Reaction of Imines with Naphthoquinones and 2-(Dicyanomethylene)-1,3-indandione

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Benzylideneanilines react with 2,3-dichloro-1,4-naphthoquinone and 2,3-dicyano-1,4-naphthoquinone to give 2-arylamino-3-chloro-1,4-naphthoquinones and 2-arylamino-3-cyano-1,4-naphthoquinones respectively together with the corresponding aldehydes. Similarly benzylideneanilines react with 2-(dicyanomethylene)-1,3-indandione to give 2-arylamino-2-(1,3-dioxo-2-indanylidene)acetonitriles.

In our previous work[1)] we reported that 4-dimethylaminobenzylideneanilines react with 2,3,5,6-tetrahalo-*p*-benzoquinones via a charge transfer complex formation followed by a chemical reaction to afford 2-arylamino-3,5,6-trihalo-*p*-benzoquinones as well as 2,5-bis(arylamino)-3,6-dihalo-*p*-benzoquinones together with the corresponding 4-dimethylaminobenzaldehyde.

Early it has been reported that imines react with alkyl halides to give a quaternary immonium salt which is converted to a secondary amine upon hydrolysis.[2)] The alkylation is usually applied to the synthesis of secondary amines, and this method is known as "Decker alkylation method".

In the present investigation we studied the behavior of benzylideneanilines **1a**—**h** towards 2,3-dichloro-1,4-naphthoquinone (DClNQ, **2a**) and 2,3-dicyano-1,4-naphthoquinone (DCNQ, **2b**) in addition to 2-(dicyanomethylene)-1,3-indandione (CNIND, **7**).

Addition of DClNQ **2a** to benzylideneanilines **1c**—**f** (1 : 1) in ethyl acetate afforded 2-arylamino-3-chloro-1,4-naphthoquinones **5a,b** together with the corresponding aldehydes **6a,b** (Scheme 1). The IR spectra of **5a,b** showed characteristic absorptions for the secondary amino group between ν=3240 and 3200 and for the carbonyl between ν=1675 and 1670 cm^{-1}. ^{1}H NMR showed chemical schifts between δ=9.25 and 9.27 for NH group. The mass spectra exhibited the correct molecular ion peaks.

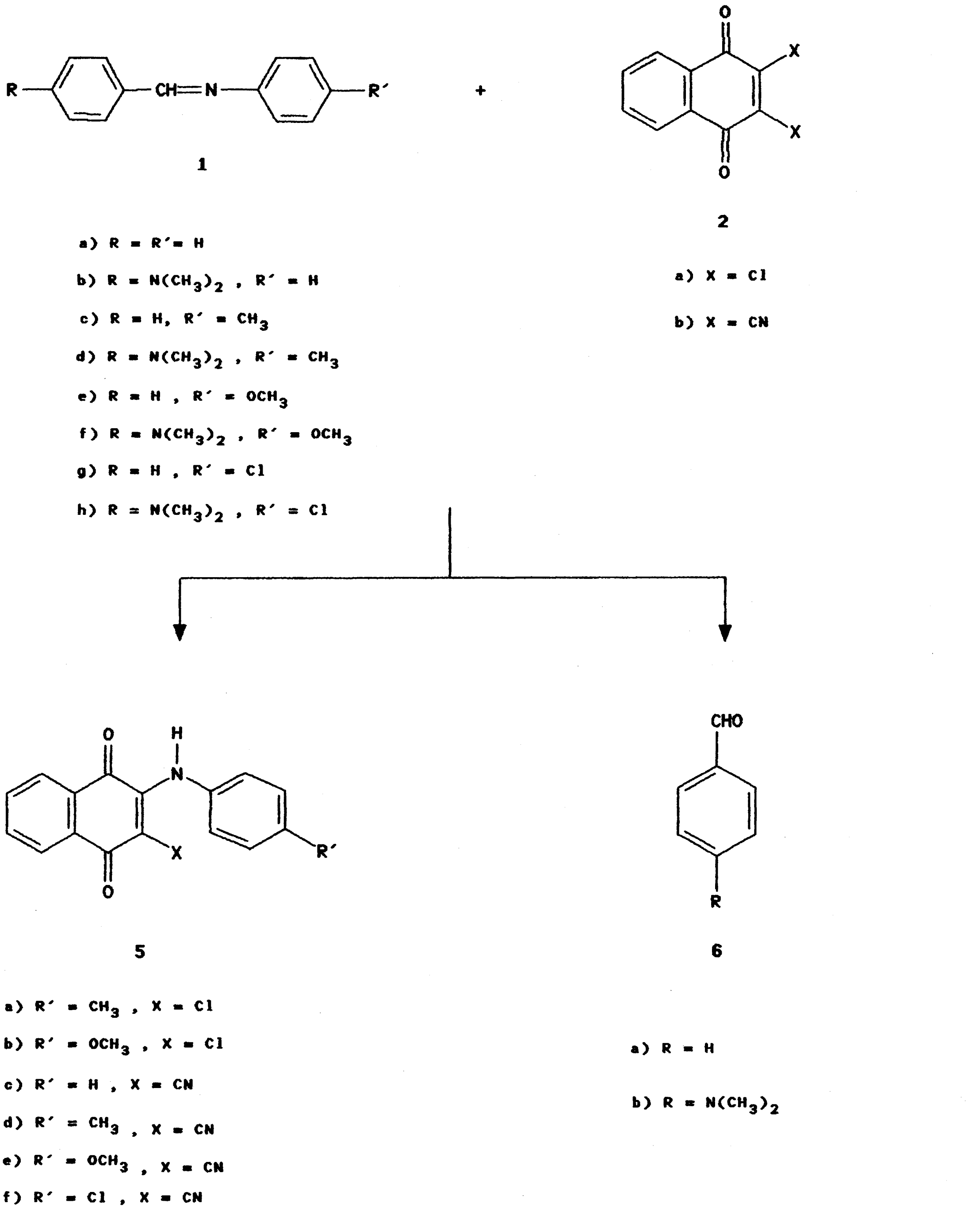
Formation of **5a,b** and **6a,b** can be rationalized as a nucleophilic attack by the imino nitrogen atom on C-2 of **2** leading to the formation of **3** which turns into immonium cation **4** which undergoes hydrolysis by taking up a molecule of water from atmosphere to afford **5** and **6**. The reaction resembles Decker alkylation method where **2** reacts like the alkyl halide RX as electrophile. In our reaction the difference is that the hydrolysis takes place spontaneously by absorption of water from atmosphere. This indicates that the intermediate **4** is relatively unstable and sensitive to moisture compared to the immonium cation of the alkyl halide. Hydrolysis of the benzylideneanilines (which should generate the aldehyde and the free amine ArNH$_2$ which in turn attack the quinone) prior to reaction with the quinone is considered unlikely, because there is no change in the benzylideneanilines under the similar conditions where a *p*-naphthoquinone is abscent.

It might be expected that the reaction between benzylideneanilines **1c**—**f** and **2a** proceeded via the nucleophilic attack mechanism rather than the charge transfer mechanism.[1)] This may be attributed to the higher electron affinity of 2,3,5,6-tetrachloro-*p*-benzoquinone than of **2a** (Scheme 2).[3)]

Benzylideneanilines **1a**—**h** reacted similarly with 2,3-dicyano-1,4-naphthoquinone (**2b**) but more rapidly (from ten minutes to one hour) than with **2a** (24 h) at room temperature. The higher reactivity of **2b** is ascribed to the cyano group is better leaving group in the *p*-naphthoquinones than the chloride anion, where naphthoquinones may be considered as vinyl analogues, so in comparison of **2a** with the vinyl chloride, it is known that the chlorine atom is unreactive towards substitution. This is due to resonance through which the C–Cl bond acquires some double bond characters, and thereby the chlorine atom will be more strongly bonded to carbon atom.

The reaction of **1a**—**h** with DCNQ **2b** afforded 2-arylamino-3-cyanonaphthoquinones **5c**—**f** and the corresponding aldehydes **6a,b**. The IR spectra showed characteristic absorptions for the secondary amino group between ν=3210 and 3150 and for the carbonyl group between ν=1695 and 1675 cm^{-1}. The mass spectra exhibited the correct molecular ion peaks.

Rationalization of the formation of these products is probably the same as described above with DClNQ **2a** i.e. by a nucleophilic substitution mechanism (see Scheme 2).

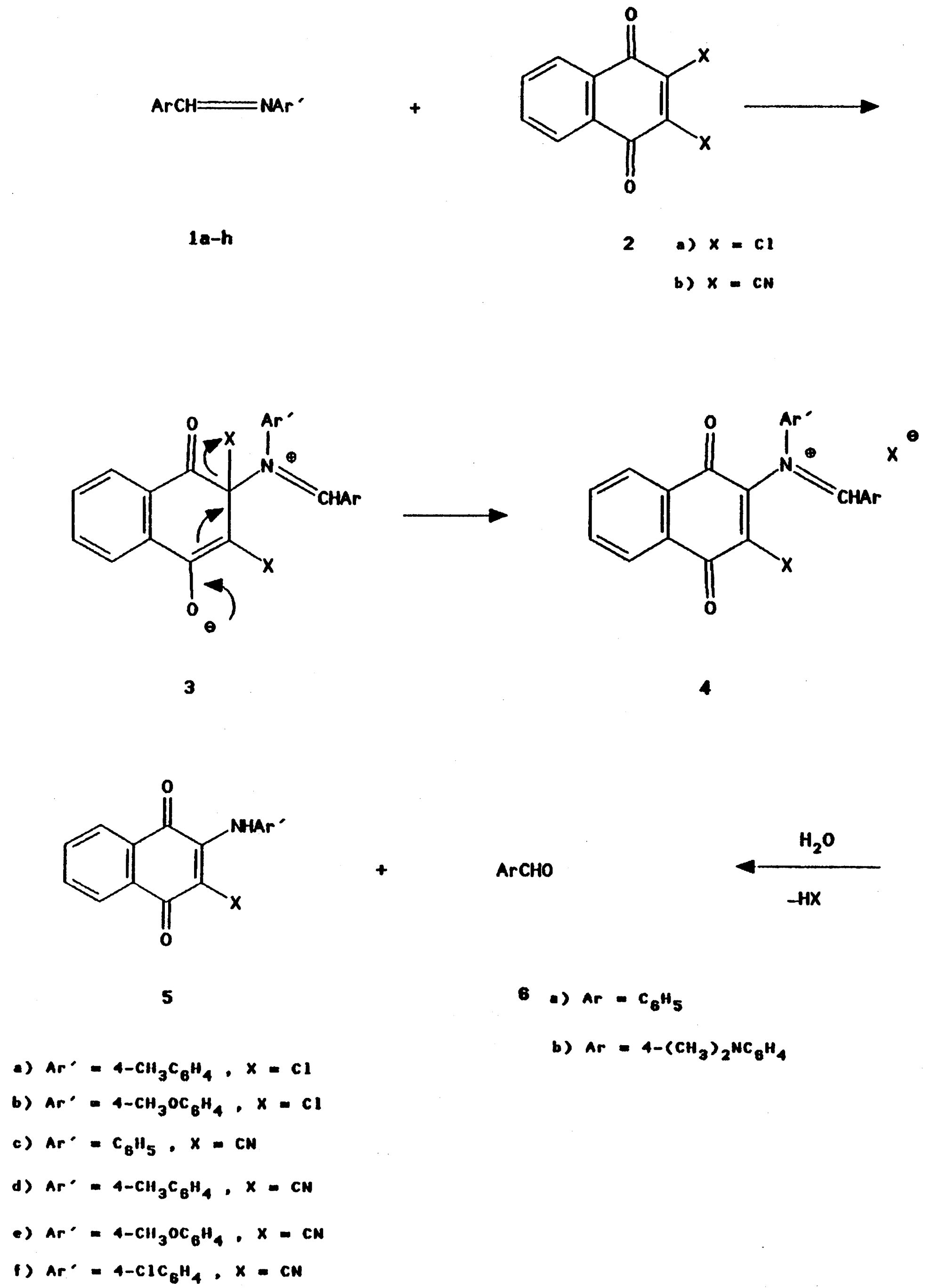


Scheme 1.

On the other hand the possibility existed that 2-(dicyanomethylene)-1,3-indandione (**7**) in the presence of electron donors **1** underwent an electron transfer mediated rearrangement to the 2,3-dicyano-1,4-naphthoquinone (**2b**.)[4] Consequently it worths to investigate the behavior of the benzylideneanilines **1a**—**h** towards **7**.

Addition of CNIND **7** to benzylideneanilines **1a**—**f** (1:1) in ethyl acetate led to the formation of 2-arylamino-2-(1,3-dioxo-2-indanylidene)acetonitriles **10a**—**c** together with the corresponding aldehydes **6a**, **b** (Scheme 3). The structure of **10a**—**c** were identified by comparison of their melting points with those reported in literature.[5,6] Aldehydes were identified either by comparing their melting points or their R_f values with the authentic samples.

These results indicate that benzylideneanilines **1a**—**f** react like amines[5] with CNIND **7** by a Michael addition –elimination mechanism through a nucleophilic attack of the imino nitrogen atom on the double bond of **7**. Where the four electron-withdrawing groups (two nitriles and two carbonyl groups) facilitate the reaction to form the intermediate **8** and **9**. The intermediate **9** undergoes an elimination of HCN followed by hydrolysis to form **10a**—**c** and **6a,b**. This result shows that there



Scheme 2.

is no an electron transfer rearrangement of **7** to the 2,3-dicyano-1,4-naphthoquinone **2b**.

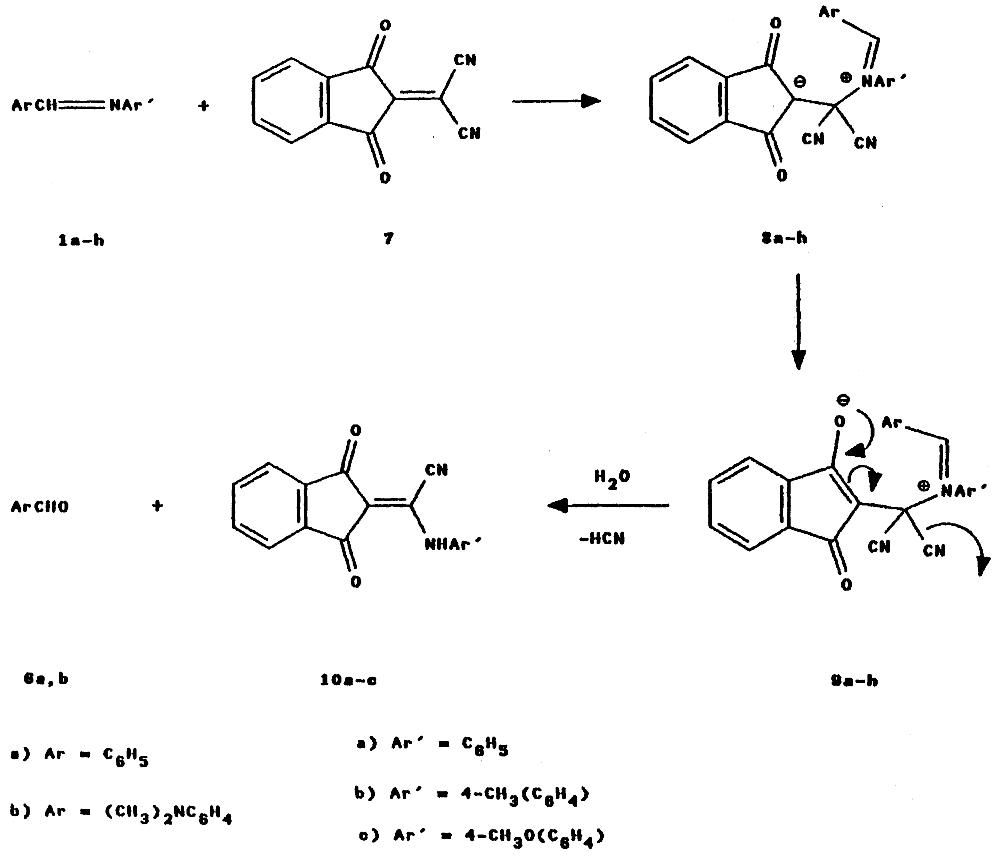
Conclusion

Aldimines showed a remarkable reactivity towards electron poor compounds through their active center, the imino nitrogen atom, which is responsible for all these reactions by the sp^2 lone pair of electrons. Thus azomethines can be used as an arylamination agent to prepare arylamino-1,4-naphthoquinones and 2-arylamino-2-(1,3-dioxo-2-indanylidene)acetonitriles.

Experimental

The melting points were determined on a Griffin Georg melting point apparatus and are uncorrected. IR spectra were obtained on a Shimadzu 470 spectrophotometer. ^{1}H NMR spectra were measured with a Bruker WP 80 spectrometer (80 MHz); chemical schifts are expressed in ppm values (δ) using Me_4Si as an internal standard. The MS spectra were recorded on MAT 311A spectrometer in connection with an AMD Dp-10 data processing system at 70 eV. Elemental analyses were performed by a Carlo ERBA strumentazione elemental analyzer Model 1106.

Preparative Layer Chromatography (PLC): Air



Scheme 3.

dried 1.0 mm thick layers of slurry applied silica gel Merck *P*f 254 on 480 cm wide and 20 cm high glass plates were employed using the solvents listed. Zones were detected by quenching upon exposure to 254 nm light and eluted with acetone.

Starting Materials: 2,3-Dichloro-1,4-naphthoquinone (**2a**) (Aldrich) was used as received, 2,3-dicyano-1,4-naphthoquinone[7] (**2b**), 2-(dicyanomethylene)-1,3-indandione[8] (**7**), and benzylideneanilines[9] were prepared according to literature procedures.

Reaction of 1c—f with DClNQ 2a. A solution of **2a** (1.0 mmol) in 20 ml of dry ethyl acetate was added dropwise to a solution of the imine **1c**—**f** (1.0 mmol) in dry of ethyl acetate under reflux for 24 h. The reaction mixture became red. Precipitates were collected by filtration and washed several times with cold ethyl acetate and identified as the unchanged starting materials. The filtrate was concentrated in vacuo and the residue was separated by PLC using toluene/ethyl acetate (10 : 1) into two zones. The upper zone contained the aldehydes **6a,b** and the lower contained compounds **5a,b**.

2-Chloro-3-(4-methylphenyl)amino-1,4-naphthoquinone (5a). This compound (59 mg (20%) and 74 mg (25%) from **1c** and **1d**, respectively) was obtained as red crystals (cyclohexane). Mp 184—185 °C; IR (KBr) 3240 (NH), 1670 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) $\delta=2.27$ (s, 3H, CH$_3$), 7.0—7.14 (m, 4H, Ar-H), 7.80—8.06 (m, 4H, Ar-H), 9.27 (s, 1H, NH); MS *m*/*z* (%) 297 (M$^+$; 5), 262 (5), 226 (80), 76 (35).

2-Chloro 3-(4-methoxyphenyl)amino-1,4-naphthoquinone (5b). This compound (47 mg (15%) and 56 mg (18%) from **1e** and **1f**, respectively) was obtained as red crystals (cyclohexane). Mp 168—170 °C; IR (KBr) 3200 (NH), 1675 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) $\delta=3.76$ (s, 3H, CH$_3$O), 6.86—8.0 (m, 8H, Ar-H), 9.24 (s, 1H, NH); MS *m*/*z* (%) 313 (M$^+$; 100), 298 (50), 278 (21), 92 (7), 76 (11). Found: C, 64.83; H, 4.12; N, 4.67%. Calcd for $C_{17}H_{12}ClNO_3$: C, 65.07; H, 3.85; N, 4.96%.

Reaction of 2,3-Dicyano-1,4-naphthoquinone DCNQ (2b) with Imines 1a—h. A solution of **2b** (0.5 mmol) in 10 ml of dry ethyl acetate was added to a solution of the imine **1a**—**h** (0.5 mmol) in 5 ml of dry ethyl acetate, the mixture was left at room temperature for one hour, then concentrated in vacuo and the residue was subjected to PLC using toluene/ethyl acetate (10 : 1) as developing solvent to give two zones, the upper contained the aldehyde **6a,b** and the lower contained **5c**—**f**.

2-Anilino-3-cyano-1,4-naphthoquinone (5c).[10] This compound (52 mg (19%) and 142 mg (51%) from **1a** and **1b**, respectively) was obtained as orange crystals (ethanol). Mp 230—234 °C (Lit, 238—239 °C); IR 3200 (NH), 1695 cm^{-1} (C=O).

2-Cyano-3-(4-methylphenyl)amino-1,4-naphthoquinone (5d). This compound (103 mg (36%) and 120 mg (44%) from **1c** and **1d**, respectively) was obtained as red crystals (ethanol). Mp 234—235 °C; IR 3210 (NH), 1675 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) $\delta=2.37$ (s, 3H, CH$_3$), 7.37 (d, 4H, Ar-H), 7.9—8.4 (m, 4H, Ar-H), 10.52 (s, 1H, NH); MS *m*/*z* (%) 288 (M$^+$; 100), 273 (25), 259 (12), 91 (10). Found: C, 74.66; H, 4.24; N, 9.55%. Calcd for $C_{18}H_{12}N_2O_2$: C, 74.98; H, 4.10; N, 9.72%.

2-Cyano-3-(4-methoxyphenyl)amino-1,4-naphtho-

quinone (5e). This compound (100 mg (33%) and 120 mg (40%) from **1e** and **1f**, respectively) was obtained as brownish orange crystals (ethanol). Mp 219—221 °C; IR 3210 (NH), 1695 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=3.78 (s, 3H, CH$_3$O), 6.8—7.3 (m, 4H, Ar-H), 7.8—8.0 (m, 4H, Ar-H), 10.52 (s, 1H, NH); MS m/z (%) 304 (M$^+$; 100), 289 (40), 261 (8), 93 (5). Found: C, 70.93; H, 4.00; N, 9.13%. Calcd for $C_{18}H_{12}N_2O_3$: C, 70.63; H, 3.95; N, 9.15%.

2-(4-Chlorophenyl)amino-3-cyano-1,4-naphthoquinone (5f). This compound (124 mg (40%) and 150 mg (49%) from **1g** and **1h**, respectively) was obtained as red crystals (ethanol). Mp 253—254 °C; IR 3150 (NH), 1695 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=7.4—7.5 (m, 4H, Ar-H), 7.9—8.2 (m, 4H, Ar-H), 10.6 (s, 1H, NH); MS m/z (%) 308 (M$^+$; 100), 288 (18), 273 (43), 76 (17). Found: C, 66.29; H, 3.06; N, 9.02%. Calcd for $C_{18}H_9N_2ClO_2$: C, 65.91; H, 2.92; N, 9.05%.

Reaction of 2-(Dicyanomethylene)-1,3-indandione (7) with Imines 1a—h. A solution of CNIND **7** (1.0 mmol) in 30 ml of dry ethyl acetate was added dropwise to a solution of the azomethine **1a**—**h** (1.0 mmol) in 10 ml of dry ethyl acetate at room temperature whereby the reaction became yellowish brown. The reaction was left standing for one hour and filtered. The precipitates were collected by filtration and washed several times with cold ethyl acetate, and identified as **10a**—**c**. The filtrate was concentrated and subjected to PLC using toluene/ethyl acetate (10 : 1) as developing solvent, to give two zones, the upper zone contained **6a,b** and the lower contained the soluble part of **10a**—**c**. The zones were extracted recrystallized and identified.

2-Anilino-2-(1,3-dioxo-2-indanylidene)acetonitrile[5,6] **(10a).** This compound (132 mg (48%) and 172 mg (62%) from **1a** and **1b**, respectively) was obtained as yellow crystals (ethanol). Mp 216—218 °C; IR 1690 and 1650 cm^{-1} (C=O).

2-(4-Methylanilino)-2-(1,3-dioxo-2-indanylidene)-acetonitrile[6] **(10b).** This compound (177 mg (61%) and 139 mg (48%) from **1c** and **1d**, respectively) was obtained as yellow crystals (ethanol). Mp 208—210 °C; IR 1695 and 1645 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=2.39 (s, 3H, CH$_3$), several multiplets at 7.2, 7.3, 7.7 and 7.9 (8H, Ar-H), 11.5 (s, 1H, NH); MS m/z (%) 288 (M$^+$; 100), 273 (19), 261 (62), 91 (13).

2-(4-Methoxyanilino)-2-(1,3-dioxo-2-indanylidene)acetonitrile[5] **(10c).** This compound (182 mg (60%) and 221 mg (72%) from **1e** and **1f**, respectively) was obtained as orange crystals (ethanol). Mp 203—207 °C; IR 1705 and 1650 cm^{-1} (C=O).

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