Tetrahedron Vol. 45, No. 24, pp. 7795 to 7804, 1989
Printed in Great Britain.

0040-4020/89 $3.00+.00

AN UNEXPECTED RING-OPENING IN THE REISSERT REACTION ON 2,3-DIPHENYLQUINOXALINE-N-OXIDE.

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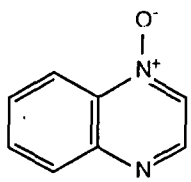
(*Received in Belgium* 27 *July* 1989)

Summary. When quinoxaline-N-oxide **1** is reacted with KCN and benzoyl chloride in water (the Reissert reaction) or methanol, the products are 2-, 5- and 6- chloroquinoxaline (the latter being the major product: 42±6 %) and small amounts of 2-cyanoquinoxaline. Using three equivalents of trimethylsilyl cyanide instead of KCN, and dichloromethane as the solvent, leads to a 72 % yield of 2-cyanoquinoxaline. The reaction of trimethylsilyl cyanide and benzoyl chloride with 2,3-diphenylquinoxaline-N-oxide **2** leads to an unexpected ring-opening product **13**; its structure is based on spectroscopic data and on an X-ray crystallographic analysis.

Introduction.

We have found previously [1] that the action of phosphoryl chloride on 2,3-diphenylquinoxaline-N-oxide **2** leads to the unexpected formation of aryl phosphates. It thus seemed interesting to test whether this apparently unusual substrate behaves normally in other reactions typical of N-oxides and we selected to study the Reissert reaction [2].



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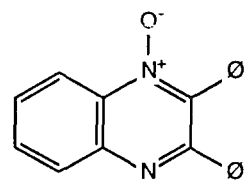


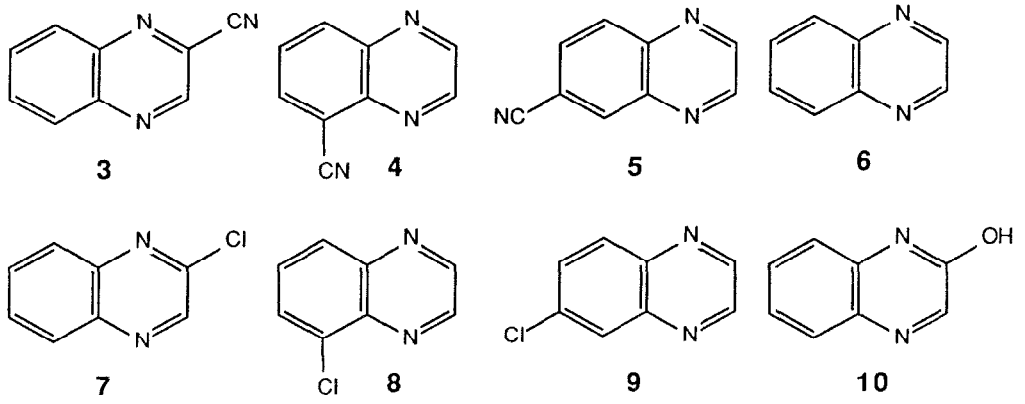
2

Henze [3] reacted quinoline-N-oxide with potassium cyanide and benzoyl chloride in water and obtained a 60 % yield of 2-cyanoquinoline. The same procedure applied to other substrates met, however, with variable results because of the poor solubility of the N-oxide and of the benzoyl chloride in water. Major improvements in this area came more recently by the use of phase transfer reagents [4] or lipophilic cyanides [5]. We thus reacted first quinoxaline-N-oxide **1** in the original Reissert conditions, *i.e.* with KCN in water, without or with phase transfer catalysis, and then with trimethylsilyl cyanide in dichloromethane or chloroform in order to test the system, and then submitted 2,3-diphenylquinoxaline-N-oxide **2** to the same reactions.

Results and discussion.

1. Quinoxaline-N-oxide.

The products isolated from the reaction have been identified by comparison with authentic samples; they are 2-cyano- (**3**), 5-cyano- (**4**) and 6-cyanoquinoxaline (**5**), the deoxygenation product (**6**), the 2-chloro- (**7**), 5-chloro- (**8**) and 6-chloroquinoxaline (**9**), and 2-hydroxyquinoxaline (**10**). The relative yields were obtained by HPLC and the results are collected in Table I.



Entries 1 to 4 disclose an astonishing result: the major product of the reactions run in a highly polar medium is 6-chloroquinoxaline; this is unexpected. First, the formation of aromatic chlorides is never mentioned in the literature of the Reissert reaction, whereas here they amount to 55 to 59 % relative yields. If 2-hydroxyquinoxaline, which is probably formed by hydrolysis of 2-chloroquinoxaline, is added, the total of non-cyanide nucleophilic attack rises to 65 - 87 % relative yields.

The second unexpected aspect is the fact that 6-chloroquinoxaline **8** results from the attack of a nucleophile in the homocycle, which is by far less activated than the heterocycle, especially in an environment as electrophilic as aqueous benzoyl chloride. This is in contrast to the results found for the nitriles in the same runs: they are formed in modest yields, but the 2-cyano isomer is always the major component, which is in good agreement with expectations. It should also be reminded that heating quinoxaline-N-oxide in $POCl_3$ (the Meisenheimer reaction) gives [6] 2-chloro- and 6-chloroquinoxaline in a 9:1 ratio.

It was then attempted to improve the solubility of the reactants by working in methanol, as suggested by Iijima [6b] and Kobayashi [7], but as shown by entry 4, this had only a minor effect on the ratio of chloro-to-cyano derivatives. The two-phase system water-chloroform including the phase-transfer catalyst Bu_4NCl gives much more nitriles which now become the major products. The yield is, however, rather low; this seems to be due to the reaction of KCN with benzoyl chloride, giving benzoyl cyanide which was found to be inert towards quinoxaline-N-oxide under these conditions. Reaction requires indeed the reflux temperature of xylene (see run 7) to give a moderate conversion and significant amounts of deoxygenation.

We finally turned to trimethylsilyl cyanide in dichloromethane. Entry 8 shows that the nitriles are definitely the major products, and entries 9 and 10 confirm Fife's findings that excess reagents appreciably improve the overall yield of nitriles. It is also interesting to notice that deoxygenation is now a really minor side-

reaction. The very high selectivity in favour of the *ortho* substitution product is probably to be interpreted as a consequence of the intramolecular cyclic mechanism suggested in the literature [8].

TABLE I. Relative product distribution in the Reissert reaction on quinoxaline-N-oxide.

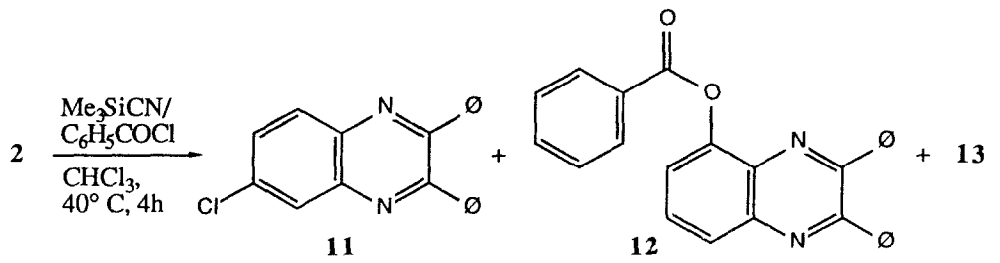
Conditions	N	t/h	3	4	5	7	8	9	6	10	yield	1
1) KCN (3 eq) H_2O	2	2.0	9	3	-	11	8	39	16	15	78	-
2) KCN (6eq) H_2O	3	1.5	8	1	1	13	1	48	21	8	77	-
3) KCN (3 eq) H_2O/MeOH	2	2.75	5	7	1	7	12	38	1	30	100	-
4) KCN (3 eq) MeOH	2	24	14	11	6	14	2	40	-	13	100	-
5) KCN (3 eq) $H_2O/CHCl_3$	2	0.5	16	-	4	9	-	50	15	6	89	-
6) KCN (3 eq) $H_2O/CHCl_3$ + Bu_4NCl (.06 eq)	1	16	43	-	20	3	-	26	8	-	52	58
7) C_6H_5COCN (6 eq) xylene, reflux	1	2	45	-	6	-	-	-	49	-	30	70
8) Me_3SiCN (1 eq) CH_2Cl_2 + 1 eq C_6H_5COCl	2	24	46	2	-	3	5.5	11	0.5	32	69	-
9) Me_3SiCN (3 eq) CH_2Cl_2 + 1 eq C_6H_5COCl	2	5	72	1	1	1	2	4	6	14	80	-
10)Me_3SiCN (3 eq) CH_2Cl_2 + 3 eq C_6H_5COCl	2	3	72	2	1	1	6	5	1	11	98	-

All reactions were run with 50 mg (0.34 mmol) of quinoxaline-N-oxide in 1 mL of solvent at room temperature. *N* is the number of independent runs; t is the time in hours.1.4 equivalents of benzoyl chloride have been used in entries 1 to 6.

2,3-Diphenylquinoxaline-N-oxide.

When 500 mg of 2,3-diphenylquinoxaline-N-oxide **2** were kept fo 4 hours at 40° C in chloroform with 1 equivalent of trimethylsilyl cyanide and one of benzoyl chloride, a TLC analysis showed that no nitriles were formed. Work-up and separation afforded a 5 % yield of 6-chloro-2,3-diphenylquinoxaline **11**, 54 mg of a first unknown **12** and 620 mg of a second unknown **13**.

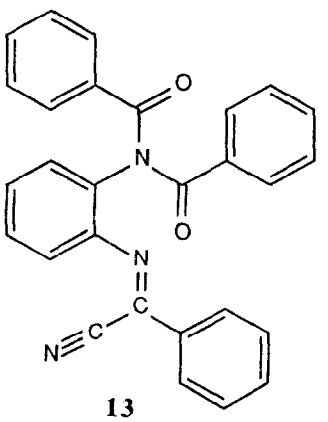
The identification of **12** is straightforward if it is assumed that the quinoxaline skeleton has been preserved; this is confirmed by the ^1H NMR spectrum exhibiting the typical AMX pattern of the 6-, 7- and 8- protons in a 5-substituted quinoxaline and by the absence of lines corresponding to pyrazinic protons. The molecular ion at m/z = 402 corresponds to $C_{27}H_{18}N_2O_2$, *i.e.* to a diphenylquinoxaline substituted by a benzoyloxy group. The benzoyl and the two phenyl groups are well defined in the ^1H NMR spectrum. These data, combined with the IR and ^{13}C NMR spectra, lead to assign the structure of 5-benzoyloxy-2,3-diphenylquinoxaline to compound **12**.



11 12

The structure of **13** was more difficult to establish. The molecular ion at m/z = 428 corresponds to $C_{28}H_{19}N_3O_2$, as confirmed by elemental analysis, *i. e.* to the sum of 2,3-diphenylquinoxaline and benzoyl cyanide. The ^1H NMR spectrum shows no lines at $\delta > 8.1$ ppm, excluding thus a quinoxalinic structure. What is definitely intriguing is the presence of three phenyl groups, two of which are rigorously identical even when changing the solvent from $CDCl_3$ to C_6D_6.

The high resolution ^{13}C NMR spectrum recorded in the presence of $Cr(acac)_3$ confirms the identity of two of the three phenyl groups, and in addition shows two identical deshielded carbon atoms belonging to carbonyl groups. A nitrile is indicated by a signal at 110.5 ppm in ^{13}C NMR and a band at 2200 cm^{-1} in the IR spectrum. **13** contains thus two identical benzoyl groups ($C_{14}H_{10}O_2$), one phenyl (C_6H_5) and a nitrile (CN). The connecting fragment which remains to justify is thus $C_7H_4N_2$. The structure compatible with all the data is that of a compound having undergone the opening of the quinoxaline heterocycle to an *ortho*-phenylene-diamine where one of the nitrogen atoms carries the two benzoyl groups and is thus an imide, and the other nitrogen atom is part of an imine which might be pictured as originating from benzoyl cyanide.



13

The structure of **13** was confirmed by an X-ray analysis, proving the Z configuration of the C=N double bond of the imine. Figure 1 shows a stereoscopic view of the molecule [9].

Compound **13** contains three phenyl groups, and comes from a reagent having one and a reactant having two phenyls. The question obviously arises: which is the one coming from the acid chloride? To answer this, the N-oxide **2** was reacted with three other acid chlorides: *meta*-methylbenzoyl chloride, *para*-nitrobenzoyl chloride and pivaloyl chloride. In all three cases was the acyl group of the reagent fond on the imide nitrogen atom, and not on the imine.

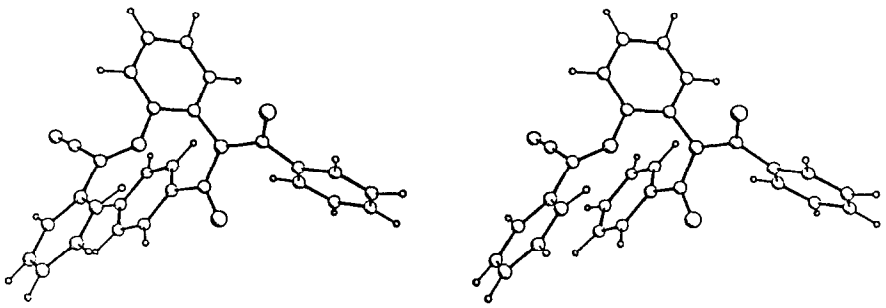
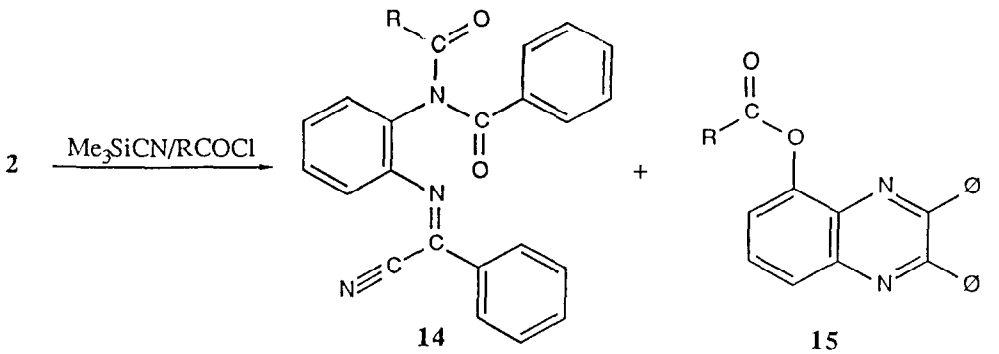


FIGURE I

The crystallographic data are as follows: $C_{28}H_{19}N_3O_2$, Mr = 429.48, monoclinic, $C2/c$ with a = 21.343(4), b = 9.169(1), c = 24.205(4) Å, β = 112.15(2)°, V = 4387(1) Å^3, Dx = 1.30 gcm^{-3} for Z = 8.The intensities of 3950 h $k\pm l$ independent reflections with (sinθ/λ) < 0.60 Å^{-1} were collected on a Huber four circle diffractometer operating in front of a RU200 rotating anode generator and with Cu$K\alpha$ graphite monochromatized radiation (λ = 1.5418 Å). 2793 reflections with $I > 2.5\ \sigma(I°)$ were considered as observed and used in the refinement. No absorption correction was applied (dimensions of the crystal: 0.25 x 0.12 x 0.10 mm, μ = 6.78 cm^{-1}).

The structure was solved by the direct method using SHELXS-86 [10]. Anisotropic least squares refinement on F with SHELX-76 [11]. All hydrogen atoms were located from a difference Fourier synthesis and included in the refinement with a common isotropic temperature factor. The final R index is 0.078 for 2793 observed reflections. The list of atomic coordinates and molecular dimensions has been deposited at the Cambridge Data Centre.

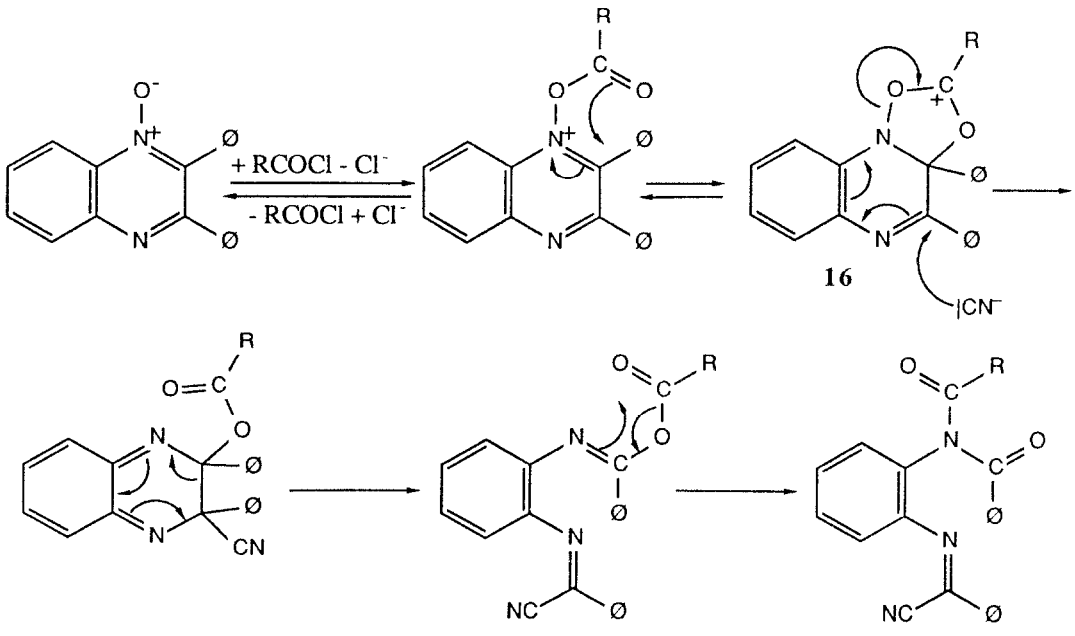


14 15

R = *m*-Me-C_6H_4	14a:	89 %	15a:	10 %
R = *p*-O_2N-C_6H_4	14b:	80 %	15b:	15 % (*)
R = ^{t}Bu	14c:	88 %	15c:	7 %

(*) A mixture of 5- and 6-*para*-nitrobenzoyloxy-2,3-diphenylquinoxalines

A tentative mechanism for the formation of **13** and its analogs **14a-c** is shown in Scheme I. The first step, the reversible acylation of the N-oxide oxygen atom by the added acid chloride is usually accepted in this type of interaction. The ring closure to the tricyclic acetoxylium **16** ion is also reversible, and finds precedent in Begtrup's work [12], as well as its opening under cyanide attack to give the hetero-cyclohexadiene **17**. A Cope rearrangement to **18** restores the aromatic ring, and a 1,3-acyl shift finally leads to the product; such a rearrangement of an α-acyloxy-imine to an imide also finds some precedent in the literature [13].



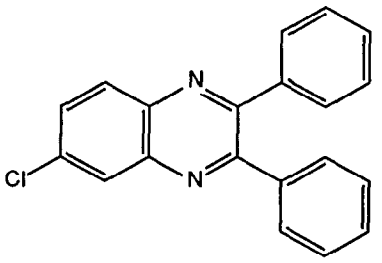
SCHEME I

This unexpected ring-opening leads one to ask whether it is typical of the reagent trimethylsilyl cyanide; we thus submitted 2,3-diphenylquinoxaline-N-oxide **2** to the classical Reissert conditions using potassium cyanide and some of the variants tried in the case of quinoxaline-N-oxide. To our surprise, the only products identified in any significant yield are 6-chloro-2,3-diphenylquinoxaline **19** and the deoxygenation product 2,3-diphenylquinoxaline **20**. The results are collected in Table II.

The most interesting results are those of runs 4, 7, 8 and 9, showing high deoxygenation, and runs 5, 6, 7 and 9 where the ring-opened product is appreciable; it should be noticed, however, that the actual yields of these products is usually low, and in the case of benzoyl cyanide as the reagent (run 5) extensive decomposition to unidentified products is the major fate.

Experimental part.

IR spectra (in KBr pellets) have been recorded on a Perkin-Elmer 237 spectrophotometer. NMR spectra were recorded with a Brucker Cryospec WM spectrometer at 250 MHz for ^{1}H and 62.89 MHz for ^{13}C. Chemi-cal shifts, relative to internal TMS, are given in ppm; couplings in Hz. Mass spectra were recorded with a VG Micromass 7070F spectrometer; peaks less than 10 % of the base peak are not mentioned.



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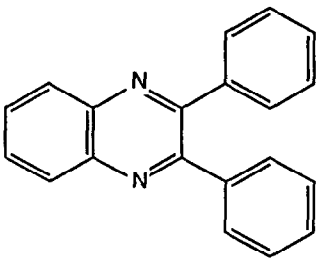

20

TABLE II. Relative product distribution in the Reissert reaction on 2,3-diphenylquinoxaline-N-oxide **2**.

Conditions	time	**19**	**20**	**13**	yield	**2**
1) KCN (3 eq), 70 °C H_2O	24 h	85	4	1	35	65
2) KCN (3 eq), 20 °C H_2O/MeOH	120 h	71	23	-	10	90
3) KCN (3 eq), reflux H_2O/MeOH	72 h	81	5	1	40	56
4) KCN (3 eq), reflux EtOH	72 h	17	83	-	11	89
5) C_6H_5COCN (10 eq) reflux,toluene	144 h	12	-	48	3	7
6) KCN (3 eq), 20 °C $H_2O/CHCl_3$	17 h	21	4	51	50	50
7) KCN (3 eq), 20 °C, $H_2O/CHCl_3$, + 0.2 eq Bu_4NCl	4 h	-	67	33	3	97
8) KCN (3 eq), 50 °C $H_2O/CHCl_3$, + 0.1 eq Bu_4NCN	24 h	-	100	-	1	99
9) Bu_4NCN (4 eq), 50 °C toluene	72 h	-	45	20	37	50

The results are based on a single run, except 6) which was duplicated. The experiments used 50 mg of 2,3-diphenylquinoxaline-N-oxide (3.17 mmol) in 1 or 2 mL solvent containig 1.1 eq of benzoyl chloride; where two solvents are mentioned, they are present in equal volumes. When the sum of the yiels of **19**, **20** and **13** do not add to 100 %, the balance corresponds to an unidentified compound which might be 6-cyano-2,3-diphenylquinoxaline or a benzoyloxy-2,3-diphenylquinoxaline and, in some runs, to some 6-hydroxy-2,3-diphenylquinoxaline.

HPLC separations, identifications and determinations were performed with a Waters chromatograph equipped with a 6000A pump, a UVR440 detector at 254 nm and an integrator. The columns were 25 cm long with a 4.6 mm internal diameter. Flash chromatography was done according to Still, Kahn and Mitra [14]; the silicagel column was 15 cm high, the diameter being adapted to the amount of material to separate.

N-oxides.

Quinoxaline-N-oxide was made according to literature data [6a]. 2,3-Diphenylquinoxaline-N-oxide was made in the same way; chromatography through alumina eluted with chloroform separates the mono-N-oxide

from the starting material and the di-N-oxide. 2,3-Diphenylquinoxaline [6c]: ^{1}H NMR ($CDCl_3$; analysis by PANIC): 8.18 (dd; 2 H; H_5, H_8; $J_{5,6} = J_{7,8} = 8.6$ Hz); 7.77 (dd; 2 H; H_6, H_7); phenyl groups at 7.52 and 7.31 (m). 2,3-Diphenylquinoxaline-N-oxide **2**: MP: 205-206 °C, lit [15]: 207 °C. ^{1}H NMR ($CDCl_3$; analysis by PANIC): 8.65 (dd, 1 H; H_8); 8.20 (dd; 1 H; H_5); 7.84 (dd; 1H; H_7); 7.76 (dd; 1 H; H_6); $J_{5,6} = 8.76$, $J_{5,7} = 1.30$, $J_{6,7} = 6.92$, $J_{6,8} = 1.43$, $J_{7,8} = 8.47$ Hz; phenyl groups at 7.39 and 7.25 (m). ^{13}C NMR: 156.4 (C_3); 144.0 (C_{4a}); 140.2 (C_2); 136.2 (C_{8a}); 119.5 (C_8); others: quat. C at 138.2; CH at 131.5, 130.8 (2 C, phenyl), 130.1, 130.0, 129.7 (2 C), 129.3, 129.0, 128.3 (2 C), 128.1 (2 C, phenyl). MS: 298 (46 %; M^+); 297 (38; $M^+ - H$); 282 (66; $M^+ - O$); 281 (100 %; $M^+ - OH$); 268 (20); 179 (24; 282 - C_6H_5CN); 178 (12; 281 - C_6H_5CN); 105 (14).

Substituted quinoxalines.

2-Chloroquinoxaline **7** [16], 5-chloroquinoxaline **8** [16b, 17,18], 6-chloroquinoxaline **9** [17, 19] and 2-hydroxyquinoxaline **10** [16a, 16c, 20] were made according to literature data. 5- and 6-chloro-2,3-diphenylquinoxaline were accessible from a previous work [1] 2-cyanoquinoxaline **3** was isolated from the reaction and found identical with the literature material [21].

5-Cyanoquinoxaline **4** was made according to the method of Newman and Boden [22] by heating 5-chloroquinoxaline **8** (200 mg, 1.2 mmol) and CuCN (200 mg, 2.2 mmol) under reflux in 1 mL N-methylpyrrolidinone for 7 h. After cooling, a solution of 0.2 mL ethylenediamine in 0.6 mL water is added, the medium left overnight at room temperature, a little water is added, and the medium extracted with chloroform; the organic phase is then washed with 10 % aqueous KCN, dried and evaporated to dryness. The residue is dissolved in the minimal amount of chloroform and flash- chromatographed (1 cm diameter) with hexane-ethyl acetate 8:2. After recrystallization from ethanol, 31 mg (0.2 mmol, 18 %) of 5-cyanoquinoxaline **4** are obtained. MP: 115-119 °C; lit [23]: 108-108.5 °C. ^{1}H NMR: 9.04 and 9.00 (d, d; 2 H; H_2 and H_3; $J_{2,3} = 1.8$ Hz); 8.39 (dd; 1 H; H_8); 8.21 (dd; 1 H; H_6); 7.87 (dd; 1 H; H_7); $J_{6,7} = 7.3$, $J_{6,8} = 1.3$, $J_{7,8} = 8.5$ Hz. MS: 155 (100 %; M^+); 154 (10; $M^+ - H$); 128 (100; $M^+ - HCN$); 101 (58; 128 - HCN); 100 (14); 91 (13); 75 (25; 101 - CN).

6-Cyanoquinoxaline **5** was made in the same way starting from 6-chloroquinoxaline and was found identical to the literature material [16b].

Reactions of 2,3-diphenylquinoxaline-N-oxide with trimethylsilyl cyanide.

The work-up of the systems starts with the addition of water or saturated aqueous $NaHCO_3$, extraction with chloroform and evaporation of the organic phase to dryness. The residue is then flash-chromatographed (2 or 3 cm diameter) with hexane-ethyl acetate 9:1, or directly submitted to HPLC analysis for the determination of the yields.

a) With benzoyl chloride.

5-Benzoyloxy-2,3-diphenylquinoxaline **12**.:recrystallized from cyclohexane. MP: 172-175 °C. ^{1}H NMR ($CDCl_3$): 8.10 (dd; 1 H; H_8); 7.78 (dd; 1 H; H_7); 7.61 (dd; 1 H; H_6); $J_{6,7} = 7.6$, $J_{6,8} = 1.2$, $J_{7,8} = 8.4$ Hz; benzoyl: 8.33 (m; 2 H; H_{ortho}); 7.70 (tt; 1 H; H_{para}); 7.18 (m; 2 H; H_{meta}). ^{13}C NMR: 165.5 (C=O); quaternary C at 153.9, 152.8 (C_{4a}, C_{8a}); 147.6 (C_5); 141.9, 139.2, 138.6 (C_2, C_3, benzoyl C1); 129.7 (2 phenyl C_1); CH at 134.6, 130.5, 130.2, 129.8, 129.2, 129.0, 128.9, 128.6, 128.4, 127.9, 127.2, 121.7. MS: 402 (100 %; m^+); 299 (7); 298 (10; $M^+ - C_6H_4O$); 194 (7); 166 (5); 149 (7); 150 (6); 106 (35; $C_6H_5COH^+$); 105 (100 %; $C_6H_5CO^+$).

2-(α-cyanobenzalimino)-N,N-dibenzoylaniline **13**: recrystallized from methanol. MP: 186-187 °C. ^{1}H NMR: very complex pattern of lines between 7.2 and 8.2 ppm. ^{13}C NMR: quaternary C at 172.8 (2 C=O); 144.6, 141.7 (diaminobenzene C_1, C_2); 134.7 (2 benzoyl C_1); 134.2, 133.3 (benzalimino C=N, C_{Ar}); 110.5 (CN). CH at 133.3; 132.4 (2C); 129.4; 129.2 (4 benzoyl C); 129.1; 129.0 (2 C); 128.7; 128.5 (2 C); 128.4 (4 benzoyl C);119.8. MS: 429 (33 %; M^+); 324 (22; $M^+ - C_6H_5CO$); 308 (10); 298 (100 %; 324 - CN); 193 (17);

106 (83); 105 (100; $C_6H_5CO^+$). Analysis: calculated for $C_{28}H_{19}N_3O_2$ (FW = 429.48): C (78.32), H (4.43), N (9.79); found: C (78.44), H (4.52), N (9.73).

b) With *meta*-methylbenzoyl chloride.

5-*meta*-methylbenzoyloxy-2,3-diphenylquinoxaline **15a**: recrystallized from cyclohexane. MP: 134-138 °C. ^1H NMR ($CDCl_3$): 8.10 (dd; 1 H; H_8); 7.78 (dd; 1 H; H_7); 7.62 (dd; 1H; H_6); $J_{6,7}$ = 7.7, $J_{6,8}$ = 1.3, $J_{7,8}$ = 8.5 Hz; phenyls at 7.45, 7.36 (m); *m*Me-phenyl: multiplets at 8.16, 7.57, 7.19; 2.47 (s; 3 H; Me). MS: 416 (94 %; M^+); 298 (24; M^+ - MeC_6H_3CO); 297 (16; M^+ - MeC_6H_4CO); 270 (13; 298 - CO); 269 (30; 297 - CO); 194 (15; 297 - C_6H_5CN); 166 (10; 194 - CO); 120 (63); 119 (100 %; $MeC_6H_4CO^+$).

2-(α-cyanobenzalimino)-N-benzoyl- N-*meta*-methylbenzoylaniline **14a**: recrystallized from methanol. MP: 153-160 °C. ^1H NMR: very complex pattern of lines between 7.1 and 8.1 ppm; 2.18 (s; 3 H; Me). ^{13}C NMR: quaternary carbons at 173.2, 173.1 (2 C=O); 144.8, 141.8 (diaminobenzene C_1, C_2); 138.5 (*m*Me-benzoyl C_3'); 134.9, 134.8 (benzoyl C_1, *m*Me-benzoyl C_1); 134.4, 133.5 (benzalimino C=N, C_{Ar}); 110.5 (CN); CH at 133.3; 132.4; 130.0; 129.6; 129.3 (2 C); 129.2; 129.1 (2 C); 128.8; 128.6 (2 C); 128.5 (2 C); 128.4; 126.3; 119.9; CH_3 at 21.2. MS: 443 (11 %; M^+); 312 (7); 298 (7); 207 (6); 119 (100 %; $CH_3C_6H_4CO^+$); 105 (50); 91 (28).

c) With *para*-nitrobenzoyl chloride.

5- and 6- *para*-nitrobenzoyloxy-2,3-diphenylquinoxaline **15b**. The two esters were not separated, but the ^1H NMR spectrum was clear enough to allow the following assignments: 5-*para*-nitrobenzoyloxy-2,3-diphenylquinoxaline: 8.14 (dd; 1 H; H_8); 7.81 (dd; 1 H; H_7); 7.64 (dd; 1 H; H_6); $J_{6,7}$ = 7.6, $J_{6,8}$ = 1.3, $J_{7,8}$ = 8.5 Hz. 6-*para*-nitrobenzoyloxy-2,3-diphenylquinoxaline: 8.26 (d; 1 H; H_8); 8.07 (d; 1 H; H_5); 7.66 (dd; 1 H; H_6); $J_{5,7}$ = 2.6, $J_{7,8}$ = 9.1 Hz. The phenyls gave multiplets at 7.52, 7.32 (m); the 4-nitrobenzoyl at 8.42.

2-(α-cyanobenzalimino)-N-benzoyl- N-*para*-nitrobenzoylaniline **14b**: recrystallized from methanol. MP: 86-87 °C. ^1H NMR: very complex pattern of lines between 7.1 and 8.2 ppm. ^{13}C NMR: quaternary C at 172.2, 171.1 (2 C=O); 149.6 (C-NO_2); 144.6, 142.2 (diaminobenzene C_1, C_2); 140.6 (nitrobenzoyl C_1); 133.7 (benzoyl C_1); 133.2, 133.1 (benzalimino C=N, C_{Ar}); 110.3 (CN). CH at 133.7; 133.0; 129.7; 129.5 (2 C); 129.4 (3 C); 129.1 (2 C); 128.8; 128.7 (2 C); 128.4 (2 C); 123.6 (2 C); 120.0.

d) With pivaloyl chloride.

5-Pivaloyloxy-2,3-diphenylquinoxaline **15c**: recrystallized from pentane. MP: 125-130 °C. ^1H NMR ($CDCl_3$): 8.05 (dd; 1 H; H_8); 7.73 (dd; 1 H; H_7); 7.45 (dd; 1 H; H_6); $J_{6,7}$ = 7.4, $J_{6,8}$ = 1.2, $J_{7,8}$ = 8.4 Hz; 1.48 (s; 9 H; ^{t}Bu); phenyls at 7.48, 7.33 (m).MS: 382 (14 %; M^+); 299 (23); 298 (100 %; M^+ - C_4H_8CO).

2-(α-cyanobenzalimino)-N-benzoyl- N-pivaloylaniline **14c**: recrystallized from methanol. MP: 136-139 °C. ^1H NMR: very complex pattern of lines between 7.1 and 8.1 ppm. 1.27 (s; 9 H; ^{t}Bu). MS: 409 (9 %; M^+); 325 (15); 298 (47); 194 (90); 105 (100 %, $C_6H_5CO^+$).

HPLC determinations.

Elution with methanol-water 85:15 (1.5 mL/min) on 5 µ RoSil C_{18}D (RSL-Alltech) gave the following retention times (in minutes): benzoyl cyanide 2.76; 2,3-diphenylquinoxaline-N-oxide 3.54; 6-hydroxy-2,3-diphenylquinoxaline 3.86; 5-hydroxy-2,3-diphenylquinoxaline 4.43; 6-cyano-2,3-diphenylquinoxaline 5.22; 2,3-diphenylquinoxaline 5.66; 5-cyano-2,3-diphenylquinoxaline 8.50; 5-chloro-2,3-diphenylquinoxaline 8.75; 6-chloro-2,3-diphenylquinoxaline 9.50. With hexane-ethyl acetate 80:20 on 5 µ RSL-CN (RSL-Alltech): 5-benzoyloxy-2,3-diphenylquinoxaline 2.42; 5-cyano-2,3-diphenylquinoxaline 2.86. With methanol-water 60:40 (1.0 mL/min) on 5 µ RoSil C_{18}D: 2-hydroxyquinoxaline 4.47; 5-cyanoquinoxaline 5.02; quinoxaline-N-oxide 4.59; 6-cyanoquinoxaline 5.72; quinoxaline 6.50; 2-cyanoquinoxaline 8.16; 5-chloroquinoxaline 8.57; benzoyl cyanide 12.46; 6-chloroquinoxaline 13.65; 2-chloroquinoxaline 14.54; with methanol-water 75:25 the corresponding retention times were definitely shorter, but in the same order.

Acknowledgements. S. H. thanks the IRSIA (Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture) for a doctoral fellowship. We express our thanks to Professor M. Begtrup for stimulating discussions about the mechanism of the ring-opening reaction. The HPLC analyses were performed by Dr F. Geerts-Evrard; the NMR spectra were recorded and skillfully scrutinized by Dr R. Ottinger; we are grateful to Dr M. Kaisin for his invaluable help in the analysis of the mass spectra recorded by Mr C. Moulard; this work was supported in part under contract n° 1.5.100.87F of the National Fund for Scientific Research.

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