Chemistry of Halonitroethenes, 1: First Synthesis of Functionalized 3-Chloroquinoxalin-2(1H)-one 4-Oxides

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Abstract: A one-pot annulation reaction of aniline and its ring-substituted derivatives with 1,1,2-trichloro-2-nitroethene (TCNiE) was developed delivering 3-chloroquinoxalin-2(1H)-one 4-oxides, exclusively, in good yields. The structure was proved by X-ray analysis. The C–N cyclization, a competing reaction to the double S_NVin reaction of 1,1,2-trichloro-2-nitroethene with amines, can be controlled by the mode of addition. Some of the resulting quinoxalines are promising candidates with respect to their prospective biological, especially pharmacological, activity.

Key words: annulation, C–N coupling, amines, halides, nitro compounds, nitrones, quinoxalines

Halonitroalkenes are valuable building blocks for the directed synthesis of four-, five-, and six-membered heterocycles with a unique substitution pattern. In particular, to date an impressive number of different reactions of pen- tachloro-2-nitrobuta-1,3-diene have been documented;2 further efforts are underway to explore the whole synthetic potential of this class of compounds. The group of known halonitroethenes is still rather small, consisting of 14 members, which have been prepared by four different synthetic routes.3,4 Synthetic applications of halonitroethenes are rare in the literature.5 In this context we became interested in the availability and chemistry of 1,1,2-trichloro-2-nitroethene (TCNiE, 2), a perchlorovinyl analogue of nitryl chloride, representing the reactive key unit of many polychloroalkanes. 1,1,2-Trichloro-2-nitroethene (2) is now easily accessible by electrophilic nitration of the inexpensive industrial solvent trichloroethene with nitric acid.3k,3k Nitration of a solution of trichloroethene in cyclohexane in a liquid–liquid extractor with nitric acid at 50 °C under isothermal conditions, to our surprise a new product precipitated, independent of the solvent used (Scheme 1).

When the mode of addition is reversed, thus the aniline solution (1 equiv) is slowly added by a syringe pump to a solution of 2 (1 equiv) at temperatures between –10 and 50 °C under isothermal conditions, to our surprise a new product precipitated, independent of the solvent used (Scheme 2). Due to the 1:1 ratio of the starting materials 2 and 1a, an intermediate such as 5 or an equivalent is formed. The low solubility of the product in combination with its high melting point and the NMR, IR, and MS spectra made formation of the 3-chloroquinoxalin-2(1H)-
one 4-oxide (6) appear likely. An unambiguous spectroscopic analysis of the product proved difficult.

Additionally, single crystals could not be obtained by recrystallization. Fortunately, the C–Cl group of the C-chloronitrone unit of 7 allowed \( S_N \) reactions. By transformation of the 7-methoxy derivative 7 into 8 using the strong nucleophile dodecane-1-thiol, the long alkyl chain improved the solubility and we were able to isolate single single crystals of 3-(dodecylsulfanyl)-7-methoxyquinoxalin-2(1H)-one 4-oxide (8) (Scheme 3). X-ray analysis confirmed the structure (Figure 1).9

The detailed mechanism of formation of the parent heterocycle 6 remains unclear. Apparently, the reaction starts with Michael addition of the aromatic amine at the C2 position of 1,1,2-trichloro-2-nitroethene (2) forming an intermediate such as 9. N-Alkylanilines do not form quinoxalinones. Then a proton shift occurs: the ammonium proton migrates to the nitro group thus forming a nitronium unit of the corresponding 4-oxide 8 (Scheme 3). X-ray analysis confirmed the structure (Figure 1).9

To evaluate the synthetic scope and limitation of this annulation reaction, all reaction conditions were modified in a stepwise process. If one equivalent of aniline or a derivative and two equivalents of a tertiary amine such as triethylamine or 1,4-diazabicyclo[2.2.2]octane were added to a solution of 2 in a solvent such as methanol, tetrahydrofuran, or toluene, the new quinoxalin-2(1H)-one 4-oxide 6 precipitated completely (Scheme 2). The product yield always depended on the reaction temperature, the addition rate of the aniline to the reaction mixture, the solvent, and the substitution pattern of the aniline.

The annulation reaction was exothermic. Under isothermal conditions the product yield increased with higher reaction temperatures. Reaction rate and yield were also dependent on the ring substituents of the aniline derivatives (Figure 2). In a number of cases the reaction was almost complete within 1–3 hours. Not all reactions were optimized with respect to time.

The product yield of 7 was not strongly dependent on the nature of the reaction solvent (Table 1); methanol and tetrahydrofuran were especially well suited. Only in the case of acetonitrile did the yield decreased.

The broad range of applicability of this annulation reaction is documented in Table 2, many different substituents are tolerated. In the case of \( m \)-anisidine the reaction was highly regioselective. Only the 3-chloro-7-methoxyquinoxalin-2(1H)-

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**Scheme 3** Transformation of 7 to a soluble derivative 8

**Scheme 4** Postulated mechanism for the formation of 6

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**Figure 1** X-ray crystal structure of the quinoxalin-2-one derivative 8

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Table 1  Yields of Quinoxalinone 7 in Various Solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Yield (%)</th>
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<tr>
<td>MeOH</td>
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<tr>
<td>THF</td>
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<tr>
<td>toluene</td>
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<tr>
<td>MeCN</td>
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*a Reaction conditions: Et$_3$N (2 equiv), r.t., 12 h.

Table 2  Range of Newly Synthesized 3-Chloroquinoxalin-2(1H)-one 4-Oxides

<table>
<thead>
<tr>
<th>R$^1$</th>
<th>R$^2$</th>
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<th>R$^4$</th>
<th>Product</th>
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</table>

*a Reaction conditions: Et$_3$N (2 equiv), MeOH, r.t. to 30 °C, 1–62 h.

Under identical reaction conditions the yields of the 3-chloroquinoxalin-2(1H)-ones 4-oxides depend strongly on the substituents of the introduced anilines, ranging from 9 to 65%. Electron-withdrawing substituents at C6,

one 4-oxide (7) could be isolated from the reaction mixture. For 3-aminophenol, we obtained 3-chloro-5-hydroxyquinoxalin-2(1H)-one 4-oxide (15) in only 6% yield and the 7-hydroxy derivative 14 in 59% yield.

In conclusion, we have found a novel one-pot synthesis of a broad range of substituted 3-chloroquinoxalin-2(1H)-ones starting from easily accessible 1,1,2-trichloro-2-nitroethene (2) and subsequent addition of substituted anilines. This addition mode is crucial. The structure of a long-chain derivative was proven by X-ray. The products should offer interesting biological, in particular pharmacological, properties. Therefore, corresponding tests of these promising compounds are presently underway.

All chemicals were obtained from commercial suppliers and used without further purification. MeOH was purchased as reagent grade. Melting points were determined with a Büchi apparatus 520 and are uncorrected. $^1$H and $^1$H-decoupled $^{13}$C NMR spectra were measured on a Bruker Avance 400 (400 MHz) or Bruker DPX 200 (200 MHz) in CDCl$_3$ or DMSO-$d_6$.

In the case of chlorinated compounds, all peak values of molecular ions as well as fragments $m/z$ refer to the isotope $^{35}$Cl.

HRMS were measured with a Finnigan MAT 95 sector field instrument (EI) or with a Bruker APEX IV 7.
Tesla FT ion cyclotron resonance mass spectrometer (ESI). TLC was performed on Merck TLC plates (aluminum-backed) silica gel 60 F 254. Flash chromatography was carried out on silica gel 60 (Merck).

1,1,2-Trichloro-2-nitroethene (2)
A mixture of concd HNO3 (900 mL, 65%) and cyclohexane (200 mL) in the extractor vessel of a rotating Normag liquid–liquid extractor for solvents lighter than H2O was heated in an oil bath to 55 °C. Trichloroethene (250 mL, 2.81 mol) and cyclohexane (100 mL) was added to the evaporator vessel. After continuous reaction and extraction for 9 h the organic layers were separated and washed with H2O and Brine. Redistillation on a Fischer Spaltrohr column HMC 500 C gave pure 2: yield: 96.9 g (32%) related to reisolated trichloroethene (139 g, 1.06 mol); bp 56–57 °C/25 mbar.

IR (NaCl): 2868, 2623, 2361, 2342, 1548, 1324, 1052, 933, 871, 819, 798, 749 cm–1.

IR (KBr): 3060, 3014, 2878, 1679, 1590, 1571, 1471, 1442, 1415, 1373, 1353, 1273, 1222, 1132, 1026, 847, 772, 677, 608 cm–1.

UV (CH2Cl2): λmax (%): 210 (M+ – O) (100), 196 (M+ – NO) (58).


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3-Chloro-7-methoxyquinoxalin-2(1H)-one 4-Oxide (7); Typical Procedure II
Under N2 at r.t. a soln of m-anisidine (1.11 mL, 10 mmol) and Et3N (2.88 mL, 20 mmol) in anhyd MeOH (20 mL) was added via syringe pump over 12 h with stirring to a soln of 2 (1.76 g, 10 mmol) in anhyd MeOH (10 mL). The product precipitated from the mixture and was isolated by filtration with suction. The solid was washed with MeOH, dil aqu HCl, H2O, and Et2O and subsequently dried in vacuo to give as a pale green solid: yield: 0.71 g (73%); mp 246–247 °C (dec).

IR (KBr)): 2729, 2943, 2902, 2824, 1665 (C=O), 1603, 1530, 1489, 1440, 1407, 1373, 1353, 1273, 1222, 1132, 1026, 847, 772, 677, 549 cm–1.

3-Chloroquinolin-2(1H)-one 4-Oxide (12); Typical Procedure III
Under N2 at r.t. a soln of p-anisidine (1.23 g, 10 mmol) and DABCO (1.12 g, 10 mmol) in anhyd MeOH (20 mL) was added via syringe pump over 12 h with stirring to a soln of 2 (1.76 g, 10 mmol) in anhyd MeOH (10 mL). The product precipitated from the mixture and was isolated by filtration with suction. The solid was washed with MeOH, dil aqu HCl, H2O, and Et2O and subsequently dried in vacuo to give 12 as a green solid: yield: 1.23 g (54%); mp 234–235 °C (dec).

IR (KBr)): 2729, 2943, 2902, 2824, 1665 (C=O), 1603, 1530, 1489, 1440, 1407, 1373, 1353, 1273, 1222, 1132, 1026, 847, 772, 677, 549 cm–1.

3-Chloro-6-7-Dimethoxyquinoxalin-2(1H)-one 4-Oxide (13)
Following typical procedure I gave 13 as a pale green solid; yield: 40%; mp 268–269 °C (dec).

IR (KBr)): 3138, 3083, 3038, 2942, 1672 (C=O), 1630, 1604, 1527, 1511, 1460, 1442, 1426, 1411, 1379, 1333, 1307, 1256, 1213, 1187,
1119, 1030, 1003, 927, 855, 830, 792, 769, 723, 688, 664, 624, 575, 541, 527 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\); \(\delta = 12.64\) (br s, 1 H, NH), 7.52 (s, 1 H, H5), 6.82 (s, 1 H, H6), 3.84 (s, 3 H, OCH\(_3\)), 3.83 (s, 3 H, OCH\(_3\)).

\(^1^3\)C NMR (100 MHz, DMSO-\(d_6\); \(\delta = 153.2\) (C6), 153.0 (C7) 146.5 (C2), 131.6 (C3), 126.1, 124.2, 100.3, 98.0, 56.3 (OCH\(_3\)), 56.2 (OCH\(_3\)).

MS (EI): \(m/z\) \(\%\) = 256 (M\(^+\)) (100), 24 (M\(^+\) – O) (10), 226 (M\(^+\) – NO) (60), 150 (30).

HRMS (ESI): \(m/z\) \(\%\) = 257.03236; found: 257.03236.

3-(Dodecylsulfanyl)-7-methoxyquinoxalin-2(1H)-one 4-Oxide (8)

Under N\(_2\) at r.t. a suspension of 3-chloro-7-methoxyquinoxalin-2(1H)-one 4-oxide (7, 1.10 g, 4.41 mmol), NaOEt (0.721 g, 10.59 mmol), and dodecan-1-thiol (1.95 g, 9.71 mmol) in anhyd MeOH (10 mL) was stirred for 1 h. Subsequently, the mixture was heated to 50 °C for 10 h. After cooling to r.t., dil qHCl was added. The product precipitated from the mixture and was isolated by filtration with suction. The solid was washed with dil qHCl, H\(_2\)O, and MeOH and then dried in vacuo to obtain 8 as a yellow solid; yield: 1.56 g (89%); mp 138–140 °C.

\(\delta = 12.56\) (br s, 1 H, NH); \(\delta = 8.8\) Hz, \(J_{HF} = 2.6\) Hz, 1 H, H5), 7.52–7.48 (m, 2 H, H7, H8), 7.41 (t, \(J = 7.4\) Hz, 2 H, SCH\(_2\)), 1.60–1.55 (m, 2 H, CH\(_2\)), 0.87 (t, \(J = 6.8\) Hz, 3 H, CH\(_3\)CH\(_2\)).

\(\delta = 160.2, 158.4, 138.0, 131.5, 125.9, 121.0, 113.2, 98.6, 55.9\) (OCH\(_3\)), 31.9, 31.8, 30.5, 29.6, 29.6, 29.5, 29.4, 29.3, 21.8, 22.6, 14.1.

Anal. Calc'd for C\(_8\)H\(_4\)ClFN\(_2\)O: C, 64.25; H, 8.22; N, 7.14; S, 8.17. Found: C, 64.37; H, 8.17; N, 7.04; S, 8.44.

3-Chloro-7-hydroxyquinoxalin-2(1H)-one 4-Oxide (14) and 3-Chloro-5-hydroxyquinoxalin-2(1H)-one 4-Oxide (15)

Following typical procedure II, addition time 62 h. The precipitated solid was a mixture of 2 regioisomers. The 7-hydroxyquinoxalinone 14 was separated by washing the solid with CHCl\(_3\) (50 ml) and acetone (50 ml). Subsequently, the second isomer 15 was isolated by evaporating the solvents.

3-Chloro-7-hydroxyquinoxalin-2(1H)-one 4-Oxide (14)

Red-brown solid; yield: 59%; mp 276–277 °C.

IR (KBr): 3072, 2978, 2908, 2863, 2819, 2706, 1667 (C=O), 1627, 1611, 1535, 1492, 1439, 1367, 1317, 1267, 1128, 1090, 974, 876, 861, 823, 798, 733, 656, 592, 483 cm\(^{-1}\).

\(\delta = 12.83\) (br s, 1 H, NH), 8.16 (dd, \(J = 9.4\) Hz, \(J_{HF} = 5.5\) Hz, 1 H, H5), 7.19–7.25 (m, 1 H, H6), 7.11 (dd, \(J = 2.7\) Hz, \(J_{HF} = 9.2\) Hz, 1 H, C8).

\(\delta = 12.6\) (br s, 1 H, NH), 8.16 (dd, \(J = 9.4\) Hz, \(J_{HF} = 5.5\) Hz, 1 H, H5), 7.19–7.25 (m, 1 H, H6), 7.11 (dd, \(J = 2.7\) Hz, \(J_{HF} = 9.2\) Hz, 1 H, C8).

\(\delta = 12.83\) (br s, 1 H, NH), 8.16 (dd, \(J = 9.4\) Hz, \(J_{HF} = 5.5\) Hz, 1 H, H5), 7.19–7.25 (m, 1 H, H6), 7.11 (dd, \(J = 2.7\) Hz, \(J_{HF} = 9.2\) Hz, 1 H, C8).

\(\delta = 12.83\) (br s, 1 H, NH), 8.16 (dd, \(J = 9.4\) Hz, \(J_{HF} = 5.5\) Hz, 1 H, H5), 7.19–7.25 (m, 1 H, H6), 7.11 (dd, \(J = 2.7\) Hz, \(J_{HF} = 9.2\) Hz, 1 H, C8).

3-Chloro-5-hydroxyquinoxalin-2(1H)-one 4-Oxide (15)

Orange solid; yield: 6%; mp 274–275 °C (dec).

IR (KBr): 3423, 3211, 3019, 2929, 2862, 1665 (C=O), 1625, 1608, 1513, 1450, 1374, 1338, 1306, 1238, 1174, 1144, 1130, 1088, 866, 810, 758, 596 cm\(^{-1}\).

\(\delta = 12.86\) (br s, 1 H, NH), 8.06 (s, 1 H, H5), 7.71 (dd, \(J = 8.8\) Hz, \(J_{HF} = 2.1\) Hz, 1 H, H7), 7.38 (d, \(J = 8.8\) Hz, 1 H, H8).

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3-Chloro-2,1,2-dihydroquinoxaline-6-carboxylic Acid 4-Oxide (22)
Following typical procedure I gave 22 as a yellow solid; yield: 77%; mp 234 °C (dec).
IR (KBr): 3454 (O–H), 3165, 3105, 2960, 2702, 2627, 2551, 1904, 1699 (C=O), 1627, 1536, 1491, 1432, 1402, 1346, 1288, 1259, 1234, 1170, 1143, 1077, 1003, 954, 920, 849, 788, 768, 740, 685, 672, 633, 571, 444 cm⁻¹.
1H NMR (200 MHz, DMSO-d₆): δ = 13.26 (br s, 1 H, NH), 8.30 (d, J = 1.9 Hz, 1 H, H5), 8.05 (dd, J = 8.6, 1.9 Hz, 1 H, H7) 7.54 (d, J = 8.6 Hz, 1 H, H8).
13C NMR (100 MHz, DMSO-d₆): δ = 153.6 (C2), 135.2 (C5), 133.6 (C3), 130.3, 124.5 (C7), 118.0, 117.9 (C8), 105.8.

3-Chloro-2,1,2-dihydroquinoxaline-6-carboxylic Acid 4-Oxide (23)
Following typical procedure I gave 23 as a yellow solid; yield: 65%; mp 243 °C (dec).
IR (KBr): 3163, 3075, 2933, 2230 (C≡N), 1665 (C=O), 1621, 1526, 1473, 1441, 1403, 1352, 1299, 1262, 1202, 1153, 1124, 1091, 953, 920, 848, 809, 741, 677, 642, 598, 588, 556, 517 cm⁻¹.
1H NMR (400 MHz, DMSO-d₆): δ = 13.26 (br s, 1 H, NH), 8.30 (d, J = 1.9 Hz, 1 H, H5), 8.05 (dd, J = 8.6, 1.9 Hz, 1 H, H7) 7.54 (d, J = 8.6 Hz, 1 H, H8).
13C NMR (100 MHz, DMSO-d₆): δ = 153.6 (C2), 135.2, 134.6, 130.4, 124.5, 118.1 (CN), 117.9, 105.8. C3 was not detected.

3-Chloro-2,1,2-dihydroquinoxaline-6-carboxylic Acid 4-Oxide (24)
Following typical procedure I gave 24 as a yellow solid; yield: 43%; mp 235 °C (dec).
IR (KBr): 3085, 3036, 2908, 2814, 1866, 1808, 1782, 1752, 1656 (C≡N), 1611, 1511, 1438, 1420, 1395, 1344, 1312, 1294, 1250, 1198, 1177, 1122, 944, 890, 849, 878, 827, 735, 708, 659, 607, 570, 523, 499, 474 cm⁻¹.
1H NMR (400 MHz, DMSO-d₆): δ = 12.56 (br s, 1 H, NH), 8.14 (d, J = 2.4 Hz, 1 H, H5), 8.06 (d, J = 2.4 Hz, 1 H, H7).
13C NMR (100 MHz, DMSO-d₆): δ = 153.6 (C2), 135.2 (C3), 132.0, 128.5, 127.6, 121.3, 118.3 (C5).

3-Chloro-2,1,2-dihydroquinoxaline-6-carboxylic Acid 4-Oxide (25)
Following typical procedure I gave 25 as a beige solid; yield: 35%; mp 236 °C (dec).
IR (KBr): 3188, 3130, 3078, 3022, 2924, 1666 (C≡N), 1601, 1589, 1502, 1456, 1439, 1350, 1293, 1252, 1165, 1119, 954, 899, 827, 813, 784, 739, 729, 654, 577, 526, 472 cm⁻¹.
1H NMR (400 MHz, DMSO-d₆): δ = 12.53 (br s, 1 H, NH), 8.12 (d, J = 9.2 Hz, 1 H, H6).

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13C NMR (100 MHz, DMSO-d6): δ = 153.8 (C2), 135.4 (C3), 134.3, 130.6, 130.5, 124.3, 119.4, 118.5 (C5).

MS (EI): m/z (%) = 264 (M+) (91), 248 (M+ − O) (12), 234 (M+ − NO) (100).

Anal. Calcd for C8H3Cl3N2O2 (263.93): C, 36.19; H, 1.14; Cl, 39.74; N, 10.49.

Acknowledgment

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References


(9) X-ray crystallographic analysis of C9H7ClN2O2 was performed at 223(2) K by using a STOE IPDS II diffractometer with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. Crystal system: triclinic, P1 (No. 2), Z = 1, a = 632.32(13) pm, b = 900.7(2) pm, c = 1395.2(4) pm, α = 84.236(9), β = 83.827(17), γ = 77.126(18), V = 1064.9(4) Å3 pm. The structure was solved by direct methods (SHELXLS-97) using 373 refined parameters. Structure refinement: full matrix least-squares methods on F2 using SHELXL-97 all nonhydrogen atoms with anisotropic displacement parameters. All hydrogen atoms were taken from a difference Fourier synthesis and were isotropically refined. The refinement converged to a final R = 0.1223 for 3704 unique reflections and R1 = 0.0540 for 2420 observed reflections [l > 2σ(l)] and 373 refined parameters with a goodness-of-fit of 1.053. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-679570. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336303, e-mail: deposit@ccdc.cam.ac.uk].

(10) (a) Sheldrick, G. M. SHELXS-97; University of Göttingen: Germany, 1997. (b) Sheldrick, G. M. SHELXL-97; University of Göttingen: Germany, 1997.

