α-Iminonitriles (Imidoyl Cyanides); Their Preparation using Phase-Transfer Catalysis and Their Reductive Dimerization

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We became interested in preparing α-iminonitriles ("imidoyl cyanides", **2**) in order to continue our studies[1] on the effect of electronegative substituents on the reductive dimerization of Schiff bases. In addition, these compounds are interesting synthetic intermediates since they possess two nitrogen-containing functional groups at different levels of oxidation[2].

α-Iminonitriles of the type **2** have been prepared by the manganese dioxide oxidation of α-aminonitriles[3], by the reaction of nitrosoarenes with phenylacetonitriles[4] or with benzylpyridinium salts[5], and by the reaction of cyanogen bromide with Schiff bases[6]. The earliest and seemingly most convenient procedure[7] involved the reaction of imidoyl chlorides (**1**) in petroleum ether with aqueous potassium cyanide.

In our hands, the procedure **1**→**2** failed since hydrolysis of the imidoyl chloride (**1**) predominated and the low solubility of **1** in petroleum ether caused operational difficulties. A substantial improvement in this procedure was effected by introducing a phase-transfer catalyst and changing the solvent to chloroform (see Table 1). Of the phase-transfer catalysts examined using *N*-phenylbenzimidoyl chloride, benzyltriethylammonium chloride and hexadecyltrimethylammonium bromide were the most effective. The latter was used to prepare successfully several substituted α-iminonitriles (**2**). Since benzimidoyl chlorides (**1**) are readily prepared from *N*-substituted benzamides and these in turn are readily available from a wide choice of aromatic carboxylic acids and amines, this procedure is both versatile and simple for the synthesis of α-iminonitriles of the type **2** (α-phenyliminophenylacetonitriles).

Exploration of the reduction of compounds **2** with alkali metals revealed a new route to benzil dianil and its substituted analogues **4**. Thus, treatment of **2** (X = H) with sodium

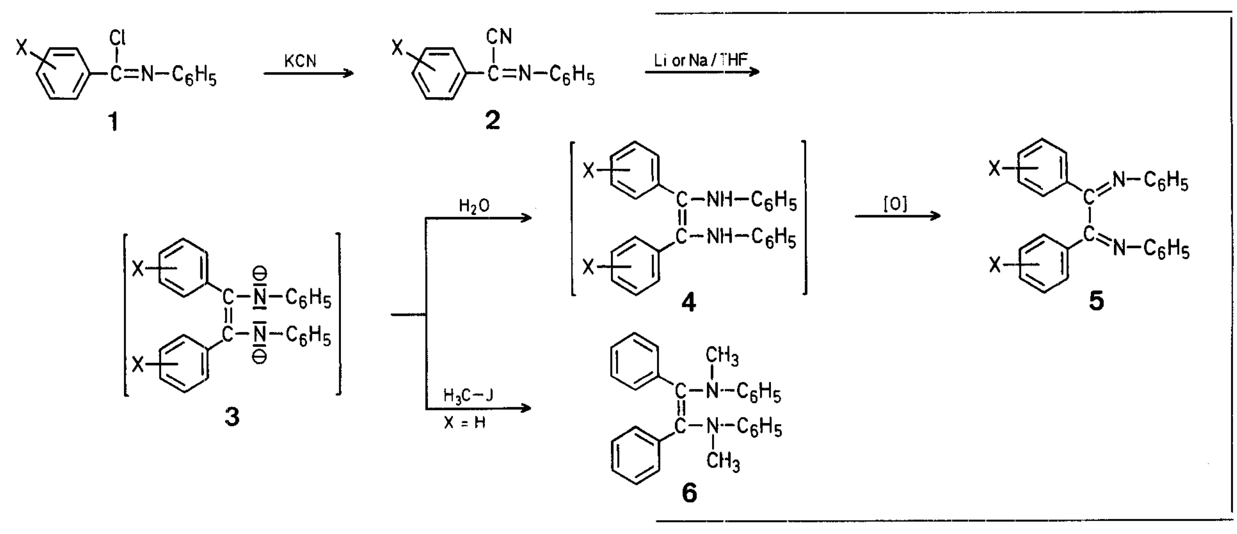

Table 1. Preparation of α-Iminonitriles (**2**)

X	Catalyst	Yield [%]	m.p.	Molecular formula or m.p. reported[11]
H	—	9		
	$(n\text{-}C_4H_9)N^{\oplus}\ Cl^{\ominus}$	41		
	$C_6H_5{-}CH_2{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	56		
	$C_6H_5{-}CH_2{-}N^{\oplus}(C_2H_5)_3\ Cl^{\ominus}$	86		
	$n\text{-}C_{16}H_{33}{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	88	71–71.5°	71–72°
4-CH_3	$n\text{-}C_{16}H_{33}{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	68	99–99.5°	97–99°
4-Cl	$n\text{-}C_{16}H_{33}{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	80	108–108.5°	107–108°
2-Cl	$n\text{-}C_{16}H_{33}{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	47	62–63°	$C_{14}H_9ClN_2$[a] (240.7)
3-Br	$n\text{-}C_{16}H_{33}{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	93	96–97°	$C_{14}H_9BrN_2$[b] (285.1)
4-OCH_3	$n\text{-}C_{16}H_{33}{-}N^{\oplus}(CH_3)_3\ Br^{\ominus}$	79	114.5–115.5°	118–119°

[a]

	C	H	N
calc.	C 69.86	H 3.77	N 11.64
found	70.08	4.01	11.65

M.S.: *m/e* (relative intensity) = 240 (M^+, 39), 219 (22), 214 (24), 205 (37), 88 (22), 77 (100).

I.R. ($CHCl_3$): ν_{max} = 2240 (CN); 1615 (C=N) cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 8.0–6.5 ppm (m, 9H).

[b]

	C	H	N
calc.	C 58.97	H 3.18	N 9.83
found	58.99	3.24	9.78

M.S.: *m/e* (relative intensity) = 286 (M^+, 66), 285 (31), 284 (68), 205 (26), 77 (100).

I.R. ($CHCl_3$): ν_{max} = 2225 (CN); 1610 (C=N) cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$): δ = 8.4–7.1 ppm (m, 9H).

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Table 2. Reaction of α-Iminonitriles (**2**) with Lithium or Sodium

X	Alkali metal	Reaction temperature	Reaction of **3** with	Product	Yield [%]	m.p.	m.p. reported
H	Li	22°	H_2O	**5**	87	142–143°	143–145°[8]
	Li	22°	CH_3J	**6**	87	170–172°	173–173.5°[8]
	Na	22°	H_2O	**5**	55		
	Na	22° (in ether)	H_2O	**5**	78		
	Na	−78°	H_2O	**5**	69		
	Na	22°	CH_3J	**6**	39		
	Na	−78°	CH_3J	**6**	77		
4-OCH_3	Na	22°	H_2O	**5**	67	154–156°	150–151°[10]
4-CH_3	Na	22°	H_2O	**5**	29	149–150°	147–148°[10]
4-CH_3	Na	22° (in ether)	H_2O	**5**	59		
4-CH_3	Li	22°	H_2O	**5**	63		

in tetrahydrofuran resulted in dimerization with loss of the cyano group to form dianion **3**. This dianion has been examined[8] before and as reported it is alkylated with methyl iodide to give the diamine **6**. Protonation gives initially **4** which oxidizes readily during isolation[8, 9, 10] to benzil dianil **5** (X=H). Several experiments were conducted (see Table 2) to optimize the yield of benzil dianil. A lower temperature of reduction or a change of solvent to diethyl ether improved yields in the case of reductions with sodium. Reduction with lithium was more satisfactory than sodium at 22°. This dimerization procedure was successfully extended to the 4-methoxy analogue and to the 4-methyl analogues. Thus, the reductive dimerization supplements existing synthetic routes[9,10] to benzil dianil and its derivatives.

The *N*-phenylbenzamides were prepared from the appropriate benzoyl chlorides and aniline and these were converted to the corresponding imidoyl chlorides (**1**) using a slight excess of thionyl chloride.

α-Phenyliminophenylacetonitriles (2); General Procedure:
To a solution of the *N*-phenylbenzimidoyl chloride (**1**; 0.007–0.01 mol) in chloroform (50 ml), a solution of potassium cyanide (3 equiv) and hexadecyltrimethylammonium bromide (1–1.5 mmol) in a minimum amount of water is added. The mixture is stirred for 24 h, the chloroform layer separated, washed with water, and dried with magnesium sulfate. This solution is evaporated onto silica gel (1 g) which is then added to the top of a silica gel column (75 g). Elution is effected with petroleum ether (30–60°) containing 5% ethyl acetate and the yellow band of **2** collected. The crude product is recrystallized from ethanol.

Reductive Dimerization of α-Phenyliminophenylacetonitriles (2):
A solution of the α-iminonitrile (**2**; 2.5 mmol) in tetrahydrofuran (75 ml; dried and distilled over lithium aluminum hydride) is stirred under nitrogen with lithium (0.07 g, 10 mg-atom) or sodium (0.23 g, 10 mg-atom) for 24 h using the special apparatus previously described[12]. After removing the excess alkali metal, the solution is cooled to −78° and water (2 ml) or methyl iodide (0.36 g, 2.5 mmol) is injected through a septum. The solution is allowed to warm to 20°, then diluted with water, extracted with chloroform, the chloroform extracts dried with magnesium sulfate, and evaporated. Chromatography on silica gel with benzene graded to benzene plus 25% ethyl acetate gives *benzil anils* (**5**) or *1,2-bis[*N*-methylanilino]-1,2-diphenylethylene* (**6**).

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