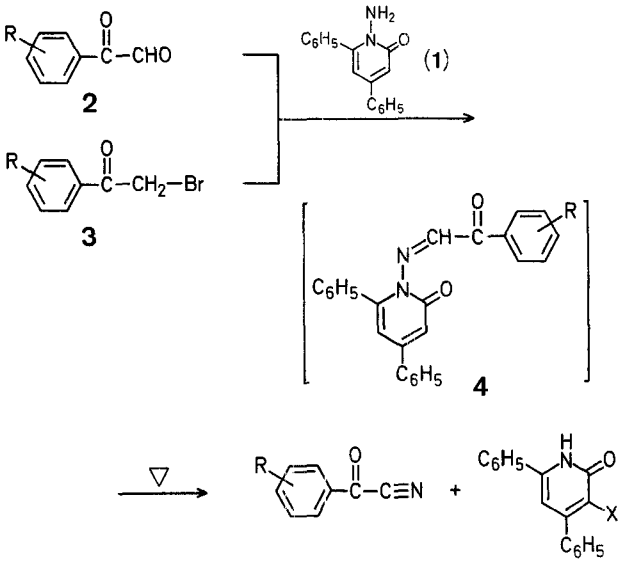

2 3 (1) 4 5 6 X = H, Br

A Convenient One-Step Synthesis of Aroyl Cyanides from Arylglyoxals or Phenacyl Bromides

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While the conversion of acyl halides into acyl cyanides (2-oxoalkanenitriles) is a well-known reaction[1,2,3] no generally useful procedure has been previously reported for the conversion of arylglyoxals or phenacyl halides into aroyl cyanides. Recently, we have shown that 1-amino-4,6-diphenyl-2-pyridone (**1**) is a useful reagent for the preparation of nitriles from aldehydes[4,5]. As a novel extension of this work, we have developed a one-step method which appears to be of considerable utility for the conversion of arylglyoxals (**2**) or phenacyl bromides (**3**) into aroyl cyanides (**5**).

The preparation of the aroyl cyanides **5** was achieved either by condensation of the aminopyridone **1** with arylglyoxals (**2**) in hot toluene (Method A), or by reaction of **1** with phenacyl bromides (**3**) in hot dimethyl sulfoxide (Method B).

The reaction presumably proceeds via formation of the aldimine **4** as an intermediate, which under the reaction conditions is thermolyzed to give a mixture of products **5** and **6** from which the desired product **5** can be extracted with ether.

The reaction appears to be quite general; it proceeds satisfactorily in the case of the representative derivates examined. Thus, phenylglyoxal is almost quantitatively converted into benzoyl cyanide. Phenacyl bromides are converted to the corresponding aroyl cyanides in yields of 70–75%. However, attempts to apply the method to the preparation of aliphatic acyl cyanides did not give satisfactory yields. The present method provides an alternative synthesis of aroyl cyanides without the use of cyanide ion.

Aroyl Cyanides (5, Arylglyoxylonitriles); General Procedures:

Method A, from Arylglyoxals: 1-Amino-4,6-diphenyl-2-pyridone (**1**; 1.32 g, 5 mmol) is dissolved in dry toluene (25 ml). The arylglyoxal (5 mmol) is added, the mixture is stirred at 110 °C for 6 h, and then allowed to stand at room temperature. The solvent is removed under reduced pressure. The residue is extracted with ether (3 × 20 ml) and the remaining solid recrystallized from ethanol to give 4,6-diphenyl-2-pyridone (**6**, X = H); m.p. 208 °C (Ref.[10], m.p. 204–208 °C). The ethereal extracts are dried with magnesium sulfate and evaporated in vacuo to leave the crude product. Purification is achieved by crystallization from pentane.

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I.R. (CCl_4) of all aroyl cyanides: $\nu = 2210–2230$ (C≡N), 1670–1700 cm^{-1} (—CO—).

Method B, from Phenacyl Bromides: A solution of the phenacyl bromide (5 mmol) in dimethyl sulfoxide (15 ml) is stirred at room temperature for 10 h. 1-Amino-4,6-diphenyl-2-pyridone (1.32 g, 5 mmol) is then added, the reaction mixture heated at 100 °C for 6 h, and poured into ice/water (50 ml). The precipitate is collected by filtration and extracted with ether (3 × 30 ml). The remaining solid is recrystallized from ethanol to give 3-bromo-4,6-diphenyl-2-pyridone (**6**, X = Br); m.p. 285 °C (Ref.[11], m.p. 287 °C). The ethereal extract is dried with magnesium sulfate and evaporated in vacuo to leave the crude product which is recrystallized from pentane.

Table. Aroyl Cyanides (**5**) from Aryl Glyoxals (**2**) or Phenacyl Bromides (**3**)

5	R	Yield[a] [%]		m.p.[b] [°C]	
		Method A	Method B	found	reported
a	H	97	70	32°	32–33°[6]
b	4-Br	93	75	67°	65–66°[2]
c	3-NO_2	90	70	34°	33–34°[3]
d	4-Cl	92	73	40°	40–41°[7]
e	4-OCH_3	95	71	59°	58–59°[8]
f	4-CH_3	86	70	48°	49°[9]

[a] Yield of recrystallized product.
[b] Uncorrected.

Received: February 25, 1980

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0039-7881/80/1032-0845 $ 03.00