimethyl-7-phenylpyrimido[4,5-*d*]-pyrimidine-2,4-dione (17a):**
A solution of **16a**[4] (2.02 g, 10 mmol) in $CH_2Cl_2$ (10 mL) was added to a suspension of **6** (1.55 g, 10 mmol) in $CH_2Cl_2$ (30 mL). After stirring for 24 h at 23°C the solvent was evaporated and the residue was crystallized from MeCN (40 mL) at −20°C. Yield: 1.74 g (61%) of a colorless powder; mp > 300°C).

**7-(4-Chlorophenyl)-1,2,3,4-tetrahydro-5-hydroxy-1,3-dimethylpyrimido[4,5-*d*]pyrimidine-2,4-dione (17b):**
A mixture of **16b**[4] (2.37 g, 10 mmol) and **6** (1.55 g, 10 mmol) in MeCN (40 mL) was stirred at 23°C for 10 h and then boiled under reflux for 2 h. After cooling to 23°C a colorless powder was filtered off (2.52 g, 79%); mp > 300°C).

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(1) Liebscher, J. *Synthesis* **1988**, 655.
(2) The nomenclature of 2-azoniaallene salts has been discussed by Jochims et al. Ref. 3.
(3) Jochims, J.C.; Hamed, A.; Huu-Phuoc, T.; Hofmann, J.; Fischer, H. *Synthesis* **1989**, 918.
(4) Ismail, A.; Jochims, J.C., unpublished results.
(5) Hamed, A.; Müller, E.; Jochims, J.C. *Tetrahedron* **1986**, *42*, 6656.
(6) Mautner, H.G. *J. Org. Chem.* **1958**, *23*, 1450.
(7) Chatterji, C.K.; Anand, N. *J. Sci. Ind. Res.* **1958**, *17B*, 63.
(8) Chatterji, C.K.; Anand, N. *J. Sci. Ind. Res.* **1959**, *18B*, 272.
(9) Taylor, E.C.; Knopf, R.J.; Meyer, R.F.; Holmes, A.; Hoefle, M.L. *J. Am. Chem. Soc.* **1960**, *82*, 5711.
(10) Druey, J.; Schmidt, P.; Eichenberger, K.; Wilhelm, M.; CIBA Corp. U.S. Patent 3055900, 1962; *Chem. Abstr.* **1963**, *59*, 8763.
(11) Bredereck, H.; Effenberger, F.; Suter, R. *Chem. Ber.* **1962**, *95*, 2049.
(12) Taylor, E.C.; McKillop, A.; Vromen, S. *Tetrahedron* **1967**, *23*, 885.
(13) Bredereck, H.; Simchen, G.; Traut, H. *Chem. Ber.* **1967**, *100*, 3664.
(14) Grabeyes, H.; Jaffe, G.E.; Pachter, I.J.; Rosenbloom, J.P.; Villani, A.J.; Wilson, J.W.; Weinstock, J. *J. Med. Chem.* **1968**, *11*, 568.
(15) Bredereck, H.; Simchen, G.; Wahl, R.; Effenberger, F. *Chem. ber.* **1968**, *101*, 512.
(16) Yoneda, F.; Higuchi, M. *J. Chem. Soc., Chem. Commun.* **1972**, 402.
(17) Yoneda, F.; Higuchi, M. *Chem. Pharm. Bull.* **1972**, *20*, 2076.
(18) Stegman, R.J.; Senft, A.W.; Brown, P.R.; Parks, R.E. *Biochem. Pharmacol.* **1973**, *22*, 459.
(19) Yoneda, F.; Higuchi, M.; Senga, K.; Kanahori, M.; Nishigaki, S. *Chem. Pharm. Bull.* **1973**, *21*, 473.
(20) Yoneda, F.; Higuchi, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3849.
(21) Grohe, K.; Heitzer, H. *Liebigs Ann. Chem.* **1974**, 2066.
(22) Niess, R.; Ellingsfeld, E. *Liebigs Ann. Chem.* **1974**, 2019.
(23) Yoneda, F.; Higuchi, M.; Yano, T. *Chem. Lett.* **1979**, 155.
(24) Pfleiderer, W.; Strauss, G. *Liebigs Ann. Chem. 1958*, *612*, 173.
(25) Scherer, O.; Kluge, F. Hoechst, AG, German Patent (DOS) 1670756, 1966; French Patent 1539486, *Chem. Abstr.* **1969**, *71*, 81404.
(26) Grohe, K.; Heitzer, H. *Liebigs Ann. Chem.* **1974**, 2066.
(27) Reck, R.; Jochims, J.C. *Chem. Ber.* **1982**, *115*, 1494.
(28) Al-Talib, M.; Jibril, I.; Jochims, J.C.; Huttner, G. *Chem. Ber.* **1984**, *117*, 3211.
(29) Al-Talib, M.; Jochims, J.C. *Chem. Ber.* **1984**, *117*, 3222.
(30) Al-Talib, M.; Jibril, I.; Huttner, G.; Jochims, J.C. *Chem. Ber.* **1985**, *118*, 1876.
(31) Müller, E.; Orama, O.; Huttner, G.; Jochims, J.C. *Tetrahedron* **1985**, *41*, 5901.
(32) Al-Talib, M.; Jochims, J.C.; Zsolnai, L.; Huttner, G. *Chem. Ber.* **1985**, *118*, 1887.
(33) Müller, E.; Jochims, J.C. *Synthesis* **1986**, 465.
(34) Hamed, A.; Müller, E.; Al-Talib, M.; Jochims, J.C. *Synthesis* **1987**, 745.
(35) Hamed, A.; Müller, E.; Jochims, J.C.; Zsolnai, L.; Huttner, G. *Tetrahedron* **1989**, *45*, 5825.
(36) Bredereck, K.; Richter, R. *Chem. ber.* **1965**, *98*, 131.
(37) Neidlein, R.; Stackebrandt, B. *Liebigs Ann. Chem.* **1977**, 914.
(38) Fenner, H.; Bauch, W. *Arch. Pharm.* **1978**, *311*, 196.
(39) Seitz, G.; Sutrisno, R.; Kämpchen, T. *Arch. Pharm.* **1980**, *313*, 959.
(40) Kokel, B.; Viehe, H.G. *Angew. Chem.* **1980**, *92*, 754; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 716.
(41) Kokel, B.; Lespagnol, C.; Viehe, H.G. *Bull. Soc. Chim. Belg.* **1980**, *89*, 651.
(42) Kapp, W.; Klaus, R. *Arch. Pharm.* **1982**, *315*, 346.
(43) Weidner, J.; Vilsmaier, E.; Fries, R. *Monatsh. Chem.* **1987**, *118*, 1039.
(44) Gregory, B.B.; Ronald, J.S.; Robert, B.M.; Robert, J.S.; Ruth, M. *J. Org. Chem.* **1977**, *42*, 221.
(45) A. Marhold In *Houben-Weyl*; Thieme: Stuttgart, 1983; H. Hagemann Ed.; Vol. E/4, p.656. Tetramethylthiuram disulfide can be used as starting material.