PALLADIUM-CATALYZED AMINATION OF PHOTOCHROMIC TRIFLATE-SUBSTITUTED 3*H*-NAPHTHO[2,1-*b*]PYRANS

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Abstract: The conversion of triflic 3*H*-naphtho[2,1-*b*]pyrans to the corresponding piperazine derivatives, using the combination of palladium acetate/BINAP as catalyst is reported. Compared to the 3,3-diphenyl-*3H*-naphtho[2,1-b]pyran, the amino group on the 8-position of naphthopyran part induces a significant bathochromic shift of the absorption of the coloured form.

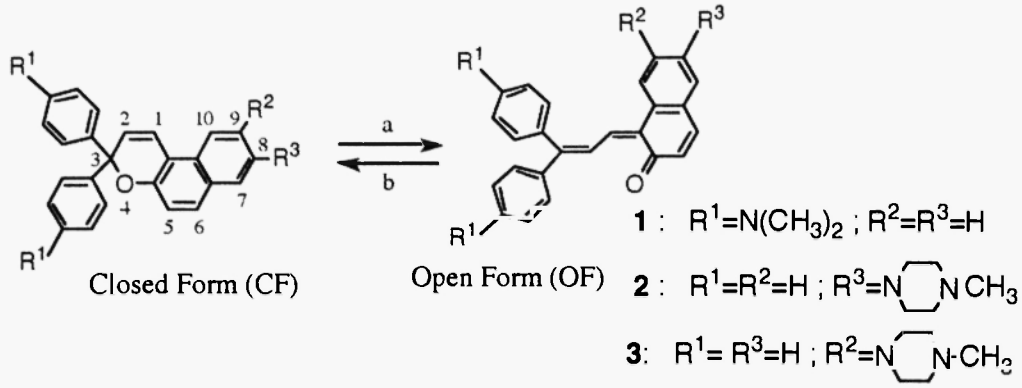
Introduction :

3*H*-naphtho[2,1-*b*]pyrans have known these last years an important development due to their interesting photochromic properties (1) and their application in the field of variable optical transmission materials (2). In a previous work (3), we reported the synthesis and the photochromic behaviour of 3*H*-naphtho[2,1-*b*]pyrans, carrying geminal 4-(N,N-dimethylamino)phenyl groups on the sp^3-carbon. Taking into account the photochromic behaviour of this compound (particularly the high bathochromic shift of the visible absorption of the coloured form), we decided to introduce amino groups on the naphthopyran part of the molecule and to study their influence on the photochromic properties. Regarding the literature, it appeared that the carbon-nitrogen bond formation can be achieved from palladium(0)-catalyzed cross coupling. Recently, many developments in palladium-catalyzed aminations of aryl halides (4) and aryl triflates (5) received considerable attention. The last approach has been used in this work because of the more attractive synthetic potentialities of triflates (for instance in the frame of Suzuki (6) and Stille (7,8) couplings).

Results and discussion :

Triflation of the commercially available 2,6-dihydroxynaphthalene with trifluoromethanesulfonic anhydride in pyridine (9) at -10°C, gave a mixture of two products: the ditriflate **4** and the triflic naphthol **5**, which were readily separated by column chromatography on silica gel, employing Et_2O/Pentane mixtures of gradually increased polarity (5 to 50%). Compounds **4** and **5** were

obtained in 24% and 48% yield respectively. Similarly, triflation of the commercial 2,7-dihydroxynaphthalene led to the ditriflate **6** (27% yield) and to the naphthol 7 (39% yield).



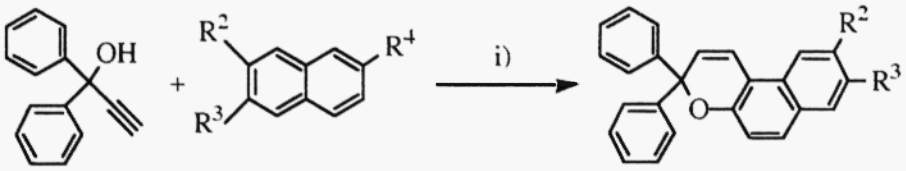
Scheme 1. a) $h\nu_1$ (UV); b) $h\nu_2$ (visible) or heat

The preparation of the triflic 3*H*-naphtho[2,1-*b*]pyrans was achieved by one pot method, starting from the suitable triflic naphthol and the commercial 1,1-diphenylpropyn-1-ol (10), in an inert solvent (toluene) under acid catalysis (11). *Para*-toluenesulfonic acid (PTSA) is generally used. We pointed out that the replacement of PTSA by pyridinium *para*-toluenesulfonate (PPTS) (12), and the use of dichloromethane as solvent, allow to increase significantly yields of the chromenisation reaction. The condensation of the triflic naphthols **5** and **7** with 1,1-diphenylpropyn-1-ol, in refluxing CH_2Cl_2 in the presence of a catalytic amount of PPTS, afforded the triflic 3*H*-naphtho[2,1-*b*]pyrans **8** and **9** (13) respectively with yields over 70% (Scheme 2) (after purification on silica gel using 10% ethyl acetate in pentane as eluent).

Coupling reaction of the triflic chromenes with amines was accomplished using the palladium-catalyzed procedure described by Buchwald (14). In this reaction, the catalytic system consisted in the combination of $Pd(OAc)_2$ and BINAP (15) (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl). The reaction of **8** and **9** with N-methylpiperazine, employing a mixture of $Pd(OAc)_2$/BINAP (2 mole% Pd) and NaOtBu (1.4 eq) in toluene at 80°C for 16h, gave the corresponding amino derivatives **2** and **3** (16) with 41% and 72% yields respectively.

As expected, chromenes **2** and **3** undergo photochromic properties in toluene at room temperature (continuous irradiation using a 150 W Xenon lamp). The maximum absorption (λ_{max}) of the coloured form for **2** and **3** are respectively 511 nm and 436 nm (in toluene). It is interesting to notice that the introduction of an amino group in the 8-position induces a high bathochromic shift (~+80 nm) compared to the unsubstituted 3,3-diphenyl-3*H*-naphtho[2,1-b]pyran (scheme 1, $R^1=R^2=R^3=H$) (λ_{max}= 432 nm, toluene) (3). In contrast, no change of the absorption is observed when the amino group is linked to the 9-position. It seems that the electronic effect of the substituent

fixed in the 8-position is more important due to a better conjugation with the π system of the photomerocyanine.



R^2=H ; R^3=R^4=OTf **4**
R^2=H ; R^3=OTf ; R^4=OH **5**
R^2=R^4=OTf ; R^3=H **6**
R^2=OTf ; R^3=H ; R^4=OH **7**

R^2=H ; R^3=OTf **8** (71%)
R^2=OTf ; R^3=H **9** (74%)

Scheme 2. i) CH_2Cl_2, PPTS, 5 days, heat.

Conclusion :

In conclusion, the cross coupling reaction using Pd(0) as catalyst can be applied to elaborated molecules as 3*H*-naphtho[2,1-*b*]pyrans and opens new perspectives for structure and photochromic property modifications in this family of compounds.

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13. Satisfactory ^{1}H NMR, ^{13}C NMR, IR and elemental analysis data were obtained.

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15. $Pd(OAc)_2$ and chelating (R)-(+)-2,2μ-Bis(diphenyl-phosphino)-1,1μ-Binaphthyl used in that work are commercially available (Aldrich and Acros respectively).

16. **2**: 41%, recryst. from MeOH/cyclohexane, mp: 209.5-210.1°C. $C_{30}H_{28}N_2O$. Mw : 432.56 Elemental analysis : Calc : H: 6.52, C : 83.20, N : 6.48 ; found : H : 6.45, C : 83.30, N : 6.50. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm): 2.32 (s, 3H), 2.58 (t, J=4.9 Hz, 4H), 3.19 (t, J=4.9 Hz, 4H), 6.19 (d, J=9.9 Hz, 1H), 6.97 (d, J=2.4 Hz, 1H), 7.07 (d, J=8.8 Hz, 1H), 7.12-7.50 (m, 13H), 7.78 (d, J=9.2 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm): 45.74 (CH_3), 49.33 ($2CH_2$), 54.93 ($2CH_2$), 82.32 (C), 111.85 (CH), 114.13 (C), 118.69, 119.65, 120.25, 122.38 (CH), 124.85 (C), 127.00 (4CH), 127.47 (2CH), 127.97 (CH), 128.06 (4CH), 128.64 (CH), 130.25 (C), 144.92 (2C), 147.12, 149.08 (C). **3**: 72%, recryst. from MeOH/cyclohexane, mp: 139-140.3°C. $C_{30}H_{28}N_2O$. Mw : 432.56 Elemental analysis : Calc : H: 6.52; C : 83.20, N : 6.48 ; found : H : 6.58, C : 83.15, N : 6.41. ^{1}H NMR (250 MHz, $CDCl_3$): δ(ppm): 2.17 (s, 3H), 2.42 (t, J=4.9 Hz, 4H), 3.12 (t, J=4.9 Hz, 4H), 6.02 (d, J=9.9 Hz, 1H), 6.80 (d, J=8.7 Hz, 1H), 6.87 (dd, J=2.3 Hz and J=9.0 Hz, 1H), 6.95-7.34 (m, 13H), 7.37 (d, J=9.0 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ(ppm): 46.35 (CH_3), 49.42 ($2CH_2$), 55.30 ($2CH_2$), 82.54 (C), 104.32 (CH), 113.33 (C), 115.74, 116.84, 120.01 (CH), 124.43 (C), 127.24 (5CH), 127.68 (2CH), 128.28 (4CH), 129.59, 129.68 (CH), 131.27 (C), 145.22 (2C), 150.02, 151.39 (C).

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