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Solvent-free condensation of arylacetonitrile with aldehydes

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Abstract—The condensation of a series of arylacetonitriles with aldehydes can be carried out by mixing equivalent amounts of reagents with neat powdered KOH at room temperature for 3–60 min depending on the aldehyde steric hindrance. At higher temperature (110 °C), yields were generally higher and purity increased within very short reaction times (1–5 min). With pentamethylphenylacetonitrile, a phase transfer agent was necessary to give a satisfactory yield.

1. Introduction

Unsaturated nitriles play a key role in several pathways proposed for the prebiotic synthesis of biological molecules.[1] Arylacrylonitriles are important synthons of the synthesis of several biologically active molecules in the preparation of flagrances,[2] flavonoïd pigments,[3] sexual pheromones[4] and vitamin A.[5] They are directly concerned for increasing soybean yield as plant growth regulators,[6] and as inhibitors of prostaglandin synthetase.[7] Recently, they were used in the field of organic materials in order to obtain high-electron affinity polymers, which can be used to produce light-emitting diodes (LEDs) with air stable electrodes.[8,9]

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

Very recently, we have proposed solvent-free procedures using neat powdered base.[17] When applied to the reaction of phenylacetonitrile with 4-methoxybenzaldehyde, excellent results were obtained using KOH at room temperature (Method I). The reactions were performed at higher temperatures (Method II, 110 °C), eventually in the presence of a phase transfer agent (PTA) (Method III). When a PTA catalyst was added (TBAB, Aliquat 336, TDA-1 or 18-C-6), under microwave irradiation (MW), new acrylonitriles with phenyl or alkyl group were obtained (whatever the base) according to a multi-step proposed mechanism.[17] With nonanenitrile, the PTA is necessary to obtain satisfactory yields, which were enhanced when using excesses of base ($KOCH_3$ or KOH) and nonanenitrile. However, a rather high temperature (130–150 °C) is needed, either under MW irradiation or conventional heating.

Strengthened by these results and in order to generalize the method, we now extend this study to the reaction of a series of aliphatic and aromatic aldehydes, including hindered ones, with substituted phenylacetonitriles.

2. Results and discussions

2.1. Reactions with phenylacetonitrile

Reactions were first carried out by mixing equivalent molar amounts of aldehyde (10 mmol), phenylacetonitrile and finely ground KOH. The main product was the α,β-unsaturated nitriles **3**(*Z*+*E*), contaminated by compound **4** resulting from Michael addition of **2a** to **3** (Eq. 1), and sometimes **5** coming from competitive Cannizzaro reaction.

Keywords: Solvent-free condensation; Microwave irradiation; Phase transfer catalysis; X-ray crystallography.
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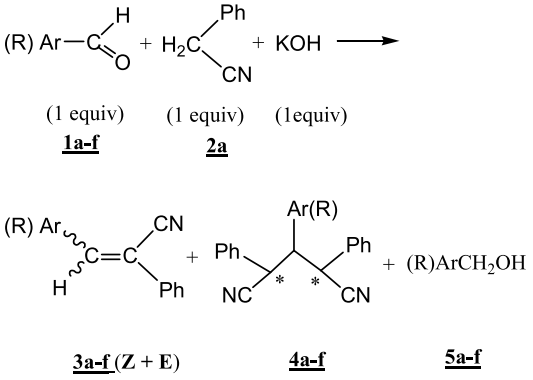


(1)

The main results are given in Table 1.

In all the cases, the major isomer was **3*Z*** with only traces of **3*E*** ($\leq$2%). The *Z* configuration of the carbon=carbon double bond in the major stereoisomer of compounds **3** was determined by X-ray single crystal analysis and by ^{13}C NMR. The ^{3}J coupling constant between the ethylenic proton and the carbon of the nitrile group was measured. In all cases, ^{3}J(C–H) values larger than 14 Hz were found.[18]

With the less hindered aromatic aldehydes **1a**–**c**, good yields (75–86%, entries 1, 3 and 6) were obtained within very short reaction time (3 min), needing a slight excess of aldehyde (1.3 equiv) when bearing a CF_3 group in position 4 (entry 6). Extended reaction times up to 10 min induced only a slight improvement, presumably due to the inefficacy of stirring as the reaction mixture became too solid (entries 2 and 4).

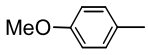
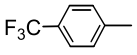
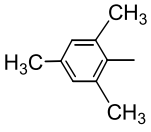
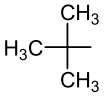
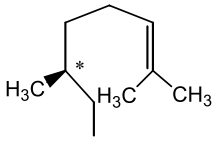
With aldehyde **1c**, an important amount of compound **4c** resulting from the Michael addition of **2a** to **3c*Z*** is obtained (8–12%, entries 5 and 6). When using an excess of nitrile (entry 7), the yield in **4c** is increased up to 20%. Furthermore, **1c** was among the tested aldehydes the only one giving amounts of the Cannizzaro product **5c**.

Where a highly hindered aromatic aldehyde such as mesitaldehyde **1d** is concerned, reaction time had to be extended up to 60 min to give a quasi-quantitative yield (98%, entry 10). Pivalaldehyde **1e**, in spite of steric hindrance due to *tert*-butyl group, led to a good yield in 10 min when using a slight excess of aldehyde (1.5 equiv) (87%, entry 12). No by-products were observed in these two last cases.

A yield of 87% in **3f*Z*** was obtained from L-(−)-citronellal **1f** in 10 min (entry 13), together with small amounts of **4f** (4%). Extension of reaction time did not allow any improvement.

The same reactions were next carried out at higher temperatures ($\geq$110 °C) under MW irradiation for very short times (1–2 min) and compared systematically with conventional heating (Δ) under strictly similar conditions (time, temperature, stirring,…) in order to check the possible non-thermal MW specific effects.[19]

Table 1. Solvent-free condensation of phenylacetonitrile **2a** with aromatic **1a**–**d** and aliphatic **1e**–**f** aldehydes, at room temperature, in the presence of KOH [Method I]

Entry	Aldehyde	(R) Ar	Reaction time (min)	Conversion[a] (%)	Yields (%)[a]			
					3*Z*	**3*E***	**4**	**5**
1	**1a**	Ph	3	96	77	1	4	0
2			10	96	81	1	6	0
3	**1b**		3	95	86	1	2	0
4			10	98	90	1	2	0
5	**1c**		3	94	63	2	12	7
6			3[b]	92	75	2	8	7
7			3[c]	—	67	2	20	5
8	**1d**		10	75	62	0	0	0
9			30	87	87	0	0	0
10			60	100	98	0	0	0
11	**1e**		10	79	77	0	0	0
12			10[d]	89	87	0	0	0
13	**1f**		10	94	87	1	4	0

[a] Conversions (based on consumption of **2a**) and yields were measured by GC using an internal standard (diethyl phthalate).
[b] **1c** (1.3 equiv).
[c] **2a** (1.2 equiv).
[d] **1e** (1.5 equiv).

Table 2. Solvent-free condensation of **2a** with a series of aldehydes **1a–f**, in the presence of KOH under MW irradiation or in a thermostated oil bath (Δ) [Method II]

Entry	Aldehyde	Activation method	Reaction time (min)	Temperature[a] (°C)	Conversion[b] (%)	Yields (%)[b]		
						3Z	**3E**	**4**
14	**1a**	MW	1	113	100	90	3	0
15		Δ	1	112	99	88	3	2
16	**1b**	MW	1	120	95	92	2	0
17		Δ	1	120	95	93	2	0
18	**1c**	MW	1	111	97	87	3	4
19		MW	2	125	99	94	1	2
20		Δ	1	101	97	83	2	5
21	**1d**	MW	1	111	42	42	0	0
22		MW	2	131	90	80	4	0
23		Δ	2	134	91	74	1	0
24	**1e**	MW	1	77	67	66	< 1	0
25		MW	2	115	84	83	< 1	0
26		Δ	1	80	60	58	< 1	0
27	**1f**	MW	1	123	98	95	3	0
28		Δ	1	107	96	90	4	2

[a] Optimal values obtained under MW (assigned temperature = 100 °C for **1a–d** and **1f**, 60 °C for **1e**) and consequently used for reactions under conventional heating Δ (values evaluated inside the reaction mixtures).
[b] Conversions and yields measured by GC using an internal standard (diethyl phthalate).

In Table 2 the results obtained under these conditions (MW and Δ) are given.

Yields were quite good (≥80%) within very short reaction times (1–2 min). Two opposite behaviours were shown:

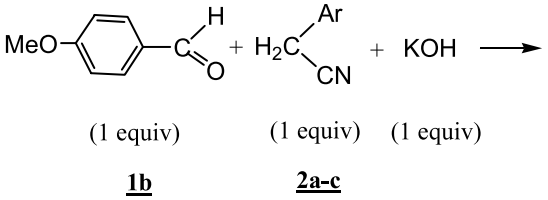
- a significant decrease in yield in the case of mesitaldehyde **1d** (80% within 2 min, entry 22) remained significantly less than the one resulting from reaction at room temperature. The yield was not next improved by extending reaction time up to 3 and 5 min as the isomer *E* was appearing (ex 3 min MW **3d*Z***: 80% **3d*E***: 10%).
- a clear increase with benzaldehyde **1a** (88–90% instead of 77–81% by Method I). The improvement is even more important with **1c** as yield was 94% versus only 63% according to Method I. Furthermore, it is of interest here to recover much less by-products (3% instead of 15–25%).

Aliphatic aldehydes **1e** and **1f** led to comparable yields but now without any traces of by-products (compare entries 25–27, respectively, with entries 11 and 13 in Table 1).

Finally, as a general rule, Method II seems to be more suitable than Method I improving the yield and reducing the secondary reactions. Nevertheless, in all these cases, results were practically identical whatever the activation mode, that is, no specific MW effects intervene here. The absence of such MW effects is justified as expected when considering the only slight modification of the polarity of the system during the reaction from the ground state to the transition state. The increase in polarity (necessary to observe MW effects) is here evidently limited due to the involvement of $PhCHCN^{-},M^{+}$ loose ion pairs concerning a charge delocalized (soft) anion.[20]

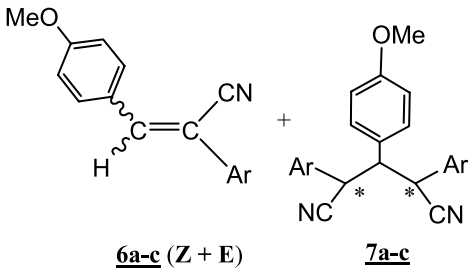
2.2. Reactions of several aromatic acetonitriles with 4-methoxybenzaldehyde

Reactions were carried out by mixing equivalent amounts of 4-methoxybenzaldehyde **1b** (10 mmol), arylacetonitrile **2a–c** and finely ground KOH. The main product was the α,β-unsaturated nitrile **6**, essentially with *Z* geometry, eventually accompanied in certain cases of compound **7** derived from Michael addition of **2** to **6** (Eq. 2).



(1 equiv) (1 equiv) (1 equiv)

1b **2a-c**



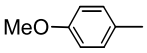
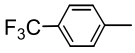
6a-c (**Z** + **E**) **7a-c** (2)

The main results are given in Table 3.

Satisfactory yields were obtained (≥74%) after short reaction times (≤10 min). The *Z* isomer was preponderant and accompanied by traces of **6*E***. However, extension of the reaction time induced slight modification presumably due to the heterogeneity of the reaction mixture. This reaction was next foreseen under MW irradiation and, for sake of comparison, with classical heating under similar conditions. Results are given in Table 4.

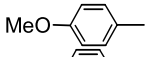
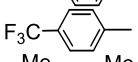
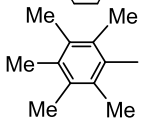
With nitriles **2a–c**, we isolated **6a–c*Z*** in high yields under

Table 3. Solvent-free condensation at room temperature of arylacetonitriles **2a–c** with 4-methoxybenzaldehyde **1b** in the presence of solid KOH [Method I]

Entry	Nitrile	Ar	Reaction time (min)	Conversion[a] (%)	Yields (%)[a]		
					6*Z*	**6*E***	**7**
3	**2a**	Ph	3	95	86	1	2
4			10	98	90	1	2
29	**2b**		3	83	65	2	0
30			10	94	74	1	0
31	**2c**		10	92	88	2	0

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

Table 4. Solvent-free condensation of $ArCH_2CN$ **2a–c** with **1b** in the presence of solid KOH under MW irradiation or in a thermostated oil bath (Δ) [Method II]

Entry	Nitrile	Ar	Activation mode	Reaction time (min)	Temperature[a] (°C)	Conversion[a] (%)	Yields (%)[b]		
							6*Z*	**6*E***	**7**
14	**2a**	Ph	MW	1	113	100	90	3	0
15			Δ	1	112	99	88	3	2
32	**2b**		MW	1	124	99	89	3	0
33			Δ	1	124	93	83	2	0
34	**2c**		MW	1	119	99	92	1	0
35			Δ	1	119	100	93	1	0
36	**2d**		MW	5	122	47	19	14	0
37			Δ	5	120	45	24	14	0
38			MW	3	140	43	17	13	0

[a] Optimal values obtained under MW (assigned temperature = 100 °C for entries 14, 32 and 34, 120 °C for 36 and 140 °C for 38) and consequently used for reactions under conventional heating Δ (values evaluated inside the reaction mixtures).
[b] Conversions and yields were measured by GC using an internal standard (diethyl phthalate).

MW within 1 min (≥89%), even with nitrile **2b** (89%), which proved to be lower at room temperature (74% after 10 min, entry 30).

With the especially hindered nitrile **2d**, the yields remained very low (33%, entry 36), even when increasing temperature to 140 °C (entry 38).

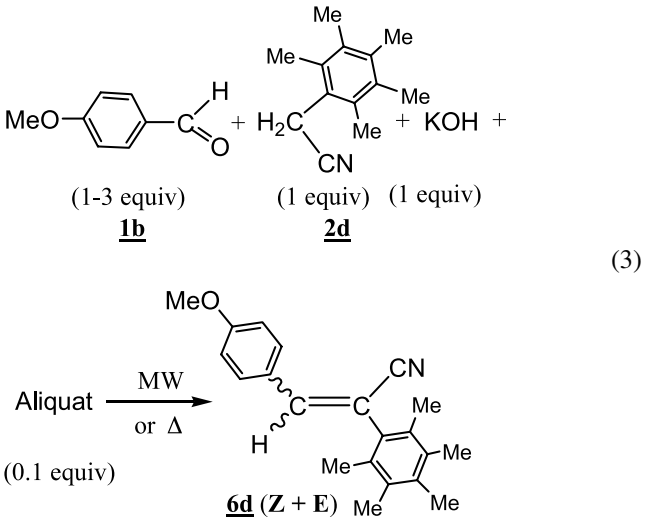
Changing the MW heating to conventional heating (entry 37) did not change the yield. In fact, as before, we did not observe any MW effects (Table 4), since yields and conversions were quite similar under conventional heating for the four nitriles (**2a**–**2d**). In order to try to improve the yield with the hindered **2d**, we also performed the reaction after addition of Aliquat 336 (Eq. 3), of which we report in Table 5 the main results obtained either under MW irradiation or classical heating with similar conditions.

The addition of Aliquat 336 allowed to noticeably increase the yields in ***6Z*** + ***E*** from 33% (entry 36, Table 4) up to 56% (entry 40, Table 5) under similar conditions (5 min at 120 °C). Yields were even more significantly improved up to 86% (entry 43) using an excess of aldehyde (1.5–3 equiv) with an optimal yield for 2 equiv. In all cases, ***Z*** is the predominant isomer. However, as discussed above, no noticeable MW specific effects were evidenced (MW = 86% versus Δ = 76%).

Table 5. Solvent-free condensation of pentamethylphenylacetonitrile **2d** with **1b** under solid–liquid phase transfer catalysis (PTC) conditions and MW irradiation or in a thermostated oil bath (Δ) [Method III]

Entry	**1b** (equiv)	Activation mode	Reaction time (min)	Temperature[a] (°C)	Conversion[b] (%)	Yields (%)[b]	
						6d*Z*	**6d*E***
39	1	MW	3	117	73	36	16
40		MW	5	120	96	36	20
41	1.5	MW	5	120	86	48	20
42	2	MW	3	120	91	55	20
43		MW	5	120	90	64	22
44		Δ	5	120	100	57	19
45		MW	7	120	91	56	20
46	3	MW	5	120	75	47	22

[a] Optimal values obtained under MW (assigned temperature = 120 °C) and consequently used for under conventional heating Δ (values evaluated into the reaction mixtures).
[b] Conversions and yields were measured by GC using an internal standard (diethyl phthalate).



2.3. Crystallographic study

The structures of compounds **3dZ**, **6cZ**, **6dZ** and **6dE** have been established by X-ray crystallography (Fig. 1). The crystal data were collected using a Bruker X8-APEX II-CCD area detector diffractometer. Intensities were given with graphite-monochromated Mo Kα radiation (0.71073 Å). The data were recorded at room temperature for **6dE** and at 100 K($\pm$1 K) for the three others (**3dZ**, **6cZ** and **6dZ**). The structures were solved by direct methods SHELX 86[21] and refined using SHELX 97[22] suite of programs. Non-H atoms were refined anisotropically by full-matrix least-squares techniques. H atoms were calculated geometrically and included in the refinement.

Crystal's data, details of data collections and structures refinements are given in the Section 4.

3. Conclusions

We have shown that solvent-free conditions, as previously established for the condensation of phenylacetonitrile with 4-methoxybenzaldehyde,[17] can be generalized to a series of aromatic and aliphatic aldehydes and to more or less hindered nitriles. At room temperature (Method I), reactions required from 3–60 min depending of the aldehyde steric hindrance. At higher temperatures ($\geq$110 °C, Method II), either under MW irradiation or conventional heating, reaction times are very short (1–5 min) and yields are generally higher and less by-products are recovered. With

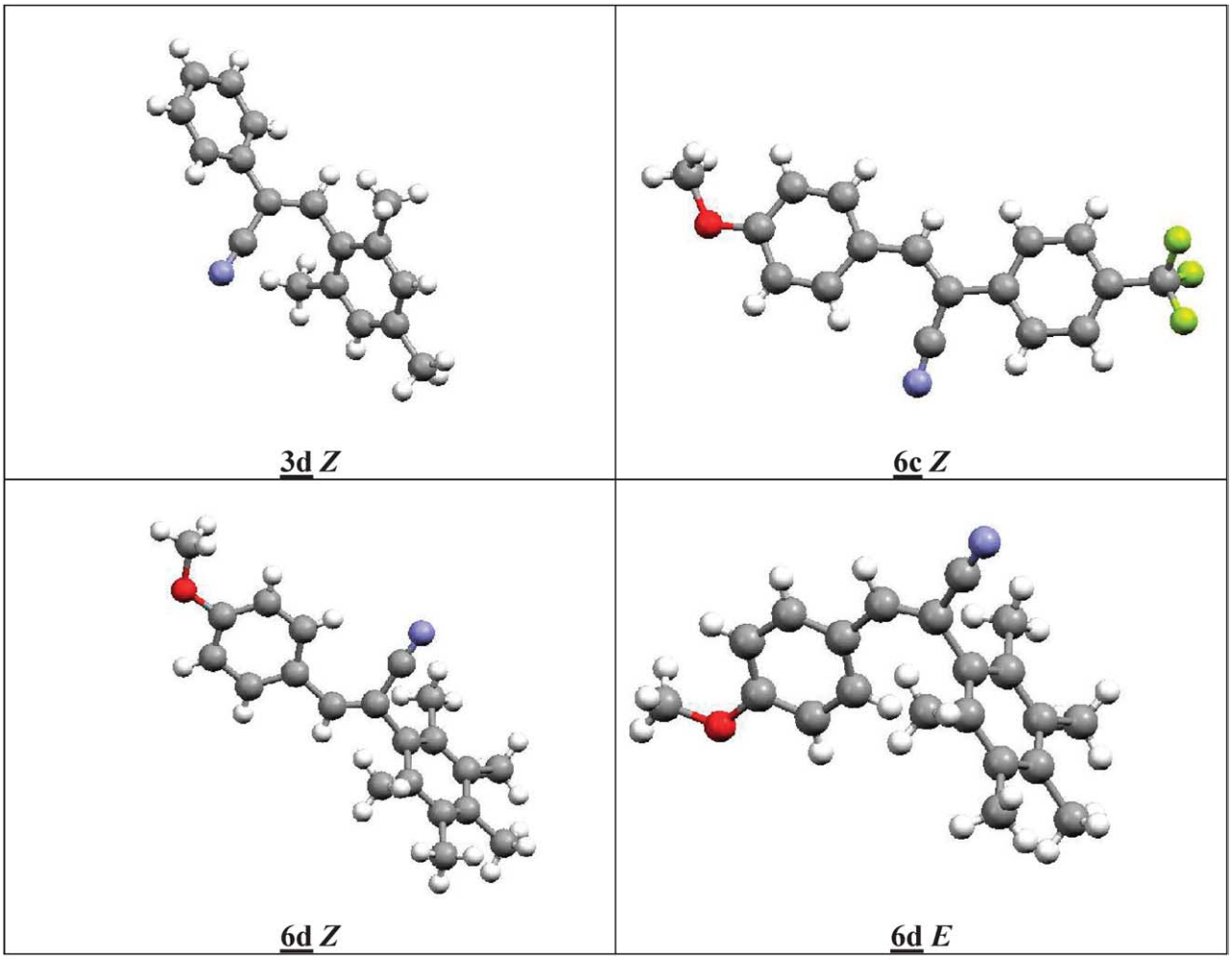


Figure 1. Crystal structures for **3dZ**, **6cZ**, **6dZ** and **6dE**.

pentamethylphenylacetonitrile, a phase transfer agent (Method III) is necessary to obtain a satisfactory yield at 120 °C. We have not observed any special MW effects neither on yields or conversions nor on the selectivity ***Z/E*** of the formed acrylonitriles.

4. Experimental

Microwave equipment

Reactions were performed in a monomode reactor Synthewave 402 microwave device from Prolabo.[23] 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 fiber thermometer (FTI-10 device from Fiso, optical fiber up to 250 °C). All reactions were conducted in a cylindrical Pyrex tube with mechanical stirring to ensure homogeneity in temperature. The 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 chromatography fitted with a capillary column DB5, 30 m, ID = 0.25 mm).

Their ^{1}H and ^{13}C NMR spectra were registered on a Bruker instrument (AC 200, AC 250 and DRX 400) as $CDCl_3$ solutions. Chemical shifts are expressed in δ units (ppm) and quoted downfield from TMS as an internal standard. Proton-coupled ^{13}C NMR experiments were performed on a Bruker DRX 400 NMR spectrometer using a classical gated decoupling technique.

X-ray crystallography

Crystallographic data:

	3dZ	**6cZ**	**6dZ**	**6d*E***
Chemical formula	$C_{18}H_{17}N$ NO	$C_{17}H_{12}F_3$ NO	$C_{21}H_{23}$ NO	$C_{21}H_{23}$ NO
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space Group	$P2_1/n$	$C2/c$	P-1	$Pbca$
a (Å)	10.27(1)	15.98(1)	12.16(1)	13.31(1)
b (Å)	9.02(1)	31.32(1)	18.27(1)	13.38(1)
c (Å)	14.72(1)	13.68(1)	18.64(1)	19.40(1)
α (°)	90	90	61.49(1)	90
β (°)	90.17(1)	125.019(1)	70.99(1)	90
γ (°)	90	90	89.87(1)	90
V (Å^3)	1363(1)	5607(1)	3382(2)	3454(2)
Z	4	16	4	8
μ (Mo Kα) (mm^{-1})	0.070	0.117	0.073	0.071
Crystal size (mm)	0.200, 0.180, 0.130	0.200, 0.120, 0.060	0.100, 0.080, 0.020	0.250, 0.300, 0.300
F (000)	528	2496	1312	1312
2θ range (°)	2.42–30.89	1.30–30.98	1.29–24.05	2.10–27.48
T (K)	100(1)	100(1)	100(1)	293(2)
Number of data collected	11,553	35,396	18,750	7461
Number of unique data	3382	8051	9317	3950
Observed data [$I>2\sigma(I)$] (nobs)	2998	5169	2757	2928
Rint (%)	2.01	4.51	8.90	2.03
Number of parameters (nvar)	176	397	365	212
R a(%)	6.67	5.71	21.94	6.03
wR b(%)	9.82	12.69	30.10	8.17
Sc	1.024	0.978	1.225	1.035
$\Delta\rho$min (e$^-$ Å^{-3})	−0.564	−0.410	−0.785	−0.282
$\Delta\rho$max (e$^-$ Å^{-3})	0.433	0.559	0.939	0.331

The dimensions of the crystal **6dZ** (20 microns thickness) did not permit to obtain data of satisfying quality to carry out a perfect refinement. The factor R for this structure is 21.94%. This structure is not deposited on Cambridge Crystallographic Data Center but this result is sufficient to prove that the compound is the expected one.

Crystallographic data for the structures reported in this paper, have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 269684–269685 and 269686. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

GC Analyses

All the yields were determined by GC with diethyl phthalate as internal standard. The GC devices (GC 9000 series Fisons, 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 is fitted with a hardware (NCI 900 series interface) and software (Turbochrom) system developed by Perkin Elmer Co.

GC conditions and retention times for reagents and products are given in Table 6.

Typical experiment

Aldehydes, arylacetonitriles, Aliquat 336 were purchased from commercial sources (Acros, Aldrich or Avocado Chemical Co.). Aldehydes **1a**, **1b** and **1c** were distilled before use. All others were used without any further purification. Commercial solid KOH (containing 15% H_2O) was finely grounded.

Table 6. GC conditions and retention times (RT) for reagents and products

Products or reagents	GC column	GC conditions	RT (min)	Internal standard RT (min)
1a	OV1, 12 m	100→250 °C (10 min)	1.18	5.87
2a	ID=0.25 mm	10 °C/min	1.73	
3a*Z*		P_{He}=50 kPa	9.78	
3a*E*			8.40	
4a			15.17+15.57	
1c	12QC2/BP1, 12 m	80→250 °C (5 min)	1.15	6.46
2a	ID=0.22 mm	10 °C/min	1.86	
3c*Z*		P_{He}=50 kPa	9.88	
3c*E*			8.53	
4c			14.44+15.03	
5c			2.27	
1b	DB1, 30 mm	100→280 °C (10 min)	5.58	9.38
2a	ID=0.25 mm	10 °C/min	4.50	
3b*Z*≡6a*Z*		P_{He}=70 kPa	16.40	
3b*E*≡6a*E*			15.12	
4b≡7a			22.43+23.24	
1d			6.33	
3d*Z*			15.17	
3d*E*			14.05	
1f		100→250 °C (10 min)	4.74	9.38
3f*Z*		10 °C/min	14.25	
3f*E*			13.93	
4f			23.00+23.42+23.80	
1e		80→250 °C (10 min)	In the solvent	11.14
2a		10 °C/min	5.40	
3e*Z*			9.71	
3eE			9.39	
1b		120→280 °C (10 min)	4.75	7.65
2b		10 °C/min	5.63	
6b*Z*			17.22	
6b*E*			15.60	
2c			4.09	
6c*Z*			13.91	
6c*E*			12.29	
2d			9.78	
6d*Z*			19.44	
6d*E*			17.69	

4.1. Solvent-free uncatalyzed reaction (Tables 1–4)

A mixture of phenylacetonitrile **2a** (10 mmol; 1.17 g), solid KOH (10 mmol; 0.65 g) and aldehyde **1a–f** (10 mmol) were introduced into a Pyrex vessel adapted to the microwave equipment fitted with a mechanical stirrer. At room temperature [Method I] or at temperatures ≥110 °C [Method II], the reactions were carried out in Pyrex vessels according to the conditions indicated in the Tables. At the end of the reaction, organic products were extracted with organic solvent (ethyl acetate) and the mixture was then filtered through sintered-glass.

The products **3a–f**(*Z*+*E*), **4a–c**, **4f** and **5c** were identified by GC–MS, NMR, X-ray crystallography, retention time by comparison with authentic samples, and analyzed by GC with an internal standard. Under conventional heating conditions (Δ) (Tables 2 and 4), the same Pyrex vessel as for MW experiments was used in the reactions carried out in the thermostated oil bath, at the same temperature as under MW irradiation. The same treatments were performed in both cases.

4.2. PTC solvent-free reaction (Tables 5 and 6)[Method III].

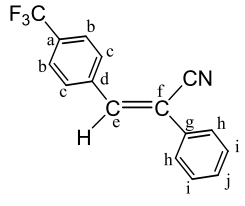
A mixture of arylacetonitrile **2a–d** (10 mmol), solid KOH (10 mmol; 0.65 g), Aliquat 336 (1 mmol; 0.4 g) and 4-methoxybenzaldehyde **1b** (10 mmol; 0.68 g) were introduced into a Pyrex vessel adapted to the microwave equipment, fitted with a mechanical stirrer.

Treatment remained exactly the same whatever the catalyzed or non-catalyzed nature of the reactions, under MW irradiation or conventional heating.

4.2.1. *Z*-2,3-Diphenylacrylonitrile 3a*Z* (RN: 2510-95-4). Commercial product (Lancaster Chemical Co.)

4.2.2. *Z*-2-Phenyl-3-(4-methoxyphenyl)acrylonitrile 3b*Z* or 6a*Z* (RN: 5432-07-5). This product was already described in earlier work.[17]

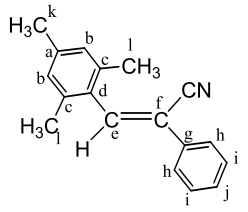
4.2.3. *Z*-2-Phenyl-3-(4-trifluoromethylphenyl]acrylonitrile 3c*Z* (RN: 147728-28-7).



Purified by flash chromatography (ether/*n*-pentane/ethanol 3:15:0.5). White crystals. Mp=112–114 °C. MS: *m*/*z* 273

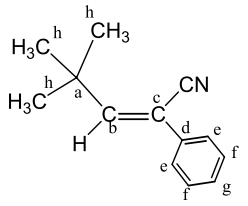
(M^+, 100%), 258 (10.7), 252 (11.4), 204 (78.2), 177 (11), 88 (11), 51 (13.5). ^{1}H NMR: 7.40–7.55 (m, 3H, H_i+H_j), 7.58 (s, 1H, H_e), 7.62–7.70 (m, 2H, H_h), 7.70–7.78 (m, 2H, H_b), 7.95–8.05 (m, 2H, H_c). ^{13}C NMR: 114.49 (C_f), 117.39 (CN) ($J_{He-CN}=14.5$ Hz), 122.22 (CF_3), 125.95 (C_b), 126.17 (C_h), 129.12 (C_i)+129.40 (C_c), 129.85 (C_j), 131.33 (C_a), 133.80 (C_g), 137.02 (C_d), 140.11 (C_e).

4.2.4. *Z*-2-Phenyl-3-(2,4,6-trimethylphenyl)acrylonitrile 3d*Z* (RN: 173975-31-0).



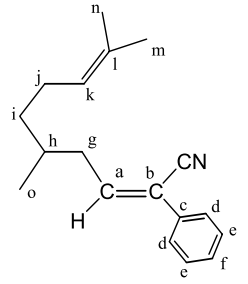
Purified by washing the crude product with cold *n*-pentane. Yellow crystals. Mp=103 °C. MS: *m/z* 247 (M^+, 100%), 231 (59.7), 205 (10.2), 115 (17.1), 91 (14.1), 77 (17.4), 51 (12.2). ^{1}H NMR: 2.31 (s, 9H, H_k+H_l), 6.91 (s, 2H, H_b), 7.34–7.45 (m, 3H, H_i+H_j), 7.64 (s, 1H, H_e), 7.65–7.70 (m, 2H, H_h). ^{13}C NMR: 20.10 (C_k), 20.97 (C_l), 116.72 (C_f), 118.50 (CN) ($J_{He-CN}=14.5$ Hz), 125.72 (C_h), 129.55 (C_b), 128.94 (C_i)+129.23 (C_j), 130.69 (C_a), 133.21 (C_g), 135.81 (C_c), 138.32 (C_d), 142.75 (C_e).

4.2.5. *Z*-2-Phenyl-3-*tert*-butylacrylonitrile 3e*Z* (RN: 110327-47-4).



Purified by distillation under reduced pressure. Colourless liquid. Bp=120–122/0.55 mbar. MS: *m/z* 185 (M^+, 73.5), 170 (100), 154 (18.6), 143 (67.4), 128 (46.3), 115 (33.7), 77 (34.2), 41 (31.6). ^{1}H NMR: 1.35 (s, 9H, H_h), 6.75 (s, 2H, H_b), 7.33–7.43 (m, 3H, H_f+H_g), 7.52–7.58 (m, 2H, H_e). ^{13}C NMR: 29.53 (C_h), 34.42 (C_a), 112.10 (C_c), 117.20 (CN) ($J_{Hb-CN}=15.0$ Hz), 125.73 (C_e), 128.63 (C_g), 128.76 (C_f), 135.08 (C_d), 157.31 (C_b).

4.2.6. *Z*-2-Phenyl-3-[(2,6-dimethyl)hept-5-en]acrylonitrile 3f*Z*.

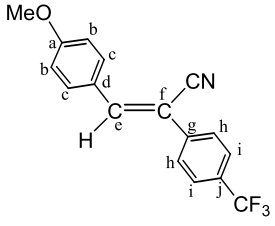


Purified by flash column chromatography on silica gel (*n*-pentane). Colourless liquid. MS: *m/z* 253 (M^+, 18.1), 238 (20.1), 154 (18.1), 115 (59.2), 109 (77.7), 81 (22.9), 69 (100), 55 (27.4), 41 (87.8). ^{1}H NMR: 0.98 (d, 3H, H_o), 1.15–1.55 (m, 2H, H_i), 1.61+1.68 (2s, 2×3H, H_n+H_m), 1.70–1.85 (m, 1H, H_h), 1.9–2.15 (m, 2H, H_j), 2.37–2.70 (m, 2H, H_g), 5.09 (m, 1H, H_k), 6.83 (t, 1H, H_a), 7.30–7.48 (m, 3H, H_e+H_f), 7.48–7.60 (m, 2H, H_d). ^{13}C NMR: 17.53 (C_n), 19.36 (C_o), 25.36 (C_j), 25.58 (C_m), 32.69 (C_h), 36.54 (C_i), 39.21 (C_g), 116.46 (CN) ($J_{Ha-CN}=14.4$ Hz), 116.55 (C_b), 124.06 (C_k), 125.41 (C_d), 128.65 (C_f), 128.73 (C_e), 131.37+133.13 (C_c+C_l), 145.83 (C_a).

4.2.7. *Z*-2-(4-Methoxyphenyl)-3-(4-methoxyphenyl)-acrylonitrile 6b*Z* (RN: 6443-74-9).

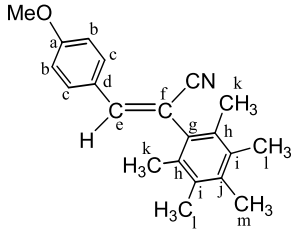
This product was already described in earlier work.[17]

4.2.8. *Z*-2-(4-Trifluoromethylphenyl)-3-(4-methoxyphenyl)acrylonitrile 6c*Z* (RN: 146725-29-3).



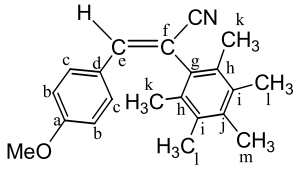
Purified by flash column chromatography on silica gel (*n*-pentane then *n*-pentane/ether 98:2). Yellow crystals. Mp=127–128 °C. MS: *m/z* 303 (M^+, 100), 284 (13,4), 272 (12.7), 240 (13.7), 234 (29), 233 (55.8), 219 (12.1), 191 (29.1), 190 (57.1). ^{1}H NMR: 3.89 (s, 3H, OCH_3), 6.94–7.06 (m, 2H, H_b), 7.54 (s, 1H, H_e), 7.64–7.85 (m, 2×2H, H_h+H_i), 7.85–8.01 (m, 2H, H_c). ^{13}C NMR: 55.24 (CH_3O), 107.07 (C_f), 114.52 (C_b), 118.03 (CN) ($J_{He-CN}=15.0$ Hz), 121.03 (CF_3), 124.00 (C_d), 125.99 (C_h), 128.43 (C_i), 129.39 C_j), 131.56 (C_c), 138.34 (C_g), 143.70 (C_e), 161.96 (C_a).

4.2.9. *Z*-2-(2,3,4,5,6-Pentamethylphenyl)-3-(4-methoxyphenyl)acrylonitrile 6d*Z*.



Purified by flash column chromatography on silica gel (*n*-pentane then *n*-pentane/ether 99:1–95:5). White solid. Mp=157 °C. MS: *m/z* 305 (M^+, 100%), 290 (37.9), 275 (29.6), 263 (8.9), 197 (10.1), 182 (17.2), 121 (16.2). ^{1}H NMR: 2.24+2.27+2.28 (3s, 15H, $H_k+H_l+H_m$), 3.87 (s, 3H, OCH_3), 6.79 (s, 1H, H_e), 6.95–7.06 (m, 2H, H_b), 7.81–7.94 (m, 2H, H_c). ^{13}C NMR: 16.59 (C_l), 16.87 (C_m), 17.87 (C_k), 55.40 (CH_3O), 108.07 (C_f), 114.28 (C_b), 118.68 (CN) ($J_{He-CN}=15.5$ Hz), 126.51 (C_d), 130.62 (C_c), 132.19 (C_h), 132.90 (C_g), 133.05 (C_i), 135.70 (C_j), 146.37 (C_e), 161.23 (C_a).

4.2.10. *E*-2-(2,3,4,5,6-Pentamethylphenyl)-3-(4-methoxyphenyl)acrylonitrile 6d*E*.



Purified by flash column chromatography on silica gel (pentane then pentane/ether 99:1–95:5). White solid. Mp = 153 °C. MS: *m/z* 305 (M^+, 100%), 290 (38.5), 275 (26), 263 (7.6), 197 (6.8), 182 (11), 121 (10.2). ^{1}H NMR: 2.19 + 2.22 + 2.28 (3s, 6H + 6H 3H, $H_k + H_l + H_m$), 3.74 (s, 3H, OCH_3), 6.66–6.74 (m, 2H, H_b), 6.89–6.98 (m, 2H, H_c), 7.31 (s, 1H, H_e). ^{13}C NMR: 16.63 (C_l), 16.94 (C_m), 17.08 (C_k), 55.20 (CH_3O), 111.05 (C_f), 114.11 (C_b), 120.46 (CN) ($J_{He-CN} = 9.3$ Hz), 127.11 (C_d), 129.58 (C_g), 131.22 (C_h), 131.35 (C_c), 133.42 (C_i), 135.94 (C_j), 144.19 (C_e), 160.87 (C_a).

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