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One-Pot Synthesis of 1,4-Dichlorophenazines

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Abstract : An efficient, generally applicable one-pot method for the synthesis of 1,4-dichlorophenazines has been established. The method is based on the use of 3,3,6,6-tetrachloro-1,2-cyclohexanedione **2** as a synthetic equivalent of 3,6-dichloro-1,2-benzoquinone **1**. The reaction of **2** with primary 1,2-arylidenediamines followed by treatment with pyridine provides the title compounds in nearly quantitative yields. 1,1,4,4-Tetrachloro-1,2,3,4-tetrahydrophenazines are isolable intermediates. The crystallographic X-ray structure of 7,7'-Bis(1,1,4,4-tetrachloro-1,2,3,4-tetrahydrophenazine) **7** has been determined. © 1997 Elsevier Science Ltd.

Chlorophenazines[1] are compounds of considerable interest. Because of the remarkable reluctance of phenazine to undergo electrophilic substitution processes, the displacement of the halogen atoms of chlorophenazines by a variety of nucleophiles has played an important role in the production of a wide variety of phenazine derivatives.[2] However, the difficulty in preparing the appropriate chlorinated starting materials frequently results in a lack of applicability of the procedure. The development of improved methods for the synthesis of chlorophenazines is, therefore, substantial. Advances in the synthesis of chlorophenazines themselves are also of interest on account of their pronounced herbicide activity.[3,4] Recent studies[5] on naturally occurring phenazines or analogues, some of them with antibiotic and antitumoral activity as well as the study of properties related to their peculiar structural features provide good examples of the renewed interest in the progress of the synthesis of phenazines. Since chlorophenazines may be used as intermediates for the synthesis of structurally complex phenazines, they may yet have much to offer in this effort.

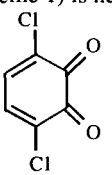
On the basis of a literature survey it is apparent that 1,4-dichlorophenazines are practically unavailable compounds. Only three examples have been prepared by applying two procedures based on reactions with low yield and a limited scope:

1. Chlorination of the parent phenazine by direct treatment with chlorine under different conditions.[6] These reactions lead to a complex mixture of monochloro and polychlorophenazines where the best yield for 1,4-dichlorophenazine reaches 25%. The prior synthesis of phenazine is required. Results of reactions applied to functionalized phenazines have not been reported.

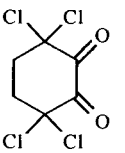
2. The Wohl-Aue reaction of 2,5-dichloronitrobenzene with aniline or chloroanilines in strongly basic medium at high temperature.[3,7] The previous synthesis of the phenazine is avoided. However, the efficiency in the formation of the three prepared 1,4-dichlorophenazines varies from low to very low yield (40, 17, 0.5%). Furthermore, the method cannot be used to prepare functionalized phenazines, since the majority of substituents are lost under the necessary extreme experimental conditions.

To summarize, the direct chlorination processes lack selectivity in the chlorination site as well as in the chlorination degree, whereas the Wohl-Aue method is remarkably deficient because of the inherent low activity of aromatic compounds towards this process. Given the precariousness of the reported synthesis of 1,4-dichlorophenazines, we focused our interest on the research of improved synthetic methods.

Regarding the described procedures for the synthesis of phenazines,[1] it is apparent that a good method for preparing 1,4-dichlorophenazines does not seem likely to be available on this basis. In concise terms, it should be noticed that, as in the Wohl-Aue reaction, drastic experimental conditions are required when only aromatic starting materials are used. On the other hand, the reaction of 1,2-arylideneamines with 1,2-cyclohexanediones with subsequent aromatization fails greatly in yield.[8,9] Moreover, the incompatibility with the presence of a wide variety of substituents, even chloro groups, is another crucial limitation. It should be noticed that the direct condensation of o-quinones with aromatic 1,2-diamines directly provides phenazines. However, this method also appears to be unsatisfactory, since the reaction of o-phenylenediamine with o-benzoquinone gives phenazine[10] in low yield (35%). Moreover, the difficulty in preparing the appropriate o-quinone sometimes is the main synthetic problem. This is just the case for the entry to 1,4-dichlorophenazines from 3,6-dichloro-1,2-benzoquinone **1**. In contrast with other quinones, **1** is a rare and difficultly available compound. Only its unisolated generation, by oxidation of 3,6-dichlorocatechol with silver oxide, has been reported.[11] However, in 3,3,6,6-tetrachloro-1,2-cyclohexanedione **2** we have found an excellent synthetic equivalent of the quinone **1**. On this basis, a new, efficient, general and easy one-pot method for the synthesis of 1,4-dichlorophenazines (Scheme 1) is here reported.

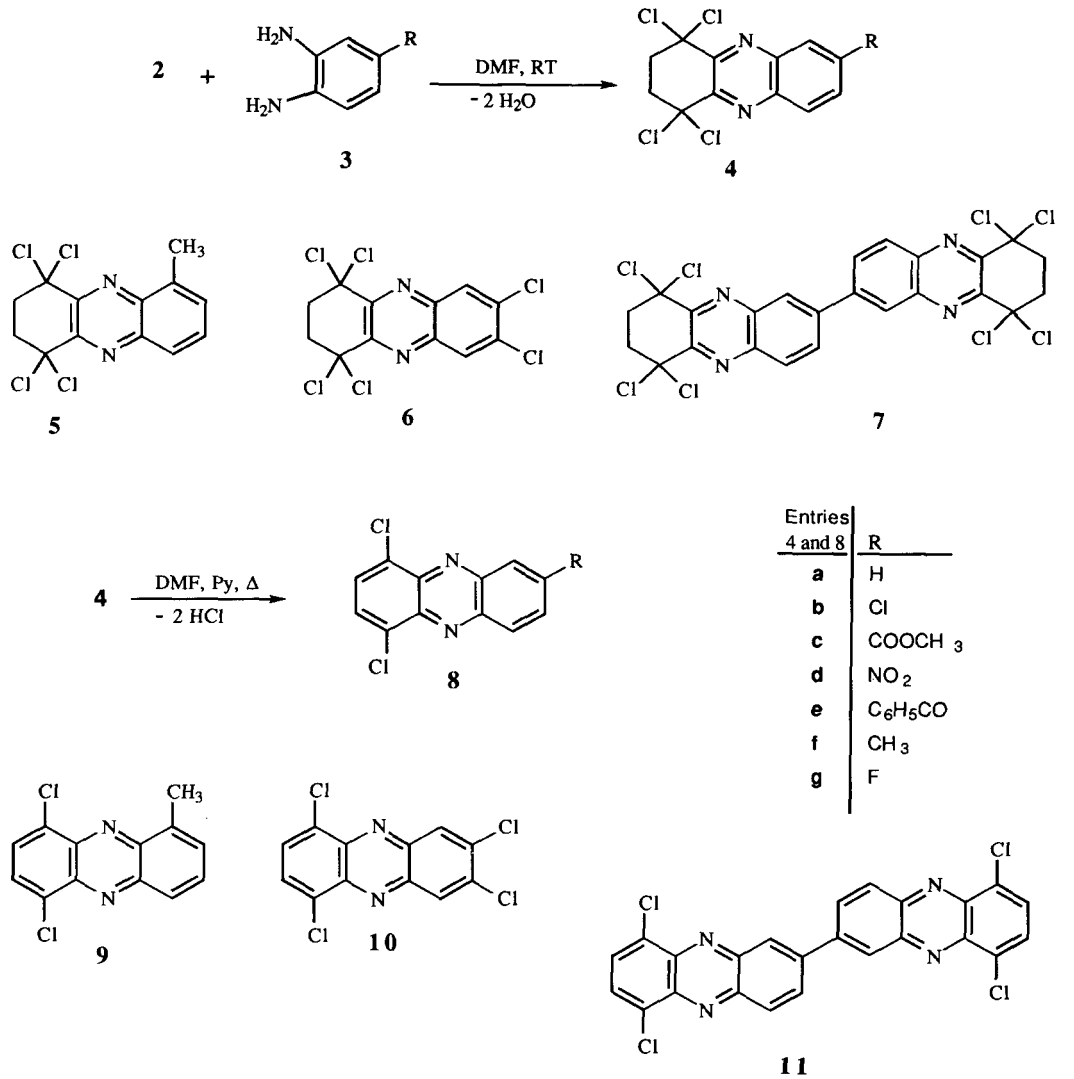


1



2

The key intermediate **2** can be easily obtained in quantitative yield by treatment of trans-cyclohexanediol with chlorine. There is no precedent for the use of **2** as a synthetic equivalent of the quinone **1**. The reactivity of **2** and its synthetic usefulness remain little known since only its preparation and its oxidation to 2,2,5,5-tetrachloroadipic acid have been previously reported.[12]



Entries 4 and 8	R
a	H
b	Cl
c	$COOCH_3$
d	NO_2
e	C_6H_5CO
f	CH_3
g	F

Scheme 1

The reaction of **2** with aromatic 1,2-diamines, under mild conditions, provided previously unknown

phenazine derivatives: 1,1,4,4-Tetrachloro-1,2,3,4-tetrahydrophenazines **4** (**a** - **g**), **5** - **7** in nearly quantitative yield. These products were easily obtained in a crystalline state and were stable enough to permit a prolonged store without receiving any special care. Unlike the other compounds, product **7** crystallized from chloroform - petroleum ether with formation of crystals solvated by chloroform. Microanalysis was in agreement with a $C_{26}H_{16}Cl_{14}N_4$ composition ≡ $C_{24}H_{14}Cl_8N_4.(CHCl_3)_2$ which was confirmed by thermogravimetric analysis. This showed only one thermal decomposition step associated to the loss of two molecules of chloroform per each solvated unit. The recorded graphic showed a peak at 75.7 °C. In order to determine the geometrical characteristics of the solvated product **7**, a single crystal was analyzed by X-ray diffraction. The molecular structure found is illustrated in Figure 1. Selected intramolecular distances (crystallographic numbering of atoms) and selected bond angles are given in Table 1. The molecular geometry was found to possess an inversion centre. The four aromatic rings are in the same plane (mean deviation = 0.044 Å). As is shown in Figure 2 there are intermolecular hydrogen interactions of each chloroform molecule with a nitrogen and a chlorine atom. Intermolecular bond distances: H···N = 2.576 (3) Å; H···Cl = 2.746 (3) Å.

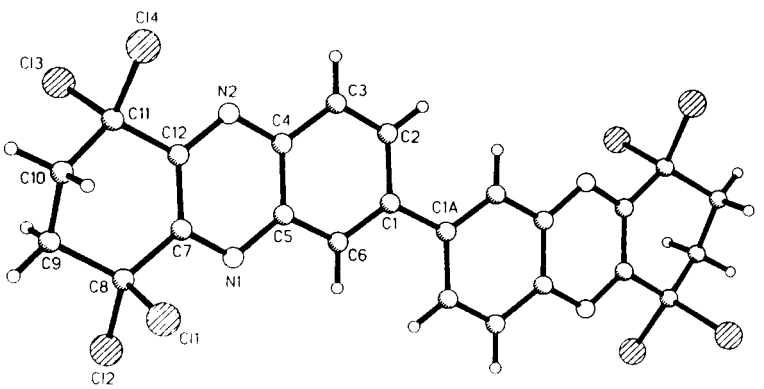


Figure 1. Molecular structure of product **7**, *showing the crystallographic numbering system used.*

lengths (Å)

Cl(1)-C(8)	1.811(2)	C(1)-C(6)	1.377(3)
N(1)-C(7)	1.311(3)	N(1)-C(5)	1.359(3)
C(1)-C(2)	1.433(3)	C(1)-C(1A)	1.490(4)
C(2)-C(3)	1.363(3)	C(3)-C(4)	1.412(3)
C(4)-C(5)	1.419(3)	C(7)-C(8)	1.520(3)
C(8)-C(9)	1.511(3)	C(9)-C(10)	1.526(3)
C(7)-C(12)	1.430(3)	C(11)-C(12)	1.520(3)

angles (°)

C(6)-C(1)-C(1A)	121.8(3)	C(12)-C(11)-C(10)	114.3(2)
C(2)-C(1)-C(1A)	120.6(3)	C(11)-C(10)-C(9)	110.4(2)
N(1)-C(7)-C(8)	118.1(2)	C(12)-C(11)-Cl(3)	105.4(2)
C(9)-C(8)-C(7)	113.2(2)	N(2)-C(12)-C(11)	117.3(2)
C(9)-C(8)-Cl(2)	109.3(2)	C(7)-N(1)-C(5)	117.5(2)
C(7)-C(8)-Cl(1)	105.9(2)	C(3)-C(2)-C(1)	122.3(2)
Cl(2)-C(8)-Cl(1)	107.14(12)	C(8)-C(9)-C(10)	110.7(2)

Symmetry transformations used to generate equivalent atoms: -x,-y+1,-z+1

Table 1. Selected Bond Lengths and Bond Angles in Crystal Structure of **7**.

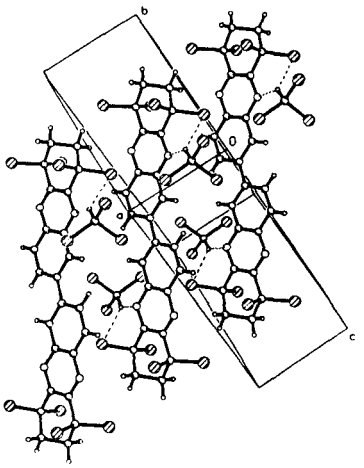


Figure 2. A perspective of the crystal packing of 7 showing the hydrogen interactions.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydrophenazines **4** (**a** - **g**), **5** - **7** undergo bisdehydrochlorination giving 1,4-dichlorophenazines **8** (**a** - **g**), **9** - **11** in almost quantitative yield. This transformation could be carried out in weak basic medium as well as in boiling solvents without using a base. The preparation of product **8a** has been previously reported,[3,6,7] whereas the other products are new phenazines. The described synthesis of 1,4-dichlorophenazines in separate steps could also be carried out in a one-pot process, which allowed a quick and very efficient preparation of the same products.

In conclusion, a simple, effective and general method for the synthesis of 1,4-dichlorophenazines is reported. Nearly quantitative yields, easy availability of starting materials and one-pot reaction process are valuable, noteworthy advantages of the method which allows the access to previously unattainable products. It is also to be noticed that this work has revealed 3,3,6,6-tetrachloro-1,2-cyclohexanedione **2** as an excellent synthetic equivalent of 3,6-dichloro-1,2-benzoquinone **1**. Since the usefulness of quinones in organic synthesis

is well known, **2** seems likely to be a promising intermediate in allowing the selective synthesis of a wide variety of specifically chlorinated compounds.

EXPERIMENTAL

NMR spectra were determined on Bruker AC-200 or Varian AC-300 Unity instruments with tetramethylsilane as internal reference. Electron-impact mass spectra were obtained on a Hewlett-Packard 5995 spectrometer with direct insertion probe and an ionizing voltage of 70 eV. i.r. spectra (nujol emulsions) were recorded on a Nicolet-5DX spectrophotometer. Microanalyses were performed on a Carlo Erba EA-1108 analyzer. A Mettler TA 3000 thermogravimetric analyzer was used. All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected.

X-Ray crystallographic analysis of 7 solvated by chloroform

Crystal Data. $C_{26}H_{16}Cl_{14}N_4$; Fwt.. 880.73; triclinic; P-1; a = 5.9049(12) Å, b = 11.148(2) Å, c = 13.966(2) Å, α = 111.172(8)°, β = 96.723(12)°, γ = 96.631(12)°; V = 839.0(3) Å^3; Z = 1, D_{calc} 1.743 g/cm^{-3}; crystal size 0.80 x 0.48 x 0.12 mm; F_{000} 438; μ(MoKα) 1.178 mm^{-1}.

Data Collection. A yellow tablet of **7** in inert oil was mounted on a glass fibre and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). Unit cell parameters were determined from a least-squares fit of 63 accurately centered reflections (14.01 < 2θ < 24.9). A total of 4208 intensity data were collected at 173(2) K with graphite monochromated Mo-Kα radiation (l = 0.71073 Å) to $2\theta_{max}$ = 50°. Merging equivalents gave 2887 unique data (R_{int}= 0.017), which were used for calculations.

Structure Solution and Refinement. The structure was solved by direct methods and refined anisotropically on F^2 (program SHELXTL)[13]. Hydrogen atoms were included using a riding model. The final R(F) was 0.0375, for 199 parameters and 2625 obseved reflections [I > 2σ(I)] and wR(F^2) was 0.1042 for all data. The weighting scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. Maximum Δ/σ = 0.001, maximum $\Delta\rho$ = 0.72 eÅ^3 near the chlorine atoms.

Preparation of 1,1,4,4-tetrachloro-1,2,3,4-tetrahydrophenazines

To a solution of 3,3,6,6-tetrachloro-1,2-cyclohexanedione **2** (4 mmol) in chloroform (10 mL) an equimolecular amount of the appropriate aromatic diamine in chloroform (10 mL) was added dropwise. The solution was stirred at room temperature for 1 h and the solvent was removed in vacuo. High purity crude

products[14] were isolated in nearly quantitative yields and were crystallized from the appropriate solvent. Products **4c**, **4d** and **7** were similarly prepared[15] in DMF instead of chloroform. In these cases the reaction mixture was poured into 400 mL of cold brine and the precipitate was collected by vacuum filtration.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydrophenazine (**4a**)

(93%), mp 222-224 °C (pet ether). (Found: C, 44.71; H, 2.52; N, 8.68. $C_{12}H_8Cl_4N_2$ requires: C, 44.76; H, 2.50; N, 8.70); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.27 (s, 4H), 7.88 - 7.94 (m, 2H), 8.23 - 8.29 (m, 2H); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.55, 84.60, 129.51, 132.43, 142.74, 146.96; m.s., m/z (%): 320 (M^+, 9), 287 (23), 285 (24), 251 (58), 249 (100), 215 (36), 214 (39), 179 (26), 50 (38); i.r.: 1480, 1438, 949, 849, 812, 769, 698 cm^{-1}.

1,1,4,4,7-Pentachloro-1,2,3,4-tetrahydrophenazine (**4b**)

(84%), mp 199-200 °C (pet ether). (Found: C, 40.50; H, 1.98; N, 7.83. $C_{12}H_7Cl_5N_2$ requires: C, 40.43; H, 1.98; N, 7.86); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.26 (s, 4H), 7.84 (dd, 1H, J = 9.0, J = 2.4), 8.20 (d, 1H, J = 9.0), 8.26 (d, 1H, J = 2.4); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.37, 42.40, 84.20, 84.27, 128.20, 130.57, 133.55, 138.66, 141.17, 142.82, 147.04, 147.80; m.s., m/z (%): 354 (M^+, 2), 285 (24), 283 (23), 136 (24), 124 (36), 110 (35), 100 (46), 75 (100), 74 (47), 61 (46), 51 (48), 50 (53); i.r.: 1605, 1443, 963, 955, 932, 855, 841, 810, 735 cm^{-1}.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydro-7-methoxycarbonylphenazine (**4c**)

(93%), mp 155-157 °C (ethanol). (Found: C, 44.09; H, 2.67; N, 7.38. $C_{14}H_{10}Cl_4N_2O_2$ requires: C, 44.24; H, 2.65; N, 7.37);^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.28 (s, 4H), 4.05 (s, 3H), 8.31 (d, 1H, J = 9.0), 8.49 (dd, 1 H, J = 9.0, J = 1.8), 8.98 (d, 1 H, J = 1.8); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): δ 42.38, 52.93, 84.18, 84.22, 129.73, 131.66, 131.99, 133.49, 141.98, 144.35, 148.04, 148.61, 165.56; m.s., m/z (%): 378 (M^+, 5), 309 (39), 307 (56), 213 (30), 103 (44), 75 (100), 74 (50), 51 (49); i.r.: 1722, 1263, 855, 809, 754, 721 cm^{-1}.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydro-7-nitrophenazine (**4d**)

(87%), mp 192-194 °C (pet ether). (Found: C, 39.32; H, 1.93; N, 11.49. $C_{12}H_7Cl_4N_3O_2$ requires: C, 39.27; H, 1.92; N, 11.45);^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.30 (s, 4H), 8.44 (dd, 1H, J = 9.3, J = 0.6), 8.67 (dd, 1H, J = 9.3, J = 2.7), 9.17 (dd, 1H, J = 2.7, J = 0.6); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.24, 83.71, 83.81, 125.49, 125.73, 131.34, 141.56, 144.63, 149.39, 149.45, 149.94; m.s., m/z (%): 365 (M^+, 11), 332 (32), 330 (36), 296 (56), 294 (79), 75 (100), 51 (58), 50 (59); i.r.: 1529, 1350, 958, 944, 857, 835, 810, 741, 723 cm^{-1}.

7-Benzoyl-1,1,4,4-tetrachloro-1,2,3,4-tetrahydrophenazine (**4e**)

(96%), mp 177-179 °C (pet ether). (Found: C, 53.50; H, 2.85; N, 6.60. $C_{19}H_{12}Cl_4N_2O$ requires: C, 53.55; H, 2.84; N, 6.57); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.28 (s, 4H), 7.55 (t, 2H, J = 7.5), 7.67 (tt, 1H, J = 7.5, J = 1.2), 7.88 (dd, 2H, J = 7.5, J = 1.2), 8.38 (d, 2H, J = 1.2), 8.58 (t, 1H, J = 1.2); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.34, 42.36, 84.20, 128.72, 129.99, 130.11, 132.00, 132.08, 133.24, 136.56, 140.47, 141.84, 144.11, 148.07, 148.51, 195.01; m.s., m/z (%): 424 (M^+, 1), 355 (4), 353 (5), 213 (9), 105 (83), 77 (100), 51 (38); i.r.: 1662, 1323, 948, 852, 812, 736, 728 cm^{-1}.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydro-7-methylphenazine (**4f**)

(95%), mp 193-194 °C (pet ether). (Found: C, 46.61; H, 2.99; N, 8.33. $C_{13}H_{10}Cl_4N_2$ requires: C, 46.46; H, 3.00; N, 8.34); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 2.63 (s, 3H), 3.25 (s, 4H), 7.73 (dd, 1H, J = 8.7, J = 2.1), 8.03 (br s, 1H), 8.13 (d, 1H, J = 8.7); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 22.01, 42.42, 42.45, 84.61, 84.63, 127.94, 128.78, 134.81, 141.18, 142.70, 143.41, 145.82, 146.62; m.s., m/z (%): 334 (M^+, 2), 265 (26), 263 (42), 114 (49), 89 (100), 75 (41), 63 (81), 51 (63); i.r.: 1488, 1438, 1348, 950, 944, 858, 839, 808 cm^{-1}.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydro-7-fluorophenazine (**4g**)

(96%), mp 179-180 °C (ethanol-chloroform). (Found: C, 42.50; H, 2.09; N, 8.26. $C_{12}H_7Cl_4FN_2$ requires: C, 42.39; H, 2.08; N, 8.24); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.26 (s, 4H), 7.67 - 7.74 (m, 1H), 7.88 (dd, 1H, J = 7.2, J = 2.7), 8.82 (dd, 1H, J = 9.4, J = 5.7); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.44, 42.48, 84.29, 84.39, 112.80 (d, J = 22.1), 123.43 (d, J = 26.7), 131.78 (d, J = 10.1), 140.05, 143.67 (d, J = 14.0), 146.37 (d, J = 3.5), 147.76, 164.27 (d, J = 273.3); m.s., m/z (%): 338 (M^+, 5), 269 (53), 267 (86), 232 (41), 197 (39), 147 (37), 146 (33), 120 (63), 116 (49), 100 (47), 94 (100) 75 (72), 50 (62); i.r.: 1621, 1484, 1437, 1197, 947, 856, 842, 806, 797 cm^{-1}.

1,1,4,4-Tetrachloro-1,2,3,4-tetrahydro-6-methylphenazine (**5**)

(97%), mp 184-185 °C (pet ether). (Found: C, 46.52; H, 3.01; N, 8.37. $C_{13}H_{10}Cl_4N_2$ requires: C, 46.46; H, 3.00; N, 8.34); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 2.86 (s, 3H), 3.26 (s, 4H), 7.69 (br d, 1H, J = 7.2), 7.76 (dd, 1H, J = 8.4, J = 7.2), 8.06 (br d, 1H, J = 8.4); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 17.10, 42.60, 42.70, 84.75, 84.99, 127.13, 131.86, 132.24, 138.42, 142.00, 142.92, 145.53, 146.38; m.s., m/z (%): 334 (M^+, 4), 265 (31), 263 (52), 228 (36), 115 (34), 114 (79), 89 (90), 63 (100); i.r.: 1435, 951, 864, 839, 813, 765, 701 cm^{-1}.

1,1,4,4,7,8-Hexachloro-1,2,3,4-tetrahydrophenazine (**6**)

(96%), mp 158-159 °C (pet ether). (Found: C, 36.92; H, 1.55; N, 7.15. $C_{12}H_6Cl_6N_2$ requires: C, 36.87;

H, 1.55; N, 7.17); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.25 (s, 4H), 8.39 (s, 2H); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.32, 84.02, 129.84, 137.62, 141.25, 148.00; m.s., m/z (%): 388 (M^+, 1), 321 (12), 319 (24), 317 (19), 111 (45), 109 (69), 75 (87), 74 (81), 61 (100), 51 (73), 50 (66); i.r.: 1449, 1166, 990, 947, 888, 863, 811 cm^{-1}.

7,7'-Bis(1,1,4,4-tetrachloro-1,2,3,4-tetrahydrophenazine) (**7**)

(94%), mp 275-277 °C (chloroform-pet ether). (Found: C, 44.72; H, 2.23; N, 8.75. $C_{24}H_{14}Cl_8N_4$ requires: C, 44.90; H, 2.20; N, 8.73); solvated product (Found: C, 35.52; H, 1.81; N, 6.40. $C_{26}H_{16}Cl_{14}N_4$ requires: C, 35.46; H, 1.83; N, 6.36); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 3.30 (s, 8H), 8.37 (dd, 2H, J = 8.9, J = 2.1), 8.43 (d, 2H, J = 8.9), 8.67 (d, 2H, J = 2.1); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 42.51, 42.54, 84.45, 84.48, 127.96, 130.53, 131.71, 142.61, 142.68, 142.91, 147.54, 147.95; m.s., m/z (%): 638 (M^+, 2), 497 (30), 428 (71), 426 (99), 392 (37), 249 (97), 248 (100), 213 (71), 85 (34); i.r.: 1485, 1422, 1350, 956, 852, 835, 808, 708 cm^{-1}.

Preparation of 1,4-dichlorophenazines

To the appropriate 1,1,4,4-tetrachloro-1,2,3,4-tetrahydrophenazine (4 mmol) in DMF (20 mL) pyridine (5 mL) was added and the solution was boiled for 1 h. After cooling the reaction mixture was poured into 400 mL of cold brine. Crude 1,4-dichlorophenazines in a high purity state[14] precipitated and were isolated by vacuum filtration and crystallized from the appropriate solvent. Yields were almost quantitative.

One-pot procedure: To a solution of 3,3,6,6-tetrachloro-1,2-cyclohexanedione **2** (4 mmol) in DMF (10 mL) a solution of the appropriare diamine (4 mmol) in DMF (10 mL) was added dropwise. The mixture was stirred at room temperature for 1 h (80 °C, 1.5 h for products **8c** and **11**). Then, pyridine (5 mL) was added and the solution was boiled for 1 h. 1,4-Dichlorophenazines were isolated[14] in almost quantitative yields and were crystallized from the appropriate solvent.

1,4-Dichlorophenazine (**8a**)

(90%), mp 203-204 °C (pet ether). (Lit[3], mp 191-192 °C; Lit[7], mp 198-199 °C). (Found: C, 58.02; H, 2.43; N, 11.22. $C_{12}H_6Cl_2N_2$ requires: C, 57.86; H, 2.43; N, 11.25);^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 7.87 (s, 2H), 7.90 - 7.96 (m, 2H), 8.34 - 8.41 (m, 2H); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 128.99, 129.82, 131.89, 132.20, 140.28, 143.40; m.s., m/z (%): 250 (M^+ + 2, 65), 248 (M^+, 100) 213 (26), 124 (9), 76 (12), 75 (13), 74 (11), 50 (12); i.r.: 1509, 1405, 1130, 958, 938, 843, 757 cm^{-1}.

1,4,7-Trichlorophenazine (**8b**)

(96%), mp 229-231 °C (ethanol). (Found: C, 51.01; H, 1.78; N, 9.90. $C_{12}H_5Cl_3N_2$ requires: C, 50.83;

H, 1.78; N, 9.88); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 7.84 (dd, 1H, J = 9.2, J = 2.4), 7.86 (d, 1H, J = 8.2), 7.87 (d, 1H, J = 8.2), 8.31 (dd, 1H, J = 9.4, J = 0.6), 8.38 (d, 1H, J = 2.4); ^{13}C n.m.r. δ ($CDCl_3$, 75.4 MHz): 128.38, 129.38, 129.78, 131,21, 132.47, 132.58, 133.45, 138.40, 140.47, 140.88, 142.03, 143.45; m.s., m/z (%): 286 (M^+ + 4, 30), 284 (M^+ + 2, 100), 282 (M^+, 86), 247 (30), 100 (35), 75 (63), 74 (49); i.r.: 1610, 1410, 1133, 1063, 969, 952, 845, 837 cm^{-1}.

1,4-Dichloro-7-methoxycarbonylphenazine (**8c**)

(94%), mp 259-260 °C (1,2-dichloroethane). (Found: C, 54.79; H, 2.66; N, 9.09. $C_{14}H_8Cl_2N_2O_2$ requires: C, 54.75; H, 2.63; N, 9.12); n.m.r. spectra could not be recorded due to its extremely low solubility in the usual spectroscopic solvents; m.s., m/z (%): 308 (M^+ + 2, 69), 306 (M^+, 92), 277 (61), 275 (100), 249 (47), 247 (66), 134 (38), 51 (81); i.r.: 1724, 1448, 1332, 1311, 1269, 1243, 1087, 971 cm^{-1}.

1,4-Dichloro-7-nitrophenazine (**8d**)

(90%), mp 207-209 °C (pet ether). (Found: C, 49.23; H, 1.70; N, 14.33. $C_{12}H_5Cl_2N_3O_2$ requires: C, 49.01; H, 1.71; N, 14.29); ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): δ 7.99 (s, 2 H), 8.54 (d, 1 H, J 9.4), 8.66 (dd, 1 H , J 9.4, J 2.4), 9.31 (d, 1H, J 2.4); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 124.75, 126.71, 130.57, 131.24, 131.94, 132.65, 132.85, 141.65, 141.73, 141.81, 144.46, 149.11; m.s., m/z (%): 295 (M^+ + 2, 63), 293 (M^+, 100), 249 (34), 247 (40), 235 (24), 212 (17); i.r.: 1531, 1351, 1343, 963, 840, 739, 699 cm^{-1}.

7-Benzoyl-1,4-dichlorophenazine (**8e**)

(96%), mp 232-234 °C (ethyl acetate). (Found: C, 64.58; H, 2.86; N, 7.91. $C_{19}H_{10}Cl_2N_2O$ requires: C, 64.61; H, 2.85; N, 7.93); ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 7.51 - 7.72 (m, 3H), 7.87 - 7.96 (m, 4H), 8.40 (d, 1H, J = 9.1), 8.47 (d, 1H, J = 8.9), 8.69 (s, 1H); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 128.76, 129.66, 130.18, 130.51, 131.34, 132.47, 133.15, 133.23, 136.78, 139.85, 140.78, 141.02, 141.20, 142.49, 144.43, 195.40; m.s., m/z (%): 352 (M^+, 7), 105 (84), 77 (100), 51 (34); i.r.: 1648, 1327, 1313, 1267, 1138, 964, 709 cm^{-1}.

1,4-Dichloro-7-methylphenazine (**8f**)

(91%), mp 207-208 °C (pet ether). (Found: C, 59.16; H, 3.09; N, 10.64. $C_{13}H_8Cl_2N_2$ requires: C, 59.34; H, 3.06; N, 10.65); ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 2.64 (s, 3H), 7.71 (dd, 1H, J = 9.0, J = 1.8), 7.80 (s, 2H), 8.07 (br s, 1H), 8.20 (d, 1H, J = 9.0); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 22.31, 127.85, 128.45, 128.84, 129.23, 132.06, 132.17, 134.94, 139.78, 140.26, 142.25, 142.96, 143.51; m.s., m/z (%): 264 (M^+ + 2, 69), 262 (M^+, 100), 191 (40), 164 (27), 89 (41), 63 (49), 51 (35); i.r.: 1475, 1410, 1175, 1140, 960, 934, 836, 828, 802 cm^{-1}.

1,4-Dichloro-7-fluorophenazine (**8g**)

(90%), mp 186-188 °C (ethanol). (Found: C, 54.15; H, 1.90; N, 10.50. $C_{12}H_5Cl_2FN_2$ requires: C, 53.96; H, 1.89; N, 10.49); ^{1}H n.m.r. δ ($CDCl_3$, 300 MHz): 7.71 - 7.78 (m, 1H), 7.86 (d, 1H, J = 8.1), 7.87 (d, 1H, J = 8.1), 7.95 (dd, 1H, J = 9.2, J = 3), 8.38 (dd, 1H, J = 9.6, J = 5.4); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 112.03 (d, J = 21.5), 124.22 (d, J = 28.7), 129.00 (d, J = 1.4), 129.78, 131.95, 132.36 (d, J = 10.5), 132.41, 139.81 (d, J = 2.6), 140.62, 141.00, 144.06 (d, J = 13.7), 163.99 (d, J = 257.9); m.s., m/z (%): 268 (M^+ + 2, 61), 266 (M^+, 100), 231 (39), 196 (21), 195 (17), 133 (19); i.r.: 1632, 1458, 1412, 1196, 1164, 963, 837 cm^{-1}.

1,4,-Dichloro-6-methylphenazine (**9**)

(93%), mp 196-198 °C (ethanol). (Found: C, 59.50; H, 3.07; N, 10.67. $C_{13}H_8Cl_2N_2$ requires: C, 59.34; H, 3.06; N, 10.65); ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 2.89 (s, 3H), 7.65 (br d, 1H, J = 6.7), 7.76 (dd, 1H, J = 8.4, J = 6.7), 7.78 (s, 2H), 8.12 (br d, 1H, J = 8.4); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 17.40, 127.53, 128.48, 128.84, 130.82, 131.88, 132.82, 138.44, 139.24, 139.82, 142.84, 143.52; m.s., m/z (%): 264 (M^+ + 2, 65), 262 (M^+, 100), 191 (24), 164 (27), 113 (16), 95 (12), 63 (14); i.r.: 1191, 955, 936, 835, 787, 755, 667, 604 cm^{-1}.

1,4,7,8-Tetrachlorophenazine (**10**)

(91%), mp 228-230 °C (ethanol). (Found: C, 45.29; H, 1.27; N, 8.84. $C_{12}H_4Cl_4N_2$ requires: C, 45.33; H, 1.27; N, 8.81); ^{1}H n.m.r. δ ($CDCl_3$, 200 MHz): 7.87 (s, 2H), 8.47 (s, 2H); ^{13}C n.m.r. δ ($CDCl_3$, 50.3 MHz): 129.98, 132.41, 137.37, 140.75, 141.80; m.s., m/z (%): 320 (M^+ + 4, 52), 318 (M^+ + 2, 100), 316 (M^+, 77), 159 (25), 158 (24), 134 (33), 109 (51), 74 (43); i.r.: 1448, 1426, 1403, 1177, 1103, 1086, 964, 944, 881 cm^{-1}.

7,7'-Bis(1,4-dichlorophenazine) (**11**)

(95%), mp > 325 °C (washed with hot ethanol). (Found: C, 57.96; H, 2.00; N, 11.31. $C_{24}H_{10}Cl_4N_4$ requires: C, 58.10; H, 2.03; N, 11.29); n.m.r. spectra could not be recorded due to its extremely low solubility in the usual spectroscopic solvents; m.s., m/z (%): 498 (M^+ + 4, 83), 496 (M^+ + 2, 100), 494 (M^+, 49), 464 (20), 462 (42), 460 (30), 69 (12); i.r.: 1621, 1502, 1432, 1345, 964, 937, 826 cm^{-1}.

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