Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 5887–5891

TETRAHEDRON

Reaction of N^1,N^2-diarylamidines with 3,4,5,6-tetrachloro-1,2-benzoquinone

Mohsen A.-M. Gomaa[a,*] and Dietrich Döpp[b]

[a]*Department of Chemistry, Faculty of Science, Minia University, 61519 El-Minia, Egypt*
[b]*Institut für Chemie, Unversität Duisburg-Essen, D-47048 Duisburg, Germany*

Received 21 March 2003; revised 15 May 2003; accepted 12 June 2003

Abstract—A synthesis of 5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-ones was found in the reaction of nitro-substituted N^1,N^2-diarylamidines with 3,4,5,6-tetrachloro-1,2-benzoquinone. In contrast, 6,7,8,9-tetrachlorodibenzodioxins were obtained from reaction of N^1,N^2-diphenylpropionamidine and N^1,N^2-di-(4-*tert*-butylphenyl)acetamidine with 3,4,5,6-tetrachloro-1,2-benzoquinone.

1. Introduction

Amidines find widespread application in organic chemistry as starting materials for the preparation of many different nitrogen-containing heterocycles.[1] In 1995 we reported on the reaction of N^1,N^2-diarylamidines with 2,3,5,6-tetrachloro-1,4-benzoquinone and isolation of tetrahydroindolones.[2] 3,4,5,6-Tetrachloro-1,2-benzoquinone often reacts as a diene at C3, C6 with dienophiles through [4+2]-cycloaddition, or as a 1,2-dione type heterodiene giving rise to either bicyclic 1,2-diones (with e.g. alkynes[3] and with 1,2-bisimines to form bicyclic iminoketones finally.[4] When double bond dienophiles are used the cycloaddition is followed by a dehydrogenation of the primary adducts to form fused dioxins.[5–7] Alternatively this quinone may undergo nucleophilic attack by e.g. the N-atoms of *N*,*N*′-dibenzylidene ethylenediamine at both carbonyl groups and at the chlorine atoms followed by condensation (elimination of either H_2O or HCl).[8] For this reason we decided to exploit the reactions of *o*-chloranil with the nucleophilic imino nitrogen atom of amidine groups.

2. Results and discussions

2.1. Formation of dibenzodiazepines 3a–d,d′ and indolone 4

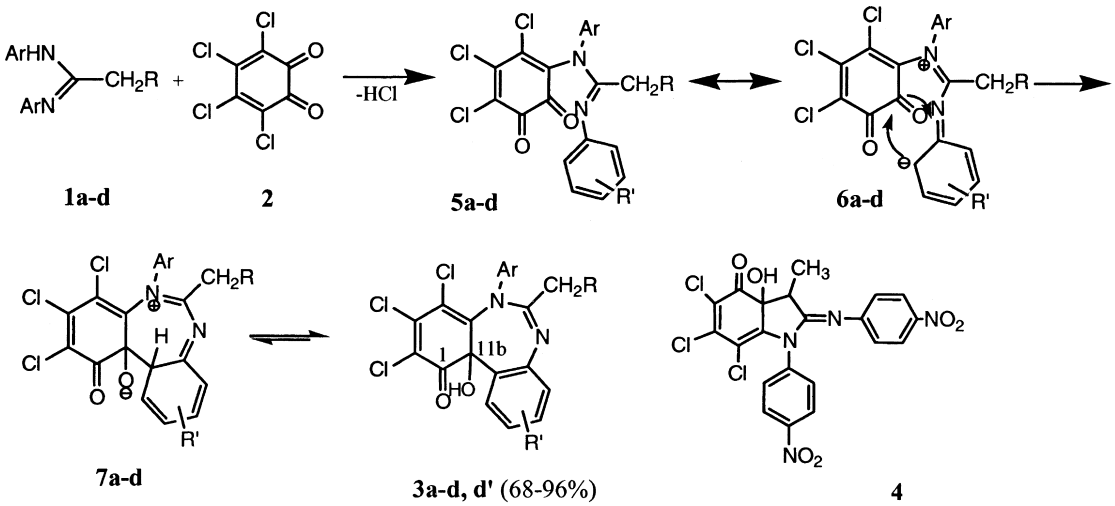
Addition of an ethyl acetate solution of 3,4,5,6-tetrachloro-1,2-benzoquinone **2** to solutions of amidines **1a–d** in the same solvent formed, after standing overnight at room temperature, products **3a–d**,**d′**. The structural assignment of products **3a–d**,**d′** is based on the following data. In their ^{13}C NMR spectra the characteristic signals for the carbonyl groups appear at δ=170.1–172.2 ppm, and a signal at 79.3 ppm with low intensity represents the quaternary carbon atom C-11b bearing a hydroxyl group (only in the case of **3a**). Due to its low intensity this signal was not observed in **3b**,**3c**,**3d** or **3d′**. In their ^1H NMR spectra characteristic D_2O exchangable signals at δ=8.92–9.19 ppm were assigned to the hydroxyl protons. In addition, the IR spectra (in potassium bromide) showed two sharp bands at ν=3261–3411 and 1670–1688 cm^{-1} which were assigned to the hydroxyl and carbonyl groups respectively.

The mass spectra revealed that the products are 1:1 condensation products formed by release of HCl. Thus the product could be either **3** or **4**. In the ^1H NMR spectra we observed only seven aromatic protons in addition to the characteristic D_2O exchangable proton, a singlet for the acetamidinic CH_3 (for **3a**,**b**), as well as triplet and quartet signals for the CH_3 and CH_2 groups (for **3c**,**d**) respectively. The ^{13}C NMR spectra showed 12 quaternary carbon atoms. Also ^{13}C DEPT spectra of **3c**,**d**,**d′** showed a signal with a negative amplitude for the methylene carbon atoms between 27.6 and 27.8 ppm; and five aryl-*C*H signals (for **3a**,**c**) or 7 aryl-*C*H signals (for **3b**,**3d**,**3d′**). Thus the presence of methyl and methylene carbon atoms and the difference observed in the number of signals attributable to aryl-carbon atoms linked to hydrogen excludes structure **4** and supports structure **3** (Scheme 1).

Since C-11b is a stereogenic center, the methylene protons in **3c**,**3d** and **3d′** are diastereotopic and their signals in the

Keywords: diazepine; amidine; benzoquinone; dibenzodioxine.
* Corresponding author. Tel.: +20-8634-7729; fax: +20-8634-2601; e-mail: mohsengomaa@link.net

0040–4020/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/S0040-4020(03)00941-4



1,3,5-7	R	Ar = C_6H_4R'	3,7	R	R'
a	H	4-NO_2-C_6H_4	**a**	H	10-NO_2
b	H	3-NO_2-C_6H_4	**b**	H	9(11)-NO_2 (one isomer)
c	CH_3	4-NO_2-C_6H_4	**c**	CH_3	10-NO_2
d	CH_3	3-NO_2-C_6H_4	**d,d'**	CH_3	9(11)-NO_2 (both isomers)

Scheme 1.

^{1}H NMR spectra each appear as quartet of quartets (qq). In the case of **3a**,**b** (R=H) all methyl protons are homotopic and thus isochronous. In addition, in **3b**,**d** the NO_2 group may be located at either C-9 or C-11, thus two positional isomers are to be expected for these products. Actually, two isomers are observed for **3d**,**3d′** only. When the ^{1}H NMR spectra of these were recorded at 60°C, all signals became sharper than at ambient temperature, most likely due to enhancement of rotation around the chiral axis coinciding with the N5-aryl bond.

A rationale for the formation of diazepines **3a**–**d**,**d′** is given as follows. Nucleophilic attack on C-3 of **2** by the imino nitrogen atom N^2 of **1a**–**d** followed by liberation of hydrogen chloride gives **5a**–**d**. In the latter the amidine moiety activates the *ortho* positions of the nitrophenyl ring which adds to the C-2 carbonyl groups of the quinone to give **3a**–**d**,**d′** (Scheme 1).

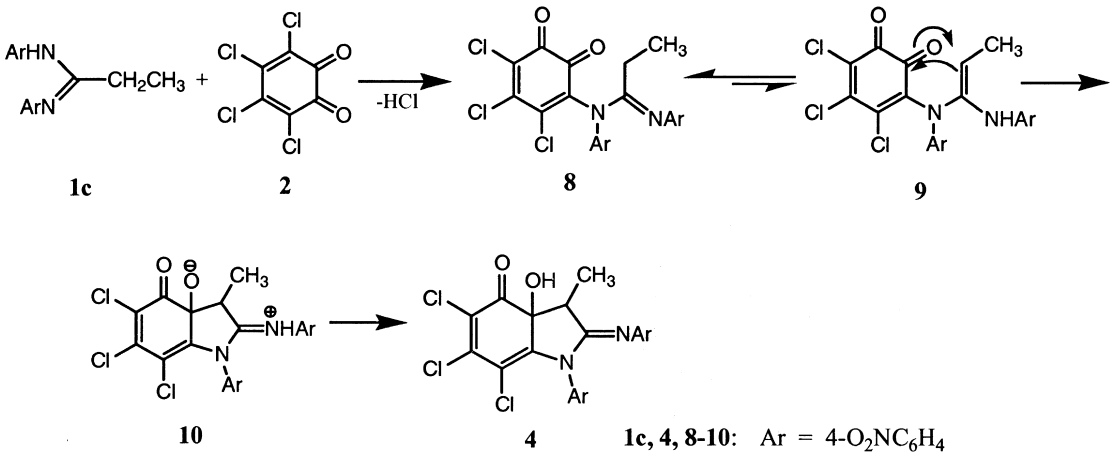
These results open a satisfactory route to dibenzodiazepines **3a**–**d** in high yield (68–96%). Diazepines are a class of heterocycles with potential pharmacological interest.[9]

In the case of reaction of **1c** with **2** the indolic ketone **4** was obtained as a minor product (23%) in addition to **3c**. ^{13}C NMR specroscopy of **4** revealed a signal at 78.5 for the quaternary aliphatic carbon atom C-3a bearing a hydroxyl group and a signal at 186.1 ppm for the carbonyl carbon atom. The ^{13}C DEPT spectrum exhibited a positive signal at higher field at δ=48.1 ppm for the tertiary aliphatic carbon atom C-3. The ^{1}H NMR spectrum revealed a doublet at 1.07 ppm for the methyl group protons and a quartet at 3.39 ppm for 3-H and a broad signal at 1.55 ppm for the hydroxyl group. In addition, its IR spectrum showed two sharp bands at ν=3411 and 1691 cm^{-1} for the hydroxyl and the carbonyl groups, respectively.

Formation of **4** may be rationalized as an initial nucleophilic substitution of chlorine at C-3 of **2** by the imino nitrogen atom N^2 of **1c** giving **8** which is in equilibrium with enamine **9**. The latter ultimately cyclizes to **4** via the intermediate **10** (scheme 2).

2.2. Formation of dibenzodioxines 11a,b

When we reacted 3,4,5,6-tetrachloro-1,2-benzoquinone (**2**) with amidines **1e**,**f** we expected to get the dibenzodiazepine **3** as with amidines **1a**–**d**, but the reaction with **1e**,**f** was dramatically different leading to the formation of dibenzodioxins **11a**,**b**. The structural assignment of products **11a**,**b** is based on the following data. Their mass spectra showed that 1:1 products are present with peak clusters characteristic of compounds bearing four chlorine atoms. Structural assignment of **11a** was confirmed from its ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum showed only six aryl protons in addition to one characteristic D_2O exchangeable proton, while its ^{13}C NMR and ^{13}C DEPT spectra revealed ten quaternary carbon atoms and only four kinds of aromatic *C*H carbons. The alternative **20** should show eight aromatic protons and 11 quaternary carbon atoms. ^{13}C Spectrum of

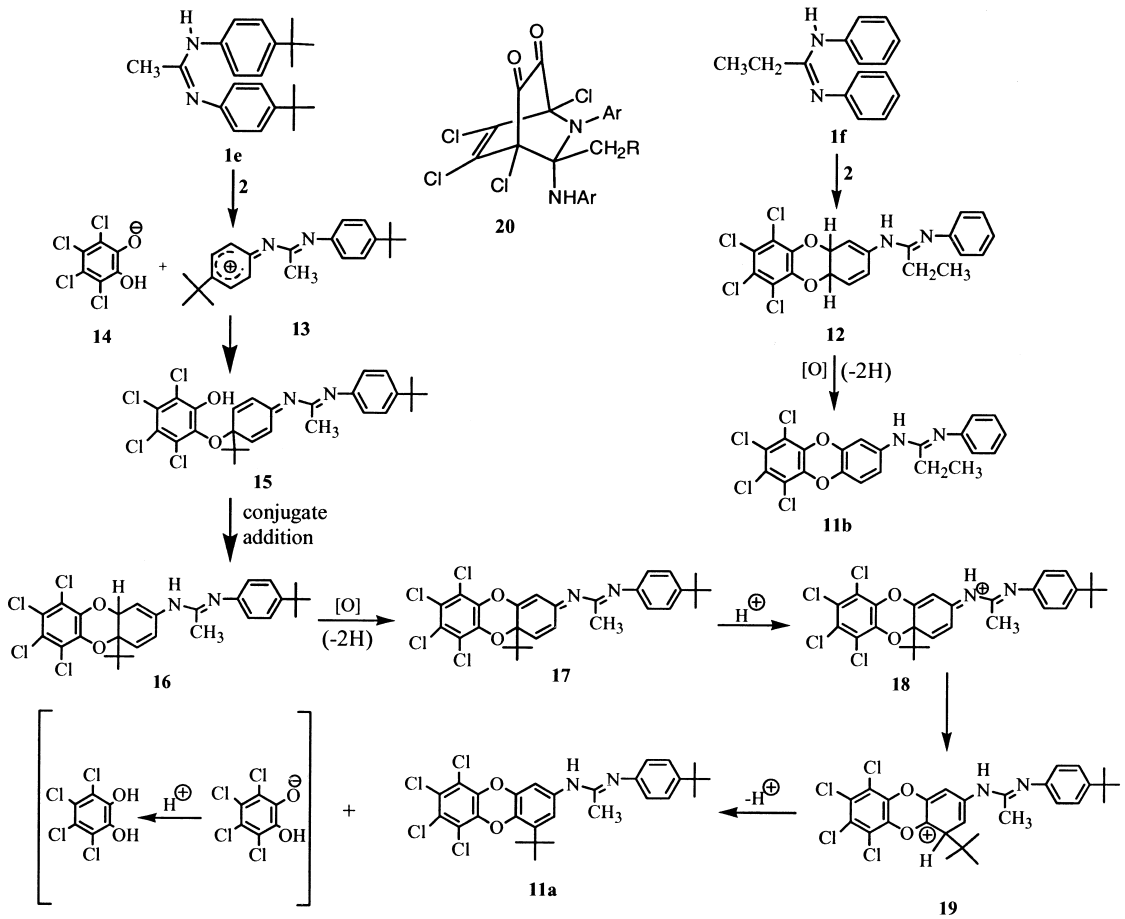


Scheme 2.

11b revealed 15 quaternary carbon atoms and its ^{13}C DEPT spectrum revealed only five aromatic CH carbon atoms. Its alternative structure **20** should show nine quaternary carbons and four signals for aromatic CH carbon atoms (scheme 3). Moreover, the ^{1}H NMR of **11b** showed eight aromatic protons in addition to one characteristic D_2O exchangeable proton, while its alternative **20** should show ten aryl protons.

To unravel whether the amidinic group is linked to C-1 or C-2 of the dioxine, coupling constants of the aromatic protons were determined from their ^{1}H NMR spectra. The ^{1}H NMR spectrum of **11b** showed that coupling constants for the proton 1-H is ^{4}J=2.3 Hz and for both 3-H and 4-H is ^{3}J=8.6 Hz. In contrast the ^{1}H NMR spectrum of **11a** showed the coupling constants for both of 1-H and 3-H as ^{4}J=2.0 Hz. These observations are consistent only with a C-2 connectivity as in **11a**,**b**.

The formation of **11a**,**b** may be rationalized as follows. Hydride transfer from the amidine **1e** to the *o*-chloranil **2** to form **13** and **14**. These two may combine to afford **15**. The



Scheme 3.

latter undergoes a conjugate addition to form **16** which is dehydrogenated by another molecule of **2** resulting in the formation of **17**. The latter rearranges to the dioxine **11a** via the intermediates **18** and **19**. Similarly **1f** reacts with **2** to afford the intermediate **12** which undergoes dehydrogenation to give **11b**.

3. Conclusion

These results demonstrated that nitro-substituted N^1,N^2-diarylamidines used in this study resemble amines in their reactions with chlorinated quinones, but due to their ambident nature allow for the synthesis of 5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-ones. In contrast in the reaction of diphenyl- or di-(4-*tert*-butylphenyl)amidines with 3,4,5,6-tetrachloro-1,2-benzoquinone, 6,7,8,9-tetrachlorodibenzodioxins were obtained.

4. Experimental

4.1. General

The uncorrected melting points were determined on a Reichert Thermovar hot stage microscope. Elemental analyses were obtained on a Carlo Erba 1106 CHN analyzer, while the IR (potassium bromide) were recorded on a Perkin–Elmer 983 spectrophotometer. The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were observed on a Bruker WM 300 instrument with TMS as the internal standard using dimethylsulfoxide-d_6 as solvent. The ^{13}C signals were assigned on the basis of DEPT 135/90 spectra. The mass spectra (70 eV, electron impact mode) were recorded on AMD 604 instrument. Preparative layer chromatography (PLC) used air-dried 1.0 mm thick layers of slurry applied silica gel Merck PF_{254} on 48 cm wide and 20 cm high glass plates and toluene/ethyl acetate (10:1) as developing solvent. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm light and eluted with acetone or ethyl acetate.

4.2. Starting materials

3,4,5,6-Tetrachloro-1,2-benzoquinone (**2**) was used as received from Aldrich. N^1,N^2-Diarylamidines **1a**–**f** were prepared according to literature procedures.[10]

4.3. General procedure for preparation of 3a–d,d′ and 4

To a solution of **1a**–**d** (1.0 mmol) in ethyl acetate at room temperature was added dropwise a solution of *o*-chloranil **2** (0.5 mmol) 10 mL of ethyl acetate. The mixture was left standing overnight. After filtration, the precipitate was identified as the amidine salt. The filtrate was subjected to PLC using toluene/ethyl acetate 2:1 as developing solvent. Zones were extracted with acetone, the fastest moving one contained **3d′** and **4**, while the second contained **3a**, **3b**, **3c**, or **3d**, respectively.

4.3.1. 2,3,4-Trichloro-11b-hydroxy-6-methyl-10-nitro-5-(4-nitrophenyl)-5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-one (3a). This compound was obtained (220 mg, 86%) as yellow crystals (ethyl acetate), mp 236–240°C; IR (KBr) ν_{max} 3264 (OH), 1676 (CO) and 1329 (NO_2) cm^{-1}; δ_H (300 MHz, acetone-d_6) 2.20 (s, 3H, CH_3), 6.78 (d, ^3J=8.7 Hz, 8-H), 7.58 (d, 1H, ^4J=2.6 Hz, 11-H), 7.74 (dd, 1H, ^3J=8.7 Hz, ^4J=2.6 Hz, 9-H), 7.83 (m, 2H, nitrophenyl-H), 8.22 (m, 2H, nitrophenyl-H), 8.92 (s, 1H, OH); δ_C (75 MHz, acetone-d_6) 24.0 (CH_3), 79.3 (C-11b), 110.5, 114.3, 122.9, 125.0, 127.7 (aryl *C*H), 124.7, 130.7, 131.5, 137.0, 137.3, 140.3, 141.3, 141.9, 144.2, 145,5, 170.0 (quart. C); *m*/*z* 510 (M^+, 16), 466 (51), 449 (18), 43 (100); Anal. calcd for $C_{20}H_{11}Cl_3N_4O_6$: C, 47.13; H, 2.18; N, 10.99. Found: C, 47.15; H, 2.18; N, 10.88.

4.3.2. 2,3,4-Trichloro-11b-hydroxy-6-methyl-9-nitro-5-(3-nitrophenyl)-5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-one (3b). This compound was obtained (210 mg, 82%) as yellow crystals (ethyl acetate), mp 295–297°C; IR (KBr) ν_{max} 3297 (OH), 1674 (CO) and 1340 (NO_2) cm^{-1}; δ_H (300 MHz dimethylsulfoxide-d_6) 2.09 (s, 3H, CH_3), 6.92 (d, 1H, ^3J=8.7 Hz, 11-H), 7.52 (d, 1H, ^4J=2.5 Hz, 8-H), 7.56 (dd, 1H, ^3J=8.7 Hz, ^4J=2.6 Hz, 10-H), several m at 7.62, 8.06 and 8.61 (4H, nitrophenyl-H), 9.19 (s, 1H, OH); δ_C (75 MHz dimethylsulfoxide-d_6) 23.8 (CH_3), 109.5, 115.9, 118.6, 119.4, 120.4, 129.3 and 130.3 (aryl *C*H) 121,8, 122.5, 128.2, 130.9, 131.4, 140.0, 140.4, 144.3, 147.4, 147.7, 170.1 (quart. C); *m*/*z* 510 (M^+, 17), 492 (18), 466 (47), 449 (24), 432 (23), 419 (15), 373 (17), 339 (10), 57 (21), 43 (100). Anal. calcd for $C_{20}H_{11}Cl_3N_4O_6$: C, 47.13; H, 2.18; N, 10.99. Found: C, 47.18; H, 2.38; N, 10.61.

4.3.3. 2,3,4-Trichloro-6-ethyl-11b-hydroxy-10-nitro-5-(3-nitrophenyl)-5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-one (3c). This compound was obtained (230 mg, 88%) as yellow crystals (ethyl acetate), mp 300–302°C; IR (KBr) ν_{max} 3346 (OH), 1688 (CO), 1329 (NO_2) cm^{-1}; δ_H (300 MHz dimethylsulfoxide-d_6) 1.09 (t, 3H, ^3J=7.3 Hz, CH_3), 2.35 (m, 2H, CH_2), 6.86 (d, 1H, $|^3J|$=8.8 Hz, 8-H), 7.46 (d, 1H, ^4J=2.4 Hz, 11-H), 7.71–7.76 several m (3H, Ar-H), 8.17 (d, 2H, ^3J=9.4 Hz, Ar-H), 9.35 (s, 1H, OH), δ_C (75 MHz dimethylsulfoxide-d_6) 8.5 (CH_3), 27.7 (CH_2), 110.2, 114.0, 121.7, 123.7, 123.8 (aryl CH), 120.2, 122.7, 123.0, 127.6, 130.6, 136.5, 140.0, 141.4, 141.6, 144.1, 145.3, 172.7 (quart. C); *m*/*z* 524 (M^+, 6), 466 (22), 449 (6), 421 (3), 373 (3), 301 (7), 57 (100). Anal. calcd for $C_{21}H_{13}Cl_3N_4O_6$: C, 48.15; H, 2.50; N, 10.70. Found: C, 47.92; H, 2.68; N, 10.42.

4.3.4. 2,3,4-Trichloro-6-ethyl-11b-hydroxy-11-nitro-5-(3-nitrophenyl)-5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-one (3d). This compound was obtained (160 mg, 51%) as yellow crystals (ethyl acetate), mp 319–320°C; IR (KBr) ν_{max} 3300 (OH), 1670 (CO), 1346 (NO_2) cm^{-1}; δ_H (300 MHz dimethylsulfoxide-d_6) 1.04 (t, 3H, ^3J=7.2 Hz, CH_3), 2.35 (m, 2H, CH_2), 6.94 (dd, 2H, ^3J=8.1 Hz, ^4J=1.1 Hz, 8-H and 10-H), 7.24 (dd, 1H, ^3J=8.6, 8.6 Hz, 9-H), several m at 7.63, 8.01and 8.62 (4H, nitrophenyl-H), 9.21 (s, 1H, OH); δ_C (75 MHz dimethylsulfoxide-d_6) 9.0 (CH_3), 27.8 (CH_2), 117.3, 118.9, 119.5, 120.3, 124.9, 129.3, 130.3 (aryl *C*H), 120.6, 121.8, 122.0, 128.5, 129.3, 132.0, 136.2, 137.6, 139.9, 140.7, 147.7, 173.2 (quart. C); *m*/*z* 524 (M^+, 5), 468 (9), 451 (19), 421 (3), 373 (3), 57 (100). Anal. calcd for $C_{21}H_{13}Cl_3N_4O_6$: C, 48.15; H, 2.50; N, 10.70. Found: C, 48.22; H, 2.48; N, 10.72.

4.3.5. 2,3,4-Trichloro-6-ethyl-11b-hydroxy-9-nitro-5-(3-nitrophenyl)-5,11b-dihydro-1*H*-dibenzo[*d*,*f*][1,3]diazepin-1-one (3d^{l}). This compound was obtained (140 mg, 45%) as yellow crystals (ethyl acetate), mp 318°C; IR (KBr) ν_{max} 3375 (OH), 1683 (CO), 1346 (NO_2) cm^{-1}; δ_H (300 MHz dimethylsulfoxide-d_6): 1.07 (t, 3H, ^3J=7.3 Hz, CH_3), 2.38 (m, 2H, CH_2), 6.92 (d, 1H, ^3J=8.8 Hz, 11-H), 7.52 (d, 1H, ^4J=2.7 Hz, 8-H), 7.56 (dd, 1H, ^3J=8.8 Hz, ^4J=2.7 Hz, 10-H), several m at 7.63, 8.06 and 8.63 (4H, nitrophenyl-H), 9.18 (s, 1H, OH), δ_C (75 MHz dimethylsulfoxide-d_6) 8.9 (CH_3), 27.6 (CH_2), 119.3, 119.5, 120.1, 120.2, 122.3, 129.1, 130.2 (aryl *C*H), 109.3, 115.7, 118.4, 128.1, 130.8, 131.3, 139.8 140.4, 144.1, 147.3, 147.5, 173.02 (quart. C); MS: *m/z* 524 (M^+, 5), 468 (9), 451 (5), 421 (2), 373 (3), 57 (100). Anal. calcd for $C_{21}H_{13}Cl_3N_4O_6$: C, 48.15; H, 2.50; N, 10.70. Found: C, 48.27; H, 2.43; N, 10.65.

4.3.6. 5,6,7-Trichloro-3a-hydroxy-3-methyl-1-(4-nitrophenyl)-2-[(4-nitrophenyl)imino]-1,2,3,3a-tetrahydro-4*H*-indol-4-one (4). This compound was obtained (70 mg, 23%) as orange crystals (ethyl acetate/cyclohexane), mp 300°C; IR (KBr) ν_{max} 3411 (OH), 1691 (CO), 1340 (NO_2) cm^{-1}; δ_H (300 MHz $CDCl_3$) 1.07 (d, 3H, ^3J=7.3 Hz, CH_3), 1.55 (br, 1H, OH), 3.39 (q, 1H, ^3J=7.2 Hz, CH_2), 6.95–8.35 several m (8H, Ar-H); δ_C (75 MHz $CDCl_3$) 13.5 (CH_3), 48.1 (C-3), 78.5 (C-3a), 121.2, 124.3, 125.3, 128.1 (aryl *C*H), 105.7, 125.4, 140.7, 144.4, 144.7, 144.9, 150.3, 153.7, 162.3, 186.1 (quart. C); *m/z* 524 (M^+, 12^{j}), 506 (10), 487 (12), 459 (21), 386 (14), 374 (12), 138 (21), 92 (8), 65 (18), 36 (100). Anal. calcd for $C_{21}H_{13}Cl_3N_4O_6$: C, 48.15; H, 2.50; N, 10.70. Found: C, 48.26; H, 2.61; N, 10.80.

4.4. General procedure for preparation of 11a,b

To a stirred solution of amidines **1e**,**f** (0.5 mmol) in 5.0 mL of ethyl acetate at room temperature was added dropwise, solution of *o*-chloranil **2** (1.0 mmol) in 5.0 mL of ethyl acetate and the mixture left standing overnight. The reaction mixture was concentrated and subjected to PLC using toluene/ethyl acetate 10:1 as developing solvent. In the case of **1e**, when the residue was dissolved in acetone, a precipitate was formed and filtered off to give a first crop of **11b**. The major zones were extracted and identified as **11a** and **11b**.

4.4.1. *N*^{1}-[4-(*tert*-Butyl)-6,7,7,9-tetrachlorodibenzodioxin-2-yl]-*N*^{2}(4-*tert*-butylphenyl)-acetamidine (11a). This compound was obtained (96 mg, 30%) as yellow crystals (cyclohexane) mp 162–164°C; IR (KBr) ν_{max} 3381 (NH), 1676 (C=N) cm^{-1}; δ_H (300 MHz $CDCl_3$): 1.22 (s, 9H, $3CH_3$), 1.30 (s, 9H, $3CH_3$), 2.15 (s, 3H, CH_3), 5.83 (s, 1H, NH), 6.72 (d, 1H, ^4J=2.0 Hz, 1-H), 6.83 (d, 1H, ^4J=2.0 Hz, 3-H), 7.30–7.39 several m (4H, Ar-H); δ_C (75 MHz $CDCl_3$): 22.4 (CH_3), 31.0 [C(*C*H_3)$_3$], 31.2 [*C*(CH_3)$_3$], 112.2, 118.4, 121.5, 123.7, 124.1, 124.6, 126.7, 129.1, 140.1, 142.7; *m/z* 566 (M^+, 73), 524 (100), 509 (31), 467 (25), 453 (13), 174 (11), 57 (39), 43 (14). Anal. calcd for $C_{28}H_{28}Cl_4N_2O_2$: C, 59.36; H, 4.98; N, 4.95 Found: C, 59.26; H, 4.90; N, 4.80.

4.4.2. *N*^{1}-(6,7,8,9-Tetrachlorodibenzodioxin-2-yl)-*N*^{2}-phenyl-propionamidine (11b). This compound was obtained (83 mg, 71%), as colorless crystals (from ethyl acetate), mp 280°C; IR (KBr) ν_{max} 3272 (NH), 1665 (C=N) cm^{-1}; δ_H (300 MHz dimethylsulfoxide-d_6): 1.03 (t, 3H, ^3J=7.3 Hz, CH_3), 2.26 (m, 2H, CH_2), 6.79 (d, 2H, ^3J=8.6 Hz, 3-H and 4-H), 6.86 (d, 1H, ^4J=2.3 Hz, 1-H), 7.18–7.47 (5H, phenyl-H), 8.59 (br, 1H, NH), δ_C (75 MHz dimethylsulfoxide-d_6) 8.6 (CH_3), 27.4 (CH_2), 115.6, 116.0, 124.6, 124.8, 125.7, 128.9 (aryl *C*H), 121.0, 122.4, 123.4, 124.2, 125.1, 127.8, 128.9, 129.6, 132.2, 140.1, 142.6 (quart. C); *m/z* 468 (M^+, 39), 446 (8), 412 (100), 376 (24), 339 (9), 77 (8). 57 (91), 43 (11). Anal. calcd for $C_{21}H_{14}Cl_4N_2O_2$: C, 53.85; H, 3.01; N, 5.95. Found: C, 54.00; H, 2.90; N, 6.04.

Acknowledgements

Generous support of this work by Fonds der Chemischen Industrie is gratefully acknowledged.

References

1. Boyd, G. V. *The Chemistry of Amidines and Imidates*; Patai, S., Rappoport, Z., Eds.; Interscience: London, 1991; Vol. 2, pp 367–426.
2. Döpp, D.; Gomaa, M. A.-M.; Henkel, G.; Nour El-Din, A. M. *J. Heterocycl. Chem.* **1995**, *32*, 603–610.
3. Pyle, J. L.; Shaffer, A. A.; Contrell, J. S. *J. Org. Chem.* **1981**, *46*, 115–118.
4. Aly, A. A.; Mohamed, N. K.; Hassan, A. A.; Mourad, A.-E. *Bull. Chem. Soc. Jpn* **1996**, *69*, 2249–2252.
5. Latif, N.; Mishriky, N.; Guiriguis, N. S.; Hussein, A. *J. Prakt. Chem.* **1973**, *315*, 419–426.
6. Latif, N.; Girgis, N. S.; Michael, F. *Tetrahedron* **1970**, *26*, 5765–5772.
7. Latif, N.; Mishriky, N.; Guiriguis, N. S. *J. Chem. Soc. Perkin Trans. 1* **1975**, 1052–1055.
8. Aly, A. A.; Hassan, A. A.; Mohamed, N. K.; Mourad, A.-E. *Pharmazie* **1997**, *52*, 282–287.
9. Fryer, R. I.; Walser, A. In *Bicyclic Diazepines*; Fryer, R. I., Ed.; Wiley: New York, 1991.
10. Taylor, E. C.; Erhart, W. A. *J. Org. Chem.* **1963**, *28*, 1108–1112.