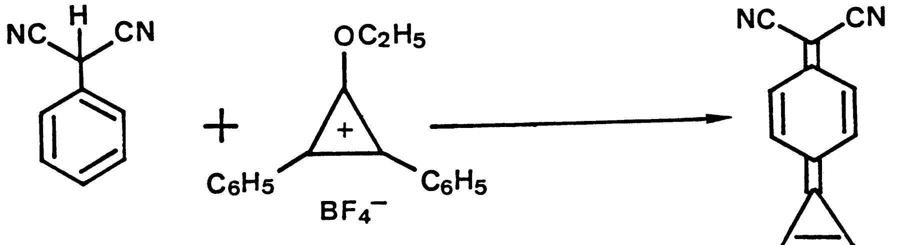
CHEMISTRY LETTERS, pp. 685-688, 1985.

A NEW APPROACH TO ARYLMALONONITRILES

Shunro YAMAGUCHI,* Hisashi ARAKI, and Terukiyo HANAFUSA
The Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka, Ibaraki, Osaka 567

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 $POCl_3$-pyridine in the second step. Finally, reduction of chlorodicyanomethylbenzenes with $Zn-CH_3CO_2H$ afforded arylmalononitriles.

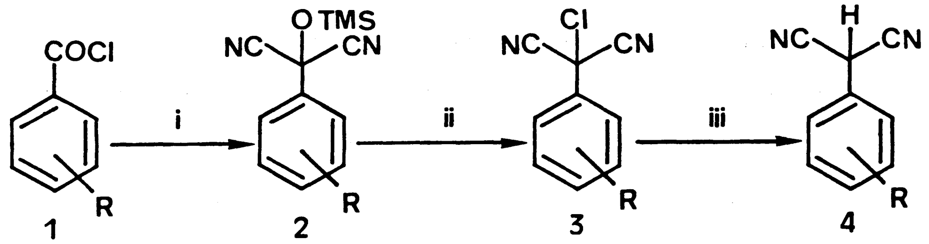
Arylmalononitriles are useful intermediates particularly for the synthesis of highly dipolar quinodimethanes, which have been studied on their unusual electronic properties and reactivities (Scheme 1).[1] To date, various preparative procedures of arylmalononitriles have been reported. These synthetic 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 dicyanotrimethyl-



Scheme 1.

siloxymethylbenzene,[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 (1a-1g) were treated with cyanotrimethylsilane in the presence of pyridine at 120 °C to give dicyanotrimethylsiloxymethylbenzenes (2a-2g) in good yields. Chlorination of the compounds 2a-2g with $POCl_3$-pyridine at room temperature gave chlorodicyanomethylbenzenes (3a-3g). The compounds 3a-3g thus obtained were reduced with zinc dust and acetic acid at room temperature to arylmalononitriles (4a-4g).



R; a) H b) o-Cl c) p-Cl d) o-CH_3 e) p-CH_3 f) p-Br g) p-OCH_3

i) TMS CN, C_5H_5N ii) $POCl_3$, C_5H_5N iii) Zn, CH_3CO_2H

Scheme 2.

A typical experimental procedure is as follows. A mixture of 4-chlorobenzoyl 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 Torr); ^{1}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 $C_{12}H_{13}N_2OSiCl$: C, 54.43; H, 4.95; N, 10.58; Cl, 13.39%]. A mixture of 1-chloro-4-dicyanotrimethylsiloxymethylbenzene 2c (0.64 g, 2.42 mmol), $POCl_3$ (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 3c in 93% yield [3c: mp 74-75 °C (sublimated under reduced pressure); ^{1}H-NMR ($CDCl_3$) δ 7.73, 7.55 (A_2B_2 like pattern, 4H); IR (Nujol) 2250 cm^{-1}. Found: C, 51.42; H, 2.11; N, 13.16; Cl, 33.48%. Calcd for $C_9H_4N_2Cl_2$: C, 51.22; H, 1.91; N, 13.27; Cl, 33.60%]. To a solution of 1-chloro-4-chlorodicyanomethylbenzene 3c (0.12 g, 0.57 mmol) in acetic 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 4c in 99% yield [4c: mp 70.5-71 °C (recrystallized from EtOH) (Lit.[2] 68-69°C); ^{1}H-NMR ($CDCl_3$) 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-methoxybenzoyl cyanide was obtained in 38% yield as side product.

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

Compound R	Yield of 2/% (Bp θ_b/°C, Torr)	Yield of 3/% (Bp θ_b/°C, Torr or Mp θ_m/°C)	Yield of 4/% (Mp θ_m /°C)
a) H	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-CH_3	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)

a) New compounds 1b-1g and 2a-2g 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.

References

1) T. Eicher and K. Eiglmeier, Chem. Ber., 104, 605 (1971);
R. Gompper, H. Wagner, and E. Kutler, ibid., 101, 4123 (1968);
R. Gompper and H. Wagner, Tetrahedron Lett., 1968, 165.
2) M. Uno, K. Seto, and S. Takahashi, J. Chem. Soc., Chem. Comm., 1984, 932;
H. Suzuki, T. Kobayashi, and A. Osuka, Chem. Lett., 1983, 589;
H. D. Hartzler, J. Am. Chem. Soc., 86, 2174 (1964).
3) W. A. Davis and M. D. Cava, J. Org. Chem. 48, 2774 (1983);
J. K. Williams, E. L. Martin, and W. A. Sheppard, ibid., 31, 919 (1966);
P. B. Russel and G. H. Hitchings, J. Am. Chem. Soc., 74, 3443 (1952);
J. C. Hessler, ibid., 32, 119 (1904).
4) D. A. Evans, G. L. Carroll, and L. K. Tuesdale, J. Org. Chem., 39, 914 (1974).
5) W. Lidy and W. Sundermeyer, Tetrahedron Lett., 1973, 1449; Chem. Ber., 106, 587 (1973).

(Received January 25, 1985)