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New Synthetic Uses of 2,3-Dihydro-3-Oxobenzo[B]Thiophene

STEPHANIE DEPRETS, NACHWA JARKAS and GILBERT KIRSCH

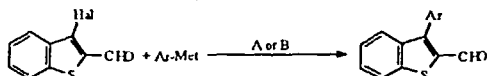
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Synthesis of benzo[b]thiophenes functionalized in the position 3 and new polycyclic systems are discussed.

Keywords: Vilsmeier-Haack-Arnold; palladium-catalysed coupling; Pomeranz-Fritsch

The 2-carboxaldehyde-3-halogeno derivatives **2(a-b)** are conveniently obtained by Vilsmeier-Haack-Arnold reaction^[1] applied to the 2,3-dihydro-3-oxobenzo[b]thiophene **1**. Compounds **2(a-b)** are reacted either under Stille conditions^[2] (with an organostannane) or under Suzuki conditions^[3] (with an organoboronic acid). The results are summarized in table I.

Table I : Stille and Suzuki cross-coupling reactions of compounds **2(a-b)**



A : Ar-SnBu₃, Pd(PPh₃)₄ (0.02 mol%), toluene, reflux

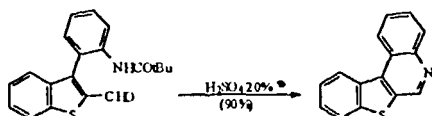
B : Ar-B(OH)₂, Pd(PPh₃)₄ (0.02 mol%), K₂CO₃ 2N (2 eq.), DME, reflux

Compound	Hal	Ar-Met	Yield (%)
3a	Cl	Ph-SnBu ₃	39
3a	Br	Ph-SnBu ₃	92
3b	Cl	Ph-B(OH) ₂	5
3b	Br	Ph-B(OH) ₂	82

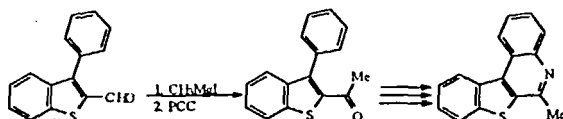
A variety of organoboronic acids, including 2-thienyl boronic acid and 2-furyl boronic acid were coupled with the 3-bromo-2-carboxaldehyde benzo[b]thiophene in very good yields.

The 2-carboxaldehyde-3-phenylbenzo[b]thiophene is a useful starting material for the synthesis of benzothieno[2,3-c]quinoline (Scheme 1) and 6-methylbenzothieno[2,3-c]quinoline (Scheme 2).

Scheme 1 : Access to benzothieno[2,3-c]quinoline

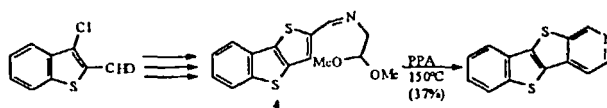


Scheme 2 : Access to 6-methylbenzothieno[2,3-c]quinoline

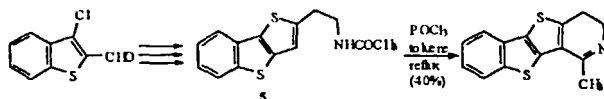


Analogues of pyridocarbazoles were synthesized from 2-carboxaldehyde-3-chlorobenzo[b]thiophene by a procedure involving a Pomeranz-Fritsch cyclisation^[4] of Schiff's base **4** (Scheme 3) or by a Bischler-Napieralski cyclisation of amide **5** (Scheme 4).

Scheme 3 : Synthesis of benzothieno[2,3-f]thieno[2,3-c]pyridine



Scheme 4: Synthesis of 1-methyl-3,4-dihydro-benzothieno[3,2-g]thieno[3,2-c]pyridine



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