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Alkynyl germatranes as alternative reagents for the preparation of biarylethynes

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Abstract—Arylalkynyl germatranes react with aryl chlorides and triflates to give the corresponding biarylethynes in good yield. The reaction proceeds under mild conditions in the presence of a palladium phosphine catalyst and fluoride ions. © 2002 Elsevier Science Ltd. All rights reserved.

The Sonogashira reaction (Scheme 1) is a highly effective procedure for the preparation of arylethynyl compounds[1] and the reaction has been widely studied.[2] The versatility of the reaction and the range of R′–X reagents available make this a powerful tool in synthetic strategies and it is often the method of choice in the preparation of biarylethynes. The reaction has been used in a variety of applications, including the preparation of dendrimers,[3] molecular wires and electronic devices,[4] polymers,[5] and novel organic materials.[6]

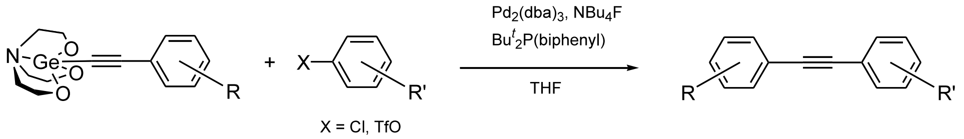
The reaction has been augmented by a number of refinements of the protocol, including the use of a phosphine-free palladium–imidazolium catalyst,[7] the use of silver oxide in place of the copper iodide[8] and the use of the reactive alkyne trimethylsilyl acetylene in a one-pot procedure for the preparation of biarylethynyl products.[9] These reactions typically use aryl bromides or iodides as substrates and even then usually employ harsh conditions, although recently a room-temperature Sonogashira coupling of aryl bromides has been reported.[10]

$$\mathrm{H}{-}{\equiv}{-}\mathrm{R} + \mathrm{X}{-}\mathrm{R'} \xrightarrow[\text{base}]{\mathrm{Pd(0)/R_3P/CuI}} \mathrm{R}{-}{\equiv}{-}\mathrm{R'}$$

Scheme 1. The Sonogashira coupling reaction.

While organosilicon and organotin compounds have well-developed roles in cross-coupling reactions[11] a recent report on the successful use of tri(2-furyl)arylgermanes in aryl coupling reactions demonstrates that organogermanium reagents may also be of use in this regard.[12] We have also recently reported upon the preparation and reactions of a variety of organogermatranes, including those of arylethynyl germatranes.[13] We have extended our studies of these reagents and now report on the utility of arylalkynyl germatranes as reagents for the Sonogashira-type coupling reaction using aryl chlorides and triflates as substrates.

Arylalkynyl germatranes react with aryl chlorides or triflates to form biarylethynes according to the reaction shown in Scheme 2, with results summarized in Table 1.[14–18] In comparison with other Sonogashira type reactions, it appears that the use of germatrane reagents enables the reaction to proceed at lower temperatures than are usually observed for the related reactions using triorganosilicon reagents. This is particularly significant because the reactions reported here are with the less



Scheme 2. Palladium-catalyzed coupling using arylalkynyl germatranes.

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Table 1. Arylethynyl coupling products prepared according to Scheme 1

Entry	R	R′	X	Temperature (°C)	Reaction time (h)[a]	Yield (%)[b]
1	H	H	Cl	78	12	76
2	4-Me	H	Cl	78	12	72
3	H	4-Me	Cl	78	12	59
4	4-Me	4-Me	Cl	78	12	62
5	H	2-Me	Cl	78	12	55
6	4-Me	2-Me	Cl	78	12	53
7	H	H	TfO	24	24	74
8	4-Me	H	TfO	24	24	81
9	H	4-Me	TfO	24	24	60
10	4-Me	4-Me	TfO	24	24	61

[a] The reaction time is not optimized.

[b] Isolated yield.

reactive aryl chlorides and triflates, substrates not normally successful under the conventional Sonogashira coupling reaction conditions.[19]

The related 2-(trimethylsilyl)ethynyl germatrane is an unsymmetrically substituted ethyne with two different main-group organometallic moieties. The two groups are both able to participate in transmetallation reactions and so this reagent, by analogy with the reactions of trimethylsilyl acetylene, can be used to prepare biarylethyne compounds by reaction with two equivalents of ArX reagents under the conditions reported here. Treatment of the silylalkynyl substituted germatrane with two equivalents of chlorobenzene in refluxing THF in the presence of the palladium phosphine catalyst and fluoride ion does indeed yield biphenyl acetylene in moderate yield (76%). Although this is a preliminary result, it appears likely that a range of symmetrical (and potentially unsymmetrical) biarylethyne products should be available from this single germatrane reagent. This greatly enhances the utility of the reagent, as it is possible to prepare a range of products without the need for the prior preparation of the specific arylethynyl reagent that would otherwise be required.

As so many useful reactions are known for organosilane and -stannane reagents, it comes as no very great surprise that organogermanes can also be useful in synthetic protocols. The paucity of publications relating to the use of organogermanium reagents is in some ways a testament to the utility and availability of reagents based upon its congeners.[20] One can anticipate that the reactivity of the germanium reagents would be intermediate between those derived from tin or silicon and thus might avoid the toxicity of tin while being more reactive than silicon. The germatrane reagents also have the advantage of being stable crystalline solids that are easily handled.

Acknowledgements

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14. *Typical reaction conditions*: To a solution of arylethynyl germatrane (5.0×10^{-4} M) in THF (15 mL) was added Pd_2dba_3 (1.2×10^{-5} M), Bu^t_2P(biphenyl) (4.0×10^{-5} M), the aryl halide or triflate (3.6×10^{-4} M) and 0.5 mL of a 1.0 M solution of $N(Bu^n)_4F$ in THF. The reaction was heated under reflux under nitrogen for 12 h (aryl chloride) or stirred at room temperature (aryl triflate). The solvent was removed under vacuum and the residue extracted

with CH_2Cl_2 (1.0 mL). Preparative TLC (silica gel, hexanes) allowed isolation of the biarylethyne product as the most mobile fraction.

15. Arylethynyl germanium trichlorides were obtained from the arylethynes and $GeCl_4$ in the presence of Et_3N according to the procedure of Lutsenko and co-workers.[16] Without distillation these trichlorides were converted into the corresponding germatranes using a two-step procedure involving alkoxylation with ethanol followed by transalkoxylation with triethanolamine.[17] In our hands overall yields of 85–95% were obtained of the arylethynyl germatranes.[13] The TMS trichloride derivative was prepared from TMSacetylene and $GeCl_4$.[18]
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