Pergamon

*Tetrahedron* Vol. 50, No. 17, pp. 5139-5146, 1994

0040-4020/94 $6.00+0.00

0040-4020(94)E0176-T

# Aromatic Iodination with the $I_2$-$HgX_2$ Combination

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***Abstract:*** The reaction of different aromatic compounds **1a-1t** with iodine and a mercury(II)-salt **2** [mercury(II) chloride, nitrate or triflate] (1:1:1 molar ratio) in dichloromethane at room temperature leads to the corresponding iodoarene **3**, the obtained regiochemistry being the expected. Concerning the mercury(II) salt, the observed reactivity decreased in the series triflate>nitrate>chloride according to their ionic character. An activation of the iodine molecule by the mercury(II) salt followed by a $S_E$ reaction with the aromatic compound is postulated as the possible mechanism.

## INTRODUCTION

Iodoarenes are useful molecules in organic synthesis[2] above all in carbon-carbon bond formation reactions. Among these processes, iodoarenes are particulary interesting in : (a) alkylation and arylation processes promoted by copper compounds[3]; (b) Heck-type reactions catalysed by palladium compounds[4]; (c) Stille-type reactions with organotin compounds[5]; (d) iodine/lithium exchange giving lithioarenes and subsequent coupling with electrophiles[6]. Some of these reactions have been used in the synthesis of pharmacologically active molecules, such as 2'-deoxycytidines[7a], methotrexane analogues[7b], benzoprostacyclins[7c], tetrahydrobenzazepinones[7d] and other compounds such as inodoles[7e] or spiroquinol ketals[7f]. In addition, there are some biologically very active molecules, in which structures, an iodinated aromatic ring is present: calicheamicine $\gamma 1$[8a] and L-thyroxine[8b] could be two important representative examples. On the other hand, radioactive labeled iodoaromatic molecules have been used in radioimmunoassay studies and in nuclear magnetic imaging[9].

Concerning aromatic iodination procedures, the most important methodologies involve the following reactions : (a) direct iodination with $I_2$; this is a thermodinamically defavoured (endothermic) and reversible reaction[10], which needs the help of an oxidant[11], a metallic salt[12] or alumina[13]. (b) Iodination with an iodide and an oxidant[14]. (c) Ioododemercuration[15] and iododetalation[16]. (d) Other more sophisticated procedures, such as the use of electrochemical reactions[17], iodoamides[18], iodonium salts[19] or transiodination processes[20]. To our best knowledgement, only one aromatic iodination reaction using a mercury(II) salt compound for the iodine activation [mercury(II) oxide] under strong acidic conditions has been described[21]. We have recently discovered that the iodine-mercury(II) salt combination is a good reagent for the direct iodofunctionalisation of different substrates such as olefins and dienes[22a-d], alkynes[22e], cyclopropanes[22f] or carbonyl compounds[22g]. In the present paper we report the application of this combination for the direct iodination of different arenes.

## RESULTS AND DISCUSSION

The reaction of arenes **1a-t** with iodine and a mercury(II) salt **2a-c** (1:1:1 molar ratio) in dichloromethane at ambient temperature overnight led to the formation of the corresponding iodoarene (Scheme 1 and Table 1).

$$\underset{\mathbf{1a\text{-}t}}{\mathrm{ArH}} + \mathrm{I_2} + \underset{\mathbf{2a\text{-}c}}{\mathrm{HgX_2}} \xrightarrow{\mathrm{i}} \underset{\mathbf{3a\text{-}t}}{\mathrm{ArI}} + \mathrm{HX} + \mathrm{HgXI}$$

**Scheme 1.** *Reagents and conditions* : i, $CH_2Cl_2$, 20°C, overnight (*ca.* 14 h).

As mercury(II) salts, commercially available mercury(II) chloride and nitrate (**2a** or **2b**, respectively) or easily prepared triflate (**2c**)[23] were used. In the case of arenes bearing electron-donating substituents ( **1f**, **h**, **i** and **1k-r**) the iodine-mercury(II) chloride combination was effective enough (Table 1, entries 6, 8, 9 and 11-19). However, for benzene itself (**1a**) or mono-, di-alkylated systems (**1b-d**) and even 1,2,3-trimethylbenzene (**1e**) was necessary to use the iodine-mercury(II) nitrate combination in order to get the corresponding iodoarene (Table 1, entries 1-5). This combination was also adequate for the iodination of *p*-methoxyacetophenone (**1j**) or 1,3-dimethylnaphthalene (**1t**): in both cases the iodination took place on the most activated aromatic ring (Table 1, entries 10 and 21, respectively). Finally, in the cases in which neither mercury(II) chloride nor nitrate were reactive enough for the activation of the iodine molecules, mercury(II) triflate was used for this purpose; thus, when the aromatic starting material beared electron-withdrawing groups, such as chlorine ( **1g**) or an ester moiety ( **1s**), the iodination was successful using the iodine-mercury(II) triflate combination (Table 1, entries 7 and 20, respectively). Finally, nitrobenzene was resistant to the iodination reaction even under the action of this last mercury(II) salt.

Concerning the regiochemistry of the iodination reaction, alkylated arenes gave only an iodinated product at the *ortho* or *para* position (Table 1, entries 1, 3-6 and 21) except in the case of toluene ( **1b**) in which a mixture of both regioisomers was obtained (Table 1, entry 2). Oxygen- or nitrogen-containing substituents gave only the corresponding *para*-iodination, unless this position was occupied: in these cases the *ortho*-iodination took exclusively place (Table 1, entries 8-11 and 13-19). In the case of aniline ( **1k**) was necessary tho use an excess of the arene (1:10) in order to obtain 4-iodoaniline (**3k**): under the standard conditions a mixture of products **3k'** and **3k''**, resulting from *ortho*- and 2,4-diiodination was, respectively, isolated (Table 1, entry 12; compare to entry 11). For chlorobenzene ( **1g**) a mixture of 4- or 2-iodo-derivatives (**3g** and **3g'**) was formed, the last one being the major compound (Table 1, entry 7). On the other hand, ethyl benzoate (**1s**) was iodinated at the *metha*-position as expected (Table 1, entry 20). Finally, only in one case, for the iodination of compound **1t** ,we obtained the corresponding 2-nitro derivative **3t'** together with the iodination product **3t** (Table 1, entry 21 and footnote g): steric hindrance is the probable cause of this strange behaviour.

**Table 1.** Preparation of Iodoarenes **3**.

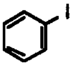
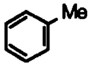
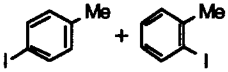
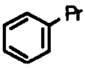
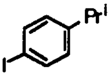
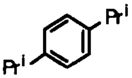
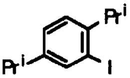
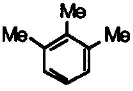
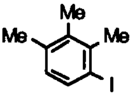
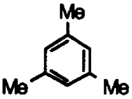
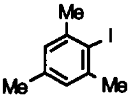
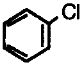
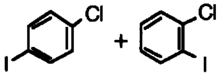
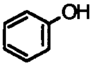
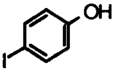
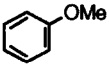
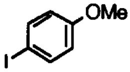
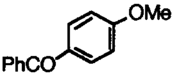
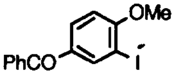
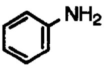
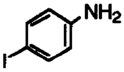
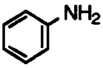
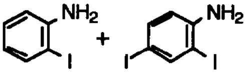
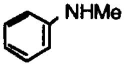
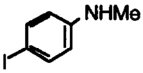
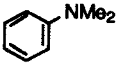
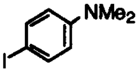
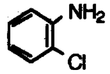
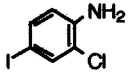
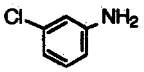
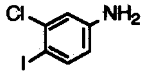
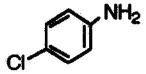
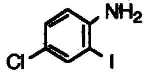
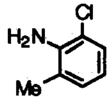
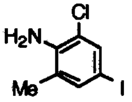
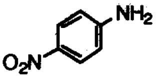
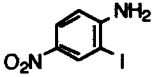
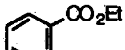
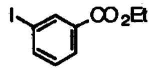
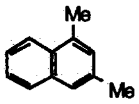
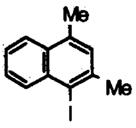
| | ArH | | $HgX_2$ | | Product[a] | | |
|---|---|---|---|---|---|---|---|
| Entry | no. | formula | no. | X[b] | no. | formula | yield (%)[c] |
| 1 | **1a** |  | **2b** | $NO_3$ | **3a** |  | 52 |
| 2 | **1b** |  | **2b** | $NO_3$ | **3b+3b'** |  | 92 (1.9:1)[d] |
| 3 | **1c** |  | **2b** | $NO_3$ | **3c** |  | 73 |
| 4 | **1d** |  | **2b** | $NO_3$ | **3d** |  | 76 |
| 5 | **1e** |  | **2b** | $NO_3$ | **3e** |  | 98 |
| 6 | **1f** |  | **2a** | Cl | **3f** |  | 54 |
| 7 | **1g** |  | **2c** | Tf | **3g+3g'** |  | 75 (11.5:1)[d] |
| 8 | **1h** |  | **2a** | Cl | **3h** |  | 71 |
| 9 | **1i** |  | **2a** | Cl | **3i** |  | 92 |
| 10 | **1j** |  | **2b** | $NO_3$ | **3j** |  | 84 |
| 11[e] | **1k** |  | **2a** | Cl | **3k** |  | 44[f] |
| 12 | **1k** |  | **2a** | Cl | **3k'+3k''** |  | 34 (1.3:1) |
| 13 | **1l** |  | **2a** | Cl | **3l** |  | 75 |
| 14 | **1m** |  | **2a** | Cl | **3m** |  | 83 |

**Table 1** (cont.)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15 | **1n** |  | **2a** | Cl | **3n** |  | 43 |
| 16 | **1o** |  | **2a** | Cl | **3o** |  | 45 |
| 17 | **1p** |  | **2a** | Cl | **3p** |  | 48 |
| 18 | **1q** |  | **2a** | Cl | **3q** |  | 37 |
| 19 | **1r** |  | **2a** | Cl | **3r** |  | 35 |
| 20 | **1s** |  | **2c** | Tf | **3s** |  | 83 |
| 21 | **1t** |  | **2b** | $NO_3$ | **3t** |  | 34[g] |

[a] The isolated products **3** were >95% pure (GLC and 300 MHz $^1$H NMR). [b] Tf=$CF_3SO_3$. [c] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting arene **1**; in parenthesis the corresponding regioisomers ratio after chromatographic separation. [d] Regioisomers ratio determined by GLC; the minor isomer could not be obtained in pure form. [e] An excess of aniline (**1k**/**2a**: 10/1) was used. [f] Isolated yield based on the mercury(II) salt **2a**. [g] 1,3-Dimethyl-2-nitronaphthalene (**3t'**) was also obtained (44%).

From a mechanistic point of view, we think that the first process is an activation of the iodine molecule, which is polarised by the soft-soft interaction with the mercury(II) salt increasing the electrophility of the iodine and , consequently, its reactivity toward the starting arene. Another posible mechanistic pathway would involve a two-steps reaction; first an aromatic mercuration followed by an iododemercuration process[15]. However, the last possibility can be ruled out, at least in the case of non-activated arenes, because their reaction in absence of iodine did not take place under the same standard reaction conditions (for instance, using alkylated arenes as starting material).

From the results included in this paper we concluded that the iodine-mercury(II) salt combination[22] is an adequate reagent for the direct iodination of aromatic compounds. According to the ionic character of the mercury(II) salt we found that the reactivity of the combination decreases in the series triflate>nitrate>chloride.

## EXPERIMENTAL PART

*General*.- M.P.'s are uncorrected and were measured on a Reichert thermovar apparatus. IR spectra were determined with a Pye Unicam SP3-200 spectrometer. $^1$H and $^{13}$C NMR spectra were recorded in a Bruker AC-300 using $CDCl_3$ as solvent and $SiMe_4$ as internal standard; chemical shifts are given in $\delta$ (ppm) and the coupling constants (*J*) are measured in Hz. MS (EI) were recorded with a Hewlett Packard EM/CG HP-5988A spectrometer. The purity of volatile distilled products and the chromatographic analyses (GLC) were determined with a flame ionization detector and a 12 m HP-1 capillary column (0.2 mm diam., 0.33 µm film thickness), using nitrogen (2 ml/min) as the carrier gas,$T_{injector}$=270°C, $T_{column}$=60°C (3 min) and 60-270°C (15°C/min). Thin layer chromatography (TLC) was carried out on Scheleicher & Schnell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel, using a mixture of hexane/ethyl acetate as eluant; $R_f$ values are given under these conditions. Microanalyses were performed in the Microanalyses Service at the University of Alicante. All reagents were commercially available (Aldrich) and were of the best grade.

*Preparation of Iodinated Arenes* **3**. *General Procedure*.- To a suspension of the aromatic derivative **1** (2.5 mmol[24]) and the mercury(II) salt **2** (2.5 mmol) in dichloromethane (10 ml) was added iodine (0.79 g, 2.5 mmol). The mixture was stirred overnight (*ca.* 14 h) at room temperature. The formed precipitate was filtered off and the filtrate washed with aqueous 0.1 M sodium thiosulfate (5 ml) and a saturated aqueous solution of potassium iodide (5 ml). The organic layer was dried with sodium sulfate, the solvent was evaporated under reduced pressure (15 Torr), and the residue was purified by distillation, column chromatography (silica gel, hexane/ethyl acetate) or recrystallisation (hexane/chloroform) to give compounds **3**. Compounds **3a-b**, **3g-i**, **3k** and **3k'** were characterised by comparison of their spectroscopic data (IR, $^1$H and $^{13}$C NMR) with commercially available authentic samples (Aldrich). For the rest of compounds **3**, yields are included in Table 1; physical and spectroscopic data follow[25].

*4-Isopropyliodobenzene* (**3c**)[26]: $R_f$ 0.68 (hexane); $\nu_{max}$ (film) 2950, 1640, 1000, 815, 710 cm$^{-1}$; $\delta_H$ 1.25 [6 H, d, *J*=6.9, $(CH_3)_2CH$], 2.85 [1 H, heptet, *J*=6.9, $CH(CH_3)_2$], 6.96 (2 H, d, *J*=8.3, ArH), 7.59 (2 H, d, *J*=8.3, ArH); $\delta_C$ 23.8 ($CH_3$), 33.7 (CH), 90.6 (CI), 128.6, 137.3, 148.5 (ArC); *m/z* 246 (M+, 74%), 231 (100), 104 (73), 77 (21), 51 (16) .

*2,5-Diisopropyliodobenzene* (**3d**)[27]: $R_f$ 0.74 (hexane); $\nu_{max}$ (film) 3030, 2950, 1600, 1400, 1020, 830, 670 cm$^{-1}$; $\delta_H$ 1.20 [6 H, d, *J*=6.8, $(CH_3)_2CH$], 1.22 [6 H, d, *J*=7.0, $(CH_3)_2CH$], 2.67-2.8 5 [1 H, m, $CH(CH_3)_2$], 3.10-3.19 [1 H, m, $CH(CH_3)_2$], 7.14 (1 H, s, ArH), 7.15 (1 H, d, *J*=1.6, ArH), 7.67 (1 H, d, *J*=1.6, ArH); $\delta_C$ 23.15 [$(CH_3)_2CH$], 23.6 [$(CH_3)_2CH$], 33.2 [$CH(CH_3)_2$], 37.65 [$CH(CH_3)_2$], 101.25 (CI), 125.6, 126.7, 137.5, 147.6, 148.4 (ArC); *m/z* 288 (M+, 50 %), 273 (100), 131 (17), 91 (10).

*2,3,4-Trimethyliodobenzene* (**3e**)[28]: $R_f$ 0.60 (hexane); $\nu_{max}$ (film) 2920, 1630, 1450, 1130, 990, 800 cm$^{-1}$; $\delta_H$ 2.19 (3 H, s, $CH_3$), 2.25 (3 H, s, $CH_3$), 2.41 (3 H, s, $CH_3$), 6.64 (1 H, d, *J*=8.0, ArH), 7.56 (1 H, d, *J*=8.0, ArH); $\delta_C$ 17.3 ($CH_3$), 20.5 ($CH_3$), 25.8 ($CH_3$), 99.25 (CI), 129.15, 136.15, 136.2, 136.55, 138.70 (ArC); *m/z* 246 (M+, 100 %), 245 (15), 127 (10), 119 (37), 91 (27), 77 (12).

*2,4,6-Trimethyliodobenzene* (**3f**)[29]: m.p. 29-30°C (hexane/chloroform); $\nu_{max}$ (KBr) 3020, 2910, 1460, 1370, 1005, 850, 755, 685 cm$^{-1}$; $\delta_H$ 2.25 (3 H, s, $CH_3$), 2.42 (6 H, s, 2x$CH_3$), 6.86 (2 H, s, ArH); $\delta_C$ 20.8 ($CH_3$), 29.45 (2x$CH_3$), 104.2 (CI), 127.9, 137.25, 141.7 (ArC); *m/z* 246 (M+, 100%), 119 (53), 117 (18), 91 (41), 51 (12).

*3-Iodo-4-methoxybenzophenone* (**3j**)[25]: m.p. 71-72°C (hexane/chloroform); $\nu_{max}$ (KBr) 3025, 3005, 2925, 1650, 1585, 1260, 1015, 700 cm$^{-1}$; $\delta_H$ 3.95 (3 H, s, $OCH_3$), 6.86 (1 H, d, *J*=8.6, ArH), 7.21 (2 H, t, *J*=7.2, ArH), 7.33 (1 H, td, *J*=7.1, 1.4, ArH), 7.73 (2 H, dd, *J*=7.2, 1.4, ArH), 7.81 (1 H, dd, *J*=8.6, 1.9, ArH), 8.28 (1 H, d, *J*=1.9, ArH); $\delta_C$ 56.5 ($OCH_3$), 85.6 (CI), 109.8, 128.2, 129.6, 131.7, 132.15, 132.4, 137.5, 141.5, 161.25 (ArC), 193.9 (C=O); *m/z* 338 (M+, 77%), 261 (100), 105 (31), 77 (29).

*2,4-Diiodoaniline* (**3k''**)[30]: m.p. 95-96°C (hexane/chloroform); $\nu_{max}$ (KBr) 3370, 3260, 1610, 1470, 1380, 1220, 1020, 760 cm$^{-1}$; $\delta_H$ 4.12 (2 H, br s, $NH_2$), 6.51 (1 H, d, *J*=8.4, ArH), 7.35 (1 H, dd, *J*=8.4, 1.9, ArH), 7.93 (1 H, d, $J$=1.9, ArH); $\delta_C$ 78.9 (CI), 84.85 (CI), 116.2, 137.8, 145.7, 146.45 (ArC); *m/z* 345 (M$^+$, 100%), 218 (16), 91 (21), 63 (10).

*4-Iodo*-N-*methylaniline* (**3l**)[31]: $R_f$ 0.38 (hexane/ethyl acetate, 10/1); $\nu_{max}$ (film) 3450, 2950, 1590, 1495, 1310, 1255, 810, 760 cm$^{-1}$; $\delta_H$ 2.82 [3 H, s, $NCH_3$], 3.69 (1 H, br s, NH), 6.41 (2 H, d, $J$=8.9, ArH), 7.42 (2 H, d, $J$=8.9, ArH); $\delta_C$ 30.5 ($CH_3$), 77.7 (CI), 114.6, 137.7, 148.8 (ArC); *m/z* 233 (M$^+$, 100%), 232 (35), 105 (10), 77 (12).

*4-Iodo*-N,N-*dimethylaniline* (**3m**)[32]: m.p. 66-67°C (hexane/chloroform); $\nu_{max}$ (KBr) 2880, 1590, 1485, 1350, 1225, 800 cm$^{-1}$; $\delta_H$ 2.90 [6 H, s, $N(CH_3)_2$], 6.48 (2 H, d, $J$=8.9, ArH), 7.45 (2 H, d, $J$=8.9, ArH); $\delta$C 40.35 [$N(CH_3)_2$], 77.2 (CI), 114.7, 137.5, 150.0 (ArC); *m/z* 247 (M$^+$, 100%), 246 (50), 119 (16), 77 (13), 42 (10).

*2-Chloro-4-iodoaniline* (**3n**)[33]: m.p. 68-70°C (hexane/chloroform); $\nu_{max}$ (KBr) 3465, 3370, 3000, 1605, 1300, 1210, 800, 730 cm$^{-1}$; $\delta_H$ 4.06 (2 H, br s, $NH_2$), 6.50 (1 H, d, $J$=8.4, ArH), 7.29 (1 H, dd, $J$=8.4, 1.8, ArH), 7.52 (1 H, d, $J$=1.8, ArH); $\delta_C$ 77.9 (CI), 117.35, 120.15, 136.25, 137.1, 142.65 (ArC); *m/z* 253 (M$^+$, 100%), 254 (30), 126 (38), 99 (14), 90 (47 ), 63 (28).

*3-Chloro-4-iodoaniline* (**3o**)[33]: m.p. 64-66°C (hexane/chloroform); $\nu_{max}$ (KBr) 3460, 3370, 3000, 1610, 1470, 1405, 1200, 900, 760 cm$^{-1}$; $\delta_H$ 4.16 (2 H, br s, $NH_2$), 6.46 (1 H, dd, $J$=8.4, 2.3, ArH), 6.72 (1 H, d, $J$=2.3, ArH), 7.51 (1 H, d, $J$=8.4, ArH); $\delta_C$ 81.0 (CI), 114.2, 119.9, 135.1, 139.59, 147.7 (ArC); *m/z* 253 (M$^+$, 100%), 255 (27), 126 (19), 90 (18), 63 (20).

*4-Chloro-2-iodoaniline* (**3p**)[33]: m.p. 42-43°C (hexane/chloroform); $\nu_{max}$ (KBr) 3470, 3370, 3010, 1610, 1475, 1215, 1110, 770, 690 cm$^{-1}$; $\delta_H$ 4.19 (2 H, br s, $NH_2$), 6.62 (1 H, d, $J$=8.6, ArH), 7.08 (1 H, dd, $J$=8.6, 2.2, ArH), 7.59 (1 H, d, $J$=2.2, ArH); $\delta_C$ 83.43 (CI), 114.92, 123.03, 129.27, 137.67, 145.48 (ArC); *m/z* 253 (M$^+$, 100%), 255 (34), 126 (33), 127 (24), 99 (19), 90 (18), 63 (20).

*2-Chloro-4-iodo-3-methylaniline* (**3q**)[25]: m.p. 61-62°C (hexane/chloroform); $\nu_{max}$ (KBr) 3480, 3390, 3000, 1610, 1475, 1210, 760, 640 cm$^{-1}$; $\delta_H$ 2.14 (3 H, s, $CH_3$), 4.03 (2 H, br s, $NH_2$), 7.25 (1 H, d, $J$=1.9, ArH), 7.42 (1 H, d, $J$=1.9, ArH); $\delta_C$ 17.5 ($CH_3$), 77.55 (CI), 119.75, 125.4, 134.75, 137.0, 141.0 (ArC); *m/z* 267 (M$^+$, 100 %), 140 (37), 104 (23), 77 (43), 51 (12).

*2-Iodo-4-nitroaniline* (**3r**)[34]: m.p. 104-105°C (hexane/chloroform); $\nu_{max}$ (KBr) 3450, 3340, 1610, 1300, 1100, 810, 680 cm$^{-1}$; $\delta_H$ 4.92 (2 H, broad s, $NH_2$), 6.69 (1 H, d, $J$=9.0, ArH), 8.04 (1 H, dd, $J$=9.0, 2.5, ArH), 8.58 (1 H, d, $J$=2.5, ArH); $\delta_C$ 80.5 (CI), 112.2, 125.7, 135.4, 139.1, 152.4 (ArC); *m/z* 264 (M$^+$, 100%), 234 (34), 91 (75), 52 (32).

*Ethyl 3-Iodobenzoate* (**3s**)[17b]: $R_f$ 0.57 (hexane/ethyl acetate, 10/1); $\nu_{max}$ (film) 3050, 2960, 1715, 1560, 1250, 740, 680 cm$^{-1}$; $\delta_H$ 1.40 (3 H, t, $J$=7.2, $CH_3$), 4.41 (2 H, q, $J$=7.2, $CH_2$), 7.17 (1 H, t, $J$=7.8, ArH), 7.86 (1 H, dd, $J$=7.8, 1.2, ArH), 8.00 (1 H, dd, $J$=7.8, 1.5, ArH), 8.37 (1 H, d, $J$=1.5, ArH); $\delta_C$ 14.25 ($CH_3$), 61.3 ($CH_2$), 93.7 (CI), 128.65, 129.95, 132.35, 138.4, 141.6 (ArC), 165.0 (C=O); *m/z* 276 (M$^+$, 70%), 248 (49), 231 (100), 203 (32), 76 (52), 50 (33).

*4-Iodo-1,3-dimethylnaphthalene* (**3t**): $R_f$ 0.62 (hexane/ethyl acetate, 20/1); $\nu_{max}$ (film) 3050, 2900, 1600, 1400, 1260, 1050, 890, 640 cm$^{-1}$; $\delta_H$ 2.56 (3 H, s, $CH_3$), 2.60 (3 H, s, $CH_3$), 7.15 (1 H, s, ArH), 7.41-7.52 (2 H, m, ArH), 7.83 (1 H, dd, $J$=8.0, 0.9, ArH), 8.20 (1 H, dd, $J$=8.8, 1.2, ArH); $\delta_C$ 19.1 ($CH_3$), 30.2 ($CH_3$), 103.15 (CI), 124.25, 125.5, 127.3, 129.0, 131.65, 132.5, 134.5, 134.8, 140.25 (ArC); *m/z* 282 (M$^+$, 100%), 153 (38), 155 (34), 127 (19).

*1,3-Dimethyl-2-nitronaphthalene* (**3t'**): m.p. 75-76°C (hexane); $\nu_{max}$ (KBr) 3005, 1600, 1520, 1210, 830, 760, 670 $cm^{-1}$; $\delta_H$ 2.43 (3 H, s, $CH_3$), 2.64 (3 H, s, $CH_3$), 7.15 (1 H, s, ArH), 7.52-7.57 (2 H, m, ArH), 7.71 (1 H, dd, $J$=7.2, 2.0, ArH), 7.95 (1 H, dd, $J$=7.8, 2.8, ArH); $\delta_C$ 17.65 ($CH_3$), 19.3 ($CH_3$), 121.6 , 124.15, 124.65, 126.3, 127.0, 127.9, 128.5, 131.1,137.5, 146.5 (ArC); *m/z* 201 ($M^+$,58%), 184 (10), 154 (21), 115 (42), 77 (14), 63 (16) (Found: C, 71.1; H, 5.6; N, 6.7. $C_{12}H_{11}NO_2$ requires: C, 71.63; H, 5.51; N, 6.96).

## ACKNOWLEDGEMENTS

This work was supported by DGICYT (no. PB91-0751). We thank Prof. C. Nájera (University of Alicante) for fruitful discussions.

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24. For compound **3a**, benzene (**1a**; 10 ml) was used as solvent instead of dichloromethane.
25. Correct microanalytical figures could not be obtained for the pure (GLC and 300 MHz $^1$H NMR) new compounds **3j** (Found: C, 48.6; H, 3.2. $C_{14}H_{11}IO_2$ requires: C, 49.73; H, 3.28) and **3q** (Found: C, 31.6; H, 2.6; N, 4.2. $C_7H_7ClNI$ requires: C, 31.43; H, 2.64; N, 5.24).
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(*Received in UK* 31 *December* 1993; *revised* 11 *February* 1994; *accepted* 18 *February* 1994)