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Preliminary communication

Synthesis of aryl- and vinyl-sydnones. Cross-coupling of 4-copper-3-phenylsydnone with aryl and vinyl halides catalyzed by palladium(0) complexes

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Abstract

A general method is suggested for introduction of substituents into the 4-position of 3-phenylsydnone by palladium(0) catalyzed cross-coupling of 4-copper-3-phenylsydnone with aryl iodides and vinyl bromides.

Sydnones are the most interesting representatives of mesoionic compounds [1]. However, up to now there have been no preparative methods for introduction of

Table 1

Compound II–V

Compound	M.p. (°C)	Yield (%)	Analyses (Found(calc.) (%))			^{1}H NMR (in $CDCl_3$) (ppm)
			C	H	N	
II	189–192	90				7.43–7.72 (m, 10 H)
III	167–170	92	59.34 (59.36)	3.34 (3.18)	14.74 (14.84)	7.48 (d, *J* 9 Hz, 2H), 7.50–7.77 (m, 5H), 8.13 (d, *J* 9Hz, 2H)
IV	146–148	91	66.89 (67.17)	4.28 (4.48)	10.32 (10.45)	3.77 (c, 3H), 6.81 (d, *J* 10.6 Hz, 2H), 7.22(d, *J* 10.6 Hz, 2H), 7.44–7.69 (m, 5H)
V	179–181	86	72.73 (72.73)	4.54 (4.54)	10.66 (10.61)	6.59 (d, *J* 16.2 Hz, 1H), 7.35–7.41 (m, 5H), 7.59–7.73 (m, 5H), 7.79 (d, *J* 16.2 Hz, 1H)

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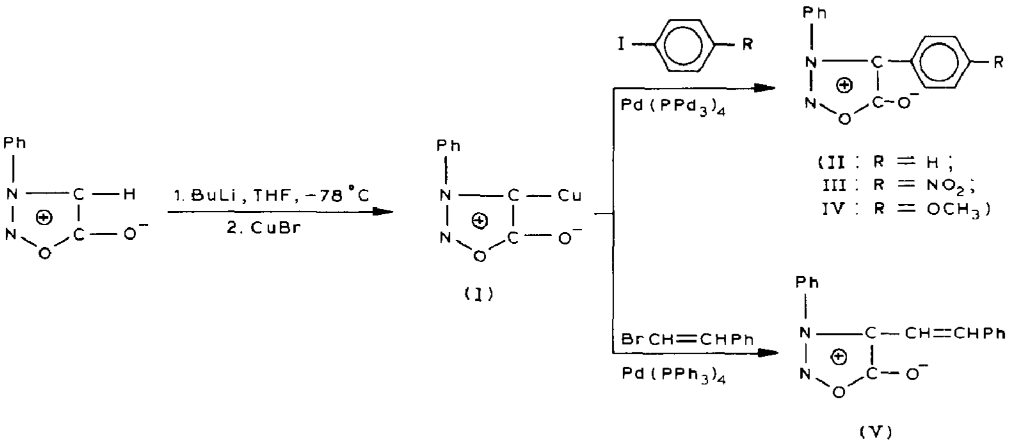
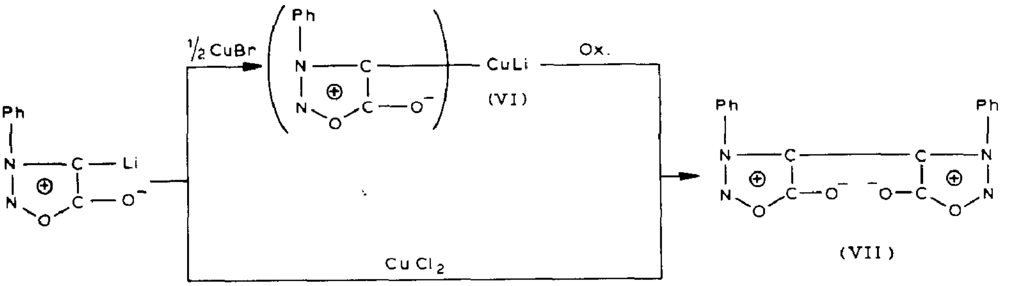


aryl and vinyl groups into 4-position of sydnone. The C-functionalisation of sydnones by 4-lithio-3-phenylsydnone is limited by the low stability of lithiosydnones in solution. They react only with very reactive organoelements compounds at low temperatures [1–4]. The conventional route to 3,4-disubstituted sydnones involves preparation of the scarcely available 2-substituted *N*-phenyl-*N*-nitrosoglicines.

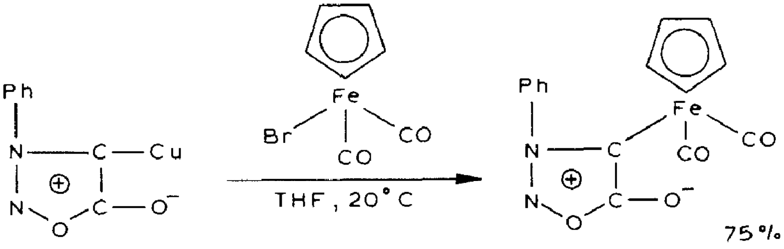
We first obtained 4-copper-3-phenylsydnone (I) in situ by the reaction of 4-lithio-3-phenylsydnone with CuBr. I is stable in solution up to 120 °C. It reacts with aryl iodides and vinyl bromides in the presence of $Pd(PPh_3)_4$ at room temperature to give 4-aryl(vinyl)-3-phenylsydnones. In the absence of the palladium, compound I reacts only with 4-iodonitrobenzene on heating in HMPA (120 °C) for a long time to yield the cross-coupling product (20%).

Depending on the reagent ratio, the action of CuBr on 4-lithio-3-phenylsydnone leads to I or cuprate VI, which on oxidation, forms the dimer bis-sydnone (VII); the latter can be also obtained by direct oxidation of 4-lithio-3-phenylsydnone with $CuCl_2$.



The yield of bis-sydnone is as low as 25%. VII has also been prepared from 4-bromosydnone [5].

I reacts with cyclopentadienyl(dicarbonyl) iron bromide to give σ-sydnon-4-yl-cyclopentadienyl(dicarbonyl)iron. This method is preferable to that requiring the use of 4-lithio-3-phenylsydnone [6].



Experimental

The general procedure for the synthesis of 4-aryl(vinyl)-3-phenylsydnones. A 1.2 *N* solution of n-BuLi (1.07 ml, 1.2 mmol) in benzene was added dropwise at −78°C to a stirred solution of 3-phenylsydnone (0.2 g, 1.2 mmol) in THF (20 ml). The mixture was stirred for 10 min, and then CuBr (0.17 g, 1.2 mmol) was added. After the mixture had been at room temperature for 15 min $Pd(PPh_3)_4$ (0.07 g, 0.06 mmol), and then aryl(vinyl) halide (1.2 mmol) were added. After stirring for 2 h the solvent was evaporated off in vacuum, and the residue was separated by column chromatography on silica gel ($CHCl_3$) (Table 1).

Bis-sydnone. A 1.3 *N* solution of n-BuLi (0.95 ml, 1.2 mmol) in benzene was added dropwise to a stirred solution of 3-phenylsydnone (0.2 g, 1.2 mmol) in THF (20 ml) at −78°C. After 10 min, CuBr (0.09 g, 0.6 mmol) was added and then the mixture was kept at room temperature for 15 min. The mixture was oxidized by dry air or $CuCl_2$ (6.0 mmol) for 1 h. The solvent was evaporated off in vacuum, and the residue was separated by column chromatography on silica gel ($CHCl_3$) to yield bissydnone (25%). Similar oxidation of 4-lithio-3-phenylsydnone by $CuCl_2$ gives bis-sydnone in a 24% yield, m.p. 182,5–183°C. MS: $m/e = 322$ $[M]^+$, 264 $[M-\mathrm{NOCO}]^+$, 206 $[M-2\mathrm{NOCO}]^+$, 103 $[\mathrm{PhNC}]^+$, 91 $[\mathrm{PhN}]^+$, 77 $[\mathrm{Ph}]^+$. Anal. Found: C, 59.61; H, 3.11; N, 17.41. $C_{16}H_{10}N_4O_4$ calc.: C, 59.62; H, 3.11; N, 17.39%.

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