Preparation and Beckmann Rearrangement of *O*-(Chlorooxalyl)oximes

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Oximes **1** react with phosgene or oxalyl chloride to give *O*-(chloroformyl)- **2**, or *O*-(chlorooxalyl)oximes **8**, which undergo Beckmann rearrangement with antimony pentachloride to afford nitrilium hexachloroantimonates **3** in high yields. With di- or triphosgene (**4** or **6**) oximes **1** form mixtures of *O*-(chloroformyl)- **2** and *O*-(trichloromethoxyformyl)oximes **5**. The *O*-(chlorooxalyl)oximes **8** are further characterized as esters **10** and amides **11**. With *N,N*-dimethylformamide the nitrilium salts **3** react to give *N*-acyl formamidinium salts **12**.

Nitrilium salts **3** have mainly been prepared[1] by alkylation of nitriles,[2-17] by the reaction of imidoyl chlorides with Lewis acids,[18-20] and by arylation of nitriles with aryl diazonium salts.[2] Only in special cases the Beckmann rearrangement[21] of oxime ethers[22] or *N*-chloro imines[23-25] has been used for the preparation of nitrilium salts. Meerwein pointed out that nitrilium salts **3** may not accumulate during Beckmann rearrangement of oximes **1** since the forming nitrilium cation reacts quickly with unreacted oxime. In fact, benzophenonoxime has been rearranged into benzanilide with *N*-phenylbenzonitrilium hexachloroantimonate as catalyst.[22] However, Olah observed NMR spectra of the *N*-methylacetonitrilium cation when acetone oxime was heated in fluorosulfonic acid/antimony pentafluoride/sulfur dioxide at 100°C for 30 min.[5]

From the work of Meerwein[22] it may be concluded that Beckmann rearrangement can only be used for the preparation of nitrilium salts if one starts with aprotic oxime derivatives.

We now describe the preparation of *O*-(chlorooxalyl)-oximes **8** and of some of their derivatives. The oxalyl chlorides **8** react with antimony pentachloride to give pure nitrilium hexachloroantimonates **3** in high yields.

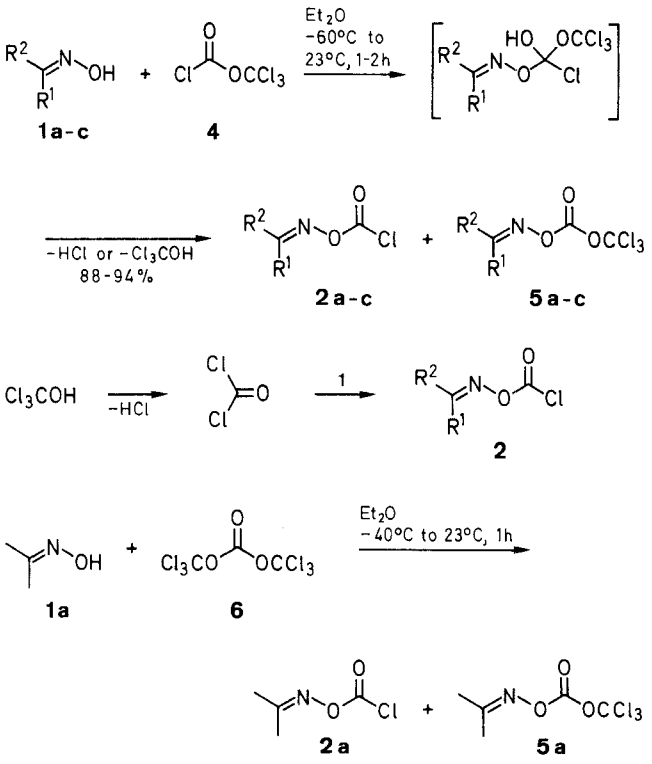
Initially, the *O*-(chloroformyl)oximes **2**[26-29] were considered to be suitable starting materials for the preparation of nitrilium salts. Compounds **2a–c** were prepared by the procedure of Jumar et al.[26] from oximes **1** and excess of phosgene. On addition, of antimony pentachloride compounds **2** undergo smooth Beckmann rearrangement with loss of carbon dioxide to give the nitrilium salts **3** almost quantitatively.

Since the use of large quantities of phosgene is obviously inconvenient we turned our attention to the so-called phosgene substitutes "di-" and "triphosgene" [trichloromethyl carbonochloridate (**4**) and bis(trichloromethyl)carbonate (**6**).[30-32]

The oximes **1a–c** react with diphosgene **4** to form mixtures of the (trichloromethoxy)formyl esters **5a–c** and the chloroformyl esters **2a–c** in variable ratios. This may be rationalized assuming an addition of the nucleophile **1** to the carbonyl group of **4** followed by elimination of either hydrogen chloride to give **5** or of trichloromethanol to render **2**.

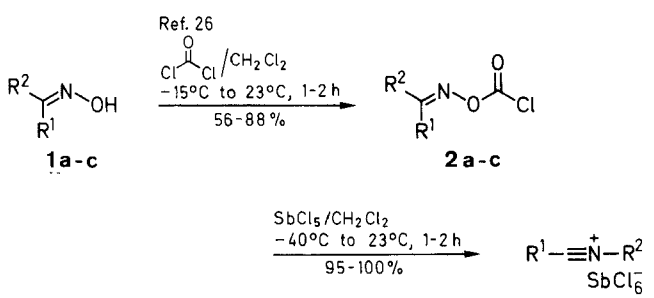
Trichloromethanol decomposes to hydrogen chloride and phosgene, which reacts with oxime **1** to give further **2**.

When the oxime **1a** is treated with triphosgene **6** again mixtures of **5a** and **2a** in variable ratios are formed.



With antimony pentachloride these mixtures give nitrilium salts **3**, which are contaminated with excess of antimony pentachloride or with excess of **5**, as the exact amount of antimony pentachloride required to transform a mixture of **2** and **5** into the corresponding nitrilium salt **3** is difficult to determine.

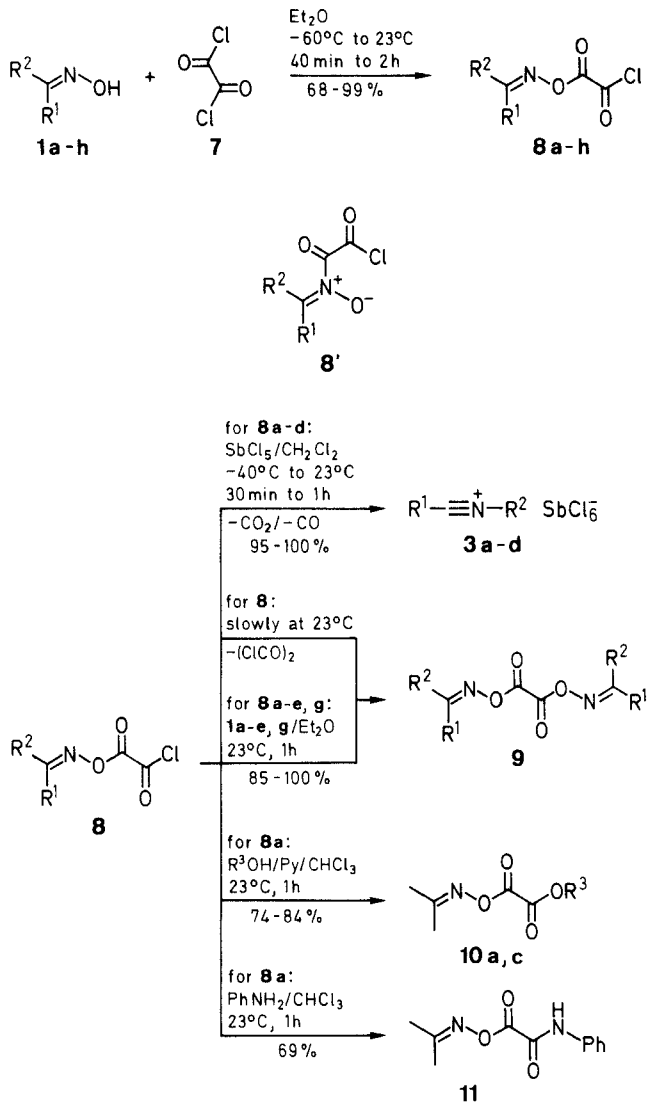
Therefore, for the rearrangement of oximes **1** to nitrilium salts **3** di- and triphosgene cannot be recommended as substitutes for phosgene. Finally, oxalyl chloride **7**

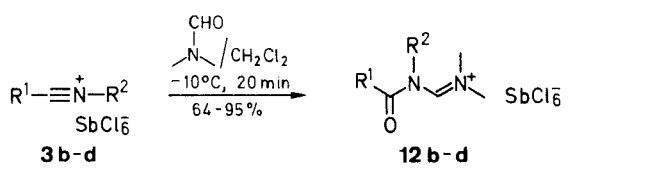


1–3	R^1	R^2
a	Me	Me
b	Me	Ph
c	Ph	Ph

proved to be the reagent of choice. The oximes **1a–h** are treated with 1.5 mole equivalents of oxalyl chloride in diethyl ether at low temperatures. A precipitate (hydrochloride of the oxime) is formed immediately, which dissolves after a few minutes. The (chlorooxalyl)oximes **8a–h** are isolated in high yields. Merely the hydroxamic chloride[33,34] **1h** requires room temperature for the formation of **8h**, which is isolated in moderate yields.

To our knowledge, there is only one instance of an *O*-(chlorooxalyl)oxime reported in the literature.[35] The ester was described to be unstable decomposing to products of a Beckmann rearrangement. The chlorooxalyl esters **8** are moisture sensitive compounds tending to disproportionate to the diesters **9** and oxalyl chloride on standing at room temperature. The acetone derivative **8a** can be distilled under reduced pressure, and compound **8h** can be sublimed without decomposition. NMR and IR data of all new compounds are presented in the Table. Although it seems most likely that compounds **8–11** are *O*-oxalyl oximes, alternative nitrone structures, e.g. **8'** instead of **8**, cannot be excluded at time. To our knowledge *N*-acyl nitrones have not been reported in the literature.





1–9, 12	R^1	R^2	1–9, 12	R^1	R^2	10	R^3
a	Me	Me	f			a	Me
b	Me	Ph				b	Et
c	Ph	Ph	g	H	Ph	c	*i*-Pr
d	Me	4-MeC_6H_4	h	Cl	CCl_3[38]		
e	$-(CH_2)_5-$						

With antimony pentachloride in dichloromethane the oxalyl derivatives **8a–d** lose carbon dioxide and carbon monoxide to give the nitrilium salts **3a–d** quantitatively. Under the same reaction conditions the derivatives **8e, f** of the cyclic ketones cyclohexanone and 9-fluorenone are decomposed to tars. Attempts to trap an intermediate nitrilium cation as imidoyl chloride or as *N*-acyl formamidinium salt[36,37] by the addition of tetraethylammonium chloride or *N,N*-dimethylformamide, respectively, to the reaction mixtures were unsuccessful. The benzaldehyde derivative **8g** undergoes fragmentation to carbon monoxide, carbon dioxide, hydrogen hexachloroantimonate, and benzonitrile when treated with antimony pentachloride. The oxalylated hydroxamic chloride **8h** decomposes to a black tar in the presence of antimony pentachloride.

Experiments to rearrange the chlorides **8** to imidoyl chlorides with a nitrilium salt as "Lewis acid" have failed. Compounds **8** do not react with nitrilium salts **3**.

With alcohols, amines and oximes the chlorooxalyl compounds **8** furnish the expected esters and amides, respectively. Thus, compounds **8** are easily transformed into the *O,O'*-oxalyldioximes **9** by treatment with oximes **1**. The acetone derivative **8a** is further characterized by transformation into esters **10a, c** and the anilide **11**. The ester **10b** is obtained directly from acetone oxime and ethyl oxalyl chloride. From the nitrilium salts **3b–d** and dimethylformamide the formamidinium salts **12b–d** are prepared.[36,37]

In conclusion, the reaction of open-chain oximes with oxalyl chloride and a Lewis acid like antimony pentachloride can be recommended as a useful method for the preparation of nitrilium salts.

All solvents are dried by standard methods. Antimony pentachloride is distilled before use. All experiments are carried out with exclusion of moisture. Compounds **2a–c** were prepared according to Ref. 26.

***N*-Methylacetonitrilium Hexachloroantimonate (3a):**[3,5,12]

1) A solution of **2a** (20.36 g, 150 mmol) in CH_2Cl_2 (80 mL) is added dropwise under stirring to a cold (−40 °C) solution of $SbCl_5$ (44.85 g, 150 mmol) in CH_2Cl_2 (30 mL). A colourless precipitate is formed immediately. The mixture is warmed to 23 °C and stirred at this temperature for 1 h. Slow addition of pentane (50 mL), filtration and washing of the residue with pentane affords a colourless powder; yield: 36.72 g (100%); mp 171–181 °C (dec) (Lit.[12] mp 178–181 °C (dec)).

2) A solution of **8a** (3.72 g, 20 mmol) in CH_2Cl_2 (10 mL) is added dropwise under stirring to a cold (−25 °C) solution of $SbCl_5$ (5.98 g, 20 mmol) in CH_2Cl_2 (30 mL). A colourless precipitate is

Table. Selected NMR- and IR-Data of Compounds **2–11** Prepared

Product	Molecular Formula[a]	IR (CCl_4) ν (cm^{-1})[b]	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)[c]	^{13}C-NMR ($CDCl_3$/TMS) δ
2a	$C_4H_6ClNO_2$ (135.6)	1810	2.07 (CH_3)	17.3, 21.5 (CH_3), 148.3, 166.5 (C=N, C=O)
2b	$C_9H_8ClNO_2$ (197.6)	1798[e]	2.44 (CH_3)[d]	15.0 (CH_3), 148.4, 165.4 (C=N, C=O), 133.0 (*i*-C), 131.4 (*p*-C), 128.8, 127.1 (*o*, *m*-C)
2c	$C_{14}H_{10}ClNO_2$ (259.7)	1794[e]		148.7, 167.0 (C=N, C=O), 128.4, 128.6, 129.0, 129.4, 130.5, 131.0, 131.7, 133.2 (phenyl)
3a	$C_3H_6Cl_6NSb$ (390.6)	2412[g]	2.83 (m, $^3J_{NH} \approx 2.4$, $^4J_{HH} \approx 2.5$, CH_3C), 3.75 (m, $^2J_{NH} \approx 2.7$, $^4J_{HH} \approx 2.5$, CH_3N)[f]	4.8 (CH_3), 31.8 (t, $^1J_{NC} = 7.4$, CH_3N), 109.4 (t, $^1J_{CN} = 47.3$, CN)[f]
3b	$C_8H_8Cl_6NSb$ (452.6)	2354[g]	3.18 (br, CH_3)[d]	6.5 (CH_3), 117.6 (t, $J = 49.1$, CN), 122.5 (t, $J = 14.8$, *i*-C), 128.5, 131.5, 135.0 (*o*, *m*, *p*-C)
3c	$C_{13}H_{10}Cl_6NSb$ (514.7)	2315[g]	decomposition in CD_3CN	
3d	$C_9H_{10}Cl_6NSb$ (466.7)	2346[g]	2.47, 3.18 (CH_3)[f]	6.5, 22.0 (CH_3), 117.4 (t, $J = 49.2$, CN), 119.6 (t, $J = 14.8$, *i*-C), 128.3, 131.9, 146.5 (*m*, *p*, *o*-C)[f]
4	$C_2Cl_4O_2$ (197.8)			108.2 (CCl_3), 143.5 (C=O)[i]
5a	$C_5H_6Cl_3NO_3$ (234.5)	1829	2.09, 2.10 (CH_3)	17.1, 21.6 (CH_3), 107.8 (CCl_3), 146.3, 166.3 (C=N, C=O)[i]
5b	$C_{10}H_8Cl_3NO_3$ (296.5)	1814, 1820[h]	2.46 (CH_3)[f,j]	14.8, 15.0 (CH_3), 107.8 (CCl_3), 146.4, 148.4, 165.0, 165.3 (C=N, C=O), 127.0, 127.1, 128.7, 128.8 (*o*, *m*-C), 131.3, 131.4 (*p*-C), 133.1, 133.4 (*i*-C)[f,j]
5c	$C_{15}H_{10}Cl_3NO_3$ (358.6)	1806, 1825		107.8 (CCl_3), 146.6, 148.7, 166.5, 167.0 (C=N, C=O)[f,k]
6	$C_3Cl_6O_3$ (296.7)			108.0 (CCl_3), 140.8 (C=O)[f]
7	$C_2Cl_2O_2$ (126.9)			159.5 (C=O)
8a	$C_5H_6ClNO_3$ (163.6)	1787	2.11, 2.12 (CH_3)	17.6, 21.8 (CH_3), 153.9 (br), 160.5, 168.5 (C=N, C=O)
8b	$C_{10}H_8ClNO_3$ (225.6)	1791	2.46 (CH_3)	14.8 (CH_3), 154.7, 160.2, 166.2 (C=N, C=O), 127.2, 128.9 (*o*, *m*-C), 131.6, 133.1 (*i*, *p*-C)[i]
8c	$C_{15}H_{10}ClNO_3$ (287.7)	1787		154.4, 160.0, 167.9 (C=N, C=O), 128.3, 128.6, 129.1, 129.4, 130.6, 130.7, 131.9, 133.2 (phenyl)
8d	$C_{11}H_{10}ClNO_3$ (239.7)	1787	2.42, 2.51 (CH_3)[d]	14.9, 21.6 (CH_3), 127.1, 129.5 (*o*, *m*-C), 130.0, 142.2 (*i*, *p*-C), 154.5 (br), 160.5, 166.1 (C=N, C=O)
8e	$C_8H_{10}ClNO_3$ (203.6)	1787	1.77 (m), 1.84 (m, 6H), 2.51 (m, 2H), 2.73 (m, 2H) (CH_2)[d]	25.1, 25.8, 26.8, 27.4, 31.8, 154.1 (br), 160.6, 172.9 (C=N, C=O)
8f	$C_{15}H_8ClNO_3$ (285.7)	1791		120.3, 120.4, 123.6, 128.5, 128.9, 129.2, 130.7, 132.6, 132.9, 133.5, 141.4, 142.6 (aryl), 153.1 (br), 160.8, 161.1 (C=N, C=O)
8g	$C_9H_6ClNO_3$ (211.6)	1791	8.55 (CH)	128.2, 128.8, 129.2, 132.9 (phenyl), 153.7 (br), 159.4, 160.4 (C=N, C=O)
8h	$C_4Cl_5NO_3$ (287.3)	1810, 1780[h]		91.0 (CCl_3), 151.3, 151.6, 158.5 (C=N, C=O)[l]
9a	$C_8H_{12}N_2O_4$ (200.2)	1771, 1785	2.11, 2.14 (CH_3)[f]	17.4, 21.7 (CH_3), 156.6 (br), 167.0 (C=N, C=O)[f]
9b	$C_{18}H_{16}N_2O_4$ (324.3)	1775, 1802[h]	2.47 (CH_3)	14.6 (CH_3), 158.7 (br), 164.4 (C=O, C=N), 127.1, 128.7, 131.2, 133.6 (phenyl)[i]
9c	$C_{28}H_{20}N_2O_4$ (448.5)	1775, 1802		159.4 (br), 165.7 (C=O, C=N), 128.1, 128.4, 129.0, 129.1, 130.2, 130.8, 131.4, 133.5 (phenyl)
9d	$C_{20}H_{20}N_2O_4$ (352.4)	1775, 1800[h]	2.37, 2.43 (CH_3)	14.5, 21.4 (CH_3), 158.9 (br), 164.2 (C=O, C=N), 127.0, 129.4, 130.8, 141.7 (aryl)
9e	$C_{14}H_{20}N_2O_4$ (280.3)	1767, 1800[f]	1.68 (m), 1.75 (m), 2.40 (m, 2H), 2.62 (m, 2H, CH_2)	25.2, 25.8, 27.7, 27.3, 31.9 (CH_2), 156.3 (br), 171.7 (C=O, C=N)[f]
9g	$C_{16}H_{12}N_2O_4$ (296.3)	1771, 1794[m]	8.55 (CH)	128.7, 129.0, 129.1, 132.4 (phenyl), 156.4, 158.3 (C=N, C=O)[i]
10a	$C_6H_9NO_4$ (159.1)	1756, 1787	2.11, 3.94 (CH_3)	17.4, 21.8, 53.6 (CH_3), 155.6, 157.8, 167.1 (C=N, C=O)[i]
10b	$C_7H_{11}NO_4$ (173.2)	1756, 1787	1.40 (d, $J = 7.1$), 2.11, 2.12 (CH_3), 4.39 (q, $J = 7.1$, CH_2)	13.9, 17.2, 21.6 (CH_3), 63.0 (CH_2), 156.3, 157.6, 166.6 (C=N, C=O)[i]
10c	$C_8H_{13}NO_4$ (187.2)	1744, 1787	1.39 (d, $J = 6.3$), 2.12, 2.13 (CH_3), 5.22 (sept, $J = 6.3$)[f]	17.4, 21.5 (2C), 21.9 (CH_3), 71.8 (CH_2), 156.1, 156.9, 167.0 (C=N, C=O)[f]
11	$C_{11}H_{12}N_2O_3$ (220.2)	1713, 1748[m]	2.13, 2.17 (CH_3), 9.14 (NH)[f]	17.5, 22.0 (CH_3), 153.2, 158.7, 167.8 (C=N, C=O), 136.2, 125.6 (*i*, *p*-C), 129.2, 119.8 (*o*, *m*-C)[f]

Table. (continued).

Product	Molecular Formula[a]	IR (CCl_4) ν (cm^{-1})[b]	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)[c]	^{13}C-NMR ($CDCl_3$/TMS) δ
12b	$C_{11}H_{15}Cl_6N_2OSb$ (525.7)	1679, 1764[m]	2.10, 2.53 (d, J = 1.0), 3.49 (d, J = 0.6, CH_3), 8.76 (CH)[d,n]	23.8, 41.3, 49.7 (CH_3), 130.0, 131.6, 132.3, 135.8 (phenyl), 154.2 (C=N), 172.8 (C=O)[n]
12c	$C_{16}H_{17}Cl_6N_2OSb$ (587.8)	1675, 1729[m]	2.74 (d, J = 1.0), 3.53 (d, J = 0.8, CH_3), 8.58 (m) (CH)[n]	42.7, 48.9 (CH_3), 157.2, 170.7 (C=N, C=O)[n]
12d	$C_{12}H_{17}Cl_6N_2OSb$ (539.8)	1679, 1764[m]	2.09, 2.44, 2.56 (d, J = 1.0), 3.48 (d, J = 0.7, CH_3), 8.73 (CH)[n]	21.4, 23.5, 41.3, 49.7 (CH_3), 129.7, 132.0, 133.2, 143.2 (aryl), 154.4 (C=N), 172.8 (C=O)[i,n]

[a] Satisfactory microanalyses obtained: C ±0.35, H ±0.26, N ±0.20. The C values obtained for the volatile compounds **8a** (−0.83%), **8e** (−0.90%), **9e** (−0.50%) are too low.
[b] Mattson Polaris FTIR Spectrophotometer.
[c] Bruker WM-250 and AC-250 spectrometers; ^{1}H-NMR at 295 K; ^{13}C-NMR at 263 K.
[d] At 263 K.
[e] In $CHCl_3$.
[f] At 273 K.
[g] In Nujol.
[h] Shoulder.
[i] At 295 K.
[j] Mixture of **5b** and **2b**.
[k] Mixture of **5c** and **2c**.
[l] Only one stereoisomer.
[m] In CH_2Cl_2.
[n] In CD_3CN.

formed immediately. After warming to 23 °C within 1 h pentane (80 mL) is added dropwise. The precipitate is filtered off and stirred under pentane (30 mL) for 10 min to give a colourless powder; yield: 7.08 g (91%); mp 178–188 °C (dec).

***N*-Phenylacetonitrilium Hexachloroantimonate (3b):**
1) From **2b** (1.98 g, 10 mmol) and $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (30 mL) as described for **3a** 1). After stirring for 30 min at −40 °C pentane (50 mL) is added dropwise at temperatures below −30 °C. The colourless precipitate is filtered off (4.28 g, 95%); mp 163–166 °C (dec).

2) From **8b** (2.26 g, 10 mmol) in CH_2Cl_2 (10 mL) and $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (20 mL) as described for **3a** 2). After stirring for 1 h at temperatures between −40 °C and −10 °C pentane (50 mL) is added slowly. The colourless precipitate (4.07 g, 90%) is filtered off; mp 162–167 °C (dec).

***N*-Phenylbenzonitrilium Hexachloroantimonate (3c):**[2,12,18,20,24]
1) From **2c** (2.60 g, 10 mmol) as described for **3a** 1). Yield: 4.99 g (97%) of a colourless powder; mp 234–238 °C (dec) (Lit.[18] mp 236–237 °C (dec)). Decomposition in CD_3CN.

2) From **8c** (2.88 g, 10 mmol) in CH_2Cl_2 (20 mL) and $SbCl_5$ (2.99 g, 10 mmol) in CH_2Cl_2 (10 mL) as described for **3a** 2). Yield: 4.65 g (90%) of an almost colourless powder; mp 228–230 °C (dec).

***N*-(4-Methylphenyl)acetonitrilium Hexachloroantimonate (3d):**
From **8d** (1.20 g, 5 mmol) as described for **3a** 2). Yield: 2.25 g (96%) of an almost colourless powder; mp 176–178 °C (dec).

Acetone *O*-(Trichloromethoxyformyl)oxime (5a):
1) A solution of **1a** (1.46 g, 20 mmol) in Et_2O (10 mL) is added dropwise under stirring to a cold (−60 °C) solution of **4** (4.95 g, 25 mmol) in Et_2O (15 mL). A precipitate is formed. The mixture is warmed to 23 °C in the course of 1 h. Stirring is continued until the precipitate is completely dissolved (ca 40 min). Evaporation of the solvent at 0 °C/13 Torr gives a colourless powder (2.21 g, 94%); mp 48–50 °C. Three attempts to reproduce this procedure led according to the NMR spectra to mixtures of various ratios of **5a** and **2a**.

2) A solution of **1a** (0.73 g, 10 mmol) in Et_2O (10 mL) is added dropwise to a cold (−40 °C) solution of **6** (4.45 g, 15 mmol) in Et_2O (10 mL). After stirring at 23 °C for 30 min the solvent is evaporated. The ^{13}C-NMR-spectrum of the solid colourless residue (3.33 g) shows the signals for **2a**, **5a**, and **6**.

Acetophenone *O*-(Trichloromethoxyformyl)oxime (5b):
From **1b** (2.70 g, 20 mmol) as described for **5a**. Yield: 4.37 g (ca 88%) of a colourless oil, which gradually solidifies when kept at 5 °C. The product decomposes within one week at 5 °C. According to the spectra the product consists of an 1:1-mixture of **5b** and **2b**.

Benzophenone *O*-(Trichloromethoxyformyl)oxime (5c):
From **1c** (3.95 g, 20 mmol) as described for **5b**. Yield: 4.69 g of a colourless powder. According to the spectra the product consists of a 2:1-mixture of **5c** and **2c**.

Acetone *O*-(Chlorooxalyl)oxime (8a):
A solution of **1a** (14.62 g, 200 mmol) in Et_2O (50 mL) is added dropwise under stirring to a cold (−20 °C) solution of **7** (38.01 g, 300 mmol) in Et_2O (50 mL). Stirring is continued for 30 min at −20 °C and then at +23 °C until the primary formed precipitate is completely dissolved (about 10 min). The Et_2O is removed at 23 °C/13 Torr and the residue is distilled to afford a colourless volatile oil, yield: 22.24 g (68%), which turns yellow within 12 h; bp 36–40 °C/0.1 Torr. The residue of the distillation (4.97 g, 25%) consists of almost pure **9a**. After standing for some hours solutions of **8a** show additional NMR signals for **9a**.

Acetophenone *O*-(Chlorooxalyl)oxime (8b):
A solution of **1b** (13.52 g, 100 mmol) in Et_2O (20 mL) is added dropwise under stirring to a cold (−60 °C) solution of **7** (19.39 g, 150 mmol) in Et_2O (20 mL). The mixture is stirred for 1 h at temperatures between −60 °C and −35 °C. Evaporation of the solvent at 0° to 23 °C/13 Torr furnishes a colourless powder; yield: 20.89 g (93%), mp 42–44 °C.

Benzophenone *O*-(Chlorooxalyl)oxime (8c):
A solution of **1c** (19.72 g, 100 mmol) in Et_2O (250 mL) is added dropwise to a cold (−40 °C) solution of **7** (19.04 g, 150 mmol) in Et_2O (25 mL). A precipitate is formed. Stirring is continued for 15 min at −40 °C and then for 1 h at 23 °C. Evaporation of the solvent at 0 °C/13 Torr affords a colourless solid; yield: 23.30 g (81%); mp 80–83 °C.

4-Methylacetophenone *O*-(Chlorooxalyl)oxime (8d):
From **1d** (1.49 g, 10 mmol) in Et_2O (10 mL) and **7** (1.90 g, 15 mmol) in Et_2O (10 mL) as described for **8c**. Yield: 2.37 g (99%) of a colourless powder, which can be crystallized from $CHCl_3$ (0.30 g from 10 mL) to render colourless leaflets; mp 58–60 °C.

Cyclohexanone *O*-(Chlorooxalyl)oxime (8e):
A solution of **1e** (1.13 g, 10 mmol) in Et_2O (20 mL) is added dropwise to a cold (−40 °C) solution of **7** (2.54 g, 20 mmol) in Et_2O (10 mL). An immediately formed precipitate dissolves when the mixture is stirred for 1 h at −20 °C. Evaporation of the solvent at low temperature (−15 °C) under reduced pressure affords an unstable colourless oil (1.98 g, 97%), which at 23 °C soon turns dark with evolution of gases.

9-Fluorenone *O*-(Chlorooxalyl)oxime (8f):
A solution of **7** (1.90 g, 15 mmol) in Et_2O (10 mL) is added dropwise to a suspension of **1f** (1.95 g, 10 mmol) in cold (−40 °C)

Et_2O (20 mL). The mixture is stirred for 1 h at −20 °C. The solvent is evaporated at 0 °C/13 Torr furnishing a pale yellow powder; yield: 2.60 g (91%); mp 97–100 °C.

Benzaldehyde *O*-(Chlorooxalyl)oxime (8g):
A solution of **1g** (1.21 g, 10 mmol) in Et_2O (10 mL) is added dropwise to a cold (−40 °C) solution of **7** (1.90 g, 15 mmol) in Et_2O (10 mL). After stirring for 1 h at −20 °C the solvent is evaporated at −10 °C/13 Torr leaving back a colourless temperature sensitive powder; yield 2.04 g (97%); dec 23–47 °C with evolution of gas and formation of benzonitrile.

***N*-(Chlorooxalyloxy)trichloroethanimidoyl Chloride (8h):**
A mixture of **1h**[34,35,38] (1.97 g, 10 mmol) and **7** (3.81 g, 30 mmol) is stirred for 2 h at 23 °C. Evaporation of excess of **7** gives a colourless powder, yield: 2.67 g (93%), which can be sublimed (23 °C, 0,1 Torr, 84%); mp 27–30 °C.

Acetone *O,O'*-Oxalyldioxime (9a):
A solution of **1a** (1.46 g, 20 mmol) in Et_2O (20 mL) is added dropwise to a cold (−40 °C) solution of **8** (1.27 g, 10 mmol) in Et_2O (10 mL). A precipitate is formed. The mixture is stirred for 20 min at −40 °C and then for 1 h at 23 °C. Evaporation of the solvent affords a colourless powder, yield: 1.70 (85%), which can be crystallized from CH_2Cl_2/pentane at −20 °C to give colourless prisms; mp 66–67 °C.

Acetophenone *O,O'*-Oxalyldioxime (9b):
From **1b** (2.70 g, 20 mmol) as described for **9a**. Yield: 3.18 g (98%) of a colourless powder, which crystallizes within 4 weeks from $CHCl_3$/pentane at −20 °C; mp 138–140 °C.

Benzophenone *O,O'*-Oxalyldioxime (9c):
From a solution of **1c** (3.94 g, 20 mmol) in Et_2O (30 mL) as described for **9a**. Yield: 4.48 g (100%) of a colourless powder, which crystallizes from CH_2Cl_2/pentane at −20 °C affording colourless platelets; mp 163–165 °C.

4-Methylacetophenone *O,O'*-Oxalyldioxime (9d):
From **1d** (2.98 g, 20 mmol) as described for **9a**. Yield: 3.21 g (91%) of a colourless powder, which slowly crystallizes from $CHCl_3$ at −20 °C; mp 128–130 °C.

Cyclohexanone *O,O'*-Oxalyldioxime (9e):
From **1e** (2.26 g, 20 mmol) as described for **9a**. Yield: 2.80 g (99%) of a volatile colourless powder; mp 53–55 °C (dec).

Benzaldehyde *O,O'*-Oxalyldioxime (9g):
From **1g** (2.42 g, 20 mmol) as described for **9a**. Yield: 2.81 g (95%) of a colourless powder of moderate solubility in most organic solvents; mp 111–114 °C.

Acetone *O*-(Methoxalyl)oxime (10a):
A solution of **8a** (3.25 g, 20 mmol) in $CHCl_3$ (15 mL) is added dropwise to a cold (−30 °C) solution of MeOH (0.64 g, 20 mmol) and pyridine (1.58 g, 20 mmol) in $CHCl_3$ (20 mL). Stirring is continued for 1 h at 23 °C. Pyridinium chloride is precipitated by slow addition of Et_2O (80 mL). Evaporation of the solvent and distillation of the residue gives a colourless oil; yield: 2.35 g (74%); bp 58–60 °C/0.1 Torr.

Acetone *O*-(Ethoxalyl)oxime (10b):
1a (3.65 g, 50 mmol) in Et_2O (20 mL) is added dropwise to a cold (−20 °C) solution of ethyl oxalyl chloride (6.83 g, 50 mmol) in Et_2O (10 mL). A colourless precipitate is formed, which dissolves when the mixture is warmed to 23 °C. Evaporation of the solvent affords a colourless oil; yield: 7.27 g (84%); bp 65–68 °C/0.1 Torr.

Acetone *O*-(Isopropoxalyl)oxime (10c):
From *i*-PrOH (1.20 g, 20 mmol) as described for **10a**. Distillation of the crude product affords a colourless oil; yield: 2.82 g (76%); bp 64–66 °C/0.1 Torr.

Acetone *O*-(Anilinooxalyl)oxime (11):
A solution of aniline (1.86 g, 20 mmol) in $CHCl_3$ (10 mL) is added dropwise under stirring to a cold (−40 °C) solution of **8a** (1.63 g, 10 mmol) in $CHCl_3$ (20 mL). After stirring for 1 h at 23 °C anilinium chloride is filtered off. Evaporation of the filtrate yields a colourless powder, yield: 1.51 g (69%), which can be purified by crystallization from $CHCl_3$ (25 mL) at −20 °C; mp 196–201 °C.

N^1-Acetyl-N^2,N^2-dimethyl-N^1-phenylformamidinium Hexachloroantimonate (12b):
A solution of DMF (0.37 g, 5 mmol) in CH_2Cl_2 (10 mL) is added dropwise to a cold (−10 °C) suspension of **3b** (2.26 g, 5 mmol) in CH_2Cl_2 (20 mL). Stirring is continued for 10 min at −10 °C. After cooling the clear solution to −40 °C slow addition of Et_2O (50 mL) affords a colourless powder; yield: 2.18 g (83%); mp 165–170 °C (dec).

N^1-Benzoyl-N^2,N^2-dimethyl-N^1-phenylformamidinium Hexachloroantimonate (12c):
From **3c** (2.57 g, 5 mmol) as described for **12b**. Yield: 2.78 g (95%) of a pale yellow powder, which can be purified by precipitation from CH_2Cl_2/Et_2O; mp 138–144 °C (dec).

N^1-Acetyl-N^2,N^2-dimethyl-N^1-(4-methylphenyl)formamidinium Hexachloroantimonate (12d):
From **3d** (2.33 g, 5 mmol) as described for **12d**. Yield: 1.20 g (64%) of a colourless powder; mp 120–124 °C (dec).

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