A Convenient Procedure for the Preparation of Bis(dialkylamino)malononitriles

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Abstract: *N*,*N*,*N*′,*N*′-Tetraalkylchloroformamidinium chlorides react with trimethylsilyl cyanide without solvent to give bis(dialkylamino)malononitriles, which can be distilled off from the reaction mixture in vacuo.

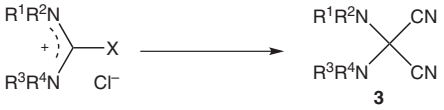
Key words: iminium salts, *N*,*N*,*N*′,*N*′-tetraalkylchloroformamidinium chlorides, trimethylsilyl cyanide, bis(dialkylamino)malononitriles

Compounds with a captodative substituent pattern very often show surprising chemical properties.[1] Bis(dialkylamino)malononitriles **3** are compounds of this type. Some time ago we showed that bis(dimethylamino)malononitrile (**3a**) can be used for the preparation of ketene aminals, 1,3-bis(*N*,*N*,*N*′,*N*′,*N*″,*N*″-hexamethylguanidinium)substituted 1,2,3-tricyanoprop-2-en-1-ides, 1,4-dimethylpiperazine-2,2,5,5-tetracarbonitrile, *N*,*N*,*N*′,*N*′-tetramethylcyanoformamidinium salts, and dimethylammonium salts of 5,5′-dicyanomethylenedibarbituric acid.[2]

Bis(dimethylamino)malononitrile (**3a**) was prepared for the first time by the reaction of *N*,*N*,*N*′,*N*′-tetramethylchloroformamidinium chloride (**1a**) with copper(I) cyanide. The complex thus obtained, which was not specified, was decomposed with aqueous potassium cyanide solution to give **3a** in 43% yield.[3] The reaction of *N*,*N*,*N*′,*N*′-tetramethylcyanoformamidinium chloride (**2a**) with potassium cyanide in a two-phase system water/diethyl ether also afforded **3a** in 72% yield.[4] Bis(dialkylamino)malononitriles **3a–f** were similarly prepared by this procedure directly from *N*,*N*,*N*′,*N*′-tetraalkylchloroformamidinium chlorides **1b–f** and potassium cyanide in 64–89% yields.[2] Recently we have found that the reaction of trimethylsilyl cyanide with the salts **1a**,**g–j** without solvent gives easy access to bis(dialkylamino)malononitriles **3a**,**g–j** (Table 1). In contrast, the reaction of trimethylsilyl cyanide with salts **1** in acetonitrile resulted in dark brown to black polymeric products.

According to this procedure symmetrically substituted malononitriles such as **3a**, and unsymmetrically substituted malononitriles, such as **3g–j**, can be prepared in 70–85% yields.

Table 1 Formation of Bis(dialkylamino)malononitriles **3**



1 X = Cl
2a X = CN
$R^1 = R^2 = R^3 = R^4 = Me$

Entry	R^1	R^2	R^3	R^4	Method[a]	Product	Yield (%)
1	Me	Me	Me	Me	A	**3a**	43
					B[b]		72
					C		85
2	Et	Et	Et	Et	B	**3b**	83
3	$(CH_2)_4$		$(CH_2)_4$		B	**3c**	76
4	$(CH_2)_5$		$(CH_2)_5$		B	**3e**	89
5	$(CH_2)_2O(CH_2)_2$		$(CH_2)_2O(CH_2)_2$		B	**3f**	64
6	Me	Me	Pr	Pr	C	**3g**	81
7	Me	Me	Bu	Bu	C	**3h**	77
8	Et	Et	Pr	Pr	C	**3i**	70
9	Et	Et	Bu	Bu	C	**3j**	77

[a] Starting from **1**, unless otherwise indicated. Method A: Ref. 3, X = Cl; (1) CuCN, MeCN; (2) KCN, H_2O; Method B: Refs. 2 and 4, X = Cl, CN; KCN, Et_2O–H_2O; Method C: this work, X = Cl; TMSCN, no solvent (–TMSCl).
[b] Starting from **2a**.

The *N*,*N*,*N*′,*N*′-tetraalkylchloroformamidinium chlorides **1a**,**g–j** were prepared according to already described procedures[2,5] from the corresponding ureas and phosgene in acetonitrile. By subsequent removal of the solvent the solid chlorides **1** were obtained and used without further purification in the reactions with trimethylsilyl cyanide.

All reactions were performed in dry glassware with magnetic stirring and exclusion of moisture. Trimethylsilylcyanide[6] and N,N,N′,N′-tetrasubstituted ureas[7] were prepared according to known procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 500 spectrometer. The refractive indices were determined using a Zeiss Abbe refractometer.

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Bis(dialkylamino)malononitriles 3; General Procedure
To solid *N*,*N*,*N*′,*N*′-tetraalkylchloroformamidinium chloride **1** (0.2 mol) in a 2-necked flask equipped with a reflux condenser and drying tube ($CaCl_2$) was added cautiously at 0 °C excess Me_3SiCN (59 g, 0.6 mol). On subsequent warming, an exothermic reaction occurred at r.t. and the chloride **1** dissolved. Then the mixture was magnetically stirred for 10–12 h at r.t. The Me_3SiCl formed and the excess Me_3SiCN were removed under reduced pressure (20 Torr). The residue was distilled in vacuo through a 25-cm Vigreux column with fractionation. The malononitriles **3** are colorless liquids when freshly distilled, and after some time become yellow-to-orange colored.

Bis(dimethylamino)malononitrile (3a)
Yield: 85%; bp 89–90 °C/40 mbar (Lit.[3] 75 °C/16 mbar); n^{20}_D = 1.4359 (Lit.[4] n^{20}_D = 1.4360).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45 [s, 12 H, $N(CH_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.2 (NCH_3), 81.6 (C_q), 110.0 (CN).

MS (EI, 70 eV): *m*/*z* = 152.1 $[M]^+$.

Anal. Calcd for $C_7H_{12}N_4$ (152.20): C, 55.24; H, 7.95; N, 36.81. Found: C, 55.18; H, 7.93; N, 36.62.

(Dimethylamino)(dipropylamino)malononitrile (3g)
Yield: 81%; bp 64–65 °C/0.013 mbar; n^{20}_D = 1.4461.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90–0.93 (t, *J* = 7.3 Hz, 6 H, CH_3), 1.57–1.62 (m, 4 H, CH_2), 2.44 [s, 6 H, $N(CH_3)_2$], 2.71–2.74 (m, 4 H, NCH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.6 (CH_3), 21.6 (CH_2), 39.2 (NCH_3), 52.5 (NCH_2), 81.1 (C_q), 111.4 (CN).

MS (EI, 70 eV): *m*/*z* = 208.1 $[M]^+$.

Anal. Calcd for $C_{11}H_{20}N_4$ (208.30): C, 63.43; H, 9.68; N, 26.90. Found: C, 63.23; H, 9.65; N, 26.81.

(Dibutylamino)(dimethylamino)malononitrile (3h)
Yield: 77%; bp 86–88 °C/0.013 mbar; n^{20}_D = 1.4473.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.95 (t, *J* = 7.4 Hz, 6 H, CH_3), 1.29–1.36 (m, 4 H, CH_2), 1.51–1.57 (m, 4 H, CH_2), 2.44 [s, 6 H, $N(CH_3)_2$], 2.74–2.78 (m, 4 H, NCH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.9 (CH_3), 20.5 (CH_2), 30.4 (CH_2), 39.1 (NCH_3), 50.5 (NCH_2), 81.1 (C_q), 114.4 (CN).

MS (EI, 70 eV): *m*/*z* = 236.2 $[M]^+$.

Anal. Calcd for $C_{13}H_{24}N_4$ (236.36): C, 66.06; H, 10.23; N, 23.70. Found: C, 66.10; H, 10.14; N, 23.76.

(Diethylamino)(dipropylamino)malononitrile (3i)
Yield: 70%; bp 84–86 °C/0.013 mbar; n^{20}_D = 1.4478.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90–0.93 (t, *J* = 7.4 Hz, 6 H, CH_3), 1.15–1.18 (t, *J* = 7.4 Hz, 6 H, CH_3), 1.56–1.61 (m, 4 H, CH_2), 2.70–2.73 (m, 4 H, NCH_2), 2.86–2.91 (m, 4 H, NCH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.6 (CH_3), 13.3 (CH_3), 21.7 (CH_2), 43.3 (NCH_2), 52.2 (NCH_2), 79.8 (C_q), 112.9 (CN).

MS (EI, 70 eV): *m*/*z* = 236.2 $[M]^+$.

Anal. Calcd for $C_{13}H_{24}N_4$ (236.36): C, 66.06; H, 10.23; N, 23.70. Found: C, 65.94; H, 10.06; N, 23.63.

(Dibutylamino)(diethylamino)malononitrile (3j)
Yield: 77%; bp 98–100 °C/0.013 mbar; n^{20}_D = 1.4491.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.92–0.95 (t, *J* = 7.4 Hz, 6 H, CH_3), 1.15–1.18 (t, *J* = 7.4 Hz, 6 H, CH_3), 1.30–1.35 (m, 4 H, CH_2), 1.51–1.55 (m, 4 H, CH_2), 2.73–2.76 (m, 4 H, NCH_2), 2.85–2.90 (q, *J* = 7.4 Hz, 4 H, NCH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.2 (CH_3), 13.9 (CH_3), 20.4 (CH_2), 30.5 (CH_2), 43.3 (NCH_2), 50.5 (NCH_2), 79.8 (C_q), 112.9 (CN).

MS (EI, 70 eV): *m*/*z* = 264.2 $[M]^+$.

Anal. Calcd for $C_{15}H_{28}N_4$ (264.41): C, 68.14; H, 10.67; N, 21.19. Found: C, 67.95; H, 10.53; N, 21.09.

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