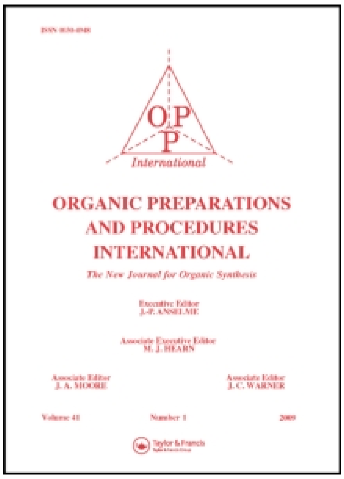

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

IMPROVED PREPARATION OF *tris*-(2-FURYL)PHOSPHINE

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To cite this Article Zapata, Antonio J. and Rondon, Ana C.(1995) 'IMPROVED PREPARATION OF *tris*-(2-FURYL)PHOSPHINE', Organic Preparations and Procedures International, 27: 5, 567 — 568
To link to this Article: DOI: 10.1080/00304949509458503
URL: http://dx.doi.org/10.1080/00304949509458503

IMPROVED PREPARATION OF *tris*-(2-FURYL)PHOSPHINE

Submitted by
(12/09/94)

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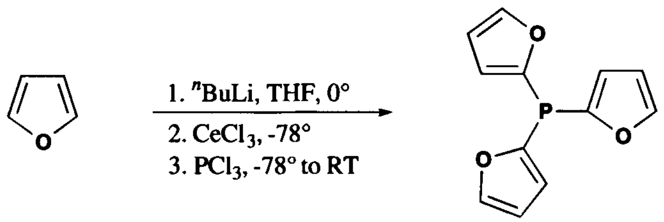
The palladium-catalyzed coupling of unsaturated electrophiles and organotin compounds, now commonly referred to as the Stille reaction, has become an important synthetic method in organic chemistry.[1] This reaction usually affords good yields of products and proceeds under mild conditions which allow the presence of a variety of functional groups on either coupling partner. Recently, the range of applications of this methodology was further extended by the interesting work of Farina and Krishnan.[2] In this study, large rate accelerations were observed using tris-(2-furyl)phosphine or triphenylarsine as palladium ligands, thus requiring lower temperatures to induce the coupling reaction. In connection with a research program directed towards the synthesis of 1,3-enynes using the Stille reaction, we found *tris*-(2-furyl)phosphine (TFP) to be more effective than triphenylarsine in the coupling of alkynyl bromides with vinyltin compounds. We also found that the reported preparations of this phosphine[3,4] were not satisfactory as they afford yields in the range of 30-40%. Consequently, we undertook the development of an improved preparation of this important and expensive additive.[5]



The published procedures for the synthesis of *tris*-(2-furyl)phosphine were based on the reaction of phosphorus tribromide[3] or trichloride[4] with α-furyllithium. Speculating that the low yields associate with these preparations could be attributed to undesirable side reactions caused by the basicity of the organolithium reagent, we decided to examined the reaction using the less basic organocerium(III) reagent[6] and phosphorus trichloride. Fortunately, this modification led to the desired *tris*-(2-furyl)phosphine in 74% yield.

EXPERIMENTAL SECTION

***tris*-(2-Furyl)phosphine.**- Cerium trichloride heptahydrate (60.00 g, 161.0 mmol) and a spin bar were placed in a 1 L two-necked flask. The flask and its contents were heated *in vacuo* (1 mmHg at 150°) with stirriring for approximately 2 hrs until a fine powder of anhydrous cerium trichloride was obtained. The flask was allowed to cool to room temperature under a dry nitrogen atmosphere and dry tetrahydrofuran was added (200 mL). In a separate 500 mL flask, a solution of α-furyllithium was prepared as follows: to a solution of furan (20.0 g, 294 mmol) in dry tetrahydrofuran (100 mL) at 0° was added, with stirring, under nitrogen, *n*-butyllithium (160 mmol, 200 mL of a 0.80 M solution in hexanes) and the mixture was stirred at room temperature for 1 hr. The resulting solution of the lithium reagent was transferred via cannula to the previously cooled (-78°) slurry of cerium trichloride. After stirring for 1 h at -78°, phosphorus trichloride (3.50 mL, 5.51 g, 40.1 mmol) was added and the reaction mixture was allowed to warm up to room temperature overnight. The reaction was poured into saturated aqueous ammonium chloride (300 mL). After partitioning the layers, the aqueous phase was extracted with ether (4 x 50 mL), and the combined organic layers were washed with brine (200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification of the oily residue by distillation afforded *tris*-(2-furyl)phosphine (6.88 g, 74%), bp 118-120°/1.25 mmHg, mp 63°, lit.[3] bp 136°/4 mmHg, mp 63°; lit.[4] bp 114°/0.6 mmHg).

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