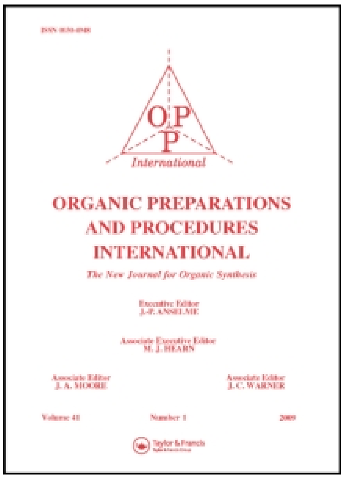

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT ONE-STEP SYNTHESIS OF AROYL CYANIDES FROM AROMATIC ALDEHYDES

Suk-Ku Kang[a]; Houng-Kyu Sohn[a]; Sung-Gyu Kim[a]
[a] Department of Chemistry, Natural Science Campus, Sung Kyun Kwan University, Suwon, KOREA

To cite this Article Kang, Suk-Ku , Sohn, Houng-Kyu and Kim, Sung-Gyu(1989) 'A CONVENIENT ONE-STEP SYNTHESIS OF AROYL CYANIDES FROM AROMATIC ALDEHYDES', Organic Preparations and Procedures International, 21: 3, 383 — 385

To link to this Article: DOI: 10.1080/00304948909356407

URL: http://dx.doi.org/10.1080/00304948909356407

2-Phenyl-4H-naphtho[2,1-e]-1,3,4-oxadiazine-6-ol. General Procedure.- 4-Acetyl-2-aryl-4H-naphtho[2,1-e]-1,3,4-oxadiazine-6-ol acetate (0.01 mol) was refluxed in 0.5% alcoholic sodium hydroxide solution on a steam bath for 30 min. The reaction mixture was cooled to 0° and neutralised with cold 1% HCl. The solid which separated was collected and crystallized from suitable solvents (Table 1).

REFERENCES

1. M. S. Rao, V. Rajeswar Rao and T. V. Padmanabha Rao, Sulfur Letters, 4, 19 (1985).
2. M. S. Rao, R. Ashok Kumar, V. Rajeswar Rao, K. Rahava Raju, S. M. Reddy and T. V. Padmanabha Rao, Ind. J. Chem., 23B, 483 (1984).
3. M. S. Rao, V. Rajeswar Rao and T. V. Padmanabha Rao, Org. Prep. Proced. Int., 18, 104 (1986).
4. M. S. Rao, V. Rajeswar Rao and T. V. Padmanabha Rao, ibid., Submitted for publication.

****

A CONVENIENT ONE-STEP SYNTHESIS OF AROYL CYANIDES FROM AROMATIC ALDEHYDES

Submitted by (11/16/88)

Suk-Ku Kang*, Houng-Kyu Sohn and Sung-Gyu Kim

Department of Chemistry, Sung Kyun Kwan University
Natural Science Campus, Suwon 440-746, KOREA

Acyl cyanides are versatile and important synthetic intermediates which have been utilized in a variety of transformations.[1] The acyl cyanides have been generally prepared by the reaction of acid halides with a variety of heavy metal (copper, silver or thallium) cyanides at high temperature.[2] Some modifications with cyanotrimethylsilane,[3] tributyltin cyanide,[4] potassium cyanide with ultrasound,[5] sodium cyanide with a phase-transfer catalyst,[6] or impregnated on Amberlite XAD resins[7] have been reported. Recently, oxidation of aromatic cyanohydrins to acyl cyanides catalyzed by $RuCl_2(PPh_3)_3$ has been described.[8] We now report a one-step method for the direct conversion of aromatic or heteroaromatic aldehydes 1 to the corresponding acyl cyanides 2.

$$\underset{\underline{\text{1a-d}}}{\text{RCHO}} \xrightarrow[\text{CrO}_3]{\text{KCN,TMSCl}} \underset{\underline{\text{2a-d}}}{\text{RCOCN}}$$

In method A (Eq. 1), the aromatic aldehyde 1 in dichloromethane was first allowed to react with two equiv. of potassium cyanide and one equiv. of trimethylsilyl chloride and stirred for 1 hr. Two equiv. of chromic anhydride was then added and the mixture was stirred until all the aldehyde had been consumed (ca. 6 hrs). The reaction presumably proceeds via formation of the O-trimethylsilylcyanohydrin as intermediate, which under the reaction conditions is oxidized to the aroyl cyanide. The yields of aroyl cyanides 2 are moderate to good (Table 1). Even with less reactive aromatic aldehydes such as 4-methoxybenzaldehyde 1b, the pure aroyl cyanide 2b was obtained without formation of the dimer as a by-product.

This synthetic method is considered to be important as a one-carbon homologation reaction.

TABLE 1. Aroyl Cyanides 2 from Aromatic Aldehydes 1

R	No	Yield (%)	Yield[a,g] (%)	mp. (°C)	lit. mp. (°C)
C_6H_5	2a	72	66[f]	35-36	32-33[b]
p-$MeOC_6H_4$	2b	67	57	62-63	58-59[c]
p-ClC_6H_4	2c	63	-	28-29	25[d]
2-Furyl	2d	66	63	43-44	40-41[e]

a) Yields have not been optimized. b) Ref. 9. c) Ref. 10. d) ref. 11. e) Ref. 12.
f) Yield is 63% without addition of acetic anhydride. g) Yield by method B.

Alternatively (method B), aromatic acyl cyanide 2 can be conveniently prepared from the corresponding aldehydes 1 by treatment with potassium cyanide, pyridinium p-toluenesulfonate (PPTS) and pyridinium chlorochromate (PCC) in the presence of acetic anhydride (Eq. 2).

$$\underset{\underline{\text{1a-c}}}{\text{RCHO}} \xrightarrow[\text{PCC, (Ac}_2\text{O)}]{\text{KCN, PPTS}} \underset{\underline{\text{2a-c}}}{\text{RCOCN}}$$

Thus, the aromatic aldehyde 1 in dichloromethane was allowed to react with two equiv. of potassium cyanide and one equiv. of PPTS followed by one equiv. of PCC. The reaction mixture was stirred for ~1 hr. If 3 equiv. of acetic anhydride are added after the PCC oxidation, the yields could be increased about 10% for 2b. The reaction presumably proceeds via formation of the cyanohydrin, which under the reaction conditions is oxidized to the aroyl cyanide. However, attempts to apply these methods to aliphatic aldehydes did not give the corresponding acyl cyanides.

EXPERIMENTAL SECTION

Typical Procedures. Benzoyl Cyanide 2a. Method A.- To a stirred solution of benzaldehyde 1a (1.20 g, 11.3 mmol) in dichloromethane (60.0 ml) was added potassium cyanide (1.48 g, 22.6 mmol) followed by trimethylsilyl chloride (1.23 g, 11.3 mmol). The mixture was stirred at room temperature for 1 hr. After that time, was added chromic anhydride (2.26 g, 22.6 mmol) and stirring was continued for 6 hrs. The reaction mixture was washed with water and then the organic layer was evaporated in vacuo to give the crude benzoyl cyanide 2a. The crude product was further purified by chromatography on silica gel using n-hexane: dichloromethane (2:5) as eluent ($R_f = 0.78$) to afford the pure benzoyl cyanide 2a (1.06 g, 72%).

Method B.- To a stirred solution of benzaldehyde 1a(1.20 g, 11.3 mmol) in dichloromethane (50.0 ml) was added potassium cyanide (1.48 g, 22.6 mmol) and PPTS (2.83 g, 11.3 mmol) followed by PCC (2.43 g, 11.3 mmol) and acetic anhydride (3.46 g, 33.9 mmol) and stirred at room temperature for 1hr. The reaction mixture was washed with water and then the organic layer was evaporated in vacuo to give the crude benzoyl cyanide 2a. The crude product was purified as above to afford 0.96 g (66%) of the pure benzoyl cyanide 2a.

Acknowledgement.- We thank the Korea Science and Engineering Foundation for financial support. One of us (S-G. Kim) also thanks the Dae Woo Foundation for a postgraduate research scholarship.

REFERENCES

1. For a recent review, see S. Hunig and R. Schaller, Angew. Chem. Int. Ed. Engl., 21, 36 (1982).
2. a) J. F. Normant and C. Piechucki, Bull. Soc. Chim. Fr., 2402 (1975); b) J. V. Nef, Ann. Chem., 287, 307 (1985); c) E. C. Taylor, J. G. Andrade, K. C. John and A. McKillop, J. Org. Chem., 43, 2280 (1978).
3. K. Herrman and G. Simchen, Synthesis, 204 (1979).
4. M. Tanaka, Tetrahedron Lett., 21, 2959 (1980).
5. T. Ando, T. Kawata, J. Yamawaki and T. Hanafusa, Synthesis, 637 (1983).
6. K. E. Koenig and W. P. Weber, Tetrahedron Lett., 2275 (1974).
7. K. Sukata, Bull. Chem. Soc. Jpn., 60, 1085 (1987).
8. S.-I. Murahashi, T. Naota and N. Nakajima, Tetrahedron Lett., 26, 925 (1985).
9. a) T. A. Bither, W. H. Knoth, R. V. Lindsey, Jr. and W. H. Sharkey, J. Am. Chem. Soc., 80, 4151 (1958); b) J. W. Zubrick, B. I. Dunbar and H. D. Durst, Tetrahedron Lett., 71 (1975).
10. F. Asinger, A. Saus, H. Offermanns and H. D. Hahn, Ann., 691, 92 (1966).
11. A. Burger and E. D. Hornbarker, J. Am. Chem. Soc., 74, 5514 (1952).
12. E. Fischer and F. Brauns, Ber., 46, 892 (1913).

****