Tin(IV) Chloride-Catalyzed Preparation of Aroyl Cyanides from Aroyl Chlorides and Cyanotrimethylsilane[1]

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Acyl cyanides (2-oxoalkanenitriles) are generally prepared by the reaction of the acid chloride with silver[2], copper(I)[3], or mercury(II)[4] cyanides. The yields in these reactions are, however, generally only moderate. The reaction has also been performed with sodium cyanide under phase-transfer conditions[5] with some improvement in yield. Aliphatic acid chlorides react with cyanotrimethylsilane (slight excess) without solvent at 20-70 °C to give the corresponding 2-oxoalkanenitriles in moderate to good yields[6]; however, aroyl chlorides do not react with cyanotrimethylsilanes under these conditions. The reaction of benzoyl chloride with cyanotrimethylsilane under pyridine catalysis proceeds with introduction of two cyano groups to afford phenyltrimethylsiloxymalononitrile[7]. 4-Dimethylamino-1-naphthoyl cyanide has been prepared from 4-dimethylamino-1-naphthoyl chloride and cyanotrimethylsilane using zinc iodide as catalyst. In our studies we found that these reaction conditions were not of general scope and reactions with a variety of aroyl halides either fail or give only very low yields. In contrast, we have found that tin(IV) chloride catalyses the reaction extremely well with a wide variety of aroyl chlorides (**1**). The yields of aroyl cyanides (**2**) are good to excellent (Table 1). The reaction fails only with 4-nitrobenzoyl chloride, yielding 4-nitrobenzoic acid as the main product along with a small amount of isolable 4-nitrophenyltrimethylsiloxymalononitrile. The presently developed method is a good alternative to the synthesis of aroyl cyanides using the readily available cyanotrimethylsilane.

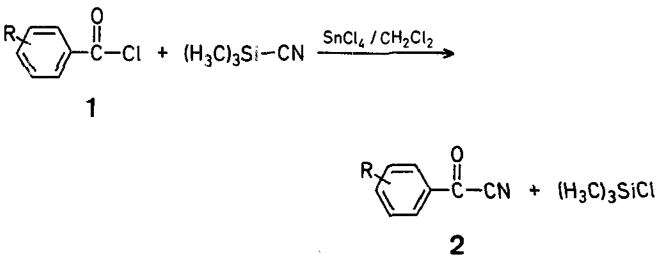

Table 1. Aroyl Cyanides (**2**) from Aryl Chlorides (**1**) and Cyanotrimethylsilane

2	R	Yield[a] [%]	m.p. or b.p./torr[b] [°C]	Molecular formula[c] or Lit. Data [°C]
a	H	91	b.p. 72-73°/0.15	b.p. 209-210°/760[9]
b	2-F	87	b.p. 85-87°/0.3	C_8H_4FNO (149.1)
c	3-F	46	b.p. 72-74°/0.25	C_8H_4FNO (149.1)
d	4-F	79	b.p. 46-48°/0.3	C_8H_4FNO (149.1)
e	4-Cl	81	m.p. 42°	m.p. 37-39°[9]
f	4-Br	85	m.p. 66-67°	m.p. 65-66°[10]
g	$4-OCH_3$	89	m.p. 59°	m.p. 58-60°[9]
h	$2-CH_3$	94	b.p. 89-90°/0.3	C_9H_7NO (145.15)
i	$3-CH_3$	91	b.p. 86-87°/0.7	C_9H_7NO (145.15)
j	$4-CH_3$	94	m.p. 49°	m.p. 49-49.5°[9]

[a] Yield of isolated product characterized by I.R., ^{1}H-N.M.R., and ^{13}C-N.M.R. data

[b] Melting and boiling points are uncorrected.

[c] The microanalyses of the new compounds were in satisfactory agreement with the calculated values: C, ±0.10; H, ±0.21; N, ±0.27; O, ±0.18.

Table 2. ^{13}C-N.M.R.-spectrometric Data of Compounds **2** ($CDCl_3/TMS_{int}$, 50 MHz, 24 °C)

2	R	C=O	C≡N	C-1	C-2	C-3	C-4	C-5	C-6	Others
a	H	167.7	112.5	133.0	130.2	129.3	136.6	129.3	130.2	
b	2-F	112.9	121.6 ($^2J_{C-F}$=7.4 Hz)	162.4 ($^1J_{C-F}$=267.2 Hz)	117.5 ($^2J_{C-F}$=20.5 Hz)	138.8 ($^3J_{C-F}$= 9.8 Hz)	132.2	125.1 ($^3J_{C-F}$=3.7 Hz)		
c	3-F	166.5	112.2	135.0 ($^3J_{C-F}$=7.4 Hz)	124.0 ($^2J_{C-F}$=22.0 Hz)	162.7 ($^1J_{C-F}$=251.5 Hz)	116.0 ($^2J_{C-F}$=23.2 Hz)	131.4 ($^3J_{C-F}$=8.5 Hz)	126.6 ($^4J_{C-F}$=2.5 Hz)	
d	4-F	165.2	112.4	129.7	133.2 ($^3J_{C-F}$=11.0 Hz)	116.9 ($^2J_{C-F}$=23.2 Hz)	168.2 ($^1J_{C-F}$=217.4 Hz)	116.9 ($^2J_{C-F}$=23.2 Hz)	133.2 ($^3J_{C-F}$=11.0 Hz)	
e	4-Cl	166.6	112.4	131.7	131.6	130.0	143.9	130.0	131.6	
f	4-Br	166.7	112.2	131.9	132.8	131.3	132.8	131.3	132.8	
g	$4-OCH_3$	165.9	113.0	126.6	133.1	114.9	166.6	114.9	133.1	OCH_3: 55.9
h	$2-CH_3$	168.3	113.2	131.1	142.6	126.6	135.5	132.6	134.7	CH_3: 21.7
i	$3-CH_3$	167.9	113.0	133.7	130.6	139.7	137.7	127.8	129.3	CH_3: 21.1
j	$4-CH_3$	167.3	112.8	131.1	130.5	130.2	148.8	130.2	130.5	CH_3: 22.1

Aroyl Cyanides (2); General Procedure:
To a stirred solution of the aroyl chloride **1** (20 mmol) and cyanotrimethylsilane (2.282 g, 21 mmol) in dry dichloromethane (50 ml) under nitrogen at room temperature is added tin(IV) chloride (0.5 ml). Stirring is continued for 2 h. The color of the solution gradually changes from initial light yellow to dark brown. After the reaction, the mixture is quenched with ice-cold water (150 ml) and extracted with dichloromethane (2 x 150 ml). The dichloromethane layer is washed with cold water (2 x 150 ml), dried with magnesium sulfate, and evaporated to provide the crude aroyl cyanide **2** which is further purified by recrystallization or distillation.

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