Tetrahedron Vol. 46, No. 3, pp. 1025-1038, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

REACTIONS OF CARBANIONS FROM 2-(DIALKYLAMINO)-ARYLACETONITRILES WITH ACETYLENE - SIMPLE SYNTHESES OF 1,3-DIENAMINES AND 1,4-DIKETONES[1]

Andrzej Jończyk*, Dariusz Lipiak and Tadeusz Zdrojewski

Department of Chemistry, Technical University (Politechnika)
Koszykowa 75, 00-662 Warsaw, Poland

(*Received in UK* 1 *September* 1989)

Abstract: It has been found that morpholinonitrile **1a** reacts with acetylene (**2**) in the presence of solid sodium hydroxide and tetrabutylammonium bromide (TBABr) as a catalyst, in DMSO, to give the vinyl derivative **3a**. Whereas aminonitriles **1b-i**, in the reaction with **2**, afford dienamines **7**. The different reactivity of **1a** as compared to **1b-i** is explained in terms of the different basicity of the amino moiety in vinyl derivatives **3**. Dienamines **7** were hydrolyzed to 1,4-diarylbutan-1,4-diones **8** in high yields.

The addition of carbon nucleophiles (organometallic reagents[2] or carbanions[3]) to acetylenes affords a new C-C(vinyl)bond and therefore, it is of immense value in organic synthesis.

While studying the transformations of carbanions of C-H acids, which are substituted by heteroatom(s)[4], we turned our attention to base mediated reactions of 2-aminonitriles **1a-i** with acetylene (**2**).[5] We have found that simple shaking of morpholinonitrile **1a** with powdered sodium hydroxide and TBABr as a catalyst, in DMSO and saturation of the above with **2** under atmospheric pressure results in the formation of the vinyl derivative **3a** and the unexpected enaminoaminonitrile **4a** in a ratio of ca 1:1 (total yield ca 70%). Minor modifications of this procedure (using an excess of **2**, lower temperature) allowed for the isolation of **3a** in a 77% yield (only minute amounts of **4a** were formed) (Scheme 1).

Table 1. The prepared dienamines **7** and diketones **8**

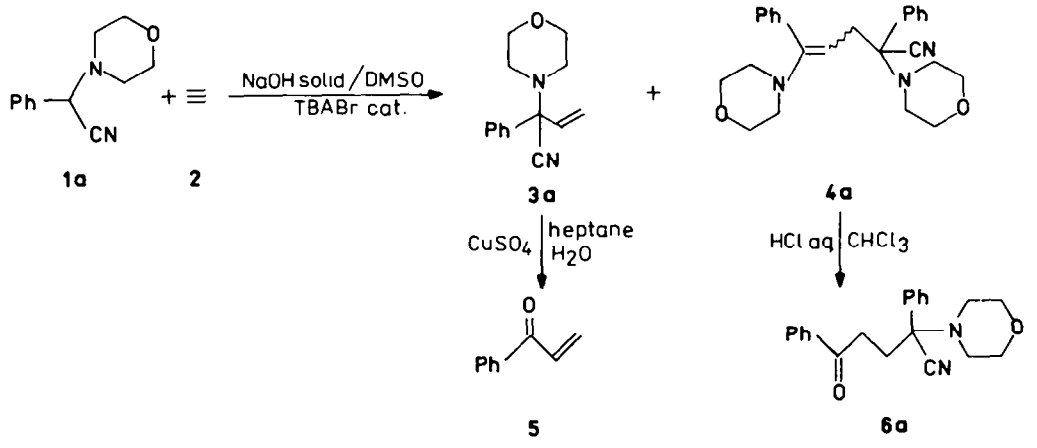
No	Aminonitriles **1** and products **7,8**		Dienamine	Yield[a] (%)	M.p. (°C)	Formula (Mol.weight)	Analysis Calcd. / Found			Diketone	Yield[b] (%)	M.p. (°C)
	Ar	R,R	**7**				C	H	N	**8**		
1	2	3	4	5	6	7	8			9	10	11
b	C_6H_5	CH_3,CH_3	**7b**	54	134-136	$C_{20}H_{24}N_2$ (292.41)	82.14 / 82.44	8.27 / 8.16	9.58 / 9.28	**8b**	70	146-147[c]
c	C_6H_5	CH_3CH_2, CH_3CH_2	**7c**	32	82-83	$C_{24}H_{32}N_2$ (348.52)	82.75 / 82.48	9.20 / 9.14	8.05 / 7.87		55	
d	C_6H_5	$(CH_2)_4$	**7d**	59(93)	135 (dec.)	$C_{24}H_{28}N_2$ (344.48)	83.72 / 83.52	8.14 / 8.18	8.14 / 7.82		89	
e	C_6H_5	$(CH_2)_5$	**7e**	97	156-158	$C_{26}H_{32}N_2$ (372.54)	83.87 / 83.79	8.60 / 8.25	7.52 / 7.76		90	
f	4-MeC_6H_4	CH_3,CH_3	**7f**	44	159-160	$C_{22}H_{28}N_2$ (320.46)	82.50 / 82.65	8.75 / 8.92	8.75 / 8.64	**8f**	72	157-158[d]

Table 1. (continued)

1	2	3	4	5	6	7	8	9	10	11
g	4-$MeOC_6H_4$	CH_3,CH_3	**7g**	26(68)	130.5-131.5	$C_{22}H_{28}N_2O_2$ (352.46)	75.00 7.95 7.95 75.08 8.09 8.08	**8g**	64	154-155[e]
h	2-ClC_6H_4	$(CH_2)_5$	**7h**	(78)	-	$C_{26}H_{30}Cl_2N_2$ (441.43)	- - -	**8h**	70	44-45[f]
i	3,4-$(MeO)_2C_6H_3$	$(CH_2)_5$	**7i**	(45)	-	$C_{30}H_{40}N_2O_2$ (460.64)	- - -	**8i**	39	178-180[g]

[a] In parentheses amounts of CN^- titrated in the aqueous phase; [b] The yields of the **4**→**8** step; [c] Lit.[6] m.p.144-145°C; [d] Lit.[7] m.p.159°C; [e] Lit.[8] m.p.154°C; [f] Physical properties of this compound are not described[9]; for $C_{16}H_{12}Cl_2O_2$ (307.17) calcd. C 62.54; H 3.91; found C 62.60; H 4.19; [g] Lit.[10] m.p. 180-181°C.

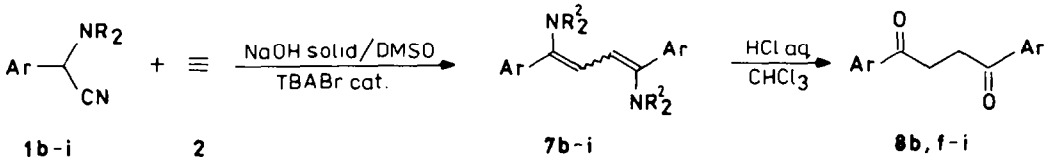
Scheme 1



Unmasking of the carbonyl groups in **3a** and **4a** gave phenyl vinyl ketone (**5**) and cyanoamino ketone **6a** in yields of 63% (calculated with regard to **1a**) and 78%, respectively.

However, much to our surprise, the aminonitriles **1b-i**, when reacted with **2**, under the above mentioned conditions, afforded products, to which the structure of dienamines **7** has been ascribed (Scheme 2, Table 1).

Scheme 2



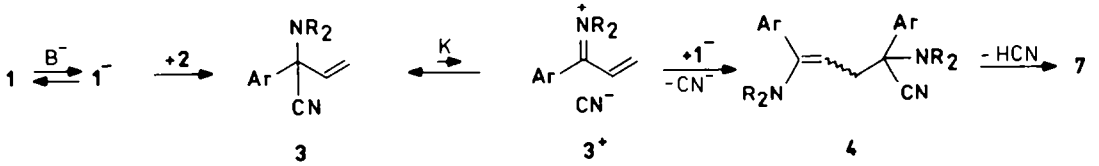
A similar reactivity pattern was observed in reactions of carbanions from **1** with substituted acetylenes.[11]

The dienamines **7** were hydrolyzed to give 1,4-diketones **8b-i** in high yields; the latter reaction was conveniently carried out using crude **7**. As a result of the limited stability of some dienamines **7**, which depends on the kind of R substituent a loss of material occured in the purification step. Nevertheless, the yields of crude **7** were usually high as it can be seen from the yields of **8** as well as the titration of CN^- in the aqueous phase (Table 1).

The addition of **1** (via its carbanion, 1^-) to **2** produces **3**, which exists in equilibrium with the immonium salt 3^+.

The 2-aminonitrile ⇌ immonium salt equilibrium has already been suggested as an explanation of the chemical transformations of these compounds.[12] Salt 3^+ being a strong electrophile, easily adds 1^- to C-3, affording **4**, which in turn eliminates hydrogen cyanide under basic conditions to give the final products **7** (Scheme 3).

Scheme 3



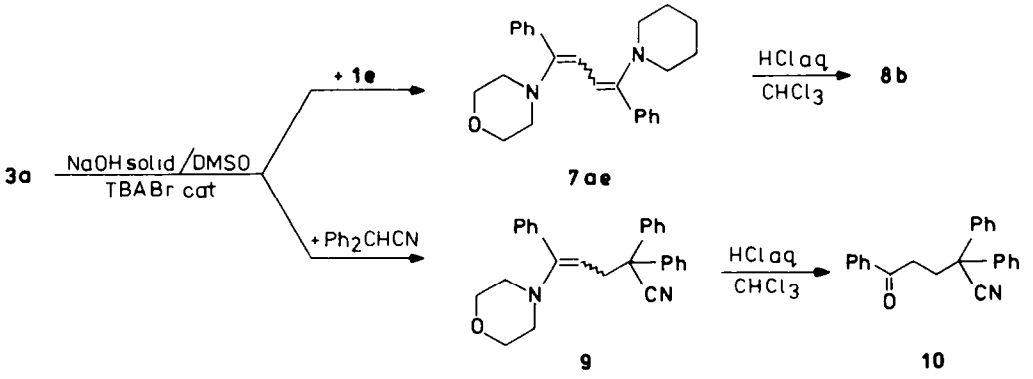
Possibly, due to steric reasons, **4a** is not able to assume an antiperiplanar arrangement with respect to hydrogen and the cyano substituent, which is required for hydrogen cyanide elimination.

There are a few known examples of substitution of the cyano group in unsaturated 2-aminonitriles by organometallic reagents or carbanions,[13] which follow the reactivity pathway mentioned above.

The value of the K constant for the $3 \rightleftharpoons 3^+$ equilibrium depends on the basicity of **3**, and may be evaluated from the pK_b of the parent amines. K in case of **3a** should be relatively small since pK_b of morpholine is higher by ca 2.5 units than that of dimethyl- or diethylamines, pyrrolidine as well as piperidine.[14] Therefore, the reaction of **1a** with **2** is arrested on the stage of **3a**, while **3b-i** reacted further with 1^- giving **4** and **7**.

The intermediacy of **3** in the formation of **4** was proved by independent reactions of isolated **3a** with some C-H acids in the solid NaOH/TBABr cat./DMSO system. As expected, these reactions proceeded slowly, affording the products **7ae** and **9** in low yields (Scheme 4).

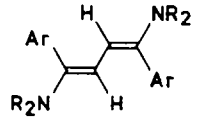
Scheme 4



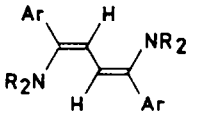
Probably for the same reasons as for **4a**, compound **9** did not eliminate hydrogen cyanide. Both **7ae** and **9** were hydrolytically cleaved to give **8b** and cyanoketone **10**, respectively.

Finally, we have noted that carbanions of lower activity, derived from relatively strong C-H acids (e.g. **1**, Ar=4-NCC_6H_4; R,R=Me,Me) do not exhibit the tendency to add to acetylene (**2**).

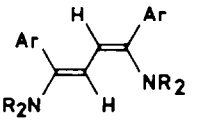
The dienamines **7** may exist as E,E-, Z,Z- or E,Z-isomers.



E,E-**7** δ_{calcd}=5.25 ppm



Z,Z-**7** δ_{calcd}=5.60 ppm



E,Z-**7**

$\delta_{obs.}$=5.62 - 5.87 ppm (s)

A relatively large difference between the calculated chemical shifts[15] of vinyl protons in E,E- and Z,Z-**7** as well as fact that the signal of vinyl protons in ^1H NMR spectra of **7** appeared as singlet, allowed us to exclude the E,Z-structure for **7**. The calculated chemical shift of the vinyl protons in **7** for the Z,Z-stereoisomer is in agreement with the measured value (singlet at δ =5.62-5.87), which indicate that this conformation is more probable.

Data confirming the structure of prepared compounds are reported in Table 1 as well as in the Experimental Part.

Summarizing, we have demonstrated that 2-(dialkylamino)arylacetonitriles enter an unusual reaction with acetylene, under basic conditions, affording dienamines **7**[16], which are a convenient source of 1,4-diarylbutane--1,4-diones.[17,18]

EXPERIMENTAL PART

Melting points were determined using a capillary tube apparatus and are not corrected. ^1H and ^{13}C NMR spectra were recorded on a Tesla BS 567A 100 MHz FT/CW and a Varian CFT-20 at 22.5 MHz spectrometers, respectively. IR spectra were obtained on Perkin-Elmer Model 577, whereas UV spectra were measured using Carl Zeiss Jena Specord in cyclohexane solution, and are quoted as λ_{max}nm (log ε). GC/MS were recorded on a LKB 2091 spectrometer.

All aminonitriles **1** were prepared by a previously reported procedure[19] and purified by vacuum distillation or crystallization. The new products were identified by spectral means and elemental analyses (Table 2).

Table 2. The prepared aminonitriles **1**

No	Ar	R,R	B.p.(°C/torr) or m.p.(°C)	yield (%)	Spectral Data	
					IR (cm^{-1}), ν	^1H NMR (TMS/$CDCl_3$), δ
1	2	3	4	5	6	7
1a	C_6H_5	$O(CH_2CH_2)_2$	68-69[a] (light petroleum)	77	-	-
1b	C_6H_5	CH_3,CH_3	59-60/0.3[b]	85	-	-
1c	C_6H_5	CH_3CH_2, CH_3CH_2	95/1.25[c]	71	-	-
1d	C_6H_5	$(CH_2)_4$	90/0.15[d]	79	2250 (neat)	1.82 (br s, 4 H, CH_2CH_2), 2.64 (br s, 4 H, CH_2N), 5.03 (s, 1 H, CH), 7.25-7.58 (m, 5 H, ArH)
1e	C_6H_5	$(CH_2)_5$	61-62[e] (light petroleum)	80	-	-
1f	4-$CH_3C_6H_4$	CH_3,CH_3	87/1[f]	70	2250 (neat)	2.31 (s, 6 H, CH_3N), 2.36 (s, 3 H, CH_3Ar), 4.80 (s, 1 H, CH), 7.16-7.43 (m, 4 H, ArH).

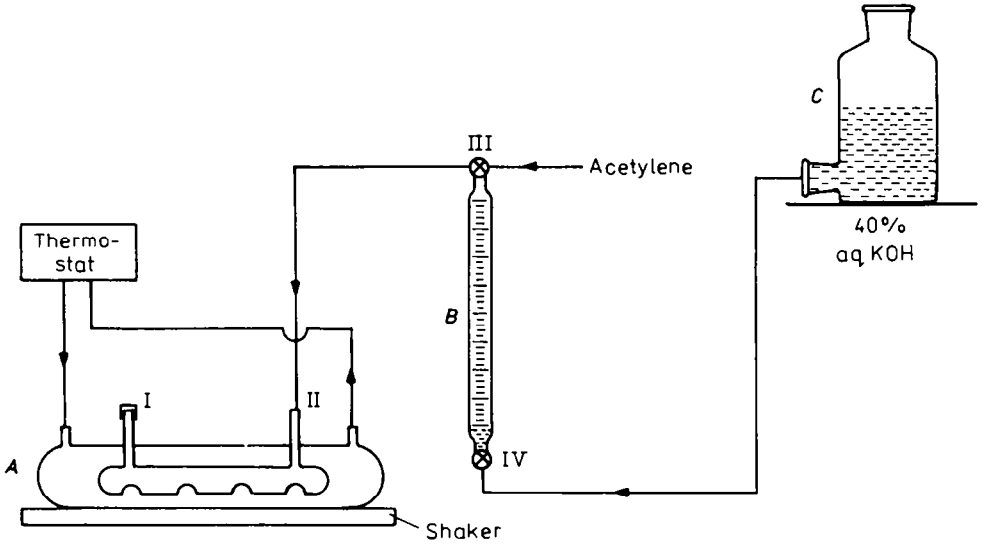
Table 2. (continued)

1	2	3	4	5	6	7
1g	4-$CH_3OC_6H_4$	CH_3,CH_3	120/1.5[g]	65	-	-
1h	2-ClC_6H_4	$(CH_2)_5$	76-78[h] (MeOH)	82	2250 (KBr)	1.50 (br s,6 H,$CH_2CH_2CH_2$) 2.51-2.56 (m, 4 H, CH_2N) 5.05 (s, 1 H, CH) 7.30-7.64 (m, 4 H, ArH)
1i	3,4-$(CH_3O)_2C_6H_3$	$(CH_2)_5$	57-59[i] (MeOH,i-PrOH mixture)	98	2245 (KBr)	1.54 (br s,6 H,$CH_2CH_2CH_2$) 2.46-2.50 (m, 4 H, CH_2N) 3.89 (s, 3 H, CH_3O) 3.90 (s, 3 H, CH_3O) 4.77 (s, 1 H, CH) 6.81-7.15 (m, 3 H, ArH)

[a]Lit.[19] m.p. 69-70°C; [b]Lit.[20] b.p. 78-79°C/1.1 torr; [c]Lit.[21] b.p. 78-80°C/0.05 torr; [d]For $C_{12}H_{14}N_2$(186.25) calcd. C 77.42; H 7.53; N 15.05; found C 77.46; H 7.49; N 15.11; [e]Lit.[21] m.p. 62-64°C; [f]For $C_{11}H_{14}N_2$(174.24) calcd. C 75.86; H 8.05; N 16.09; found C 75.99; H 7.89; N 15.88; [g]Lit.[22] b.p. 107-109°C/0.8 torr, m.p. 36.5-38°C; [h]For $C_{13}H_{15}ClN_2$(234.72) calcd. C 66.52; H 6.40; N 11.94; found C 66.47; H 6.53; N 11.81; [i]For $C_{15}H_{20}N_2O_2$(260.33) calcd. C 69.23; H 7.69; N 10.77; found C 68.97; H 7.73; N 10.73.

Acetylene was obtained from a gas-cylinder and separated from acetone as previously described.[3] Other chemicals were commercially available.

Fig.



2-Phenyl-2-(N-morpholino)but-3-enenitrile **(3a)** and 2,5-diphenyl-2,5-di(N-morpholino)pent-4-enenitrile **(4a):** The apparatus used for reactions with acetylene **(2)** is shown in the Fig. DMSO(15 ml), powdered sodium hydroxide (4.0 g, 100 mmol) and TBABr (0.2 g, 0.62 mmol) were added through inlet I to reactor A (volume of ca 25 ml, with a water-jacket connected to a thermostat), placed on a shaker. The reactor was joined with a calibrated gas-burette B (volume of ca 800 ml) through inlet II. The burette was connected to bottle-flask C (volume ca 1000 ml). Reactor A was washed a few times with **2** by means of the three-way stopcock III and stopcock IV. The level of **2** was maintained in the gas-burette B. Aminonitrile **1a** (4.04 g, 20 mmol) was then added to A, after which inlet tube I was closed. The temperature of water in the thermostat was kept constant at 40(±1)°C, and a stream of **2** was allowed to enter reactor A under slight overpressure created by 40% aq KOH present in bottle-flask C (stopcock IV was open). The shaker was started and the reaction was carried out until no more of **2** was absorbed in reactor A (ca 20 h). Reactor A was then disconnected, the mixture was poured into water (100 ml) and reactor A was washed with a small amount of water and benzene. The mixture was extracted with benzene (3x50 ml), the organic extracts were washed with water and dried (Na_2SO_4).

After the removal of solvent on a rotary evaporator, the residue was dissolved in methanol (20 ml), which contained traces of sodium hydroxide. The solution was then cooled and the solid was filtered to give colorless crystals of **4a**, yield 1.90 g (47%), m.p.134-135°C (dec.). IR (KBr): ν 2220 (C≡N), 1620 (C=C) cm^{-1}; ^1H NMR (C_6D_6/TMS): δ 2.11-2.51 (m, 9 H, CH_2N and =C-CH_2), 2.77-2.99 (m, 1 H, =C-CH_2, part of ABX pattern of =CH-CH_2, ^2J = 13.85 Hz), 3.24-3.41 (m, 8 H, CH_2O), 4.20-4.35 (m, 1 H, =CH, part X of ABX pattern of =CH-CH_2),7.03-7.54 (m, 10 H, ArH). For $C_{25}H_{29}N_3O_2$(403.50) calcd. C 74.44; H 7.19; N 10.42; found C 74.42; H 7.18; N 10.22.
The filtrate, after isolation of **4a**, was concentrated on a rotary evaporator and the residue was distilled on the Kugelrohr apparatus to give **3a**, b.p.145-150°C/0.1 torr, yield 1.03 g (22.5%). IR (neat): ν 2220 (C≡N), 1635 cm^{-1}; ^1H NMR (C_6D_6/TMS): δ 2.35-2.78 (m, 4 H, CH_2N), 3.60-3.78 (m, 4 H, CH_2O), 5.20-5.60 (m, 3 H, $CH=CH_2$), 7.26-7.67 (m, 5 H, ArH).

2-Phenyl-2-(N-morpholino)but-3-enenitrile **(3a):** As described above, DMSO(8 ml) powdered sodium hydroxide (4.0 g, 100 mmol) and TBABr (0.2 g, 0.62 mmol) were placed in reactor A. Inlet tube I was closed by means of a septum, the temperature of the thermostat water was maintained at 15(±1)°C. The mixture was saturated with **2** while the shaker was on. The solution of **1a** (4.04 g, 20 mmol) in DMSO (8 ml) was then slowly added by means of a syringe through inlet I (during addition, the shaker was off). The reaction was carried out for 4 h, left overnight and worked-up as described above. The products were distilled on the Kugelrohr apparatus to give **3a**, b.p.145-150°C/0.1 torr, yield 3.50 g (77%).

Phenyl vinyl ketone **(5):** Aminonitrile **3a** (1.03 g, 4.5 mmol), heptane (6 ml), a solution of cupric sulfate pentahydrate (1.12 g, 4.5 mmol) in water (8 ml) was stirred and refluxed for 20 min. The mixture was cooled and the insoluble products were filtered off. The filtrate was separated and the water phase was extracted with heptane (2x20 ml and 1x10 ml). The combined organic phases were washed with 1% aq hydrochloric acid (30 ml), then water and dried (Na_2SO_4). The solvent was evaporated, and the residue was distilled on the Kugelrohr apparatus to give **5**, b.p.50-55°C/0.3 torr, yield 0.48 g, (81%), lit.[23] b.p.117-118°C/20 torr, IR (neat): ν 1670 (C=O), 1605, 1595 (C=C) cm^{-1}; ^1H NMR (acetone-d_6/TMS): δ 5.88-7.48 (m, 3 H, $CH=CH_2$), 7.50-8.06 (m, 5 H, ArH).

2-Phenyl-2-(N-morpholino)-4-benzoylbutyronitrile **(6a):** Enaminoaminonitrile **4a** (0.30 g, 0.75 mmol), chloroform (5 ml) and 1% aq hydrochloric acid (10 ml) were stirred at 20°C for 1 h. The phases were separated and the water phase was extracted with chloroform (3x10 ml). The combined organic phases were washed with water and dried (Na_2SO_4). The residue, after evaporation of solvent, was crystallized from cyclohexane to give 0.195 g (yield 78%) of **6a**, m.p.139-140°C. IR (KBr): ν 2230 (C≡N), 1680 (C=O) cm^{-1}; ^1H NMR (C_6D_6/TMS): δ 2.15-2.55 (m, 8 H, CH_2N and $COCH_2CH_2$), 3.28-3.49 (m, 4 H, CH_2O), 6.93-7.68 (m, 10 H, ArH). For $C_{21}H_{22}N_2O_2$ (334.41) calcd. C 75.45; H 6.59; N 8.38; found C 75.85; H 6.55; N 8.20 .

Dienamines **7b-q** and Diketones **8b,f-i.** General Procedure: Reactions were carried out as described above in the apparatus shown in the Fig. Starting materials: aminonitriles **1b-i** (20 mmol), DMSO (10 ml), TBABr (0.2 g , 0.62 mmol) and powdered sodium hydroxide (4.0 g, 100 mmol). The temperature of water in the thermostat was maintained at 20(±1)°C for 0.5 h and 40(±1)°C until no more **2** was absorbed by the reaction mixture (ca 15 h). The mixture was worked-up as previously described. After evaporation of solvent, the crude dienamines were dissolved in methanol (20 ml) containing a small amount of sodium hydroxide, and the solution was cooled in dry ice. The resulting solid was filtered-off and crystallized from petroleum ether to give yellow crystals of dienamines **7b-i**. The yields and physical properties of **7b-i** are listed in Table 1.

7b - IR (KBr): ν 1550 (C=C) cm^{-1}; UV: 360 (4.21); ^1H NMR (C_6D_6/TMS): δ 2.31 (s, 12 H, CH_3N), 5.69 (s, 2 H, =CH-), 7.06-7.66 (m, 10 H, ArH); ^{13}C NMR (C_6D_6/TMS), NBD and off-resonance: δ 41.35 (CH_3N), 105.21 (=C-), 127.47, 128.30, 130.41, 139.43(C_{arom}), 147.25 (>C=); MS m/e (relative intensity): 292 (M^+, 100), 147 (59).

7c - IR (KBr): ν 1555 (C=C) cm^{-1}; UV: 370 (4.21); ^1H NMR (C_6D_6/TMS): δ 0.85 (t, J=7.04 Hz, 12 H, $\underline{CH_3}CH_2N$), 2.76 (q, J=7.04 Hz, 8 H, CH_2N), 5.68 (s, 2 H, =CH-), 7.16-7.65 (m, 10 H, ArH); ^{13}C NMR (C_6D_6/TMS) NBD: δ 12.04 (CH_3), 43.64 (CH_2N), 107.15 (=CH-), 127.16, 128.14, 130.55, 139.98 (C_{arom}), 143.80 (>C=).

7d - IR (KBr): ν 1560 (C=C) cm^{-1}; UV: 368 (4.10); ^1H NMR (C_6D_6/TMS): δ 1.41 (m, 8 H, CH_2CH_2), 2.74 (m, 8 H, CH_2N), 5.62 (s, 2 H, =CH-), 7.14-7.68 (m, 10 H, ArH).

7e - IR (KBr): ν 1550 (C=C) cm^{-1}; UV: 362 (3.77); ^1H NMR (C_6D_6/TMS): δ 1.26 (br s, 12 H, $CH_2CH_2CH_2$), 2.64 (br s, 8 H, CH_2N), 5.87 (s, 2 H, =CH-), 7.16-7.76 (m, 10 H, ArH); ^{13}C NMR (C_6D_6/TMS) NBD: δ 24.66 ($NCH_2CH_2\underline{CH_2}$), 26.35 ($NCH_2\underline{CH_2}$), 50.87 (NCH_2), 106.34 (=CH-),127.49, 128.27, 130.46, 139.75 (C_{arom}), 148.28 (>C=).

7f - IR (KBr): ν 1550 (C=C) cm^{-1}; UV: 357 (4.20); ^1H NMR (C_6D_6/TMS): δ 2.16 (s, 6 H, CH_3Ar), 2.36 (s, 12 H, CH_3N), 5.77 (s, 2 H, =CH-),7.04-7.62 (m, 8 H, ArH); ^{13}C NMR (C_6D_6/TMS) NBD: δ 21.16 (CH_3Ar), 41.48 (CH_3N), 105.34 (=CH-),129.09, 130.40, 136.60, 136.86 (C_{arom}), 147.20 (>C=).
7g - IR (KBr): ν 1560 (C=C) cm^{-1}; UV: 348 (3.83); ^1H NMR (C_6D_6/TMS): δ 2.38 (s, 12 H, CH_3N), 3.35 (s, 6 H, CH_3O), 5.75 (s, 2 H, =CH-),6.83-7.62 (m, 8 H, ArH); ^{13}C NMR (C_6D_6/TMS) NBD: δ 41.50 (CH_3N), 54.63 (CH_3O), 105.23 (=CH-),113.84, 131.57, 131.72 (C_{arom}), 146.73 (>C=), 159.41 (C_{arom}).
8b - IR (KBr): ν 1675 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 3.46 (s, 4 H, CH_2CH_2), 7.46-8.09 (m, 10 H, ArH); ^{13}C NMR ($CDCl_3$/TMS) NBD and off resonance: δ 32.65 (CH_2), 128.17, 128.62, 133.12, 136.96 (C_{arom}), 198.63 (C=O).
8f - IR (KBr): ν 1670 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 2.40 (s, 6 H, CH_3Ar), 3.40 (s, 4 H, CH_2CH_2), 7.21-7.97 (m, 8 H, ArH).
8g - IR (KBr): ν 1665 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 3.36 (s, 4 H, CH_2CH_2), 3.84 (s, 6 H, CH_3O), 6.87-8.03 (m, 8 H, ArH).
8h - IR (KBr): ν 1695 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 3.40 (s, 4 H, CH_2CH_2), 7.30-7.67 (m, 8 H, ArH).
8i - IR (KBr): ν 1672 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 3.42 (s, 4 H, CH_2CH_2), 3.94 (s, 6 H, CH_3O), 3.96 (s, 6 H, CH_3O), 7.56-7.78 (m, 6 H, ArH).

Cyanide anions, contained in the water phases after work-up of reaction mixtures, were titrated using the Liebig-Denings method (Table 1).

Crude dienamine **7** was dissolved in chloroform (45 ml), 5% aq hydrochloric acid (71 ml) was added and the mixture was stirred and refluxed for 1-5 h (the progress of reaction was checked by TLC). The mixture was then cooled and poured into water (100 ml). The organic phase was separated and the water phase was extracted with chloroform (3x40 ml). The combined organic phases were washed with water and dried (Na_2SO_4). The solvent was evaporated on a rotary evaporator and the residue was dissolved in methanol (ca 20 ml), cooled (by means of a dry ice) acetone bath, and the resulting solid was filtered off to give colorless crystals of diketones **8b,f-i** (Table 1).

1,4-Diphenyl-1-(N-morpholino)-4-(N-piperidino)buta-1,3-diene **(7ae):** Vinyl - aminonitrile **3a** (1.02 g, 4.5 mmol), aminonitrile **1e** (0.92 g, 4.6 mmol), DMSO (5.0 ml), TBABr(0.05 g,0.155 mmol) and powdered sodium hydroxide (0.9 g, 22.5 mmol) were stirred and heated at 40°C for 32 h under nitrogen. The mixture was then poured into water (100 ml), extracted with benzene (3x40 ml) and the organic extracts were washed with water and dried (Na_2SO_4). The solvent was evaporated, the residue was dissolved in methanol (10 ml) containing a trace of sodium hydroxide and the solution was cooled.

The solid was filtered off to give 0.62 g (yield 36%) of **7ae**, m.p.132-134°C. IR (KBr): ν 1555 (C=C) cm^{-1}; UV: 361 (4.18); ^1H NMR (C_6D_6/TMS): δ 1.13-1.40 (m, 6 H, $CH_2CH_2CH_2$), 2.40-2.68 (m, 8 H, CH_2N), 3.28-3.45 (m, 4 H, CH_2O), 5.80 (s, 2 H, =CH-), 7.20-7.71 (m, 10 H, ArH). For $C_{25}H_{30}N_2O$ (374.51) calcd. C 80.21; H 8.02; N 7.49; found C 80.08; H 8.25; N 7.65.
The product was hydrolyzed as described above to afford diketone **8b** (Table 1).

2,2,5-Triphenyl-5-(N-morpholino)pent-4-enenitrile **(9):** The reaction was carried out as described above, starting from **3a** (0.83 g, 3.6 mmol),diphenylacetonitrile (0.715 g, 3.7 mmol), DMSO(4 ml), TBABr(0.036 g, 0.11 mmol) and powdered sodium hydroxide (0.8 g, 18.5 mmol). Nitrile **9**: yield 0.4 g (28%), m.p.129-130°C. IR (KBr): ν 2230 (C≡N), 1630 (C=C) cm^{-1}; ^1H NMR (C_6D_6/TMS): δ 2.42-2.51 (m, 4 H, CH_2N), 3.06 (d, ^3J=7.04 Hz, 2 H, CH_2), 3.29-3.38 (m, 4 H, CH_2O), 4.76 (t, ^3J=7.04 Hz, 1 H, =CH-), 6.91-7.31 (m, 15 H, ArH). For $C_{27}H_{26}N_2O$ (394.50) calcd. C 82.23; H 6.60; N 7.11; found C 82.28; H 6.63; N 7.02.

2,2-Diphenyl-4-benzoylbutyronitrile **(10):** From enaminonitrile **9** (0.10 g, 0.25 mmol), following the procedure for **6a**, the product **10** (0.07 g, yield 86%), m.p.118.5-119.5°C (methanol) was obtained. IR (KBr): ν 2235 (C≡N), 1680 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$/TMS): δ 2.85-2.95 (m, 2 H, CH_2CH_2CO), 3.06-3.16 (m, 2 H, CH_2CO), 7.25-7.93 (m, 15 H, ArH). For $C_{23}H_{19}NO$ (325.39) calcd. C 84.92; H 5.85; N 4.31; found C 84.70; H 6.10; N 4.32.
Acknowledgement. We wish to thank the Polish Academy of Sciences for financial support, Grant CPBP 01.13.

REFERENCES AND NOTES

1. Reactions of Organic Anions, Part 167; Part 166, see: Jończyk, A.; Lipiak, D.; Sienkiewicz, K. J.Am.Chem.Soc. submitted.
2. Review: Normant, J.F.; Alexakis, A. Synthesis 1981, 841. Ishimo, Y.; Wakamoto, K. Chemistry Lett. 1984, 765. Epsztein, R.; Le Goff, N. Tetrahedron 1985, **41**, 5347.
3. Mąkosza, M.; Czyżewski, J.; Jadwosiuk, M. Org.Synth. 1976, **55**, 99 and references cited therein.
4. Jończyk, A.; Radwan-Pytlewski, T. Chemistry Lett. 1983, 1557.
Jończyk, A.; Owczarczyk, Z. Synthesis 1986, 297.
Jończyk, A.; Owczarczyk, Z.; Makosza, M.; Goliński, M.; Winiarski, J. Bull.Soc.Chim.Belg. 1987, **96**, 303.
Jończyk, A.; Goliński, M.; Winiarski, J. Liebigs Ann.Chem. 1989, 203.

5. Preliminary communication: Jończyk, A.; Lipiak, D.; Stępniewski, P.; Zdrojewski, T. Bull.Soc.Chim.Belg. 1988, **97**, 165.
6. Kapf, S.; Paal, C. Ber. 1888, **21**, 3053.
7. Claus, A. Ber. 1887, **20**, 1374.
8. Hollemann, M.A.F. Rec. Trav. Chim. Pays Bas 1891, **10**, 211.
9. Iyoda, M.; Sakaitami, M.; Kojima, A.; Oda, M. Tetrahedron Lett. 1985, **26**, 3719.
10. Haworth, R.D.; Kellog, W. J.Chem.Soc. 1937, 1645.
11. Zdrojewski, T.; Jończyk, A. in preparation.
12. Chauviere, G.; Tchoubar, M.B.; Welvart, Z. Bull.Soc.Chim.Fr. 1963, 1428. Taillades, J.; Commeyras, A. Tetrahedron 1974, **30**, 127.
13. Grierson, D.S.; Harris, M.; Husson, H.P. J.Am.Chem.Soc. 1980, **102**, 1064. Ahlbrecht, H.; Dollinger, H. Synthesis 1985, 743.
14. Methoden der Organischen Chemie Houben-Weyl, Stickstoff-Verbindungen II, Amine Band XI/1, Teil 1, Georg Thieme Verlag, Stuttgart, 1957, p.5. Streitweiser, A.Jr.; Heathcock, C.H. Introduction to Organic Chemistry, second ed. Macmillan Publishing Co. New York, 1981, p.735.
15. Pascual, C.; Meier, J.; Simon, W. Helv.Chim.Acta 1969, **48**, 164.
16. Jończyk, A.; Lipiak, D.; Zdrojewski, T. Polish Pat. Appl. No P 273217 (1988).
17. Jończyk, A.; Lipiak, D.; Zdrojewski, T. Polish Pat. Appl. No P 273219 (1988).
18. Recent paper on synthesis of 1,4-dicarbonyl compounds: Fiandanese, V.; Marchese, G.; Naso, F. Tetrahedron Lett. 1988, **29**, 3587 and literature cited therein.
19. Bennett, D.J.; Kirby, G.W.; Moss, V.A. J.Chem.Soc.(C) 1970, 2049.
20. Hauser, C.R.; Taylor, H.M.; Ledford, T.G. J.Am.Chem.Soc. 1960, **82**, 1786.
21. Goodson, L.J.; Christopher, H. J.Am.Chem.Soc. 1950, **72**, 358.
22. Morris, G.F.; Hauser, C.R. J.Org.Chem. 1961, **26**, 4741.
23. Straus, F.; Berkow, A. Ann. 1913, **401**, 121.