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Applications of Br_2- and I_2-Cucurbit[6]uril Complexes in Synthetic Organic Chemistry

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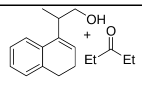
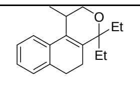
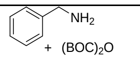
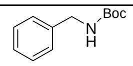
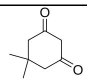
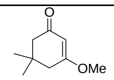
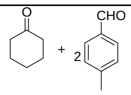
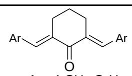
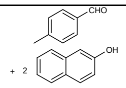
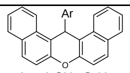
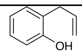
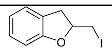
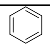
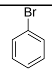
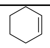
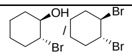
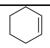
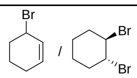
Introduction

The different available cavity and portal sizes in the rigid macrocyclic CB[*n*] molecules makes possible to include guest species of different sizes.[1] The CB[6] complex has been successfully used in many transformations. The use of molecular iodine has received considerable attention as an inexpensive, non-toxic, readily available catalyst for various organic transformations.[2] The bromination of organic substrates is a hot topic in the list of useful transformations in organic synthesis.[3] For this purpose, molecular bromine has been extensively used, even though its volatile, irritating and corrosive nature. Prof. Grégoire recently succeed in synthesis of Br_2 and I_2 encapsulated CB[6] complexes. Considering our expertise in synthetic organic chemistry and our interest in reactions promoted by I_2, we decide to investigate the behavior of new Br_2 and I_2-CB[6] complexes.

Results and Discussion

To achieve this goal, known reactions using Br_2 and I_2 were selected in the literature, and the reactivity was compared with Br_2 and I_2-CB[6] complexes. The catalytic activity of I_2-CB[6] complex (entry 1-5) indicated that I_2-CB[6] is source of I_2. Iodocyclization of 2-allylphenols (entry 6) also supported that I_2-CB[6] complex is also useful in stoichiometric application as a I_2. We also studied the reaction nature of I_2 in CB, i.e the reactivity of molecular iodine would be inside or outside of cavity. The obtained result (entry 2c, 6c) shows that the encapsulated I_2 leaves with solvent from the cavity and participate in reaction. We find out during our comparative analysis of Br_2-CB[6] complex with Br_2 and NBS (entry 7-9), that Br_2-CB[6] complex can be use as substitute of Br_2 and NBS.

Table 1. Reactivity of Br_2 and I_2-CB[6] complexes.

Entry	Substrate	Product	conditions	Yield % this work (lit)
1			a. I_2 (5 mol%), CH_2Cl_2.	75 (-)
			b. I_2-CB (1.25 mol%), CH_2Cl_2.	82 (-)
2			a. I_2 (10 mol%), CH_2Cl_2	94 (95[4])
			b. I_2-CB (2.5 mol%), CH_2Cl_2	92 (-)
			c. Filtered solution of I_2-CB (2.5 mol%), CH_2Cl_2..	93 (-)
3.			a. I_2 (3.0 mol %), MeOH.	88 (96[5])
			b. I_2-CB (0.75 mol%), MeOH.	92 (-)
4.		 Ar= 4-CH_3-C_6H_4	a. I_2 (30. mol %), CH_2Cl_2.	94 (94[6])
			b. I_2-CB (7.5 mol%), CH_2Cl_2.	70 (-)
5		 Ar= 4-CH_3-C_6H_5	a. I_2 (2.5 mol%).	92 (93[7])
			b. I_2-CB (0.62 mol%).	73 (-)
6			a. I_2 (1.5 eq), H_20.	87 (84[8])
			I_2-CB (0.37 eq), H_20.	71 (-)
			b. I_2-CB (0.37 eq), H_20:EtOH (1:1).	69 (77[8])
			c. Filtered solution of I_2-CB (0.37 eq), H_20:EtOH (1:1).	37 (-)
7			a. Br_2 (1.4 eq), pyridin (0.1 eq).	54 (60[9])
			b. Br_2-CB (0.35 eq), pyridin (0.1 eq), CH_2Cl_2.	56 (-)
8			a. NBS (1.1 eq), H_2O:Me_2CO (1;4).	85/ 0 (91[10]/-)
			b. Br_2-CB (0.27), H_2O:Me_2CO (1;4).	19/15 (-)
			c. Br_2-CB (0.27), H_2O.	70/0 (-)
			d. Br_2-CB (0.27), Me_2CO, 10 min.	0/35 (-)
9			a. NBS (1.1 eq), benzyl peroxide (5 mol%).	56/0 (60[9]/-)
			b. Br_2-CB (0.27 eq), benzyl peroxide (5 mol%).	0/65 (-)
			c. Br_2-CB (0.27 eq), benzyl peroxide (5 mol%).	0/54 (-)
			d. Br_2-CB (0.27 eq).	0/40 (-)

note: I_2-CB = CB[6]$(I_2)_4$.6H_2O, Br_2-CB = CB[6]$(Br_2)_4$.6H_2O

Conclusion

On the basis of our results, we can conclude that Br_2 and I_2-cucurbit[6]uril complexes can be used as a source of molecular bromine, NBS and molecular iodine.

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