New Route Synthesis of Some Quinolin-2-one Derivatives

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New synthesis of some quinoline derivatives was achieved through the fusion of ylidenecyanoacetates with aminoarene in the presence of sulfuric acid as catalyst.

Polyfunctionally substituted heteroaromatics are biologically interesting molecules and their chemistry has received considerable recent attention [1—3]. These new heterocycles were required as potential biodegradable agrochemicals [4—8]. Reactions of 6-arylamino-7-bromoquinoline-5,8-dione with butylamine, sodium methoxide and phenoxide have been studied [9]. An *o*-substituted aryl group in this class of compounds renders the arylamino residue noncoplanar to the quinone ring. Arylidenemalononitrile reacts with phenols, naphthols, and active methylene azoles forming benzopyrans [4, 6], pyranoazoles [8], and pyrano[3,2-*c*]quinoline [10]. Also the behaviour of thiophenol, 2-sulfanylphenol, naphthols, and aminopyrazoles toward ylidenemalononitrile yields 1:2 mole ratio adducts [11]. In conjunction with that work, results of the investigation on the behaviour of aminoarene derivatives toward arylidenecyanoacetates and methylenecyanoacetates are here reported. It was found that ylidenecyanoacetates *Ia*—*Ic* reacted by fusion with aminoaryl to yield quinoline derivatives. Thus, equimolar amounts of 2-aminoanthraquinone with acrylonitrile (0.01 mol) in the presence of 1 cm^3 of concentrated sulfuric acid yielded the corresponding quinoline derivatives *IIIa*—*IIIc*. These compounds were assumed to be formed *via* addition of 2-aminoanthraquinone to acrylonitriles (*Ia*—*Ic*) yielding intermediate (zwitterions) *IIa*—*IIc* that cyclized and hydrolyzed under the reaction conditions into the final products. The structures of the new compounds were confirmed by microanalysis data, mass spectra, infrared and ^{1}H NMR spectra (*cf.* Tables 1 and 2).

Compounds *IVa*—*IVc* were also obtained by fusion of equimolar amounts of anthranilic acid with acrylonitrile derivatives *Ia*—*Ic* in the presence of concentrated sulfuric acid.

m-Phenylenediamine, *p*-aminoaniline, *p*-bromoaniline, and *p*-nitroaniline reacted similarly with *Ia*—*Ic* in the presence of concentrated sulfuric acid to yield quinoline derivatives (*Va*—*Vc*—*VIIIa*—*VIIIc*).

The quinoline derivatives are highly coloured compounds and their ethanolic solutions exhibited deep colours accompanied with green fluorescence.

So, the electronic absorption spectra of quinoline derivatives (*IIIa*—*IIIc, VIIIa*—*VIIIc*) in 95 % ethanol exhibited absorption bands due to the type of substituents present in the molecules. In this connection it has to be pointed out that the auxochromic groups of oxygen and nitrogen atoms cause remarkable high absorptivity. This may be attributed to the partial mixing of the lone pair orbitals of oxygen or nitrogen with the π-system of the heterocyclic ring leading to a modified set of energy levels and this moves the bands intensity to high absorptivity. As a representative example, it is clear that the spectra of the compound *Vc* are characterized by two absorption bands at 385 nm and 465 nm, which can be assigned to an intramolecular charge-transfer transitions [12, 13]. This charge transfer inside the molecule is shown in Scheme 1.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were recorded on a Perkin— Elmer 1650 FT-IR spectrometer, ^{1}H NMR spectra on an EM-390 90 MHz NMR spectrometer, and mass spectra on an instrument Ms 5988. Analytical data were determined with a CE 440 Elemental Analyzer-Automatic Injector at the Cairo University, Egypt.

(1*H*)-Quinolin-2-one Derivatives (*IIIa*—*IIIc*, *IVa*—*IVc*, *Va*—*Vc*, *VIa*—*VIc*, *VIIa*—*VIIc*, *VIIIa*—*VIIIc*)

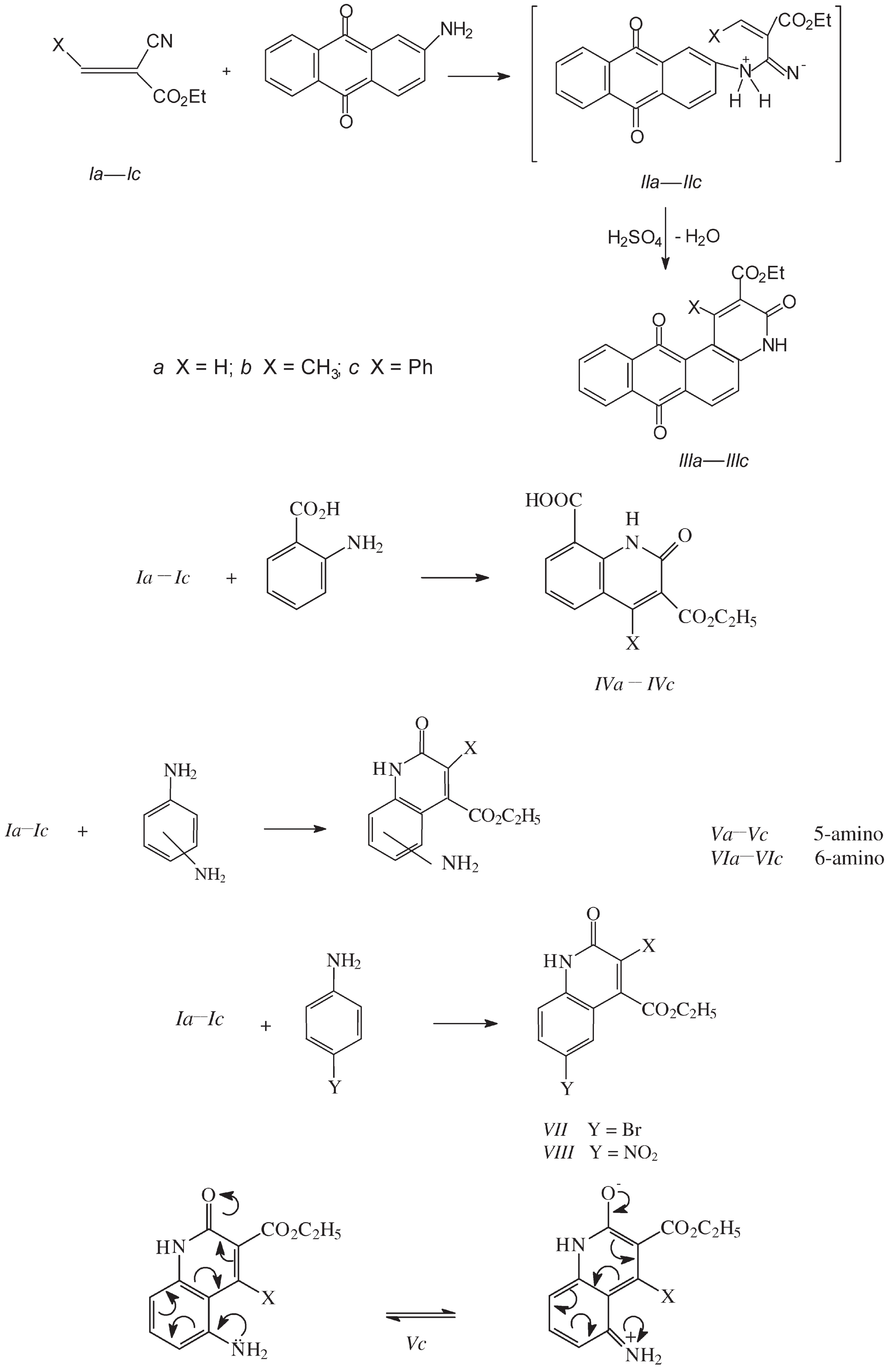
Aromatic amines (0.01 mol) and cyanoacetates *Ia*—*Ic* (0.01 mol) were heated at 150 ℃ in sand bath with 1 cm^3 of concentrated sulfuric acid for 15 min. The mixture was allowed to cool at room temperature. The isolated solid product so formed was washed with water and crystallized from ethanol.

Table 1. Characterization of the Synthesized Compounds

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%			Yield	M.p.	Mass spectra m/z
			C	H	N	%	°C	
IIIa	$C_{20}H_{13}NO_5$	347	69.16 69.15	3.75 3.75	4.03 4.01	47	213—215	347
IIIb	$C_{21}H_{15}NO_5$	361	69.81 69.81	4.15 4.16	3.88 3.91	46	242—245	361
IIIc	$C_{26}H_{17}NO_5$	423	73.76 73.74	4.02 4.00	3.31 3.29	47	189—192	422
IVa	$C_{13}H_{11}NO_5$	361	59.77 59.77	4.21 4.21	5.36 5.38	30	227—230	360
IVb	$C_{14}H_{13}NO_5$	275	61.09 61.08	4.73 4.75	5.09 4.98	17	>300	276
IVc	$C_{19}H_{15}NO_5$	337	67.65 67.71	4.45 4.48	4.15 4.13	35.5	217—220	337
Va	$C_{12}H_{12}N_2O_3$	232	62.07 62.08	5.17 5.16	12.07 12.07	10	>300	231
Vb	$C_{13}H_{14}N_2O_3$	246	63.41 63.40	5.69 5.68	11.38 11.40	14	>300	247
Vc	$C_{18}H_{16}N_2O_3$	308	70.13 70.14	5.19 5.21	9.09 8.97	26	132—135	307
VIa	$C_{12}H_{12}N_2O_3$	232	62.07 62.03	5.17 5.16	12.07 12.05	14	>300	233
VIb	$C_{13}H_{14}N_2O_3$	246	63.41 63.44	5.69 5.68	11.38 11.35	16	>300	246
VIc	$C_{18}H_{16}N_2O_3$	308	70.13 70.10	5.19 5.17	9.09 8.97	24	>300	308
VIIa	$C_{12}H_{10}NO_3Br$	396	36.36 36.35	2.52 2.47	3.53 3.58	15	187—190	296
VIIb	$C_{13}H_{12}NO_3Br$	310	50.32 50.34	3.87 3.87	4.52 4.49	19	135—138	309
VIIc	$C_{18}H_{14}NO_3Br$	372	58.06 58.04	3.76 3.76	3.76 3.76	19	172—175	373
VIIIa	$C_{12}H_{10}N_2O_5$	262	54.96 54.79	3.82 3.82	10.69 10.66	12	149—151	261
VIIIb	$C_{13}H_{12}N_2O_5$	276	56.52 56.49	4.34 4.34	10.14 10.16	32	>300	276
VIIIc	$C_{18}H_{14}N_2O_5$	338	63.91 63.93	4.14 4.13	8.28 8.32	12	287—290	339

Table 2. Selected IR and ^{1}H NMR Spectral Data for the Synthesized Compounds

Compound	IR, $\tilde{\nu}$/cm^{-1}	^{1}H NMR, δ
IIIa—IIIc	1600 (C=C or C=N), 1750 (C=O)	6—8 (m, 7H, H_{arom}), 1.8 (q, 2H, CH_2), 1.2 (t, 3H_3, CH_3)
IVa—IVc	1600 (C=C), 1700 (C=O)	6—8 (m, 5H, H_{arom}), 1.8 (q, 2H, CH_2), 1.4 (t, 3H, CH_3), 1.2 (s, 1H, COOH)
Va—Vc, *VIa—VIc,* *VIIa—VIIc,* *VIIIa—VIIIc*	1600 (C=C or C=N), 1760 (C=O)	6—8 (m, 4H, H_{arom}), 3.8 (br, 2H, NH_2), 1.8 (q, 2H, CH_2), 1.2 (t, 3H, CH_3); 6—8 (m, 3H, H_{arom}), 3.8 (br, 2H, NH_2), 1.8 (q, 2H, CH_2), 1.2 (t, 3H, CH_3); 6—8 (m, 8H, H_{arom}), 3.8 (br, 2H, NH_2), 1.8 (q, 2H, CH_2), 1.2 (t, 3H, CH_3); 6—8 (m, 6H, H_{arom}), 3.8 (br, 2H, NH_2), 1.8 (q, 2H, CH_2), 1.2 (t, 3H, CH_3)


X
CN
CO2Et
NH2
Ia—Ic
IIa—IIc
H2SO4 - H2O
NH
IIIa—IIIc
a X = H; b X = CH3; c X = Ph
CO2H
HOOC
CO2C2H5
IVa—IVc
Ia—Ic
Va—Vc 5-amino
VIa—VIc 6-amino
Y
VII Y = Br
VIII Y = NO2
HN
Vc

Scheme 1

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