On the Formation and ^{1}H NMR-spectroscopic Characterization of *N,N*-Diaryl-substituted Formamide Chlorides

Jens Schönewerk[a] and Horst Hartmann

Department Chemie, Technische Universität Dresden, 01062 Dresden, Germany
[a] Present address: SEMA GmbH, Industriestraße 12, 06869 Coswig, Germany

Reprint requests to Prof. Dr. Horst Hartmann. Fax: +49-3514-6339485. E-mail: Hartmann@iapp.de

Z. Naturforsch. **2012**, *67b,* 277 – 284; received January 16, 2012

Dedicated to Prof. Klaus Müllen to the occasion of his 65th birthday

The reaction of *N*,*N*-diaryl-substituted formamides with oxalyl chloride gives rise, instead to the formation of the expected salt-like formamide chlorides, to the formation of corresponding non-ionic *N*-dichloromethyl-substituted diarylamines.

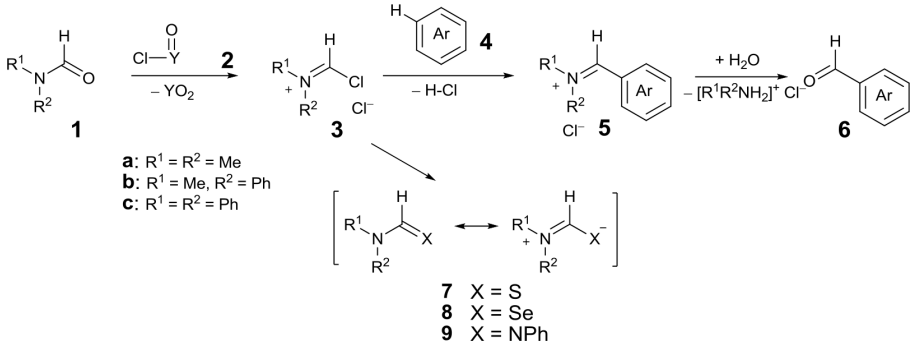
Key words: Vilsmeier Reaction, *N*,*N*-Diaryl-Formamides, *N*-Dichloromethyl-substituted Diarylamines, ^{1}H NMR Spectroscopy

Introduction

As known, the Vilsmeier-Haak reaction (VR) is a versatile method for preparing aromatic or heteroaromatic aldehydes in an enormous variety [1]. Originally a mixture of *N*-methylformanilide (**1b**) and $POCl_3$ (**2a**, Y = PCl_2) was used for this method [2]. Later on, instead of these reagents the cheaper DMF (**1a**) as well as other inorganic and organic acid chlorides, especially phosgene (**2b**, Y = CCl) or oxalyl chloride (**2c**, Y = CCOCl), were used [3].

In the course of the VR both reactants, the *N*,*N*-disubstitued formamides **1** and the acid chlorides **2**, are transformed into reactive chloroformamidinium chlorides **3** which are able to react with suitable nucleophilic substrates, like an aromatic or heteroaromatic compound of the general formula **4**, to yield, in a first step, the corresponding iminium salts **5** [4] from which the aldehydes **6** could finally be obtained by hydrolysis (Scheme 1).

In contrast to the formamides **1a** and **1b**, *N*,*N*-diaryl-substituted formamides have not been applied for the VR hitherto. The parent *N*,*N*-diphenylformamide **1c** was used, however, for the synthesis of certain products containing the *N*,*N*-diphenylaminomethine moiety. Thus, *N*,*N*,*N*′-triphenyl-formamidine [5] *N*,*N*-diphenyl-cyanamide [6], *N*,*N*-diphenylamino-trifluoromethane [7], and 1,2-bis-(*N*,*N*-diphenylamino)-1,2-dichloroethylene [8], have been prepared by starting with this formamide derivative. Although for all these reactions the formation of the corresponding *N*,*N*-diphenyl-substituted formamide chloride **3c** can be assumed, an unambiguous proof for this compound has not been given as yet, however. Such proof was envisaged by us now by means of NMR measurements.



Scheme 1. Formation of iminium salts **5** and aldehydes **6**.

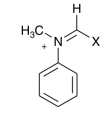
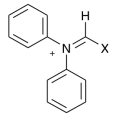
	X	**1** (X = O^-)	**3** (X = Cl)	**7** (X = S^-)	**8** (X = Se^-)	**9** (X = $^-NC_6H_5$)
a		7.93[a] [9, 10] 7.92[b] [11] 8.02[c] [25] 7.95[d] [25]	10.10[a] [9, 10] 11.08[b] [11]	9.21[d] [15] 9.21[d] [16]	10.56[d] [17] 10.62[d] [18] 10.32[d] [19]	7.40[d] [20]
b		8.48 [21] 8.53[c] [25] 8.48[d] [25]	9.51[a] [9] 9.36 / 9.46[b] [14]	9.64[e] [12]	11.17[d] [18] 11.22[d] [22]	8.10[d] [13]
c		8.55[d] [23] 8.64[d] [24]	7.60[d,f]	10.0[d] [16] 8.67[d] [20]	11.75[d] [16]	8.18[d] [25]

Table 1. Chemical shifts of the $R_2N{=}CHX$ protons in compounds **1**, **3**, **7**–**9**.

[a] In CD_2Cl_2; [b] in CD_3CN; [c] in $[D_6]DMSO$; [d] in $CDCl_3$; [e] in CCl_4; [f] own measurement.

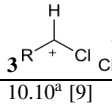
	R	**3**  **10**	**1** 	**2** 	**8** 	**9** 
a	Me_2N	10.10[a] [9]	7.93[a] [9]	9.21[a] [15]	10.62[a] [18] 10.32[b] [19]	7.40[a] [20]
b	MePhN	9.51[a] [9]	8.48[a] [25]	9.64[c] [12]	11.22 / 11.71[a] [22]	8.10[a] [13]
c	Ph_2N	7.60	8.64[a] [24]	10.0[a] [16]	11.75[a] [16]	8.18[a] [25]
d	MeO	7.33[a] [30]	8.07[a] [40]	9.66[a] [26]		
e	MeS	7.08[c] [31]	10.12[d] [26]	11.33[a] [27]		
f	Cl	7.26[d] [41]	9.70[a] [29]	9.74[a] [28]		

Table 2. ^{1}H NMR chemical shifts of methine protons of some formamide derivatives.

[a] In $CDCl_3$; [b] in C_6D_6; [c] in CCl_4; [d] neat.

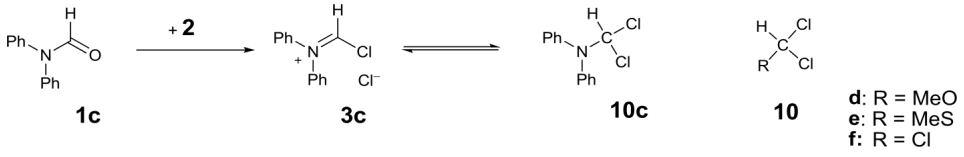
Results and Discussion

Formamide chlorides **3a** and **3b** exhibit, similar to other *N*,*N*-dialkyl substituted formamide chlorides [9], in the ^{1}H NMR spectra characteristic singlets at $\delta \approx$ 10 ppm, and a signal in the same region was thus expected also for the proton at the methine-iminium moiety in **3c**. To our surprise, this was not the case, however. Independently of the acyl chloride **2** used for the transformation of *N*,*N*-diphenylformamide (**1c**) into its formamide chloride **3c**, no signals for the methine proton at about 10 ppm could be detected. Thus, with $POCl_3$ as example, no reaction was observed, whereas with $(COCl)_2$ a transformation of the starting material **1c** into a product occurs. For this product, a new ^{1}H NMR signal at higher field at $\delta \approx 7.7$ ppm could be detected.

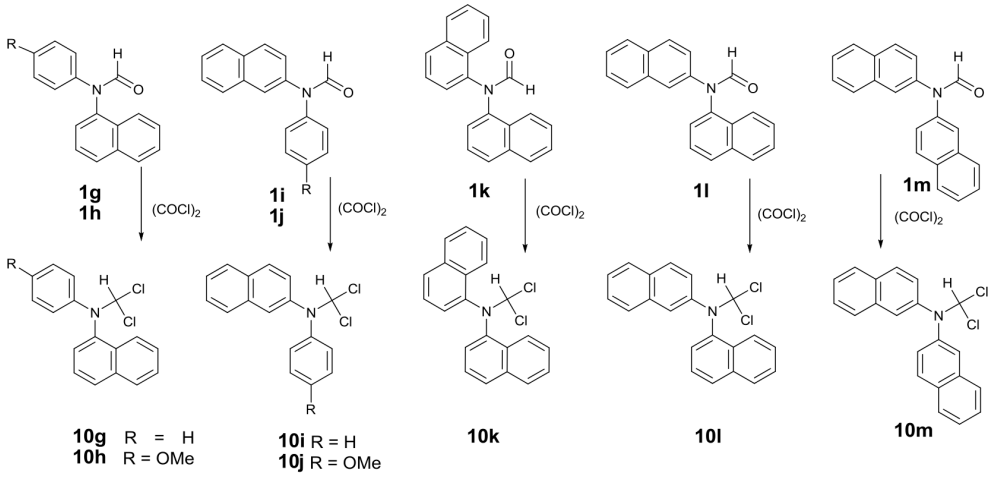
To check whether this finding is a speciality for *N*,*N*-diphenylformamide (**1c**), the ^{1}H NMR spectra of several other *N*,*N*-diaryl-substituted formamides were measured after the reaction with oxalyl chloride and compared with those of other *N*,*N*-diaryl-substituted formamide derivatives, such as *N*,*N*-diaryl-substituted thioformamides **7**, selenoformamides **8**, and formamides **9** (Scheme 1). The results obtained are summarized in Table 1 and Table 2 and discussed below.

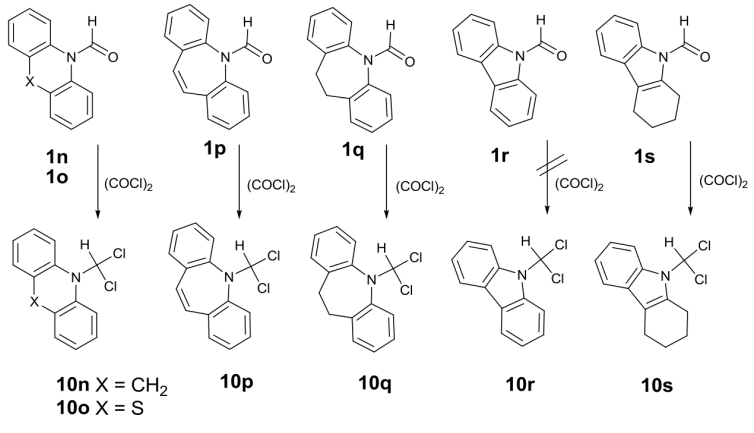
As can be seen from Table 1, the transformation of the formamides **1a** and **1b** into the corresponding formamide chlorides **3a** and **3b** is accompanied by a shift of the proton signal at the formyl moiety to lower field. This shift is larger for the *N*,*N*-dimethyl-substituted compound **3a** than for the *N*-methyl-*N*-phenyl-substituted compound **3b** and goes in line with the shifts observed by going from these formamides to the appropriate thioformamides **7a** and **7b** and selenoformamides **8a** and **8b**. The shift of the signals of these compounds is obviously due to the corresponding heteroatoms S and Se, which polarize the C=X bond more strongly than the oxygen due their lower π-π overlap strength.

In contrast, by going from *N*,*N*-diphenyl-formamide (**1c**) to the putative formamide chloride derivate **3c** a shift of the signals to higher field is observed in contrast to the shift observed by going from **1c** to the thio- and selenoformamide derivatives **7c** and **8c**, respectively. A shift to higher field is also found for *N*,*N*,*N*′-triphenyl-formamidine (**9c**) relative to *N*,*N*-diphenyl-formamide (**1c**).



Scheme 2.



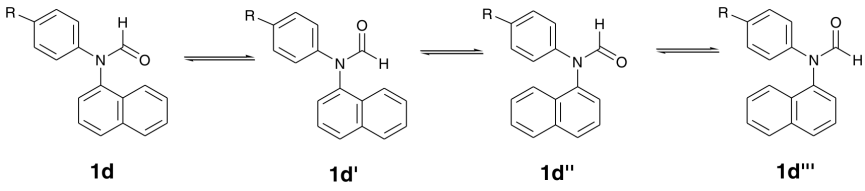


Scheme 3.

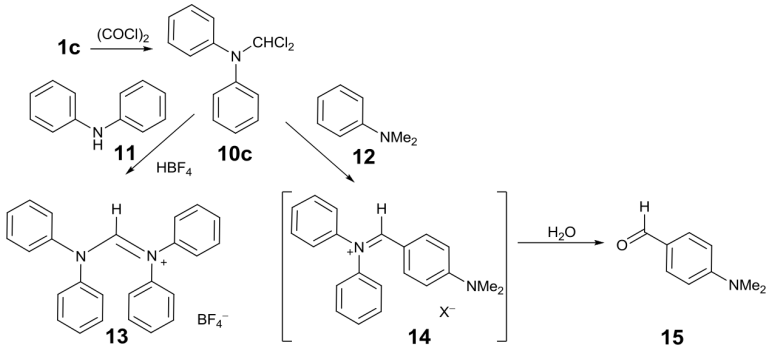
The observed abnormality in the chemical shift of the proton signal of compound **3c** can be explained by assuming that this compound exists contrary to compounds **3a** and **3b** in the non-ionic structure **10c** (Scheme 2) in which both chlorine atoms are covalently bound at the methine C atom. This statement is supported by the values of the proton signals at $\delta \approx$ 7.33, 7.08 and 7.26 ppm found for compounds **10d**, **10e** and **10f**, respectively, in which both chlorine atoms are also covalently bound at the methine C atom. In compounds **10a** and **10b** the proton signals are found at significantly higher field than the same signals in the thiono compounds **7a** and **7b** and in the seleno compounds **8a** and **8b** (Table 2).

A similar behavior is found for some other *N*,*N*-diaryl-substituted formamides, such as compounds **1g** – **1q** (Scheme 3). By reaction with oxalyl chloride **2b**, these compounds are transformed into products the ^{1}H NMR spectra of which indicate the exclusive existence of the non-ionic dichloro compounds **10d** – **10q** and not of the corresponding formamide chlorides. The same result was also found with the methoxy-substituted *N*,*N*-diarylformamides **1h** and **1j** which contain a donor-substituent able to stabilize cationic structures at the phenyl groups.

It is worth mentioning that the formamide derivative **1r** derived from carbazole can not be transformed neither into the corresponding formamide chloride **3r**



Scheme 4. Stereoisomers of the naphthyl-substituted formamide **1d**.



Scheme 5. Formation of the salts **13** and **14** and the aldehyde **15**.

Table 3. ^{1}H NMR chemical shifts of methine protons of some formamide derivatives.

Compound	Chem. shift δ	Compound	Chem. shift δ
1g	9.06 / 8.57	**10g**	7.57
1h	8.92 / 8.54	**10h**	7.65
1i	8.78 / 8.75	**10i**	7.71
1j	8.79 / 8.65	**10j**	7.71
1k	8.85	**10k**	7.84
1l	9.09 / 8.58	**10l**	7.66
1m	8.81	**10m**	7.81
1n	8.88	**10n**	7.72
1o	8.65	**10o**	7.54
1p	8.31	**10p**	7.25
1q	8.58	**10q**	7.57
1r	9.68	**10r**	–
1s	9.11 / 9.50	**10s**	7.81

nor into the dichloro compound **10r**, and that the formamide derivative **1l** derived from 1,1-dinaphthylamine needs an excess of oxalyl chloride and a longer reaction time for a complete transformation into the product **10l**. Obviously, the 1,1-dinaphthylamine moiety in **1k** on the one hand strongly screens the reactive formyl group, and the carbazole moiety is, on the other hand, a much weaker electron donor than the other *N*,*N*-diarylamines used as formamide building blocks. The last-mentioned fact is reflected also by the ^{1}H NMR signal of the formyl proton in compound **1r** at $\delta \approx 9.69$ ppm which is significantly shifted to lower field in comparison to the signals of the other formamide derivatives considered (Table 3).

By inspecting the ^{1}H NMR spectra of the *N*,*N*-diaryl-substituted formamides containing different aryl moieties at their N atoms, such as the formamides **1g** – **1j** and **1l**, another peculiarity was found. These compounds exhibit two separated singlets for the methine protons at the CH=O groups. This separation obviously is caused by the existence of stereoisomers and goes in line with observations in the ^{1}H NMR spectra of other unsymmetrically *N*,*N*-substituted formamides, *e. g. N*-alkyl-substituted *N*-naphthylformamides [32] and *N*-methyl-*N*-phenyl-thioformamide (**8c**) [12], each of which also exist as two stereoisomers. Although for the naphthyl-substituted formamides **1g** – **1j**, as exemplified for **1g** in Scheme 4, four different stereoisomers **1g**, **1g′**, **1g″**, and **1g‴** are possible, only **1g** and **1g′** seem to exist according to the NMR detected signals.

The separation of the signals of the stereoisomers vanishes, however, by going from the formyl derivatives **1g** – **1j** and **1l** to the corresponding dichloro compounds **10g** – **10j** and **10l**. The signal separation in the formamides **1g** – **1j** and **1l** is observed not only for the signals of the formyl protons at $\delta \approx 8.8$ ppm but also for the signals of all other protons in these compounds. The size of the signal separation depends, however, on the relative position of these protons with respect to the formyl groups and is rather large for the naphthalene protons at C-8 and significantly smaller for the other naphthalene protons.

The existence of the *N*,*N*-diaryl-substituted formamide chlorides **3** as isomeric dichloro-compounds **10** stimulated us to investigate the reactivity of these nonionic compounds towards some nucleophilic reagents,

e. g. towards electron-rich aromatics. Therefore, *N*,*N*-diphenyl-formamide **1c** was allowed to react – after its transformation into the dichloro compound **10c** by reaction with oxalyl chloride – with diphenylamine (**11**) and with *N*,*N*-dimethyl-aniline (**12**). In both cases a reaction occurs giving rise to the formation of the salts **13** and **14**, respectively (Scheme 5). The formamidinium salt **13** was isolated by addition of tetrafluoroboric acid to the pristine reaction mixture diluted with methanol, whereas **14** was not isolated but transformed into 4-(*N*,*N*-dimethylamino)benzaldehyde (**15**) by pouring the reaction mixture into an aqueous sodium carbonate solution and extracting the deeply colored reaction product with dichloromethane followed by purification by column chromatography.

Although these results demonstrate the aptness of *N*,*N*-diaryl-substituted formamides for VR, the rather complicated isolation procedure, by which the product has to be separated from the diarylamine by-product, suggests that it is of little synthetic value.

Experimental Section

^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker DRX 500 P instrument at 500.13 MHz. Mass spectra were obtained with a Bruker Esquire-LC 00084 instrument at 10 V with electrospray ionization using methanol containing 0.1 % ammonium acetate. The melting points were measured with a Boetius heating-table microscope and are uncorrected.

*Preparation of N,N-diaryl-substituted formamides **1** (General procedure)*

All the formamides studied were prepared by refluxing of a mixture of an appropriate diarylamine (10 mmol) in formic acid (25 mL) for 6 h and subsequent removing the formic acid at a rotary evaporator *in vacuo*. Solid products were recrystallized from toluene/hexane, and liquid products were purified by vacuum distillation using a microdistiller.

*N,N-Diphenyl-formamide (**1c**)*

From diphenylamine; m. p. 73 °C (ref. [33]: m. p. 71 – 72 °C). – ^{1}H NMR ($CDCl_3$): δ = 7.15 – 7.17 (m, 2 arom. H), 7.25 – 7.32 (m, 4 arom. H), 7.37 – 7.42 (m, 4 arom. H), 8.64 (s, 1H, CH=O). – $C_{13}H_{11}NO$ (197.23): calcd. C 79.16, H 5.62, N 7.10; found C 79.16, H 5.89, N 7.16.

*N-(1-Naphthyl)-N-phenyl-formamide (**1g**)*

From *N*-phenyl-1-naphthylamine; m. p. 74 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.16 – 7.25 (m, 2 arom. H), 7.29 – 7.34 (m, 2 arom. H), 7.41 – 7.56 (m, 5 arom. H), 7.78, 7.85 (dd, *J* = 8.4 Hz, 1 arom. H), 7.91 – 7.96 (m, 2 arom. H), 8.57, 9.06 (ds, 1H, CH=O). – $C_{17}H_{13}NO$ (247.1): calcd. C 82.57, H 5.30, N 5.66; found C 82.81, H 5.61, N 5.81.

*N-(4-Methoxyphenyl)-N-(1-naphthyl)-formamide (**1h**)*

From *N*-(4-methoxyphenyl)-1-naphthylamine, prepared according to ref. [39]; oil. – ^{1}H NMR ($CDCl_3$): δ = 3.76/3.77 (ds, 3H, OCH_3), 6.85 (dd, *J* = 9.1 Hz, 2 arom. H), 7.33 (d, 1 arom. H), 7.47 – 7.56 (m, 3 arom. H), 7.86 – 7.94 (m, 3 aromat. H), 8.00 (s, 1 arom. H), 8.54, 8.92 (ds, 1H, CH=O). – $C_{18}H_{15}NO$ (277.3): calcd. C 77.96, H 5.45, N 5.05; found C 77.68, H 5.61, N 4.81.

*N-(2-Naphthyl)-N-phenyl-formamide (**1i**)*

From *N*-phenyl-2-naphthylamine; m. p. 106 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.20 – 7.29 (m, 2 arom. H), 7.33 – 7.40 (m, 4 arom. H), 7.47 – 7.52 (m, 1 arom. H), 7.53 – 7.58 (m, 1 arom. H), 7.76, 7.85 (dd, *J* = 2.1 Hz, 1 arom. H), 7.82 – 7.86 (m, 3 arom. H), 8.75, 8.78 (ds, 1H, CH=O). – $C_{17}H_{13}NO$ (247.1): calcd. C 82.57, H 5.30, N 5.66; found C 82.97, H 5.64, N 5.75.

*N-(4-Methoxyphenyl)-N-(2-naphthyl)formamide (**1j**)*

From *N*-(4-methoxyphenyl)-2-naphthylamine, prepared according to ref. [39]; m. p. 70 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.81, 383 (ds, 3H, OCH_3), 6.93 – 9.95 (dd, *J* = 6.8 Hz, 2 arom. H), 7.18 (dd, *J* = 14.5 Hz, 1 arom. H), 7.25 (dd, *J* = 4.6 Hz, 1 arom. H), 7.45 – 7.47 (m, 1 arom. H), 7.50 – 7.54 (m, 1 arom. H), 7.64, 7.78 (dd, *J* = 2.1 Hz, 1 arom. H), 7.77 – 7.85 (m, 2 arom. H), 7.81, 8.01 (ds, 1 arom. H), 8.65, 8.79 (ds, 1H, CH=O). – $C_{18}H_{15}NO$ (277.3): calcd. C 77.96, H 5.45, N 5.05; found C 77.81, H 5.41, N 5.18.

*N,N-Bis(1-naphthyl)formamide (**1k**)*

From *N*,*N*-bis-(1-naphthyl)amine; m. p. 210 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.32 – 7.40 (m, 2 arom. H), 7.44 – 7.47 (m, 2 arom. H), 7.54 – 7.64 (m, 4 arom. H), 7.81 – 7.88 (m, 2 arom. H), 7.92 – 7.94 (m, 2 arom. H), 8.10 – 8.18 (m, 2 arom. H), 8.85 (s, 1H, CH=O). – $C_{21}H_{15}NO$ (297.1): calcd. C 84.82, H 5.08, N 4.71; found C 84.38, H 4.89, N 4.73.

*N-(1-Naphthyl)-N-(2-naphthyl)formamide (**1l**)*

From *N*-(1-naphthyl)–*N*-(2-naphthyl)amine; m. p. 62 – 65 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.20 (dd, *J* = 2.1, 7.5 Hz, 1 arom. H), 7.36 – 7.55 (m, 13 arom. H), 7.64 – 7.66 (m, 2 arom. H), 7.73 – 7. 81 (m, 8 arom. H), 7.88 – 7.90 (m, 3 arom. H), 7.93 (d, *J* = 7.5 Hz, 1 arom. H), 8.58, 9.09 (ds, 2H, CH=O). – $C_{21}H_{15}NO$ (297.1): calcd. C 84.82, H 5.080, N 4.71; found C 84.38, H 4.89, N 4.73.

*N,N-Bis(2-naphthyl)formamide (**1m**)*

From *N,N*-bis-(2-naphthyl)amine; m. p. 124 °C. – ^{1}H NMR ($CDCl_3$): δ = 7.19 (dd, *J* = 2.2, 8.8 Hz, 1 arom. H), 7.39 (dd, *J* = 2.1, 8.8 Hz, 1 arom. H), 7.43 – 7.47 (m, 2 arom. H), 7.48 – 7.52 (m, 2 arom. H), 7.71 – 7.73 (m, 2 arom. H), 7.77 (d, *J*= 1.9 Hz, 1 arom. H), 7.79 – 7.84 (m, 5 arom. H), 8.81 (s, 1H, CH=O). – $C_{21}H_{15}NO$ (297.1): calcd. C 84.82, H 5.08, N 4.71; found C 84.69, H 5.07, N 4.73

*N-Formyl-9H-acridane (**1n**)*

From 9*H*-acridane; m. p. 88 °C; (ref. [34]: m. p. 110 °C). – ^{1}H NMR ($CDCl_3$): δ = 4.88 (s, 2H, CH_2), 7.27 – 7.33 (m, 4 arom. H), 7.73 (t, *J* = 3.8 Hz, 1 arom. H), 7.93 (d, *J* = 7.0 Hz, 1 arom. H), 8.03 (t, *J* = 7.4 Hz, 1 arom. H), 8.17 (d, *J*= 8.4 Hz, 1 arom. H), 8.88 (s, 1H, CH=O). – $C_{14}H_{11}NO$ (209.2): calcd. C 80.36, H 5.30, N 6.69; found C 80.65, H 4.39, N 6.89.

*N-Formyl-10H-phenothiazine (**1o**)*

From 10*H*-phenothiazine; m. p. 140 °C; (ref. [35]: m. p. 144 °C). – ^{1}H NMR ($CDCl_3$): δ = 7.22 – 7.28 (m, 3 arom. H), 7.31 – 7.40 (m, 4 arom. H), 7.73 (d, *J*= 7.4 Hz, 1 arom H), 8.65 (s, 1H, CH=O). – $C_{13}H_9NOS$ (227.3): calcd. C 68.70, H 3.99, N 6.16, S 14.11; found C 68.55, H 3.99, N 6.19, S 13.98.

*N-Formyl-5H-dibenz[b,f]azepine (**1p**)*

From 5*H*-dibenz[b,f]azepine; m. p. 128 °C; (ref. [36]: m. p. 135 – 136 °C. – ^{1}H NMR ($CDCl_3$): δ = 6.86 (dd, *J* = 11.7 Hz, 14,6 Hz, 2 arom. H), 7.26 – 7.28 (m, 1 arom. H), 7.33 – 7.42 (m, 5 arom. H), 7.43 – 7.46 (m, 2 arom. H), 8.31 (s, 1H, CH=O). – $C_{15}H_{11}NO$ (221.3): calcd. C 81.43, H 5.01, N 6.33; found C 80.26, H 4.97, N 6.24.

*N-Formyl-10,11-dihydro-5H-dibenz[b,f]azepine (**1q**)*

From 10,11-dihydro-5*H*-dibenz[b,f]azepine; m. p. 118 °C; (ref. [35]: m. p. 137 °C). – ^{1}H NMR ($CDCl_3$): δ = 2.84 – 2.95 (m, 2H, CH_2), 3.39 – 3.45 (m, 2H, CH_2), 7.19 – 7.28 (m, 7 arom. H), 7.35 (d, *J* = 3.2 Hz, 1 arom. H), 8.58 (s, 1H, CH=O). – $C_{15}H_{13}NO$ (223.3): calcd. C 80.69, H 5.87, N 6.27; found C 80.58, H 5.97, N 6.25.

*N-Formyl-carbazole (**1r**)*

From carbazole; m. p. 98 – 100 °C; (ref. [37]: m. p. 94 °C). – ^{1}H NMR ($CDCl_3$): δ = 7.40 – 7.43 (m, 2 arom. H), 7.47 – 7.5 (m, 2 arom H), 7.71 (d, *J* = 6.5 Hz, 1 arom. H), 7.97 (s, br, 2 arom. H), 8.57 (d, *J* = 6.5 Hz, 1 arom. H), 9.68 (s, 1H, CH=O). – $C_{13}H_9NO$ (195.2): calcd. C 79.98, H 4.65, N 7.17; found C 80.33, H 4.90, N 7.32.

*N-Formyl-1,2,3,4-tetrahydrocarbazole (**1s**)*

From 1,2,3,4-tetrahydrocarbazole; m. p. 63 °C; (ref. [38]: m. p. 64 – 65 °C). – ^{1}H NMR ($CDCl_3$): δ = 1.30 (t, *J* = 5.4 Hz, 2H, CH2), 1.38 (s, 2H, CH2), 2.05 (q, 2H, CH2), 2.29 (s, 2H, CH2), 7.26 – 7.30 (m, 2 arom. H), 6.79 (q, 1 arom. H), 8.35 (d, *J* = 6.8 Hz, 1 arom. H), 9.11, 9.50 (ds, 1H, CH=O). – $C_{13}H_{131}NO$ (199.3): calcd. C 78.36, H 6.58, N 7.03; found C 79.12, H 7.14, N 7.15.

*Preparation of N-dichloromethyl-N,N-diarylamines **10** (General procedure)*

The *N*-dichloromethyl-*N,N*-diarylamines **10** were prepared by the addition of oxalyl dichloride or $POCl_3$ to a solution of the corresponding *N,N*-diarylformamide **1** in dichloromethane. After some standing at r. t. the mixture was transferred into an NMR tube, and the ^{1}H signals of the formed product were recorded. The following compounds were identified:

*N-Dichloromethyl-N,N-diphenylamine (**10c**)*

^{1}H NMR ($CDCl_3$): δ = 7.19 – 7.25 (m, 6 arom. H), 7.35 – 7.40 (m, 4 arom. H), 7.60 (s, 1H, $CHCl_2$).

*N-Dichloromethyl-N-(1-naphthyl)-N-phenylamine (**10g**)*

^{1}H NMR ($CDCl_3$): δ = 7.01 – 7.03 (m, 1 arom. H), 7.13 – 7.15 (m, 2 arom. H), 7.23 – 7.26 (m, 2 arom H), 7.50 – 7.55 (m, 4 arom. H), 7.57 (s, 1H, $CHCl_2$), 7.91 – 7.96 (m, 3 arom. H).

*N-Dichloromethyl-N-(4-methoxyphenyl)-N-(1-naphthyl)-amine (**10h**)*

^{1}H NMR ($CDCl_3$): δ = 6.79 (d, *J* = 9.2 Hz, 2 arom. H), 7.20 (d, *J* = 9.2 Hz, 2 arom. H), 7.49 – 7.53 (m, 2 arom. H), 7.62 (dd, *J* = 1.2, 7.3 Hz, 1 arom H), 7.65 (s, 1H, $CHCl_2$), 7.87 – 7.91 (m, 2 arom. H), 7.96 – 7.98 (m, 1 arom. H).

*N-Dichloromethyl-N-(2-naphthyl)-N-phenylamine (**10i**)*

^{1}H NMR ($CDCl_3$): δ = 7.22 – 7.25 (m, 2 arom. H), 7,27 – 7.7.29 (m, 2 arom. H), 7.38 – 7.40 (m, 2 arom. H), 7.46 – 7.50 (m, 2 arom. H), 7.71 (s, 1H, $CHCl_2$), 7.78 – 7.85 (m, 4 arom. H).

*N-Dichloromethyl-N-(4-methoxyphenyl)-N-(2-naphthyl)-amine (**10j**)*

^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 3H, OCH_3), 6.95 (dd, *J* = 6.7 Hz, 2 arom. H), 7.12 (dd, *J* = 2.4 Hz, 1 arom H), 7.71 (dd, *J* = 6.7 Hz, 2 arom. H), 7.83 – 7.7.41 (m, 1 arom. H), 7.44 – 7.48 (m, 1 arom. H), 7.63 (d, *J* = 2.3 Hz, 1 arom. H), 7.70 (d, *J* = 8.8 Hz, 1 arom. H), 7.71 (s, 1H, $CHCl_2$), 7.75 – 7.78 (m, 2 arom. H).

*Dichloromethyl-di-(1-naphthyl)amine (**10k**)*

^{1}H NMR ($CDCl_3$): δ = 7.43 – 7.49 (m, 7 arom. H), 7.76 (d, *J* = 8.2 Hz, 4 arom. H), 7.84 (s, 1H, $CHCl_2$), 7.85 – 7.92

(m, 1 arom. H), 7.94 – 7. 96 (m, 1 arom.), 8.10 – 8.13 (m, 1 arom. H).

*Dichloromethyl-(1-naphthyl)-(2-naphthyl)amine (**10l**)*

^{1}H NMR ($CDCl_3$): δ = 7.11 (dd, *J* = 2.4, 9.2 Hz, 1 arom. H), 7.33 – 7.36 (m, 1 arom. H), 7.40 – 7.43 (m, 1 arom. H), 7.48 – 7.57 (m, 3 arom. H), 7.63 – 7.65 (m, 2 arom. H), 7.66 (s, 1H, $CHCl_2$), 7.70 – 7.7.75 (m. 3 arom. H), 7.93 (d, *J* = 8.2 Hz, 1 arom. H), 8.00 (d, *J* = 7.6 Hz, 1 arom. H).

*Dichloromethyl-di-(2-naphthyl)amine (**10m**)*

^{1}H NMR ($CDCl_3$): δ = 7.28 (dd, *J* = 2.4, 8.5 Hz, 2 arom. H), 7.45 – 7. 50 (m, 4 arom. H), 7.89 – 7.82 (m, 8 arom. H), 7.81 (s, 1H, $CHCl_2$).

*N-Dichloromethyl-9H-acridane (**10n**)*

^{1}H NMR ($CDCl_3$): δ = 3.80 (s, 2H, CH_2), 7.09 – 7.12 (m, 2 arom. H), 7.22 (dd, *J* = 0.9, 7.4 Hz, 2 arom. H), 7.27 – 7.30 (m, 2 arom. H), 7.64 (d, *J* = 8.1 Hz, 2 arom. H), 7.72 (s, 1H, $CHCl_2$).

*N-Dichloromethyl-10H-phenothiazine (**10o**)*

^{1}H NMR ($CDCl_3$): δ = 7.13 (dt, 7.6, Hz, 1.2 Hz, 2 arom. H), 7.25 – 7. 31 (m, 4 arom. H), 7.54 (s, 1H, $CHCl_2$), 7.75 (dd, *J* = 8.2 Hz, 1.1 Hz, 2 arom. H).

*5-Dichloromethyl-5H-dibenzo[b,f]azepine (**10p**)*

^{1}H NMR ($CDCl_3$): δ = 6.78 (s, 2 arom. H), 7.23 – 7.27 (m, 4 arom. H), 7.25 (s, 1H, $CHCl_2$), 7.40 – 7.42 (m, 2 arom. H), 7.90 (dd, *J* = 7.9 Hz, 0.8 Hz, 2 arom. H).

*5-Dichloromethyl-10,11-dihydro-5H-dibenzo[b,f]azepine (**10q**)*

^{1}H NMR ($CDCl_3$): δ = 2.80 (s, br, 2H, CH_2), 3.38 (s, br, 2H, CH_2), 7.16 – 7.18 (m, 4 arom. H), 7.23 – 7.27 (m, 2 arom. H), 7.57 (s, 1H, $CHCl_2$), 7.86 (d, *J* = 7.8 Hz, 2 arom. H).

*N-Dichloromethyl-1,2,3,4-tetrahydrocarbazole (**10s**)*

^{1}H NMR ($CDCl_3$): δ = 1.88 – 1.90 (m, 2H, CH_2), 1.98 – 2.02 (m, 2H, CH_2), 2.68 – 2.71 (m, 2H, CH_2), 7.22 – 7.25 (m, 1 arom. H), 7.47 (d, *J* = 7.7 Hz, 1 arom. H), 7.81 (s, 1H, $CHCl_2$), 7.84 (s, br, 1 arom. H).

*Preparation of N,N'-tetraphenyl-formamidinium tetrafluoroborate (**13**)*

To a solution of *N*,*N*-diphenylformamide (**1c**, 2.0 g, 0.01 mol) in dichloromethane (25 mL) oxalyl chloride (2.5 g, 0.02 mol) was added under cooling. The resulting mixture was concentrated *in vacuo* after 30 min and mixed with a solution of diphenylamine (**11**, 1.7 g, 0.01 mol) in methanol (25 mL). By addition of aqueous HBF_4 the formamidinium salt **13** precipitated and was isolated by filtration in a yield of 2.0 g (45 %), m. p. 296 °C. – ^{1}H NMR ([D_6]DMSO): δ = 7.15 – 7.18 (m, 5 arom. H), 7.19 – 7.22 (m, 5 arom. H), 7.49 – 7.52 (m. 10 arom. H), 9.14 (s, 1H, N=CH–N). – $C_{25}H_{21}BF_4N_2$ (436.3): calcd. C 68.83, H 4.85, N 6.42; found C 67.88, H 4.83, N 6.38.

*Preparation of 4-dimethylamino-benzaldehyde (**15**)*

To a solution of N,N-diphenylformamide (**1c**, 2.0 g, 0.01 mol) in dichloromethane (25 mL) oxalyl chloride (2.5 g, 0.02 mol) was added under cooling. The resulting mixture was concentrated in vacuo after 30 min and mixed with N,N-dimethylaniline (**12**, 2.5 g, 0.02 mol). The mixture was heated at 50 °C for 1 h, then poured into water, extracted with dichloromethane (100 mL) and dried with magnesium sulfate. The filtered solution was concentrated and the deeply colored residue purified by column chromatography on silica using toluene as eluent to yield 4-(dimethylamino)benzaldehyde in an amount of 0.8 g (53 %), m. p. 73 °C. – ^{1}H NMR ($CDCl_3$): δ = 3.00 (s, 6H, NCH_3), 6.65 (d, J = 9.0 Hz, 2 arom. H), 7.69 (d, J = 9.0 Hz, 2 arom. H), 9.70 (s, 1H, CH=O).

[1] G. Jones, S. P. Stanforth, *Org. React.,* Vol. 49; John Wiley & Sons, London, **1997**, pp. 1 – 330.

[2] A. Vilsmeier, A. Haak, *Ber. Dtsch. Chem. Ges*. **1927**, *60*, 119.

[3] a) H. H. Bosshard, R. Mory, H. Schmid, H. Zollinger, *Helv. Chim. Acta* **1959**, *42*, 1653 – 1658; b) H. H. Bosshard, H. Zollinger, *Helv. Chim. Acta* **1959**, *42*, 1659 – 1671.

[4] W. Kantlehner in *Comprehensive Organic Synthesis,* Vol. 6 (Eds.: B. Trost, M. Fleming), Pergamon Press, Oxford, **1991**, chapter 2.7, pp. 485 – 599.

[5] S. Enthaler, K. Schröder, S. Inoue, B. Eckhardt, K. Junge, M. Beller, M. Drieß, *Eur. J. Org. Chem*. **2010**, 4893 – 4901.

[6] R. Imhof, D. W. Ladner, J. M. Muchowski, *J. Org. Chem.* **1977**, *42*, 3709 – 3713.

[7] B. Baesner, G.-M. Petruck, H. Hagemann, E. Klauke, DE 3044216, **1982**.

[8] H. Böhme, P. Sutoyo, *Tetrahedron Lett.* **1981**, *22*, 1671 – 1674.

[9] M. L. Martin, G. Ricolleau, S. Poignant, G. J. Martin, *J. Chem. Soc., Perkin Trans. 2* **1976**, 182 – 186.

[10] C. Rabiller, J. P. Renou, G. J. Martin, *J. Chem. Soc., Perkin Trans. 1* **1977**, 536 – 541.

[11] H. Mayr, A. R. Ofial, E.-U. Würthwein, N. C. Aust, *J. Am. Chem. Soc.* **1997**, *119*, 12727 – 12733.
[12] W. Walter, R. F. Becker, *Tetrahedron* **1972**, *28*, 1705 – 1720.
[13] J. Oszczapowicz, M. Kuminska, *J. Chem. Soc., Perkin Trans. 2* **1994**, 103 – 107.
[14] A. Hamed, E. Müller, J. C. Jochims, *Tetrahedron* **1986**, *42*, 6645 – 6656.
[15] U. Pathak, L. K. Pandey, R. Tank, *J. Org. Chem.* **2008**, *73*, 2890 – 2893.
[16] F. Shibahara, R. Sugiura, T. Murai, *Org. Lett.* **2009**, *11*, 3064 – 3067.
[17] G. M. Li, R. A. Zingano, *J. Chem. Soc., Perkin Trans. 1* **1998**, 647 – 649.
[18] L. Henriksen, *Synthesis* **1974**, 501 – 502.
[19] J. Bethka, K. Karaghiosoff, L. A. Wessjohann, *Tetrahedron Lett.* **2003**, *44*, 6911 – 6913.
[20] R. N. Loeppky, H. Yu, *J. Org. Chem.* **2004**, *69*, 3015 – 3024.
[21] G. Bencivenni, T. Lanza, R. Leardini, M. Minozzi, D. Nanni, P. Spagnolo, G. Zanardi, *J. Org. Chem.* **2008**, *73*, 4721 – 4724.
[22] M. Segi, A. Kojima, T. Nakajima, S. Suga, *Synlett* **1981**, 105 – 106.
[23] M. Hosseini-Sarvari, H. Sharghi, *J. Org. Chem.* **2006**, *71*, 6652 – 6654.
[24] M. Rahman, D. Kundu, A. Hajra, A. Majee, *Tetrahedron Lett.* **2010**, *51*, 2896 – 2899.
[25] R. J. Abraham, J. J. Bryne, L. Griffiths, M. Perez, *Magn. Res. Chem*. **2006**, *44*, 491 – 509.
[26] G. Gattow, R. Engler, *Angew. Chem.* **1971**, *83*, 444 – 445; *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 415 – 416.
[27] T. Gandhi, M. Nethaji, B. R. Jagirdar, *Inorg. Chem.* **2003**, *42*, 4798 – 4800.
[28] C. J. Borths, J. Chan, B. J. Burke, R. D. Larsen, *Synlett* **2009**, *19*, 3139 – 3142.
[29] A. Bagno, W. Kantlehner, G. Saielli, *J. Phys. Org. Chem.* **2008**, *21*, 682 – 687.
[30] H. Gross, D. Habisch, E. Gründemann, *J. Prakt. Chem.* **1968**, *38*, 190 – 198.
[31] J. C. Dyer, S. A. Evans, Jr., *J. Org. Chem,* **1980**, *45*, 5350 – 5355.
[32] J. Leis, K. D. Klika, M. Karelson, *Tetrahedron* **1998**, *54*, 7497 – 7504.
[33] G. Olah, S. Kuhn, *Chem. Ber.* **1956**, *89*, 2211 – 2212.
[34] K. Brewster, R. A. Chitten, J. M. Harrison, T. D. Indi, C. Brown, *J. Chem. Soc., Perkin Trans. 1* **1976**, 1291 – 1296.
[35] U. Pindur, H. Witzel, *Archiv Pharm.* **1990**, *323*, 439 – 442.
[36] J. Querner, Dissertation, TU Dresden, Dresden, **2004**.
[37] a) H. Witzel, U. Pindur, *J. Heterocycl. Chem.* **1988**, *25*, 907 – 910; b) C. Flo, U. Pindur, *Liebigs Ann. Chem.* **1987**, 509 – 513.
[38] Y. Marakami, H. Ishii, *Chem. Pharm. Bull.* **1981**, *29*, 699 – 703.
[39] E. Knoevenagel, *J. Prakt. Chem.* **1914**, *89*, 1 – 50.
[40] K. Griesbaum, G. Zwick, *Chem. Ber.* **1986**, *119*, 229 – 243.
[41] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512 – 7515.