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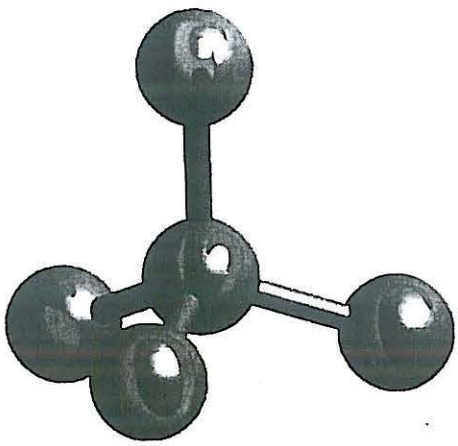


Palladium-catalyzed cyclisation and deprotection of *o*-halodiarylacetamides, obtained by C-N copper assisted coupling, to the corresponding 6*H*-thieno-[2,3-*c*]carbazole

Isabel C.F.R. Ferreira[a], Maria-João R.P. Queiroz[a] and Gilbert Kirsch[b]

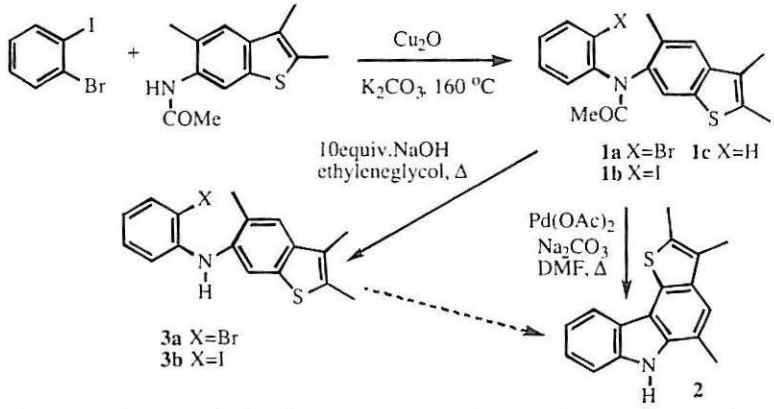
[a]Departamento de Química, Universidade do Minho, 4700-320 Braga, Portugal

[b]Groupe de Synthèse Organique et Hétérocyclique, Université de Metz, 57045 Metz, France

e-mail: mjrpq@quimica.uminho.pt

With the aim of obtaining potential anti-tumoural thienocarbazoles by a ring B convergent method of synthesis, *o*-halodiarylacetamides were prepared by copper assisted C-N coupling[1] from 2-bromo-iodobenzene and 6-acetamido-2,3,5-trimethylbenzo[*b*]thiophene, prepared from the 6-acetyl compound. A mixture of *o*-bromo and *o*-iododiarylacetamides **1a,b** was obtained (~40% yield) which was impossible to separate chromatography. Dehalogenation also occurred in the coupling reaction, **1c** being isolated (10%).

Palladium catalyzed cyclisation and deprotection of the mixture **1a,b** occurred in a one pot reaction giving 2,3,5-trimethyl-6*H*-thieno-[2,3-*c*]carbazole **2** in quantitative yield.



The same mixture **1a,b** was submitted to hydrolysis under drastic conditions, giving a mixture of the corresponding amine compounds **3a,b** that can also cyclise to compound **2**.

Thanks are due to FCT-IBQF-UM(Portugal), to Fundação Calouste Gulbenkian and to Escola Superior Agrária do I.P.Bragança for supporting in part I.C.Ferreira.

1- Peixoto, F.M.C. ; Queiroz, M.-J. R. P; Kirsch, G, *J.Chem.Res.*, 1998, (S)172-173, (M)0801-0812.

Palladium-catalyzed amination to obtain *o*-halodiarylamines precursors of thienocarbazoles

Isabel C.F.R. Ferreira[a], Maria-João R.P. Queiroz[a] and Gilbert Kirsch[b]

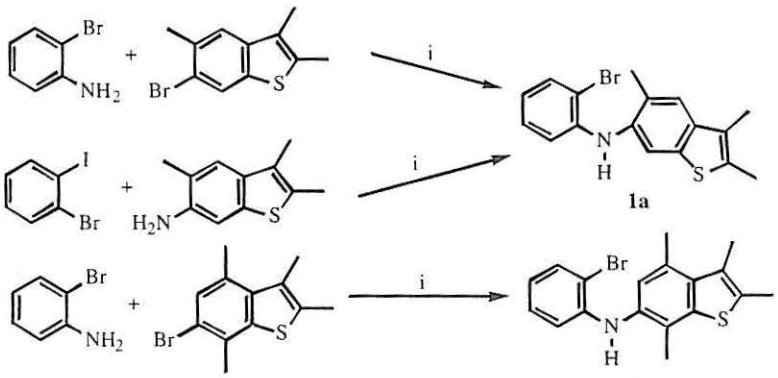
[a]Departamento de Química, Universidade do Minho, 4700-320 Braga, Portugal

[b]Groupe de Synthèse Organique et Hétérocyclique, Université de Metz, 57045 Metz, France

e-mail: mjrpq@quimica.uminho.pt

o-Bromodiarylamines **1** were prepared by palladium-catalyzed amination of 2-bromo-iodobenzene or 6-bromobenzo[*b*]thiophenes, using Buchwald conditions[1]. The yield for *o*-bromodiarylamine **1a** doubled when the starting materials were 2-bromo-iodobenzene and 6-amino-2,3,5-trimethylbenzo[*b*]thiophene (40%) instead of 2-bromoaniline and the corresponding 6-bromo benzo[*b*]thiophene (20%). No *o*-iododiarylamine was isolated neither from the experiment using 2-bromo-iodobenzene as starting material nor from the one using 2-iodoaniline and 6-bromo benzo[*b*]thiophene, in this case only decomposition took place.

o-Bromodiarylamine **1b** was obtained in low yield (10%) using 6-bromo-2,3,4,7-tetramethyl benzo[*b*]thiophene.



i) $Pd(OAc)_2$, BINAP, *t*-OBuNa, dry toluene, Δ, Ar

1a **1b**

Compounds **1a** and **1b** can be cyclised to the corresponding potential anti-tumour thienocarbazoles by an intramolecular Heck reaction[2].

Thanks are due to the FCT-IBQF-UM(Portugal) and to Escola Superior Agrária do I.P.Bragança for supporting in part I.C.Ferreira.

1- Wolfe, J., Buchwald, L., *J. Org.Chem.*, 2000, *65*, 1144-1157.

2- Iwaki, T.; Yasuhara, A.; Sakamoto, T., *J. Chem.Soc. Perkin 1*, 1999, 1505-1510.