A Simple Route to New *N*(3)-Substituted 5-Aryl-2-(dialkylamino)-1,3-oxazolium Salts and *N*(1)-Substituted 4-Aryl-2-(dialkylamino)-1*H*-imidazoles

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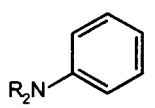
Dedicated to Prof. Dr. *S. Daehne* on the occasion of his 70th birthday

In the reaction of *N,N*-dialkyl-dichloromethaniminium chlorides **11** with 2-aminoacetophenones **12**, a general and simple route to heretofore unknown 5-aryl-substituted 2-(dialkylamino)-1,3-oxazolium salts **13** and 5-aryl-substituted 2-(dialkylamino)oxazoles **14** was found. From the 2-(dialkylamino)-1,3-oxazoles **14**, the corresponding oxazolium salts **13** were obtained after alkylation with $(MeO)_2SO_2$. The new oxazolium salts **13** were converted to 1-substituted 4-aryl-2-(dialkylamino)-1*H*-imidazoles **9** by treatment with NH_4OAc. The possible use of these 1*H*-imidazoles as dye educts was explored. Analytical data, as well as AM1 calculations, reveal some remarkable differences between the structures of the neutral imidazoles **9** and their positively charged oxazolium precursors **13**.

Introduction. – *N,N*-Dialkylanilines **1** are versatile starting materials for the preparation of organic dyes [1]. Due to the high reactivity at C(4), they are able to react with various types of electrophilic reagents, *e.g.*, with aromatic diazonium salts [2], squaric acid [3] or other reactive carbonyl derivatives [4], to give products that are important as dyestuffs or their intermediates [5]. The iso-electronic structure of the five-membered 2-(dialkylamino)-substituted heterocycles **2**–**6** to *N,N*-dialkylanilines led to an increasing interest in these compounds for the same or similar fields of application. For instance, *N,N*-disubstituted 2-aminothiophenes **2** [6], 2-aminoselenophenes **3** [7], 2-aminothiazoles **4** [8], and 2-aminoselenazoles **5** [9] were successfully transformed into different types of organic dyes by the reaction with appropriate dye-forming reagents at C(5) [10]. Some of these dyes exhibit unconventional properties, *e.g.*, interesting for NLO applications [11].



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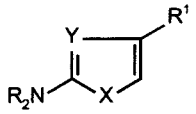

2-6

	2	3	4	5	6
X	S	Se	S	Se	NR^2
Y	CH	CH	N	N	N

Although *N,N*-disubstituted 2-aminoimidazoles **6** are also structurally analogous to *N,N*-dialkylanilines, only little is known about their chemistry [12] and ability to form organic dyes [13][14]. Because of their biological activity, they have attracted more attention for pharmaceutical purposes [15].

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Currently, the mostly applied synthetic route to five-membered 2-amino heterocycles is the well-known *Hantzsch* reaction of a halogenomethyl ketone with amides or urea derivatives [7][16–19]. However, while the unsubstituted 2-aminoimidazole **6** ($R_2N = H_2N$, $R^1 = R^2 = H$) was not isolable in this way when simple guanidine was used as starting material [20], 1,2-diaminoimidazoles **6** were obtained from *N*-anilinoguanidines [13][21] or guanylhydrazones [22]. Other synthetic pathways leading to **6**, *e.g.*, the reaction of isothioureas with aminoacetaldehyde diethyl acetal [15] and of 3-(pyrimidin-2-yl)oxazolin-2-imines with secondary amines [23], or the ring transformation of 2-amino-3-phenacyl-1,3,4-oxadiazolium salts [14], are of special synthetic value and have no claim to generality.

A simple and common access to electron-rich 2-(dialkylamino)-1*H*-imidazoles **6**, which could be transformed into different types of organic dyes, seemed, therefore, to be non-trivial. We report here on a new and comfortable two-step route to 1,4-disubstituted 2-(dialkylamino)-1*H*-imidazoles.

Results and Discussion – Attempts to prepare *N*(1)-substituted 2-(dialkylamino)-1*H*-imidazoles **9** by a *Hantzsch*-type synthesis, as depicted in *Scheme 1*, were not successful. Even applying a wide variation of reaction conditions, the reaction of *N,N*-dialkyl-*N*′-arylguanidines **7** ($R^1 = Ph$) [24] with phenacyl bromide **8** gave 2-(dialkylamino)-1,4-diphenyl-1*H*-imidazoles **9** ($R^1 = Ph$) in only low yields (*Table 1*, *Method A*). Instead of the also possible *N,N*-disubstituted 2-amino-1,5-diphenyl-1*H*-imidazoles **10**, resulting from an inverse attack of **8** at **7**, the starting guanidines **7** were mainly recovered as hydrobromides. Hence, the *N,N*-dialkyl-*N*′-arylguanidines act here as *Brønsted* bases decomposing the phenacyl bromide under the applied reaction conditions [21].

Since the known synthetic methods for 1-substituted 2-aminoimidazoles were, obviously, somehow restricted, we tried to find a new route to 2-(dialkylamino)-1*H*-imidazoles **9**. Encouraged by the successful transformation of 2-(dialkylamino)-1,3-oxathiolium salts into corresponding thiazoles by ammonia [25], we envisaged the extension of this technique to appropriate 1,3-oxazolium salts. Although such a

Scheme 1

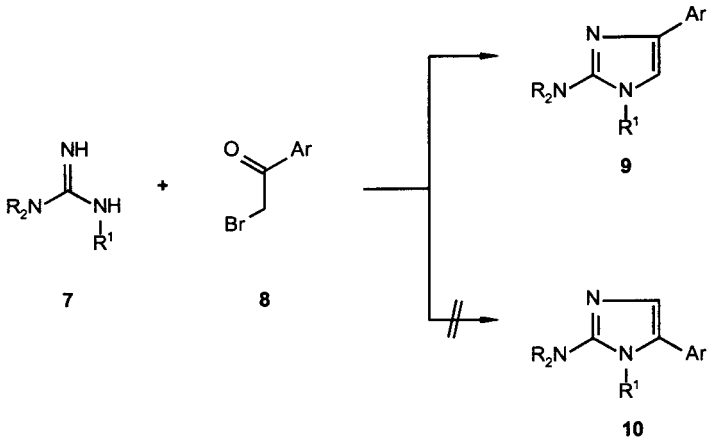


Table 1. *4-Aryl-2-(dialkylamino)-1*H*-imidazoles* ***9*** *and Their Hydrogenperchlorates* **9 • HClO$_4$**

No.	R_2N	R^1	Ar	Yield [%] [a])	M.p. [°]
9a	Me_2N	4-Cl–C_6H_4	4-Cl–C_6H_4	69 (11)	137–138
9b	Et_2N	4-Cl–C_6H_4	4-Cl–C_6H_4	98 (6)	70–71
9c	Pyrrolidin-1-yl	4-Cl–C_6H_4	4-Cl–C_6H_4	93 (7)	146–147
9d	Morpholino	4-Cl–C_6H_4	4-Cl–C_6H_4	95 (16)	146–147
9e • HClO$_4$	Me_2N	Ph	Ph	77	185–188
9f	Me_2N	4-Me–C_6H_4	Ph	83	102–104
9g	Me_2N	4-Cl–C_6H_4	Ph	94	95–98
9h • HClO$_4$	Me_2N	Ph	4-Me–C_6H_4	73	180–184
9i • HClO$_4$	Me_2N	4-Me–C_6H_4	4-Me–C_6H_4	82	182–184
9j	Me_2N	4-Me–C_6H_4	4-Cl–C_6H_4	84	106–108
9k	Me_2N	4-MeO–C_6H_4	4-Cl–C_6H_4	63	105–106
9l • HClO$_4$	Et_2N	4-Me–C_6H_4	Ph	75	185–186
9m	Pyrrolidin-1-yl	4-Me–C_6H_4	Ph	89	97–99
9n	Pyrrolidin-1-yl	4-Cl–C_6H_4	Ph	95	108–110
9o	Pyrrolidin-1-yl	4-Me–C_6H_4	4-Cl–C_6H_4	83	102–103
9p	Pyrrolidin-1-yl	4-MeO–C_6H_4	4-Cl–C_6H_4	92	97–99
9q	Piperidino	4-Cl–C_6H_4	Ph	99	134–136
9r	Piperidino	4-MeO–C_6H_4	4-Cl–C_6H_4	94	110–111
9s	Morpholino	4-Cl–C_6H_4	Ph	87	128–130
9t	Morpholino	4-MeO–C_6H_4	4-Cl–C_6H_4	91	137–138
9u • HClO$_4$	Me_2N	–	Ph	35	215–217
9v • HClO$_4$	Me_2N	–	4-Me–C_6H_4	55	155–157
9w	Me_2N	–	4-Cl–C_6H_4	47	60–62

[a]) By the method depicted in Scheme 3; values in parentheses refer to the *Hantzsch* method shown in *Scheme 1*.

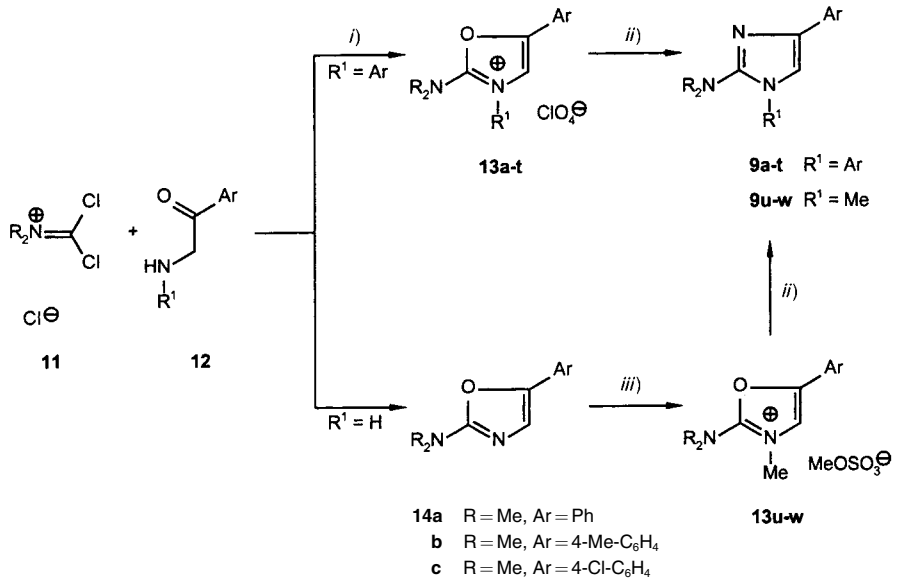
conversion is a well-known method for preparing imidazoles from 2-alkyl- or 2-aryloxazolium salts [26][27], it was hitherto not used for the synthesis of 2-amino-substituted derivatives. The reason for this is that the necessary *N*(3)-substituted 2-(dialkylamino)-1,3-oxazolium salts are essentially unknown.

1,3-Oxazolium salts are usually prepared by the alkylation of oxazoles [27][28], which are in turn available from the reaction of urea derivatives with halogenomethyl ketones [19][27], or of aminomethyl ketones with carbonic-acid derivatives [26]. Unfortunately, these methods could not be applied here, since the resulting oxazolium salts do not have the desired substitution pattern to form 2-(dialkylamino)-1*H*-imidazoles **9** by a simple O/N exchange reaction.

We found that the easily available and relatively stable 2-amino-1-arylethanones **12** or their hydrobromides **12 • HBr** [29] react with *N,N*-dialkyl-dichloromethaniminium chlorides **11** [30] to give 2-(dialkylamino)-1,3-oxazole derivatives under mild conditions in good yields. This cyclization was performed by heating a 2-amino-1-arylethanone **12** or its hydrobromide **12 • HBr** with a slight excess of **11** in dry MeCN until the evolution of HCl ceased. Depending on the substituent R^1 of **12**, 2-(dialkylamino)-substituted 5-aryl-1,3-oxazolium salts **13** or 5-aryl-1,3-oxazoles **14** were isolated (*Scheme 2*).

When 2-(arylamino)ethanones **12** (R^1 = Ph) were used in this reaction, 2-(dialkylamino)-3,5-diaryl-1,3-oxazolium perchlorates **13a**–**13t** precipitated directly from the reaction mixture after addition of equimolar amounts of $HClO_4$. In the case of 5-aryl-2-

Scheme 2



i) $HClO_4$. *ii*) NH_4OAc. *iii*) $(MeO)_2SO_2$

(dialkylamino)-1,3-oxazoles **14** prepared from *N*-unsubstituted 2-amino-1-arylethanone hydrobromides **12**•**HBr** ($R^1 = H$), the products were obtained from the reaction mixture after extraction with Et_2O as greasy crystals. These oxazoles **14** were converted to 5-aryl-3-methyl-1,3-oxazolium methyl sulfates **13u**–**13w** by subsequent alkylation with $(MeO)_2SO_2$. The *N*(3)-substituted 5-aryl-2-(dialkylamino)-1,3-oxazolium salts **13** listed in *Table 2* are crystalline compounds, which are sufficiently stable at moisture-free air.

The 2-(dialkylamino)-1,3-oxazolium salts **13** were converted to corresponding 2-(dialkylamino)-1*H*-imidazoles **9** by heating with NH_4OAc in EtOH (*Scheme 3*). Depending on their substitution pattern, the imidazoles **9** were separated as crystals or as oily layers after addition of H_2O to the reaction mixture. The oily products were transformed into non-hygroscopic hydrogenperchlorates **9**•**HClO$_4$** by addition of $HClO_4$. The 5-aryl-2-(dialkylamino)-1*H*-imidazoles **9**, as well as their hydrogenperchlorate salts **9**•**HClO$_4$**, are listed in *Table 1*.

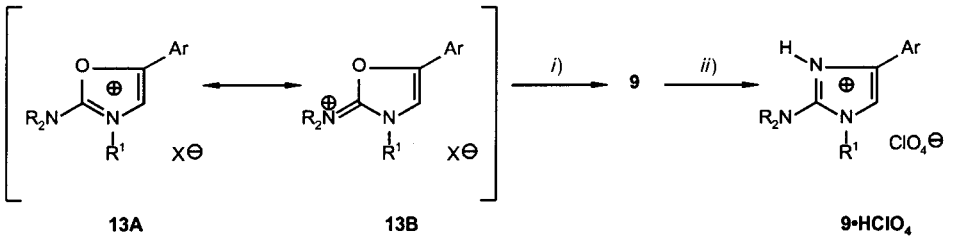
The new heterocyclic compounds **13**, **14**, and **9**, as well as their salts, were characterized by elemental analyses, IR and NMR measurements. *Tables 3* and *4* in *Exper. Part* summarize these data, which confirm the proposed structures. Some remarkable properties of the oxazolium salts **13** and the corresponding imidazoles **9** should be mentioned.

The IR spectra of the 2-(dialkylamino)-substituted 5-aryl-1,3-oxazolium salts **13** show typically an intense absorption at *ca.* 1690 cm^{-1}, accompanied by a somewhat weaker band at *ca.* 1650 cm^{-1}. Both absorptions were assigned to bond-stretching modes of the localized double bonds in the (dialkylamino)-1,3-oxazolium moiety and refer to the resonance structure **13B** (*cf. Scheme 3*). An additional very strong band at *ca.* 1100 cm^{-1} occurs only in the perchlorates **13a**–**13t** and originates from the ClO_4^-

Table 2. *5-Aryl-2-(dialkylamino)-1,3-oxazolium Salts* **13**

No.	R_2N	R^1	Ar	X^-	Yield [%]	M.p. [°]
13a	Me_2N	4-Cl–C_6H_4	4-Cl–C_6H_4	ClO_4^-	80	300–302
13b	Et_2N	4-Cl–C_6H_4	4-Cl–C_6H_4	ClO_4^-	72	267–269
13c	Pyrrolidin-1-yl	4-Cl–C_6H_4	4-Cl–C_6H_4	ClO_4^-	74	280–281
13d	Morpholino	4-Cl–C_6H_4	4-Cl–C_6H_4	ClO_4^-	50	307–309
13e	Me_2N	Ph	Ph	ClO_4^-	88	230–231
13f	Me_2N	4-Me–C_6H_4	Ph	ClO_4^-	72	155–157
13g	Me_2N	4-Cl–C_6H_4	Ph	ClO_4^-	91	215–216
13h	Me_2N	Ph	4-Me–C_6H_4	ClO_4^-	84	229–231
13i	Me_2N	4-Me–C_6H_4	4-Me–C_6H_4	ClO_4^-	77	221–222
13j	Me_2N	4-Me–C_6H_4	4-Cl–C_6H_4	ClO_4^-	77	269–271
13k	Me_2N	4-MeO–C_6H_4	4-Cl–C_6H_4	ClO_4^-	74	239–241
13l	Et_2N	4-Me–C_6H_4	Ph	ClO_4^-	73	225–226
13m	Pyrrolidin-1-yl	4-Me–C_6H_4	Ph	ClO_4^-	77	228–229
13n	Pyrrolidin-1-yl	4-Cl–C_6H_4	Ph	ClO_4^-	65	257–259
13o	Pyrrolidin-1-yl	4-Me–C_6H_4	4-Cl–C_6H_4	ClO_4^-	80	254–256
13p	Pyrrolidin-1-yl	4-MeO–C_6H_4	4-Cl–C_6H_4	ClO_4^-	77	218–220
13q	Piperidino	4-Cl–C_6H_4	Ph	ClO_4^-	68	269–271
13r	Piperidino	4-MeO–C_6H_4	4-Cl–C_6H_4	ClO_4^-	72	205–207
13s	Morpholino	4-Cl–C_6H_4	Ph	ClO_4^-	65	278–280
13t	Morpholino	4-MeO–C_6H_4	4-Cl–C_6H_4	ClO_4^-	71	250–251
13u	Me_2N	–	Ph	$MeOSO_3^-$	68	178–180
13v	Me_2N	–	4-Me–C_6H_4	$MeOSO_3^-$	80	197–199
13w	Me_2N	–	4-Cl–C_6H_4	$MeOSO_3^-$	84	214–216

Scheme 3



i) NH_4OAc. *ii*) $HClO_4$

anion. In contrast, the most important IR absorptions of the imidazoles **9** are two groups of three sharp single bands between 1500 and 1600 cm^{-1}, as well as between 1400 and 1500 cm^{-1}. It is noteworthy that the IR spectra of the imidazole hydrogenperchlorates **9**•**HClO$_4$** and their corresponding oxazolium precursors **13** are very similar.

Characteristic in the ^{1}H-NMR spectra of the 2-(dialkylamino)-1,3-oxazolium salts **13** are sharp *singlets* at *ca.* 7.9–8.2 ppm, arising from the protons at C(5). Further signals at *ca.* 3.3 ppm, and between 7.0 and 7.8 ppm were attributed to the aminoalkyl and aryl moieties, respectively. The ^{1}H-NMR signals of H–C(5) in the 1*H*-imidazoles **9**, which were found at *ca.* 7.5 ppm, result from a higher shielding in the electron-rich imidazole compared to the oxazolium precursor. The proton signals of the dialkylamino groups in **9** appear between 2.5 and 3.1 ppm, depending on their type, and they are slightly shifted to lower fields in the case of the hydrogenperchlorates **9**•**HClO$_4$**.

The mass spectra of the 1,4-diaryl-2-(dialkylamino)-1*H*-imidazoles **9** are dominated by their molecular-ion peaks. In contrast to the HCN extrusion typical for 2*H*-imidazoles [31], the corresponding fragmentation of dialkylcyanamides is less favored. Formation of ethynylbenzene was found to be the main fragmentation process, accompanied by dehydration of the aminoalkyl groups, or dealkylation in the cases of $NR_2 = NMe_2$.

To get a deeper insight into the electronic structures of the new 1,4-diaryl-2-(dialkylamino)-1*H*-imidazoles **9** and their oxazolium precursors **13**, quantum-chemical calculations using the AM1 hamiltonian [32] were performed. The results obtained for the 2-(dimethylamino)-3,5-diphenyl-1,3-oxazolium ion (**13e**) and the corresponding imidazole **9e** are shown in the Figure.

The results reveal significant differences between the optimized structures of these compounds caused by different charges on both molecules. For instance, the planarity of the amino-N-atom, as well as the calculated bond length between C(2) and the

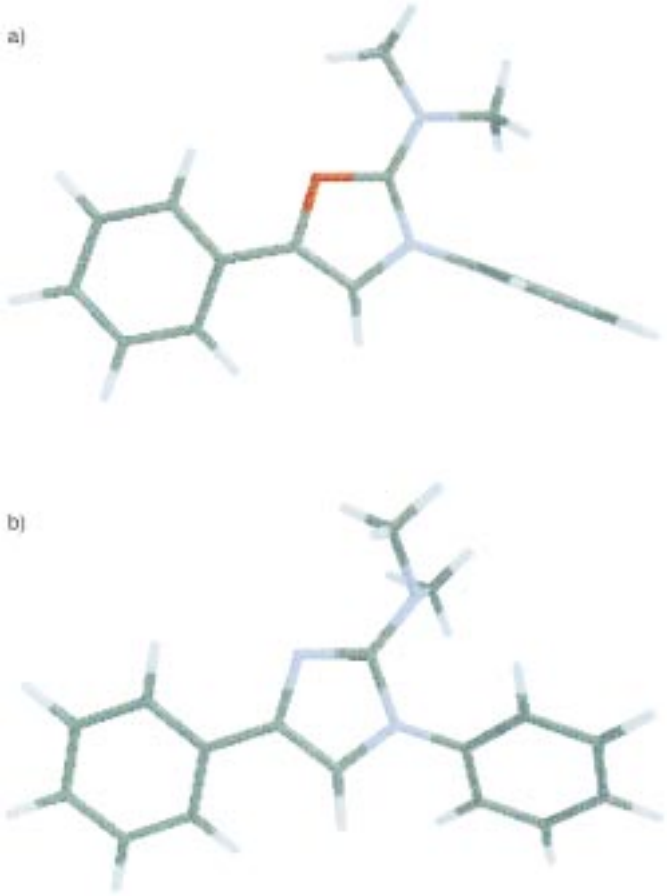


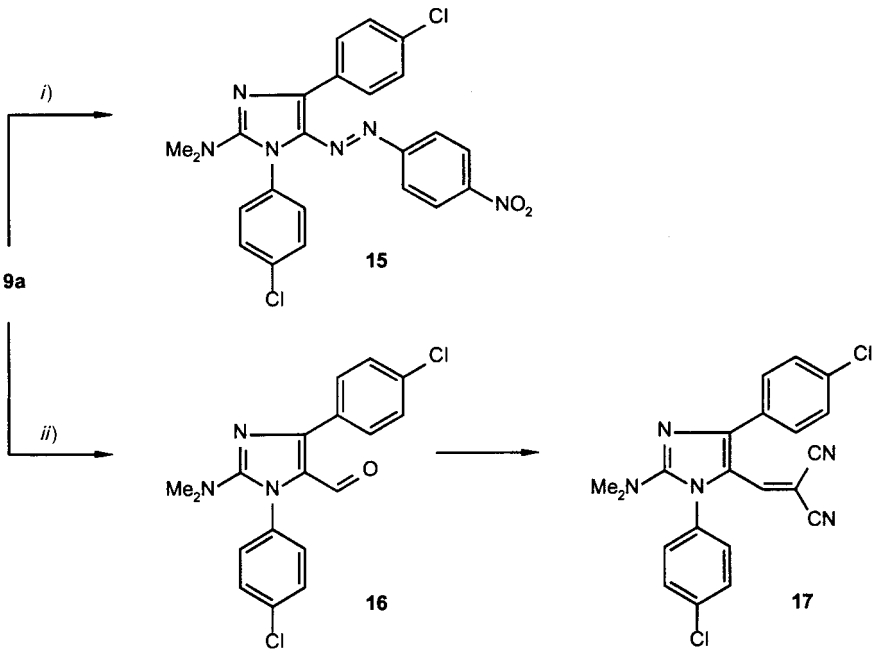
Fig. 1. *AM-1-Optimized geometry of* a) *the 2-(dimethylamino)-3,5-diphenyl-1,3-oxazolium salt* (**13e**) *and* b) *of the 2-(dimethylamino)-1,4-diphenyl-1*H-*imidazole* **9e**

amino-N-atom of only 135.1 pm in **13e**, indicate a strong involvement of the amino group in the stabilization of the positive charge. These facts also support the strong contribution of the resonance structure **13B** to the electronic ground state of the oxazolium salts **13**. Consequently, the exocyclic amino group forces the relatively weakly bonded Ph ring at *N*(3) to twist nearly perpendicular to the oxazolium plane. In the imidazole **9e**, the C–N bond length of 143.5 pm, as well as the torsion angle of *ca.* 81° between the amino-N lone pair and the imidazole plane, indicate a clearly weaker interaction. Again, the calculated structure of the imidazolium ion **9e**•**H**$^+$, which is not shown here, is very similar to that of the corresponding oxazolium ion **13e**.

Different molecular charges also influence the energies of the π-type frontier orbitals of the compounds **13e** and **9e**. The cationic charge and the electronegative O-atom lower the HOMO energy of the oxazolium salt **13e** ($E^{HOMO} = -12.08$ eV) by *ca.* 3.7 eV compared to the neutral imidazole **9e** ($E^{HOMO} = -8.34$ eV). The LUMO energy of **13e** ($E^{LUMO} = -4.09$ eV) is also much lower than that of the imidazole **9e** ($E^{LUMO} = -0.20$ eV). Hence, a comparatively strong electrophilicity of **13e** and a high electron-donating ability of **9e** is expected.

It could be easily derived from the *Lewis* structure and the calculated electronic properties that the exocyclic dialkylamino group and the N(1)-atom enable the new (dialkylamino)-1*H*-imidazoles **9** to react in their 5-position with various electrophilic reagents. As shown in *Scheme 4*, the 2-(dimethylamino)-1*H*-imidazole **9a** reacts with the (4-nitrophenyl)diazonium hydrogen sulfate and the *Vilsmeier* reagent to give the

Scheme 4



i) 4-NO_2–$C_6H_4N_2^{\oplus}$. *ii*) $POCl_3$/DMF. *iii*) $H_2C(CN)_2$/NEt_3.

violet 5-arylazo dye **15** and the imidazole-carbaldehyde **16**, respectively. The dicarbonitrile **17** was prepared from **16** by condensation with malononitrile.

The preparation and characterization of dyes derived from the new 5-aryl-2-(dialkylamino)-1*H*-imidazoles **9**, as well as the corresponding carbaldehydes **16**, was extended and will be published in a forthcoming paper.

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Experimental Part

General. M.p.: *Boëtius* heating-table microscope; uncorrected. IR Spectra: in KBr pellets on a *Philips FT-IR* spectrometer *PU 9624*. NMR Spectra: *Varian* 300-MHz spectrometer *Gemini 300*; chemical shifts in ppm at the δ scale. The elemental analyses were performed on a *LECO* analyser *CHNS 932*.

3,5-Diaryl-2-(dialkylamino)-1,3-oxazolium Perchlorates **13a**–**13t** (*General Procedure*). A mixture of an *1-aryl-2-(arylamino)ethanone* **12** (0.01 mol) and a *N,N*-dialkyl-dichloromethaniminium chloride **11** (0.012 mol) in MeCN (50 ml) was heated for *ca.* 3 h until the evolution of HCl ceased. After addition of aq. $HClO_4$ (70%, 0.01 mol) to the cooled soln., the crystallization was initiated by addition of Et_2O. The precipitated oxazolium perchlorate was isolated by filtration, washed with AcOEt, and recrystallized from AcOH. M.p. and anal. data of **13a**–**13t** are given in *Tables 2–4*.

Table 3. *^{1}H- and ^{13}C-NMR Data of the 4-Aryl-2-(dialkylamino)-1*H*-imidazoles* **9**, *the Hydrogenperchlorates* **9**•**HClO$_4$**, *and the 5-Aryl-2-(dialkylamino)-1,3-oxazolium Salts* **13**

No.	δ(^{1}H)	δ(^{13}C)
9a	2.68 (*s*, 2 Me); 7.35 (*d*, 2 CH); 7.50 (*s*, 1 CH); 7.56 (*d*, 2 CH); 7.65 (*d*, 2 CH); 7.82 (*d*, 2 CH) [a])	42.9; 115.9; 127.2; 127.4; 129.9; 131.1; 132.7; 133.8; 135.2; 138.2; 138.8; 154.3 [a])
9b	0.97 (*t*, 2 Me); 3.02 (*q*, 2 CH_2); 7.32 (*d*, 2 CH); 7.49 (*d*, 2 CH); 7.53 (*s*, 1 CH); 7.60 (*d*, 2 CH); 7.80 (*d*, 2 CH) [a])	12.1; 45.8; 114.2; 125.9; 126.7; 128.4; 129.5; 131.2; 132.4; 133.8; 137.1; 151.1 [a])
9c	1.79 (*quint.*, 2 CH_2); 3.15 (*t*, 2 CH_2); 7.32 (*d*, 2 CH); 7.38 (*s*, 1 CH); 7.54 (*s*, 4 CH); 7.79 (*d*, 2 CH) [a])	25.8; 50.9; 114.8; 126.6; 127.5; 129.1; 130.2; 131.1; 131.8; 133.3; 134.7; 138.3; 150.9 [a])
9d	2.99 (*t*, 2 CH_2); 3.64 (*t*, 2 CH_2); 7.34 (*d*, 2 CH); 7.55 (*d*, 2 CH); 7.58 (*s*, 1 CH); 7.80 (*d*, 2 CH) [a])	50.9; 51.0; 66.7; 66.8; 115.4; 126.2; 126.7; 129.2; 130.4; 130.5; 132.1; 133.2; 134.2; 137.6; 152.0 [a])
9e•**HClO$_4$**	3.02 (*s*, 2 Me); 3.25 (*s*, 1 NH); 7.39 (*t*, 1 CH); 7.46 (*t*, 2 CH); 7.57 (*s*, 1 CH); 7.61 (*t*, 1 CH); 7.64 (*t*, 2 CH); 7.73 (*d*, 2 CH); 7.77 (*d*, 2 CH) [a])	41.1; 116.7; 126.1; 126.8; 127.7; 129.7; 129.8; 130.7; 130.8; 130.9; 136.8; 149.3 [a])
9f	2.35 (*s*, Me); 2.63 (*s*, 2 Me); 7.13 (*t*, 1 CH); 7.28 (*d*, 2 CH); 7.30 (*d*, 2 CH); 7.34 (*s*, 1 CH); 7.42 (*d*, 2 CH); 7.79 (*d*, 2 CH) [a])	21.0; 42.2; 114.9; 124.7; 125.1; 126.8; 129.0; 130.8; 135.8; 136.9; 137.8; 138.2; 150.5 [a])
9g	2.65 (*s*, 2 Me); 7.16 (*t*, 1 CH); 7.31 (*t*, 2 CH); 7.46 (*s*, 1 CH); 7.54 (*d*, 2 CH); 7.62 (*d*, 2 CH); 7.80 (*d*, 2 CH) [a])	42.2; 114.7; 125.1; 126.4; 127.0; 129.1; 130.4; 132.9; 135.5; 138.1; 138.6; 148.2 [a])
9h•**HClO$_4$**	2.34 (*s*, Me); 3.01 (*s*, 2 Me); 3.26 (*s*, NH); 7.28 (*d*, 2 CH); 7.50 (*s*, 1 CH); 7.55–7.72 (*m*, 7 CH) [a])	21.2; 41.2; 116.1; 125.0; 126.1; 126.6; 129.4; 130.1; 130.5; 131.0; 136.8; 139.8; 149.4 [a])
9i•**HClO$_4$**	2.32 (*s*, Me); 2.41 (*s*, Me); 3.01 (*s*, Me); 3.27 (*s*, NH); 7.26 (*d*, 2 CH); 7.43 (*d*, 2 CH); 7.46 (*s*, 1 CH); 7.59 (*d*, 2 CH); 7.64 (*d*, 2 CH) [a])	21.1; 21.2; 41.0; 116.2; 124.9; 126.0; 126.6; 128.7; 130.4; 131.3; 134.3; 139.7; 140.9; 149.1 [a])
9j	2.36 (*s*, Me); 2.63 (*s*, 2 Me); 7.31 (*d*, 2 CH); 7.32 (*d*, 2 CH); 7.42 (*s*, 1 CH); 7.44 (*d*, 2 CH); 7.79 (*d*, 2 CH) [a])	20.9; 42.1; 115.5; 124.8; 126.6; 129.1; 129.9; 130.8; 131.8; 134.5; 138.0; 138.1; 149.3 [a])
9k	2.64 (*s*, 2 Me); 3.83 (*s*, Me); 7.03 (*d*, 2 CH); 7.32 (*d*, 2 CH); 7.35 (*s*, 1 CH); 7.44 (*d*, 2 CH); 7.80 (*d*, 2 CH) [a])	41.6; 55.4; 114.9; 115.2; 126.1; 128.4; 131.2; 131.7; 134.2; 136.4; 153.2; 159.2; 162.1 [a])

Table 3 (cont.)

9l • HClO$_4$	1.02 (*t*, 2 Me); 2.39 (*s*, Me); 3.22 (*q*, 2 CH$_2$); 7.43 (*m*, 3 CH); 7.53 (*m*, 4 CH); 7.76 (*d*, 2 CH); 7.82 (*s*, 1 CH); 12.9 (*s*, NH) [b])	12.7; 20.9; 44.6; 117.0; 125.5; 125.8; 127.3; 128.0; 129.2; 130.7; 133.4; 140.0; 147.5 [b])
9m	1.72 (*quint.*, 2 CH$_2$); 2.32 (*s*, Me); 3.11 (*t*, 2 CH$_2$); 7.10 (*t*, 1 CH); 7.20 (*s*, 1 CH); 7.25 (*m*, 4 CH); 7.31 (*t*, 2 CH); 7.78 (*d*, 2 CH) [a])	21.0; 25.8; 50.8; 114.4; 125.1; 125.8; 126.6; 129.0; 130.6; 136.0; 137.1; 137.8; 138.2; 152.1 [a])
9n	1.76 (*quint.*, 2 CH$_2$); 3.14 (*t*, 2 CH$_2$); 7.13 (*s*, 1 CH); 7.29 (*t*, 1 CH); 7.30 (*s*, 1 CH); 7.50 (*s*, 4 CH); 7.78 (*d*, 2 CH) [a])	25.8; 50.9; 114.1; 125.1; 126.8; 127.3; 129.0; 130.1; 133.0; 135.7; 138.3; 138.6; 151.8 [a])
9o	1.75 (*quint.*, 2 CH$_2$); 2.35 (*s*, Me); 3.12 (*t*, 2 CH$_2$); 7.26–7.35 (*m*, 7 CH); 7.77 (*d*, 2 CH) [a])	21.0; 25.8; 50.7; 115.0; 125.8; 126.5; 129.0; 130.6; 131.5; 134.9; 136.9; 137.0; 130.0; 152.2 [a])
9p	1.75 (*quint.*, 2 CH$_2$); 3.13 (*t*, 2 CH$_2$); 3.83 (*s*, Me); 7.02 (*d*, 2 CH); 7.24 (*s*, 1 CH); 7.30 (*d*, 2 CH); 7.37 (*d*, 2 CH); 7.70 (*d*, 2 CH) [a])	25.8; 50.6; 55.8; 115.2; 126.5; 127.6; 128.0; 131.4; 132.3; 134.9; 136.8; 152.4; 159.8; 162.0 [a])
9q	1.51 (*quint.*, 3 CH$_2$); 2.97 (*t*, 2 CH$_2$); 7.16 (*t*, 1 CH); 7.30 (*t*, 2 CH); 7.48 (*s*, 1 CH); 7.53 (*d*, 2 CH); 7.70 (*d*, 2 CH); 7.79 (*d*, 2 CH) [a])	24.8; 26.1; 51.8; 114.4;125.2; 125.9; 127.0; 129.1; 130.3; 132.8; 135.6; 138.1; 138.8; 152.9 [a])
9r	1.50 (*quint.*, 3 CH$_2$); 2.96 (*t*, 2 CH$_2$); 3.83 (*s*, Me); 7.04 (*d*, 2 CH); 7.32 (*d*, 2 CH); 7.43 (*s*, 1 CH); 7.53 (*d*, 2 CH); 7.80 (*d*, 2 CH) [a])	24.3; 25.7; 51.1; 55.4; 114.9; 125.4; 126.1; 128.6; 131.2; 131.7; 134.3; 136.6; 152.6; 159.1; 162.2 [a])
9s	2.98 (*t*, 2 CH$_2$); 3.62 (*t*, 2 CH$_2$); 7.16 (*t*, 1 CH); 7.31 (*t*, 2 CH); 7.48 (*s*, 1 CH); 7.52 (*d*, 2 CH); 7.68 (*d*, 2 CH); 7.79 (*d*, 2 CH) [a])	51.0; 66.7; 114.8; 125.2; 126.2; 127.1; 129.1; 130.4; 133.0; 135.3; 137.7; 138.9; 151.8 [a])
9t	2.97 (*t*, 2 CH$_2$); 3.60 (*t*, 2 CH$_2$); 3.82 (*s*, Me); 7.04 (*d*, 2 CH); 7.32 (*d*, 2 CH); 7.43 (*s*, 1 CH); 7.52 (*d*, 2 CH); 7.79 (*d*, 2 CH) [a])	50.8; 55.9; 66.8; 115.4; 115.8; 126.2; 126.6; 129.2; 129.9; 131.7; 131.8; 134.6; 137.2; 152.1 [a])
9u	3.12 (*s*, NH); 3.26 (*s*, Me); 3.83 (*s*, Me); 7.42 (*m*, 3 CH); 7.51 (*s*, 1 CH); 7.68 (*d*, 2 CH) [a])	35.7; 41.3; 117.1; 124.5; 125.9; 127.9; 129.6; 129.9; 150.6 [a])
9v • HClO$_4$	2.33 (*s*, Me); 3.10 (*s*, NH); 3.25 (*s*, 2 Me); 3.82 (*s*, Me); 7.46 (*s*, 1 CH); 7.26 (*d*, 2 CH); 7.57 (*d*, 2 CH) [a])	20.3; 34.9; 40.5; 124.2; 149.6; 115.7; 125.0; 127.6; 129.7; 138.8; 149.6 [a])
9w • HClO$_4$	3.06 (*s*, NH); 3.27 (*s*, 2 Me); 3.86 (*s*, Me); 7.48 (*d*, 2 CH); 7.57 (*s*, 1 CH); 7.71 (*d*, 2 CH) [a])	32.5; 43.0; 115.6; 126.2; 129.0; 131.2; 135.0; 136.4; 154.6 [a])
13a	3.05 (*s*, 2 Me); 7.63 (*d*, 2 CH); 7.77 (*m*, 6 CH); 8.34 (*s*, 1 CH) [b])	40.0; 118.1; 123.8; 125.4; 129.0; 129.6; 130.1; 135.9; 134.4; 135.6; 142.1; 154.0 [b])
13b	1.12 (*t*, 2 Me); 3.42 (*q*, 2 CH$_2$); 7.66 (*d*, 2 CH); 7.78 (*d*, 2 CH); 7.81 (*d*, 2 CH); 7.91 (*d*, 2 CH); 8.27 (*s*, 1 CH) [b])	12.3; 44.6; 118.4; 123.9; 125.4; 129.2; 129.6; 130.4; 133.1; 134.3; 136.0; 142.1; 153.5 [b])
13c	1.15 (*quint.*, 3 CH$_2$); 3.46 (*q*, 2 CH$_2$); 7.66 (*d*, 2 CH); 7.78 (*d*, 2 CH); 7.81 (*d*, 2 CH); 7.92 (*d*, 2 CH); 8.32 (*s*, 1 CH) [b])	25.0; 50.2; 117.6; 123.9; 125.4; 129.5; 129.6; 129.8; 132.0; 134.3; 135.7; 142.3; 152.0 [b])
13d	3.46 (*t*, 2 CH$_2$); 3.68 (*t*, 2 CH$_2$); 7.63 (*d*, 2 CH); 7.78 (*s*, 4 CH); 7.80 (*d*, 2 CH); 8.37 (*s*, 1 CH) [b])	47.2; 64.7; 117.9; 123.8; 125.6; 128.3; 129.6; 130.6; 132.8; 134.5; 135.7; 142.5; 153.2 [b])
13e	3.22 (*s*, 2 Me); 7.47–7.56 (*m*, 3 CH); 7.68 (*t*, 3 CH); 7.77 (*d*, 2 CH); 7.83–7.86 (*m*, 2 CH); 8.03 (*s*, 1 CH) [a])	39.8; 117.6; 123.7; 125.0; 127.2; 129.4; 129.8; 130.1; 130.9; 134.1; 143.0; 154.0 [b])
13f	2.40 (*s*, Me); 3.02 (*s*, 2 Me); 7.45 (*t*, 1 CH); 7.46 (*d*, 2 CH); 7.53 (*t*, 1 CH); 7.63 (*d*, 2 CH); 7.73 (*d*, 2 CH); 8.24 (*s*, 1 CH) [b])	20.8; 39.7; 117.6; 123.6; 125.0; 126.9; 129.4; 130.4; 131.6; 140.8; 142.9; 153.9 [b])
13g	3.26 (*s*, 2 Me); 7.48–7.56 (*m*, 3 CH); 7.73 (*d*, 2 CH); 7.76 (*d*, 2 CH); 7.90 (*d*, 2 CH); 8.06 (*s*, 1 CH) [a])	40.0; 117.4; 123.7; 125.0; 129.1; 129.5; 129.9; 130.2; 133.0; 135.6; 143.1; 154.0 [b])
13h	2.37 (*s*, Me); 3.22 (*s*, 2 Me); 7.35 (*d*, 2 CH); 7.64–7.70 (*m*, 5 CH); 7.84 (*d*, 2 CH); 7.96 (*s*, 1 CH) [a])	21.1; 39.8; 116.8; 122.3; 123.7; 127.2; 130.0; 130.1; 130.9; 134.2; 139.7; 143.4; 153.9 [b])

Table 3 (cont.)

13i	2.37 (*s*, Me); 2.42 (*s*, Me); 3.02 (*s*, 2 Me); 7.37 (*d*, 2 CH); 7.46 (*d*, 2 CH); 7.62 (*d*, 2 CH); 7.65 (*d*, 2 CH); 8.18 (*s*, 1 CH) [b])	20.7; 20.9; 39.7; 116.7; 122.1; 123.4; 126.7; 129.7; 130.2; 131.4; 139.4; 140.6; 143.0; 153.7 [b])
13j	2.44 (*s*, Me); 3.22 (*s*, 2 Me); 7.48 (*d*, 2 CH); 7.56 (*d*, 2 CH); 7.71 (*d*, 2 CH); 7.70 (*d*, 2 CH); 8.03 (*s*, 1 CH) [a])	20.9; 39.8; 118.3; 124.0; 125.4; 126.9; 129.6; 130.5; 131.6; 134.2; 141.0; 142.0; 154.0 [b])
13k	3.04 (*s*, 2 Me); 3.85 (*s*, Me); 7.18 (*d*, 2 CH); 7.63 (*d*, 2 CH); 7.69 (*d*, 2 CH); 7.78 (*d*, 2 CH); 8.28 (*s*, 1 CH) [b])	39.2; 55.7; 114.7; 118.4; 123.8; 125.2; 126.3; 128.5; 129.4; 134.0; 141.6; 153.9; 160.6 [b])
13l	1.12 (*t*, 2 Me); 2.42 (*s*, Me); 3.42 (*q*, CH_2); 7.47 (*m*, 3 CH); 7.55 (*t*, 2 CH); 7.72 (*m*, 4 CH); 8.23 (*s*, 1 CH) [b])	12.5; 21.0; 44.5; 118.1; 123.6; 125.2; 127.0; 129.5; 129.8; 130.7; 131.9; 141.3; 142.9; 153.5 [b])
13m	1.87 (*quint.*, 2 CH_2); 2.41 (*s*, Me); 3.39 (*t*, 2 CH_2); 7.43 (*d*, 2 CH); 7.45 (*t*, 1 CH); 7.54 (*t*, 2 CH); 7.63 (*d*, 2 CH); 7.72 (*d*, 2 CH); 8.30 (*d*, 2 CH) [b])	20.9; 25.0; 50.0; 117.2; 123.6; 125.2; 127.5; 129.4; 129.7; 130.1; 140.9; 143.2; 152.1; 172.0 [b])
13n	1.91 (*quint.*, 2 CH_2); 3.42 (*t*, 2 CH_2); 7.48 (*t*, 1 CH); 7.56 (*t*, 2 CH); 7.73 (*d*, 4 CH); 7.80 (*d*, 2 CH); 8.31 (*s*, 1 CH) [b])	24.8; 49.9; 116.8; 123.4; 124.8; 129.3; 129.4; 129.5; 129.6; 131.9; 135.4; 143.1; 151.8 [b])
13o	1.86 (*quint.*, 2 CH_2); 2.40 (*s*, Me); 3.35 (*t*, 2 CH_2); 7.43 (*d*, 2 CH); 7.61 (*d*, 2 CH); 7.62 (*d*, 2 CH); 7.74 (*d*, 2 CH); 8.32 (*s*, 1 CH) [b])	21.0; 25.0; 50.0; 117.9; 124.1; 125.3; 127.5; 129.6; 130.2; 130.7; 134.2; 141.0; 142.2; 152.1 [b])
13p	1.86 (*quint.*, 2 CH_2); 3.39 (*t*, 2 CH_2); 3.83 (*s*, Me); 7.15 (*d*, 2 CH); 7.61 (*d*, 2 CH); 7.67 (*d*, 2 CH); 7.73 (*d*, 2 CH); 8.28 (*s*, 1 CH) [b])	24.9; 49.9; 55.8; 115.0; 118.0; 124.1; 125.3; 125.6; 129.3; 129.6; 134.1; 142.0; 152.2; 160.8 [b])
13q	1.58 (*quint.*, 3 CH_2); 3.42 (*t*, 2 CH_2); 7.46 (*t*, 1 CH); 7.54 (*t*, 2 CH); 7.78 (*m*, 6 CH); 8.29 (*s*, 1 CH) [b])	22.4; 24.1; 48.2; 117.2; 123.7; 125.0; 128.2; 129.4; 129.9; 130.5; 133.4; 135.5; 143.2; 153.3 [b])
13r	1.56 (*quint.*, 3 CH_2); 3.43 (*t*, 2 CH_2); 3.83 (*s*, Me); 7.19 (*d*, 2 CH); 7.61 (*d*, 2 CH); 7.68 (*d*, 2 CH); 7.77 (*d*, 2 CH); 8.26 (*s*, 1 CH) [b])	22.5; 24.2; 48.0; 55.9; 115.5; 118.4; 124.1; 125.4; 127.0; 127.8; 129.6; 134.2; 141.7; 153.1; 160.7 [b])
13s	3.45 (*t*, 2 CH_2); 3.68 (*t*, 2 CH_2); 7.47 (*t*, 1 CH); 7.54 (*t*, 2 CH); 7.78 (*m*, 6 CH); 8.33 (*s*, 1 CH) [b])	47.1; 64.7; 117.2; 123.8; 124.8; 128.4; 129.5; 130.0; 130.6; 132.8; 135.6; 143.5; 153.2 [b])
13t	3.45 (*t*, 2 CH_2); 3.67 (*t*, 2 CH_2); 3.83 (*s*, Me); 7.19 (*d*, 2 CH); 7.62 (*d*, 2 CH); 7.67 (*d*, 2 CH); 7.79 (*d*, 2 CH); 8.30 (*s*, 1 CH) [b])	46.9; 55.9; 64.7; 115.6; 118.4; 124.0; 125.5; 126.4; 128.0; 129.6; 134.4; 142.2; 153.2; 160.8 [b])
13u	3.34 (*s*, 2 Me); 3.49 (*s*, Me); 3.74 (*s*, Me); 7.43 (*t*, 1 CH); 7.51 (*t*, 2 CH); 7.63 (*d*, 2 CH); 7.95 (*s*, 1 CH) [b])	35.9; 39.7; 117.6; 123.5; 125.1; 129.4; 129.6; 142.4; 155.6 [b])
13v	2.35 (*s*, Me); 3.34 (*s*, 2 Me); 3.38 (*s*, Me); 7.32 (*d*, 2 CH); 7.53 (*d*, 2 CH); 7.88 (*s*, 1 CH) [b])	21.0; 35.9; 39.7; 52.9; 116.9; 122.4; 123.7; 129.9; 139.5; 142.9; 155.6 [b])
13w	3.34 (*s*, 2 Me); 3.74 (*s*, Me); 7.58 (*d*, 2 CH); 7.66 (*d*, 2 CH); 7.99 (*s*, 1 CH) [b])	36.0; 39.7; 118.4; 124.3; 125.5; 129.7; 134.2; 141.6; 155.8 [b])

[a]) In (D_6)acetone. [b]) In (D_6)DMSO.

5-Aryl-2-(dimethylamino)-1,3-oxazoles **14**. To a suspension of an 2-amino-1-arylethanone hydrobromide **12**•**HBr** (R^1 = H, 0.01 mol) in MeCN (100 ml), dichloro-*N*,*N*-dimethylmethaniminium chloride **11** (R = Me, 2.0 g, 0.012 mol) was added, and the mixture was refluxed until the evolution of hydrochloride has ceased. The resulting suspension was poured onto ice (50 g) and neutralized with aq. NaOH. The oily layer was extracted with Et_2O (3 × 50 ml) and dried. After evaporation of Et_2O, the following oxazoles **14** were obtained as greasy crystals.

2-(Dimethylamino)-5-phenyl-1,3-oxazole (**14a**). Yield 89%. M.p. 52°. IR: 1625, 1429, 1263, 1141. ^{1}H-NMR ($CDCl_3$): 3.10 (*s*, 2 Me); 7.03 (*s*, 1 CH); 7.17 (*t*, 1 CH); 7.32 (*t*, 2 CH); 7.45 (*d*, 2 CH). ^{13}C-NMR ($CDCl_3$): 37.7; 122.4; 122.5; 122.6; 126.5; 128.7; 129.0; 145.2. Anal. calc. for $C_{11}H_{12}N_2O$ (188.0): C 70.21, H 6.38, N 14.89; found: C 70.05, H 6.55, N 14.77.

2-(Dimethylamino)-5-(4-methylphenyl)-1,3-oxazole (**14b**). Yield 69%. M.p. 69°. IR: 1626, 1433, 1425, 1263, 1140. ^{1}H-NMR ($CDCl_3$): 2.31 (*s*, Me); 3.08 (*s*, 2 Me); 6.97 (*s*, 1 CH); 7.12 (*d*, 2 CH); 7.35 (*d*, 2 CH). ^{13}C-NMR ($CDCl_3$): 21.1; 37.7; 121.6; 122.4; 126.1; 129.3; 136.2; 145.3; 161.8. Anal. calc. for $C_{12}H_{14}N_2O$ (202.0): C 71.29, H 6.93, N 13.86; found: C 71.55, H 7.08, N 13.74.

Table 4. *Most Important IR and MS Data of Some 1,4-Diaryl-2-(dialkylamino)-1*H*-imidazoles* **9** *and 3,5-Diaryl-2-(dialkylamino)-1,3-oxazolium Salts* **13**

No.	IR [cm^{-1}]	MS [*m*/*z*] (rel. intensity)
9a	1558, 1537, 1496, 1483, 1456, 1433, 1417, 1360, 1149, 1086, 1012, 931, 847, 837, 829	331 (100, M^+), 207 (30), 195 (19), 180 (55), 166 (16), 160 (29), 151 (15)
9b	1593, 1579, 1570, 1560, 1529, 1496, 1483, 1460, 1421, 1213, 1088, 834	359 (100, M^+), 330 (33), 316 (18), 221 (36), 207 (14), 194 (37)
9c	1602, 1579, 1562, 1537, 1494, 1457, 1427, 1408, 1352, 1217, 1091, 1085, 1014, 935, 837, 820	357 (100, M^+), 330 (14), 220 (19), 193 (23)
9d	1560, 1531, 1496, 1485, 1452, 1425, 1113, 1091, 920, 835	373 (100, M^+), 316 (42)
9f	1608, 1570, 1543, 1516, 1454, 1408, 1252, 1234, 1160, 935, 823	277 (M^+, 100), 262 (13), 172 (16), 159 (40), 145 (12)
9k	1560, 1537, 1512, 1483, 1444, 1412, 1255, 1155, 1091, 1036, 937, 837	327 (100, M^+), 191 (23), 176 (58), 160 (11), 121 (19)
13a	1697, 1655, 1493, 1456, 1427, 1284, 1155, 1091, 1012, 939, 922, 837	
13b	1689, 1653, 1493, 1456, 1211, 1090, 1014, 941, 835	
13c	1680, 1645, 1493, 1448, 1313, 1144, 1120, 1091, 1010, 914, 833	
13d	1697, 1655, 1516, 1464, 1429, 1221, 1155, 1105, 1093, 1082, 941, 922	
13f	1697, 1655, 1589, 1516, 1493, 1464, 1458, 1427, 1304, 1255, 1093	
13k	1697, 1655, 1516, 1493, 1456, 1429, 1271, 1221, 1157, 1092, 1010, 941, 924, 829	

5-(4-Chlorophenyl)-2-(dimethylamino)-1,3-oxazole (**14c**). Yield 67%. M.p. 98°. IR: 1635, 1487, 1431, 1280, 1265, 1146, 1091. ^{1}H-NMR ($CDCl_3$): 3.09 (*s*, 2 Me); 7.03 (*s*, 1 CH); 7.27 (*d*, 2 CH); 7.36 (*d*, 2 CH). ^{13}C-NMR ($CDCl_3$): 37.7; 122.8; 123.5; 128.5; 128.8; 131.2; 144.1; 161.9. Anal. calc. for $C_{11}H_{11}ClN_2O$ (222.5): C 59.33, H 4.94, N 12.58; found: C 59.45, H 5.12, N 12.38.

5-Aryl-2-(dialkylamino)-3-methyl-1,3-oxazolium Methyl Sulfates **13u**–**13w** (*General Procedure*). A soln. of an 1,3-oxazole **14** (0.01 mol) and freshly distilled $(MeO)_2SO_2$ (1.4 g, 0.011 mol) in MeCN (50 ml) was refluxed for 2 h. After cooling and addition of Et_2O, the precipitated oxazolium salt was isolated by filtration and recrystallized from EtOH. M.p. and anal. data of the compounds **13u**–**13w** are given in *Tables 2–4*.

*1,4-Diaryl-2-(dialkylamino)-1*H*-imidazoles* **9** (*General Procedures*) *Method A:*

A mixture of a *N,N*-disubstituted *N′*-(4-chlorophenyl)guanidine **7** (R = alkyl, R^1 = 4-Cl–C_6H_4) and 4-chlorophenacyl bromide **8** (Ar = 4-Cl–Ph) (2.3 g, 0.01 mol) in EtOH (30 ml) was refluxed for 8 h. After standing overnight, the precipitated product was isolated by filtration and recrystallized from aq. EtOH (90%).

Method B: A suspension of a 5-aryl-2-(dialkylamino)-1,3-oxazolium salt **13** (0.01 mol) and NH_4OAc (3.9 g, 0.05 mol) in EtOH (50 ml) was refluxed for 1 h. After cooling, the mixture was alkalized with aq. NH_3. While crystalline imidazoles were isolated by filtration, oily products were extracted with Et_2O and precipitated from the Et_2O soln. as hydroperchlorates after addition of $HClO_4$ (70%, 0.01 mol) and 5 ml of EtOH. The free imidazoles **9**, as well as their hydrogenperchlorates **9**•**HClO$_4$**, were recrystallized from aq. EtOH (90%). M.p. and anal. data are given in *Tables 1*, *3* and *4*.

*1,4-Bis(4-chlorophenyl)-2-(dimethylamino)-5-(4-nitrophenylazo)-1*H*-imidazole* (**15**). A soln. of 4-nitrophenyldiazonium hydrogensulfate, prepared by diazotization of 4-nitroaniline (1.38 g, 0.01 mol) in AcOH (25 ml) and H_2SO_4 (5 ml), was added dropwise to a stirred soln. of *1,4-bis(4-chlorophenyl)-2-(dimethylamino)-1*H*-imidazole* (**9a**; 3.32 g, 0.01 mol) in MeOH (25 ml) at 0°. After 30 min, the mixture was diluted with H_2O (100 ml) and neutralized with aq. NH_3. The crystals formed were isolated by filtration, dried, and recrystallized from DMF. Yield: 3.6 g (74%). M.p. 182–183°. UV (CH_2Cl_2): λ_{max} 517 (4.40). ^{1}H-NMR ((D$_6$)DMSO): 2.87 (*s*, 2 Me); 7.26 (*d*, 2 CH); 7.41 (*d*, 2 CH); 7.51–5.59 (*m*, 4 CH); 8.16 (*d*, 2 CH); 8.25 (*d*, 2 CH). Anal. calc. for $C_{23}H_{18}Cl_2N_6O_2$ (481.0): 57.38, H 3.74, N 17.46; found: C 57.69, H 4.51, N 17.26.

*1,4-Bis(4-chlorophenyl)-2-(dimethylamino)-1*H*-imidazole-5-carbaldehyde* (**16**). To a soln. of **9a** (3.32 g, 0.01 mol) in DMF (25 ml), $POCl_3$ (3.8 g, 0.025 mol) was added dropwise under stirring. The mixture was kept at 75° for 3 h, poured onto ice (50 g), and neutralized with 0.1N NaOH. The precipitate was isolated by filtration, dried, and recrystallized from EtOH. Yield: 3.24 g (90%). M.p. 196–198°. IR: 1651 (C=O). ^{1}H-NMR ((D$_6$)DMSO): 2.73 (*s*, 2 Me); 7.49 (*d*, 2 CH); 7.51 (*d*, 2 CH); 7.54 (*d*, 2 CH); 7.82 (*d*, 2 CH); 9.36 (*s*, CHO). Anal. calc. for $C_{18}H_{15}Cl_2N_3O$ (360.0): C 60.00, H 4.17, N 11.67; found: C 59.91, H 4.43, N 11.71.

*2-[1,4-Bis(4-chlorophenyl)-2-(dimethylamino)-1*H*-imidazole-5-yl]ethene-1,1-dicarbonitrile* (**17**). A mixture of **16** (3.32 g, 0.01 mol), malononitrile (0.8 g, 0.012 mol), and NEt_3 (0.5 ml) in MeCN (25 ml) was refluxed for 1 h. After cooling, the precipitate was isolated by filtration, dried, and recrystallized from EtOH. Yield: 3.6 g (88%). M.p. 227–228°. UV (CH_2Cl_2): λ_{max} 456 (4.31). ^{1}H-NMR ($CDCl_3$): 2.82 (*s*, 2 Me); 6.93 (*s*, 1 CH); 7.28 (*d*, 2 CH); 7.43 (*d*, 2 CH); 7.51 (*d*, 2 CH); 7.54 (*d*, 2 CH). Anal. calc. for $C_{21}H_{15}Cl_2N_5$ (408.0): C 61.76, H 3.68, N 17.16; found: C 61.61, H 3.95, N 16.99.

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