

4*H*-Pyrans from α -Benzoylcinnamionitriles

M. Quinteiro, C. Seoane and J. L. Soto*

Departamento de Química Orgánica, Facultad de Química,
Universidad Complutense, Ciudad Universitaria, Madrid-3, Spain

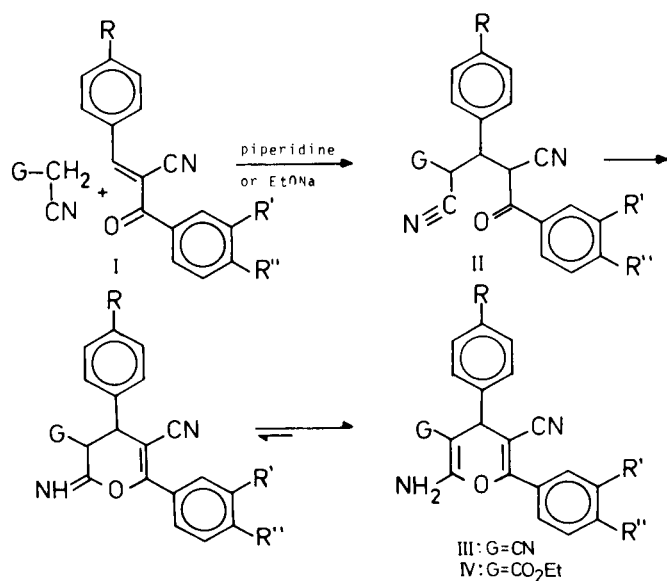
Received June 20, 1977

A new synthesis of substituted 4*H*-pyrans is reported. The base catalyzed reaction of substituted α -benzoylcinnamionitriles (I) with malononitrile yields 6-amino-2,4-diaryl-3,5-dicyano-4*H*-pyrans (III). Similarly, 6-amino-2,4-diaryl-5-carbomethoxy-3-cyano-4*H*-pyrans (IV) have been prepared from ethyl cyanoacetate.

J. Heterocyclic Chem., 15, 57 (1978)

In a preliminary communication (1), the reaction of α -benzoylcinnamionitriles (I) with either malononitrile or ethyl cyanoacetate has been described. 6-Amino-2,4-diaryl-3,5-dicyano-4*H*-pyrans (III) and 6-amino-2,4-diaryl-5-carbomethoxy-3-cyano-4*H*-pyrans (IV) were thus obtained. Compounds I are easily accessible from the appropriate aromatic aldehydes and benzoylacetonitriles.

The reaction sequence begins with a Michael addition of malononitrile or ethyl cyanoacetate to the α -benzoylcinnamionitrile to yield the adduct II, followed by cyclization to III or IV through a nucleophilic attack by the carbonyl oxygen at the cyano group (Scheme I).



By this one step reaction two new series of 4*H*-pyrans have been prepared (Table I).

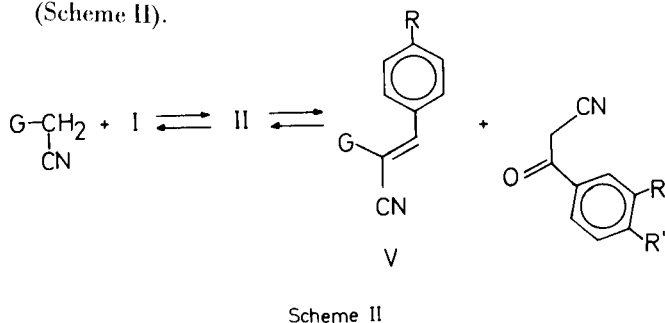
The structure was assigned on the basis of analytical and spectral data. The ir spectra of both series of pyrans (III and IV) show a very strong C=C band (1660-1680 cm^{-1}) and two strong bands (1135-1160 and 1250-1270 cm^{-1}), due to the enolic C-O bond; all these bands are characteristic of the γ -pyran ring (2,9). They show also a cyano stretching band (2200 cm^{-1}) and an amino bending band (1620 cm^{-1}). Stretching N-H bands appear at 3150-3450 cm^{-1} as three bands in III pyrans and two in IV pyrans.

Table I

Starting α -Benzoylcinnamionitrile	R	R'	R''	4 <i>H</i> -Pyran
Ia	H	H	H	IIIa
Ib	Cl	H	H	IIIb
Ic	OH	H	H	IIIc
Id	NO ₂	H	H	IIIc
Ie	CH ₃	H	H	IIIe
If	OCH ₃	H	H	IIIf
Ig	H	H	Cl	IIIg
Ih	H	NO ₂	H	IIIh
Ii	H	H	CH ₃	IIIi
Ij	NO ₂	H	OCH ₃	IIIj
Ik	NO ₂	H	CH ₃	IIIk
II	OCH ₃	H	CH ₃	IIIl
Im	(CH ₃) ₂ N	H	H	—
In	(CH ₃) ₂ N	H	Cl	—
Ia	H	H	H	IVa
Id	NO ₂	H	H	—
Ie	CH ₃	H	H	IVe
If	OCH ₃	H	H	IVf
Ii	H	H	CH ₃	IVi
Ij	NO ₂	H	OCH ₃	IVj
Ik	NO ₂	H	CH ₃	IVk
II	OCH ₃	H	CH ₃	IVl

This, together with the lower frequency shift of the C=O ester band, show the intramolecular association between the amino and the carbomethoxy groups in IV pyrans. The nmr spectra of all these compounds show a singlet ($\delta = 4.1-4.9$), assigned to the proton at the 4 position of γ -pyran ring (4). The uv spectra show a single maximum (296-305 nm) in both series. The mass spectra are also consistent with the proposed structures.

The elimination of benzoylacetonitrile from the II adducts is a side reaction which competes with the cyclization (Scheme II).



Thus, the reaction of ethyl cyanoacetate with α -(*p*-methoxybenzoyl)-*p*-nitrocinnamionitrile (Ij) yields the expected 4*H*-pyran (IVj) and a certain amount of ethyl α -cyano-*p*-nitrocinnamate (V; R = NO₂, G = CO₂Et) (10). In the case of α -benzoyl-*p*-nitrocinnamionitrile (Id) only ethyl α -cyano-*p*-nitrocinnamate was isolated in almost quantitative yield.

This side reaction has also been observed in the III series, but the formation of the 4*H*-pyran is prevented only when a *p*-dimethylamino group is present in the starting α -benzoylcinnamionitrile (Im and In). In that case, the isolated product is α -cyano-*p*-*N,N*-dimethylaminocinnamionitrile (V; R = (CH₃)₂N, G = CN) (11) or its reaction product with malononitrile: 6-amino-3,5-dicyano-2-ethoxy-4-(*p*-dimethylaminophenyl)pyridine (12).

EXPERIMENTAL

Melting points are uncorrected. The uv spectra were recorded on a Perkin Elmer I37 and a PYE Unicam SP 1700 spectrophotometer. The ir spectra were recorded on a Perkin Elmer 237 and PYE Unicam SP 1100. The nmr spectra were recorded on a JEOL Minimar 60; chemical shifts are quoted in δ values against tetramethylsilane as the internal standard. Mass spectra were recorded on a Varian MAT 711 spectrometer. Microanalysis are by "Centro Nacional de Química Orgánica" de Madrid.

α -Benzoylcinnamionitriles (I).

α -Benzoylcinnamionitrile (Ia), α -benzoyl-*p*-dimethylaminocinnamionitrile (Im) and α -benzoyl-*p*-nitrocinnamionitrile (Id) were prepared by the method described by Kaufman (13). α -Benzoyl-*p*-chlorocinnamionitrile (Ib), α -benzoyl-*p*-hydroxycinnamionitrile (Ic) and α -(*p*-chlorobenzoyl)-*p*-dimethylaminocinnamionitrile (In) were obtained by the method described by Drapkina (14) and α -(*p*-chlorobenzoyl)cinnamionitrile (Ig) by the method reported by Meyer (15). The remaining α -benzoylcinnamionitriles, which have not been described in the literature, were prepared by the following general procedure: Equimolar amounts of aldehyde and benzoylacetonitrile (16) were dissolved in dry ethanol, a few drops of piperidine were added and the solution was stirred either at room temperature or with heating. The exact conditions varied with the compounds to be prepared. These were isolated by filtration and crystallized.

α -(*m*-Nitrobenzoyl)cinnamionitrile (Ih).

The reaction mixture was refluxed for three hours. Compound Ih was obtained in 60% yield, m.p. 135-136° (crystallized from ethanol, methanol or methylene chloride); ir (potassium bromide): 3080, 2220, 1675, 1610, 1580, 1565, 1525, 1490, 1470, 1450, 1350, 1315, 1300, 1265, 1210, 1190, 1125, 1100 cm⁻¹; nmr (deuterioacetone): δ = 7.0-8.5 (m, 9H arom. and =CH).

Anal. Calcd. for C₁₆H₁₀N₂O₃: C, 69.06; H, 3.62; N, 10.07. Found: C, 69.43; H, 3.82; N, 10.26.

α -(*p*-Methylbenzoyl)cinnamionitrile (Ii).

The reaction mixture was stirred at room temperature until total solution was obtained (2-3 hours). Compound Ii was obtained in 62% yield, m.p. 95-96° (ethanol); ir (potassium bromide): 2920, 2220, 1662, 1605, 1580, 1560, 1495, 1450, 1410, 1360, 1312, 1300, 1270, 1210, 1182, 1115, 1100, 1080, 1020 cm⁻¹; nmr (deuteriochloroform): δ = 7.1-8.2 (m, 9H arom. and =CH); 2.6 (s, 3H, -CH₃).

Anal. Calcd. for C₁₇H₁₃NO: C, 82.59; H, 5.26; N, 5.67. Found: C, 82.53; H, 5.08; N, 5.48.

α -(*p*-Methoxybenzoyl)-*p*-nitrocinnamionitrile (Ij).

This compound was prepared as described above, yield, 81%, m.p. 145-146° (dry ethanol); ir (potassium bromide): 3170, 2900, 2265, 1695, 1630, 1600, 1552, 1545, 1445, 1375, 1350, 1300, 1240, 1212, 1130, 1060, 1050 cm⁻¹; nmr (deuterioacetone): δ = 6.5-8.0 (m, 9H arom. and =CH); 3.85 (s, 3H, -OCH₃).

Anal. Calcd. for C₁₇H₁₂N₂O₄: C, 66.23; H, 3.90; N, 9.09. Found: C, 66.28; H, 4.09; N, 9.09.

α -(*p*-Methylbenzoyl)-*p*-nitrocinnamionitrile (Ik).

This compound was obtained as Ii and Ij, yield 64%, m.p. 152-153° (ethyl acetate); ir (potassium bromide): 3120, 3030, 2860, 2220, 1675, 1605, 1590, 1570, 1520, 1490, 1450, 1410, 1375, 1350, 1315, 1300, 1270, 1210, 1185, 1120, 1105, 1035, 1015 cm⁻¹; nmr (deuteriochloroform): δ = 7.3-8.6 (m, 8H arom. and =CH); 2.55 (s, 3H, -CH₃).

Anal. Calcd. for C₁₇H₁₂N₂O₃: C, 69.85; H, 4.14; N, 9.59. Found: C, 70.10; H, 4.24; N, 9.81.

α -(*p*-Methylbenzoyl)-*p*-methoxycinnamionitrile (Il).

The reaction mixture was gently heated for 30 minutes. Compound Il was obtained in 52% yield, m.p. 94-96° (ethanol); ir (potassium bromide): 2920, 2840, 2220, 1660, 1610, 1590, 1580, 1560, 1520, 1470, 1430, 1370, 1320, 1275, 1220, 1185, 1140, 1110, 1030 cm⁻¹; nmr (deuterioacetone): δ = 6.7-8.0 (m, 8H arom. and =CH); 3.9 (s, 3H, -OCH₃); 2.4 (s, 3H, -CH₃).

Anal. Calcd. for C₁₈H₁₅NO₂: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.85; H, 5.43; N, 5.18.

Preparation of 4*H*-Pyrans. General Procedure.

Series III.

To a suspension of 0.005 mole of the appropriate α -benzoylcinnamionitrile in ca. 15 ml. of dry ethanol, a solution of 0.005 mole of malononitrile in ca. 10 ml. of dry ethanol with a very small piece of sodium (less than 0.0005 mole) or a few drops of piperidine was added. The mixture is stirred at room temperature until total solution occurred (a few minutes). After a few hours standing a rapid crystallization begins. The resulting solid was filtered off and recrystallized from benzene, ethanol or methylene chloride.

Series IV.

The procedure was as above, using 0.005 mole of ethyl cyanoacetate and a few drops of piperidine as the catalyst.

6-Amino-3,5-dicyano-2,4-diphenyl-4*H*-pyran (IIIa).

This compound was obtained in 91% yield, m.p. 181-182° (recrystallized from ethanol, methylene chloride or benzene); ir (potassium bromide): 3460, 3400, 3310, 3185, 2200, 1680, 1630, 1600, 1495, 1460, 1415, 1345, 1270, 1150, 1080, 1030 cm⁻¹; nmr (deuteriochloroform): δ = 6.9-7.6 (m, 10H arom.); 4.7 (s, 2H, -NH₂), 4.2 (s, 1H); uv λ max (ethanol): 298 nm (ϵ = 7,100); ms: m/e = 299 (M⁺, 13), 298 (3), 255 (5), 233 (33), 232 (15), 222 (33), 154 (26), 145 (3), 127 (23), 105 (100), 103 (12), 77 (60).

Anal. Calcd. for C₁₉H₁₃N₃O: C, 76.25; H, 4.34; N, 14.04. Found: C, 75.89; H, 4.08; N, 13.95;

6-Amino-3,5-dicyano-4-(*p*-chlorophenyl)-2-phenyl-4*H*-pyran (IIIb).

This compound was obtained in 84% yield, m.p. 175-176° (recrystallized from benzene or ethyl acetate); ir (potassium bromide): 3450, 3320, 3180, 2220, 1680, 1630, 1595, 1490, 1445, 1415, 1400, 1340, 1265, 1140, 1090, 1020 cm⁻¹; nmr (deuteriochloroform): δ = 7.2-7.9 (m, 9H arom.), 5.15 (s, 2H, -NH₂), 4.5 (s, 1H);

uv λ max (ethanol): 295.6 nm ($\epsilon = 6,424$); ms: $m/e = 333$ (M^+ , 11), 332 (2), 289 (5), 267 (15), 240 (10), 222 (31), 188 (19), 153 (24), 145 (3), 105 (100), 77 (57).

Anal. Calcd. for $C_{19}H_{12}ClN_3O$: C, 68.37; H, 3.62; N, 12.59; Cl, 10.65. Found: C, 68.11; H, 3.76; N, 12.71; Cl, 10.98.

6-Amino-3,5-dicyano-4-(*p*-hydroxyphenyl)-2-phenyl-4*H*-pyran (IIIc).

This compound was obtained in 48% yield, m.p. 184-185° (recrystallized from acetone or ethyl acetate); ir (potassium bromide): 3360, 3180, 2230, 2210, 1725, 1680, 1615, 1600, 1520, 1490, 1450, 1410, 1375, 1340, 1265, 1175, 1150, 1110, 1030 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 9.05$ (s, 1H, OH), 6.9 (s, 2H, -NH₂), 6.3-7.6 (m, 9H, arom.) 4.15 (s, 1H); uv λ max (ethanol): 298 nm ($\epsilon = 10,154$); ms: $m/e = 315$ (M^+ , 10), 314 (4), 271 (7), 249 (25), 222 (27), 170 (30), 145 (5), 106 (13), 105 (100), 77 (72).

Anal. Calcd. for $C_{19}H_{13}N_3O_2$: C, 72.37; H, 4.16; N, 13.33. Found: C, 72.39; H, 3.98; N, 13.19.

6-Amino-3,5-dicyano-4-(*p*-nitrophenyl)-2-phenyl-4*H*-pyran (IIIId).

This compound was obtained in 90% yield, m.p. 204-205° (recrystallized from ethanol or methylene chloride); ir (potassium bromide): 3405, 3280, 3160, 3090, 3060, 2220, 2200, 1660, 1615, 1590, 1505, 1480, 1430, 1400, 1340, 1258, 1170, 1150, 1135, 1100, 1015 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 7.0$ -8.0 (m, 9H arom.), 7.1 (s, 2H, -NH₂), 4.6 (s, 1H); uv λ max (ethanol): 296 nm ($\epsilon = 34,025$); ms: $m/e = 344$ (M^+ , 7), 300 (1), 278 (9), 261 (13), 223 (5), 222 (28), 199 (12), 153 (10), 145 (3), 126 (11), 106 (10), 105 (100), 77 (62).

Anal. Calcd. for $C_{19}H_{12}N_4O_3$: C, 66.27; H, 3.51; N, 16.27. Found: C, 66.34; H, 3.39; N, 16.13.

6-Amino-3,5-dicyano-4-(*p*-methylphenyl)-2-phenyl-4*H*-pyran (IIIe).

This compound was obtained in 86% yield, m.p. 199-200° (recrystallized from ethanol, benzene or methylene chloride); ir (potassium bromide): 3400, 3310, 3190, 3020, 2900, 2220, 1680, 1630, 1610, 1510, 1448, 1410, 1350, 1270, 1160, 1140, 1030 cm^{-1} ; nmr (deuterioacetone): $\delta = 7.3$ -8.2 (m, 9H arom), 6.75 (s, 2H, -NH₂), 4.65 (s, 1H), 2.55 (s, 3H, -CH₃); uv λ max (ethanol): 297 nm ($\epsilon = 9,189$); ms: $m/e = 313$ (M^+ , 9), 312 (2), 269 (5), 247 (14), 232 (27), 222 (19), 168 (14), 145 (2), 141 (11), 140 (10), 105 (100), 77 (57).

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 76.96; H, 4.58; N, 13.32.

6-Amino-3,5-dicyano-4-(*p*-methoxyphenyl)-2-phenyl-4*H*-pyran (IIIIf).

This compound was obtained in 73% yield, m.p. 199-200° (recrystallized from methylene chloride); ir (potassium bromide): 3400, 3300, 3180, 3040, 2920, 2830, 2210, 1670, 1625, 1600, 1515, 1490, 1460, 1440, 1410, 1350, 1300, 1260, 1180, 1140, 1115, 1030 cm^{-1} ; nmr (deuterioacetone): $\delta = 6.7$ -7.7 (m, 9H arom.), 6.5 (s, 2H, -NH₂); 4.5 (s, 1H), 3.9 (s, 3H, -OCH₃); uv λ max (ethanol): 299.2 nm ($\epsilon = 10,406$); ms: $m/e = 329$ (M^+ , 9), 285 (8), 263 (19), 222 (8), 184 (43), 145 (3), 141 (12), 114 (17), 106 (10), 105 (100), 77 (60).

Anal. Calcd. for $C_{20}H_{15}N_3O_2$: C, 72.93; H, 4.59; N, 12.76. Found: C, 72.32; H, 4.68; N, 12.43

6-Amino-3,5-dicyano-2-(*p*-chlorophenyl)-4-phenyl-4*H*-pyran (IIIg).

This compound was obtained in 71% yield, m.p. 209-210° (recrystallized from benzene); ir (potassium bromide): 3420, 3320, 3140, 3000, 2210, 2183, 1660, 1620, 1585, 1485, 1445, 1390,

1330, 1260, 1210, 1140, 1105, 1090, 1010 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 6.9$ -7.6 (m, 9H arom), 6.9 (s, 2H, -NH₂), 4.35 (s, 1H); uv λ max (ethanol): 298 nm ($\epsilon = 25,000$); ms: $m/e = 333$ (M^+ , 6), 289 (4), 267 (22), 266 (14), 256 (17), 232 (15), 179 (4), 154 (28), 141 (35), 140 (10), 139 (100), 127 (27), 113 (15), 111 (44), 103 (15), 77 (10), 76 (10).

Anal. Calcd. for $C_{19}H_{12}ClN_3O$: C, 68.37; H, 3.62; N, 12.59; Cl, 10.65. Found: C, 68.36; H, 3.60; N, 12.68; Cl, 10.92.

6-Amino-3,5-dicyano-2-(*m*-nitrophenyl)-4-phenyl-4*H*-pyran (IIIh).

This compound was obtained in 83% yield, m.p. 211-212° (recrystallized from ethanol); ir (potassium bromide): 3420, 3300, 3190, 3080, 2210, 1670, 1620, 1598, 1520, 1450, 1400, 1345, 1320, 1258, 1158, 1100, 1010 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 7.0$ -8.4 (m, 9H arom.), 7.0 (s, 2H, -NH₂); 4.35 (s, 1H); uv λ max (ethanol): 296 nm ($\epsilon = 7,160$); ms: $m/e = 344$ (M^+ , 7), 300 (2), 279 (11), 278 (56), 277 (44), 267 (16), 190 (2), 154 (19), 151 (11), 150 (100), 128 (12), 127 (18), 104 (50), 103 (13), 77 (19), 76 (42), 75 (16).

Anal. Calcd. for $C_{19}H_{12}N_4O_3$: C, 66.27; H, 3.48; N, 16.27. Found: C, 66.29; H, 3.60; N, 16.62.

6-Amino-3,5-dicyano-2-(*p*-methylphenyl)-4-phenyl-4*H*-pyran (IIIi).

This compound was obtained in 81% yield, m.p. 195-196° (recrystallized from ethanol); ir (potassium bromide): 3420, 3330, 3190, 2220, 2200, 1675, 1625, 1600, 1450, 1400, 1345, 1320, 1260, 1250, 1190, 1160, 1140, 1080 cm^{-1} ; nmr (deuterioacetone): $\delta = 7.2$ -8.8 (m, 9H arom.), 6.5 (s, 2H, -NH₂), 4.45 (s, 1H), 2.4 (s, 3H, -CH₃); uv λ max (ethanol): 299.2 nm ($\epsilon = 8,922$).

Anal. Calcd. for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 76.90; H, 4.60; N, 13.56.

6-Amino-3,5-dicyano-2-(*p*-methoxyphenyl)-4-(*p*-nitrophenyl)-4*H*-pyran (IIIj).

This compound was obtained in 68% yield, m.p. 216-217° (recrystallized from ethanol); ir (potassium bromide): 3400, 3350, 3215, 2960, 2840, 2210, 1685, 1610, 1520, 1460, 1440, 1410, 1350, 1335, 1315, 1265, 1190, 1155, 1035 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 7.1$ -8.5 (m, 8H, arom.), 7.75 (s, 2H, -NH₂), 4.9 (s, 1H), 4.0 (s, 3H, -OCH₃); uv λ max (ethanol): 303 nm ($\epsilon = 19,897$).

Anal. Calcd. for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.74; N, 14.97. Found: C, 64.29; H, 3.54; N, 14.87.

6-Amino-3,5-dicyano-2-(*p*-methylphenyl)-4-(*p*-nitrophenyl)-4*H*-pyran (IIIk).

This compound was obtained in 97% yield, m.p. 214-215° (recrystallized from methylene chloride); ir (potassium bromide): 3430, 3320, 3200, 3080, 2225, 2200, 1675, 1630, 1610, 1600, 1520, 1405, 1350, 1270, 1200, 1170, 1150, 1135, 1115, 1035, 1023 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 6.9$ -8.1 (m, 8H arom.), 7.1 (s, 2H, -NH₂), 4.65 (s, 1H), 3.37 (s, 3H, -CH₃); uv λ max (ethanol) = 301 nm ($\epsilon = 7,442$).

Anal. Calcd. for $C_{20}H_{14}N_4O_3$: C, 67.03; H, 3.94; N, 15.63. Found: C, 67.06; H, 4.08; N, 15.73;

6-Amino-3,5-dicyano-4-(*p*-methoxyphenyl)-2-(*p*-methylphenyl)-4*H*-pyran (IIIl).

This compound was obtained in 87% yield, m.p. 216-217° (recrystallized from methylene chloride); ir (potassium bromide): 3460, 3340, 3180, 2840, 2220, 2200, 1675, 1610, 1597, 1512, 1470, 1450, 1395, 1330, 1310, 1260, 1240, 1215, 1180, 1150, 1120, 1030 cm^{-1} ; nmr (deuteriodimethylsulfoxide): $\delta = 6.6$ -7.7 (m, 8H, arom.), 7.1 (s, 2H, -NH₂), 4.35 (s, 1H), 3.75 (s, 3H, -OCH₃), 2.4 (s, 3H, -CH₃); uv λ max (ethanol) = 300 nm ($\epsilon = 9,368$).

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.40; H, 5.04; N, 12.50.

6-Amino-5-carbomethoxy-3-cyano-2,4-diphenyl-4H-pyran (IVa).

This compound was obtained in 46% yield, m.p. 145-146° (recrystallized from benzene); ir (potassium bromide): 3438, 3320, 3020, 2980, 2910, 2220, 1695, 1650, 1615, 1535, 1460, 1450, 1410, 1365, 1340, 1300, 1260, 1230, 1170, 1110, 1040, 1000 cm^{-1} ; nmr (deuteriochloroform): δ = 6.8-7.0 (m, 10H, arom.), 6.3 (s, 2H, -NH₂), 4.55 (s, 1H), 4.1 (q., 2H, -CH₂-), 1.1 (t., 3H, -CH₃); uv λ max (ethanol): 296 nm (ϵ = 5.968); ms: m/e = 346 (M^+ , 44), 317 (12), 274 (23), 273 (100), 270 (20), 269 (99), 241 (15), 233 (9), 223 (34), 201 (8), 156 (16), 105 (70), 77 (43).

Anal. Calcd. for $C_{21}H_{18}N_2O_3$: C, 72.82; H, 5.24; N, 8.09. Found: C, 72.67; H, 5.31; N, 7.91.

6-Amino-5-carbomethoxy-3-cyano-4-(*p*-methylphenyl)-2-phenyl-4H-pyran (IVe).

This compound was obtained in 34% yield, m.p. 142-143° (recrystallized from ethanol-water or methanol); ir (potassium bromide): 3420, 3300, 2990, 2220, 1698, 1650, 1615, 1530, 1405, 1340, 1330, 1290, 1260, 1230, 1160, 1100, 1035 cm^{-1} ; nmr (deuterioacetone): δ = 6.8-7.8 (m, 9H arom.), 7.2 (s, 2H, -NH₂), 4.5 (s, 1H), 4.05 (q., 2H, -CH₂-), 2.35 (s, 3H, -CH₃), 1.15 (t, 3H, -CH₃); uv λ max (ethanol): 296 nm (ϵ = 6.424).

Anal. Calcd. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.11; H, 5.62; N, 7.76.

6-Amino-5-carbomethoxy-3-cyano-4-(*p*-methoxyphenyl)-2-phenyl-4H-pyran (IVf).

This compound was obtained in 53% yield, m.p. 183-184° (recrystallized from benzene); ir (potassium bromide): 3420, 3300, 2980, 2940, 2218, 1692, 1650, 1610, 1512, 1410, 1300, 1250, 1235, 1180, 1160, 1090, 1035 cm^{-1} ; nmr (deuteriopyridine): δ = 6.7-7.8 (m, 9H arom.), 2H, -NH₂), 4.75 (s, 1H), 4.15 (q., 2H, -CH₂-), 3.65 (s, 3H, -OCH₃), 1.15 (t., 3H, -CH₃); uv λ max (ethanol): 300 nm (ϵ = 7.964); ms: m/e = 376 (M^+ , 51), 347 (19), 331 (12), 330 (19), 329 (12), 304 (23), 303 (82), 287 (10), 286 (16), 270 (10), 269 (33), 263 (22), 241 (10), 236 (10), 232 (10), 231 (16), 223 (23), 186 (12), 156 (10), 106 (10), 105 (100), 77 (57).

Anal. Calcd. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 69.99; H, 5.27; N, 7.40.

6-Amino-5-carbomethoxy-3-cyano-2-(*p*-methylphenyl)-4-phenyl-4H-pyran (IVi).

This compound was obtained in 66% yield, m.p. 154-155° (recrystallized from benzene); ir (potassium bromide): 3400, 3295, 2980, 2220, 1690, 1650, 1620, 1530, 1455, 1403, 1335, 1300, 1260, 1250, 1230, 1190, 1150, 1100, 1020 cm^{-1} ; nmr (deuterioacetone): δ = 7.0-7.7 (m, 9H arom. 2H, -NH₂), 4.5 (s, 1H), 4.05 (q., 2H, -CH₂-), 2.4 (s, 3H, -CH₃), 1.1 (t., 3H, -CH₃); uv λ max (ethanol): 297 nm (ϵ = 6.750); ms: m/e = 361 (11), 360 (M^+ , 30), 331 (11), 288 (16), 287 (65), 284 (19), 283 (81), 255 (11), 247 (19), 246 (11), 237 (30), 201 (8), 170 (13), 119 (100), 91 (46), 77 (8).

Anal. Calcd. for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found: C, 73.09; H, 5.72; N, 7.49.

6-Amino-5-carbomethoxy-3-cyano-2-(*p*-methoxyphenyl)-4-(*p*-nitrophenyl)-4H-pyran (IVj).

Ethyl α -cyano-*p*-nitrocinnamate (10) (0.25 g.) was separated first from the reaction mixture. After a few days at room temperature, IVj was obtained from the mother liquors in 26% yield, m.p. 213-214° (recrystallized from benzene); ir (potassium bromide): 3440, 3320, 2980, 2220, 1690, 1660, 1630, 1610, 1520, 1465,

1350, 1310, 1260, 1230, 1180, 1150, 1100, 1030 cm^{-1} ; nmr (deuterioacetone): δ = 6.5-7.9 (m, 8H arom. 2H, -NH₂), 4.5 (s, 1H) 3.9 (q., 2H, -CH₂-), 3.75 (s, 3H, -OCH₃), 1.1 (t., 3H, -CH₃); uv λ max (ethanol): 305 nm (ϵ = 17,100).

Anal. Calcd. for $C_{22}H_{19}N_3O_6$: C, 62.70; H, 4.55; N, 9.97. Found: C, 62.82; H, 4.49; N, 9.75.

6-Amino-5-carbomethoxy-3-cyano-2-(*p*-methylphenyl)-4-(*p*-nitrophenyl)-4H-pyran (IVk).

This compound was obtained in 65% yield, m.p. 214-215° (benzene); ir (potassium bromide): 3440, 3315, 2985, 2220, 1695, 1665, 1630, 1592, 1530, 1405, 1350, 1300, 1262, 1250, 1230, 1190, 1150, 1100, 1030, 1015 cm^{-1} ; nmr (deuteriochloroform): δ = 6.7-7.8 (m, 8H arom.), 6.15 (s, 2H, -NH₂), 4.45 (s, 1H), 3.9

(q, 2H, -CH₂-), 2.31 (s, 3H, -CH₃), 1.1 (t, 3H, -CH₃); uv λ max (ethanol): 302 nm (ϵ = 10,528); ms: m/e = 405 (M^+ , 20), 333 (18), 332 (70), 292 (8), 284 (15), 283 (69), 255 (7), 246 (8), 237 (21), 218 (12), 201 (9), 170 (7), 120 (11), 119 (100), 91 (45), 77 (4).

Anal. Calcd. for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.37. Found: C, 65.27; H, 4.45; N, 10.26.

6-Amino-5-carbomethoxy-3-cyano-4-(*p*-methoxyphenyl)-2-(*p*-methylphenyl)-4H-pyran (IVl).

This compound was obtained in 48% yield, m.p. 154-155° (methanol); ir (potassium bromide): 3420, 3310, 2980, 2840, 2220, 1695, 1650, 1615, 1530, 1520, 1405, 1385, 1365, 1330, 1310, 1290, 1260, 1235, 1185, 1160, 1105, 1040 cm^{-1} ; nmr (deuteriochloroform): δ = 6.6-7.6 (m, 8H arom.), 6.2 (s, 2H, -NH₂), 4.4 (s, 1H), 4.0 (q, 2H, -CH₂-), 3.2 (s, 3H, -OCH₃), 2.4 (s, 3H, -CH₃), 1.15 (t, 3H, -CH₃); uv λ max (ethanol): 299 nm (ϵ = 8,370).

Anal. Calcd. for $C_{23}H_{22}N_2O_4$: C, 70.53; H, 5.63; N, 6.96. Found: C, 70.77; H, 5.64; N, 7.18.

Reaction of α -Benzoyl-*p*-dimethylaminocinnamitrile (Im) with Malonitrile.

Following the general procedure and using sodium as catalyst, 6-amino-3,5-dicyano-2-ethoxy-4-(*p*-dimethylaminophenyl)pyridine (12) was obtained in 15% yield, m.p. 274-275° (lit. 270-271°). α -Cyano-*p*-*N,N*-dimethylaminocinnamitrile (V, G = CN, R = (CH₃)₂N) (11).

This compound was obtained in 79% yield when piperidine was used instead of sodium as the catalyst, m.p. 179-180° (lit. 179°).

Reaction of α -(*p*-Chlorobenzoyl)-*p*-dimethylaminocinnamitrile (In) with Malonitrile.

α -Cyano-*p*-*N,N*-dimethylaminocinnamitrile was obtained using piperidine as the catalyst.

Reaction of α -Benzoyl-*p*-nitrocinnamitrile (Id) with Ethyl Cyanoacetate.

Ethyl α -cyano-*p*-nitrocinnamate (V, R = NO₂, G = CO₂Et) (10) was obtained in 81% yield, m.p. 169-170° (lit. 169-70°).

REFERENCES AND NOTES

- (1) M. Quinteiro, C. Seoane and J. L. Soto, *Tetrahedron Letters*, 1835 (1977)
- (2) J. Ficini and A. Krief, *ibid.*, 1427 (1969)
- (3) J. Ficini and A. Krief, *ibid.*, 885 (1970)
- (4) H. S. Hauer, Doctoral Thesis, Purdue University (1969); *Chem. Abstr.*, 73, 3740j (1970).
- (5) A. Balaban, G. Michai and C. Nenitzescu, *Tetrahedron*, 18, 257 (1962).

- (6) A. Saffiedine, J. Royer and J. Dreux, *Bull. Soc. Chim. France*, 707 (1972).
- (7) J. Royer, A. Saffiedine and J. Dreux, *ibid.*, 1646 (1972).
- (8) R. Gomper and O. Christmann, *Angew. Chem.*, 71, 32 (1959).
- (9) R. Gomper and O. Christmann, *Chem. Ber.*, 94, 1784 (1961).
- (10) E. Fiquet, *Ann. Chim. Phys.*, 29, 489 (1894).
- (11) W. Walter, *Ber.*, 35, 1320 (1902).
- (12) A. Alvarez-Insua, M. Lora-Tamayo and J. L. Soto, *J. Heterocyclic Chem.*, 7, 1305 (1970).
- (13) H. Kaufman, *Ber.*, 50, 5150 (1917).
- (14) D. Drapkina, V. Brudz and B. Bolotin, *Tr., Vses. Nauch.-Isled. Inst. Khim. Reaktivou Osobo Chist. Khim Veshehestv.*, No. 30, 333 (1967); *Chem. Abstr.*, 69, 6727p (1968).
- (15) E. V. Meyer, *J. Prakt. Chem.*, [2], 92, 183 (1915).
- (16) R. Long, *J. Am. Chem. Soc.*, 69, 990 (1947).