Chemistry of Polyhalogenated Nitrobutadienes, 2: Synthesis of *N*-Tetrachloroallylidene-*N*′-arylhydrazines by a Formal Synproportionation Reaction

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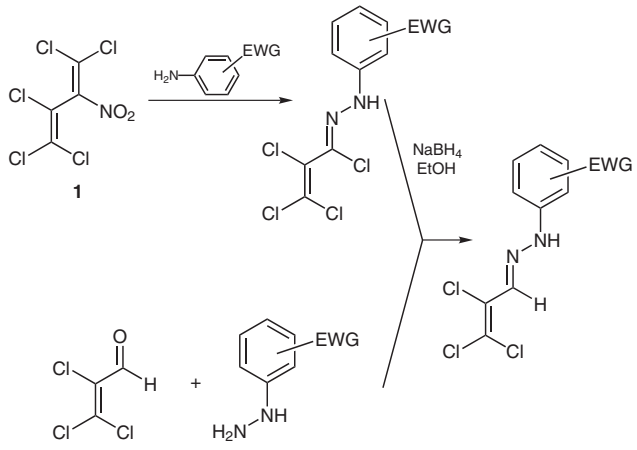
Abstract: The reaction of 2-nitropentachlorobuta-1,3-diene with a variety of anilines substituted with electron-withdrawing groups generates, contrary to expectations, *N*-tetrachloroallylidene-*N*′-arylhydrazines instead of 1,1-bisaminated substitution products. The imidoyl-type chlorides are capable of undergoing nucleophilic substitution with amines or hydrides. The resulting compounds should exhibit physiological activity, especially for use in crop science.

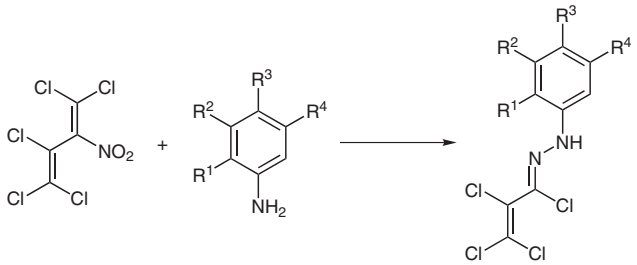
Key words: nitro compounds, halides, hydrazones, N–N couplings, nucleophilic substitutions

2-Nitroperchlorobuta-1,3-diene (**1**) is a valuable precursor for various synthetic applications.[1] In this context, it is well known that the reaction of **1** with aromatic amines follows a classical S_NVin pathway that leads to the formation of 1,1-diamino-2-nitroperchlorobutadienes.[2,3] While this type of reaction requires amines bearing electron-donating substituents, in the present work an unprecedented reaction is presented starting from nitrodiene **1** and different aromatic amines with an electron-withdrawing group, such as nitroanilines (Scheme 1).



Scheme 1

Starting from these less basic aniline derivatives, the reaction takes a different route: after an initial nucleophilic substitution by the aniline derivative the second C(1)–Cl bond of nitrodiene **1** is attacked by an oxygen of the nitro group. We found that the conversion of **1** with 4-nitroaniline (**2**), 2-nitroaniline (**3**), 3-nitroaniline (**4**), 2-methyl-5-nitroaniline (**5**), 4-cyanoaniline (**6**), and 4-trifluoromethylaniline (**7**) led, predominantly, to *N*-(tetrachloroallylidene)-*N*′-arylhydrazines **8**–**13**. The chemical yields of these rare compounds[4] range from 17–63% (Scheme 2).



1 **2–7** **8–13**

2,**8**:	$R^1 = R^2 = R^4 = H$, $R^3 = NO_2$	63%
3,**9**:	$R^1 = NO_2$, $R^2 = R^3 = R^4 = H$	35%
4,**10**:	$R^1 = R^3 = R^4 = H$, $R^2 = NO_2$	17%
5,**11**:	$R^1 = Me$, $R^2 = R^3 = H$, $R^4 = NO_2$	28%
6,**12**:	$R^1 = R^2 = R^4 = H$, $R^3 = CN$	45%
7,**13**:	$R^1 = R^2 = R^4 = H$, $R^3 = CF_3$	50%

Scheme 2

In the course of this reaction a butyl unit (butadiene derivative **1**) is losing one carbon atom as carbon dioxide resulting in an unusual *N*-perchloroallylidene unit. To the best of our knowledge, such a transformation of a nitro group is unique. Formally, it may be regarded as a synproportionation reaction of an unsaturated nitro compound with an aniline derivative, accompanied by migration of a chloride anion.

Recently, it was published that the LUMO of 2-nitroperchlorobuta-1,3-diene (**1**) is located preferentially at the dihalogeno-nitrovinyl fragment, and to an extent of 67–85% at the C-1 carbon atom.[2] Therefore, independent of the nucleophilicity of the aniline derivatives the first substitution reaction always takes place at the C-1 position of **1**.

But in the second step the imidoyl chloride **II** now preferentially reacts with the nitronic acid unit of **II** in competition with the electron-deficient anilines. In addition, this conversion occurs stereospecifically with respect to the configuration of the double bonds. A plausible mechanism is shown in Scheme 3.

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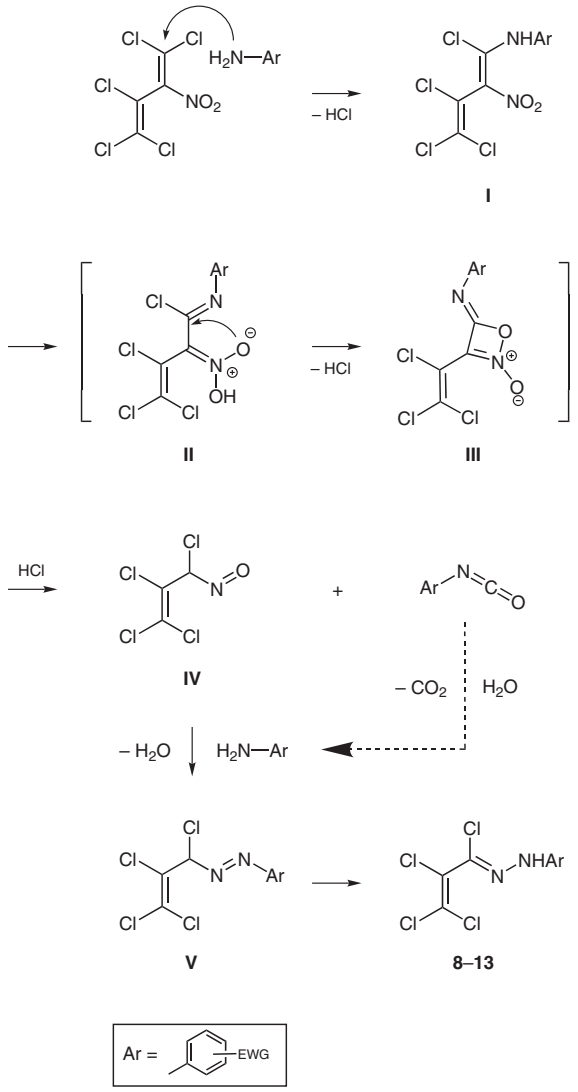


Scheme 3 Assumed mechanism for the formation of hydrazones from **1**

The initial step, apparently, is the nucleophilic attack of the aniline at the positively charged C-1 position of the nitrodiene. After tautomerization to a reactive imidoyl chloride **II** one of the oxygens of the newly formed conjugated nitronic acid attacks the C-1 carbon generating an oxazetine ring **III** with elimination of hydrochloric acid. Acid-supported cycloreversion then affords both the nitroso compound **IV** and the corresponding aryl isocyanate. Condensation of **IV** with the aniline derivatives primarily leads to the formation of azo compounds **V** with elimination of water. The following isomerization gives the more stable hydrazones **8**–**13**. The aryl isocyanates can either add additional anilines to build up ureas or react with the water formed to give carbamic acids which decompose readily. The extruded carbon dioxide was trapped and detected by its reaction with an aqueous solution of barium hydroxide. This sequence selectively yields the *Z*-isomers of allylidene hydrazines.[5]

In addition to the standard IR and NMR spectroscopic investigations, an X-ray structural analysis was carried out with *N*-(1,2,3,3-tetrachloroallylidene)-*N*′-(2-methyl-5-nitrophenyl)hydrazine (**11**). Only one single stereoisomer, the postulated *Z*-compound, was found (Figure 1).

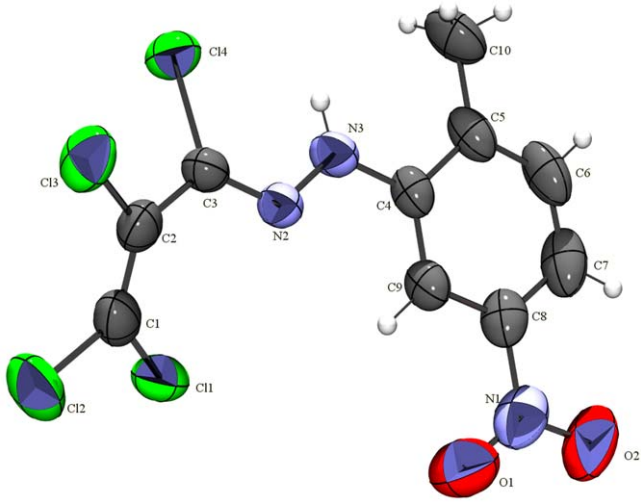


Figure 1 X-ray crystal structure of compound **11**[6,7]

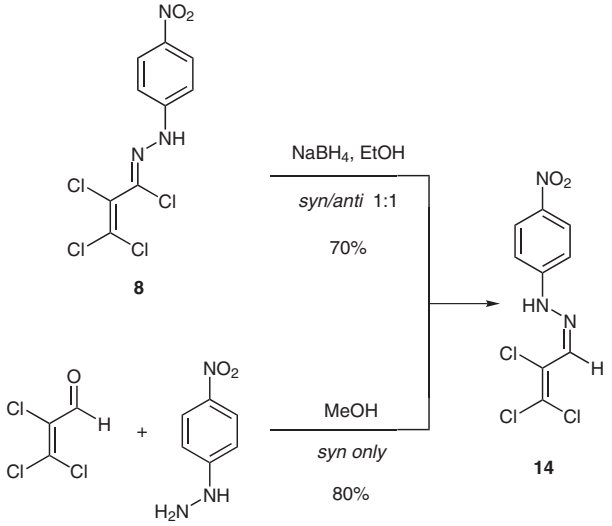
The reaction of nitrodiene **1** with 2-bromo-4-nitroaniline fails. The additional electron-withdrawing effect of the bromine diminishes the basicity, hence the reactivity, to such an extent that no reaction takes place. Switching from room temperature conditions to refluxing THF or toluene led to destruction of the starting material. Interestingly, when 4-nitroaniline (**2**) was employed as the nucleophile, apart from the corresponding hydrazone, we also isolated 1,3-bis(4-nitrophenyl)urea (10% yield), an important finding to support the proposed mechanism.

Additionally, not only for reactivity reasons but also due to our interest in physiologically active compounds, we tested some subsequent reactions of the hydrazones, namely with **8** as an exemplary starting compound. First of all, we attempted to reduce the imidoyl-type chlorine. The reduction was accomplished with sodium borohydride in ethanol at ambient temperature and provided *N*-2,3,3-trichloroallylidene-*N*′-(4-nitrophenyl)hydrazine (**14**) as a mixture of *Z*- and *E*-isomers (1:1) in 70% yield (Scheme 4).

Independently, we synthesized **14** by the reaction of trichloroacrolein with 4-nitrophenylhydrazine under reflux conditions in methanol. The *Z*-isomer was the single product which was isolated in 80% yield. Its structure was confirmed on the basis of ^{1}H and ^{13}C NMR spectroscopy.

The assumption that the chlorine atom at the C-1 position of the allylidene unit in the hydrazones **8**–**13** is activated by the strong electron-withdrawing C=N group stimulated our interest in nucleophilic substitutions at this position.

Indeed, by means of aliphatic or aromatic amines, hydrazone **8** was converted to the corresponding yellow or red *N*-(1-organylamino-2,3,3-trichloroallylidene)-*N*′-(4-nitro-



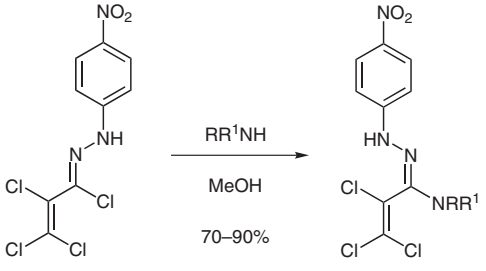
Scheme 4

phenyl)hydrazines **15**–**19** in a highly selective manner (yields 70–90%; Scheme 5).

An attempt to react hydrazone **8** with 4-methylthiophenol and sodium ethoxide in ethanol did not succeed at ambient temperature and led to decomposition upon warming to 50 °C.

Finally, we focused again on the mechanism for the formation of **8**–**13**. The question as to whether 2,3,3-trichloroacryloyl chloride could be a key intermediate was answered by the independent reaction of the acid chloride with 4-nitroaniline (**2**), which provided 2,3,3-trichloro-*N*-(4-nitrophenyl)acrylamide (**20**) in 40% yield (r.t., THF) and not the hydrazone **8** (Scheme 6). The structure was confirmed by NMR and IR spectroscopy as well as by mass spectrometry; all spectra were in accordance with literature data.[8]

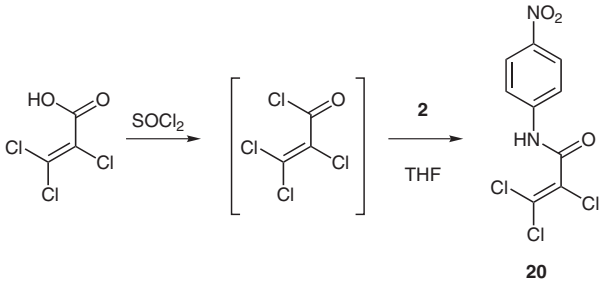
Numerous attempts to realize a straightforward synthesis starting from 2,3,3-trichloroacryloyl chloride and 4-nitro-



15: R, R^1 = -$(CH_2)_4$- 80%
16: R, R^1 = -$(CH_2)_2O(CH_2)_2$- 90%
17: R = Me, R^1 = Bn 70%
18: R = Me, R^1 = 6-CP-methyl 80%
19: R = H, R^1 = 4-Ethoxyphenyl 70%

6-CP = 6-Chloropyrid-3-yl

Scheme 5



Scheme 6

phenylhydrazine (THF, chloroform, different temperatures) resulted in unreacted starting materials only.

Apart from the synthetic point of view, it is interesting to note that quite a number of aromatic hydrazones exhibit extensive biological activity. Phenyl(phenylchloromethylidene)hydrazine, for example, shows fungicidal and fungistatic activity against *Trichophyton rubrum*, *Trichophyton mentagraphytes*, and *Microsporum canis*. Additionally, it possesses antibacterial activity against *E. coli* and *Staphylococcus aureus*,[9] and anthelmintic activity against mouse helminths as well as activity against some sheep parasites.[10] Furthermore, phenyl[(4-nitro)phenylchloromethylidene]hydrazine is also a potent fungicide and fungistatic, and shows antibacterial activity with a similar application band width.[9] Finally, it is worth mentioning that phenyl[(4-chloro)phenylamino-(4-chlorophenyl)methylidene]hydrazine is an inhibitor of soy bean lipoxygenase.[11] Investigations concerning the biological activity and applicability in, for example, crop science, of the compounds presented herein are underway.

In summary, we have developed a novel formal synproportionation reaction between a perchlorinated, unsaturated nitro compound and a deactivated aniline derivative. This unusual transformation that we accomplished with 2-nitroperchlorobuta-1,3-diene (**1**) requires an aniline derivative bearing an electron-withdrawing substituent (e.g. a nitro- or trifluoromethyl group) as the attacking nucleophile and, finally, yields a C=CC(Cl)=N unit.

Thus, it appears that the butyl building block is fragmented into a propyl unit and carbon dioxide accompanied by migration of a chloride anion within the butyl fragment. It is interesting to note that in contrast to the formation of isothiazoles from **1** and sulfur,[12] which necessitates a reaction temperature of 200 °C, the N–N coupling reaction presented herein almost proceeds at room temperature.

Melting points were determined with a Buchi apparatus 520 and are uncorrected. ^{1}H NMR and ^{1}H-decoupled ^{13}C NMR spectroscopy were performed on a Bruker Avance 400 (400 MHz) or Bruker DPX 200 (200 MHz) in $CDCl_3$ or DMSO-d_6. All NMR data are reported downfield from TMS as the internal standard unless otherwise stated. IR spectral data were obtained for liquids as film and for solids as KBr discs on a Bruker Vector 22 FT-IR. Mass spectra were obtained on a Hewlett Packard MS 5989B spectrometer, usually in direct mode with electron impact (70 eV). In the case of chlorinated compounds, all peak values of molecular ions as well as fragments

refer to the isotope ^{35}Cl. The elemental composition was confirmed either by combustion analysis or by high-resolution EI mass spectrometry. All HRMS results were satisfactory in comparison to the calculated accurate mass of the molecular ion (+/–2 ppm, R ~10000); for this reason, only calculated values are stated. TLC was performed on Merck TLC-plates (aluminum based) silica gel 60 F 254. Column chromatography was carried out on silica gel 60 (Merck). EtOH was purchased as reagent grade and used as received. PE had a boiling range 60–70 °C.

2-Nitropentachlorobuta-1,3-diene (**1**) was synthesized according to the literature[13] from 2*H*-pentachlorobuta-1,3-diene with a solution of 63% HNO_3–98% H_2SO_4 (10:1) in 53% yield (bp 69–71 °C, 1 mbar). Trichloroacrolein was found as a side product (8%) and separated by distillation (bp 57–58 °C at 12 mbar).

N-(1,2,3,3-Tetrachloroallylidene)-*N*′-(4-nitrophenyl)hydrazine (8); Typical Procedure

Under a nitrogen atmosphere, nitrodiene **1** (500 mg, 1.84 mmol) was added with stirring to a solution of 4-nitroaniline **2** (534 mg, 3.87 mmol) in anhyd THF (20 mL). Subsequently, the reaction mixture was stirred for 14 h at r.t. After evaporation of the solvent the residue was dissolved in CH_2Cl_2 (50 mL), washed with H_2O (3 × 50 mL), and dried over $CaCl_2$. The product was purified via column chromatography (PE–EtOAc, 1:1) to give hydrazone **8** as a yellow solid; yield: 381 mg (63%); mp 173–175 °C. In addition, 1,3-bis(4-nitrophenyl)urea was isolated as a side product.

IR (KBr): 3278, 1601, 1585, 1529, 1502, 1469, 1329, 1270, 1130, 1110, 885, 864, 844, 750, 710 cm^{-1}.

^1H NMR (200 MHz, DMSO-d_6): δ = 11.07 (br s, 1 H, NH), 8.20 [d, *J* = 9.2 Hz, 2 H, Ph(H-3,5)], 7.44 [d, *J* = 9.2 Hz, 2 H, Ph(H-2,6)].

^{13}C NMR (50 MHz, DMSO-d_6): δ = 148.8 (CNH), 141.3 (CNO_2), 125.9 [2 C, Ph(C-3,5)], 125.4 (CCl), 124.7 [C(Cl)=N], 117.3 (Cl_2C), 114.0 [2 C, Ph(C-2,6)].

EIMS: *m*/*z* (%) = 327 (M^+) (55), 292 (M^+ – Cl) (30), 136 (*p*-NO_2PhN^+) (100).

HRMS (EI): *m*/*z* calcd for $C_9H_5Cl_4N_3O_2$ (M^+): 326.9136; found: 326.9136.

1,3-Bis(4-nitrophenyl)urea

Yield: 10%; mp 301–303 °C.

IR (KBr): 3369, 1736, 1622, 1599, 1578, 1498, 1337, 1301, 1252, 1180, 1115, 847, 752, 658 cm^{-1}.

^1H NMR (200 MHz, DMSO-d_6): δ = 9.68 (br s, 2 H, NH), 8.35 (d, *J* = 9.1 Hz, 4 H), 7.85 (d, *J* = 9.1 Hz, 4 H).

EIMS: *m*/*z* (%) = 301 (M^+) (25), 138 (*p*-$NO_2PhNH_2^+$) (100).

N-(1,2,3,3-Tetrachloroallylidene)-*N*′-(2-nitrophenyl)hydrazine (9)

A solution of nitrodiene **1** (500 mg, 1.84 mmol) in toluene (10 mL) was added dropwise to 2-nitroaniline (534 mg, 3.87 mmol) dissolved in the same solvent (20 mL). Subsequently, the reaction mixture was heated to reflux for 5 h. After evaporation of the solvent the residue was suspended in Et_2O (50 mL). Then the precipitate was filtered off, washed with dilute HCl (20 mL), H_2O (2 × 20 mL), and PE (20 mL). The solid was dried in vacuo and purified by column chromatography (PE) to give **9** as a yellow solid; yield: 214 mg (35%); mp 122–124 °C.

IR (KBr): 3287, 1616, 1562, 1525, 1498, 1417, 1342, 1323, 1283, 1223, 1128, 887, 735, 707 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 11.30 (br s, 1 H, NH), 8.23 [dd, *J* = 8.5, 1.4 Hz, 1 H, Ph(H-3)], 7.83 [dd, *J* = 8.5, 1.4 Hz, 1 H, Ph(H-6)], 7.53–7.67 [m, 1 H, Ph(H-4)], 6.95–7.10 [m, 1 H, Ph(H-5)].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.4 (CNH), 136.3 [Ph(C-5)], 126.0 [Ph(C-3)], 120.8 [Ph(C-4)], 116.6 [Ph(C-6)]; the carbon atoms of the tetrachloroallylidene group as well as the carbon attached to the nitro group were not detected due to poor solubility.

EIMS: *m*/*z* (%) = 327 (M^+) (40), 292 (M^+ – Cl) (86), 246 (M^+ – Cl – NO_2) (14), 51 ($C_4H_3^+$) (100).

HRMS (EI): *m*/*z* calcd for $C_9H_5Cl_4N_3O_2$ (M^+): 326.9136; found: 326.9136.

Anal. Calcd for $C_9H_5Cl_4N_3O_2$ (328.97): C, 32.86; H, 1.53; Cl, 43.11; N, 12.77. Found: C, 32.75; H, 1.51; Cl, 42.71; N, 12.63.

N-(1,2,3,3-Tetrachloroallylidene)-*N*′-(3-nitrophenyl)hydrazine (10)

Synthesized according to the typical procedure, with a reaction time of 5 d. Yield: 17%; mp 148–149 °C.

IR (KBr): 3285, 1624, 1595, 1568, 1538, 1526, 1350, 1275, 1263, 1133, 871, 831, 735, 713 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 8.26 (br s, 1 H, NH), 7.60–8.10 (m, 1 H), 7.80–7.86 (m, 1 H), 7.40–7.51 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.2 (CNH), 143.2 (CNO_2), 130.3 [Ph(C-5)], 126.3 (CCl), 124.2 [C(Cl)=N], 119.4 [Ph(C-6)], 118.4 (CCl_2), 116.8 [Ph(C-4)], 108.6 [Ph(C-2)].

EIMS: *m*/*z* (%) = 327 (M^+) [14], 292 (M^+ – Cl) (14), 246 (M^+ – Cl – NO_2) (5), 211 (M^+ – 2 Cl – NO_2) (5), 136 (*m*-NO_2PhN^+) (50), 90 (PhN^+) (100).

HRMS (EI): *m*/*z* calcd for $C_9H_5Cl_4N_3O_2$ (M^+): 326.9136; found: 326.9136.

N-(1,2,3,3-Tetrachloroallylidene)-*N*′-(2-methyl-5-nitrophenyl)hydrazine (11)

Synthesized according to the typical procedure. Initially, the reaction was carried out at r.t. for 1 d and was then heated to reflux for 3 h. Yield: 28%; mp 128–130 °C.

IR (KBr): 3349, 1618, 1588, 1566, 1525, 1383, 1345, 1273, 1185, 1138, 949, 887, 862, 739, 706 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 8.25 [d, *J* = 2.4 Hz, 1 H, Ph(H-6)], 8.06 (br s, 1 H, NH), 7.76 [dd, *J* = 8.3, 2.4 Hz, 1 H, Ph(H-4)], 7.28 [d, *J* = 8.3 Hz, 1 H, Ph(H-3)], 2.38 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.8 (CNH), 140.8 (CNO_2), 131.2 [Ph(C-3)], 128.4 (CH_3), 126.6 [C(Cl)=N], 124.1 (CCl), 119.3 (CCl_2), 116.4 [Ph(C-4)], 108.6 [Ph(C-6)], 17.0 (CH_3).

EIMS: *m*/*z* (%) = 341 (M^+) (15), 306 (M^+ – Cl) (9), 260 (M^+ – Cl – NO_2) (4), 150 (PhN^+) (65), 104 (PhN^+ – NO_2) (100).

HRMS (EI): *m*/*z* calcd for $C_{10}H_7Cl_4N_3O_2$ (M^+): 340.9292; found: 340.9292.

Detailed X-ray analysis data are given in ref. 6; selected bond lengths in Å are C=N 1.271, (C=)C–Cl 1.735, and =N–N 1.338 (within the typical range for C=N, C–Cl, and =NNH, respectively); C–N–N 119.65°.

N-(1,2,3,3-Tetrachloroallylidene)-*N*′-(4-cyanophenyl)hydrazine (12)

A mixture of nitrodiene **1** (500 mg, 1.84 mmol) and 4-cyanoaniline (217 mg, 1.84 mmol) in anhyd THF (20 mL) was heated to reflux for 5 d. The solution was concentrated in vacuo, the precipitate was removed by suction filtration, and washed with MeOH (2 × 10 mL) to give hydrazine **12** as a white powder; yield: 255 mg (45%); mp 200–202 °C.

IR (KBr): 3238, 2222, 1611, 1575, 1523, 1418, 1273, 1130, 883, 855, 829, 705 cm^{-1}.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 10.85 (br s, 1 H, NH), 7.72 [d, *J* = 8.7 Hz, 2 H, Ph(H-3,5)], 7.39 [d, *J* = 8.7 Hz, 2 H, Ph(H-2,6)].

^{13}C NMR (50 MHz, DMSO-d_6): δ = 146.9 (CNH), 133.9 [2 C, Ph(C-3,5)], 125.1, 124.8 (2 C, Cl_2C=CCl), 119.6 (C=N), 116.2 (CN), 114.5 [Ph(C-2,6)], 103.2 [Ph(C-4)].

EIMS: *m*/*z* (%) = 306 (M^+) (55), 271 (M^+ – Cl) (18), 236 (M^+ – 2 Cl) (5), 116 (PhN^+) (100).

HRMS (EI): *m*/*z* calcd for $C_{10}H_5Cl_4N_3$ (M^+): 306.9238; found: 306.9238.

N-(1,2,3,3-Tetrachloroallylidene)-*N*′-(4-trifluoromethylphenyl)hydrazine (13)

Synthesized according to the typical procedure with a reaction time of 3 d at 40 °C. Yield: 50%; viscous oil; R_f 0.40 (PE–EtOAc, 3:1).

IR (NaCl): 3334, 1618, 1528, 1418, 1325, 1271, 1126, 1065, 966, 880, 836, 705 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.20 (br s, 1 H, NH), 7.56 [d, *J* = 8.6 Hz, 2 H, Ph(H-3,5)], 7.19 [d, *J* = 8.6 Hz, 2 H, Ph(H-2,6)].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.7 (CNH), 126.8 [Ph(C-3,5)], 126.1 (C=N), 125.5 (CCl), 124.1 [Ph(C-4)], 121.6 (CCl_2), 120.5 ($^1J_{C,F}$ = 270.4 Hz, CF_3), 113.5 [Ph(C-2,6)].

EIMS: *m*/*z* (%) = 349 (M^+) (20), 314 (M^+ – Cl) (8), 279 (M^+ – 2 Cl) (5), 159 [$Ph(CF_3)N^+$] (100).

HRMS (EI): *m*/*z* calcd for $C_{10}H_5Cl_4F_3N_2$ (M^+): 349.9159; found: 349.9159.

N-(2,3,3-Trichloroallylidene)-*N*′-(4-nitrophenyl)hydrazine (14)

Method A

To a suspension of $NaBH_4$ (38 mg, 1.0 mmol) in EtOH (20 mL) was added hydrazone **8** (329 mg, 1.0 mmol) portionwise with stirring. The resulting mixture was kept for 3 d at r.t. Then the solution was neutralized by the addition of dilute HCl at 0 °C. After evaporation of the solvent, the residue was removed by suction filtration, washed with H_2O (2 × 10 mL), PE (2 × 10 mL), and then dried in vacuo. The crude product was purified by column chromatography (PE–EtOAc, 4:1). The substituted hydrazine (*E*/*Z*)-**14** was isolated as an orange solid; yield: 206 mg (70%), mp 229–232 °C.

IR (KBr): 3336, 3258, 1733, 1596, 1500, 1300, 1276, 1109, 841, 801, 751 cm^{-1}.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 11.77 (br s, 1 H, NH, *Z*), 9.66 (br s, 1 H, NH, *E*), 8.20 (m, 6 H), 7.72 [d, *J* = 8.9 Hz, 2 H, Ph(H-2,6), *E*], 7.15 [d, *J* = 8.9 Hz, 2 H, Ph(H-2,6), *Z*].

^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.6 (CNH, *Z*), 145.9 (CNH, *E*), 141.7 (CNO_2, *E*), 140.0 (CNO_2, *Z*), 133.6 (CH=N, *Z*), 128.8 (CH=N, *E*), 128.0 (CCl, *Z*), 126.3 [Ph(C-3,5), *Z*], 125.9 (CCl, *E*), 125.3 [2 C, Ph(C-3,5), *E*], 125.2 (CCl_2, *E*), 121.8 (CCl_2, *Z*), 118.1 [2 C, Ph(C-2,6), *E*], 112.3 [2 C, Ph(C-2,6), *Z*].

EIMS: *m*/*z* (%) = 293 (M^+) (82), 258 (M^+ – Cl) (93), 212 (M^+ – Cl – NO_2) (67), 64 (100).

HRMS (EI): *m*/*z* calcd for $C_9H_6Cl_3N_3O_2$ (M^+): 292.9526; found: 292.9526.

Method B

A mixture of trichloroacrolein (0.50 g, 3.14 mmol) and 4-nitrophenylhydrazine (0.43 g, 2.82 mmol) in MeOH (20 mL) was refluxed for 6 h. After cooling to r.t., the solid product formed was removed by suction filtration, washed with H_2O (3 × 10 mL), MeOH (3 × 10 mL), and acetone (3 × 10 mL). The solvents were removed under reduced pressure to afford (*Z*)-**14** as an orange solid; yield: 0.66 g (80%); mp 238–239 °C.

IR (KBr): 3252, 1593, 1497, 1302, 1275, 1108, 838, 799, 750 cm^{-1}.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 11.74 (br s, 1 H, NH), 8.15 (s, 1 H, CH=N), 8.14 [d, *J* = 9.2 Hz, 2 H, Ph(H-3,5)], 7.11 [d, *J* = 9.2 Hz, 2 H, Ph(H-2,6)].

^{13}C NMR (50 MHz, DMSO-d_6): δ = 149.6 (CNH), 140.0 (CNO_2), 133.6 (CH=N), 128.0 (CCl), 126.3 [2 C, Ph(C-3,5)], 121.8 (CCl_2), 112.3 [2 C, Ph(C-2,6)].

N-(1-Organylamino-2,3,3-trichloroallylidene)-*N*′-(4-nitrophenyl)hydrazines (15–19); General Procedure

To a suspension of hydrazone **8** (500 mg, 1.52 mmol) in MeOH (20 mL) was added with stirring a solution of the corresponding amine (3.19 mmol) in MeOH (5 mL) at 0 °C over 10 min. The resulting reaction mixture was stirred for 3–8 h at r.t. Subsequently, the supernatant liquid was concentrated in vacuo to a volume of about 10 mL and treated with dilute HCl (30 mL). The precipitate was isolated, washed with H_2O (3 × 50 mL), PE (3 × 10 mL), and finally dried under reduced pressure.

N-(1-Pyrrolidino-2,3,3-trichloroallylidene)-*N*′-(4-nitrophenyl)hydrazine (15)

Yield: 80%; mp 73–75 °C.

IR (KBr): 3291, 2970, 2867, 1597, 1576, 1498, 1461, 1300, 1272, 1174, 1110, 946, 897, 836, 751 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.11 [d, *J* = 9.3 Hz, 2 H, Ph(H-3,5)], 6.96 (br s, 1 H, NH), 6.90 [d, *J* = 9.3 Hz, 2 H, Ph(H-2,6)], 3.30–3.50 (m, 4 H, NCH_2), 1.95–2.05 (m, 4 H, CH_2).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.2 (C=N), 146.4 (CNH), 138.5 (CNO_2), 126.1 [2 C, Ph(C-3,5)], 125.2 (CCl), 119.0 (CCl_2), 110.9 [2 C, Ph(C-2,6)], 46.9 (2 C, NCH_2), 25.0 (2 C, CH_2).

EIMS: *m*/*z* (%) = 362 (M^+) (12), 326 (M^+ – HCl) (9), 292 (M^+ – 2 HCl) (92), 70 (100).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{13}Cl_3N_4O_2$ (M^+): 362.0104; found: 362.0104.

Anal. Calcd for $C_{13}H_{13}Cl_3N_4O_2$ (363.63): C, 42.94; H, 3.60; N, 15.41. Found: C, 42.43; H, 3.43; N, 15.14.

N-(1-Morpholino-2,3,3-trichloroallylidene)-*N*′-(4-nitrophenyl)hydrazine (16)

Yield: 90%; mp 145–147 °C.

IR (KBr): 3252, 2843, 1599, 1532, 1498, 1475, 1316, 1302, 1277, 1252, 1109, 938, 893, 837, 752.3 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.13 [d, *J* = 9.2 Hz, 2 H, Ph(H-3,5)], 7.22 (br s, 1 H, NH), 6.96 [d, *J* = 9.2 Hz, 2 H, Ph(H-2,6)], 3.75–3.85 (m, 4 H, CH_2O), 3.25–3.35 (m, 4 H, CH_2N).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.4 (C=N), 145.0 (CNH), 139.4 (CNO_2), 126.8 (CCl), 126.1 [2 C, Ph(C-3,5)], 117.5 (CCl_2), 111.3 [2 C, Ph(C-2,6)], 66.2 (2 C, CH_2O), 46.3 (2 C, CH_2N).

EIMS: *m*/*z* (%) = 378 (M^+) (6), 343 (M^+ – Cl) (2), 308 (M^+ – 2 Cl) (2), 86 (100).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{13}Cl_3N_4O_3$ (M^+): 378.0053; found: 378.0053.

N-[1-(*N*-Benzyl-*N*-methylamino)-2,3,3-trichloroallylidene]-*N*′-(4-nitrophenyl)hydrazine (17)

Yield: 70%; mp 115–116 °C.

IR (KBr): 3268, 1595, 1578, 1522, 1493, 1472, 1458, 1392, 1297, 1274, 1223, 1176, 1112, 1087, 893, 840, 748 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.11 [d, *J* = 9.3 Hz, 2 H, Ph(H-3,5)], 7.32 (m, 5 H, Bn), 7.09 (br s, 1 H, NH), 6.91 [d, *J* = 9.3 Hz, 2 H, Ph(H-2,6)], 4.56 (d, *J* = 15.3 Hz, 1 H, CH_2), 4.44 (d, *J* = 15.3 Hz, 1 H, CH_2), 2.90 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.8 (C=N), 146.8 (CNH), 139.0 (CNO_2), 136.9 (CCH_2), 128.7 (2 C, *m*-Ph), 127.6 (2 C, *o*-Ph), 127.6 (*p*-Ph), 126.3 (CCl), 126.1 [2 C, Ph(C-3,5)], 118.1 (CCl_2), 111.1 [2 C, Ph(C-2,6)], 53.8 (CH_2), 35.5 (CH_3).

EIMS: *m*/*z* (%) = 412 (M^+) (6), 285 (10), 274 (3), 91 (100).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{15}Cl_3N_4O_2$ (M^+); 412.0261; found: 412.0261.

_N_-[_N_-(6-Chloropyridin-3-ylmethyl)-_N_-methylamino-2,3,3-trichloroallylidene]-_N′_-(4-nitrophenyl)hydrazine (18)
Yield: 80%; mp 48–49 °C.

IR (KBr): 3285, 2910, 1598, 1499, 1476, 1461, 1387, 1317, 1302, 1273, 1109, 898, 838, 752 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 2.2 Hz, 1 H, CH=N), 8.10 [d, *J* = 9.2 Hz, 2 H, Ph(H-3,5)], 7.67 (dd, *J* = 8.1, 2.2 Hz, 1 H), 7.34 (d, *J* = 8.1 Hz, 1 H), 7.22 (br s, 1 H, NH), 6.90 [d, *J* = 9.2 Hz, 2 H, Ph(H-2,6)], 4.58 (d, *J* = 15.2 Hz, 1 H, CH_2), 4.48 (d, *J* = 15.2 Hz, 1 H, CH_2), 2.92 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.8 [C(Cl)=N or C=NN], 150.4 [C=NN or C(Cl)=N], 149.0 (CH=N), 145.5 (CNH), 139.2 (CNO_2), 138.2, 131.7 (CCH_2), 126.8 (CCl), 126.1 [2 C, Ph(C-3,5)], 124.4, 117.6 (CCl_2), 111.2 [2 C, Ph(C-2,6)], 50.6 (CH_2), 35.9 (C_3).

EIMS: *m*/*z* (%) = 447 (M^+) (8), 412 (M^+ – Cl) (3), 376 (M^+ – Cl – HCl) (2), 155 (100).

HRMS (EI): *m*/*z* calcd for $C_{16}H_{13}Cl_4N_5O_2$ (M^+): 446.9823; found: 446.9823.

_N_-[1-(4-Ethoxyphenylamino)-2,3,3-trichloroallylidene]-_N′_-(4-nitrophenyl)hydrazine (19)
Yield: 70%; mp 94–95 °C.

IR (KBr): 3301, 1599, 1511, 1320, 1298, 1267, 1110, 888, 840, 751 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.35 (br s, 1 H, NH), 8.03 [d, *J* = 8.2 Hz, 2 H, Ph(H-3,5)], 7.50 (br s, 1 H, NH), 7.02 [d, *J* = 8.3 Hz, 2 H, Ph(H-2,6)], 6.91 (d, *J* = 8.8 Hz, 2 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 4.00 (q, *J* = 6.9 Hz, 2 H, OCH_2), 1.41 (t, *J* = 6.9 Hz, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 156.6 (COEt), 150.1 (C=NH), 142.3 (CNH), 140.3 (CNO_2), 130.3 (CCl), 126.7 (CNH), 125.9 [2 C, Ph(C-3,5)], 122.5 (2 C), 122.2 (CCl_2), 115.2 (2 C), 112.5 [2 C, Ph(C-2,6)], 63.8 (CH_2), 14.8 (CH_3).

EIMS: *m*/*z* (%) = 428 (M^+) (20), 358 (M^+ – 2 Cl) (9), 275 (25), 137 (100).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{15}Cl_3N_4O_3$ (M^+): 428.0210; found: 428.0210.

2,3,3-Trichloro-_N_-(4-nitrophenyl)acrylamide (20)
Trichloroacrylic acid (1.76 g, 10 mmol) was added at r.t. with stirring to $SOCl_2$ (20 mL). After 15 min, the reaction mixture was slowly heated to reflux (3 h). Further addition of $SOCl_2$ (20 mL) gave 2,3,3-trichloroacryloyl chloride (1.54 g, 8 mmol, 80%). After evaporation of the chlorination reagent, the crude product was dissolved immediately in anhyd THF (50 mL) and then 4-nitroaniline (1.66 g, 12 mmol) was added. After 24 h the solvent was removed in vacuo to give a crude solid which was dissolved in $CHCl_3$ (100 mL), washed with H_2O (3 × 100 mL), and dried over $CaCl_2$. The product was purified by column chromatography (PE–EtOAc, 10:1) to give the amide **20**; yield: 0.94 g (40%); mp 183–185 °C (lit.[8] 188 °C).

IR (KBr): 3374, 1706, 1614, 1600, 1566, 1504, 1342, 1249, 1199, 933, 851, 748 cm^{-1}.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 11.56 (br s, 1 H, NH), 8.26 (d, *J* = 9.2 Hz, 2 H), 7.85 (d, *J* = 9.2 Hz, 2 H).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 159.4 (C=O), 143.8 (CNH), 143.6 (CNO_2), 125.3 (2 C, *m*-Ph), 124.0, 123.1 ($CCl=CCl_2$), 119.9 (2 C, *o*-Ph).

EIMS: *m*/*z* (%) = 293 (M^+) (42), 258 (M^+ – Cl) (68), 212 (M^+ – Cl – NO_2) (60), 157 (C_3Cl_3O) (100).

HRMS (EI): *m*/*z* calcd for $C_9H_5Cl_3N_2O_3$ (M^+): 293.9366; found: 293.9366.

Anal. Calcd for $C_9H_5Cl_3N_2O_3$ (295.51): C, 36.58; H, 1.71; Cl, 35.99; N, 9.48. Found: C, 36.79; H, 1.79; Cl, 35.55; N, 9.23.

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(6) X-ray crystallographic analysis of $C_{10}H_7Cl_4N_3O_2$ was performed at 223 (2) K by using a STOE IPDS II diffractometer with Mo Kα radiation (λ= 0.71073 Å) and a graphite monochromator. Crystal system: orthorhombic, SG Pbca (No. 61), Z = 8, *a* = 738.22 (9) pm, *b* = 1551.6 (3) pm, *c* = 2399.4 (3) pm, V_{EZ} = 2748.3 (7) 10^6 pm^3. The structure was solved by direct methods (SHELXS-97[7a]) using 2093 independent reflections. Structure refinement: full matrix least-squares methods on F^2 using SHELXL-97[7b] all non-hydrogen 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 w*R*2 = 0.0878 for 2093 unique reflections and *R*1 = 0.0429 for 1563 observed reflections [$I_0 > 2\sigma(I_0)$] and 200 refined parameters with a goodness-of-fit of 1.052. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-245642. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033, e-mail: deposit@ccdc.cam.ac.uk]
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