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Silver Salts as New Catalyst for Coupling Reactions; Synthesis of Epoxyenyne

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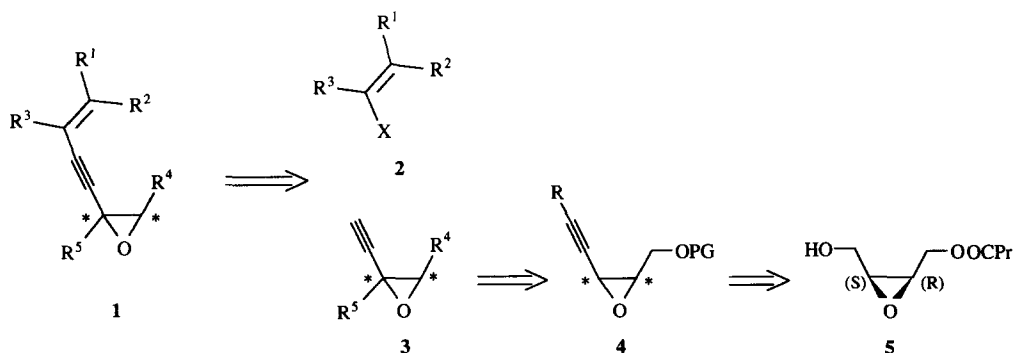
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Abstract: The coupling of ethynyl oxiranes with alkenyl triflates have been achieved by treatment with the following association of catalysts: silver salt and tetrakis(triphenylphosphine) palladium. This new set of catalysts allowed for the direct formation of epoxyenyne in rather good yields.

For a program in connection with our interest in the chemistry of ethynyl oxiranes¹⁻⁴ and devoted to the total synthesis of several natural products,⁵⁻⁷ we required a mild access to chiral epoxyenyne (**1** in Scheme 1). We have recently shown that protected derivatives of (2*S*, 3*R*)-4-butyryloxy-2,3-epoxybutan-1-ol (**5** in Scheme 1), obtained by enzymatic hydrolysis of *cis*-1,4-bis(butyryloxy)-2,3-epoxybutane⁸ are suitable enantiomerically pure starting materials for the asymmetric synthesis of ethynyl oxiranes (**4** in Scheme 1).^{4,5} This led us to envisage the use of ethynyl oxiranes (**3** in Scheme 1) as optically pure key building-blocks for the synthesis of natural products containing an epoxyenyne moiety (**1** in Scheme 1).

The most convenient access to this class of compounds relies on the convergent strategy based on coupling reactions between a terminal acetylene and an activated alkene.⁹ The literature offers numbers of methods for such couplings.⁹⁻¹⁰ Among those, the coupling of vinyl triflates with terminal acetylenes in the presence of palladium complexes are the most convenient and therefore the most widely used.^{9,11-12} However, to the best of our knowledge, the coupling of a terminal acetylene bearing an epoxy group (**3** in Scheme 1) with an activated alkene (**2** in Scheme 1) has never been reported in the literature.



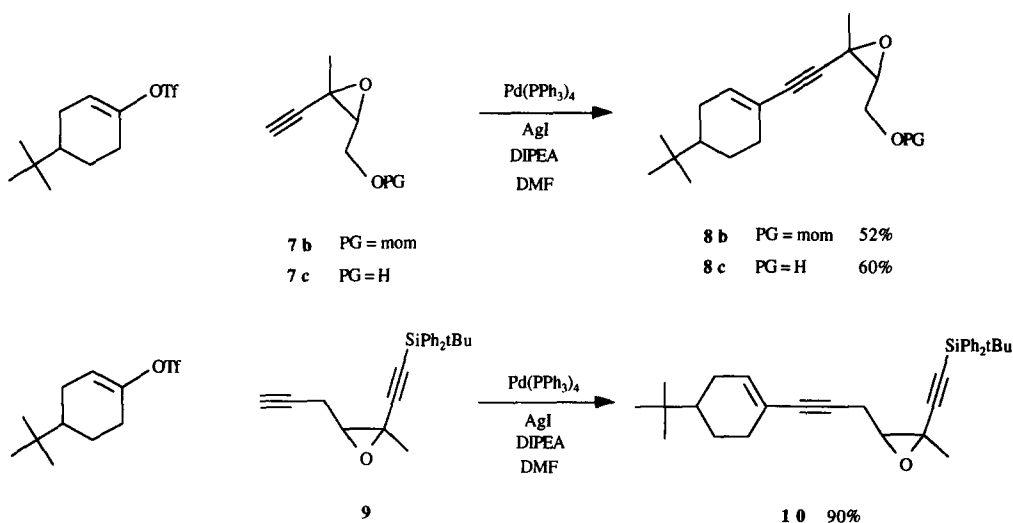
Scheme 1

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When exposed to the conditions described with cuprous iodide but with silver iodide instead as a cocatalyst, the starting materials **6** and **7** were slowly consumed in a very clean reaction and the expected product were isolated with a yield modest (Table 1, entry 5) but comparable to the best one obtained with cuprous iodide (Table 1, entry 4). We found in this case that modifications of the relative proportions of the reagents improved the yield of recovered coupling product and the best conditions are the one described in entry 6.

Other silver salts such as silver nitrate and silver carbonate proved to be also efficient catalysts in this coupling reaction but both were slightly less effective than silver iodide (Table 1, entries 7-10 vs 5-6). In order to minimize any counter-ion effect, silver triflate was also experimented. Although it was also effective as a catalyst, this salt was probably too electrophilic for use with the sensitive epoxyenyne unit and some decomposition occurred (Table 1, entry 11).

In order to expand the scope of the reaction, other epoxyalkynes was also engaged in coupling reactions with our model triflate **6** using the optimized conditions set above. Representative examples are collected in Scheme 2. Even a non-protected acetylenic epoxyalcohol **7c** was able to be coupled, but in this case, the epoxyenyne **8c**¹⁵ was isolated with a yield lower than the one observed with the corresponding silylated compound (**7a-8a**, see Table 1, entry 6). Another decrease in yield was also observed when a chelating group - a mom group - was present in the coupling partner: **7b** gave the epoxyenyne **8b**¹⁵ with a 52% yield. However, with an epoxydiyne, **9**,¹⁷ an almost quantitative yield of coupling product **10**¹⁵ was obtained but a slight decomposition occurred during chromatography.



Scheme 2

These examples showed that this new set of catalysts can be used for various couplings and seems to accommodate different functional groups.

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