chemistry proceedings

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Synthesis of Benzo[*B*]Carbazols by Tandem Au(I)-Catalyzed Cyclization/Migration/Cyclization †

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† Presented at the 24th International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2020; Available online: https://ecsoc-24.sciforum.net/.

Published: date

Abstract: The initial results on a novel procedure for the synthesis of benzo[*b*]carbazols via gold(I)-catalyzed tandem cyclization/Migration/cyclization is described. The procedure allowed the access to a highly functionalized benzo[*b*]carbazols in a one-pot process starting from tertiary anilines. The mechanism of this reaction by using gold(I) catalysis, interestingly proceeded via 5-*endo*-dig cyclization with successively migration of benzyl substituent on 2 and 3 position of indole, leading to the formation of benzyl substituted indole derivatives. We are proposing a cyclodimerization and aromatization via *6-exo-dig* with the help of gold(I)-carbene. Initial optimization with Tertiary Aniline 4, 5mol% of (Acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate as Gold(I)-catalyst, Dry-DCM or Dry-DCE at 23 °C. But unfortunately, we do not get result. Then we rise the temp of reaction in Dry-DCE upto 60 °C with 10mol% of gold(I) catalyst and then we get substituted indole as a cyclized product with 95% yield which is confirmed by H^1, C^{13} and NOE spectrum. Overall, we get first intermolecular cyclized product of benzyl substituted indole with excellent yield.

Keywords: Gold(I)Catalyst; Benzo(b)carbazole; bisalkylation; synthesis; cyclization; migration

1. Introduction

Carbazole derivatives are known to have important photo physical and biological properties. Carbazoles represent an important class of nitrogen containing heterocyclic compounds, many of which have found a wide range of applications as Natural product, Anticancer and biologically active agents in medicinal chemistry (Figure 1).

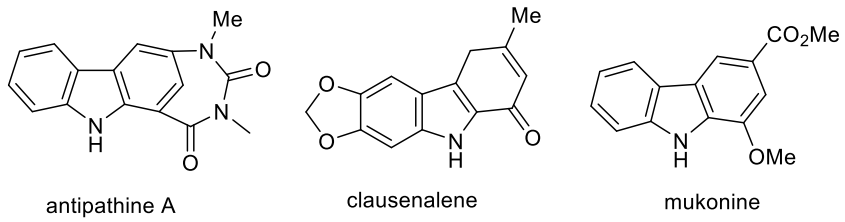
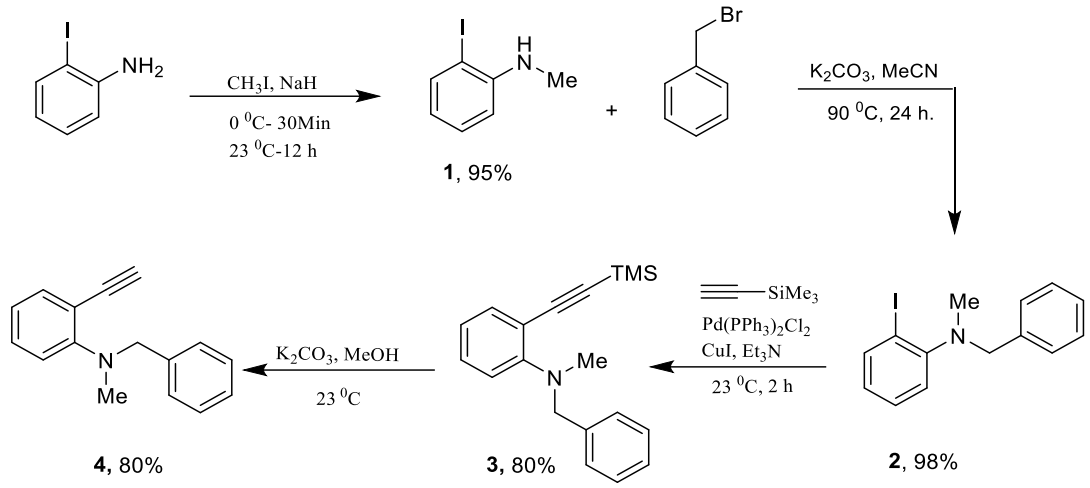


Figure 1. Natural product containing carbazole moiety.

Inspired from carbazole application and above discussion. We decide to Synthesis of Benzo(*b*)carbazols by tandem Au(I)-Catalyzed cyclization/migration/cyclization. Our aim to synthesized Benzo(*b*)carbazole with different substituents on that and make broad scope in this methodology.

2. Results and Discussion-

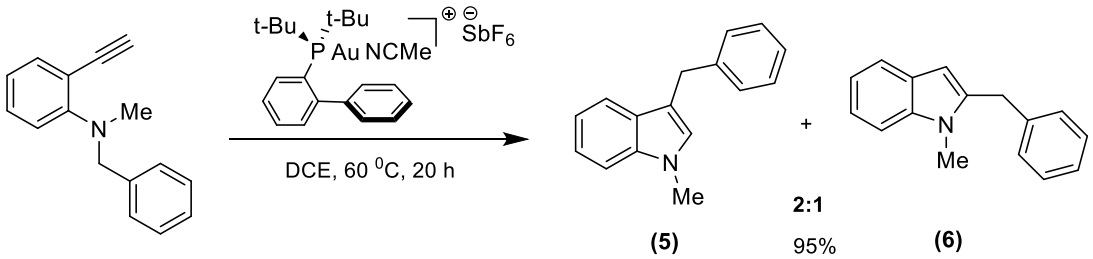
Starting material preparation:



Scheme 1. Starting material synthesis.

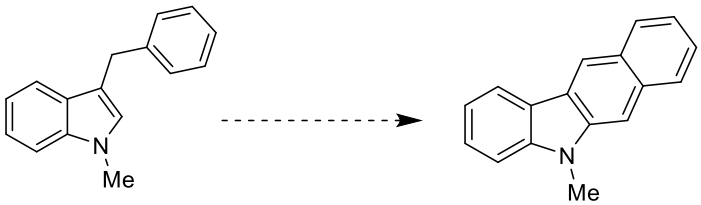
First our target to prepare tertiary Aniline **4,** as a starting material from 2-Iodo Aniline. Starting material tertiary aniline required four step which is shown in above reaction.

Gold-Catalyzed Reaction:



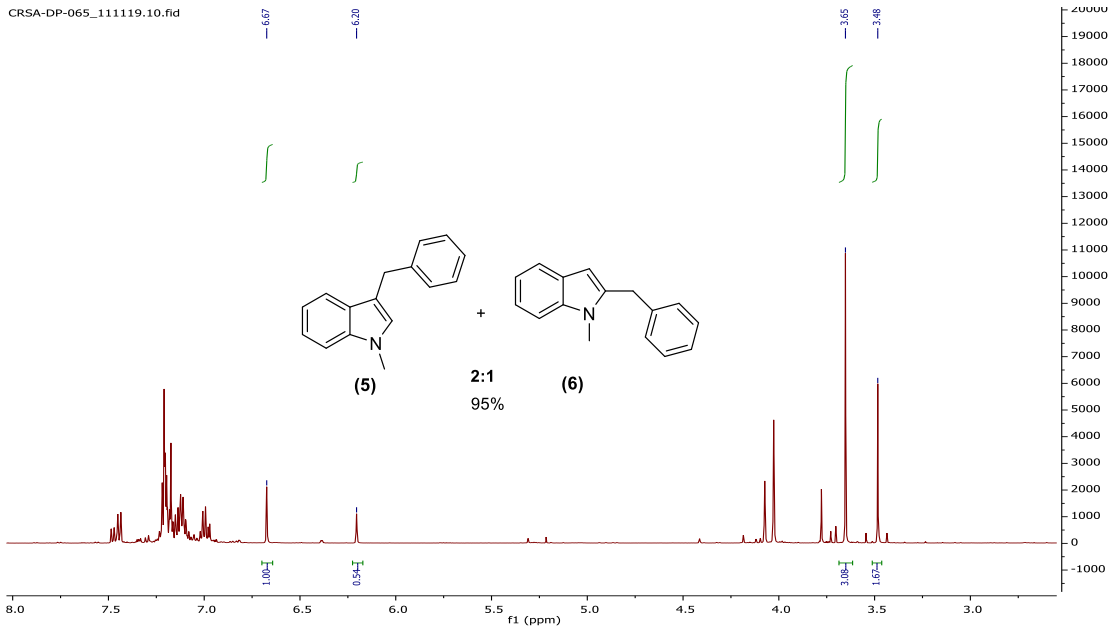
Scheme 2. Gold(I)-catalyzed reaction.

Target in future

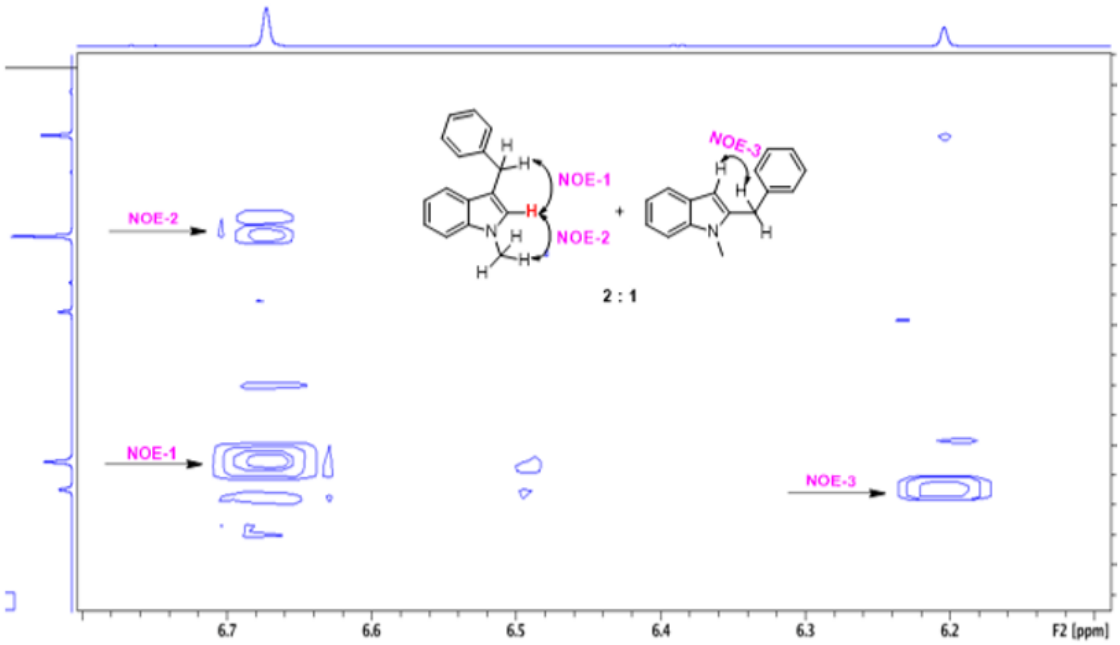


According to Gold catalyzed reaction which shown in above. Starting material tertiary aniline 4, was inserted into Gold catalyst in DCM as a solvent at 60 °C for 20-hour. In this reaction first cyclization was happen with indole formation and the benzyl group was migrate to 2 and 3 position. Benzyl group migrate on 3-position (5) is major product than that of migrate on 2-position (6) and we get 2:1 as a ratio of two compound. The migratory aptitude of benzyl group is more than methyl group.

Proton spectrum



NOE Spectrum



3. Experimental Section

Entry	Au(I)-Catalyst (mol.%)	Solvent	T (°C)	Yield (%)
1.	5	DCM	23 °C	n.r.
2.	10	DCE	60 °C	95

4. Conclusions

(i) Bis alkylation on 2-iodo aniline with two different substituted benzyl moiety is difficult.
(ii) Migratory aptitude of benzyl group is more as compared to methyl group.
(iii) Cyclization and migration were happen in same reaction and condition.
(iv) We get first intermolecular cyclized product of benzyl substituted indole with excellent yield.

Author Contributions: All authors contributed equally to this work. All authors have read and agreed to the published version of the manuscript.

Acknowledgments: This work was supported by CONACyT (CB-2013/220836). We acknowledge the facilities of the DCNyE, the Chemistry Department, and the National Laboratory UG-CONACyT (LACAPFEM) at the University of Guanajuato, for full characterization. We thank CONACyT for Ph.D. fellowships to Dipak Bhatu Patil.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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