

Solvent-free condensation of phenylacetonitrile and nonanenitrile with 4-methoxybenzaldehyde: optimization and mechanistic studies

André Loupy,^{*a} Michèle Pellet,^b Alain Petit^a and Giang Vo-Thanh^a

^a Laboratoire des Réactions Sélectives sur Supports, ICMMO, CNRS UMR 8615, Bâtiment 410, Université Paris-Sud, 91405, Orsay cedex, France

^b Laboratoire des Carbocycles, ICMMO, CNRS UMR 8615, Bâtiment 420, Université Paris-Sud, 91405, Orsay cedex, France

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The condensation of phenylacetonitrile with 4-methoxybenzaldehyde can be carried out by two solvent-free methods: i) using neat powdered KOH at room temperature with equivalent amounts of aldehyde, nitrile and base for 3 min, and ii) using K_2CO_3 in the presence of a phase transfer agent for 3 min under microwave activation or conventional heating. By extending the reaction time up to 10 min, four different products were obtained from phenyl or nitrile group migration. With nonanenitrile, only the second method could be applied to give two kinds of condensed compounds with or without phenyl (or nitrile) group migration. The intervention of non-thermal MW-specific effects was proved in some cases and interpreted.

Introduction

Unsaturated nitriles play a key role in many of the pathways proposed for the prebiotic synthesis of biological molecules.¹ Arylacrylonitriles are important synthons for the synthesis of several biologically active molecules in the preparation of perfumes,² flavonoid pigments,³ sexual pheromones⁴ and vitamin A.⁵ They are directly involved in increasing soybean yield as plant growth regulators,⁶ and as inhibitors of prostaglandin synthetase.⁷ Recently, they have been used within the area of organic materials for the obtention of high electron affinity polymers which can be used to manufacture light-emitting diodes (LEDs) with air-stable electrodes.^{8,9}

The traditional preparation of arylacrylonitriles involves the reaction of aromatic aldehydes with arylacetonitriles (Meyer and Frost reaction).¹⁰ Thus, they can be obtained under basic conditions in a polar solvent (NaOH, KOH, NaOEt or K_2CO_3 in MeOH, EtOH or THF)^{11–15} or under liquid–liquid phase-transfer catalysis conditions.^{3,16}

The replacement of organic solvents, which inevitably lead to solvent emission and/or waste, is nowadays one of the most important goals in green chemistry.^{17,18} The environmentally friendly goal of making organic compounds without using solvents has come several steps closer in recent years and, as stated by D. C. Dittmer:¹⁷ “The day may be coming when more drastic restrictions on solvent pollution will require the adoption of no-solvent reaction conditions”. Two solvent-free syntheses have been reported in the literature: i) by J. G. Verkade *et al.*¹⁵ using a tricyclic non-ionic strong Lewis base, and ii) by D. Villemin *et al.*¹⁹ working with supported bases on inorganic solids (e.g. $KF-Al_2O_3$) in “dry media” under microwave (MW) irradiation.

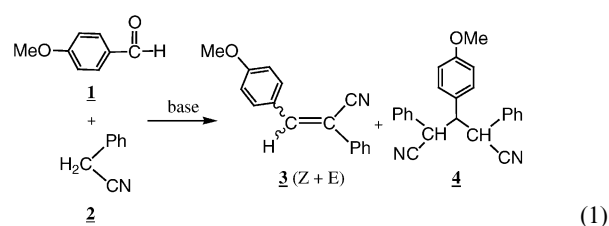
Encouraged by the results obtained by Toda *et al.*²⁰ for solvent-free aldolizations, we have studied here various solvent-free conditions according to the nature of the base, the presence of a phase transfer agent and, if necessary, MW activation. To this end, we have chosen to optimize conditions for the representative condensation of 4-methoxybenzaldehyde (because of its lower reactivity) with phenylacetonitrile (an aromatic compound) and nonanenitrile (an aliphatic one).

Results and discussion

Reaction with phenylacetonitrile

Non-catalyzed solvent-free conditions. Reactions were carried out as a slurry of equivalent amounts (10 mmol) of 4-

methoxybenzaldehyde **1**, phenylacetonitrile **2** and finely ground base. The main product was the α,β -unsaturated nitrile **3**, occasionally accompanied by compound **4** resulting from Michael addition of **2** to **3** (eqn. (1)).



The influence of the nature of the base was first checked at room temperature (Table 1) and then under MW irradiation using a monomode reactor²¹ with accurate control of temperature and MW power (Table 2).

It is noticeable that the simplest reaction using KOH for 3 min at r.t. led to a very high yield (Table 1, entry 7). These condensation reactions proceed very efficiently in the absence of solvent, as shown in some aldolization–condensations.^{20,22} Using weaker bases (Table 1, entries 1–6), yields were very low and reactions appeared to stop (similar results obtained in 10 or 60 min with K_2CO_3 , Table 1, entries 1 and 2). Some amounts of the Michael reaction by-product **4** were characterized (Table 1, entries 5 and 8).

Under MW irradiation, with KOH as the base, the yield (**3E** + **3Z**) rose to 99% with a higher purity: yield and conversion values are rather similar and no traces of **4** were detected (Table 2, entry 6). Other available bases such as Cs_2CO_3 and KF/Al_2O_3 afforded excellent yields (Table 2, entries 4 and 5). In the case of K_2CO_3 and K_3PO_4 (Table 2, entries 2 and 3), yields could presumably be optimized by extending the reaction time.

Phase-transfer catalysis^{23,24}. When the reactions were performed using K_2CO_3 , KOH or Cs_2CO_3 as the base, TBAB ($n-Bu_4N^+ Br^-$), TDA-1 (tris[2-(2-methoxyethoxy)ethyl]amine)²⁵, Aliquat 336 (mainly $MeNOct_3^+ Cl^-$) or 18-crown-6 (18-C-6) as the phase-transfer agent (PTA), five different products were obtained (eqn. (2)). Their structures were assigned by ¹H and ¹³C NMR spectroscopy. The main results are given in Table 3.

Table 1 Effect of the base nature on the reaction depicted in eqn. (1) at room temperature

Entry	Base (1 equiv.)	Reaction time/min	Conversion ^{a,b} (%)	Yields (%) ^b		
				3Z	3E	4
1	K ₂ CO ₃	10	4	tr ^c	0	0
2		60	5	5	0	0
3	K ₃ PO ₄ ·3H ₂ O	10	3	tr	0	0
4	Cs ₂ CO ₃	10	14	10	tr	tr
5	KF/Al ₂ O ₃ ^d	10	39	23	tr	6
6	NaOH	3	60	28	tr	13
7	KOH	3	95	86	1	2
8	KOCH ₃	3	90	73	tr	4

^a Conversion based on phenylacetonitrile consumption. ^b Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate).

^c Traces were detected by GC. ^d KF/Al₂O₃ = 2 : 3 w/w.

Table 2 Effect of the base nature on the reaction depicted in eqn. (1) under MW irradiation

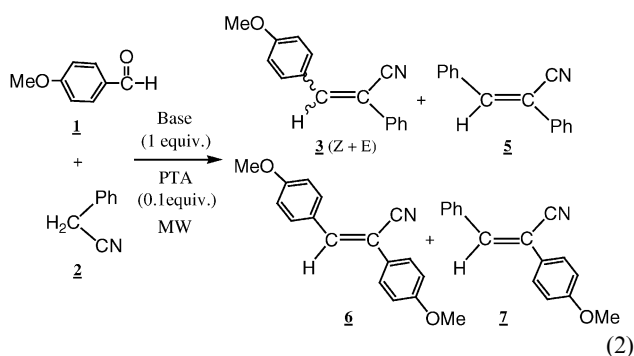
Entry	Base (1 equiv.)	Reaction time/min	Final ^a temperature /°C	Conversion ^{b,c} (%)	Yields (%) ^c	
					3Z	3E
1	K ₂ CO ₃	5	110	4	4	0
2		30	131	44	43	1
3	K ₃ PO ₄ ·3H ₂ O	3	161	31	30	1
4	Cs ₂ CO ₃	3	145	93	90	3
5	KF/Al₂O₃	3	142	95	90	5
6	KOH	2	117	99	96 (95)^d	3

^a Final temperature at the end of MW irradiation was measured with an optical fibre. ^b Conversion was based on consumption of **2**. ^c Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate). ^d Isolated yield is given in brackets.

Table 3 Effects of the base and nature of the PTA on the reaction depicted in eqn. (2) in dry media under MW irradiation (10 mmol scale)

Base	PTA	Reaction time/min	Final ^a temperature/°C	Conversion ^{b,c} (%)	Yields (%) ^c				
					3Z	3E	5	6	7
K ₂ CO ₃	TBAB	3	133	93	89 (78) ^d	1	4	0	0
	TBAB	10	151	98	40	1	22	16	21
	TBAB	30	173	98	39	2	20	19	20
	Aliquat	10	137	98	34	1	20	15	18
	TDA-1	10	137	84	73	3	1	0	0
	18-C-6	10	139	100	30	1	22	18	18
KOH	TBAB	3	156	100	27	1	20	18	17
Cs ₂ CO ₃	TBAB	3	148	100	33	1	23	20	20

^a Final temperature at the end of MW irradiation measured with an optical fibre. ^b Conversion was based on consumption of **2**. ^c Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate). ^d Isolated yield was given in brackets.



Using potassium carbonate/TBAB, after a very short irradiation time (3 min) and at a final temperature of 133 °C, mainly **3Z** was formed. By extension of the reaction time up to 10 or 30 min, we obtained a mixture of **3Z** + **3E** + **5** + **6** + **7**. Whatever the conditions of base or catalyst (except with TDA-1), rather similar mixtures of products were obtained with constant composition.

In order to keep the reaction temperature at around 100 °C, 1 mL of *n*-heptane, a non-polar solvent (*i.e.* transparent to MW

exposure) was added. After 10 min under MW we obtained, at a final temperature of 105 °C, mainly product **3Z** (88 : 0 : 2 : 3 : 0 for products **3Z** : **3E** : **5** : **6** : **7**). It is consequently clear that, for short reaction times and relatively low temperatures, **3Z** was the predominant product, whereas mixtures were obtained under harsher conditions.

Comparison of microwave irradiation vs. conventional heating.

In order to check the possible intervention of specific non-thermal MW effects,^{26,27} the same reactions were performed inside a thermostated oil bath under identical conditions (vessel, medium, temperature, reaction time, *etc.*). The main results are given in Table 4.

Specific non-thermal MW effects only appeared in two cases, which correspond to the less reactive systems, either using a weak base (K₂CO₃) in the absence of PTA (Table 4, entry 1, conversion 31% for MW, 16% for Δ) or under PTC conditions in the presence of *n*-heptane (Table 4, entry 6, conversion 93% for MW, 42% for Δ).

In all other cases, employing a stronger base (Table 4, entries 2 and 3) or with a weak one in the presence of PTA–K₂CO₃ (Table 4, entry 4), excellent yields were obtained (≥94%). They are similar whatever the mode of activation (Table 4, entries 2–5,

Table 4 Comparison of MW vs. conventional heating (Δ) under similar sets of conditions for the reaction depicted in eqn. (2) (10 mmol scale)

Entry	Base	Activation mode	Reaction time/min	Temperature/ $^{\circ}$ C	Conversion ^a (%)	Yields (%) ^b				
						3Z	3E	5	6	7
1	K ₂ CO ₃	MW	15	129	31	27	1	0	0	0
		Δ	15	131	16	16	0	0	0	0
2	KOH	MW	2	117	99	96	3	0	0	0
		Δ	2	115	95	89	3	0	0	0
3	KF/Al ₂ O ₃	MW	3	142	95	90	5	0	0	0
		Δ	3	141	95	90	0	0	0	0
4	K ₂ CO ₃ + TBAB	MW	3	133	93	89	1	4	0	0
		Δ	3	128	86	81	4	1	0	0
5	K ₂ CO ₃ + TBAB	MW	10	151	98	40	1	22	16	21
		Δ	10	145	98	40	2	20	18	20
6	K ₂ CO ₃ + TBAB/n-heptane	MW	7	104	93	88	0	2	3	0
		Δ	7	98	42	37	0	0	0	0

^a Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate). ^b Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate).

for which yields and conversions are roughly the same) within very short reaction periods (2–3 min).

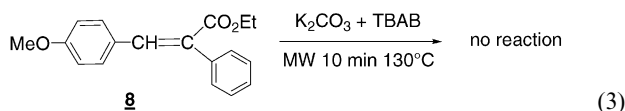
The importance of the specific MW effect observed here is consistent with the previous assessment that the effect is greater when the difficulty of the reaction is increased^{26–28} (*i.e.* higher values of activation energy). When the transition states lie further along the reaction coordinate they are more prone to develop extended polarity, and consequently MW effects are more pronounced. Here, it is the case with the less reactive system involving K₂CO₃ for 15 min at 130 $^{\circ}$ C (conversion 31% for MW, 16% for Δ) or dilution of K₂CO₃/TBAB in heptane (a non-polar, *i.e.* MW-transparent solvent) inducing extension of reaction time and decrease in temperature (no solvent: 3 min, 128–133 $^{\circ}$ C, MW, conversion 93% for MW, 86% for Δ ; heptane: 7 min, 98–104 $^{\circ}$ C, conversion 93% for MW, 42% for Δ).

Presumably, the intervention of specific MW effects is masked at elevated temperature^{29–31} which yet induces very good yields under conventional heating. These effects could be observed when the reaction was performed at lower temperature, as shown for instance when n-heptane was added to the K₂CO₃-TBAB system (Table 4, entries 5 and 6).

Mechanistic considerations

The obtention of the compounds **5–7** in the transformation of **3** at temperatures higher than 120 $^{\circ}$ C in the presence of a base and a PTA is shown in Table 5.

This reaction is specific to the nitrile moiety as no reaction occurred when using the corresponding ethyl ester **8** (eqn. (3)).



Radical mechanisms can be excluded as similar products and yields were obtained in the presence of a radical inhibitor (benzoquinone) and a promoter (benzoyl peroxide), or even by carrying out the reaction in the dark.

Finally, in order to justify the formation of products **5–7** from **3**, one could propose a multi-step mechanism (Scheme 1) involving:

1) the base-promoted β -elimination of HCN leading to alkyne **9**,^{32,33}

2) the [2 + 2] cycloaddition of **3** to alkyne **9**, presumably with formation of cyclobutadiene **10** after elimination of HCN,

3) the opening of **10** by two pathways (a and b), giving access to alkynes **9**, **11** and **12**,

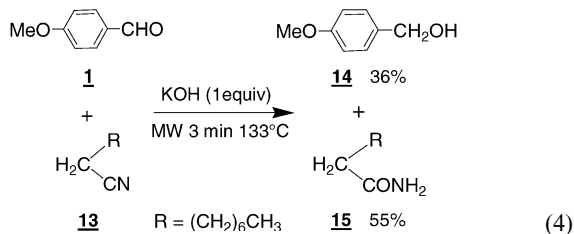
4) the nucleophilic addition of CN⁻ to these alkynes,³⁴ leading to **3**, **7**, **5** and **6** respectively.

Unfortunately, attempts to isolate intermediates or to trap them by more reactive alkynes failed. On the other hand, the intermediate **9** could be synthesized by Sonogashira coupling as reported in the literature.³⁵ However, no formation of **3** or **7** was observed by addition of CN⁻, derived from KCN or Bu₄NCN, into the reaction medium under phase-transfer catalysis conditions. Moreover, attempts to perform the [2 + 2] cycloaddition between **9** and **3** failed.

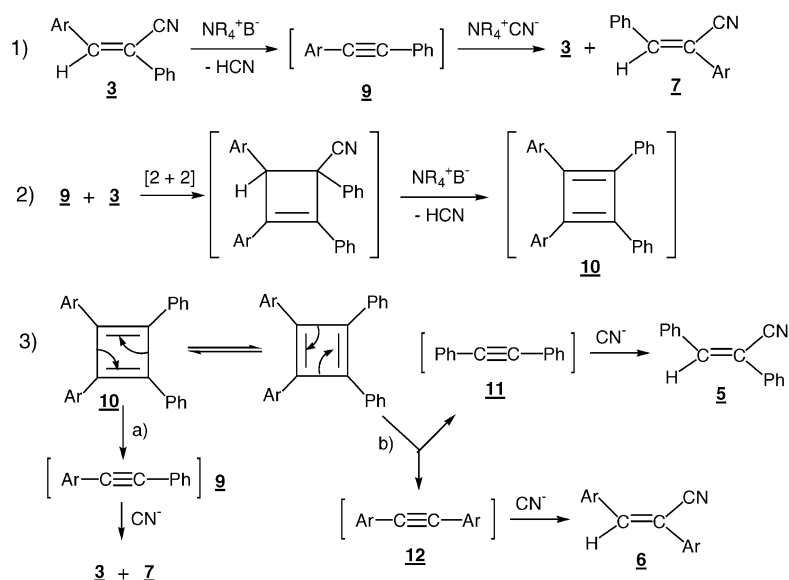
Reaction with nonanenitrile

We subsequently studied the behaviour of a long chain aliphatic nitrile (nonanenitrile **13**), to the best of our knowledge never studied in the literature. Only two isolated cases of aliphatic nitriles were described: i) the base-catalyzed condensation of acetonitrile with carbonyl compounds using KOH in CH₃CN (acting both as reagent and solvent), giving access to aliphatic α,β -unsaturated nitriles,^{36–38} and ii) the condensation of RCH₂CN (R = H, C₂H₅) with several aldehydes and ketones using lithium alkylamides in HMPA³⁹ which led to β -hydroxynitriles.

We therefore extended the previous methods to the case of **13**. In the absence of any PTA, we only obtained products from the Cannizzaro reaction (**14**) and hydrolysis of the nitrile (**15**) when using KOH for 3 min at 133 $^{\circ}$ C under MW irradiation (eqn. (4)).

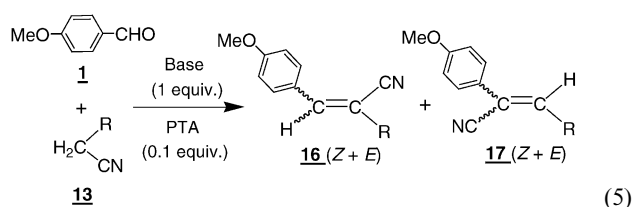
**Table 5** Conversion of **3Z** under different conditions in 10 min at 130 $^{\circ}$ C under MW irradiation

Reagents	3Z (%)	3E (%)	5 (%)	6 (%)	7 (%)
3Z + K ₂ CO ₃	97	3	0	0	0
3Z + TBAB	91	7	0	0	0
3Z + K ₂ CO ₃ + TBAB (0.1 equiv.)	38	1	18	15	20



Scheme 1 Proposed multi-step mechanism for the reaction depicted in eqn. (2).

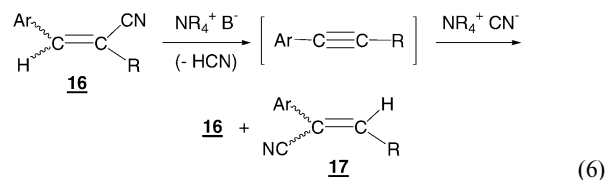
On the other hand, when a PTA was added, two condensation products **16** and **17** were obtained, each as *E* and *Z* isomers (eqn. (5)).



(5)

Different bases were also studied. We obtained two isomers **16** and **17** (*Z*+*E*) which differ in the relative positions of the R and CN groups, indicative of possible migration of these two groups. Consequently, the mechanism could be more or less similar to

the one proposed for phenylacetonitrile (eqn. (6)). The main results are given in Table 6.



(6)

The effects of the amounts of nonanenitrile (OctCN) and KOCH_3 were next studied for the TBAS-catalyzed reaction (Table 7).

We got finally satisfactory yields of condensation products when using TBAS as PTA for 3 min under solvent-free PTC conditions either conventional heating (Δ) or MW irradiation.

Table 6 Effects of the base and PTA on the reaction depicted in eqn. (4) in dry media under MW irradiation for 3 min

Base	PTA	Temperature/ $^{\circ}\text{C}$	Conversions ^a nitrile/aldehyde (%)	Yields (%) ^a			
				16 (<i>Z</i> + <i>E</i>)	17 (<i>Z</i> + <i>E</i>)	13	14
KOH	TBAB	135	48/67	37+2	6+5	7	0
	Aliquat	164	80/99	24+2	6+4	16	2
	TBAS ^b	153	64/88	34+2	8+7	10	0
	TDA-1	156	95/100	5+0	4+1	27	38
KOCH_3	TBAB	135	48/64	27+2	6+5	7	0
	TBAS ^b	123	51/63	31+2	7+6	5	0

^a Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate). ^b $\text{Bu}_4\text{N}^+\text{HSO}_4^-$.

Table 7 Effects of the amounts of reagents on the reaction depicted in eqn. (4) in dry media for 3 min with TBAS as the catalyst (10 mol% versus the base) and KOCH_3 as the base

OctCN (equiv.)	KOCH_3 (equiv.)	Activation mode	Temperature/ $^{\circ}\text{C}$	Conversion ^a nitrile/aldehyde (%)	Yields (%) ^a		
					16 (<i>Z</i> + <i>E</i>)	17 (<i>Z</i> + <i>E</i>)	14
1	1	MW	123	51/63	31+2	7+6	5
1.5	1	MW	133	55/62	34+2	8+6	1
1.5	1.5	MW	138	64/77	39+2	9+7	3
2	2	MW	138	70/83	44+3	10+7	2
3	3	MW	142	76/92	49+3	12+8	3
3	3	Δ	124	96/94	55+3	12+8	0

^a Conversions and yields were evaluated by GC using an internal standard (diethyl phthalate).

Table 8 GC conditions and retention times (R_i) for reactants and products

Products or reactants	GC column	GC conditions	R_i /min	Internal standard R_i /min
1	DB1, 30 m, ID = 0.25 mm	100→280 °C (10 min), 10 °C min ⁻¹ , P_{He} = 70 kPa	5.58	9.38
2			4.58	
3Z			16.40	
3E			15.12	
4			22.43 + 23.24	
5			13.34	
6			19.04	
7			16.26	
8			15.50	
1	12QC2/BP1, 12 m ID = 0.22 mm	100→250 °C (7 min), 10 °C min ⁻¹ , P_{He} = 50 kPa	2.87	6.19
13			2.32	
14			3.15	
15			4.99	
16Z			12.84	
16E			12.35	
17Z			12.47	
17E			11.74	

Yields were substantially enhanced when larger amounts of nitrile and base were used.

Conclusions

With phenylacetonitrile, two solvent-free methods can be used efficiently: i) neat powdered KOH or KOCH₃ at room temperature with aldehyde : nitrile : base = 1 : 1 : 1 with very short reaction times (3–10 min), and ii) with K₂CO₃, addition of a phase-transfer agent and reaction for 3 min at 133 °C under MW irradiation or conventional heating. By extending the reaction time up to 10 min, five different products were obtained resulting from phenyl or nitrile group migration. With nonanenitrile, only the second method could be used to give access to two kinds of condensed compounds with or without phenyl (or nitrile) group migration.

Generalization of these conditions to a series of aliphatic carbonyl compounds is under progress.⁴⁰

Experimental

Microwave equipment

Reactions were performed in a monomode reactor Synthewave 402 microwave device from Prolabo.²¹ The temperature was measured during the reaction by infrared detection, which indicates the surface temperature after previous calibration of emissivity in each case with an optical fibre thermometer (FTI-10 device from Fiso). All reactions were conducted in a cylindrical Pyrex tube under mechanical stirring to establish homogeneity in temperature. The emitted MW power was monitored during irradiation to maintain a constant temperature.

Characterization of products

Solid products were characterized by their melting points. All the products were also characterized by GC-MS (Delsi-NerMag spectrometer with an ionising energy of 70 eV coupled to a gas chromatograph fitted with a capillary column DB5, 30 m, ID = 25 µm). ¹H and ¹³C NMR spectra were recorded on a Bruker instrument (AC 200, AC 250 and DRX 400) as CDCl₃ solutions. Chemical shifts are expressed in δ units (ppm) and quoted downfield from TMS as an internal standard.

GC Analyses

All yields were determined by GC with diethyl phthalate as internal standard. The GC devices (GC 9000 series, Fisons, and GC 5160 Vega series 2, Carlo Erba) were fitted with a non-polar capillary column, film thickness = 0.1 µm, carrier gas = helium. GC equipment was fitted with hardware (NCI 900 series interface) and software (Turbochrom) systems developed

by Perkin-Elmer Co. GC conditions and retention times for reactants and products are given in Table 8.

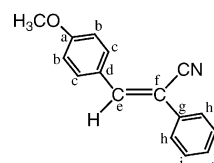
Typical experiments

Phenylacetonitrile, nonanenitrile (n-octyl cyanide), phase transfer agents (TBAB, Aliquat 336, 18-crown-6, TDA-1) and bases (K₂CO₃, NaOH, KOH, KOCH₃, K₃PO₄·3H₂O, Cs₂CO₃) were purchased from commercial sources (Acros, Aldrich or Fluka Chemical Co.) and were used without further purification. 4-Methoxybenzaldehyde (Acros) was distilled before use.

Solvent-free uncatalyzed reaction (Tables 1, 2 and 4). Phenylacetonitrile **2** (10 mmol; 1.17 g), finely ground solid KOH containing 15% H₂O (10 mmol; 0.65 g) and 4-methoxybenzaldehyde **1** (10 mmol; 0.68 g) were introduced successively into a Pyrex vessel adapted to the microwave equipment and fitted with a mechanical stirrer. MW irradiation was carried out according to the conditions indicated in Table 2. At the end of the reaction, organic products were extracted with ethyl acetate and the mixture was filtered next through sintered-glass. The products were identified (GC-MS, NMR, retention time by comparison with authentic samples), and analyzed by GC with an internal standard. At room temperature (Table 1), the same Pyrex vessel was used and the mixture was mechanically stirred. Under conventional heating conditions (Table 4), the Pyrex vessel was introduced into a thermostatted oil bath, at the same temperature as the final temperature under MW irradiation, with a mechanical stirrer. The same treatment was performed in both cases.

PTC solvent-free reaction (Tables 3–7). Phenylacetonitrile **2** (10 mmol; 1.17 g), finely ground solid KOH (10 mmol; 0.65 g), TBAB (1 mmol; 0.32 g) and 4-methoxybenzaldehyde **1** (10 mmol; 0.68 g) were introduced successively into a Pyrex vessel adapted to the microwave equipment, fitted with a mechanical stirrer. Treatment was exactly the same whether the reactions were catalyzed or non-catalyzed, conducted under MW irradiation or with conventional heating.

Z-2-Phenyl-3-(4-methoxyphenyl)acrylonitrile **3Z** (RN:5432-07-5)



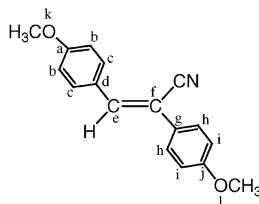
Purified by flash chromatography on silica gel (pentane-ether 60 : 40 v/v) as white crystals. Mp 95 °C (lit.⁴¹ 93.5–94.5 °C).

MS: m/z 235 (M^+ , 100%), 191 (13.6), 190 (23.2), 165 (36.8), 88 (10.4). $^1\text{H NMR}$: 3.82 (s, 3H, OCH_3), 6.93–6.99 (m, 2H, H_b), 7.35–7.48 (m, 3H, H_i and H_j), 7.45 (s, 1H, H_l), 7.63–7.69 (m, 2H, H_h), 7.86–7.91 (m, 2H, H_c). $^{13}\text{C NMR}$: 55.29 (CH_3O), 108.46 (C_f), 114.26 (C_b), 118.45 (CN), 125.63 (C_h), 126.38 (C_d), 128.64 (C_i), 128.89 (C_j), 131.09 (C_e), 134.70 (C_g), 141.75 (C_c), 161.30 (C_a).

Z-2,3-Diphenylacrylonitrile 5 (RN:2510-95-4)

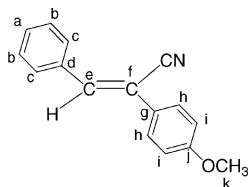
Commercial product (Lancaster Chemical Co.).

Z-2-(4-methoxyphenyl)-3-(4-methoxyphenyl)acrylonitrile 6 (RN:6443-74-9)



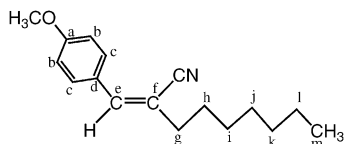
Purified by flash chromatography on silica gel (pentane) as white crystals. Mp 113 °C (lit.³⁸ 107–107.5 °C). MS: m/z 265 (M^+ , 100%), 250 (37.4), 191 (12.5), 190 (24.6), 178 (18.3), 152 (11.2). $^1\text{H NMR}$: 3.82 (s, 3H, H_i), 3.84 (s, 3H, H_k), 6.87–7.00 (2 m, 2 × 2H, $\text{H}_i + \text{H}_b$), 7.33 (s, 1H, H_c), 7.52–7.62 (m, 2H, H_h), 7.78–7.88 (m, 2H, H_e). $^{13}\text{C NMR}$: 55.33 ($\text{C}_k + \text{C}_i$), 108.20 (C_f), 114.23 (C_i), 114.29 (C_b), 118.62 (CN), 126.65 + 127.24 ($\text{C}_d + \text{C}_g$), 126.97 (C_h), 130.81 (C_e), 139.81 (C_c), 160.01 (C_j), 161.00 (C_a).

Z-2-(4-Methoxyphenyl)-3-phenylacrylonitrile 7 (RN:5840-59-5)



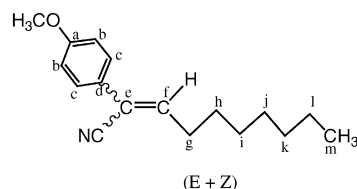
Purified by recrystallization (MeOH) as yellow crystals. Mp 92–93 °C (lit.¹⁹ 90–91 °C). MS: m/z 235 (M^+ , 100%), 219 (12.9), 204 (21.5), 190 (21.8), 177 (21.7), 165 (48.8). $^1\text{H NMR}$:¹⁹ 3.81 (s, 3H, H_c), 6.87–7.01 (m, 2H, H_i), 7.33–7.51 (m, 4H, $\text{H}_a + \text{H}_b + \text{H}_e$), 7.52–7.68 (m, 2H, H_h), 7.84–7.93 (m, 2H, H_c). $^{13}\text{C NMR}$: 55.29 (C_k), 111.09 (C_f), 114.32 (C_i), 118.05 (CN), 127.01 (C_g), 127.18 (C_h), 128.76 + 128.93 ($\text{C}_b + \text{C}_e$), 130.01 (C_a), 133.84 (C_d), 139.96 (C_c), 160.33 (C_j).

Z-2-Heptyl-3-(4-methoxyphenyl)acrylonitrile 16Z



Purified by flash chromatography on silica gel (pentane then pentane–ether 99 : 1 to 98 : 2 v/v) as pale yellow oil. MS: m/z 257 (M^+ , 52.5%), 172 (100), 121 (71.2), 115 (18.0), 41 (13.7). $^1\text{H NMR}$: 0.83 (t, 3H, H_m), 1.26–1.44 (m, 8H, $\text{H}_i + \text{H}_j + \text{H}_k + \text{H}_l$), 1.61–1.72 (m, 2H, H_h), 2.35–2.44 (m, 2H, H_g), 3.87 (s, 3H, OCH_3), 6.78 (s, 1H, H_c), 6.91–6.98 (m, 2H, H_b), 7.71–7.77 (m, 2H, H_e). $^{13}\text{C NMR}$: 14.02 (C_m), 22.56 + 28.35 + 28.62 + 28.91 + 31.66 ($\text{C}_g + \text{C}_h + \text{C}_i + \text{C}_j + \text{C}_k + \text{C}_l$), 55.28 (CH_3O), 108.52 (C_f), 114.06 (C_b), 119.34 (CN), 126.55 (C_d), 130.15 (C_e), 142.73 (C_c), 160.67 (C_a).

E,Z-2-(4-Methoxyphenyl)-3-heptylacrylonitrile 17E + 17Z



Purified by flash chromatography on silica gel (pentane then pentane–ether 99 : 1 to 98 : 2 v/v) as pale yellow oil. MS (E isomer): m/z 257 (M^+ , 49.6%), 172 (100), 121 (88.4), 108 (19.1), 41 (18.3). MS (Z isomer): m/z 257 (M^+ , 27.3%), 172 (9.7), 121 (100), 108 (33.8), 41 (13.7). $^1\text{H NMR}$ ($E_{\text{major}} + Z_{\text{minor}}$): 0.9 (t, 3H, H_m), 1.25–1.42 (m, 8H, $\text{H}_i + \text{H}_j + \text{H}_k + \text{H}_l$), 1.42–1.51 (m, 2H, H_h), 2.46–2.51 (m, 2H, H_g), 3.45 (s, 3H, OCH_3) (E), 3.81 (s, 3H, OCH_3) (Z), 6.16–6.21 (m, 1H, H_f), 6.87–6.91 (m, 2H, H_b), 7.12–7.16 (m, 2H, H_e) (Z), 7.27–7.31 (m, 2H, H_c) (E). $^{13}\text{C NMR}$ ($E_{\text{major}} + Z_{\text{minor}}$): 14.09 (C_m) ($E + Z$), 22.54 (C_i) ($E + Z$), 28.21 + 28.56 + 28.75 + 29.07 + 29.43 ($\text{C}_j + \text{C}_k + \text{C}_l$) ($E + Z$), 31.52 + 31.71 (C_h) ($E + Z$), 36.21 + 39.54 (C_g) ($E + Z$), 55.23 (CH_3O), 113.56 + 114.18 (C_c) ($E + Z$), 114.15 (C_c) ($E + Z$), 117.68 + 120.96 (CN) ($E + Z$), 126.84 + 128.73 (C_d) ($E + Z$), 129.79 (C_b) ($E + Z$), 143.58 + 148.35 (C_f) ($E + Z$), 158.72 + 160.33 (C_a) ($E + Z$).

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