Phase Transfer Catalysis without Solvent: Selective Mono- or Di-alkylation of Malononitrile

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Monoalkyl and symmetrical or unsymmetrical dialkylmalononitriles have been prepared selectively by phase transfer catalysis in the absence of solvent. Exclusive formation of a particular compound is achieved in all cases except for benzylmalononitrile **2f** (79%) and prop-2-ynylmalononitrile **2g** (62%).

Syntheses of alkylmalononitriles can be classified into two groups; direct synthesis, by alkylation of malononitrile with alkyl halides, or indirect synthesis, by transformation of compounds possessing the functionality or the skeleton of an alkylmalononitrile.

Direct methods are suitable for the preparation of dialkylmalononitriles[1-8] but the preparation of monoalkylmalononitriles needs indirect methods, such as dehydration of diamides[9-10] or cyanoacetamides,[11] reduction of alkylidenemalononitriles[12-16] or cycloalkane-1,1-dicarbonitriles,[17] reaction of dicyanosulphonium ylides with triphenylphosphine,[18] intramolecular dehydration of malononitrile and alcohols in the presence of diethyl azodicarboxylate[19] or reaction of *N*-stannylketenimines with alcohols.[20]

However, in spite of the synthetic importance of malononitrile and its alkyl derivatives,[21] there is no general procedure for the selective synthesis of either mono- or di-alkylmalononitriles.

We report the selective synthesis of mono- and di-alkylmalononitriles by phase transfer catalysis without solvent. The application of this technique to several substrates yields excellent results, employing mild and economic conditions.[22]

In previous papers we have evaluated theoretically[23] and chemically[24] the influence of various factors on selectivity and yield of the benzylation of malononitrile, the nature of the base and the malononitrile:alkyl halide:base mole ratio being the most important factors.

The best conditions will vary according to the nature of the alkyl halide and the desired selectivity. These conditions need consideration as malononitrile is a highly reactive molecule which may react with the base[2] or dimerize.[21] Some of these side reactions are also possible in the mono- or di-alkylmalononitriles obtained.

Results

Monoalkylmalononitriles **2**.—Reactions were performed by stirring the appropriate proportions of malononitrile, alkyl halide and base in the presence of tetrabutylammonium bromide (TBAB) as phase transfer agent. The best results are collected in Table 1.

$$\underset{\mathbf{1}}{CNCH_2CN} + RX \xrightarrow[TBAB]{Base} \underset{\mathbf{2}}{RCH(CN)_2}$$

Potassium carbonate and potassium *tert*-butoxide were the best bases, as they were found to be in the study of benzylation of malononitrile.[24] Potassium carbonate was used with the more reactive halides because, as a non-nucleophilic base, it reduces the side reactions and as a consequence produces higher yields. However, potassium *tert*-butoxide is the most appropriate base with the less reactive halides. Reactions with potassium carbonate are less selective with these halides because, as the alkylation is slow, potassium carbonate may produce the second deprotonation.

Owing to the high reactivity of prop-2-ynyl bromide, sodium hydrogen carbonate was used to obtain higher selectivity. The use of potassium carbonate produced diprop-2-ynylmalononitrile **3g** as the main product, whilst when using potassium *tert*-butoxide, a violent decomposition took place.

A malononitrile:alkyl halide:base 2:1:1 mole ratio produced the best results. A 2:1:2 ratio is also suitable with the more reactive halides but produced lower yields. However, with the less reactive halides a 2:1:1.5 ratio was used in order to improve the yields. This fact is related to an increase in the rate of deprotonation. Further increases in the proportion of base produced a decrease in the selectivity.

The time and temperature of the reaction depend on the nature of the base and alkyl halide used.

The nature and reactivity of the alkyl halide is an important factor to be considered. It dictates the base, mole ratio, time and temperature used and also the yield and selectivity observed. A decrease in the yield was observed with the less reactive alkyl halides due to the importance of the side reactions. Secondary alkyl halides also produced low yields due to elimination from the halide. However the reaction with octyl and isopropyl bromides is very selective due to the low reactivity of the halide and the low accessibility of the monoalkylmalononitrile owing to steric hindrance.

Monoalkylmalononitriles were obtained exclusively, except with prop-2-ynyl and benzyl bromides.

This different behaviour, especially with respect to allyl bromide, may be due to the higher acidity of benzyl **2f** and prop-2-ynylmalononitrile **2g**, or to the higher reactivity of benzyl and prop-2-ynyl bromide in this case.

We have attempted to evaluate the relative acidities of allyl, benzyl and prop-2-ynylmalononitrile by measuring the relative isotope exchange with deuterium, by ^1H and ^{13}C NMR spectroscopy or by competitive reactions.

The exchange in deuterium oxide is immediate in all cases even at pH *ca.* 5, which makes it impossible to explain the observed results.

^{13}C and ^1H NMR chemical shifts of the methine group of monoalkylmalononitriles are gathered in Tables 2 and 3.

A higher acidity will produce an increase in the charge density on the carbon, producing a shift to higher field. However, the chemical shifts observed do not correlate with the expected ones. This may be due to a different acidity from that expected, or probably, in this case, there is no linear relationship between charge density and chemical shift owing to the various components of the shielding constant.

Table 1 Synthesis of monoalkylmalononitriles

Compound[a]	R–X	Base	Mole ratio[b]	Time	Yield (%)[c]
2a	ICH_3	KBu^tO	2:1:1	10 min	79
2b	ICH_2CH_3	K_2CO_3	2:1:1	15 min	90
2c	$Br(CH_2)_3CH_3$	KBu^tO	2:1:1	5 h	71
2d	$Br(CH_2)_7CH_3$	KBu^tO	2:1:1.5	5 h	66
2e	$BrCH_2CH{=}CH_2$	K_2CO_3	2:1:1	12 h	78
2f[d]	$BrCH_2Ph$	K_2CO_3	2:1:1	5 h	76
2g[e,f]	$BrCH_2C{\equiv}CH$	$NaHCO_3$	2:1:2	24 h	51
2h	$BrCH(CH_3)_2$	KBu^tO	2:1:1.5	24 h	44

[a] TBAB, 4%; room temperature. [b] Malononitrile:alkyl halide:base. [c] Yield of isolated product 2. [d] 21% of dibenzylmalononitrile **3f**. [e] 31% of diprop-2-ynylmalononitrile **3g**. [f] Temperature, 60 °C.

Table 2 ^{13}C NMR Spectra of the CH of monoalkylmalononitriles (internal reference TMS)

Compound R	δ(CH)
2e $CH_2CH{=}CH_2$	22.7
2f CH_2Ph	24.7
2g $CH_2C{\equiv}CH$	22.8

Table 3 ^1H NMR Spectra of the CH of monoalkylmalononitriles (internal reference TMS)

Compound	R	δ(CH)
2a	CH_3	3.78
2b	CH_2CH_3	3.80
2c	$(CH_2)_3CH_3$	3.66
2d	$(CH_2)_7CH_3$	3.68
2e	$CH_2CH{=}CH_2$	3.78
2f	CH_2Ph	3.86
2g	$CH_2C{\equiv}CH$	3.93
2h	$CH(CH_3)_2$	3.54

Table 4 Competitive reactions[a]

Base	Time	Mole ratio[b]	Yield (%)
K_2CO_3	5 h	53:47	24
K_2CO_3	96 h	51:49	97
KBu^tO	10 min	54:46	82

[a] Allylmalononitrile:benzylmalononitrile:benzyl bromide:base (1:1:1:1). Room temperature. TBAB 4%. [b] Dibenzylmalononitrile:allylbenzylmalononitrile.

Although the chemical shifts do not correlate with the expected ones in the case of the ^{13}C NMR data, the downfield shifts of these signals for the benzyl and prop-2-ynylmalononitrile relative to other derivatives in the ^1H NMR spectra are evidence for higher acidity induced by these substituents (Table 3). However the differences are not so significant as to determine which of the above reasons is responsible for the different selectivity.

We also performed a competitive reaction. A mixture of allyl- **2e** and benzyl-malononitrile **2f** was allowed to react with benzyl bromide (Table 4). A higher acidity of benzylmalononitrile **2f** would produce a major proportion of dibenzylmalononitrile **3f** in the final mixture. A higher reactivity of benzyl bromide would produce similar proportions of dibenzyl- and allylbenzyl-malonitrile.

The low selectivity found indicates that the higher reactivity of benzyl and prop-2-ynyl bromides in this case must be the reason for the decrease in selectivity with these alkyl halides.

Symmetrical Dialkylmalononitriles **3**.—Considering previous reports and the excellent results obtained in the monoalkylation of malononitrile, phase transfer catalysis in the absence of solvent was expected to be a good procedure for the dialkylation of malononitrile.

Reactions were performed by stirring the appropriate proportion of malononitrile, alkyl halide and base in the presence of TBAB as phase transfer agent. The best results are collected in Table 5.

$$\underset{\mathbf{1}}{CNCH_2CN} + RX \xrightarrow[TBAB]{Base} \underset{\mathbf{3}}{R_2C(CN)_2}$$

Again, potassium carbonate and potassium *tert*-butoxide are the best bases. Potassium hydroxide produced exclusive dialkylation but with a significant decrease in yield due to its nucleophilic character. Again, potassium carbonate can only be used with the most reactive alkyl halides.

A malononitrile:alkyl halide:base 1:2.2:2.2 mole ratio produces the best results and has only been modified to minimize side reactions.

With long-chain alkyl halides an increase in temperature is necessary to achieve complete conversion and improve the selectivity, owing to the lower reactivity of the alkyl halide and to the lower accessibility of the monoalkylmalononitrile due to steric hindrance.

Unsymmetrical Dialkylmalononitriles **4**.—The preparation of monoalkylmalononitriles permits the synthesis of unsymmetrical dialkylmalononitriles in two steps, monoalkylation of malononitrile and a second alkylation with a different alkyl halide.

The synthesis of unsymmetrical dialkylmalononitriles has been performed by dehydration of cyanoacetamides,[11] alkylation of alkylmalononitriles in liquid ammonia or alkylation of *N*-stannylketenimines.[20]

We have performed the synthesis of benzylethylmalononitrile **4a** and allylprop-2-yn-ylmalononitrile **4b** by phase transfer catalysis in the absence of solvent. Results are collected in Table 6.

$$\underset{\mathbf{2}}{RCH(CN)_2} + R'X \xrightarrow[TBAB]{Base} \underset{\mathbf{3}}{RR'C(CN)_2}$$

The synthesis of benzylethylmalononitrile **4a** was performed by alkylation of benzylmalononitrile **2f** with ethyl iodide, but the opposite reaction is also possible. These conditions can be used with any alkyl halide or alkylmalononitrile.

The synthesis of allylprop-2-ynylmalononitrile **4b** was performed by reaction of allylmalononitrile **2e** with prop-2-ynyl bromide, and not the reverse, owing to the probable instability of prop-2-ynylmalononitrile and the high reactivity of prop-2-

Table 5 Synthesis of symmetrical dialkylmalononitriles

Compound[a]	R–X	Base	Mole ratio[b]	Time	Yield (%)[c]
3a	ICH_3	KBu^{t}O	1:2.2:2	2 h	76
3b	ICH_2CH_3	KBu^{t}O	1:2:2	10 min	85
3c	ICH_2CH_3	KOH	1:2:2	60 min	63
3d	$Br(CH_2)_3CH_3$	KBu^{t}O	1:2.2:2.2	18 h	76
3e[d]	$Br(CH_2)_7CH_3$	KBu^{t}O	1:2.2:2.2	13 h	45
3f	$BrCH_2CH{=}CH_2$	KBu^{t}O	1:2.2:2.2	6 h	68
3g	$BrCH_2Ph$	K_2CO_3	1:2.2:2.2	96 h	100
3h	$BrCH_2C{\equiv}CH$	K_2CO_3	1:2.2:2.2	14 h	100

[a] TBAB 4%. Room temperature. [b] Malononitrile:alkyl halide:base. [c] Yield of isolated product **3**. [d] Temperature 60 °C.

Table 6 Synthesis of unsymmetrical dialkylmalononitriles

Compound[a]	R	R′–X	Base	Mole ratio[b]	Time	Yield[c]
4a	CH_2Ph	ICH_2CH_3	KBu^{t}O	1:1.1:1.1	10 min	90
4b	$CH_2CH{=}CH_2$	$BrCH_2C{\equiv}CH$	K_2CO_3	1:1.5:1.5	90 h	80

[a] TBAB 4%. Room temperature. [b] Alkylmalononitrile:alkyl halide:base. [c] % Yield of isolated product **4**.

ynyl bromide. The use of prop-2-ynyl bromide implies the use of potassium carbonate as base.

Conclusion

The reaction of malononitrile with a great variety of alkyl halides permits the selective preparation of mono- and di-alkylmalononitriles. Monoalkylmalononitriles were obtained exclusively in all cases, except with benzyl and prop-2-ynyl bromides.

Phase transfer catalysis in the absence of solvent is a useful method for the selective preparation of monoalkylmalononitriles and symmetrically or unsymmetrically substituted dialkylmalononitriles, owing to the yields and selectivities obtained, and also to the simplification of the experimental procedure and the mild conditions used.

The high selectivity observed in the preparation of monoalkylmalononitriles may be due to the association of the bulky quaternary ammonium–carbanion ion-pair in the apolar medium which disfavours further alkylation.

Experimental

M.p.s were determined on a Gallenkamp apparatus and are uncorrected. B.p.s were determined by ball-to-ball distillation on a Büchi GKR-51 apparatus. IR spectra were recorded on a Philips PV 9500 spectrometer and NMR spectra on a Bruker AW80 at 80 MHz (^{1}H NMR) and on a Varian VXR-300 at 75 MHz (^{13}C NMR) in $CDCl_3$ solution and using tetramethylsilane (TMS) as standard reference. *J* values are in Hz. Microanalyses were performed at the Faculty of Pharmacy, University of Navarra.

Synthesis of Monoalkylmalononitriles **2**.—*General procedure.* (Using potassium carbonate or potassium *tert*-butoxide).

In a two-necked flask provided with a reflux condenser, malononitrile (25 mmol) and the calculated proportions of alkyl halide and TBAB were stirred for 30 min at the desired temperature. Potassium carbonate or potassium *tert*-butoxide were added with a Schlenk tube at 0 °C and the stirring was continued for the appropriate time (Table 1).

The crude mixture was extracted with dichloromethane (200 ml). Removal of the solvent and column chromatography on silica gel (Merck, 70–230 mesh) afforded the pure compound.

Methylmalononitrile **2a**. Using dichloromethane as eluent. B.p. 165 °C/40 mbar (lit.,[26] 90–100 °C/20 mbar); ν_{max}(KBr)/cm^{-1} 2260 (CN); δ_H 3.78 (1 H, q, *J* 7.2, CH) and 1.74 (3 H, d, *J* 7.2, CH_3).

Ethylmalononitrile **2b**. Using dichloromethane as eluent. B.p. 170 °C/40 mbar (lit.,[27] 100 °C/20 mbar). ν_{max}(KBr)/cm^{-1} 2260 (CN); δ_H 3.80 (1 H, t, *J* 6.4, CH), 2.26–1.90 (2 H, m, CH_2) and 1.24 (3 H, t, *J* 7.2, CH_3).

Butylmalononitrile **2c**. Using light petroleum (b.p. 50–70 °C) ethyl acetate (9:1) as eluent. B.p. 120 °C/27 mbar (lit.,[28] 111–120 °C/35 mbar); ν_{max}(KBr)/cm^{-1} 2256 (CN); δ_H 3.66 (1 H, t, *J* 6.4, CH) and 2.16–0.86 [9 H, m, $(CH_2)_3CH_3$].

Octylmalononitrile **2d**. Using light petroleum–ethyl acetate (9:1) as eluent. B.p. 115 °C/0.03 mbar; ν_{max}(KBr)/cm^{-1} 2256 (CN); δ_H 3.68 (1 H, t, *J* 6.4, CH) and 2.25–0.72 [17 H, m, $(CH_2)_7CH_3$] (Found: C, 74.2; H, 10.4; N, 15.5. $C_{11}H_{18}N_2$ requires C, 74.1; H, 10.2; N, 15.7%).

Allylmalononitrile **2e**. Using light petroleum–ethyl acetate (9:1) as eluent. B.p. 115 °C/0.03 mbar; ν_{max}(KBr)/cm^{-1} 2256 (CN) and 1642 (C=C), δ_H 6.12–5.25 (3 H, m, $CH{=}CH_2$), 3.78 (1 H, t, *J* 6.8, CH) and 2.73 (2 H, t, *J* 6.8, CH_2); δ_C 128.9 (=CH), 112.2 (=CH_2) 112.0 (CN), 34.4 (CH_2) and 22.7 (CH) (Found: C, 67.6; H, 26.1. $C_6H_6N_2$ requires C, 67.9; H, 5.7; N, 26.4%).

Benzylmalononitrile **2f**: Using toluene as eluent. M.p. 90.5–91.5 °C (ethanol) (lit.,[15] 91–92 °C); ν_{max}(KBr)/cm^{-1} 2256 (CN); δ_H 7.30 (5 H, s, Ph), 3.86 (1 H, t, *J* 7.2, CH) and 3.24 (2 H, d, *J* 7.2, CH_2); δ_C 128.4, 128.9, 132.9 (Ph), 112.2 (CN), 36.2 (CH_2) and 24.6 (CH).

Prop-2-ynylmalononitrile **2g**. In a two-necked flask provided with a reflux condenser, malononitrile (25 mmol) and the calculated proportion of sodium hydrogen carbonate and TBAB were stirred at 60 °C for 30 min. Prop-2-ynyl bromide was added and the stirring was continued for 24 h at 60 °C. Work-up was performed as in the general method. Elution with toluene afforded di- and mono-prop-2-ynylmalononitrile (Table 1). B.p. 100 °C/0.01 mbar; ν_{max}(KBr)/cm^{-1} 2264 (CN) and 2132 (C≡C); δ_H 3.93 (1 H, t, *J* 6.9, CH), 2.93 (2 H, dd, *J* 6.9 and 2.4, CH_2), 2.37 (1 H, t, *J* = 2.4, ≡CH); δ_C 113 (CN), 74.9 (≡C–), 74.7 (≡CH), 22.8 (CH) and 21.6 (CH_2).

Isopropylmalononitrile **2h**. Using dichloromethane as eluent. B.p. 65 °C/0.01 mbar (lit.,[15] 85–86 °C/7 mbar); ν_{max}(KBr)/cm^{-1} 2256 (CN), δ_H 3.54 [1 H, d, *J* 5.6, $CH(CN)_2$], 2.55–2.15 (1 H, m, CH) and 1.23 (6 H, d, *J* 7.2, CH_3).

Synthesis of Symmetrical Dialkylmalononitriles **3**.—Following the general procedure and conditions collected in Table 5.

Dimethylmalononitrile **3a**. Using dichloromethane as eluent. B.p. 120 °C/33 mbar (lit.,[1] 52 °C/7 mbar). ν_{max}(KBr)/cm^{-1} 2251 (CN); δ_H 1.78 (6 H, s, CH_3).

Diethylmalononitrile **3b**. Using dichloromethane as eluent. B.p. 145 °C/25 mbar (lit.,[11] 47–50 °C/3 mbar); ν_{max}(KBr)/cm^{-1} 2247 (CN); δ_H 1.97 (4 H, q, *J* 7.4, CH_2) and 1.25 (6 H, t, *J* 7.4, CH_3).

Dibutylmalononitrile **3c**. Using dichloromethane as eluent. B.p. 90 °C/0.03 mbar (lit.,[29] 104 °C/0.5 mbar); ν_{max}(KBr)/cm^{-1} 2247 (CN); δ_H 2.00–0.80 [18 H, m, $(CH_2)_3CH_3$].

Dioctylmalononitrile **3d**. Using light petroleum–ethyl acetate (9:1) as eluent. B.p. 175 °C/0.02 mbar; ν_{max}(KBr)/cm^{-1} 2248 (CN); δ_H 2.20–0.68 [34 H, m, $(CH_2)_7CH_3$] (Found: C, 78.5; H, 12.1; N, 9.4. $C_{19}H_{34}N_2$ requires C, 78.6; H, 11.8; H, 9.6%).

Diallylmalononitrile **3e**. Using dichloromethane as eluent. M.p. 35–36 °C (light petroleum) (lit.,[3] 36 °C); ν_{max}(KBr)/cm^{-1} 2252 (CN) and 1642 (C=C); δ_H 6.15–5.25 (6 H, m, $CH{=}CH_2$) and 2.64 (4 H, d, *J* 7.2, CH_2).

Dibenzylmalononitrile **3f**. Using toluene as eluent. M.p. 130–131 °C (ethanol) (lit., 131–132 °C); ν_{max}(KBr)/cm^{-1} 2248 (CN); δ_H 7.30 (10 H, s, Ph) and 3.21 (4 H, s, CH_2).

Diprop-2-ynylmalononitrile **3g**. Using dichloromethane as eluent. M.p. 75–76 °C (hexane); ν_{max}(KBr)/cm^{-1} 2256 (CN) and 2128 (C≡C); δ_H 3.05 (4 H, d, *J* 2.8, CH_2) and 2.40 (2 H, t, *J* 2.8, CH) (Found: C, 76.1; H, 4.2; N, 19.7. $C_9H_6N_2$ requires C, 76.0; H, 4.3; N, 19.7%).

Synthesis of Unsymmetrical Dialkylmalononitriles **4**.—Following the same general procedure but using the appropriate monoalkylmalononitrile (25 mmol) and conditions of Table 6.

Benzylethylmalononitrile **4a**. Using dichloromethane as eluent. M.p. 62–63 °C (hexane) (lit.,[25] 61–61.5 °C); ν_{max}(KBr)/cm^{-1} 2248 (CN); δ_H 7.31 (5 H, s, Ph), 3.15 (2 H, s, CH_2Ph), 1.96 (2 H, q, *J* 7.5, CH_2CH_3) and 1.26 (3 H, t, *J* 7.5, CH_3).

Allylprop-2-ynylmalononitrile **4b**. Using light petroleum–ethyl acetate (9:1) as eluent. B.p. 95 °C/0.03 mbar; ν_{max}(KBr)/cm^{-1} 2252 (CN), 2132 (C≡C) and 1642 (C=C); δ_H 6.16–5.31 (3 H, m, $CH{=}CH_2$), 2.90 (2 H, d, *J* 2.4, $CH_2C{\equiv}$), 2.80 (2 H, d, *J* 6.8, $CH_2C{=}$) and 2.38 (1 H, t, *J* 2.4, CH) (Found: C, 74.9; H, 5.6; N, 19.6. $C_9H_8N_2$ requires C, 75.0; H, 5.6; N, 19.4%).

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