Reactions of 2-(Dialkylamino)arylacetonitriles with Acetylenes Under Basic Conditions. A Simple Synthesis of Substituted Mono and Diketones[1]

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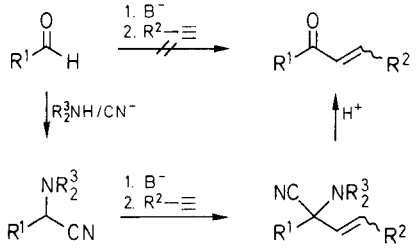
2-(Dialkylamino)arylacetonitriles **1** react with acetylenes **2a,b** in dimethyl sulfoxide, powdered sodium hydroxide and triethylbenzylammonium chloride as a catalyst to give **3** and/or **4**. The latter are formed via addition of anion **8** to immonium salt **9**. The type of product formed depends on the basicity of amino moiety in **3**. Furthermore, compound **1** adds to C-1 of acetylene **2c** affording the vinyl derivatives **15**. The products **3**, **4**, **11** and **15** are hydrolyzed to give ketones **5–7**, **12** and **16**, respectively.

While direct formation of an acyl anion via deprotonation of a formyl group is difficult to accomplish,[2] proper masking of this group is used to prepare compounds, the carbanions of which act as acyl anion equivalents.[3,4] In pursuit of novel syntheses of α,β-unsaturated carbonyl compounds, we examined the reaction of acyl anion equivalents, carbanions of 2-(dialkylamino)arylacetonitriles[4] with acetylenes. Due to electrophilic properties of the triple bond, acetylenes add to organometallic reagents[5] and carbanions,[6] giving *C*-vinyl derivatives. Unmasking of the carbonyl group in these vinyl derivatives should afford α,β-unsaturated ketones (Scheme **A**).

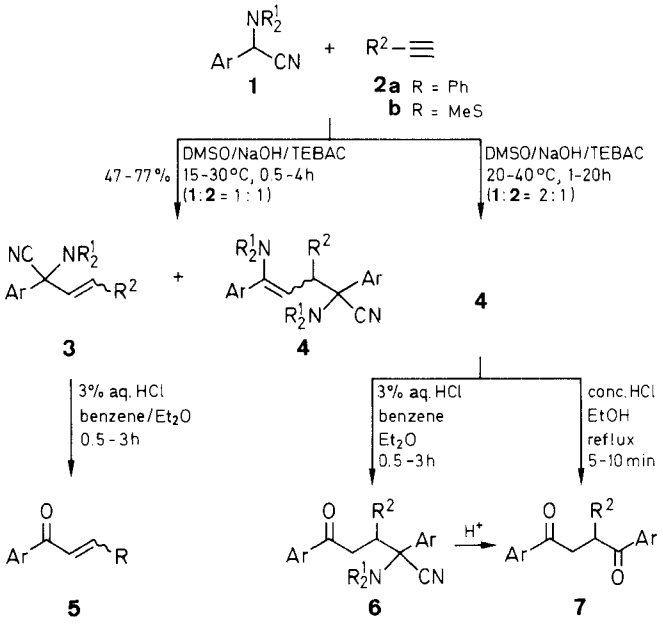


Scheme **A**

We have synthesized a series of 2-(dialkylamino)arylacetonitriles **1a–i** and reacted them, under basic conditions, with phenylacetylene **(2a)**, methylthioacetylene **(2b)** and ethoxyacetylene **(2c)**.[7] We found that simple stirring of amino nitriles **1** with acetylenes **2a,b** in powdered sodium hydroxide/triethylbenzylammonium chloride (TEBAC)/dimethyl sulfoxide system results in the formation of various products depending on the type of amino moiety in **1**, and the reaction conditions (Scheme **B**, Tables 1 and 2).

Two products, namely vinyl derivatives **3** and the unexpected enamino nitriles **4** were detected in the reaction mixtures. Reactions of morpholino- **1a**, *N*-methylpiperazino- **1b**, and thiomorpholino- **1c** nitriles with phenylacetylene **(2a)** gave the corresponding vinyl derivatives **3a,b** and **c**, whereas the formation of **4** required an excess of **1**, longer reaction times, and higher temperatures. Under these conditions **4a** and **4b** were isolated in good yields, while only traces of **4c** were detected in the mixture.

The amino nitriles **1d–h** (derivatives of dimethylamine, pyrrolidine and piperidine) reacted easily with **2a** to form



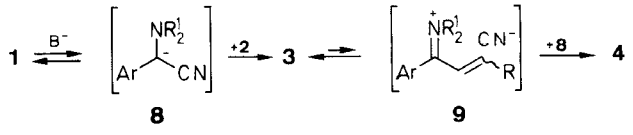
TEBAC = triethylbenzylammonium chloride

1	Ar	NR_2^1
a	Ph	morpholino
b	Ph	N-methylpiperazino
c	Ph	thiomorpholino
d	Ph	NMe_2
e	Ph	pyrrolidino
f	Ph	piperidino
g	4-MeC_6H_4	NMe_2
h	4-$MeOC_6H_4$	NMe_2
i	Ph	N(Me)Ph

Scheme **B**

4. A large excess of **2a** and mild reaction conditions were required for the isolation of **3** in good yields. The formation of products **3** and **4** in the reaction of **1** with methylthioacetylene **(2b)** did not depend significantly on the amino moiety in **1** (Tables 1 and 2).

The products **3** are formed via a simple addition of the anion **8** to the triple bond of **2**. It seems reasonable to assume that enamino nitriles **4** are formed as a result of either by attack of the anion **8** on C-3 of the initial product **3** in a S_N2' process, or more probably by the addition of **8** to the immonium salt **9** (Scheme **C**).

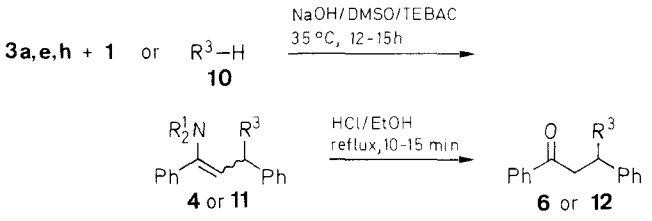


Scheme **C**

A few examples of such substitution of the cyano group in β,γ-unsaturated amino nitriles by carbanions or organometallic reagents are known.[8] Moreover, many reactions of 2-amino nitriles are thought to proceed via an immonium salt, which exists in equilibrium with 2-amino nitrile.[9]

The reason why the reaction of amino nitriles **1a–c** with **2a** is arrested at the stage of **3** is not fully clear at present. The concentration of the immonium salt **9** is a decisive factor, which depends on the basicity of amino moieties in **3**. The relatively low basicity of **3a–c** evaluated on the basis of pK_b of the corresponding amines R^1_2NH (pK_b ca. 5) compared to **3d–h** (pK_b ca. 3) causes the equilibrium **3**⇌**9** to shift to the left in the former case.[10]

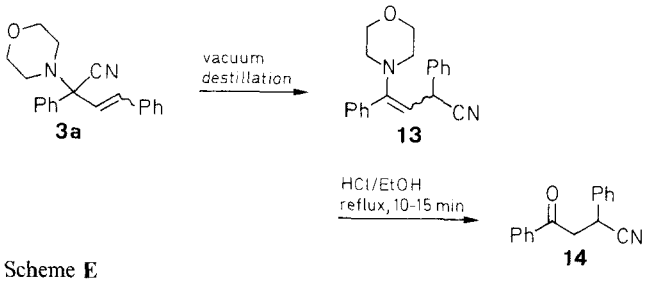
We have independently shown that **4** is formed via the vinyl derivative **3**; visualized in Scheme **C**. Thus stirring **3a**, **3e** or **3h** with amino nitriles **1** or with other compounds **10** containing an acidic CH group under the above cited conditions, afforded the products **4** or **11** in low to moderate yields (Scheme **D**, Table 2). Compounds **11** decomposed during purification and were directly transformed into ketones **12**.



10, 12	R^3
a	$PhC(CH_3)CN$
b	Ph_2CCN
c	$PhCOC(Ph)C_2H_5$

Scheme **D**

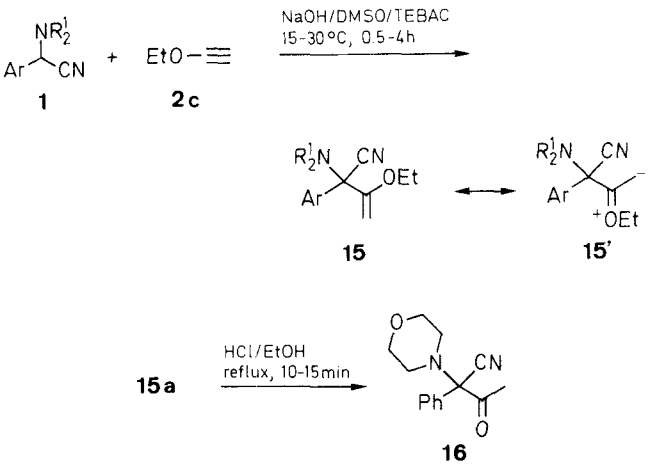
The products **3** and **4** were isolated by column chromatography and/or crystallization. In one case, e.g., the reaction of **1a** with **2a**, we attempted to isolate the product by vacuum distillation. However, the ^{1}H-NMR spectrum of the distilled material, and also cleavage under acidic conditions, revealed a compound identified as **13** (Scheme **E**).



Scheme **E**

The formation of **13** can be explained as a thermal 1,3-shift of the cyano group in **3a**.

Furthermore we have found that amino nitrile carbanions add readily to C-1 of ethoxyacetylene (**2c**). In these cases, the simple vinyl derivatives **15** were formed exclusively. Further reactions of **15** with **8**, the anion of **1**, have not been observed (Scheme **F**, Table 1). This fact may be explained by the resonance structure **15'**, in which the negative charge on C-3 hampers the attack of the nucleophile.



Scheme **F**

All the prepared products contain a masked carbonyl group. Therefore they are precursors of carbonyl compounds of different structures. Hydrolysis of vinyl derivatives **3**, enamines **4**, **11** and vinyl ethers **15** with hydrochloric acid afforded α,β-unsaturated ketones **5**, ketoamino nitriles **6**, 1,4-diketones **7**, ketones **12**, and acetyl derivative **16**, in good to high yield (Schemes **B**, **D**, **F**, Tables 3, 4).

The 1,4-diketones **7** were prepared via the unmasking of **6** or directly from **4** (**4** → **7**) without isolation of **6**. In many cases, hydrolysis was conveniently carried out using crude reaction mixtures, containing intermediates with masked carbonyl groups.

The stereochemistry of the products requires an additional comment. Analysis of crude reaction mixtures by of ^{1}H-NMR spectroscopy, showed that the *Z* isomer is the major isomer in compounds **3** and a higher *Z*/*E*-ratio for **3f–h** compared to **3a–e**. Preferred formation of *Z* isomers in the addition of CH acidic compounds to acetylenes under these conditions is well documented.[6,11] Some pure *Z* and *E* isomers of **3** were separated, and their structures were unambiguously determined. Due to the presence of a double bond and two chiral centres in **4** and in some cases also in **11**, each of the *Z* and *E* isomers can exist as a mixture of two diastereoisomers. Partial hydrolysis of **4** and **11** destroys the *Z*/*E* stereoisomerism but the chiral centres remain unchanged in the products **6** and **12**. While, the *Z*/*E* stereochemistry of **4** and **11** remains unknown, in the case of morpholine derivatives **4a**, **4h**, we were able to show the presence of two diastereoisomers. Compounds **4** and **11** containing other amino groups decomposed during attempted separation of isomers by column chromatography.

Finally, carbanions of relatively low nucleophilicity, e.g. generated from **1** (Ar = 4-NCC_6H_4; $R^1 = CH_3$) or those

Table 1. Vinylamino Nitriles **3** and **15** Prepared

Starting Materials	Reaction Conditions		Ratio of **3**/**4**[a]	Isolated Product	Yield (%)	Ratio of *Z*/*E*[a]	mp (°C) (solvent) or bp (°C)/Torr[c]	Molecular Formula[b]	IR (KBr) ν (cm^{-1}) C≡N, C=C	^{1}H-NMR ($CDCl_3$/TMS) δ, *J* (Hz)
	Ratio of **1**/**2**	Temp. (°C)/ Time (h)								
1a + **2a**	1 : 1	25–30/4	6 : 1	**3a**	70[c]	12/10	*Z*: 80–81 (EtOH)	$C_{20}H_{20}N_2O$ (304.4)	2220, 1593	2.23–2.44, 2.58–2.79 (m, 4H, CH_2NCH_2), 3.64–3.74 (m, 4H, CH_2OCH_2), 5.85, 6.76 (2d, 1H each, *J* = 12.15, CH=CH), 6.97–7.08 (m, $2H_{arom}$), 7.23–7.46 (m, $6H_{arom}$), 7.54–7.65 (m, $2H_{arom}$)
							E: 90.5–92 (EtOH)	$C_{20}H_{20}N_2O$ (304.4)	2220, 1593	2.40–2.82 (m, 4H, CH_2NCH_2), 3.69–3.79 (m, 4H, CH_2OCH_2), 6.11, 6.98 (AB system, 2H, *J* = 16.02, CH=CH), 7.22–7.46 (m, $8H_{arom}$), 7.62–7.73 (m, $2H_{arom}$)
1b + **2a**	1 : 1	25–30/4	7 : 1	**3b**	66[c]	17/10	*Z*: 86–87 (hexane)	$C_{21}H_{23}N_3$ (317.4)	2220, 1596	2.26 (s, 3H, CH_3N), 2.30–2.80 (m, 8H, NCH_2CH_2N), 5.85, 6.73 (2d, 1H each, *J* = 12.16, CH=CH), 6.97–7.08 (m, $2H_{arom}$), 7.24–7.46 (m, $6H_{arom}$), 7.54–7.64 (m, $2H_{arom}$)
							E: 108–109 (hexane/ cyclohexane)	$C_{21}H_{23}N_3$ (317.4)	2222, 1595	2.29 (s, 3H, CH_3N), 2.40–2.75 (m, 8H, NCH_2CH_2N), 6.11, 6.97 (AB system, 2H, *J* = 16.04, CH=CH), 7.24–7.46 (m, $8H_{arom}$), 7.62–7.73 (m, $2H_{arom}$)
1c + **2a**	1 : 1	25–30/3	–[d]	**3c**	77[c]	12/10	*Z*: 128–130 (cyclohexane)	$C_{20}H_{20}N_2S$ (320.5)	2240, 1603	2.50–3.10 (m, 8H, NCH_2CH_2S), 5.78, 6.73 (2d, 1H each, *J* = 12.14, CH=CH), 6.97–7.08 (m, $2H_{arom}$), 7.24–7.64 (m, $8H_{arom}$)
							E: 142–143 (cyclohexane)	$C_{20}H_{20}N_2S$ (320.5)	2240, 1600	2.65–3.10 (m, 8H, NCH_2CH_2S), 6.05, 6.95 (AB system, 2H, *J* = 16.04, CH=CH), 7.24–7.46 (m, $8H_{arom}$), 7.62–7.74 (m, $2H_{arom}$)
1d + **2a**	1 : 10	15–20/4	5/3	**3d**	47[c]	1/1	–[e]	–	–	2.22, 2.32 (2s, 6H each, CH_3NCH_3), 5.92, 6.70 (AB system, 2H, *J* = 12.16, CH=CH), 6.17, 6.96 (AB system, 2H, *J* = 16.04, CH=CH), 6.97–7.76 (m, $20H_{arom}$)[f]
1f + **2a**	10 : 1	15–20/4	23/10	**3e**	58[c]	21/10	–[e]	–	–	1.40–1.75 (m, 12H, $CH_2CH_2CH_2$), 2.15–2.75 (m, 8H, CH_2NCH_2), 5.83, 6.67 (AB system, 2H, *J* = 12.23, CH=CH), 6.11, 6.94 (AB system, 2H, *J* = 16.05, CH=CH), 6.97–7.77 (m, $20H_{arom}$)[f]
1a + **2b**	1 : 1	25–30/0.5	–[d]	**3f**	70	–[d]	*Z*: 106–107 (cyclohexane)	$C_{15}H_{18}N_2OS$ (274.4)	2220, 1600	2.26 (s, 3H, CH_3S), 2.33–2.80 (m, 4H, CH_2NCH_2), 3.71–3.81 (m, 4H, CH_2OCH_2), 5.58, 6.12 (AB system, 2H, *J* = 10.71, CH=CH), 7.33–7.41 (m, $3H_{arom}$), 7.63–7.74 (m, $2H_{arom}$)
1c + **2b**	1 : 1	25–30/0.5	–[d]	**3g**	76	–[d]	*Z*: 79–80 (cyclohexane)	$C_{15}H_{18}N_2S_2$ (290.4)	2220, 1596	2.25 (s, 3H, CH_3S), 2.65–3.05 (m, 8H, NCH_2CH_2S), 5.52, 6.09 (AB system, 2H, *J* = 10.71, CH=CH), 7.30–7.40 (m, $3H_{arom}$), 7.59–7.70 (m, $2H_{arom}$)

Table 1. (continued)

Starting Materials	Reaction Conditions: Ratio of **1**/**2**	Reaction Conditions: Temp. (°C)/ Time (h)	Ratio of **3**/**4**[a]	Isolated Product	Yield (%)	Ratio of *Z*/*E*[a]	mp (°C) (solvent) or bp (°C)/Torr[c]	Molecular Formula[b]	IR (KBr) ν (cm^{-1}) C≡N, C=C	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
1f + **2b**	1 : 1	25–30/0.5	–[d]	**3h**	58	42/10	*Z*: 73–74 (hexane)	$C_{16}H_{20}N_2S$ (272.4)	2220, 1608	1.45–1.70 (m, 6H, $CH_2CH_2CH_2$), 2.24 (s, 3H, CH_3S), 2.20–2.65 (m, 4H, CH_2NCH_2), 5.57, 6.05 (AB system, 2H, J = 10.68, CH=CH), 7.30–7.42 (m, 3H_{arom}), 7.61–7.71 (m, 2H_{arom}) *E*: 2.20 (s, CH_3S), 5.27, 6.65 (2d, J = 15.30, CH=CH)[f]
1a + **2c**	1 : 1	25–30/2	–	**15a**	68	–	98–99 (hexane/ cyclohexane)	$C_{16}H_{20}N_2O_2$ (272.3)	2230, 1650	1.21 (t, 3H, J = 7.00, CH_3), 2.34–2.74 (m, 4H, CH_2NCH_2), 3.67 (q, 2H, J = 7.00, CH_2O), 3.69–3.79 (m, 4H, CH_2OCH_2), 4.12, 4.83 (2d, 1H each, J = –3.35, $=CH_2$), 7.30–7.40 (m, 3H_{arom}), 7.67–7.77 (m, 2H_{arom})
1d + **2c**	1 : 1	25–30/2	–	**15b**	59	–	66–68/0.05	$C_{14}H_{18}N_2O$ (230.3)	2220, 1650	1.21 (t, 3H, J = 7.00, CH_3), 2.28 (s, 6H, CH_3NCH_3), 3.66, 3.70 (dq, 2H, J = 7.00), 4.08, 4.84 (2d, 1H each, J = –3.40, $=CH_2$), 7.28–7.38 (m, 3H_{arom}), 7.66–7.76 (m, 2H_{arom})
1f + **2c**	1 : 1	25–30/2.5	–	**15c**	70	–	60–61 (EtOH)	$C_{17}H_{22}N_2O$ (270.4)	2220, 1650	1.20 (t, 3H, J = 7.00, CH_3), 1.45–1.75 (m, 6H, $CH_2CH_2CH_2$), 2.25–2.65 (m, 4H, CH_2NCH_2), 3.65 (q, 2H, J = 7.00, CH_2O), 4.05, 4.80 (2d, 1H each, J = –3.22, $=CH_2$), 7.26–7.37 (m, 3H_{arom}), 7.65–7.75 (m, 2H_{arom})
1g + **2c**	1 : 1	25–30/4	–	**15d**	55	–	76–78/0.05	$C_{15}H_{20}N_2O$ (244.3)	2220, 1650	1.22 (t, 3H, J = 7.00, CH_3), 2.27 (s, 6H, CH_3NCH_3), 2.33 (s, 3H, CH_3Ar), 3.67, 3.70 (dq, 2H, J = 7.00, CH_2O), 4.07, 4.82 (2d, 1H each, J = –3.35, $=CH_2$), 7.09–7.63 (m, 4H_{arom})

[a] Determined by ^{1}H-NMR spectra at 100 MHz.
[b] Satisfactory microanalyses obtained: C ±0.17, H ±0.16, N ±0.29, S ±0.17.
[c] Calculated on the basis of ^{1}H-NMR spectra; the yield corresponds to the crude *Z* + *E*-mixture; analytically pure samples of isomers were prepared by column chromatography using basic Al_2O_3 as adsorbent and an EtOAc/hexane mixture (1 : 10) as eluent.
[d] Not determined; only traces of other products or isomers were detected by means of ^{1}H-NMR spectroscopy.
[e] Attempted purification by vacuum distillation or column chromatography failed (decomposition of material).
[f] Individual isomer resonance signals, separated from the spectra of crude reaction mixture.

Table 2. Compounds **4** Prepared

Starting Materials	Reaction Conditions		Product	Isomer Ratio[a] I/II	Yield (%)	mp (°C) (solvent)	Molecular Formula[b]	IR (KBr) ν (cm^{-1}) C≡N, C=C	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
	Ratio of **1**/**2** or **2**/**3**	Temp. (°C)/ Time (h)							
1a + **2a**	2 : 1	35–40/20	**4a**	1 : 1	I + II: 68	141–151 (cyclohexane/ acetone)	$C_{31}H_{33}N_3O_2$ (479.6)	–	I: 3.92, 4.99 (2d, 1H each, J = 10.72, CHCH=C)[d]
					II[c]: 33	150–152 (acetone)	$C_{31}H_{33}N_3O_2$ (479.6)	2215, 1622	2.27–2.60 (m, 4H, CH_2NCH_2), 2.68–2.83 (m, 4H, CH_2NCH_2), 3.56–3.76 (m, 8H, CH_2OCH_2), 4.11, 4.84 (2d, 1H each, J = 10.68, CHCH=C), 6.60–6.72 (m, 2H_{arom}), 6.95–7.40 (m, 13H_{arom})
1b + **2a**	2 : 1	35–40/10	**4b**	1 : 1	≥ 80[e]	–	–	–	2.28, 2.32 (2s, 3H each, CH_3N), 2.35–2.95 (m, 16H, NCH_2CH_2N), 3.90, 4.98 (2d, 1H each, J = 10.73, CHCH=C), 4.10, 4.85 (2d, 1H each, J = 10.60, CHCH=C), 6.60–6.75 (m, 4H_{arom}), 7.00–7.45 (m, 26H_{arom})
1d + **2a**	2 : 1	35/5	**4c**	1 : 1	≥ 68[e]	–	–	–	2.12, 2.16, 2.52, 2.56 (4s, 3H each, CH_3NCH_3), 3.78, 4.82 (2d, 1H each, J = 10.44, CHCH=C), 4.01, 4.55 (AB system, 2H, J = 10.84, CHCH=C), 6.80–7.45 (m, 30H_{arom})
1e + **2a**	2 : 1	35/6	**4d**	1 : 2	I + II: 55	119–122 (pentane/ cyclohexane)	$C_{31}H_{33}N_3$ (447.6)	2220, 1620	1.60–1.88 (m, 8H, CH_2CH_2), 2.35–2.65 (m, 4H, CH_2NCH_2), 2.74–3.00 (m, 4H, CH_2NCH_2), 3.75, 4.57 and 3.87, 4.37 (2d, J = 10.55 and AB system, J = 11.08, 2H together, CHCH=C), 6.60–6.75 (m, 2H_{arom}), 6.95–7.40 (m, 13H_{arom})
1f + **2a**	2 : 1	40/5	**4e**	1 : 1	I + II: 71				
					I[c]: 35	125–127 (hexane)	$C_{33}H_{37}N_3$ (475.7)	2215, 1620	1.54 (br s, 12H, $CH_2CH_2CH_2$), 2.26 (br s, 4H, CH_2NCH_2), 2.77 (br s, 4H, CH_2NCH_2), 3.91, 4.97 (2d, 1H each, J = 10.76, CHCH=C), 6.60–6.70 (m, 2H_{arom}), 6.95–7.35 (m, 13H_{arom})
					II[c]: 30	133–135 (hexane)	$C_{33}H_{37}N_3$ (475.7)	2220, 1622	1.35–1.65 (m, 12H, $CH_2CH_2CH_2$), 2.15–2.70 (m, 4H, CH_2NCH_2), 2.78 (br s, 4H, CH_2NCH_2), 4.19, 4.76 (AB system, 2H, J = 10.79, CHCH=C), 6.60–6.75 (m, 2H_{arom}), 7.00–7.35 (m, 13H_{arom})
1g + **2a**	2 : 1	35/8	**4f**	–[f]	I: 76	138–140 (hexane/ benzene)	$C_{29}H_{33}N_3$ (423.6)	2210, 1620	2.10 (s, 6H, CH_3NCH_3), 2.34 (s, 6H, CH_3Ar), 2.52 (s, 6H, CH_3NCH_3), 3.77, 4.78 (2s, 1H each, J = 10.50, CHCH=C), 6.60–6.70 (m, 2H_{arom}), 6.84–7.24 (m, 11H_{arom})
1h + **2a**	2 : 1	30/16	**4g**	2 : 1	≥ 62[e]	–	–	–	I and II: 2.06, 2.04 (2s, 6H together, CH_3NCH_3), 2.32, 2.35 (2s, 6H together, CH_3NCH_3), 3.21 (s, 6H, CH_3O), 3.98, 4.90 and 4.20, 4.68 (2d, J = 10.55 and AB system, J = 10.45, 2H together, CHCH=C), 6.60–7.30 (m, 13H_{arom})
1a + **2b**	2 : 1	30/6	**4h**	1 : 1	I + II: 88	168–171 (cyclohexane/ benzene)	$C_{26}H_{31}N_3O_2S$ (449.6)	2240, 1630	1.69 (s, 3H, CH_3S), 2.22–2.32 (m, 4H, CH_2NCH_2), 2.70–2.80 (m, 4H, CH_2NCH_2), 3.55–3.75 (m, 8H, CH_2OCH_2), 3.81, 4.36 (AB system, 2H, J = 10.95, CHCH=C), 7.35–7.45 (m, 8H_{arom}), 7.65–7.75 (m, 2H_{arom})
					I[c]: 24				
					II[c]: 31	158–160 (hexane/ EtOH)	$C_{26}H_{31}N_3O_2S$ (449.6)	2240, 1620	1.70 (s, 3H, CH_3S), 2.30–2.70 (m, 8H, CH_2NCH_2), 3.57–3.75 (m, 8H, CH_2OCH_2), 3.78, 3.94 (AB system, 2H, J = 10.80, CHCH=C), 7.33–7.50 (m, 8H_{arom}), 7.70–7.80 (m, 2H_{arom})

Table 2. (continued)

Starting Materials	Reaction Conditions: Ratio of **1/2** or **2/3**	Reaction Conditions: Temp. (°C)/ Time (h)	Product	Isomer Ratio[a] I/II	Yield (%)	mp (°C) (solvent)	Molecular Formula[b]	IR (KBr) ν (cm^{-1}) C≡N, C=C	^{1}H-NMR ($CDCl_3$/TMS) δ, J (Hz)
1e + 2b	1 : 1	25–30/1	**4i**	1 : 3	II: 57	141–145 (hexane/ benzene)	$C_{26}H_{31}N_3S$ (417.6)	2220, 1612	1.70–1.87 (m, 8H, CH_2CH_2), 1.75 (s, 3H, CH_3S), 2.42–2.70 (m, 4H, CH_2NCH_2), 2.75–3.00 (m, 4H, CH_2NCH_2), 3.47, 3.78 (AB system, 2H, J = 11.06, CHCH=C), 7.30–7.50 (m, 8H_{arom}), 7.70–7.80 (m, 2H_{arom}) I: 3.57, 3.98 (AB system, J = 11.00, CHCH=C)[d]
1f + 2b	2 : 1	35/5	**4j**	3 : 4	II: 55	135–137 (hexane)	$C_{28}H_{35}N_3S$ (445.7)	2219, 1608	1.49 (br s, 12H, $CH_2CH_2CH_2$), 1.68 (s, 3H, CH_3S), 2.25–2.55 (m, 4H, CH_2NCH_2), 2.67 (br s, 4H, CH_2NCH_2), 3.74, 3.99 (AB system, 2H, J = 10.90, CHCH=C), 7.30–7.50 (m, 8H_{arom}), 7.70–7.80 (m, 2H_{arom}) I: 1.57 (s, CH_3S), 3.81, 4.37 (AB system, J = 10.95, CHCH=C)[d]
1g + 2b	2 : 1	35/3	**4k**	2 : 3	I + II: 81	106–130 (cyclohexane/ hexane)	$C_{24}H_{31}N_3S$ (393.6)		I: 1.66 (s, CH_3S), 2.05, 2.54 (2s, CH_3NCH_3), 2.38 (s, CH_3Ar), 3.67, 4.17 (AB system, J = 10.75, CHCH=C)[d]
					II[c]: 34	119–121 (hexane)	$C_{24}H_{31}N_3S$ (393.6)	2212, 1612	1.73 (s, 3H, CH_3S), 2.24, 2.48 (2s, 6H each, CH_3NCH_3), 2.38 (s, 3H, CH_3Ar), 3.62, 3.84 (AB system, 2H, J = 10.81, CHCH=C), 7.14–7.66 (m, 13H_{arom})
1g + 3a	1 : 1	35/14	**4l**	–[f]	I: 27[g]	141–143 (hexane/ benzene)	$C_{30}H_{33}N_3O$ (451.6)	2220, 1620	2.10 (s, 6H, CH_3NCH_3), 2.36 (s, 3H, CH_3Ar), 2.68–2.78 (m, 4H, CH_2NCH_2), 3.68–3.78 (m, 4H, CH_2OCH_2), 3.84, 4.98 (2d, 1H each, J = 10.55, CHCH=C), 6.60–6.72 (m, 2H_{arom}), 7.03–7.35 (m, 12H_{arom})
1i + 3a	1 : 1	35/18	**4m**	–[f]	I: 24[g]	137–140 (cyclohexane/ benzene)	$C_{34}H_{33}N_3O$ (499.7)	2215, 1615	2.64–2.74 (m, 4H, CH_2NCH_2), 2.66 (s, 3H, CH_3N), 3.65–3.75 (m, 4H, CH_2OCH_2), 4.02, 5.01 (2d, 1H each, J = 9.92, CHCH=C), 6.55–6.70 (m, 4H_{arom}), 6.98–7.35 (m, 16H_{arom})
1g + 3h	1 : 1	30/5	**4n**	6 : 10	II: 31[g]	141–144 (hexane)	$C_{26}H_{33}N_3S$ (419.6)	2240, 1620	1.49 (br s, 6H, $CH_2CH_2CH_2$), 1.69 (s, 3H, CH_3S), 2.24 (s, 6H, CH_3NCH_3), 2.38 (s, 3H, CH_3Ar), 2.70 (br s, 4H, CH_2NCH_2), 3.83, 3.90 (AB system, 2H, J = 11.0, CHCH=C), 7.15–7.65 (m, 9H_{arom}) I: 1.64 (s, CH_3S), 2.03 (s, CH_3NCH_3), 2.38 (s, CH_3Ar), 3.73, 4.34 (AB system, J = 10.80, CHCH=C)[d]

[a] Ratio for one isomer I whose $\delta H_a - \delta H_b$ for $CH_a-CH_b=C$ is higher then that of the other II, determined by ^{1}H-NMR spectra at 100 MHz.

[b] Satisfactory microanalyses obtained: C ±0.29, H ±0.16, N ±0.21.

[c] Analytically pure samples of isomers were prepared by fractional crystallization.

[d] Individual isomer resonance signals, separated from the spectra of the I + II-mixture.

[e] Crude I + II-mixture; yield estimated from the yield of the corresponding diketone **7**.

[f] Not determined.

[g] Overall yield based on starting aminonitrile **1**. Reaction without isolation of the intermediate vinylaminonitrile **3**, carried-out according to the one-pot procedure (see Experimental).

containing bulky substituent at nitrogen atom (MeNPh) did not react with **2a** under the described conditions.

In summary, the reactions of 2-(dialkylamino)arylacetonitrile carbanions with acetylenes readily afford carbonyl compounds of different structures.

Boiling and melting points are uncorrected, the latter were determined in a capillary tube. ^{1}H-NMR spectra were obtained on a Bruker WP-100 spectrometer at 100 MHz with TMS as internal standard. IR spectra were measured on Perkin-Elmer Mod. 577 or Specord M80 spectrophotometers. Microanalyses were obtained using a Perkin-Elmer 240 CHN analyser. Analytical TLC plates and silica gel (230–400 mesh) were purchased from Merck, while

Table 3. Compounds **6** and **16** Prepared

Starting Materials[a]	Product[a]	Yield (%)	mp (°C) (solvent)	Molecular Formula[b] or Lit. mp (°C)	IR (KBr) ν(cm^{-1}) C≡N, C=O	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
4a (II)	**6a** (II)	89	128–129 (EtOH)	$C_{27}H_{26}N_2O_2$ (410.5)	2250, 1670	2.44–2.94 (m, 4H, CH_2NCH_2), 3.60–3.70 (m, 4H, CH_2OCH_2), 3.58, 3.89 (part AB of ABX system, 2H, J_{AX} = 9.36, J_{BX} = 3.54, J_{AB} = −17.43, CH_2CO), 4.64 (part X of ABX system, 1H, CH), 7.07 (s, 5H$_{arom}$), 7.27 (s, 5H$_{arom}$), 7.40–7.55 (s, 3H$_{arom}$), 7.86–7.96 (m, 2H$_{arom}$)
4a (I + II)	**6a** (I)	43	171–172 (EtOH)	$C_{27}H_{26}N_2O_2$ (410.5)	2220, 1680	2.65–2.80 (m, 4H, CH_2NCH_2), 3.54, 3.59 (part AB of ABX system, 2H, J_{AX} = 12.28, J_{BX} = 0.97, J_{AB} = −15.1, CH_2CO), 3.70–3.85 (m, 4H, CH_2OCH_2), 4.41 (part X of ABX system, 1H, CH), 6.60–6.72 (m, 2H$_{arom}$), 7.00–7.50 (m, 11H$_{arom}$), 7.80–7.90 (m, 2H$_{arom}$)
4c (I + II)[c]	**6b**	54[d]	165–167 (cyclohexane/benzene)	166–170[12]	2220, 1670	2.42 (s, 6H, CH_3NCH_3), 3.47, 3.74 (part AB of ABX system, 2H, J_{AX} = 11.58, J_{BX} = 1.67, J_{AB} = −17.8, CH_2CO), 4.36 (part X of ABX system, 1H, CH), 6.62–6.72 (m, 2H$_{arom}$), 7.00–7.50 (m, 11H$_{arom}$), 7.80–7.90 (m, 2H$_{arom}$)
4e (I)	**6c**	76	123.5–125 (cyclohexane)	$C_{28}H_{28}N_2O$ (408.5)	2210, 1680	1.57 (br s, 6H, $CH_2CH_2CH_2$), 2.61 (br s, 4H, CH_2NCH_2), 3.49, 3.63 (part AB of ABX system, 2H, J_{AX} = 11.67, J_{BX} = 1.62, J_{AB} = −17.75, CH_2CO), 4.44 (part X of ABX system, 1H, CH), 6.60–6.70 (m, 2H$_{arom}$), 7.00–7.53 (m, 11H$_{arom}$), 7.80–7.90 (m, 2H$_{arom}$)
4e (II)	**6c**	70				
4f	**6d**	80	121–122.5 (EtOH)	$C_{27}H_{28}N_2O$ (396.5)	2215, 1675	2.38 (s, 12H, CH_3Ar and CH_3NCH_3), 3.44, 3.65 (part AB of ABX system, 2H, J_{AX} = 11.58, J_{BX} = 1.63, J_{AB} = −17.70, CH_2CO), 4.32 (part X of ABX system, 1H, CH), 6.60–6.70 (m, 2H$_{arom}$), 7.00–7.25 (m, 9H$_{arom}$), 7.65–7.80 (m, 2H$_{arom}$)
4h (I)	**6e** (I)	86	159–160 (cyclohexane/benzene)	$C_{22}H_{24}N_2O_2S$ (380.5)	2240, 1685	2.28 (s, 3H, CH_3S), 2.57–2.72 (m, 4H, CH_2NCH_2), 3.13, 3.49 (part AB of ABX system, 2H, J_{AX} = 11.03, J_{BX} = 1.29, J_{AB} = −17.47, CH_2CO), 3.65–3.80 (m, 4H, CH_2OCH_2), 4.08 (part X of ABX system, 1H, CH), 7.35–7.60 (m, 6H$_{arom}$), 7.68–7.80 (m, 2H$_{arom}$), 7.83–7.95 (m, 2H$_{arom}$)
4h (II)	**6e** (II)	79	112–113 (hexane/benzene)	$C_{22}H_{24}N_2O_2S$ (380.5)	2235, 1695	2.07 (s, 3H, CH_3S), 2.40–2.80 (m, 4H, CH_2NCH_2), 3.14, 3.56 (part AB of ABX system, 2H, J_{AX} = 9.21, J_{BX} = 2.79, J_{AB} = −17.7, CH_2CO), 3.67–3.77 (m, 4H, CH_2OCH_2), 4.24 (part X of ABX system, 1H, CH), 7.30–7.72 (m, 8H$_{arom}$), 7.82–7.95 (m, 2H$_{arom}$)
4k (I + II)	**6f**	30	133–134.5 (cyclohexane)	$C_{22}H_{26}N_2OS$ (366.5)	2216, 1680	2.28 (s, 3H, CH_3S), 2.32 (s, 6H, CH_3NCH_3), 2.40 (s, 6H, CH_3Ar), 3.04, 3.55 (part AB of ABX system, 2H, J_{AX} = 11.0, J_{BX} = 1.30, J_{AB} = −17.63, CH_2CO), 4.01 (part X of ABX system, 1H, CH), 7.19–7.27 (m, 4H$_{arom}$), 7.55–7.84 (m, 4H$_{arom}$)
4l	**6g**	76	142–144 (EtOH)	$C_{26}H_{26}N_2O$ (382.5)	2220, 1670	2.39 (s, 9H, CH_3NCH_3 and CH_3Ar), 3.46, 3.69 (part AB of ABX system, 2H, J_{AX} = 11.54, J_{BX} = 1.74, J_{AB} = −17.83, CH_2CO), 4.33 (part X of ABX system, 1H, CH), 6.60–6.72 (m, 2H$_{arom}$), 7.00–7.20 (m, 6H$_{arom}$), 7.35–7.55 (m, 4H$_{arom}$), 7.80–7.92 (m, 2H$_{arom}$)
4m	**6h**	86	132–134 (EtOH)	$C_{30}H_{26}N_2O$ (430.5)	2220, 1685	2.89 (s, 3H, CH_3N), 3.27, 3.80 (part AB of ABX system, 2H, J_{AX} = 11.48, J_{BX} = 2.26, J_{AB} = −17.19, CH_2CO), 4.29 (part X of ABX system 1H, CH), 6.60–6.72 (m, 2H$_{arom}$), 7.00–7.70 (m, 18H$_{arom}$)
15a	**16**	98	137–138 (hexane/benzene)	$C_{14}H_{16}N_2O_2$ (244.3)	2225, 1670	2.22 (s, 3H, CH_3), 2.40–2.75 (m, 4H, CH_2NCH_2), 3.77–3.87 (m, 4H, CH_2OCH_2), 7.27–7.47 (m, 3H$_{arom}$), 7.65–7.75 (m, 2H$_{arom}$)

[a] For defenition I and II, see Table 2.

[b] Satisfactory microanalyses obtained: C ±0.20, H ±0.08, N +0.28.

[c] Crude mixture containing **4** was used (see Table 2).

[d] Yield of pure isolated product based on **2**.

basic alumina from Fluka Chemical Co. DMSO and phenylacetylene (Merck) were distilled before use. Ethoxyacetylene,[14] methylthioacetylene,[14] 2-phenylpropionitrile (**10a**),[5] 2-phenylbutyrophenone (**10c**),[16] and amino nitriles **1**[17] were prepared according to literature procedures. New amino nitriles **1b** and **1c** were identified by ^{1}H-NMR spectra and elemental analyses. 126–128 °C/0.3 Torr. **1b**; yield: 79%; bp.

$C_{13}H_{17}N_3$ (215.3) calc. C 72.52 H 7.96 N 19.52; found 72.44 7.89 19.56

^{1}H-NMR ($CDCl_3$): δ = 2.28 (s, 3H, CH_3N), 2.35–2.70 (m, 8H, NCH_2CH_2N), 4.83 (s, 1H, CH), 7.34–7.58 (m, 5H_{arom}).

1c; yield: 74%; mp 80–81 °C (cyclohexane).

$C_{12}H_{14}N_2S$ (218.3) calc. C 66.02 H 6.46 N 12.83; found 66.11 6.40 12.77

^{1}H-NMR ($CDCl_3$): δ = 2.62–2.92 (m, 8H, SCH_2CH_2N), 4.81 (s, 1H, CH), 7.35–7.58 (m, 5H_{arom}).

All carbanionic reactions of amino nitriles were carried out under N_2.

Vinylamino Nitriles 3 and 15 (except 3d and 3e); General Procedure:
A solution of amino nitrile **1** (10 mmol) in DMSO (10 mL) is placed in a 3-necked round-bottomed flask fitted with a mechanical stirrer and thermometer. The mixture is stirred while powdered NaOH (2.4 g, 60 mmol) and TEBAC (about 0.1 g, 0.5 mmol) are added all at once. A solution of acetylene **2a**, **2b** or **2c** (10 mmol) in DMSO (2 mL) is then introduced with a syringe (a slight exothermal effect is observed, the temperature is kept at 25–30 °C). The mixture is stirred at the temperature and time indicated in Table 1. The mixture is poured into water (100 mL) and extracted with benzene (100 mL). The organic phase is washed with water, dried ($MgSO_4$), and the solvent is evaporated *in vacuo*. In the case of **2b** or **2c** the residue is crystallized or distilled *in vacuo*. Crude *E*/*Z* mixtures, obtained from **2a**, are separated by column chromatography on basic alumina (EtOAc/hexane, 1:10 as eluent) and crystallized to give pure *Z* and *E* isomers of **3** (Table 1).

***E*/*Z*-2-Dimethylamino-2,4-diphenyl-3-butenenitrile (3d) and *E*/*Z*-2,4-Diphenyl-2-piperidino-3-butenenitrile (3e):**
A mixture of powdered NaOH (9.0 g, 200 mmol), TEBAC (0.5 g, 2.2 mmol), phenylacetylene (**2a**; 40.8 g, 400 mmol) in DMSO (50 mL) is vigorously stirred, while a solution of amino nitrile **1d** or **1f** (40 mmol) in DMSO (30 mL) is added dropwise at 15–20 °C for 3 h. The mixture is stirred for 1 h, poured into water, the organic phase separated and washed with water as quickly as possible, with cold 3% aq. HCl (5 × 30 mL) in order to remove the side-product **4**. Finally the organic phase is washed with 5% aq. $NaHCO_3$ (30 mL), dried ($MgSO_4$), and the excess of **2a** is distilled off under reduced pressure. The residue consists of crude vinylamino nitriles **3d** or **3e**, which decompose during attempted purification (Table 1).

Enaminoamino Nitriles 4 (except 4l,m,n); General Procedure:
The reactions are carried out as described for vinylamino nitriles **3**, starting from amino nitrile **1** (10 mmol), acetylene **2a** or **2b** (5 mmol), powdered NaOH (60 mmol) and TEBAC (ca. 0.1 g, 0.5 mmol). The reaction conditions, purification methods as well as properties of the products **4** are collected in Table 2.

Enaminoamino Nitriles 4l,m,n:
Crude vinylamino nitriles **3a** and **3h** are prepared first starting from powdered NaOH (2.4 g, 60 mmol), TEBAC (0.1 g, 0.5 mmol), DMSO (10 mL), amino nitrile **1a** (1.01 g, 5 mmol) or **1f** (1.0 g, 5 mmol) and acetylene **2a** (0.51 g, 5 mmol) or **2b** (0.36 g, 5 mmol), respectively, as described above (Table 1). Amino nitrile **1a** (0.87 g, 5 mmol) or **1i** (1.11 g, 5 mmol) is then added and the reaction is stirred at the temperature and time indicated in Table 2. The mixtures are worked-up as described for **3** to give the products (Table 2).

Table 4. Diketones **7** Prepared

Starting Materials	Product	Yield (%)	mp (°C) (solvent)	Molecular Formula[a] or Lit. mp (°C)	IR (KBr) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)
4b[b]	**7a**	80[c]	126–128 (EtOH)	126[13]	1675	3.29, 4.22, 5.33 (3dd, 1H each, AMX system, J_{AM} = −17.98, J_{AX} = 3.75, J_{MX} = 10.00, $CH_AH_MCH_X$), 7.20–7.52 (m, 11H_{arom}), 7.90–8.10 (m, 4H_{arom})
4c[b]	**7a**	68[c] (88)				
4d[b]	**7a**	68[c]				
4e[b]	**7a**	76[c]				
4f[b]	**7b**	59[c]	125.5–127 (EtOH)	$C_{24}H_{22}O_2$ (342.4)	1670, 1675	2.34, 2.39 (2s, 3H each, CH_3Ar), 3.26, 4.16, 5.30 (3dd, 1H each, AMX system, J_{AM} = −17.90, J_{AX} = 3.90, J_{MX} = 9.90, $CH_AH_MCH_X$), 7.10–7.40 (m, 9H_{arom}), 7.80–8.00 (m, 4H_{arom})
4g[b]	**7c**	62[c]	109–110 (*i*-PrOH/H_2O)	$C_{24}H_{22}O_4$ (374.4)	1665, 1675	3.82, 3.87 (2s, 3H each, CH_3O), 3.21, 4.15, 5.28 (3dd, 1H each, AMX system, J_{AM} = −17.74, J_{AX} = 3.86, J_{MX} = 9.84, $CH_AH_MCH_X$), 6.80–6.94 (m, 4H_{arom}), 7.15–7.35 (m, 5H_{arom}), 7.90–8.06 (m, 4H_{arom})
4j	**7d**	88	98–99 (cyclohexane)	$C_{17}H_{16}O_2S$ (284.4)	1666, 1678	2.02 (s, 3H, CH_3S), 3.42, 4.09, 4.87 (3dd, 1H each, AMX system, J_{AM} = −17.83, J_{AX} = 3.98, J_{MX} = 9.75, $CH_AH_MCH_X$), 7.20–7.60 (m, 6H_{arom}), 7.94–8.14 (m, 4H_{arom})
4k	**7e**	50	101–102 (cyclohexane)	$C_{19}H_{20}O_2S$ (312.4)	1670	2.01 (s, 3H, CH_3S), 2.41 (s, 6H, CH_3Ar), 3.38, 4.04, 4.85 (3dd, 1H each, AMX system, J_{AM} = −17.75, J_{AX} = 4.13, J_{MX} = 9.61, $CH_AH_MCH_X$), 7.20–7.40 (m, 4H_{arom}), 7.83–8.03 (m, 4H_{arom})
4l	**7f**	83	116–118 (EtOH)	$C_{23}H_{20}O_2$ (328.4)	1670, 1675	2.33 (s, 3H, CH_3Ar), 3.27, 4.20, 5.31 (3dd, 1H each, AMX system, J_{AM} = −17.95, J_{AX} = 3.85, J_{MX} = 9.86, $CH_AH_MCH_X$), 7.13–7.55 (m, 10H_{arom}), 7.90–8.03 (m, 4H_{arom})
4n	**7g**	77	62.5–64 (hexane/EtOH)	$C_{18}H_{18}O_2S$ (298.4)	1680	2.01 (s, 3H, CH_3S), 2.42 (s, 3H, CH_3Ar), 3.40, 4.08, 4.86 (3dd, 1H each, AMX system, J_{AM} = −17.81, J_{AX} = 4.03, J_{MX} = 9.62, $CH_AH_MCH_X$), 7.25–7.60 (m, 5H_{arom}), 7.95–8.05 (m, 4H_{arom})

[a] Satisfactory microanalyses obtained: C ± 0.21, H ± 0.18, S ± 0.16. [b,c] Refers to footnotes c and d in Table 3.

Reaction of Vinylamino Nitriles 3 with CH-Acidic Compounds 10; General Procedure:
To crude vinylamino nitrile **3a** prepared as above is added **10a**, **10b** or **10c** (5 mmol) and the mixture is stirred at 35 °C for 15 h or 12 h for **10a** or **10b** and **10c**, respectively. The mixture is worked up as described for **3** to give crude enamines **11**, which decompose during attempted purification. Therefore crude **11**, EtOH (30 mL) and conc. HCl (1 mL) are refluxed for 10–15 min, the solvent is evaporated, the residues are dissolved in benzene (30 mL), washed with water, dried ($MgSO_4$), and evaporated.

4-Benzoyl-2-methyl-2,3-diphenylbutyronitrile **(12a)**; yield: 0.4 g (24%); purified by column chromatography on silica gel (eluent: EtOAc/hexane 1:4) and crystallization from EtOH; mp 111–112 °C.

$C_{24}H_{21}NO$	calc.	C 84.92	H 6.24	N 4.13
(339.4)	found	84.97	6.26	4.08

IR (KBr): ν = 2240 (C≡N), 1682 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 1.48 (s, 3H, CH_3), 2.80–3.10 and 3.68–3.97 (m, 3H together, signals not assigned to appropriate protons in CH_2CH), 7.20–7.80 (m, 15 H_{arom}).

4-Benzoyl-2,2,3-triphenylbutyronitrile **(12b)**; yield: 1.0 g (50%); purified by crystallization from EtOH with active charcoal); mp 136–137 °C.

$C_{29}H_{23}NO$	calc.	C 86.75	H 5.77	N 3.49
(401.5)	found	86.80	5.69	3.41

IR (KBr): ν = 2240 (C≡N), 1680 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 3.38, 4.18, 4.73 (3 dd, 1H each, AMX system J_{AM} = −17.66 Hz, J_{AX} = 1.90 Hz, J_{MX} = 10.58 Hz, $CH_AH_MCH_X$), 7.08 (br s, 5 H_{arom}), 7.20–7.50 (m, 6 H_{arom}), 7.68–7.90 (m, 4 H_{arom}).

2-Ethyl-1,2,3,5-tetraphenyl-1,5-pentanedione **(12c)**; yield: 0.52 g (24%); purified by column chromatography on silica gel (eluent EtOAc/hexane 1:4) and crystallization from EtOH; mp 163–164 °C.

$C_{31}H_{28}O_2$	calc.	C 86.08	H 6.52
(432.6)	found	86.10	6.58

IR (KBr): ν = 1675, 1664 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 0.84 (t, 3H, J = 7.35 Hz, CH_3), 2.01 (q, 2H, J = 7.35 Hz, CH_2), 2.98, 3.81, 4.46 (3 dd, 1H each, AMX system, J_{AM} = −15.70 Hz, J_{AX} = 11.45 Hz, J_{MX} = 2.65 Hz, $CH_AH_MCH_X$), 6.62–6.72 (m, 2 H_{arom}), 7.03–7.56 (m, 16 H_{arom}), 7.86–7.96 (m, 2 H_{arom}).

4-Benzoyl-2,2,3-triphenylbutyronitrile (12b) from 3e:
A mixture of crude **3e** (1.4 g, 4.5 mmol) and nitrile **10b** (0.9 g, 4.5 mmol), DMSO (10 mL), powdered NaOH (1.0 g, 25 mmol) and TEBAC (0.1 g, 0.5 mmol) is stirred at 30 °C for 5 h and worked up as described above to give the crude enamine **11b**.

11b; ^{1}H-NMR ($CDCl_3$): δ = 1.42 (br s, $CH_2CH_2CH_2$), 2.50–2.70 (m, CH_2NCH_2), 4.08, 5.05 (2 d, J = 10.0 Hz, CHCH=C), 6.90–7.40 (m, 20 H_{arom}).
Crude **11b** is hydrolyzed as described above, affording **12b**; yield: 1.26 g (63%); mp 136–137 °C (EtOH).

Ketoamino nitriles 6 and 2-Morpholino-3-oxo-2-phenylbutyronitrile (16); General Procedure:
A solution of **4** (5 mmol) in benzene (30 mL) or **15a** in Et_2O (30 mL) and 3% aq. HCl (50 mL) is placed in a separatory funnel and shaken vigorously from time to time until the turbidity of the water phase disappears (0.5–3 h). The organic phase is separated, washed with 5% aq. $NaHCO_3$ (30 mL), dried ($MgSO_4$), and evaporated. Crude **6** or **16** are crystallized from an appropriate solvent (Table 3).

Diketones 7; General Procedure:
For **7a–c, f**: Enaminoamino nitrile **4** (5 mmol) is dissolved in EtOH (30 mL) and conc. HCl (1 mL) is added. The mixture is refluxed for 5–10 min. and the solvent is then evaporated *in vacuo*. The residue is dissolved in benzene (30 mL), washed with water and dried ($MgSO_4$). Benzene is distilled off and crude **7** is recrystallized from an appropriate solvent (Table 4).

For **7d, e, g**: These are obtained from the enamines **4** by acidic hydrolysis as described for the preparation of ketoamino nitriles **6** (Table 4).

Benzylideneacetophenone (5a):
Obtained as described for diketones **7** from crude mixtures of vinylamino nitriles **3a–c**; yield: 71% from **3a**, 74% from **3b**, and 80% from **3c**; mp 55–57 °C (EtOH) (Lit.[18] mp 57–58 °C).

***E/Z*-4-Morpholino-2,4-diphenyl-3-butenenitrile (13):**
The crude vinylaminonitrile **3a**, prepared from amino nitrile **1a** (4.0 g, 20 mmol) and acetylene **2a** (2.0 g, 20 mmol) is distilled, the fraction boiling at 200–205 °C/0.2 Torr (4.1 g) is collected, treated with MeOH (10 mL) and chilled. The solid is filtered and crystallized from MeOH to give **13**; yield: 1.9 g (31%); mp 140–141 °C.

$C_{20}H_{20}N_2O$	calc.	C 78.92	H 6.62	N 9.20
(304.4)	found	79.13	6.59	8.99

IR (KBr): ν = 2240 (C≡N), 1620 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 2.74–2.84 (m, 4H, CH_2NCH_2), 3.36–3.73 (m, 4H, CH_2OCH_2), 4.37, 4.65 (AB system, 2H, J = 10.06 Hz, CHCH=C), 7.30 (br s, 5 H_{arom}), 7.40 (br s, 5 H_{arom}).

3-Benzoyl-2-phenylpropionitrile (14):
Obtained from **13** (0.3 g, 1 mmol) by acidic hydrolysis as described for ketoamino nitriles **6**. Yield: 0.23 g (97%); mp 125–126 °C (EtOH) (Lit.[19] mp 126–127 °C).

$C_{16}H_{13}NO$	calc.	C 81.86	H 5.57	N 5.95
(235.3)	found	81.57	5.47	5.85

IR (KBr): ν = 2240 (C≡N), 1680 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): δ = 3.50, 3.72 (part AB of ABX system, 2H, J_{AB} = −17.91 Hz, J_{AX} = 6.17 Hz, J_{BX} = 7.77 Hz, CH_2CO), 4.57 (part X of ABX system, 1H, CHCN), 7.30–7.60 (m, 6 H_{arom}), 7.88–8.00 (m, 4 H_{arom}).

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(1) Reactions of Organic Anions, 168; for part 167 see: Jończyk, A.; Lipiak, D.; Zdrojewski, T. *Tetrahedron*, in press.
(2) Beak, P.; Zajdel, W.J.; Reitz, D.B. *Chem. Rev.* **1984**, *84*, 471.
(3) Gröbel, B.T.; Seebach, D. *Synthesis* **1977**, 357.
(4) Albright, J.D.A. *Tetrahedron* **1983**, *39*, 3207.
Arsenyadis, S.; Kyler, K.S.; Watt, D.S. *Org. React.* **1984**, *31*, 1.
(5) Normant, J.F.; Alexakis, A. *Synthesis* **1981**, 841.
(6) Mąkosza, M.; Czyzewski, J.; Jawdosiuk, M. *Org. Synth.* **1976**, *55*, 99.
(7) Preliminary communication: Jończyk, A.; Lipiak, D.; Stępniewski, P.; Zdrojewski, T. *Bull. Soc. Chim. Belg.* **1988**, *97*, 165; *C.A.* **1988**, *109*, 169969.
(8) Grierson, D.S.; Harris, M.M.; Husson, H.P. *J. Am. Chem. Soc.* **1980**, *102*, 1064.
Ahlbrecht, H.; Dollinger, H. *Synthesis* **1985**, 743.
(9) Chauviere, G.; Tchoubar, M.B.; Welvart, Z. *Bull. Soc. Chim. Fr.* **1963**, 1428.
Taillades, J.; Commeyras, A. *Tetrahedron* **1974**, *30*, 129.
(10) *Houben-Weyl*, 4th ed., Vol. XI/I, Georg Thieme Verlag, Stuttgart, 1957, p. 5.
Streitweiser, A.Jr.; Heathcock, C.H. *Introduction to Organic Chemistry*, 2nd. ed., Macmillan Publishing Co., New York, 1981, p. 735.
(11) Mąkosza, M.; Jawdosiuk, M. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1968**, *16*, 589; *C.A.* **1969**, *71*, 30193 y.
(12) Taylor, H.M.,; Hauser, Ch.R. *J. Am. Chem. Soc.* **1960**, *82*, 1790.
(13) Smith, A. *J. Chem. Soc.* **1980**, *57*, 643.
(14) Brandsma, L. *Preparative Acetylenic Chemistry*, Elsevier Publishing Co., Amsterdam, 1971.

(15) Jończyk, A.; Ludwikow, M.; Mąkosza, M. *Org. Prep. Proced. Int.* **1979**, *11*, 275.
(16) Mąkosza, M.; Jończyk, A.; Serafinowa, B.; Mroczek, Z. *Roczniki Chem.* **1973**, *47*, 77; *C.A.* **1973**, *79*, 18305.
(17) Hauser, C.R.; Taylor, H.M.; Ledford, T.G. *J. Am. Chem. Soc.* **1960**, *82*, 1786.
(18) Claisen, L.; Claparéde, A. *Ber. Dtsch. Ges.* **1881**, *14*, 2460.
(19) Hann, A.C.O.; Lapworth, A. *J. Chem. Soc.* **1904**, *85*, 1355.