



Reactions of bis-propargyl cycloalkanones with gold and silver catalysts

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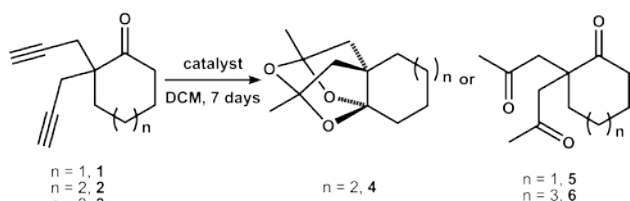
Keywords: bis-propargyl cycloalkanones, gold/silver catalysis, internal tris-ketal

INTRODUCTION

We have already demonstrated that the reactions of 2,2-bis-allyl cycloheptenones with Pd and Ru catalysts lead to intriguing internal tris-ketal molecules such as **4**.¹ We have now extended our studies to include the related bis-propargyl derivatives (**1-3**), with the use of gold catalysts, with and without silver compounds as co-catalysts.

RESULTS AND DISCUSSION

The bis-propargyl compounds (**1-3**) were prepared from the corresponding cycloalkanones, by reaction with propargyl bromide and base. (**1-3**) were then subjected to reactions catalyzed by gold (5 mol%) and silver (10 mol%) compounds in dichloromethane, with the addition of 6 equivalents of water. The products (**4-6**) were obtained as described in Table 1 (see Scheme 1).



Scheme 1.

Table 1. Reactions of **1** leading to **4**, **2** to **5** and **3** to **6**.

Entry	Catalyst	1→4	2→5	3→6
1	HAuCl ₄ ·3H ₂ O	83%	92%	21%
2	AuCl	18%	44%	4%
3	Au(PPh ₃)Cl	0%	0%	0%
4	AuCl/AgBF ₄	8%	40%	2%
5	Au(PPh ₃)Cl/AgBF ₄	100%	99%	3%
6	AuCl/AgSbF ₆	7%	57%	2%
7	Au(PPh ₃)Cl/AgSbF ₆	66%	99%	4%
8	AgBF ₄	7%	4%	1%
9	AgSbF ₆	7%	8%	1%

The ring size is obviously conclusive in directing the reaction towards the internal tris-ketal **4** (7-member), or the bis-acetonide derivatives **5** and **6**.

In order to rationalize the influence of the size of the fused ring on quite distinct reaction pathways (Scheme 1), we proposed a theoretical study of the products' Gibbs free energies. After a search for the lowest energy conformations of each of the possible products (Figure 1), the Free energies of each compound were calculated, and

grouped in pairs of the same ring size. The results are presented in Table 2, using the B3LYP/6-31+G(d,p) level of theory.

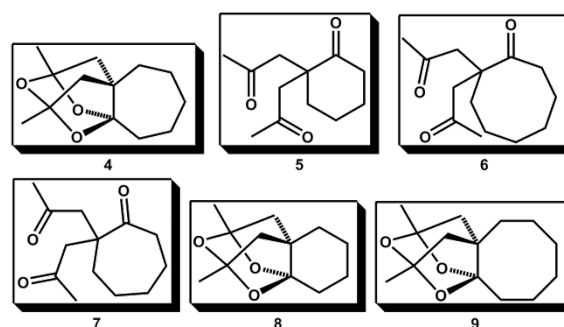


Figure 1.

Table 2. Free energies of compounds **4** to **9**.

Compound	Energy	ΔE (ketal-keto)
4	-732.847444	-0.198290
7	-732.847128	
8	-693.55814	3.702877
5	-693.564041	
9	-772.125118	3.437445
6	-772.130596	

CONCLUSION

We have found that the 7-member substrate **2** leads to the intriguing internal tris-ketal **4**, whereas the 6- and 8-member analogues **1** and **3** give the expected hydration products **5** and **6**. The presence of silver co-catalysts and additional water has a substantial effect on the yields. The experimental results have found agreement with the calculations shown in Table 2, which express a very unusual thermodynamic stability for the seven-membered fused system **4**, when compared to the 6- and 8-membered analogues **8** and **9**.

ACKNOWLEDGEMENTS

Thanks are due to the São Paulo Research Foundation (FAPESP, grants 2011/13993-2, 2013/02311-3 and 2013/06532-4), CNPq, and CAPES: and Firmenich for the donation of (*R*)-(-)-carvone.

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