

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

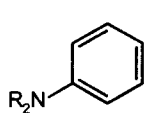
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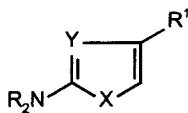
Dedicated to Prof. Dr. S. Daehne on the occasion of his 70th birthday

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)₂SO₂. The new oxazolium salts **13** were converted to 1-substituted 4-aryl-2-(dialkylamino)-1*H*-imidazoles **9** by treatment with NH₄OAc. 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].



1



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*-anilino-guanidines [13][21] or guanylhya-zones [22]. Other synthetic pathways leading to **6**, e.g., the reaction of isothiureas 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

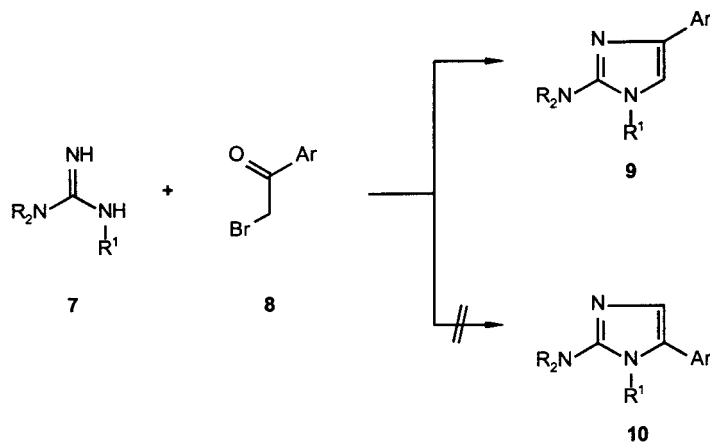


Table 1. 4-Aryl-2-(dialkylamino)-1H-imidazoles **9** and Their Hydrogenperchlorates **9**•HClO₄

No.	R ₂ N	R ¹	Ar	Yield [%] ^{a)}	M.p. [°]
9a	Me ₂ N	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	69 (11)	137–138
9b	Et ₂ N	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	98 (6)	70–71
9c	Pyrrolidin-1-yl	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	93 (7)	146–147
9d	Morpholino	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	95 (16)	146–147
9e •HClO ₄	Me ₂ N	Ph	Ph	77	185–188
9f	Me ₂ N	4-Me–C ₆ H ₄	Ph	83	102–104
9g	Me ₂ N	4-Cl–C ₆ H ₄	Ph	94	95–98
9h •HClO ₄	Me ₂ N	Ph	4-Me–C ₆ H ₄	73	180–184
9i •HClO ₄	Me ₂ N	4-Me–C ₆ H ₄	4-Me–C ₆ H ₄	82	182–184
9j	Me ₂ N	4-Me–C ₆ H ₄	4-Cl–C ₆ H ₄	84	106–108
9k	Me ₂ N	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	63	105–106
9l •HClO ₄	Et ₂ N	4-Me–C ₆ H ₄	Ph	75	185–186
9m	Pyrrolidin-1-yl	4-Me–C ₆ H ₄	Ph	89	97–99
9n	Pyrrolidin-1-yl	4-Cl–C ₆ H ₄	Ph	95	108–110
9o	Pyrrolidin-1-yl	4-Me–C ₆ H ₄	4-Cl–C ₆ H ₄	83	102–103
9p	Pyrrolidin-1-yl	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	92	97–99
9q	Piperidino	4-Cl–C ₆ H ₄	Ph	99	134–136
9r	Piperidino	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	94	110–111
9s	Morpholino	4-Cl–C ₆ H ₄	Ph	87	128–130
9t	Morpholino	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	91	137–138
9u •HClO ₄	Me ₂ N	–	Ph	35	215–217
9v •HClO ₄	Me ₂ N	–	4-Me–C ₆ H ₄	55	155–157
9w	Me ₂ N	–	4-Cl–C ₆ H ₄	47	60–62

^{a)} By the method depicted in Scheme 3; values in parentheses refer to the *Hantzsch* method shown in Scheme 1.

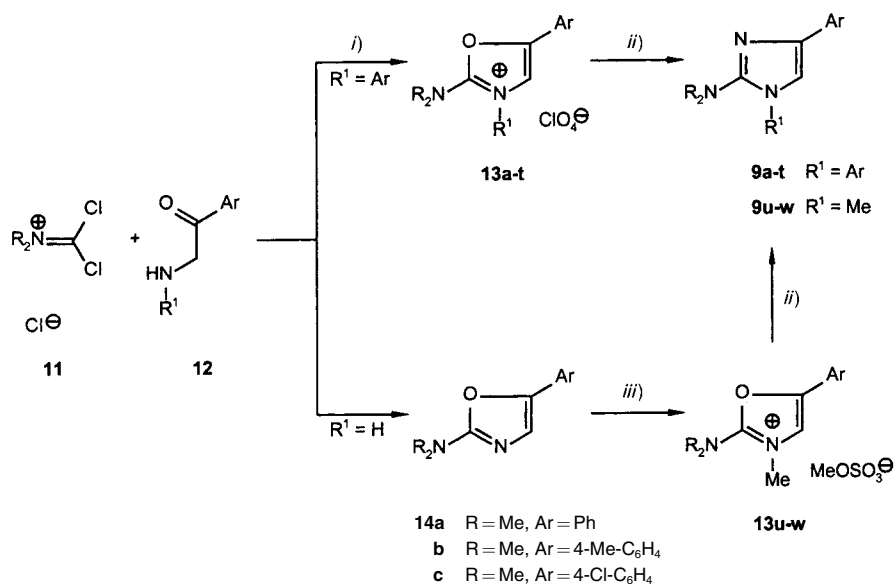
conversion is a well-known method for preparing imidazoles from 2-alkyl- or 2-aryloxazolium salts [26][27], it was hitherto not used for the synthesis of 2-amino-substituted derivatives. The reason for this is that the necessary *N*(3)-substituted 2-(dialkylamino)-1,3-oxazolium salts are essentially 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 R¹ 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** (R¹ = 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 HClO₄. In the case of 5-aryl-2-

Scheme 2



i) HClO_4 . ii) NH_4OAc . iii) $(\text{MeO})_2\text{SO}_2$

(dialkylamino)-1,3-oxazoles **14** prepared from *N*-unsubstituted 2-amino-1-arylethanone hydrobromides **12·HBr** ($\text{R}^1 = \text{H}$), 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 $(\text{MeO})_2\text{SO}_2$. 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·HClO₄** by addition of HClO_4 . The 5-aryl-2-(dialkylamino)-1*H*-imidazoles **9**, as well as their hydrogenperchlorate salts **9·HClO₄**, are listed in Table 1.

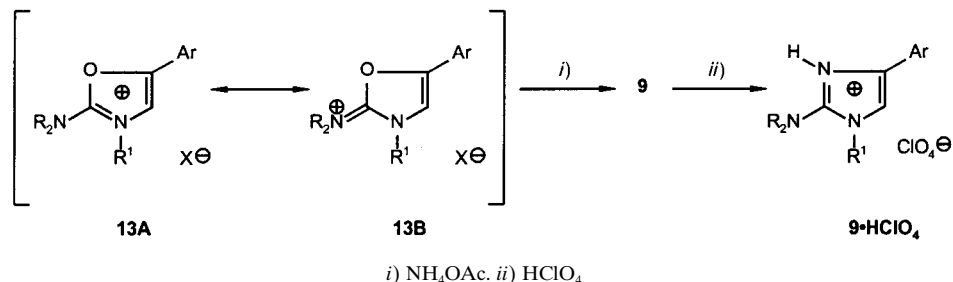
The new heterocyclic compounds **13**, **14**, and **9**, as well as their salts, were characterized by elemental analyses, IR and NMR measurements. Tables 3 and 4 in *Exper. Part* summarize these data, which confirm the proposed structures. Some remarkable properties of the oxazolium salts **13** and 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 ₂ N	R ¹	Ar	X [−]	Yield [%]	M.p. [°]
13a	Me ₂ N	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	80	300–302
13b	Et ₂ N	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	72	267–269
13c	Pyrrolidin-1-yl	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	74	280–281
13d	Morpholino	4-Cl–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	50	307–309
13e	Me ₂ N	Ph	Ph	ClO ₄ [−]	88	230–231
13f	Me ₂ N	4-Me–C ₆ H ₄	Ph	ClO ₄ [−]	72	155–157
13g	Me ₂ N	4-Cl–C ₆ H ₄	Ph	ClO ₄ [−]	91	215–216
13h	Me ₂ N	Ph	4-Me–C ₆ H ₄	ClO ₄ [−]	84	229–231
13i	Me ₂ N	4-Me–C ₆ H ₄	4-Me–C ₆ H ₄	ClO ₄ [−]	77	221–222
13j	Me ₂ N	4-Me–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	77	269–271
13k	Me ₂ N	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	74	239–241
13l	Et ₂ N	4-Me–C ₆ H ₄	Ph	ClO ₄ [−]	73	225–226
13m	Pyrrolidin-1-yl	4-Me–C ₆ H ₄	Ph	ClO ₄ [−]	77	228–229
13n	Pyrrolidin-1-yl	4-Cl–C ₆ H ₄	Ph	ClO ₄ [−]	65	257–259
13o	Pyrrolidin-1-yl	4-Me–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	80	254–256
13p	Pyrrolidin-1-yl	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	77	218–220
13q	Piperidino	4-Cl–C ₆ H ₄	Ph	ClO ₄ [−]	68	269–271
13r	Piperidino	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	72	205–207
13s	Morpholino	4-Cl–C ₆ H ₄	Ph	ClO ₄ [−]	65	278–280
13t	Morpholino	4-MeO–C ₆ H ₄	4-Cl–C ₆ H ₄	ClO ₄ [−]	71	250–251
13u	Me ₂ N	–	Ph	MeOSO ₃ [−]	68	178–180
13v	Me ₂ N	–	4-Me–C ₆ H ₄	MeOSO ₃ [−]	80	197–199
13w	Me ₂ N	–	4-Cl–C ₆ H ₄	MeOSO ₃ [−]	84	214–216

Scheme 3



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·HClO₄** and their corresponding oxazolium precursors **13** are very similar.

Characteristic in the ¹H-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 ¹H-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·HClO₄**.

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 $\text{NR}_2 = \text{NMe}_2$.

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

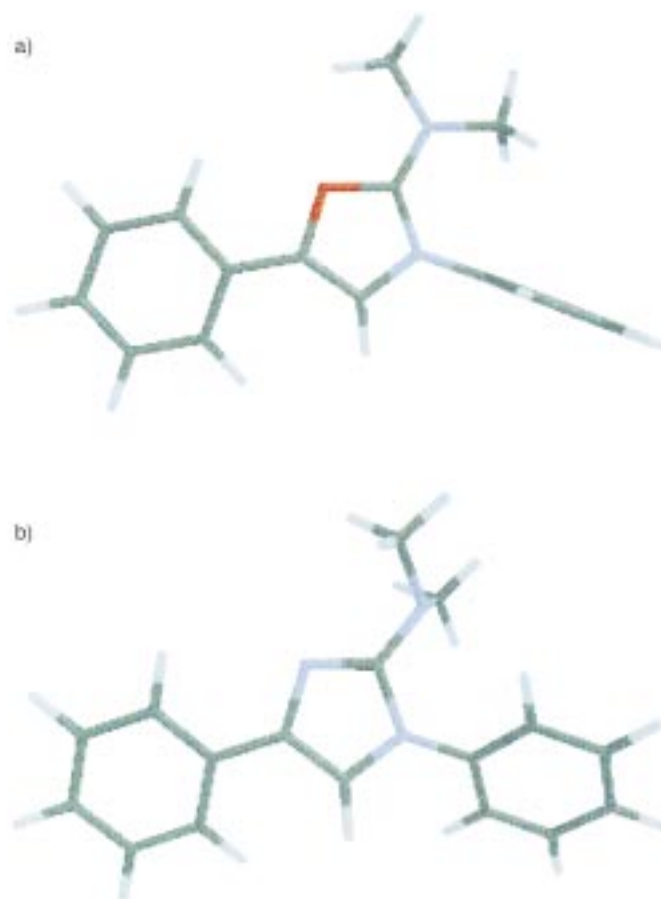


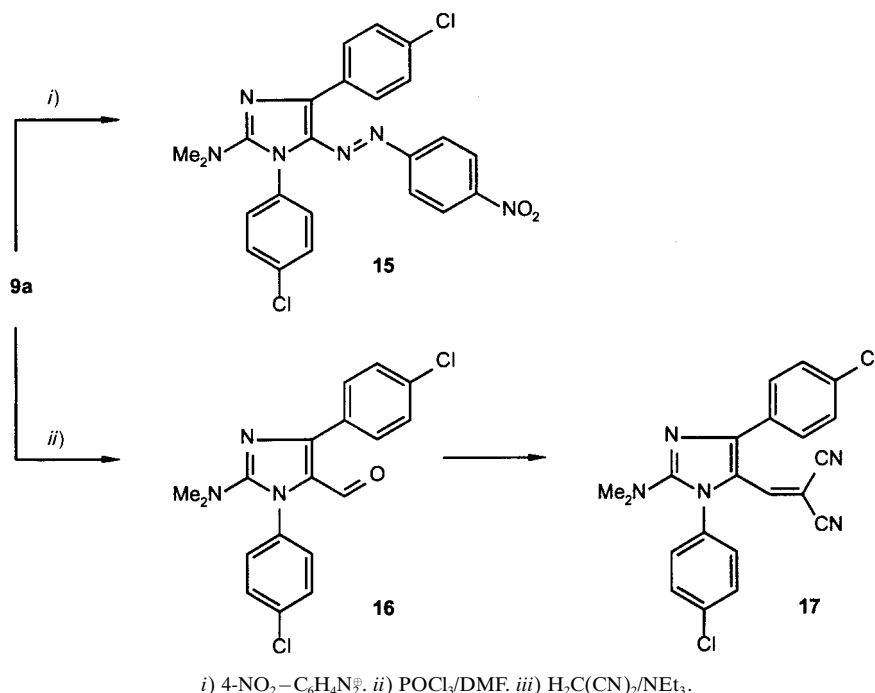
Fig. 1. AM-1-Optimized geometry of a) the 2-(dimethylamino)-3,5-diphenyl-1,3-oxazolium salt (**13e**) and b) of the 2-(dimethylamino)-1,4-diphenyl-1*H*-imidazole **9e**

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** ($E^{\text{HOMO}} = -12.08$ eV) by *ca.* 3.7 eV compared to the neutral imidazole **9e** ($E^{\text{HOMO}} = -8.34$ eV). The LUMO energy of **13e** ($E^{\text{LUMO}} = -4.09$ eV) is also much lower than that of the imidazole **9e** ($E^{\text{LUMO}} = -0.20$ 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



violet 5-aryldye **15** and the imidazole-carbaldehyde **16**, respectively. The dicyanitrile **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 *I*-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. HClO₄ (70%, 0.01 mol) to the cooled soln., the crystallization was initiated by addition of Et₂O. 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. ¹H- and ¹³C-NMR Data of the 4-Aryl-2-(dialkylamino)-1*H*-imidazoles **9**, the Hydrogenperchlorates **9•HClO₄**, and the 5-Aryl-2-(dialkylamino)-1,3-oxazolium Salts **13**

No.	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
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•HClO₄	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•HClO₄	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•HClO₄	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•HClO₄	1.02 (<i>t</i> , 2 Me); 2.39 (<i>s</i> , Me); 3.22 (<i>q</i> , 2 CH ₂); 7.43 (<i>m</i> , 3 CH); 7.53 (<i>m</i> , 4 CH); 7.76 (<i>d</i> , 2 CH); 7.82 (<i>s</i> , 1 CH); 12.9 (<i>s</i> , 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 (<i>quint.</i> , 2 CH ₂); 2.32 (<i>s</i> , Me); 3.11 (<i>t</i> , 2 CH ₂); 7.10 (<i>t</i> , 1 CH); 7.20 (<i>s</i> , 1 CH); 7.25 (<i>m</i> , 4 CH); 7.31 (<i>t</i> , 2 CH); 7.78 (<i>d</i> , 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 (<i>quint.</i> , 2 CH ₂); 3.14 (<i>t</i> , 2 CH ₂); 7.13 (<i>s</i> , 1 CH); 7.29 (<i>t</i> , 1 CH); 7.30 (<i>s</i> , 1 CH); 7.50 (<i>s</i> , 4 CH); 7.78 (<i>d</i> , 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 (<i>quint.</i> , 2 CH ₂); 2.35 (<i>s</i> , Me); 3.12 (<i>t</i> , 2 CH ₂); 7.26–7.35 (<i>m</i> , 7 CH); 7.77 (<i>d</i> , 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 (<i>quint.</i> , 2 CH ₂); 3.13 (<i>t</i> , 2 CH ₂); 3.83 (<i>s</i> , Me); 7.02 (<i>d</i> , 2 CH); 7.24 (<i>s</i> , 1 CH); 7.30 (<i>d</i> , 2 CH); 7.37 (<i>d</i> , 2 CH); 7.70 (<i>d</i> , 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 (<i>quint.</i> , 3 CH ₂); 2.97 (<i>t</i> , 2 CH ₂); 7.16 (<i>t</i> , 1 CH); 7.30 (<i>t</i> , 2 CH); 7.48 (<i>s</i> , 1 CH); 7.53 (<i>d</i> , 2 CH); 7.70 (<i>d</i> , 2 CH); 7.79 (<i>d</i> , 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 (<i>quint.</i> , 3 CH ₂); 2.96 (<i>t</i> , 2 CH ₂); 3.83 (<i>s</i> , Me); 7.04 (<i>d</i> , 2 CH); 7.32 (<i>d</i> , 2 CH); 7.43 (<i>s</i> , 1 CH); 7.53 (<i>d</i> , 2 CH); 7.80 (<i>d</i> , 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 (<i>t</i> , 2 CH ₂); 3.62 (<i>t</i> , 2 CH ₂); 7.16 (<i>t</i> , 1 CH); 7.31 (<i>t</i> , 2 CH); 7.48 (<i>s</i> , 1 CH); 7.52 (<i>d</i> , 2 CH); 7.68 (<i>d</i> , 2 CH); 7.79 (<i>d</i> , 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 (<i>t</i> , 2 CH ₂); 3.60 (<i>t</i> , 2 CH ₂); 3.82 (<i>s</i> , Me); 7.04 (<i>d</i> , 2 CH); 7.32 (<i>d</i> , 2 CH); 7.43 (<i>s</i> , 1 CH); 7.52 (<i>d</i> , 2 CH); 7.79 (<i>d</i> , 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 (<i>s</i> , NH); 3.26 (<i>s</i> , Me); 3.83 (<i>s</i> , Me); 7.42 (<i>m</i> , 3 CH); 7.51 (<i>s</i> , 1 CH); 7.68 (<i>d</i> , 2 CH) ^a	35.7; 41.3; 117.1; 124.5; 125.9; 127.9; 129.6; 129.9; 150.6 ^a)
9v•HClO₄	2.33 (<i>s</i> , Me); 3.10 (<i>s</i> , NH); 3.25 (<i>s</i> , 2 Me); 3.82 (<i>s</i> , Me); 7.46 (<i>s</i> , 1 CH); 7.26 (<i>d</i> , 2 CH); 7.57 (<i>d</i> , 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•HClO₄	3.06 (<i>s</i> , NH); 3.27 (<i>s</i> , 2 Me); 3.86 (<i>s</i> , Me); 7.48 (<i>d</i> , 2 CH); 7.57 (<i>s</i> , 1 CH); 7.71 (<i>d</i> , 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 (<i>s</i> , 2 Me); 7.63 (<i>d</i> , 2 CH); 7.77 (<i>m</i> , 6 CH); 8.34 (<i>s</i> , 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 (<i>t</i> , 2 Me); 3.42 (<i>q</i> , 2 CH ₂); 7.66 (<i>d</i> , 2 CH); 7.78 (<i>d</i> , 2 CH); 7.81 (<i>d</i> , 2 CH); 7.91 (<i>d</i> , 2 CH); 8.27 (<i>s</i> , 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 (<i>quint.</i> , 3 CH ₂); 3.46 (<i>q</i> , 2 CH ₂); 7.66 (<i>d</i> , 2 CH); 7.78 (<i>d</i> , 2 CH); 7.81 (<i>d</i> , 2 CH); 7.92 (<i>d</i> , 2 CH); 8.32 (<i>s</i> , 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 (<i>t</i> , 2 CH ₂); 3.68 (<i>t</i> , 2 CH ₂); 7.63 (<i>d</i> , 2 CH); 7.78 (<i>s</i> , 4 CH); 7.80 (<i>d</i> , 2 CH); 8.37 (<i>s</i> , 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 (<i>s</i> , 2 Me); 7.47–7.56 (<i>m</i> , 3 CH); 7.68 (<i>t</i> , 3 CH); 7.77 (<i>d</i> , 2 CH); 7.83–7.86 (<i>m</i> , 2 CH); 8.03 (<i>s</i> , 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 (<i>s</i> , Me); 3.02 (<i>s</i> , 2 Me); 7.45 (<i>t</i> , 1 CH); 7.46 (<i>d</i> , 2 CH); 7.53 (<i>t</i> , 1 CH); 7.63 (<i>d</i> , 2 CH); 7.73 (<i>d</i> , 2 CH); 8.24 (<i>s</i> , 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 (<i>s</i> , 2 Me); 7.48–7.56 (<i>m</i> , 3 CH); 7.73 (<i>d</i> , 2 CH); 7.76 (<i>d</i> , 2 CH); 7.90 (<i>d</i> , 2 CH); 8.06 (<i>s</i> , 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 (<i>s</i> , Me); 3.22 (<i>s</i> , 2 Me); 7.35 (<i>d</i> , 2 CH); 7.64–7.70 (<i>m</i> , 5 CH); 7.84 (<i>d</i> , 2 CH); 7.96 (<i>s</i> , 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 (D₆)acetone. ^b) In (D₆)DMSO.

5-Aryl-2-(dimethylamino)-1,3-oxazoles 14. To a suspension of an 2-amino-1-arylethanone hydrobromide **12·HBr** (R¹ = 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 Et₂O (3 × 50 ml) and dried. After evaporation of Et₂O, 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. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 37.7; 122.4; 122.5; 122.6; 126.5; 128.7; 129.0; 145.2. Anal. calc. for C₁₁H₁₂N₂O (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. ¹H-NMR (CDCl₃): 2.31 (s, Me); 3.08 (s, 2 Me); 6.97 (s, 1 CH); 7.12 (d, 2 CH); 7.35 (d, 2 CH). ¹³C-NMR (CDCl₃): 21.1; 37.7; 121.6; 122.4; 126.1; 129.3; 136.2; 145.3; 161.8. Anal. calc. for C₁₂H₁₄N₂O (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)-1H-imidazoles 9 and 3,5-Diaryl-2-(dialkylamino)-1,3-oxazolium Salts 13*

No.	IR [cm ⁻¹]	MS [<i>m/z</i>] (rel. intensity)
9a	1558, 1537, 1496, 1483, 1456, 1433, 1417, 1360, 1149, 1086, 1012, 931, 847, 837, 829	331 (100, <i>M</i> ⁺), 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, <i>M</i> ⁺), 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, <i>M</i> ⁺), 330 (14), 220 (19), 193 (23)
9d	1560, 1531, 1496, 1485, 1452, 1425, 1113, 1091, 920, 835	373 (100, <i>M</i> ⁺), 316 (42)
9f	1608, 1570, 1543, 1516, 1454, 1408, 1252, 1234, 1160, 935, 823	277 (<i>M</i> ⁺ , 100), 262 (13), 172 (16), 159 (40), 145 (12)
9k	1560, 1537, 1512, 1483, 1444, 1412, 1255, 1155, 1091, 1036, 937, 837	327 (100, <i>M</i> ⁺), 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. ¹H-NMR (CDCl₃): 3.09 (s, 2 Me); 7.03 (s, 1 CH); 7.27 (d, 2 CH); 7.36 (d, 2 CH). ¹³C-NMR (CDCl₃): 37.7; 122.8; 123.5; 128.5; 128.8; 131.2; 144.1; 161.9. Anal. calc. for C₁₁H₁₁ClN₂O (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)₂SO₂ (1.4 g, 0.011 mol) in MeCN (50 ml) was refluxed for 2 h. After cooling and addition of Et₂O, 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)-1H-imidazoles 9 (General Procedures) Method A:

A mixture of a *N,N*-disubstituted *N'*-(4-chlorophenyl)guanidine **7** (R = alkyl, R¹ = 4-Cl–C₆H₄) 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 NH₄OAc (3.9 g, 0.05 mol) in EtOH (50 ml) was refluxed for 1 h. After cooling, the mixture was alkalized with aq. NH₃. While crystalline imidazoles were isolated by filtration, oily products were extracted with Et₂O and precipitated from the Et₂O soln. as hydrop perchlorates after addition of HClO₄ (70%, 0.01 mol) and 5 ml of EtOH. The free imidazoles **9**, as well as their hydrogenperchlorates **9•HClO₄**, 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)-1H-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 H₂SO₄ (5 ml), was added dropwise to a stirred soln. of 1,4-bis(4-chlorophenyl)-2-(dimethylamino)-1H-imidazole (**9a**; 3.32 g, 0.01 mol) in MeOH (25 ml) at 0°. After 30 min, the mixture was diluted with H₂O (100 ml) and neutralized with aq. NH₃. The crystals formed were isolated by filtration, dried, and recrystallized from DMF. Yield: 3.6 g (74%). M.p. 182–183°. UV (CH₂Cl₂): λ_{max} 517 (4.40). ¹H-NMR ((D₆)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 C₂₃H₁₈Cl₂N₆O₂ (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)-1H-imidazole-5-carbaldehyde (**16**). To a soln. of **9a** (3.32 g, 0.01 mol) in DMF (25 ml), POCl₃ (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). ¹H-NMR ((D₆)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 C₁₈H₁₅Cl₂N₃O (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)-1H-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). $^1\text{H-NMR}$ (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 $\text{C}_{21}\text{H}_{15}\text{Cl}_2\text{N}_5$ (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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