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A NEW APPROACH TO ARYLMALONONITRILES

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Arylmalononitriles were prepared from the corresponding benzoyl chlorides by three reaction steps . Treatment of the starting substances with cyanotrimethylsilane in the presence of pyridine gave dicyanotrimethylsiloxymethylbenzenes, which were transformed into chlorodicyanomethylbenzenes with POCl₃-pyridine in the second step. Finally, reduction of chlorodicyanomethylbenzenes with Zn-CH₃CO₂H afforded arylmalononitriles.

Arylmalononitriles are useful intermediates particularly for the synthesis of highly dipolar guinodimethanes, which have been studied on their unusual electronic properties and reactivities (Scheme 1).¹⁾ To date, various



Scheme 1.

preparative procedures of arylmalononitriles have been reported. These synthetic methods were divided into two classes. One of the methods is substitution of aryliodide with malononitriles in the presence of proper catalysts.²⁾ The other is cyanation of phenylacetonitriles with the use of such cyanation reagents as cyanogen chloride, N-cyano-N-methylaniline or 2-chlorobenzylthiocyanate.³⁾ Recently, cyanotrimethylsilane has been employed as the useful cyanation reagent for aldehydes and ketones.⁴⁾ Lidy and Sundermeyer reported that the reaction of benzoyl chloride with this reagent gave dicyanotrimethylsiloxymethylbenzene,⁵⁾ which may be used as a precursor for phenylmalononitrile.

We report here a new approach to arylmalononitriles from the corresponding benzoyl chlorides in the following sequence (Scheme 2). Benzoyl chloride derivatives (<u>1a-1g</u>) were treated with cyanotrimethylsilane in the presence of pyridine at 120 °C to give dicyanotrimethylsiloxymethylbenzenes (<u>2a-2g</u>) in good yields. Chlorination of the compounds <u>2a-2g</u> with POCl₃-pyridine at room temperature gave chlorodicyanomethylbenzenes (<u>3a-3g</u>). The compounds <u>3a-3g</u> thus obtained were reduced with zinc dust and acetic acid at room temperature to arylmalononitriles (<u>4a-4g</u>).



A typical experimental procedure is as follows. A mixture of 4chlorobenzoyl chloride 1c (0.88 g, 5.0 mmol), cyanotrimethylsilane (1.47 ml, 11.0 mmol) and pyridine (0.10 ml, 1.24 mmol) was heated at 120 °C under nitrogen atmosphere for 6.5 h. After concentration of the reaction mixture, the residue was distilled under reduced pressure to give 1.05 g of 1-chloro-4-dicyanotrimethylsiloxymethylbenzene 2c as colorless oil in 79% yield [2c: bp 73-74 °C $(0.14 \text{ Torr}); {}^{1}\text{H-NMR(CDCl}_{3})$ δ 7.64-7.62, 7.50-7.48(AA'BB' 4H), 0.38(s 9H); IR(neat) 2250, 1260 cm⁻¹. Found: C, 54.19; H, 5.11; N, 10.59%. Calcd for C12H13N2OSiCl: C, 54.43; H, 4.95; N, 10.58; Cl, 13.39%]. A mixture of 1chloro-4-dicyanotrimethylsiloxymethylbenzene 2c (0.64 g, 2.42 mmol), POCl₃ (2.3 ml, 25 mmol) and pyridine (0.20 ml, 2.47 mmol) was stirred at room temperature for 17 h. To the reaction mixture was added methylene chloride. After usual work-up, the products were purified by silica gel column chromatography to obtain 0.45 g of 1-chloro-4-chlorodicyanomethylbenzene <u>3c</u> in 93% yield [<u>3c</u>: mp 74-75 °C (sublimated under reduced pressure); ¹H-NMR (CDCl₃) δ 7.73, 7.55 (A₂B₂) like pattern, 4H); IR (Nujol) 2250 cm⁻¹. Found: C, 51.42; H, 2.11; N, 13.16; Cl, 33.48%. Calcd for C₉H₄N₂Cl₂: C, 51.22; H, 1.91; N, 13.27; Cl,

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33.60%]. To a solution of 1-chloro-4-chlorodicyanomethylbenzene $\underline{3c}$ (0.12 g, 0.57 mmol) in acétic acid (1.0 ml) was added zinc dust (0.1 g, 1.53 mmol) at one time. After stirring for 2 min, methylene chloride was added and filtered. After usual work-up, the crude product was chromatographed on silica gel with methylene chloride to give 0.10 g of 1-chloro-4-dicyanomethylbenzene $\underline{4c}$ in 99% yield [$\underline{4c}$: mp 70.5-71 °C (recrystallized from EtOH) (Lit.²⁾ 68-69°C); ¹H-NMR (CDCl₃) δ 7.52-7.45 (AA'BB' 4H), 5.06 (s 1H); IR (Nujol) 2250 cm⁻¹].

The yields and properties of other arylmalononitriles and their precursors were summarized in Table 1. In the case of the chlorination of 2g, 4-methoxy-benzoyl cyanide was obtained in 38% yield as side product.

Compound		Yield of $2/$ %	Yield of $3/$ %	Yield of <u>4</u> /%
	R	(Bp θ _b /°C, Torr)	(Bp $\theta_{\rm b}$ /°C, Torr or Mp $\theta_{\rm m}$ /°C)	(Mp 0 _m /°C)
a)	н	81	70	80
		(66.5-67, 0.2)	(30-30.5, 0.15) ^{b)}	(65.5-66.5)
b)	o-Cl	74	84	79
		(85-86, 0.15)	(68-69)	(63.5-64)
c)	p-Cl	79	93	99
		(73-74, 0.14)	(74-75)	(70,5-71)
d)	o-CH ₃	74	70	91
		(69-69.5, 0.2)	(41-43, 0.17) ^b)	(42-42.5)
e)	p-CH3	69	72	73
		(70-71.5, 0.15)	(41-44, 0.18) ^{b)}	(55.5-56.5)
f)	p-Br	75	72	73
		(85.5-86, 0.12)	(90.5-91)	(86.5-87.5)
g)	p-OCH ₃	77	20	70
		(88-88.5, 0.15)	(59-60)	(67-69)

Table 1. Yields and properties of arylmalononitriles and their precursors^a)

- a) New compounds <u>1b-1g</u> and <u>2a-2g</u> gave satisfactory elemental analysis and spectral data.
- b) molecular distillation ; bath temperatures are shown.

In this approach, it may be notified that all the materials used are commercially available and relatively safe and that all the reaction conditions are mild.

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