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Aryliodonium Derivatives of 2-Amino-1,4-quinones : Preparation and Reactivity

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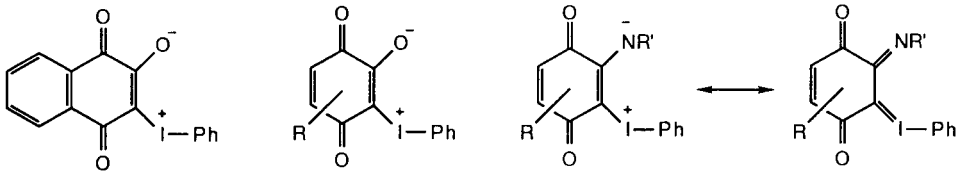
Abstract. The reaction of 2-amino-1,4-quinones with [(hydroxy)(tosyloxy)iodo]arenes affords stable 2-amino-3-aryliodonio-1,4-quinones in high yields. The latter, upon treatment with alkali, are converted to the corresponding zwitterionic 3-aryliodonio-1,4-quinone-2-imides. This new class of compounds exhibits an interesting reactivity: upon heating, aryl migration from iodine to nitrogen is observed, while photochemical reaction with aromatic compounds and 2,3-dihydrofuran leads to substitution products. Nucleophilic attack of sodium alkoxides on these zwitterions results in opening of the quinone ring affording synthetically interesting multifunctional products.

Introduction

The chemistry of organic polyvalent iodine compounds has lately witnessed a great expansion which continues at a steady pace. After publication of a book on the subject,[1] several reviews dealing with various aspects of hypervalent iodine chemistry have recently appeared in the literature,[2] as well as another book.[3] The term zwitterionic iodonium compounds includes several members of considerable diversity in which iodine is linked to two ligands and bears a positive charge compensated by a negative charge within the molecule. These compounds can be classified as 1,2-dipoles (ylides), 1,3-,etc. up to 1,7-dipoles, depending on the position of the formal negative charge relatively to iodine.[1]

Aryliodonium 1,4-dipoles are usually phenolates resulting from phenols bearing electron withdrawing substituents,[4] 1,3-dihydroxybenzene and naphthalene derivatives[5] as well as hydroxy quinolines;[6] all of them exhibit an interesting reactivity pattern.

In the past we reported the preparation and reactivity of the phenyliodonium dipole **1** resulting from 2-hydroxy-1,4-naphthoquinone (lawsone)[7] and recently we extended our studies[8] to the oxido-1,4-benzoquinone analogues, **2**.



1 2 3a 3b

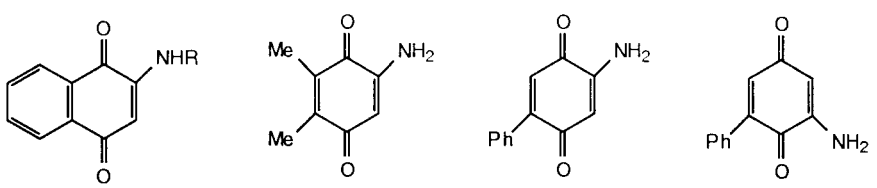
The combination of phenyliodonium and oxoquinone moieties offers some interesting synthetic possibilities regarding substitution, cycloaddition and ring contraction reactions. This diverse reactivity of dipoles **1** and **2** prompted us to investigate the possibility of preparing the corresponding iodine-nitrogen 1,4-dipoles **3** and their naphtho-analogues by replacing the hydroxy group with an amino group.

There are a few examples of 1,4 iodine-nitrogen dipoles in the literature including the relatively unstable phenyliodonium compounds derived from indole[9] and 3-amino-5,5-dimethyl-cyclohex-2-enone[10] and also a delocalised phenyliodonium dipole from imidazolo[1,2-a]pyrimidine-5(1*H*)-one.[11] Recently, we reported the preparation of the stable 3-phenyliodonium dipole of 4-amino-coumarin.[12]

The first experiments with 2-amino-1,4-naphthoquinone were successful, as we reported in a preliminary communication;[13] in this paper we describe the preparation and reactivity of this new class of iodine-nitrogen dipoles, i.e. 3-aryliodonio-1,4-quinone-2-imides. In order to avoid writing localised dipole structures, the double bond notation (e.g. **3b**) for all such compounds has been adopted in this paper.

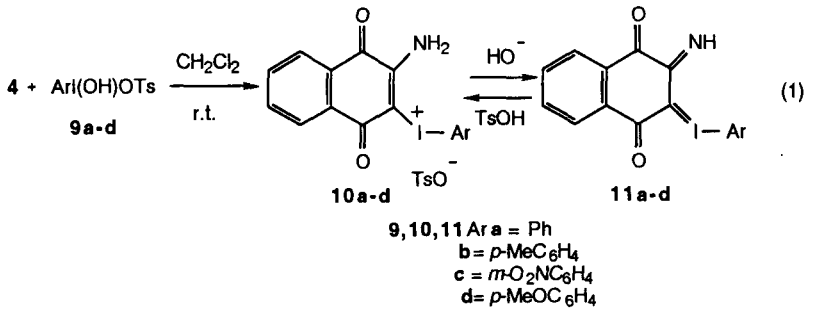
Results and Discussion

Preparation of 2-amino-1,4-quinones. The starting amino-1,4-naphthoquinones **4** and **5**- and amino-1,4-benzoquinones **6**, **7**, **8**, were prepared by standard methods (see experimental).



4 R = H, **5** R = Ph **6** **7** **8**

Preparation of aryliodonium derivatives. The reaction of naphthoquinone **4** with [(hydroxy)(tosyloxy)iodo]arenes **9** gave readily the iodonium salts **10** in high yield (80-97%)(eq 1).

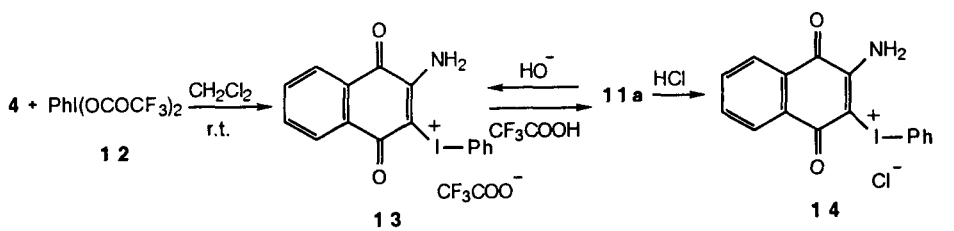


(1)

It must be noted that compounds **9** were prepared by reaction of the corresponding (diacetoxyiodo)arenes with *p*-toluenesulfonic acid, according to literature methods[14] and were reasonably stable, with the exception of the *p*-methoxy derivative **9d** The latter, when dry, decomposed violently in our hands and could not be characterized. It was used for the reaction with **4** in crude form.

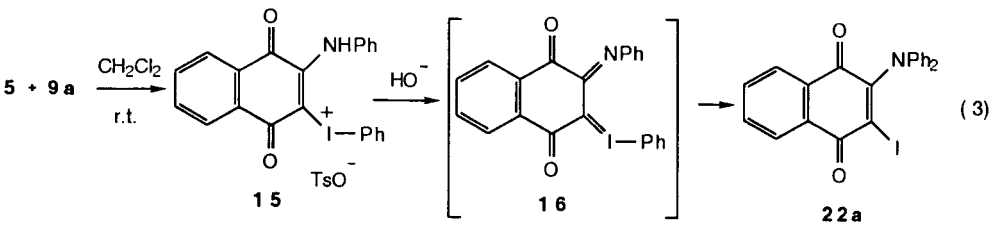
Iodonium salts **10**, were fully characterized by their spectroscopic data; upon treatment with dilute alkali, they were converted into the corresponding stable zwitterions **11** in good yield (65-80%). The reaction is reversible and the zwitterions **11** afforded again the initial iodonium salts **10** upon the addition of *p*-toluenesulfonic acid. Compounds **11** are microcrystalline solids that can be stored in the refrigerator for long periods without decomposition.

Another hypervalent iodine reagent, [bis(trifluoroacetoxy)iodo]benzene **12**, on reaction with **4** gave the corresponding trifluoroacetate **13**, which was converted to zwitterion **11a**. The latter was transformed to the chloride **14** when treated with aqueous HCl (eq 2).



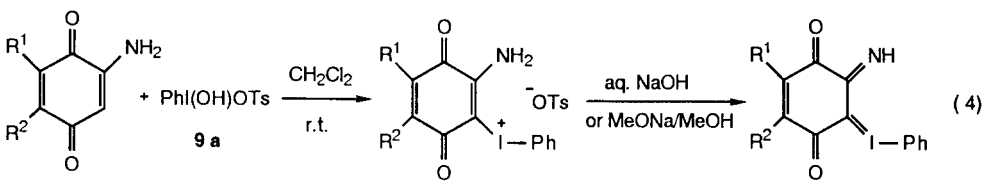
(2)

Phenylaminonaphthoquinone **5** also forms the relatively stable iodonium salt **15**, but the latter upon treatment with aqueous NaOH gave as the only isolable product **22a**, resulting from phenyl migration of the unstable intermediary zwitterion **16** (eq 3).



(3)

On the other hand, substituted 2-amino-1,4-benzoquinones **6**, **7**, **8** afforded readily both iodonium salts **17** and zwitterions **18** (eq 4).



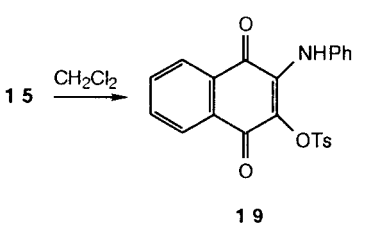
(4)

6 $R^1 = R^2 = Me$
7 $R^1 = H$, $R^2 = Ph$
8 $R^1 = Ph$, $R^2 = H$

17,18 **a** $R^1 = R^2 = Me$
b $R^1 = H$, $R^2 = Ph$
c $R^1 = Ph$, $R^2 = H$

Zwitterions **18** are isolable and were characterized by their spectroscopic data; however, they are not stable enough to obtain satisfactory elemental analyses since their decomposition starts already at room temperature.

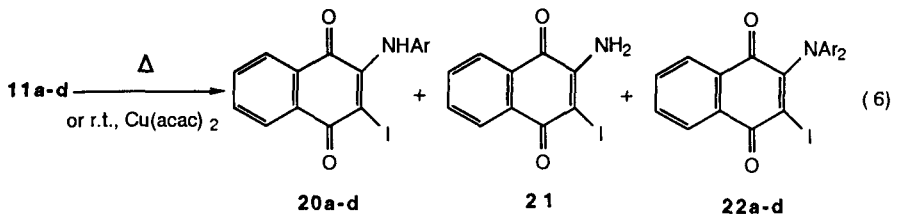
Reactivity of aryliodonio derivatives. All iodonium tosylates are fairly stable, with the exception of the phenylamino derivative **15** which in dichloromethane solution was quantitatively converted into the tosyloxy quinone **19** in 24 hours at room temperature (eq 5). The reaction probably involves nucleophilic attack of the tosylate anion to C-3, a substitution reaction common with iodonium salts.[1]



(5)

This substitution is presumably facilitated by the phenylamino group, since an analogous reaction is not observed with the corresponding amino derivatives. Since the substitution reaction proceeds at r.t., i t was not possible to obtain a satisfactory elemental analysis for **15**.

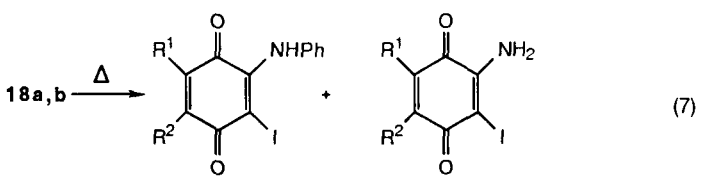
All zwitterions **11**, upon attempted recrystallization, rearranged thermally to iodoquinones **20**. In boiling acetonitrile this isomerization was quantitative in one hour (eq 6).



20a-d **21** **22a-d**

The rearrangement of zwitterions **11** to iodoquinones **20** constitutes a typical example of the Smiles rearrangement, taking place at the *ipso* carbon of the aryl ring.The substituent on the aryl ring has no noticeable effect on the rate of rearrangement. On the other hand, this aryl migration takes place at room temperature in the presence of catalytic amounts of $Cu(acac)_2$. This time the formation of **20** is accompanied by small amounts of **21** and the blue-colored 2-diarylamino-3-iodo-1,4-naphthoquinones **22**, in equal proportions, due probably to disproportionation of **20.**

Phenyl migration occurred to a limited extent in the imido benzoquinone zwitterions **18a,b** since in boiling acetonitrile **23** was the minor and **24** the major product. (eq 7).

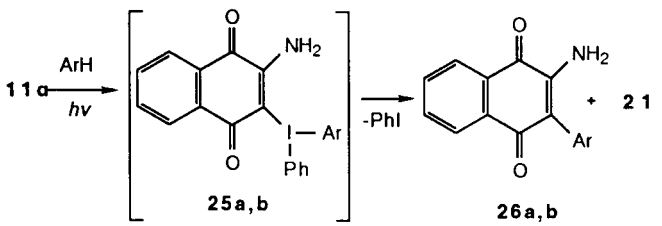


23a,b **24a,b**

a $R^1 = R^2 = Me$
b $R^1 = H$, $R^2 = Ph$

It is interesting to note the difference in reactivity between the imido quinone zwitterions and their oxido counterparts. Under the same thermal conditions imido zwitterions afford only aryl migration products, whereas oxido zwitterions give ring contraction products : 3-phenyliodonio-2-oxido-1,4-naphthoquinone **1** afforded indanedione in 91% yield[7] and the benzoquinone analogs **2** provided substituted 1,3-cyclopentenediones in good yield.[8] In this case iodoethers, resulting from aryl migration from iodine to oxygen, are minor products, as the reaction takes a different route : fission of I - C bond gives rise to carbenes and Wolff rearrangement products.[8]

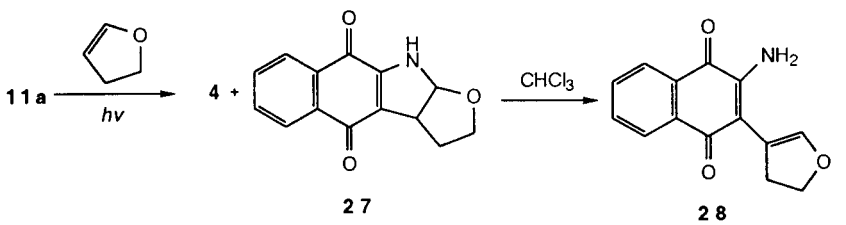
Since imido aryliodonium zwitterions under thermal conditions are converted mainly to aryl migration products, we tried some reactions under photochemical conditions. Zwitterion **11a** in benzene or furan afforded aryl quinones **26** in 60% and 70% yield respectively (eq 8). The reaction proceeds probably through the intermediacy of unstable iodanes **25**; **21** was always a by-product of the reaction.



(8)

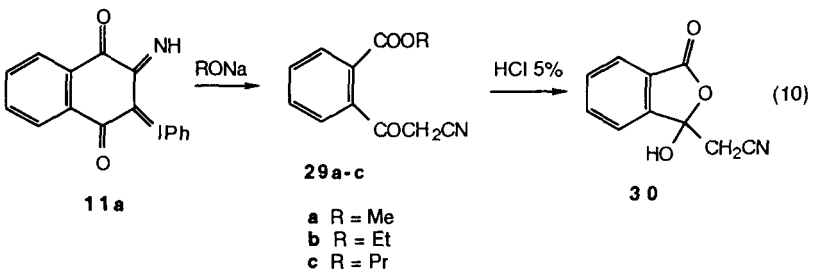
a, Ar = phenyl 60%
b, Ar = α-furyl 70%

Also, some photocyclization reactions of zwitterion **11a** were attempted. A variety of unsaturated compounds were examined, but the only isolable cyclization product **27** was from the reaction with 2,3-dihydrofuran, obtained in 12% yield, along with **4** (eq 9). Although stable when solid, **27** was rapidly isomerized to the tautomeric amino enol ether **28** in chloroform solution at room temperature.



(9)

The action of a number of nucleophiles (amines, phenoxides, β-diketonates, etc) on zwitterion **11a** even at r.t. resulted only in thermolysis products such as the phenyl migration product **20a**, the parent quinone **4** and the iodo amino quinone **21**. However, a most interesting reaction occurred with alkoxides which attacked a carbonyl group of zwitterion **11a**; this was followed by ring opening, and eventually alkyl 2-(cyanoacetyl)benzoates **29** (eq 10) were obtained in satisfactory yield (58-64%).



11a

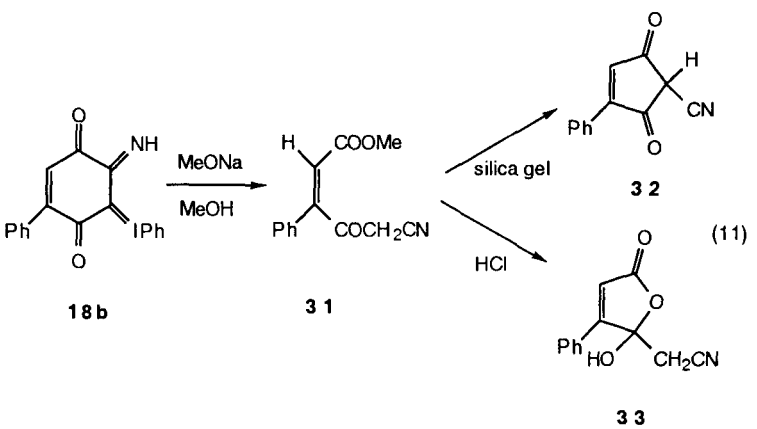
29a-c

a R = Me
b R = Et
c R = Pr

30

The formation of esters **29** was always accompanied by small amounts of lactone **30**, which is a transformation product of **29**. Indeed, **29** was quantitatively converted to **30** by the action of hydrochloric acid in an independent reaction. The structure of compounds **29a** and **30** was verified by X-ray analysis, thus establishing this novel ring opening.

When the same reaction was applied to benzoquinone zwitterions **18**, the dimethyl derivative **18a** and the 6- phenyl derivative **18c** did not react at all. However, the 5-phenyl derivative **18b**, on treatment with MeONa in MeOH, gave the corresponding ester **31** through ring opening (eq 14). The latter is the main product of the reaction and is unstable. On attempted chromatographic separation, it was converted to dione **32**, whereas the action of HCl afforded the hydroxy lactone **33**, analogously to the corresponding naphthoquinone derivatives.



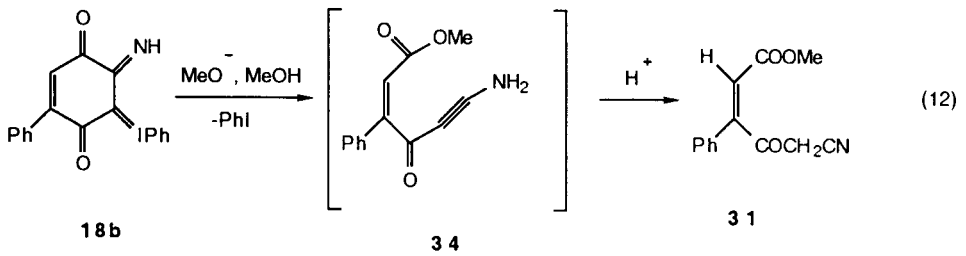
18b

31

32

33

An X-ray structure determination of **33**, verified the proposed structure with the phenyl group next to carbon bearing the hydroxy group. The formation of **33** proves that, of two possible regioisomers, **31** is the correct one. It is likely that the reaction starts with attack of methoxide on C-1 of the quinone ring; ring opening and tautomerization of the resulting unstable ynamine **34** leads to ester **31**(eq. 12).



18b **34** **31** (12)

An entirely analogous mechanism also explains the ring opening of **11a** to esters **29a-c**.

Conclusions

In conclusion, we described the preparation of aryliodonium salts and zwitterions resulting from 2-amino-1,4-naphthoquinone and 2-amino-1,4-benzoquinones, in good yield, under mild conditions. The reactivity of the zwitterions under thermal and photochemical conditions was explored. Especially noteworthy is the ring opening of the quinone system in the reaction with alkoxides which leads to multifunctional compounds, interesting from a synthetic point of view.

Experimental

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The IR-spectra were determined in Nujol and expressed in cm^{-1}. ^1H-NMR spectra were recorded on 80 and on 300 MHz spectrometers using tetramethylsilane as an internal standard. The MS spectra were recorded at 70 eV. Column chromatography was performed on silica gel.

The starting 2-amino-1,4 naphthoquinone **4** and the corresponding phenylamino derivative **5** were prepared by the action, respectively, of sodium azide[15] and aniline[16] on 1,4-naphthoquinone.

2,3-Dimethylhydroquinone and 2-phenylhydroquinone were oxidised to the corresponding quinones by $NaClO_3$, according to the literature method.[17]

Preparation of 2,3-dimethyl-4-amino-1,4-benzoquinone (6). A solution of NaN_3 (1.43 g, 22 mmol) was added to a solution of 1,3-dimethyl-1,4-benzoquinone (2.1 g, 15.4 mmol) in AcOH (50 mL). After 24 h at room temperature (monitoring by TLC), H_2O (30 mL) and a solution of $FeCl_3.6H_2O$ (12.5 g, 46.2 mmol) in H_2O (30 mL) was added to the initial solution. The resultng solution was extracted with CH_2Cl_2 (5X50 mL), dried and evaporated to dryness. The residue was dissolved in MeOH (15 mL), Pd/C 10% (75 mg, 0.7 mmol) was added under Ar and the resulting mixture remained under a stream of H_2 for 8 h. The catalyst was filtered off, $FeCl_3.6H_2O$ (5.41 g, 20 mmol) in H_2O (40 mL) was added and the mixture was extracted with CH_2Cl_2 (5X50 mL). After dryness and evaporation the residue was chromatographed on column (hexanes-AcOEt 1: 1) to afford 1 g (43% yield) of the desired amino quinone **6** as red crystals : mp 243-245 °C ; IR 3420, 3290, 1600 ; ^1H NMR (80 MHz, $CDCl_3$) δ 1.98 (s, 6H), 4.80 (s, br, 2H), 5.66 (s, 1H) ; MS m/z 151, (M^+,81), 123 (25), 95 (12). Anal. Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.27. Found : C, 63.48; H, 6.00; N, 9.14.

Preparation of 2-amino-5-phenyl-1,4-benzoquinone (7) and 2-amino-6-phenyl-1,4-benzoquinone (8). By the same procedure, starting from 2-phenyl-1,4-benzoquinone a mixture of the two isomeric amino quinones **7** and **8** was isolated. The mixture was chromatographed on column , (hexanes-AcOEt 2: 1) to afford as first fraction amino quinone **7** in 25 % yield as red crystals : mp 147-148 °C ; IR 3420, 3280, 1660 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (s, br, 2H), 5.84 (s, 1H), 6.71 (s, 1H), 7.45 (m, 5H); MS m/z 199, (M^+,49), 171 (13), 143 (8), 77 (100). Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found : C, 72.13; H, 4.48; N, 6.98.

The second fraction was aminoquinone **8**. Yield 20%, red crystals : mp 167-169 °C ; IR 3320,-3120, 1670 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.09 (s, br, 2H), 5.83 (d, J = 2.5 Hz, 1H), 6.71 (d, J = 2.5 Hz, 1H), 7.45 (m, 5H); MS m/z 199, (M^+, 81), 171 (72), 77 (24). Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found : C, 72.11; H, 4.40 N, 6.88.

Aminoquinone **7** was also prepared by another route described in literature method.[18]

Preparation of [(hydroxy)(tosyloxy)iodo]arenes (9a-d). A solution of *p*-CH_3-C_6H_4-SO_3H. H_2O (3.8 g, 20 mmol) in CH_3CN (20 mL) was added to a solution of the corresponding (diacetoxy iodo)arene (10 mmol) in CH_3CN (20 mL). Compounds **8** were crystallized from the solution, filtered, washed successively with acetone and ether and dried in vacuo.

[(Hydroxy)(tosyloxy)iodo]benzene (9a). Yield 87% , mp 135-137 °C; lit[14a] mp 136-138.5 °C.

[(Hydroxy)(tosyloxy)iodo]-*p*-toluene (9b) Yield 86% , mp 134-136 °C; lit[14b] mp 115-118 °C.

[(Hydroxy)(tosyloxy)iodo]-*m*-nitrobenzene (9c). Yield 80%, mp 157-159 °C ; IR 3130, 1590, 1520, 1225, 1110 ; ^{1}H NMR (80 MHz, DMSO-d_6) δ 2.32 (s, 3H), 5.51 (s, br, 1H), 7.09 (d, J = 8 Hz, 2H), 7.60 (m, 3H), 8.37 (m, 3H), 8.84 (s, 1H) ; MS m/z 248, (100), 202 (27), 127 (6), 90 (77). Anal. Calcd for $C_{13}H_{12}INO_6S$: C, 35.71; H, 2.77; N, 3.20. Found : C, 35.81; H, 2.68; N, 3.10.

(Hydroxy)(tosyloxy)iodo]-*p*-methoxybenzene (9d). Methoxy compound **9d** as it has already been described, is unstable and decomposes violently at room temperature within 20 min after its isolation by filtration. It was used directly for the next step.

Preparation of 3-aryliodonio-2-amino-1,4-naphthoquinone tosylates (10a-d) and 2-amino-1,4-benzoquinone tosylates (17a-c). The [(hydroxy)(tosyloxy)iodo]arene **9** (5.05 mmol) was added to a solution of 2-amino-1,4-naphthoquinone **4** (0.865 g, 5 mmol) in CH_2Cl_2 (30 mL) under continous stirring. After 1 h the resulting iodonium tosylate was filtered, washed successively with CH_2Cl_2 and ether and dried in vacuo to afford pure **10**. By the same procedure (addition of **9a** to the proper amino benzoquinone **6**, **7**, **8**) the tosylates **17** were obtained.

3-Phenyliodonio-2-amino-1,4-naphthoquinone tosylate (10a). Yield 95% : mp 213-216 °C ; IR 3310-3160, 1635, 1195, 1030 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.32 (s, 3H), 7.10-8.32 (m, 13H); MS m/z 204 (18), 176 (6), 105 (100), 91 (10). Anal. Calcd for $C_{23}H_{18}INO_5S$: C, 50.47; H, 3.31; N, 2.56. Found : C, 50.45; H, 3.36 N, 2.55.

3-(*p*-Tolyliodonio)-2-amino-1,4-naphthoquinone tosylate (10b). Yield 97% : mp 207-209°C ; IR 3270-3150, 1690, 1190, 1035 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.22 (s, 3H), 2.38 (s, 3H) 7.10-7.30 (m, 4H), 7.53-8.35 (m, 8H) ; MS m/z 561 (M^+, 15) 218 (93), 172 (6), 91 (10). Anal. Calcd for $C_{24}H_{20}INO_5S$: C, 51.35; H, 3.59; N, 2.49. Found : C, 51.51; H, 3.52 N, 2.31.

3-[(*m*-Nitrophenyl)iodonio]-2-amino-1,4-naphthoquinone tosylate (10c). Yield 91% : mp 210-212 °C ; IR 3380-3140, 1690, 1270, 1020 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.33 (s, 3H), 7.10-7.46 (m, 2H), 7.50-8.00 (m 5H), 8.05-8.30 (m, 2H), 8.31-8.59 (m, 2H), 8.98 (s, 1H) ; MS m/z 249 (67), 105 (24), 91 (26), 75 (100). Anal. Calcd for $C_{23}H_{17}IN_2O_7S$: C, 46.63; H, 2.89; N, 4.73. Found : C, 46.74; H, 3.00 N, 4.70.

3-[(*p*-Methoxyphenyl)iodonio]-2-amino-1,4-naphthoquinone tosylate (10d). Yield 80% : mp 197-199 °C ; IR 3280, 3150, 1695, 1270, 1195 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.34 (s, 3H), 3.81 (s, 3H), 6.92(d, J = 10 Hz, 2H), 7.19 (d, J = 8 Hz, 2H), 7.60-8.35 (m, 8H); MS m/z 234 (56), 172 (13), 155 (14), 105 (44), 91 (100). Anal. Calcd for $C_{24}H_{20}INO_6S$: C, 49.92; H, 3.49; N, 2.43. Found : C, 50.08; H, 3.61 N, 2.37.

4,5-Dimethyl-3-phenyliodonio-2-amino-1,4-benzoquinone tosylate (17a). Yield 79% : mp 205-207 °C ; IR 3300, 3160, 1630, 1165 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.02 (s, 3H), 2.13 (s, 3H), 2.36 (s,3H), 6.99-8.22 (m, 9H); MS m/z 204 (47), 155 (8), 138 (100), 91 (37). Anal. Calcd for $C_{21}H_{20}INO_5S$: C, 48.01; H, 3.84; N, 2.67. Found : C, 47.88; H, 3.89; N, 2.76.

5-Phenyl-3-phenyliodonio-2-amino-1,4-benzoquinone tosylate (17b). Yield 70% : mp 186-188 °C ; IR 3280, 3130, 1645, 1190 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.36 (s, 3H), 6.89 (s, 1H), 7.15-7.75 (m, 12H), 8.02 (m, 2H); MS m/z 204 (8), 172 (64), 107 (45), 91 (100). Anal. Calcd for $C_{25}H_{20}INO_5S$: C, 52.37; H, 3.52; N, 2.44. Found : C, 52.22; H, 3.73; N, 2.28.

6-Phenyl-3-phenyliodonio-2-amino-1,4-benzoquinone tosylate (17c). Yield 82% : mp 210-212 °C (dec.) ; IR 3320, 3100, 1630, 1195 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.37 (s, 3H), 7.06 (s, 1H), 7.15-7.83 (m, 12H), 8.15 (m, 2H); MS m/z 369 (26) 204(43), 172 (37), 91 (100). Anal. Calcd for $C_{25}H_{20}INO_5S$: C, 52.37; H, 3.52; N, 2.44. Found : C, 52.19; H, 3.60; N, 2.48.

Preparation of 3-phenyliodonio-2-amino-1,4-naphthoquinone trifluoroacetate (13) and chloride (14). [Bis(trifluoroacetoxy)iodo]benzene **12** (2.193 g, 5.05 mmol) was added to a solution of aminoquinone **4** (0.865 g, 5 mmol) in CH_2Cl_2 (30 mL). After 5 h at room temperature the solvent was concentrated, in vacuo without heating, until it was 1/3 of the initial volume. Ether was added and the precipitated yellow iodonium salt **13** was filtered, washed with ether and dried under vacuum. Yield 93% : mp 137-139 °C ; IR 3300-3110, 1680, 1640, 1190 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 7.31-8.40 (m); MS m/z 375 (M^+-CF_3COO^-, 38), 204 (44), 172 (18), 105 (20), 77 (100). Anal. Calcd for $C_{18}H_{11}F_3INO_4$: C, 44.19; H, 2.23; N, 2.86. Found : C, 44.09; H, 2.25 N, 2.78.

The corresponding iodonium chloride **14** was prepared by the addition of a solution of concentrated HCl (1 mL) in EtOH (5 mL) to a suspension of the zwitterion **11a** (0.375 g, 1mmol) in EtOH (15 mL). The precipitated salt was filtered, washed with H_2O and Et_2O and dried in vacuo. Yield 95% : mp 183-185 °C ; IR 3220, 3160, 1685, 1580; ^{1}H NMR (80 MHz, $CDCl_3$-DMSO-d_6) δ 7.23-8.61 (m); MS m/z 376 (M^+-Cl, 11), 375 (62), 248 (72), 204 (24), 77(100). Anal. Calcd for $C_{16}H_{11}ClINO_2$: C, 46.69; H, 2.69; N, 3.40. Found : C, 46.57; H, 2.62; N, 3.34.

Preparation of zwitterions 11a-d and 18a. A suspension of the tosylate **10a-d** or **17a** (4 mmol) in H_2O 10mL) was treated with a cold solution of NaOH (6.5%, 8mmol). The suspension remained at 3-5 °C till the yellow iodonium salt was converted to the corresponding orange-red zwitterion (ca 1.5 h). The precipitate was filtered, washed successively with cold H_2O, CH_2Cl_2 and Et_2O to afford zwitterions **11a-d** and **18a** as orange-red solids.

3-Phenyliodonio-1,4-naphthoquinone-2-imide (11a). Yield 70% (64% from iodonium trifluoroacetate **13**) : mp 110 °C (dec.) ; IR 3225, 1670, 1580 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 7.35-8.29 (m); MS m/z 375 (M^+,15), 299(42), 248 (66), 204 (81). Anal. Calcd for $C_{16}H_{10}INO_2$: C, 51.22; H, 2.69; N, 3.73. Found : C, 51.30; H, 2.65; N, 3.83.

3-(*p*-Tolyliodonio)-1,4-naphthoquinone-2-imide (11b). Yield 78% : mp 109-111 °C ; IR 3210, 1670, 1575 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 2.30 (s, 3H), 6.80-7.30 (m, 2H), 7.40-8.40 (m, 6H); MS m/z 389 (M^+,74), 299 (67), 218 (63), 91 (100). Anal. Calcd for $C_{17}H_{12}INO_2$: C, 52.46; H, 3.11; N, 3.60. Found : C, 52.60; H, 3.26; N, 3.80.

3-[(*m*- Nitrophenyl)iodonio)]-1,4-naphthoquinone-2-imide (11c). Yield 69% : mp 187-189 °C (dec.) ; IR 3260, 1660, 1575 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 7.50-8.00 (m, 3H), 8.04-8.25 (m, 2H), 8.30-8.64 (m, 2H), 8.90 (s, 1H); MS m/z 420 (M^+, 17), 298 (100). Anal. Calcd for $C_{16}H_9IN_2O_4$: C, 45.74; H, 2.16; N, 6.67. Found : C, 45.81; H, 2.27; N, 6.65.

3-[(*p*-Methoxyphenyl)iodonio)]-1,4-naphthoquinone-2-imide (11d). Yield 80% : mp 122-123 °C ; IR 3220, 1670, 1575 ; ^{1}H NMR (80 MHz, $CDCl_3$-CF_3COOH) δ 3.85 (s, 3H), 6.97 (d, J = 10 Hz, 2H), 7.37-840 (m, 6H) ; MS m/z 405 (M^+,49), 234 (65), 172 (82),128 (100). Anal. Calcd for $C_{17}H_{12}INO_3$: C, 50.39; H, 2.98; N, 3.40. Found : C, 50.56; H, 3.00; N, 3.40.

4,5-Dimethyl-3-phenyliodonio-1,4-benzoquinone-2-imide (18a). Yield 51% : mp 69-73 °C (dec.); IR 3260, 1650, 1510, 1270, 1190; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.08 (s, 3H), 7.09-7.47 (m, 3H), 7.50-7.84 (m,2H) ; MS m/z 353 (M+, 25), 277 (100), 204 (97), 77 (93)..

Preparation of zwitterions 18b,c. A methanolic solution of MeONa (55 mg Na, 2.4 mmol in 5 mL of MeOH) was added to a stirring suspension of tosylate **17b** or **17c** (1.146 g, 2 mmol) in MeOH (10 mL) at 0 °C and the mixture was allowed to reach room temperature (30 min). H_2O (40 mL) was added, the resulting mixture was extracted with CH_2Cl_2 (3X50 mL) and the combined extracts were dried with $MgSO_4$. The solvent was removed in vacuo without heating, the residue was triturated with cold Et_2O and the zwitterion was crystallized and filtered.

5-Phenyl-3-phenyliodonio-1,4-benzoquinone-2-imide (18b). Yield 57% : mp 104-107 °C ; IR 3300, 3200, 1610, 1585 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.67 (s, 1H), 7.00-7.90 (m, 8H), 8.1 (m, 2H). MS m/z 401 (M+, 22), 325 (83), 204 (93), 77 (93). Due to its instability no satisfactory elemental analysis could be obtained.

6-Phenyl-3-phenyliodonio-1,4-benzoquinone-2-imide (18c). Yield ca 40%. The zwitterion was rapidly decomposed and its formation was deduced by its decomposition products.

Preparation of 3-phenyliodonio-2-phenylamino-1,4-naphthoquinone tosylate (15) and 3-iodo-2-diphenylamino-1,4-naphthoquinone (22a). [(Hydroxy)(tosyloxy)iodo]benzene **9a** (0.804 g, 2.05 mmol) was added to a solution of quinone **5** (0.498 g, 2mmol), in CH_2Cl_2 (20 mL) at 0 °C. The resulting solution was left to reach room temperature (3 h) and the solvent was removed in vacuo without heating. The residue was washed with ether and crystallized from ether/hexane to afford tosylate **15** as a yellow solid. Yield 65% : mp 115-117 °C (dec.) ; IR 3260, 1670, 1580 ; ^{1}H NMR Decomposition to tosyloxy derivative **19** starts as soon as **15** is dissolved in $CDCl_3$; MS m/z 451 (M^+-tosyloxy,traces), 419 (59), 249 (98), 220 (98) 204 (100). Due to its instability no satisfactory elemental analysis could be obtained.

A cold solution of NaOH in H_2O (1%, 10 mL, 2mmol NaOH) was added to **15** (0.623, 1 mmol) and the resulting suspension remained under stirring at 3-5 °C for 1 h. The mixture was extracted with CH_2Cl_2 (3X20 mL) and the combined extracts after drying and evaporation were chromatographed on column (hexanes/AcOEt, 1:1). After PhI the blue-colored iodo naphthoquinone **22a** was eluted. Yield 50% : mp 165-166 °C ; IR 1665, 1650, 1585 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.90-7.45 (m, 6H), 7.60-7.90 (m, 4H), 7.91-8.10 (m, 2H), 8.12-8.35 (m, 2H); MS m/z 451 (M^+, 66), 326 (100), 105 (52). Anal. Calcd for $C_{22}H_{14}INO_2$: C, 58.56; H, 3.13; N, 3.10. Found : C, 58.31; H, 3.01; N, 2.99.

Preparation of 3-tosyloxy-2-phenylamino-1,4-naphthoquinone (19). Solutions of tosylate **15** in CH_2Cl_2 after 1 day at room temperature afforded **19** as the only product. After column chromatography , (hexanes/AcOEt) **19** was isolated as red crystals. Yield 82% : mp 173-175 °C ; IR 3280, 1655, 1630 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.39 (s, 3H), 6.87-7.30 (m, 7H), 7.48 (m, 2H), 7.68 (m, 2H), 8.09 (m, 2H) ; MS m/z 264 (17), 236 (39), 104 (100). Anal. Calcd for $C_{23}H_{17}NO_5S$: C, 65.86; H, 4.09; N, 3.34. Found : C, 66.00; H, 4.17; N, 3.38.

Thermal rearrangement of zwitterions11a-d and 18a-b. A suspension of the proper zwitterion (1 mmol) in CH_3CN (15 mL) (or CH_2Cl_2 or $CHCl_3$) was refluxed for 3h. After evaporation the residue either was subjected to column chromatography (hexanes/AcOEt) or the rearrangement product was isolated by crystallization from EtOH.

3-Iodo-2-phenylamino-1,4-naphthoquinone (20a) and 3-iodo-2-amino-1,4-naphthoquinone (21). Column chromatography gave as first fraction **20a**. Yield 85% : mp 171-172 °C ; IR 3265, 1655, 1625 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.00-7.46 (m, 5H), 7.51-7.90 (m, 2H), 7.91-8.38 (m, 2H) ; MS m/z 375 (M^+, 100), 248 (59), 105 (58), 77 (82). Anal. Calcd for $C_{16}H_{10}INO_2$: C, 51.22; H, 2.69; N, 3.73. Found : C, 51.28; H, 2.80; N, 3.61.

As second fraction, **21** was isolated in 10% yield : mp 194-196 °C (EtOH). Lit[19] mp 192-193 °C; IR 3440, 3300 1670, 1610 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 5,74 (s, br, 2H), 7.50-7.85 (m, 2H), 7.90-8.29 (m, 2H) ; MS m/z 299 (M^+, 100), 172 (98), 105 (30).

3-Iodo-2-(*p*-tolyl)amino-1,4-naphthoquinone (20b). Isolation by crystallization from EtOH. Yield 87% : mp 173-175 °C ; IR 3280, 1665, 1630 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.01 (d, J = 10 Hz, 2H), 7.18 (d, J = 10 Hz, 2H) 7.60-7.85 (m, 2H), 7.95-8.30 (m, 2H); MS m/z 389 (M^+,100), 262 (64), 218 (15), 105 (41). Anal. Calcd for $C_{17}H_{12}INO_2$: C, 52.46; H, 3.11; N, 3.60. Found : C, 52.40; H, 3.11; N, 3.59.

3-Iodo-2-(*m*-nitrophenyl)amino-1,4-naphthoquinone (20c). Isolation by crystallization from EtOH. Yield 86% : mp 206-208 °C ; IR 3270, 1665, 1635 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.30-8.40 (m) ; MS m/z 420 (M^+, 65), 294 (10), 248 (84), 105 (20). Anal. Calcd for $C_{16}H_9IN_2O_4$: C, 45.74; H, 2.16; N, 6.67. Found : C, 45.68; H, 2.20; N, 6.48.

3-Iodo-2-(*p*-methoxyphenyl)amino-1,4-naphthoquinone (20d). Isolation by crystallization from EtOH. Yield 85% : mp 179-180 °C ; IR 3380, 1665, 1620 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.82 (s, 3H), 6.88 (d, J = 10 Hz, 2H), 7.06 (d, J = 10 Hz, 2H), 7.60-7.90 (m, 2H), 8.00-8.30 (m, 2H); MS m/z 405 (M^+,100), 278 (43), 234 (22), 105 (50). Anal. Calcd for $C_{17}H_{12}INO_3$: C, 50.39; H, 2.98; N, 3.46. Found : C, 50.44; H, 2.95; N, 3.38.

5,6-Dimethyl-3-iodo-2-phenylamino-1,4-benzoquinone (23a) and 5,6-dimethyl-3-iodo-2-amino-1,4-benzoquinone (24a). Column chromatography afforded as first fraction **23a**. Yield 20% : mp 120-123 °C (EtOH); IR 3220, 1660, 1510 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (s, 3H), 2.15 (s, 3H), 7.06 (m, 2H), 7.21-7.34 (m, 3H), 7.53 (s, br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.24, 14.41, 83.21, 125.29, 125.62, 128.57, 136.78, 137.12, 143.11, 147.04, 180.43, 181.43 ; MS m/z 353 (M^+,12), 352 (100), 226 (30), 77 (16). Anal. Calcd for $C_{14}H_{12}INO_2$: C, 47.61; H, 3.42; N, 3.97. Found : C, 47.70; H, 3.51; N, 4.00.

Amino compound **24a** was obtained as second fraction. Yield 42% : mp 143-145 °C (EtOH) ; IR 3460, 3340, 1670, 1640 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.12 (s, 3H), 5.53 (s, br, 2H) ; MS m/z 277 (M^+, 100), 249 (18). Anal. Calcd for $C_8H_8INO_2$: C, 34.68; H, 2.91; N, 5.05. Found : C, 34.60; H, 3.00; N, 4.99.

5-Phenyl-3-iodo-2-phenylamino-1,4-benzoquinone (23b) and 5-phenyl-3-iodo-2-amino-1,4-benzoquinone (24b). Column chromatography afforded as first fraction **31b**. Yield 18% : mp 137-139 °C (EtOH); IR 3290, 1640, 1555, 1280 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 6.79 (s, 1H), 7.02-7.85 (m, 10H); MS m/z 401 (M^+, traces), 325 (30), 274 (56), 144 (96), 77 (100). Anal. Calcd for $C_{18}H_{12}INO_2$: C, 53.89; H, 3.01; N, 3.49. Found : C, 53.68; H, 2.99; N, 3.40.

Amino compound **32b** was obtained as second fraction. Yield 26% : mp 130-139 °C (EtOH) ; IR 3440, 3320, 1660, 1580 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 5.64 (s, br, 2H), 6.67 (s, 1H), 7.36-7.77 (m, 5H) ; MS m/z 325 (M^+, 97), 297 (10), 198 (22), 77 (44), 68 (100). Anal. Calcd for $C_{12}H_8INO_2$: C, 44.33; H, 2.48; N, 4.31. Found : C, 44.11; H, 2.28; N, 4.21.

Thermal rearrangement of zwitterions 11a-d in the presence of Cu(acac)$_2$. A catalytic amount of $Cu(acac)_2$ (10 mg) was added to a stirring suspension of the proper zwitterion (1 mmol) in CH_2Cl_2 (20 mL). After 0.5 h (4h for **11c**) the resulting clear solution, after evaporation, was chromatographed on column (hexanes/AcOEt or CH_2Cl_2).

Zwitterion **11b** afforded in the order of eluance: **22a** (10%), **20a** (60%) and **21** (10%).

Zwitterion **11b** afforded **3-iodo-2[di(*p*-tolyl)]amino-1,4-naphthoquinone. (22b)**. Yield 8% : mp 151-153 °C (EtOH) ; IR 1670, 1645, 1530 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 2.30 (s, 6H), 6.91 (d, J = 10 Hz, 4H), 7.10 (d, J = 10 Hz, 4H), 7.50-7.90 (m, 2H), 8.00-8.30 (m, 2H); MS m/z 479 (M^+, 69), 352 (79), 105 (50), 84 (100). Anal. Calcd for $C_{24}H_{18}INO_2$: C, 60.14; H, 3.78; N, 2.92. Found : C, 60.08; H, 2.80; N, 3.80 , **20b** (65%) and **21** (8%).

Zwitterion **11c** afforded **21** (5%), **20c** (67%) and finally **3-iodo-2[di(*m*-nitrophenyl)]amino-1,4-naphthoquinone (22c)**. Yield 5% : mp 128-130 °C (EtOH) ; IR 1665, 1585 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.30-8.40 (m), MS m/z 542 (M^+, 16), 425 (10), 105 (44). Anal. Calcd for $C_{22}H_{12}IN_3O_6$: C, 48.82; H, 2.23; N, 7.76. Found : C, 48.51; H, 2.08; N, 7.89

Zwitterion **11d** afforded **21** (4%), **20d** (60%) and finally **3-iodo-2[di(*p*-methoxyphenyl)]amino-1,4-naphthoquinone 22d**. Yield 4% : mp 168-170 °C (EtOH) ; IR 1670, 1645, 1590 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.78 (s, 6H), 6.76 (d, J = 10Hz, 4H), 6.96 (d, J = 10Hz, 4H), 7.50-7.90 (m, 2H), 8.00-8.35 (m, 2H); MS m/z 511 (M^+, 11), 278 (100), 105 (32). Anal. Calcd for $C_{24}H_{18}INO_4$: C, 56.38; H, 3.55; N, 2.74. Found : C, 56.26; H, 3.61; N, 2.70.

Photochemical reactions of zwitterion 11a. A suspension of **11a** (1 mmol) in benzene, furan or 2,3-dihydrofuran (15 mL) in a Pyrex vessel was irradiated with a 250-Watt low pressure Hg

lamp for 6h. The resulting solution was chromatographed on column (hexanes/AcOEt) to afford in order of eluance:

In benzene : PhI, **21** (30%) and **2-amino-3-phenyl-1,4-naphthoquinone (26a)** as red crystals. Yield 60%, mp 170-173 °C (EtOH) (lit.[20] mp 173.5-174 °C); IR 3405, 3260, 1665, 1590 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 5.20 (s, br, 2H), 7.25-7.55 (m, 5H), 7.58-7.80 (m, 2H), 7.95-8.30 (m, 2H); MS m/z 250 (M^++1, 70), 249 (M^+, 48) 105 (18), 77 (100).

In furan : PhI, **2-amino-3-(α-furyl)-1,4-naphthoquinone (26b)** as violet crystals. Yield 70%, mp 132-133 °C ; IR 3460, 3340, 1650, 1590 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.21 (s, br, 2H), 6.61 (dd, J = 3.5 Hz, 1.7Hz, 1H), 7.45 (d, J = 3.5 Hz, 1H), 7.54 (d, J = 1.7 Hz, 1H), 7.59-7.74 (m, 2H), 8.02-8.14 (m, 2H); MS m/z 239 (M^+, 100), 211 (19), 182 (15), 154 (23). Anal. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.85. Found : C, 70.31; H, 3.80; N, 6.00, and **21** (6%) .

In 2,3-dihydrofuran : PhI, **4** (traces), **21** (5%), **26a** (5%) and finally **2,3,4,12-tetrahydro-furo[2,3-b]-naphtho[2,3-b]pyrrolo-5,10-quinone (27)**. Yield 12%, mp 126-129 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.24-2.33 (m, 2H), 3.54-3.63 (m, 1H), 4.07 (dd, J = 7.5 Hz, 7.3 Hz, 2H), 5.88(s, br, 1H), 5.92 (d, J = 7.2 Hz, 1H), 7.58-7.73 (m, 2H), 7.98-8.09 (m, 2H); MS m/z 242 (M^++1, 100), 213 (73), 105 (17). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found : C, 69.78; H, 4.45; N, 5.96.

When solutions of quinone **27** were allowed to stand at room temperature, **2-amino-3-[6-(2',3'-dihydrofurylo)]-1,4-naphthoquinone (28)** started to crystallize, the transformation being quantitative in 2h. Red crystals, mp 200-203 °C ; IR 3450, 3150, 1640, 1580 ; ^{1}H NMR (300 MHz, $CDCl_3$-DMSO-d_6) δ 3.14 (t, J = 6Hz, 2H), 3.95 (t, J = 6Hz, 2H), 7.02 (s, 1H), 7.58-7.70 (m, 2H), 7.90-8.10 (m, 2H); ^{13}C NMR (75MHz, $CDCl_3$-DMSO-d_6) δ 28.49, 60.63, 123.05, 123, 48, 124.94, 125.33, 125.41, 131.81, 132.07, 132.56, 133.61, 174.06, 180.76 ; MS m/z 241 (M^+, 15), 212 (46), 155 (100), 105 (28). Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.60; N, 5.81. Found : C, 69.58; H, 4.41 N, 5.80.

Reaction of 11a with alkoxides. Zwitterion **11a** (1 mmol) was added to an alcoholic solution of RONa (92 mg Na, 4 mmol in 15 mL of the proper alcohol) at °C. After 24h water (15 mL) was added and the solution was adjusted to pH 6 by addition of 5% HCl. It was then extracted with CH_2Cl_2 (3X30 mL) and after evaporation the residue was chromatographed on column with mixtures of hexanes with CH_2Cl_2 or AcOEt.

Reaction with sodium methoxide. Chromatography with hexanes/CH_2Cl_2 gave in order of eluance : PhI, **20a** and **21** in traces, **methyl 2-cyanoacetyl-benzoate (29a)** (60%), mp 114-116 °C ; IR 2250, 1700, 1300 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.82 (s, 2H), 3.93 (s, 3H), 7.35 (m, 1H), 7.58 (m, 2H), 8.00 (m, 1H); MS m/z 172 (16), 164 (100), 105 (24). Anal. Calcd for $C_{11}H_9NO_3$: C, 65.02; H,4.46; N, 6.89. Found : C, 65.14; H, 4.70; N, 7.00 and, by changing the eluant to hexanes/AcOEt, **7-hydroxy-7-cyanomethyl-benzo[c]-2-furanone (30)** in 5% yield, mp 134-136 °C ; IR 3360, 2240, 1750, 1600 ; ^{1}H NMR (300 MHz, $CDCl_3$-DMSO-d_6) δ 3.24 (s, 2H), 7.70 (m, 1H), 7.80 (m, 2H), 7.92 (m, 1H)) ; MS m/z 190 (M^+, 29), 172 (8), 149 (100). Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.40. Found : C, 63.28; H, 3.60 N, 7.21.

Compound **29a** was quantitatively converted to **30** by addition of 5% HCl (10 mL for 0.5 mmol of **29a**) and 2h reflux. The structure of both compounds was verified by X-ray analysis.

Reaction with sodium ethoxide. Under the same conditions as previously: PhI, **20a** and **21** in traces, and **ethyl 2-cyanoacetyl-benzoate (29b)** (64%), mp 59-60 °C ; IR 1695, 1590 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.41 (t, J = 7 Hz, 3H), 3.89 (s, 2H), 4.41 (q, J = 7 Hz, 2H), 7.35 (d, J = 7 Hz, 1H), 7.56-7.68 (m, 2H), 8.04 (d, J = 7Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.11, 32.77, 62.27, 114.01, 126.30, 128.09, 130.22, 130.83, 133.13, 140.70, 165.94, 193.61; MS m/z 177 (31), 172 (22), 149 (100), 104 (11). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H,.5.10; N, 6.45. Found : C, 66.41; H, 5.20; N, 6.60 and finally **30** in 4% yield.

Reaction with sodium propoxide. Chromatography with hexanes/AcOEt : PhI, **20a** and **21** in traces, **propyl 2-cyanoacetyl-benzoate (29c)** (58%), mp 49-50 °C ; IR 2250, 1690, 1590 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.00 (t, J = 8 Hz, 3H), 1.59-195 (m, 2H), 3.82 (s, 2H), 4.28 (t, J = 6 Hz, 2H), 7.36 (m, 1H), 7.59 (m, 2H), 8.00 (m, 1H); MS m/z 192 (78), 191 (62), 172 (78), 76 (100). Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H,.5.67; N, 6.00 Found : C, 67.34; H, 5.50; N,5.91 and finally **30** in 4% yield.

Both **29b** and **29c** were converted to **30** by addition of 5% HCl at room temperature after 2h.

Reaction of 18b with sodium methoxide. Tosylate **17b** was converted to zwitterion **18b** and the latter, without isolation, reacted with sodium methoxide under the previous conditions. ^{1}H NMR and TLC of the crude reaction mixture indicate that **methyl 3-phenyl-4-oxo-5-cyano-*Z*-2-pentenoate (31)** is the only product of the reaction. After the usual work-up, column chromatography (hexanes/AcOEt 1:1) gave : PhI, **2-cyano-4-phenyl-cyclopentene-1,3-dione (32)** in 36% yield, mp 156-158 °C ; IR 3070, 2200, 1750, 1630, 1600 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.26 (s, 1H), 6.48 (s, 1H), 7.43-7.46 (m, 2H), 7.52-7.60 (m, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 80.16, 113.04, 119.42, 128.00, 128.08, 129.59, 131.68, 155.82, 162.18, 164.96; MS m/z 197 (M^+, 6), 168 (7), 102 (17), 67 (100). Anal. Calcd for $C_{12}H_7NO_2$: C, 73.09; H,.3.59; N, 7.10. Found : C, 72.97; H, 3.74; N, 7.17, then **31**in traces, oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 2H), 3.82 (s, 3H), 6.32 (s, 1H), 7.43-7.48 (m, 5H); MS m/z 229 (M^+, 31), 196 (11), 187 (100), 105 (25) and finally **5-hydroxy-5-cyanomethyl-4-phenyl-2-furanone (33)** in 5% yield, mp 153-155 °C ; IR 3300, 3120, 2240, 1720, 1605 ; ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.12 (s, 2H), 6.40 (s, 1H), 7.30-7.58 (m, 3H), 7.60-7.90 (m, 2H) ; MS m/z 216 (M^+, 26), 198 (7), 175 (22), 147 (27) 102 (100). The structure of **33** was verified by X-ray analysis[21].

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