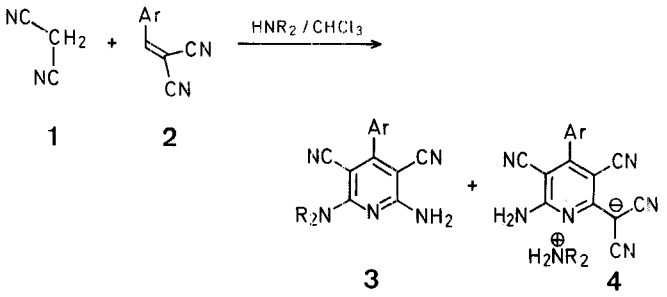
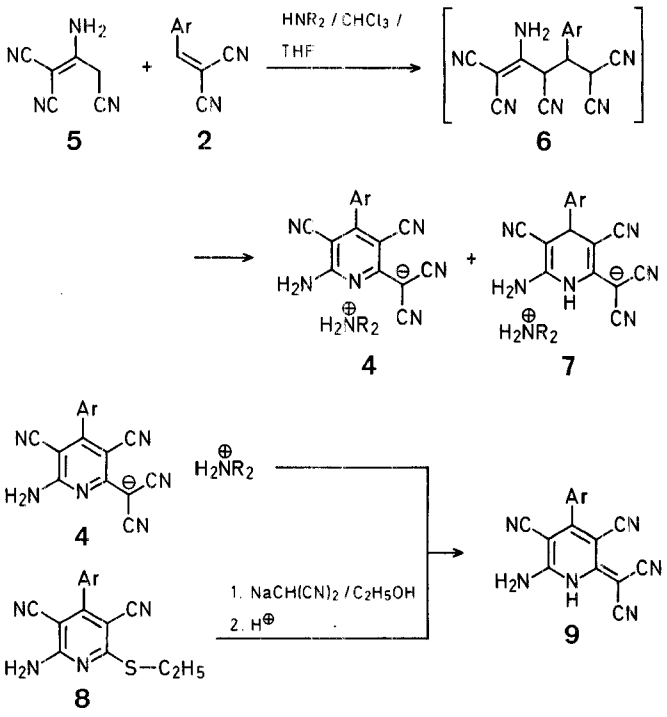


The intervention of 2-amino-1,1,3-tricyanopropene **(5)** in the formation of compounds **4** was indicated by the formation of a mixture of salts **4** and **7** from the reaction of **5**, previously synthesized[4,5], with benzylidenemalononitriles **(2)** and amine in chloroform/tetrahydrofuran. The reaction is initiated by a 1,4-addition of the 2-amino-1,1,3-tricyanopropene **(5)** to the corresponding benzylidenemalononitrile **2** to afford the adduct **6** which cyclizes to **4** and **7** via intramolecular attack of the enamine nitrogen atom at the cyano groups of the dicyanomethyl moiety of **6**. The salt mixture is oxidized completely to **4** by treatment with dichlorodicyanobenzoquinone (DDQ).



The structures assigned to the salts **4** and 1,2-dihydropyridines **9**, liberated from **4** in acid medium, are based on the preparation of **9a** (Ar = C_6H_5) by treatment of 2-amino-3,5-dicyano-6-ethylthio-4-phenylpyridine **(8a)**[6] with malononitrile in ethanol/ethoxide, and subsequent liberation of **9a** from the sodium salt thus formed.

The 1,4-dihydropyridine salts **(7)** can be isolated if tetrahydrofuran is used as reaction medium. Due the easy decomposition and readiness to oxidation of these compounds, we only describe the pyrrolidinium salt in which Ar = C_6H_5.

Melting points are uncorrected. Infrared spectra were recorded on Perkin-Elmer 257 and 599 spectrometers. ^{1}H-N.M.R. spectra were recorded on a Varian T-60 apparatus. For the column chromatography, Merck 60 alumina was used.

Synthesis of Heterocyclic Compounds, XXIII. Pyridines from Malononitrile Dimer and Benzylidenemalononitriles

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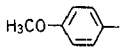
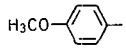
In the reaction of malononitrile **(1)** with benzylidenemalononitriles **(2** and amines, from which the 1-dialkylaminopyridines **(3)** were isolated[1], we observed that malononitrile showed a great tendency to undergo dimerization[2,3]. In the present work the intervention in that reaction of the malononitrile dimer in the formation of diethylammonium, pyrrolidinium, and piperidinium salts **(4)** of 2-amino-4-aryl-3,5-dicyano-6-dicyanomethylpyridines as side-products is proved and a synthesis for these salts **4** and the 6-amino-4-aryl-3,5-dicyano-2-dicyanomethylene-1,2-dihydropyridines **9** is described.

0039-7881/32/0432-0320 $ 03.00

Table. Compounds **4** and **9** prepared

Product No.	R	R	Ar	Yield [%]	m.p. [°C][a]	Molecular formula[b]	I.R. (KBr) [cm^{-1}] $\nu_{NH\text{-stretch}}$	$\nu_{C\equiv N}$	$\nu_{NH\text{-bend, C=C and C=N-stretch}}$	^{1}H-N.M.R. (DMSO-d_6) δ [ppm]
4a	$-(CH_2)_4-$			68	243–244°	$C_{20}H_{17}N_7$ (355.4)	3400, 3320, 3220	2220, 2190, 2155	1645, 1580, 1550, 1525, 1495	1.6–2.1 (m, 4H); 2.8–3.3 (m, 4H); 6.70 (br, 2H); 7.3 (m, 5H); 4.7–8.3 (br, 2H)
4b	$-(CH_2)_4-$			68	224–225°	$C_{21}H_{17}N_7O$ (383.5)	3390, 3330, 3225	2210, 2195, 2165	1655, 1615, 1545, 1510	1.6–2.0 (m, 4H); 2.8–3.2 (m, 4H); 3.73 (s, 3H); 6.66 (br, 2H); 6.91, 7.22 (A_2B_2, J=8 Hz, 4H); 5.0–8.6 (br, 2H)
4c	$-(CH_2)_4-$			61	253–254°	$C_{20}H_{16}ClN_7$ (389.9)	3400, 3340, 3320, 3215	2190, 2160	1645, 1600, 1575, 1550, 1530, 1500	1.6–2.0 (m, 4H); 2.9–3.3 (m, 4H); 6.70 (br, 2H); 7.28, 7.32 (2m, 4H); 3.5–8.3 (br, 2H)
4d	$-(CH_2)_4-$			60	259–260°	$C_{20}H_{16}N_8O_2$ (400.4)	3480, 3280, 3170	2190, 2150	1630, 1575, 1550, 1505	1.5–2.1 (m, 4H); 2.8–3.3 (m, 4H); 6.76 (br, 2H); 7.3–9.0 (m, 6H)
4e	$-(CH_2)_5-$			66	247–248°	$C_{21}H_{19}N_7$ (369.4)	3390, 3320, 3220, 3085	2220, 2190, 2160	1645, 1610, 1545, 1525, 1500	1.4–1.8 (m, 6H); 2.8–3.1 (m, 4H); 6.70 (br, 2H); 7.3 (m, 5H); 3.7–6.3 (br, 2H)
4f	C_2H_5	C_2H_5		68	244–245°	$C_{20}H_{19}N_7$ (357.4)	3430, 3330, 3210, 3180	2220, 2190, 2160	1640, 1585, 1555, 1520, 1490	1.13 (t, J=7 Hz, 6 H); 2.86 (q, 4 H, J=7 Hz); 6.70 (br, 2H); 7.3 (m, 5H); 4.5–6.4 (br, 2H)
7a	–	–		see experimental		—	—	—	—	—
9a	–	–		–[c]	302–307° (dec)	$C_{16}H_8N_6$ (284.3)	3360, 3300, 3260, 3210	2230, 2220, 2190	1640, 1555, 1475	7.35 (s, 5H); 7.58 (br, 3H)
9b	–	–		–[c]	312–317° (dec)	$C_{17}H_{10}N_6O$ (314.3)	3380, 3300, 3250, 3200	2220, 2210, 2180	1650, 1605, 1550, 1520, 1510, 1475	3.78 (s, 3H); 6.91, 7.22 (A_2B_2, J=8 Hz, 4H); 6.5–7.6 (br, 3H)
9c	–	–		–[c]	316–321° (dec)	$C_{16}H_7ClN_6$ (318.7)	3360, 3300, 3260, 3200	2220, 2190	1650, 1595, 1570, 1555, 1500, 1480	7.35, 7.38 (2s, 4H); 7.50 (br, 3H)
9d	–	–		–[c]	278–282° (dec)	$C_{16}H_7N_7O_2$ (329.3)	3360, 3300, 3250, 3200	2210	1645, 1610, 1550, 1520, 1475	7.40 (br, 3H); 7.6–8.0, 8.1–8.4 (2m, 4H)
		$Na^{\oplus}$		see experimental		—	—	—	—	—

[a] Compounds **4** are recrystallized from chloroform/ethanol.
[b] Satisfactory microanalyses obtained: C ±0.35, H ±0.17, N ±0.31, Cl ±0.02.
[c] 100% yield from salt **4**.

Diethylammonium, Pyrrolidinium, and Piperidinium Salts of 2-Amino-4-aryl-3,5-dicyano-6-dicyanomethylpyridines 4; General Procedure:
A solution of 2-amino-1,1,3-tricyanopropene (**5**; 0.66 g, 5 mmol) in tetrahydrofuran (6 ml) is slowly added to a stirred mixture of the corresponding benzylidenemalononitrile **2** (5 mmol) in chloroform (40 ml). The mixture is maintained for 45 min at 35–40 °C and the crude product (mixture of **4** and **7**) is separated by filtration. This mixture is dissolved in tetrahydrofuran (20 ml) and treated dropwise with a solution of DDQ in tetrahydrofuran [6–7 ml of a solution of DDQ (0.9 g, 4 mmol) in tetrahydrofuran (50 ml)] with stirring for 1 h at room temperature. Salt **4** precipitates and is filtered. The isolation of **4** that remains in the filtrate is achieved by passage through an alumina column (12 g) using acetone as eluent.

Pyrrolidinium Salt of 1,4-Dihydropyridine (7a):
To a solution of benzylidenemalononitrile (0.77 g, 5 mmol) and pyrrolidine (0.36 g, 5 mmol) in tetrahydrofuran (15 ml) is added slowly and with stirring for 1 h to 0 °C, a solution of 2-amino-1,1,3-tricyanopropene (**5**; 0.66 g, 5 mmol) in tetrahydrofuran (15 ml). When the addition is complete, the mixture is left stirring for 5 h, after which time a precipitate of **7a** has separated; yield: 0.95 g (53%). Recrystallization from water gives a white product; m.p. 212–213 °C.

$C_{20}H_{19}N_7$	calc.	C 67.21	H 5.36	N 27.44
(357.4)	found	67.46	5.37	27.88

I.R. (KBr): ν = 3470, 3420, 3360, 3340 (N—H stretch); 2200, 2170, 2160 (C≡N); 1655, 1595, 1490 cm^{-1} (N—H bending, C=C and C=N stretch).

^{1}H-N.M.R. DMSO-d_6): δ = 1.5–2.1 (m, 4H); 2.8–3.3 (m, 4H); 3.87 (s, 1H); 5.77 (s, 2H); 6.1–7.7 (br, 3H); 7.0 ppm (m, 5H).

6-Amino-4-aryl-3,5-dicyano-2-dicyanomethylene-1,2-dihydropyridines 9; General Procedure:

A solution of **4** (0.05 mol) in ethanol (20 ml) is poured over a water/ice mixture weakly acidified by hydrochloric acid. The yellow precipitate formed in each case is recrystallized from dimethylformamide/water.

Product 9a from 2-Amino-3,5-dicyano-6-ethylthio-4-phenylpyridine (8):

From a mixture of **8** (1.12 g, 4 mmol) and malononitrile (**1**; 0.33 g, 5 mmol) in absolute ethanol/sodium ethoxide (30 ml, 5 mmol) is heated for 6 h under reflux and allowed to stand for 12 h at room temperature, a precipitate (0.6 g) of the sodium salt of 2-amino-3,5-dicyano-6-dicyanomethyl-4-phenylpyridine **(9)** is formed. Removal of the solvent in vacuo leaves an oily material which is treated with chloroform and a few drops of ethanol to afford 0.28 g more of the salt. Recrystallization from ethanol gives the pure compound: yield: 0.80 g (68%); m.p. >340°C.

$C_{16}H_7N_6Na \cdot H_2O$	calc.	C 59.25	H 2.79	N 25.92
(324.3)	found	58.95	2.75	25.67

I.R. (KBr): ν = 3470, 3360 (N—H stretch); 2220, 2200, 2160 (C≡N); 1620, 1580, 545, 1505, 1495 cm^{-1} (N—H bending, C=C and C=N stretching).

^{1}H-N.M.R. DMSO-d_6): δ = 6.66 (br, 2H); 7.3 ppm (m, 5H).

Product **9a** is isolated from the above sodium salt as described for the salt **4** above.

Received: October 7, 1981

[1] L. Fuentes, J. J. Vaquero, J. L. Soto, *An. Quim.* **76** C, 68 (1980).
[2] F. Freeman, *Chem. Rev.* **69**, 591 (1969); *Synthesis* **1981**, 925.
[3] A. J. Fatiadi, *Synthesis* **1978**, 165, 241.
[4] R. A. Carboni, D. D. Coffman, E. G. Howard, *J. Am. Chem. Soc.* **80**, 2838 (1958).
[5] P. Walther, P. Pollak, *Chem. Ind. (Düsseldorf)* **27**, 25 (1975).
[6] J. J. Vaquero, *Thesis*, University of Alcalá de Henares, Madrid, Spain, 1981.

0039-7881/82/0432-0322 $ 03.00