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A. M. El-Sayed [a] & A. Khodairy [a]
[a] Department of Chemistry, Faculty of Science , Sohag, Egypt
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SYNTHESIS OF SOME NEW HETEROCYCLES DERIVED FROM ARYLMETHYLENEMALONONITRILES

A. M. El-Sayed* and A. Khodairy

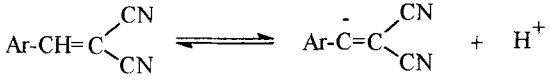
Department of Chemistry, Faculty of Science, Sohag, Egypt

Abstract- Arylmethylenemalononitriles **1** were treated with halo compounds under phase transfer catalysis (PTC) conditions to yield α-polyfunctional arylmethylene-malononitrile derivatives **2-4.** The treatment of compounds **2-4** with hydrazine hydrate gave pyridinones **5,6** and pyridine **7**, respectively. Triazines, triazepines, tetrazines, and triazoles **8-15** fused with pyridinone were synthesized by treating pyridinones **5** with a suitable reagent.

Arylmethylenemalononitriles, as α,β-unsaturated nitriles, have attracted considerable interest as potential building blocks for the synthesis of many nitrogen-containing heterocyclic compounds[1-7]. The spectral studies of several arylmethylenemalononitriles point to the acidic nature of the olefinic C-H bond.[8,9] The NMR spectra of series of arylmethylenemalono-nitriles were examined in various solvents. The chemical shift of the oliefinic

* To whom correspondence should be addressed

proton is found to be susceptible to a large solvent effects, interpreted as an association of a polar solvent molecule with the olefinic proton, which leads to downfield shift from values observed in chloroform.[10] The presence of an electron withdrawing substituent in the phenyl ring increases the downfield shift. Issa et. al[11] studied the U.V spectra of arylmethylenemalononitriles in buffer solutions of different pH. They found that the intensity of the charge transfer bands of the nonionic forms I of these molecules were decreased, while the bands corresponding to the charged forms II increased with increasin of pH values. Moreover, spectra of the investigated compounds showed a clear isosbestic points confirming the presence of acid- base equilbria for these compounds:



I II

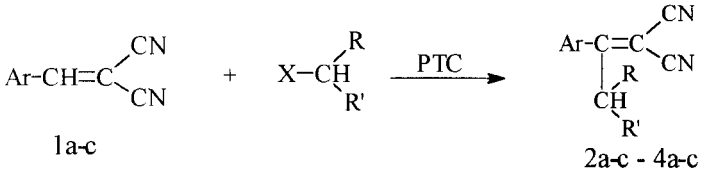
The plots of A_{max} (absorbance at λ_{max}) as a function of pH presented typical dissociation and association curves confirming the existence of an acid-base reaction. The determined pK_a values of these molecules[11,12] ranging from 6.00 to 11.10 were found to depend on the nature of the substituent on the aromatic ring and linearly related to Hammett σ values. The ease of ionization of this hydrogen is brought about by the strong acceptor character of the two nitrile groups in conjugation with it. These physical evidences along with the synthetic argument mentioned by Bastus,[13] that the treatment of benzylmethylenemalononitrile with diazomethane yielded its methyl derivative in a good yield, infer the measurable acidic character of the tested compounds.

So, in the present investigation it is intended to use the acidic character of the arylmethylenemalononitriles to synthesize some poly functional

derivatives of these compounds via phase-transfer catalysis (PTC) technique. These compounds were used for the synthesis of some new fused heterocyclic systems.

The low stability of arylmethylenemalononitriles towards strong alkaline medium[14-20] prompted us to apply the solid-liquid PTC technique [benzene or dioxan/K_2CO_3/ tetrabutylammonium bromide (TBAB)] which offers suitable conditions for alkylation of these compounds, scince it has been reported that many reactions with C-H acidic compounds can be efficiently carried out using anhydrous sodium or potassium carbonate as base and tetraalkylammonium salts as catalyst[21-25]

The reaction of arylmethylenemalononitriles 1_{a-c} with some reactive halo compounds, namely diethyl bromomalonate, ethyl chloroacetate or chloroacetonitrile under PTC conditions [benzene or dioxane /K_2CO_3/ tetrabutylammonium bromide (TBAB)] afforded the corresponding polyfunctional compounds $\mathbf{2}_{a-c}$ - $\mathbf{4}_{a-c}$ respectively. IR and ^{1}H NMR spectra are consistent with their structures. (cf. Scheme I, Table I).



1a, Ar = C_6H_5-
b, = *p*-ClC_6H_4-
c, = *p*-$NO_2C_6H_4$-

X= Cl, Br

2a-c, R= $COOC_2H_5$, R'= $COOC_2H_5$
3a-c, R= H, R'= $COOC_2H_5$
4a-c, R= H, R'=CN

Scheme I

Table I : Analytical and Spectral data of the prepared compounds.

Product No.	React. time (h) React.Temp. °C React. Solvent	M.P.[a] (cryst.Solv.)	Yield %	Mol. Form. . (Mol.wt.)	Analytical Data[b] Cal./ (Found) C	H	N	Cl
2a	8/25 (benzene)	72 (benzene)	95	$C_{17}H_{16}N_2O_4$ (312.31)	65.37 65.02	5.16 5.36	8.96 8.99	
2b	6/55 (benzene)	90-92 (ethanol)	80	$C_{17}H_{15}ClN_2O_4$ (346.76)	58.87 58.95	4.36 4.76	8.07 8.09	10.22 10.00
2c	6/25 (benzene)	108-110 (ethanol)	95	$C_{17}H_{15}N_3O_6$ (357.31)	57.14 57.44	4.23 4.63	11.76 11.79	
3a	4.5/65 (benzene)	90-92 (ethanol)	42	$C_{14}H_{12}N_2O_2$ (240.25)	69.98 69.80	5.03 5.13	11.66 11.68	
3b	4.5/60 (benzene)	110 (benzene)	35	$C_{14}H_{11}ClN_2O_2$ (274.69)	61.21 61.00	4.03 4.23	10.19 10.17	12.95 12.81
3c	3/55 (benzene)	130 (ethanol)	40	$C_{14}H_{11}N_3O_4$ (285.24)	58.94 58.77	3.88 3.70	14.73 14.70	
4a	45/60 (dioxane)	296 (benzene)	40	$C_{12}H_7N_3$ (193.19)	74.60 74.50	3.65 3.41	21.75 21.70	
4b	6/65 (dioxane)	231 (ethanol)	47	$C_{12}H_6ClN_3$ (227.64)	63.31 63.00	2.65 2.90	18.45 18.42	15.57 15.30
4c	5/50 (dioxane)	315 (benzene)	50	$C_{12}H_6N_4O_2$ (238.19)	60.50 60.11	2.53 2.59	23.52 23.72	
5a	6/25 (ethanol)	120 (ethanol)	70	$C_{15}H_{14}N_4O_3$ (298.29)	60.39 60.30	4.73 4.43	18.78 18.98	
5b	3/50 (ethanol)	265 (ethanol)	65	$C_{15}H_{13}ClN_4O_3$ (332.73)	54.14 54.00	3.93 3.70	16.83 16.67	10.65 10.40
5c	4.5/55 (ethanol)	320 (ethanol)	60	$C_{15}H_{13}N_5O_5$ (343.28)	52.47 52.30	3.81 3.65	20.40 20.27	
6b	3/ref. (ethanol)	162 (ethanol)	55	$C_{12}H_9ClN_4O$ (260.67)	55.28 55.00	3.48 3.21	21.49 21.30	13.60 13.45
7b	4/ref. (ethanol)	201 (ethanol)	35	$C_{12}H_{10}ClN_5$ (259.68)	55.49 55.19	3.88 3.65	26.96 26.75	13.65 13.55
8b	4/25 (benzene)	219 (ethanol)	68	$C_{18}H_{18}N_4O_3$ (338.35)	63.89 63.69	5.36 5.50	16.55 16.77	
8c	4/25 (benzene)	295 (dioxane)	75	$C_{18}H_{17}N_5O_5$ (383.35)	56.39 56.00	4.47 4.31	18.26 18.40	
9a	6/25 (benzene)	207 (ethanol)	85	$C_{17}H_{14}N_4O_4$ (338.31)	60.34 60.22	4.17 4.00	16.56 16.45	
9c	6/25 (benzene)	315 (dioxane)	80	$C_{17}H_{13}N_5O_6$ (283.30)	72.06 72.11	4.62 4.90	24.72 24.81	
10a	5/25 (benzene)	221 (benzene)	85	$C_{17}H_{12}N_4O_5$ (352.29)	57.95 57.75	3.43 3.83	15.9 15.66	

Table I (continued)

10c	5/25 (benzene)	341 (benzene)	75	$C_{17}H_{11}N_5O_7$ (397.29)	51.39 51.11	2.79 2.60	17.62 17.45	
11a	3/25 (benzene)	265 (dioxane)	71	$C_{18}H_{12}N_6O_3$ (360.31)	59.99 59.66	3.35 3.30	23.32 23.11	
11c	4/25 (benzene)	305 (ethanol)	75	$C_{18}H_{11}N_7O_5$ (405.31)	53.33 53.00	2.73 2.93	24.19 24.39	
12a	10/ref. (ethanol)	> 350 (ethanol)	35	$C_{16}H_{12}N_4O_3S$ (340.34)	44.65 44.45	2.81 2.70	13.01 13.11	
13a	10/ref. (ethanol)	310 (ethanol)	40	$C_{22}H_{17}N_5O_3$ (393.39)	66.15 66.00	4.29 4.30	17.53 17.70	
14a	4/ref. (ethanol)	> 350 (ethanol)	40	$C_{16}H_{14}N_4O_3$ (310.3)	61.92 61.73	4.54 4.84	18.05 18.30	
15a	2/0-5°C	138 (benzene)	75	$C_{13}H_{11}N_5O_3$ (309.27)	58.25 58.30	3.58 3.67	22.64 22.40	
15b	2/0-5°	195 (ethanol)	75	$C_{15}H_{10}ClN_5O_3$ (343.71)	52.41 52.11	2.93 2.70	20.37 20.57	10.31 10.50
15c	2/0-5°	188 (dioxane)	80	$C_{13}H_{10}N_6O_5$ (354.27)	50.85 50.71	2.84 2.44	23.72 23.89	

a) Uncorrected b) Satisfactory microanalysis obtained C; ± 0.35, H; ±0.40, N; ±0.20

(continued)

Compounds $\mathbf{2}_{a\text{-}c}$, $\mathbf{3}_b$ or $\mathbf{4}_b$ were allowed to react with hydrazine hydrate in equimolar ratio in ethanol at temperatures ranging from 25-70 °C for different periods of time, to give the corresponding pyridinone $\mathbf{5}_{a\text{-}c}$, $\mathbf{6}_b$ or pyridine $\mathbf{7}_b$ derivatives, respectively. The structures of the investigated products $\mathbf{5}_{a\text{-}c}$, $\mathbf{6}_b$ and $\mathbf{7}_b$ were established by IR and ^{1}H-NMR spectra data. (cf. Scheme II, Table I).

1,6-Diamino-4-aryl-5-cyano-3-ethoxycarbonyl-2-pyridinones $\mathbf{5}_{a,c}$ were treated with some reactive dihalo compounds, namely, 1,3-dibromo-propane, chloroacetyl chloride, oxalyl chloride, or dibromomalononitrile in presence of two moles of triethylamine at room temperature to give tetra-

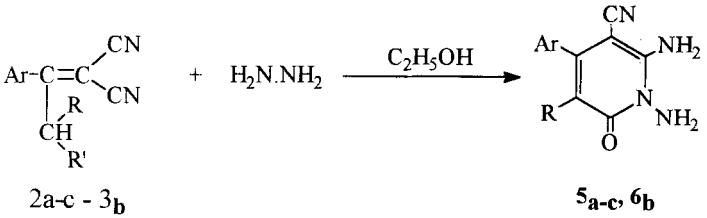
Table I (continued)

Product. No	I.R (cm^{-1})[c]	^1H-NMR[d] (δ ppm)
2_a	2980-2870 (CH_{aliph}), 2240 (C ≡ N), 1745 (C = O).	7.5-7.3 (s, 5H, aromatic), 4.4-4.1 (q, 4H,$2CH_2$), 3.8 (s, 1H, CH), 1.4-1.1 (t, 6H, $2CH_3$).
2_b	2950-2810 (CH_{aliph}), 2220 (C ≡ N), 1745 (C=O).	7.7-7.3 (m, 4H, aromatic), 4.4-4.1 (q, 4H, $2CH_2$), 4.0 (s, 1H, CH), 1.5-1.2 (t, 6H, $2CH_3$).
2_c	2990-2895 (CH_{aliph}), 2250 (C ≡ N), 1741 (C=O).	5-5.9 (m, 4H, aromatic), 3.8-3.5 (q, 4H, $2CH_2$), 3.1 (s, 1H, CH), 1.2 (t, 6H, $2CH_3$).
3_a	2980-2890 (CH_{aliph}), 2195 (C ≡ N), 1740 (C= O),1090 (C-O-C).	7.6-7.3 (m, 5H, aromatic), 4.2-4.0 (q, 2H, CH_2), 3.9 (s, 2H, CH_2 CO), 1.6-1.4 (t, 3H, CH_3).
3_b	2970-2850 (CH_{aliph}), 2189 (C ≡ N), 1755 (C = O), 1110 (C-O-C).	7.5-7.2 (m, 4H, aromatic), 4.4-4.2 (q, 2H, CH_2), 4.1 (s, 2H, CH_2CO), 1.3-1.0 (t, 3H, CH_3).
3_c	2900-2810 (CH_{aliph}), 2190 (C ≡ N), 1741 (C = O) 1090 (C-O-C).	7.1-6.8 (m, 4H, aromatic), 4.4-4.2 (q, 2H, CH_2), 3.8 (s, 2H, CH_2CO), 1.3-1.1 (t, 3H, CH_3).
4_a	2959-2800 (CH_{aliph}), 2191 (C ≡ N).	7.7-7.3 (m, 5H, aromatic), 3.7 (s, 2H, CH_2).
4_b	2950-2900 (CH_{aliph}), 2190 (C ≡ N).	7.8-7.5 (m, 4H, aromatic), 3.6-3.4 (br, 2H, CH_2).
4_c	2950-2910 (CH_{aliph}), 2193 (C ≡ N).	8.7-8.2 (m, 4H, aromatic), 3.3 (s, 2H, CH_2).
5_a	3395,3340,3270,3240($2NH_2$),2970-2810(CH_{aliph}), 2184 (C≡N), 1740 ($C=O_{ester}$) 1677 ($C=O_{amidic}$).	7.7-7.3 (m, 5H, aromatic), 6.2-6.0(br,2H,C-NH_2), 4.3-4.1(m,4H,N-NH_2 + CH_2), 1.3-1.0 (q, 3H, CH_3).
5_b	3368,3340, 3290, 3240 (2 NH_2), 2970 - 2850 (CH_{aliph}), 2189(C ≡ N), 1734 (C=O), 1687 ($C=O_{amidic}$	7.7-7.3(m, 4H,aromatic), 6.3-6.1(br,2H,C-NH_2), 4.6-4.2(m,4H, N-NH_2 + CH_2), 1.6-1.3 (t, 3H, CH_3).
5_c	3368,3340,3296,3245 (2 NH_2), 2975 - 2860(CH_{aliph}) 2187 (C ≡ N), 1737 (C=O), 1675 ($C=O_{amidic}$).	8.4-7.6 (m, 4H, aromatic), 6.2 (s, 2H,C- NH_2), 4.4-4.0 (m, 4H, N-NH_2 + CH_2), 1.3-1.1 (t, 3H, CH_3).
6_b	3390,3340, 3285, 32304 (2 NH_2), 2180 (C ≡ N), 1695 (C=O).	7.7-7.2 (m, 4H, aromatic), 6.2-6.0(s,1H,=CH), 4.4-4.0 (br, 4H, 2 NH_2).
7_b	3340, 3230, 3150 (NH, NH_2), 2190(C ≡ N).	9.2 (s, 1H, NH) , 7.7-7.0 (m, 4H, aromatic), 6.0 (s, 1H, =CH), 4.4-4.0 (br, 4H, $2NH_2$).
8_a	3220,3190 (NH), 2980-2800(CH_{aliph}), 2180 (C ≡ N), 1725 (C = O_{ester}), 1670 (C = O).	9.1 (br, 2H, 2NH), 8-0-7.7 (m, 5H, aromatic) 4.3-4.0 (q, 2H, CH_2), 3.6 -3.7(m, 2H, CH_2), 3.4 - 3.2 (m, 2H, CH_2), 3.0-2.8(m.2H,CH_2), 1.3-1.1 (t, 3H, CH_3).
8_c	3290,3160(NH),2970-2810(CH_{aliph}),2178 (C ≡ N), 1740 (C = O), 1670 (C = O).	9.2 (s, 2H, 2NH), 7-7-6.9 (m, 4H, aromatic), 4.3-4.1 (q, 2H, CH_2), 3.8-3.6 (m, 2H, CH_2), 3.5-3.2 (m, 2H, CH_2),3.0-2.8(m,2H,CH_2),1.3-1.0 (t, 3H, CH_3).
9_a	3283,3170 (NH), 2910 (CH_{aliph}), 2182 (C ≡ N), 1740 (C = O_{ester}), 1675,1666 (C = O).	9.2(s,1H,C-NH). 8.3-7.9 (m, 7H, aromatic+ 2NH), 4.4-4.1 (m, 3H, CH_2 + CH), 4.0 (s, 2H, CH_2 CO), 1.3 - 1.0 (t, 3H, CH_3).
9_c	3290,3160(NH), 2940-2870(CH_{aliph}), 2200 (C ≡ N), 1720 (C = O_{ester}), 1675,1660 (C = O).	9.3(s,1H,C-NH), 8.4-7.7 (m, 4H, aromatic), 6.1(s, 1H, NH), 4.4-4.0 (q, 2H,CH_2), 3.8(s, 2H, CH_2 CO), 1.4 - 1.2 (t, 3H, CH_3).

Table I (continued)

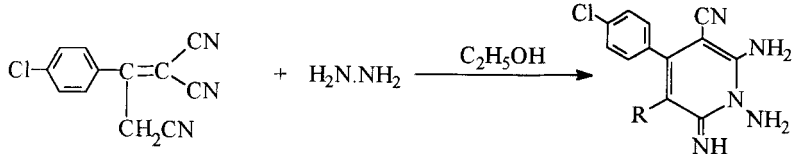
10_a	3280,3170(NH), 2920-2815(Ch_{aliph}), 2180(C ≡ N), 1730 (C = O_{ester}), 1675, 1660 (C = O)	8.5-7.8 (m, 6H, aromatic +2 NH), 4.4-4.1 (m, 2H, CH_2), 1.4 - 1.1 (t, 3H, CH_3).
10_c	3210,3170(NH), 2930-2830(Ch_{aliph}), 2175 (C ≡ N), 1730 (C = O_{ester}), 1676 (C = O).	8.3-7.4 (m, 6H, aromatic +2 NH), 4.3-4.0 (q, 2H, CH_2), 1.3 - 1.0 (t, 3H, CH_3).
11_a	3200,3150 (NH), 2970 - 2820(CH_{aliph}), 2170(C ≡ N), 1725 (C = O_{ester}), 1670 (C = O).	9.0 (s, 1H,C- NH), 8-3-7.5 (m, 6H, aromatic+NH), 4.2-3.9 (m,2H, CH_2),1.3-1.1(t, 3H, CH_3).
11_c	3290,3150 (NH), 2970 - 2810(CH_{aliph}), 2180 (C ≡ N) 1730 (C = O_{ester}), 1680 (C = O).	9.2 (s,1H,C-NH), 8.5-7.8 (m, 6H, aromatic+NH) 4.2-3.9 (q,2H, CH_2),1.3-1.0(t, 3H, CH_3).
12_a	3230,3147 (NH), 2980 - 2810(CH_{aliph}), 2224 (C ≡N 1725 (C = O_{ester}), 1680 (C = O), 1140 (C = S).	7.5-7.0(m,7H,aromatic+2 NH), 4.1-3.9(m,2H,CH_2) 1.7 - 1.3 (t, 3H, CH_3).
13_a	3200,3150 (NH), 2980 - 2820(CH_{aliph}), 2180 (C ≡ N) 1740 (C = O_{ester}), 1680 (C = O).	10.0(s,1H,C- NH), 7.7-7.0 (m, 11H, aromatic+NH) 4.1-3.9 (q, 2H, CH_2), 1.3-1.1 (t, 3H, CH_3).
14_a	3260,3140 (NH), 2850 - 2795(Ch_{aliph}), 2145 (C ≡ N) , 1729 (C = O_{ester}), 1675 (C = O).	7.7-7.2 (m, 6H, aromatic + NH), 4.3-4.0 (q, 2H, CH_2),), 3.2 (s, 2H, N-CH_2), 1.4-1.2 (t, 3H, CH_3).
15_a	3230,3167 (NH), 2980 - 2810 (CH_{aliph}), 2190(C≡N) 1740 (C = O_{ester}), 1690(C = O).	8.2-7.7(m,6H aromatic+ NH), 4.4-4.2 (q, 2H, CH_2), 1.3-1.1 (t, 3H, CH_3).
15_b	3211,3166(NH), 2970-2810(CH_{aliph}),2180 (C≡N), 1739 (C = O_{ester}), 1689(C = O)	7.7-7.0(m, 5H, aromatic+NH), 4.3-4.0 (q, 2H, CH_2) 1.3-1.0 (t, 3H, CH_3).
15_c	3321, 3210 (NH), 2980 - 2800 (CH_{aliph}), 2195(C≡N) 1740 (C = O_{ester}), 1670 (C = O).	8.6-7.5 (m, 4H aromatic),7.0(s,1H,NH), 4.4-4.0 (q, 2H, CH_2), 1.3-1.0 (t, 3H, CH_3).

c) Measured by Nicolet FT-IR 710 spectrophotometer.
d) Measured by a varian EM 360 L spectrometer at 60 MHZ using TMS as internal standard and DMSO as a sovent.



2a-c - 3_b 5_{a-c}, 6_b

5a, Ar= C_6H_5-, R=$COOC_2H_5$
b, Ar=*p*-ClC_6H_4-, R=$COOC_2H_5$
c, Ar=*p*-$NO_2C_6H_4$-, R=$COOC_2H_5$
6_b, Ar=*p*-ClC_6H_4-, R=H



4_b 7_b

Scheme II

hydrotriazepino-pyridinone $\mathbf{8}_{a,c}$, oxotriazino-pyridinone $\mathbf{9}_{a,c}$, dioxotriazino-pyridinone $\mathbf{10}_{a,c}$, or triazolo-pyridinone $\mathbf{11}_{a,c}$, derivatives, respectively. Furthermore thioxotriazolo-pyridinone $\mathbf{12}_{a}$, triazolo-pyridinone derivatives $\mathbf{13}_{a}$ or $\mathbf{14}_{a}$ were obtained through the addition reaction of $\mathbf{5}_{a}$ to CS_2, phenylisothiocyanate or formaldehyde followed by elimination of H_2S or H_2O molecule

Diazotizations of compounds $\mathbf{5}_{a-c}$ using sodium nitrite and a mixture of hydrochloric acid and acetic acid at 0 °C, led to the formation of tetrazolo-pyridinones $\mathbf{15}_{a-c}$ via self coupling with the N-NH_2 group. IR and ^{1}H NMR spectra of products **8-15** are consistent with their structures. (cf. Scheme III, Table I).

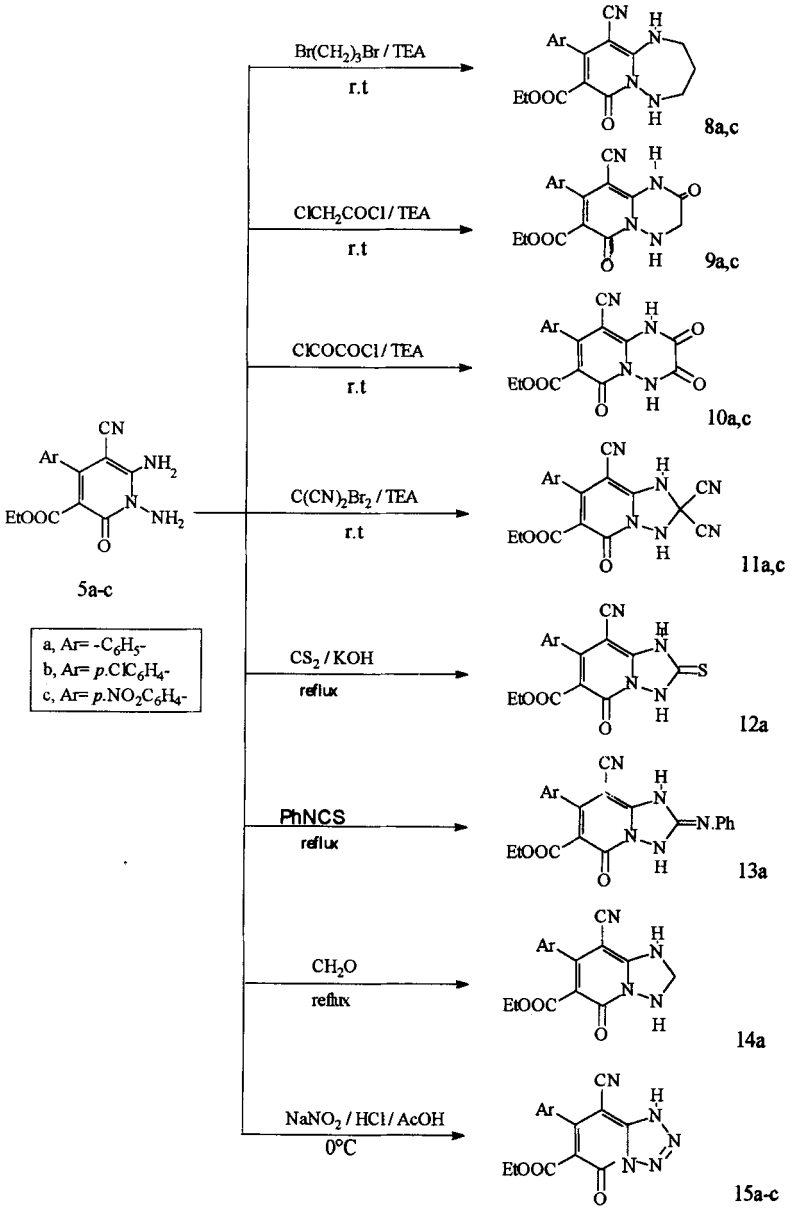
EXPERIMENTAL

The MS were recorded on a Micromass 7070 E spectrometer operating at 70 eV, using direct inlet

Synthesis of compounds 2_{a-c} - 4_{a-c}

General procedure:

To a mixture of anhydrous potassium carbonate (3g), dry benzene or dioxane (40 mL), compounds $\mathbf{1}_{a-c}$ (0.01 mol) and catalytic amount of tetrabutylammonium bromide (TBAB), was added an equimolar amount of diethyl bromomalonate, ethyl chloroacetate or chloroacetonitrile. The reaction mixtures were vigorously stirred over different periods of time at the appropriate temperatures, (cf, Table I), till completion of the reaction (TLC). The reaction mixtures were filtered off and the filterate was washed thoroughly with water, dried over anhydrous $MgSO_4$ and evaporated in



Scheme III

vacuo. The residual solid was crystallized from the appropriate solvent, where compounds $\mathbf{2}_{a-c}$ and $\mathbf{3}_{a-c}$ were obtained.

The solid potassium carbonate was dissolved in distilled water (50 mL). The separated solid was collected by filteration and crystallized from the proper solvent, where compounds $\mathbf{4}_{a-c}$ were obtained. (cf. Table I).

Synthesis of pyridinones 5_{a-c}, 6_b and pyridine derivative 7_b:

An equimolar mixture of compound $\mathbf{2}_{a-c}$, $\mathbf{3}_b$ or $\mathbf{4}_b$ and hydrazine hydrate (0.003 mol) in 30 mL of ethanol was stirred at the appropriate temperature or refluxed till the completion of the reaction (TLC). The reaction mixture was evaporated in vacuo, and the residual solid was crystallized from ethanol (cf. Table I). MS of compound $\mathbf{5}_b$: m/z (relative intensity): 332(4.00),306 (3.56), 303 (36.43), 286 (44.31), 190 (100), 98 (10.20).

Reaction of 1,6-diamino-4-aryl-5-cyano-3-ethoxycarbonyl-2-pyridinones $5_{a,c}$ with dihalo compounds: $8_{a,c}$ -$11_{a,c}$.

To a solution of compound $\mathbf{5}_{a,c}$ (0.025 mol) in 20 mL of dry benzene, a suitable dihalo compound (0.025 mol) and (0.7 mL, 0.05 mol) of triethylamine were added. The reaction mixture was stirred at room temperature (20-35 °C) for 3-6 h, and the solvent was evaporated under reduced pressure The residual solid was washed with water, and crystallized from appropriate solvent (cf. Table I).

Synthesis of thioxotrizolopyridinone derivative 12_a .

A mixture of compound $\mathbf{5}_a$ (1.5 g, 0.005 mol) , carbon disulphide (0.4 mL, 0.005 mol) and potassium hydroxide (0.3 g, 0.005 mol) in 20 mL of

ethanol was refluxed until the evolution of H_2S stopped. The reaction mixture was concentrated, cooled, poured on ice-water and acidified with dil. HCl. The precipitant was collected by filteration and crystallized from ethanol. MS of compound **12**$_a$: m/z (relative intensity) : 340 (8.65), 331 (24.46), 303 (29.43), 210 (44.52), 140 (66), 115 (66.77), 103 (100), 77 (80.8).

Synthesis of compound 13$_a$:

A solution of compound **5**$_a$ (0.6 g, 0.002 mol) and phenyl isothiocyanate (0.24 mL, 0.002 mol) in 10 mL of ethanol was refluxed until the evolution of H_2S finished. The reaction mixture was evaporated in vacuo and the residul solid was crystallized from ethanol. (cf. Table I).

Synthesis of triazolopyridinone derivative 14$_a$:

A mixture of compound **5**$_a$ (1.5 g, 0.005 mol) and 30% formaldehyde solution (1.5 mL) in 15 mL of ethanol was refluxed for 7 h. The reaction mixture was filtered on hot, and the precipitant was washed with water, dried and crystallized from ethanol (cf.Table I). MS of compound **14**$_a$: m/z (relative intensity) : 310 (20.5), 267 (17.27), 212 (100), 194 (19.3), 141 (63.8), 105 (17.92).

Diazotization of compounds 5$_{a-c}$: Compounds 15$_{a-c}$:

A solution of compound **5**$_{a-c}$ (0.003 mol) in a mixture of acetic acid (5 mL) and hydrochloric acid (10 mL) was cooled to 0-2° C. A cooled solution of sodium nitrite (0.25 g) in water (2 mL) was added dropwise at 0-5 °C with stirring. The reaction mixture was kept overnight at room

temperature. The separated solid was collected by filteration and crystallized from ethanol (cf. Table 1).

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