4(3*H*)-Quinazolinones from the Reaction of *N*-Arylnitrilium Salts with Isocyanates

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N-Arylnitrilium salts **1** react with isocyanates **2** to give salts **3** of 4(3*H*)-quinazolinones **4**, from which compounds **4** can be obtained with base. A metathesis of an isocyanate with a nitrilium salt is reported.

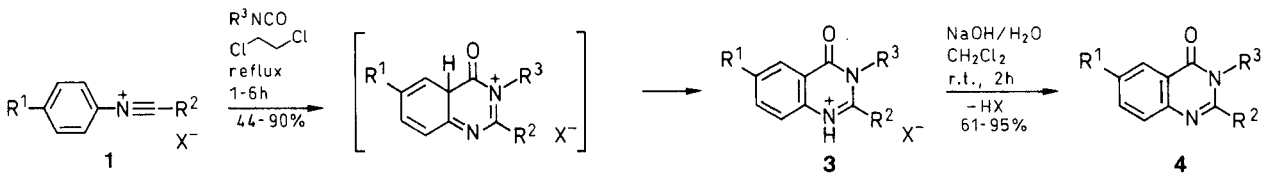
N-Arylnitrilium salts **1** have been reported to react with nitriles to form quinazolines.[1,2] This reaction, referred to as Meerwein's quinazoline synthesis, has been extended to other nucleophiles, e.g. to phenyl acetylene[3] and an azomethine.[4] For these polar $[4^+ + 2]$ cycloadditions concerted or multistep mechanisms may be discussed.[2] Isocyanates **2** are usually regarded as electrophiles[5] although oligo- and polymerizations under the influence of acids or Lewis acids are known.[6] Recently, we observed a number of reactions, in which isocyanates behave as moderately strong nucleophiles. Here we wish to report that isocyanates undergo cycloaddition to *N*-arylnitrilium salts **1** to furnish salts **3**, from which 4(3*H*)-quinazolinones **4** can be obtained with base (Scheme 1).

Compounds **4** are well known for their biological activities.[6-9] Some 4-quinazolinones are natural products.[10] Recently, it has been shown that the atropisomers of 2-methyl-3-(2-methylphenyl)-4(3*H*)-quinazolinone ("methaqualone") show different anticonvulsive activities.[11]

N-Arylnitrilium salts **1** can be prepared either by treating *N*-aryl imidoyl chlorides with Lewis acids or by reacting aryldiazonium salts with nitriles.[1] Alternatively, *N*-arylnitrilium salts are obtained by Beckman rearrangement of *o*-(chlorooxalyl)oximes of aryl ketones.[12]

N-Arylnitrilium salts **1** are sparingly soluble in boiling 1,2-dichloroethane. However, if one adds one to two mol equivalents of an isocyanate to the hot suspension of **1** in 1,2-dichloroethane, the nitrilium salt dissolves in the course of 1 to 6 hours and the salt **3** precipitates (Table).

Regarding scope and limitation of the reaction, it should be noted that no reaction is observed between *N-alkyl*nitrilium salts and isocyanates, e.g. between *N*-isopropylbenzonitrilium hexachloroantimonate and methyl isocyanate. While phenyl isocyanate (**1d**) does not react with *N*-phenyl*benzo*nitrilium hexachloroantimonate (**1f**) it reacts with *N*-phenyl*aceto*nitrilium hexachloroantimonate (**1a**) to afford the salt **3d** in 49% yield. However, the nitrilium salt **1a** does not react with the less nucleophilic 4-chlorophenyl isocyanate. In boiling 1,2-dichloroethane *N*-phenylacetonitrilium salt **1a** reacts smoothly with 4-methylphenyl isocyanate (**2e**) to give **3e**. However, under the same conditions no reaction could be achieved between **1a** or **1t** and 2-methylphenyl isocyanate to furnish salts **3**, which would give with base pharmaceutically interesting 3-(2-methylphenyl) substituted quinazolinones **4**.[11] While the *N*-phenylbenzonitrilium salt **1g** does not react with 4-methylphenyl isocyanate (**2e**) in boiling 1,2-dichloroethane (bp 83 °C) it reacts in boiling chlorobenzene (bp 132 °C). However, even in boiling chlorobenzene a salt **3** is not formed from the less nucleophilic phenyl isocyanate (**2d**) and **1g**. Thus, the formation of **3** depends critically on sufficient nucleophilicity of the isocyanate and electrophilicity of the nitrilium salt as well as on steric effects.

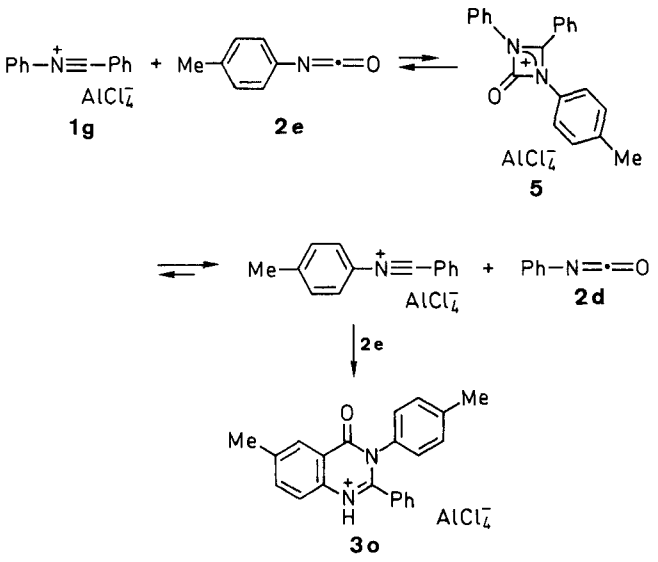


1 3 4

1–4	R^1	R^2	R^3	X	1–4	R^1	R^2	R^3	X
a	H	Me	Me	$SbCl_6$	**n**	H	Ph	4-MeC_6H_4	$AlCl_4$
b	H	Me	Pr	$SbCl_6$	**o**	Me	Ph	4-MeC_6H_4	$AlCl_4$
c	H	Me	*i*-Pr	$SbCl_6$	**p**	Cl	Me	Me	$SbCl_6$
d	H	Me	Ph	$SbCl_6$	**q**	Cl	Me	Pr	$SbCl_6$
e	H	Me	4-MeC_6H_4	$SbCl_6$	**r**	Cl	Me	*i*-Pr	$SbCl_6$
f	H	Ph	Me	$SbCl_6$	**s**	Cl	Me	4-MeC_6H_4	$SbCl_6$
g	H	Ph	Me	$AlCl_4$	**t**	Cl	4-ClC_6H_4	Me	$SbCl_6$
h	H	Ph	Pr	$SbCl_6$	**u**	Cl	4-ClC_6H_4	Pr	$SbCl_6$
i	H	Ph	Pr	$FeCl_4$	**v**	Cl	4-ClC_6H_4	*i*-Pr	$SbCl_6$
j	H	Ph	Pr	$AlCl_4$	**w**	Cl	4-ClC_6H_4	4-MeC_6H_4	$SbCl_6$
k	H	Ph	*i*-Pr	$SbCl_6$	**x**	MeO	Me	Me	$SbCl_6$
l	H	Ph	*i*-Pr	$FeCl_4$	**y**	MeO	Me	Pr	$SbCl_6$
m	H	Ph	*i*-Pr	$AlCl_4$	**z**	MeO	Me	*i*-Pr	$SbCl_6$

Scheme 1

No reactions are observed between nitrilium salts and isothiocyanates. For the reaction of *N*-arylnitrilium salts **1** with isocyanates **2** a Diels–Alder mechanism may be discussed.[2] Alternatively, a stepwise or concerted [2+2] cycloaddition, in which four or six electrons[13] are involved, has to be considered. An observation supporting a four-membered intermediate or transition state comes from the reaction of **1g** with 4-methylphenyl isocyanate (**2e**). In boiling chlorobenzene a 1:1 mixture of the expected salt **3n** and the unexpected product **3o** is formed. Treatment with aqueous sodium hydroxide gives the corresponding mixture of **4n** + **4o**. The fast atomic bombardment mass spectrum (with 4-nitrobenzylic alcohol as matrix) shows the molecular peaks $M + H^+/e =$ 313 for **4n** and 327 for **4o** with almost equal intensities.[14] In the ^1H NMR spectrum a singlet (broadened by long-range couplings) at $\delta = 8.11$ (in CD_3CN) can be assigned to H5 of **4o**. The formation of **3o** requires a metathesis of an isocyanate and a nitrilium salt via a four-membered intermediate or transition state **5** (Scheme 2). The question remains open whether **5** is also in intermediate or transition state of the formation of **3** from **1** and **2**. The metathesis via **5** could well be a side reaction being of importance only at higher temperatures.



Scheme 2

All solvents were dried by standard methods. All experiments were conducted with exclusion of moisture. The nitrilium salts **1a**,[12] **f**,[12] **g**,[22] **i**[23] were obtained according to the procedure described.[12]

Table. Selected NMR and IR Data, Yields and Melting Points of, and Reflux Times for the Preparations of the New Compounds

Product	Molecular Formula[a]	^1H NMR (CD_3CN/TMS) δ, J (Hz)[b]	^{13}C NMR (CD_3CN/TMS) δ, J (Hz)	IR (KBr) ν (cm^{-1})[c]	Yield (%)	mp (°C)	R[d] (h)
1p	$C_8H_7Cl_6NSb$ (487.1)	3.24 (CH_3)	6.6 (CH_3), 120.9 (t, J = 17, *i*-C), 130.0, 131.6 (*m*, *o*-C), 140.7 (*p*-C), 118.0 (?), (t, J = 49, C≡N)	2358[e]	92	181–182[f]	
1t	$C_{13}H_8Cl_6NSb$ (583.5)			2315[e]	90	210–215[f]	
1x	$C_9H_{10}Cl_6NOSb$ (482.7)	3.14 (br), 3.91 (CH_3)	6.4, 56.9 (CH_3), 114.0 (t, J = 16, *i*-C), 116.6 (*m*-C), 130.4 (*o*-C), 164.2 (*p*-C)	2350[e]	82	165–167[f]	
3a	$C_{10}H_{11}Cl_6N_2OSb$ (509.7)	2.87, 3.67 (CH_3), 12.02 (NH)	21.2, 32.8 (CH_3), 118.9, 119.3, 128.9, 130.7, 136.9, 138.0 (aryl), 159.3, 163.0 (C=O, C=N)	1655, 1713	84	194–196	1
3b	$C_{12}H_{15}Cl_6N_2OSb$ (537.7)	1.04 (t, J = 7.4), 2.90 (CH_3), 1.79 (m), 4.12 (m, CH_2), 11.99 (NH)	11.4, 20.7, 21.7, 48.4 (CH_3, CH_2), 119.1, 119.2, 128.8, 130.6, 136.9, 137.9 (aryl), 159.2, 162.5 (C=O, C=N)	1655,[g] 1682	85	203–206[f]	3
3c	$C_{12}H_{15}Cl_6N_2OSb$ (537.7)	1.66 (d, J = 6.8), 2.90 (CH_3), 4.75 (sept, J = 6.8, CH), 11.90 (NH)	19.4, 21.6 (CH_3), 55.8 (CH), 118.9, 120.4, 128.5, 130.5, 136.7, 137.7 (aryl), 159.5, 162.5 (C=O, C=N)	1655, 1683,[g] 1729	87	198–199[f]	3
3d	$C_{15}H_{13}Cl_6N_2OSb$ (571.7)	2.49 (CH_3), 12.27 (NH)	21.9 (CH_3), 119.7, 119.8, 128.5, 129.1, 131.0, 131.5, 132.0, 135.2, 137.1, 138.3 (aryl), 159.5, 163.4 (C=O, C=N)	1652, 1706	49	212–213[f]	6
3e	$C_{16}H_{15}Cl_6N_2OSb$ (585.8)	2.47, 2.49 (CH_3), 12.18 (NH)	21.4, 21.9 (CH_3), 119.6, 119.8, 128.2, 129.1, 131.0, 132.0, 132.6, 137.1, 138.3, 142.5 (aryl), 159.6, 163.6 (C=O, C=N)	1648, 1721	73	202–204[f]	6
3f	$C_{15}H_{13}Cl_6N_2OSb$ (571.7)	3.55 (CH_3), 12.17 (NH)	35.8 (CH_3), 119.2, 119.9, 127.1, 128.6, 129.4, 130.4, 134.8, 137.1, 138.0 (aryl), 159.8, 161.2 (C=O, C=N)	1644, 1694	85	281–282[f]	6
3g	$C_{15}H_{13}AlCl_4N_2O$ (406.0)	3.54 (CH_3), 12.18 (NH)	35.8 (CH_3), 119.2, 119.9, 127.1, 128.6, 129.4, 130.4, 134.7, 137.1, 137.9 (aryl), 159.8, 161.2 (C=O, C=N)	1640, 1725	75	223–225	4
3h	$C_{17}H_{17}Cl_6N_2OSb$ (599.8)	0.80 (t, J = 7.6, CH_3), 1.71 (m), 3.99 (m, CH_2), 12.10 (NH)	11.3 (CH_3), 22.3, 50.2 (CH_2), 119.8, 119.9, 127.2, 128.8, 129.0, 130.6, 131.1, 134.5, 137.2, 138.2 (aryl), 159.5, 161.5 (C=O, C=N)	1636, 1725	68	230–232[f]	3
3i	$C_{17}H_{17}Cl_4FeN_2O$ (463.0)			1644, 1675	78	205–208[f]	2

Table. (continued)

Product	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS) δ, J (Hz)[b]	^{13}C NMR (CD_3CN/TMS) δ, J (Hz)	IR (KBr) ν (cm^{-1})[c]	Yield (%)	mp (°C)	R[d] (h)
3k	$C_{17}H_{17}Cl_6N_2OSb$ (599.8)	1.60 (d, J = 6.8, CH_3), 4.47 (sept, J = 6.8, CH), 12.02 (NH)	19.6 (CH_3), 58.3 (CH), 119.6, 121.1, 127.9, 128.6, 128.7, 130.7, 131.0, 134.4, 136.9, 138.0 (aryl), 159.9, 161.8 (C=O, C=N)	1632, 1686	85	237–239	2
3l	$C_{17}H_{17}Cl_4FeN_2O$ (463.0)			1644,[g] 1682	84	237–239[f]	2
3m	$C_{17}H_{17}AlCl_4N_2O$ (434.1)	1.60 (d, J = 6.7, CH_3), 4.48 (sept, J = 6.7, CH), 12.09 (NH)	19.7 (CH_3), 58.2 (CH), 117.8, 121.2, 128.0, 128.4, 128.7, 130.5, 130.8, 134.1, 137.2, 137.7 (aryl), 159.9, 161.7 (C=O, C=N)	1644, 1682, 1710[g]	87	231–233	6
3p	$C_{10}H_{10}Cl_7N_2OSb$ (544.1)	2.90, 3.68 (CH_3), 12.10 (NH)	21.3, 33.1 (CH_3), 120.1, 121.4, 128.1, 135.4, 135.9, 138.0 (aryl), 158.3, 163.1 (C=O, C=N)	1567, 1640, 1679,[g] 1737	85	189–191[f]	4
3q	$C_{12}H_{14}Cl_7N_2OSb$ (572.2)	1.04 (t, J = 7.4), 2.90 (CH_3), 1.80 (m, CH_2), 4.13 (m, CH_2), 11.97 (NH)	11.3, 20.8, 21.7, 48.7 (CH_3, CH_2), 120.6, 121.4, 128.2, 135.7, 136.1, 138.1 (aryl), 158.3, 162.9 (C=O, C=N)	1571, 1640, 1729	90	183–185	2
3s	$C_{16}H_{14}Cl_7N_2OSb$ (620.2)	2.46, 2.50 (CH_3), 12.36 (NH)	21.4, 21.9 (CH_3), 121.0, 121.6, 127.8, 128.1, 131.9, 132.1, 135.5, 136.1, 138.2, 142.4 (aryl), 158.5, 163.5 (C=O, C=N)	1551, 1648, 1721	60	200–203[f]	6
3t	$C_{15}H_{11}Cl_8N_2OSb$ (640.6)	3.56 (CH_3)	36.1 (CH_3), 120.6, 122.2, 125.5, 128.1, 130.9, 131.4, 135.8, 136.6, 138.3, 141.0 (aryl), 158.9, 160.6 (C=O, C=N)	1640, 1679,[g] 1737	82	252–255[f]	4
3u	$C_{17}H_{15}Cl_8N_2OSb$ (668.7)	0.82 (t, J = 7.5, CH_3), 1.70 (m), 3.97 (m) (CH_2)	11.2, 22.2, 50.5 (CH_3, CH_2), 121.1, 121.9, 125.4, 128.1, 130.7, 130.8, 135.7, 136.6, 138.2, 140.6 (aryl), 158.4, 160.6 (C=O, C=N)	1640, 1729	77	120–122	2
3v	$C_{17}H_{15}Cl_8N_2OSb \cdot Et_2O$ (742.8)	1.11 (t, J = 7.0), 1.59 (d, J = 6.8) (CH_3), 3.41 (q, J = 7.0, CH_2), 4.46 (sept, J = 6.8, CH), 12.22 (NH)	15.6, 19.5 (CH_3), 58.7 (CH), 66.2 (CH_2), 121.8, 122.4, 126.2, 127.9, 130,5, 131.0, 135.5, 136.5, 138.1, 140.4 (aryl), 158.8, 160.9 (C=O, C=N)	1640, 1729	69	173–176	3
3w	$C_{21}H_{15}Cl_8N_2OSb$ (716.7)	2.33 (CH_3	21.2 (CH_3), 121.5, 122.3, 125.9, 128.4, 129.1, 130.1, 131.2, 131.8, 132.4, 136.0, 137.0, 138.5, 140.2, 142.0 (aryl), 158.7, 160.6 (C=O, C=N)	1640, 1727, 1730[g]	44	238–240[f]	3
3y	$C_{13}H_{17}Cl_6N_2O_2Sb$ (567.8)	1.04 (t, J = 7.4), 2.87, 3.95 (CH_3), 1.79 (m, CH_2), 4.12 (m, CH_2), 11.96 (NH)	11.4, 20.5, 21.7, 48.2, 57.0 (CH_3, CH_2), 108.9, 120.5, 121.0, 126.8, 130.9, 158.9, 159.8, 160.9 (aryl, C=O, C=N)	1648, 1679	76	190–192[f]	2
3z	$C_{13}H_{17}Cl_6N_2O_2Sb$ (567.8)	1.66 (d, J = 6.7), 2.88, 3.95 (CH_3), 4.74 (sept, J = 6.7, CH), 11.87 (NH)	19.3 (2C), 21.4, 57.0 (CH_3), 55.6 (CH), 108.7, 120.7, 121.8, 126.6, 130.6, 159.2, 159.8, 160.9 (aryl, C=N, C=O)	1582, 1652,[g] 1679, 1724[g]	73	205–207[f]	2
4a	$C_{10}H_{10}N_2O$ (174.2)	2.60, 3.60 (CH_3)[h]	23.4, 30.9 (CH_3), 120.4, 126.2, 126.7, 133.9, 147.4, 154.2, 162.1 (aryl, C=N, C=O)[h]	1605, 1682[i]	70[l, m]	105–106 Ref 15: 108–109	
4b	$C_{12}H_{14}N_2O$ (202.3)	1.03 (t, J = 7.5), 2.63 (CH_3), 1.77 (m, CH_2), 4.04 (m, CH)[h]	11.4, 22.0, 23.1, 46.1 (CH_3, CH_2), 120.6, 126.3, 126.6, 126.7, 134.1, 147.3, 154.1, 162.0 (aryl, C=O, C=N)[h]	1601, 1679[i]	87[j, k]	81–82 Ref. 15: 81–82	
4c	$C_{12}H_{14}N_2O$ (202.3)	1.67 (d, J = 6.9), 2.66 (CH_3), 4.63 (br, CH)[h]	19.7 (2C), 24.3 (CH_3), 51.7 (br, CH), 121.9, 126.2, 126.3, 126.4, 134.0, 147.0, 154.2, 162.5 (aryl, C=O, C=N)[h]	1601, 1679[i]	86[j, l]	83–84 Ref. 16: 88–91	
4d	$C_{15}H_{12}N_2O$ (236.3)	2.22 (CH_3)[h]	24.3 (CH_3), 120.7, 126.5, 126.7, 126.9, 128.1, 129.2, 129.9, 134.5, 137.8, 147.5, 154.1, 162.1 (aryl, C=O, C=N)[h]	1605, 1694[i]	74[j, l]	142–143 Ref. 15: 145–146	
4f	$C_{15}H_{12}N_2O$ (236.3)	3.46 (CH_3)[h]	34.1 (CH_3), 120.4, 126.5, 126.8, 127.3, 128.0, 128.7, 129.9, 134.1, 135.4, 147.2, 156.0, 162.4 (aryl, C=O, C=N)[h]	1567,[g] 1590,[g] 1605, 1682[i]	95[j, k]	131–132 Ref. 17: 133	
4j	$C_{17}H_{16}N_2O$ (264.3)	0.76 (t, J = 7.4, CH_3), 1.65 (m, CH_2), 3.95 (m, CH)[h]	11.2, 22.0, 47.4 (CH_3, CH_2), 120.7, 126.6, 126.8, 127.2, 127.5, 128.6, 129.6, 134.1, 135.3, 146.9, 156.0, 161.9 (aryl, C=O, C=N)[h]	1605, 1679[i]	81[k, m]	97–98 Ref. 18: 88–91	
4m	$C_{17}H_{16}N_2O$ (264.3)	1.59 (d, J = 6.8, CH_3), 4.35 (sept, J = 6.8, CH)[h]	19.6 (CH_3), 54.0 (CH), 122.1, 126.3, 126.7, 127.0, 127.1, 128.8, 129.5, 134.0, 136.4, 146.7, 156.5, 162.4 (aryl, C=O, C=N)[h]	1567, 1586, 1605, 1679[i]	77[k, m]	136–137 Ref. 16: 138–140	
4n[n]	$C_{21}H_{16}N_2O$ (312.4)	2.28 (CH_3), 8.34 (d, J = 7.4, H5)[h]	21.1 (CH_3)	1559, 1594, 1616,[g] 1675[i, n]	61[l, m, n]	201–205[n] Ref. 19: **4n** 180–181	

Table. (continued)

Product	Molecular Formula[a]	^{1}H NMR (CD_3CN/TMS) δ, J (Hz)[b]	^{13}C NMR (CD_3CN/TMS) δ, J (Hz)	IR (KBr) ν (cm^{-1})[c]	Yield (%)	mp (°C)	R[d] (h)
4o[n]	$C_{22}H_{18}N_2O$ (326.4)	2.28, 2.49 (CH_3), 8.12 (s, H 5)[h]	21.1, 21.4 (CH_3)[h]	see **4n**			
4p	$C_{10}H_9ClN_2O$ (208.7)	2.59, 3.59 (CH_3)[h]	23.4, 31.1 (CH_3), 121.3, 125.9, 128.4, 131.9, 134.3, 145.8, 154.6, 161.0 (aryl, C=O, C=N)[h]	1598, 1686[i]	73[j,l]	145–147 Ref. 20: 151–152	
4q	$C_{12}H_{13}ClN_2O$ (236.7)	1.03 (t, J = 7.4), 2.63 (CH_3), 1.77 (m, CH_2), 4.03 (m, CH_2)[h]	11.3, 21.9, 23.1, 46.3 (CH_3, CH_2), 121.6, 126.1, 128.4, 131.9, 134.5, 145.8, 154.4, 161.0 (aryl, C=O, C=N)[h]	1598, 1679[i]	89[j,l]	82–84	
4r	$C_{12}H_{13}ClN_2O$ (236.7)	1.67 (d, J = 6.8), 2.65 (CH_3), 4.63 (br, CH)[h]	19.6 (2C), 24.2 (CH_3), ≈ 51 (br, CH), 123.0, 125.9, 128.1, 132.0, 134.4, 145.5, 154.5, 161.5 (aryl, C=O, C=N)[h]	1598, 1679[i]	61[l,m]	83–84	
4t	$C_{15}H_{10}Cl_2N_2O$ (305.2)	3.49 (CH_3)[h]	34.2 (CH_3), 121.6, 126.0, 129.1, 129.2, 129.5, 132.9, 133.7, 134.6, 136.5, 145.8, 155.1, 161.4 (aryl, C=O, C=N)[h]	1598, 1686[i]	74[l,m]	178–179	
4u	$C_{17}H_{14}Cl_2N_2O$ (333.2)	0.79 (t, J = 7.4, CH_3), 1.64 (m), 3.93 (m) (CH_2)[h]	11.1, 22.0, 47.5 (CH_3, CH_2), 121.7, 125.9, 128.9, 129.0, 129.1, 129.4, 132.7, 133.5, 134.6, 136.0, 145.3, 155.2, 160.8 (aryl, C=O, C=N)[h]	1698, 1686[i]	77[j,l]	124–125	
4v	$C_{17}H_{14}Cl_2N_2O$ (333.2)	1.59 (d, J = 6.8, CH_3), 4.32 (sept, J = 6.8, CH)[h]	19.6 (CH_3), 54.5 (CH), 123.2, 125.9, 128.8, 128.9, 129.3, 132.8, 134.5, 134.6, 136.1, 145.2, 155.8, 161.4 (aryl, C=O, C=N)[h]	1598, 1690[i]	81[l,m]	122–124	
4x	$C_{11}H_{12}N_2O_2$ (204.2)	2.58, 3.61, 3.90 (CH_3)[h]	23.4, 31.0, 55.7 (CH_3), 105.8, 120.7, 124.3, 128.0, 141.7, 151.9, 157.8, 162.9 (aryl, C=O, C=N)[h]	1601, 1675[i]	71[l,m]	128–129 Ref. 21: 133	
4y	$C_{13}H_{16}N_2O_2$ (232.2)	1.04 (t, J = 7.5), 2.63, 3.90 (CH_3), 1.78 (m), 4.05 (m) (CH_2)[h]	11.4, 22.0, 22.9, 46.1, 55.7 (CH_3, CH_2), 105.9, 121.1, 124.3, 128.1, 141.8, 151.6, 157.8, 161.7 (aryl, C=O, C=N)[h]	1598, 1600,[g] 1675[i]	75[j,l]	92–93	
4z	$C_{13}H_{16}N_2O$ (232.2)	1.68 (d, J = 6.7), 2.64, 3.89 (CH_3), 4.62 (br, CH)[h]	19.7, 24.4, 56.4 (CH_3), 52.5 (br, CH), 106.6, 118.3, 123.7, 124.5, 129.0, 142.9, 153.6, 158.8, 162.9 (aryl, C=O, C=N)	1598, 1679[i]	71[j,l]	118–119	

[a] Satisfactory microanalyses obtained: C ±0.31, H ±0.59, N ±0.36.
[b] At 250 MHz at 295 K in CD_3CN with TMS as internal standard; Bruker WM-250 and AC-250 spectrometers.
[c] Mattson Polaris FTIR Spectrometer.
[d] Reflux time for the preparation of **3** from **1** and **2**.
[e] In Nujol.
[f] With decomposition.
[g] Shoulder.
[h] In $CDCl_3$.
[i] In CCl_4.
[j] Yield relative to the corresponding salt **3**.
[k] Yield before recrystallization.
[l] Yield after recrystallization.
[m] Yield relative to the corresponding salt **1**.
[n] 1:1 Mixture of **4n** and **4o**.

***N*-(4-Chlorophenyl)acetonitrilium Hexachloroantimonate (1p):**
A solution of $SbCl_5$ (14.95 g, 50 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a cold (−40 °C) solution of 4-chloroacetophenone *O*-(chlorooxalyl)oxime (15.60 g, 60 mmol, prepared without further characterization according to Ref.[12]) in CH_2Cl_2 (20 mL). The mixture was stirred at −40 °C for 1 h, then at 23 °C for 30 min. The precipitate was filtered off and washed with CH_2Cl_2 (2 × 30 mL) affording a colorless powder (44.81 g, 92%); mp 181–182 °C (dec).

4-Chloro-*N*-(4-chlorophenyl)benzonitrilium Hexachloroantimonate (1t):
A solution of $SbCl_5$ (5.98 g, 20 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a cold (−30 °C) mixture of 4-chloro-*N*-(4-chlorophenyl)benzimidic chloride[24] (5.69 g, 20 mmol) in CH_2Cl_2 (30 mL). The temperature was raised to 23 °C in the course of 1 h and the precipitate was filtered off and washed with CH_2Cl_2 (2 × 20 mL). Yield: 10.51 g (90%) of a pale yellow powder; mp 210–215 °C (dec). The product is sparingly soluble in most organic solvents and reacts within a few min with MeCN[1,25] or acetone. Therefore, NMR spectra could not be obtained.

***N*-(4-Methoxyphenyl)acetonitrilium Hexachloroantimonate (1x)**
From 4-methoxyacetophenone *O*-(chlorooxalyl)oxime (15.34 g, 60 mmol, prepared without further characterization according to Ref.[12]) as described for **1t**. Yield: 19.79 g (82%) of a yellow powder; mp 165–167 °C (dec).

3,4-Dihydro-4-oxoquinazolinium Salts (3); General Procedure:
A mixture of the nitrilium salt **1** (10 mmol) and the isocyanate **2** (20 mmol) in $ClCH_2CH_2Cl$ (30 mL) was boiled under reflux for the time specified in Table 1 (1 to 6 h). During this time the nitrilium salt dissolved and part of the product (yellow or colorless) precipitated. After cooling to 23 °C Et_2O (50 mL) was added. The mixture was stirred for 30 min. Filtration afforded the analytically pure product as a pale yellow or brownish or colorless powder. Recrystallization from MeCN/Et_2O was possible. However, organic solvents were persistently included in the crystals. Drying at 60 °C and 10^{-1} Torr for at least 24 h was required to get solvent-free products.

4(3*H*)-Quinazolinones (4): General Procedure:
A mixture of nitrilium salt **1** (10 mmol) and isocyanate **2** (20 mmol) in $ClCH_2CH_2Cl$ (30 mL) was boiled under reflux for 3 h. After cooling to 23 °C Et_2O (50 mL) was added. The mixture was stirred for 30 min. The salt **3** was filtered off and suspended in CH_2Cl_2 (30 mL). Aq NaOH (20%, 40 mL) was added. After stirring for 2 h the organic layer was separated and washed with H_2O (4 × 50 mL). Drying (Na_2SO_4) and evpaporation of the solvent furnished **4** as a colorless powder, which can be crystallized at −20 °C from CH_2Cl_2 (3 mL)/pentane (20 mL).

3-(4-Methylphenyl)-2-phenyl-4(3*H*)-quinazolinone (4n) and 6-Methyl-3-(4-methylphenyl)-2-phenyl-4(3*H*)-quinazolinone (4o):
No reaction occured if a mixture of **1g** (3.49 g, 10 mmol) and **2e**

(2.66 g, 20 mmol) in CH_2ClCH_2Cl (30 mL) was boiled under reflux for 24 h. However, if the same mixture of **1f** and **2e** was boiled under reflux for 4 h in chlorobenzene a clear red solution was formed, from which a mixture of the salts **3n, o** crystallized on cooling. The salts were suspended in CH_2Cl_2 (30 mL). Stirring with aq NaOH and workup as described above afforded a 1:1 mixture of **4n, o**, which was crystallized at −20 °C from CH_2Cl_2 (3 mL)/pentane (30 mL) to give a colorless crystalline powder (1.90 g, 61 %), which according to the ^1H NMR spectrum still consisted of a 1:1 mixture of **4n, o**; mp 201–205 °C.

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