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11th Paul Walden Symposium on Organic Chemistry



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11th Paul Walden Symposium on Organic Chemistry

PROGRAM AND ABSTRACT BOOK

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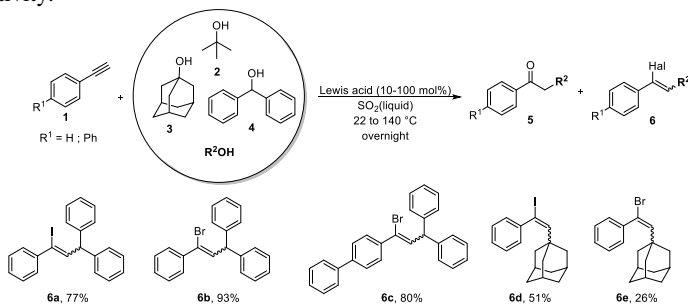
Addition of carbenium ion-nucleophile pairs to alkynes in liquid sulfur dioxide

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Ketones and alkenyl halides are both highly valuable building blocks and intermediates in many cross-coupling reactions. Alkyne coupling with alcohols is atom-economical manner to form alkenyl cation intermediates which further with subsequent nucleophilic halogen or hydroxide ion attack are converted to substituted ketones and vinyl halides. Many groups have recently demonstrated Lewis acid (especially FeCl_3) catalyzed reactions using equivalent amounts of Lewis acid.¹ We have designed the aforementioned coupling reactions with catalytic amounts of transition metal triflate catalysts and group I metal halides in suitable reaction medium. We have previously demonstrated that liquid SO_2 is highly polar Lewis acidic solvent suitable for such carbenium ion intermediate reactions.² Herein we report study of substituted ketone synthesis from alkynes with transition metal Lewis acid catalysis in liquid SO_2 medium. While employing catalytic amounts of Cu^{2+} , In^{3+} , Al^{3+} , Bi^{3+} , Sc^{3+} triflates and FeCl_3 Lewis acid catalysts with various alcohols **2-4** we observed formation of ketone **5** in good yields. As for synthesis of vinyl halides, among various group I and group II metals Li^+ and Mg^{2+} cations were found to be most efficient catalysts. The halide nucleophile reactivity order was: $\text{I}^- > \text{Br}^- > \text{Cl}^-$. The isolated products **6a-e** were obtained in good to excellent yields with *E*-selectivity.



Scheme 1. Lewis acid catalyzed carbohydration and carbohalogenation of alkynes.

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References

1. a) Biswas, S.; Maiti, S.; Jana, U. *Eur. J. Org. Chem.* **2009**, 2354; b) Jana, U.; Biswas, S.; Maiti, S. *Eur. J. Org. Chem.* **2008**, 5798; c) Li, M. M.; Zhang, Q.; Yue, H. L.; Ma, L.; Ji, J. X. *Tetrahedron Lett.* **2012**, 53, 317.
2. a) Suta, K.; Turks, M. *ACS Omega* **2018**, 3, 18065; b) Posevins, D.; Suta, K.; Turks, M. *Eur. J. Org. Chem.* **2016**, 1414.