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Short communication

Hexabromoacetone: An efficient reagent for bromination of saturated hydrocarbons catalyzed by oxidovanadium(IV) picolinate complex

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ABSTRACT

The efficient brominating agent, hexabromoacetone (HBA) worked very well with oxidovanadium(IV) picolinate catalyst in selective bromination of saturated hydrocarbons with no competing C–H oxidation. Cyclododecyl bromide was fruitfully obtained as a major product from the bromination of cyclododecane with trace amount of oxidized product(s). The selectivity attained for the reaction was excellent. Competitive bromination using selected alkane and alcohol revealed that alkyl bromide occurred *via* alkane substrate directly.

1. Introduction

Saturated hydrocarbons are the most abundant and widely used as a fuel source. The attempts to functionalize these compounds to useful organic chemicals by direct functionalization have been studied for years. The breaking of inertness C–H bonds usually requires vigorous conditions. The efficient transformation applied with transition metal catalyst has been carried out under mild conditions with high selectivity is challenging for chemical industries. Several studies [1–3] have been stated that productive and selective C–H functionalization is still not achieved and only a few complexes revealed their potential as a good catalyst under mild conditions. Therefore, a number of methods were developed with new metal complex catalysts for functionalization of various alkanes. In the past decade, these transformations usually often catalyzed by expensive transition metals [4].

Bromination of organic compounds provides important organic intermediates for chemical and pharmaceutical industries. The bromination of saturated hydrocarbons generally proceeds *via* radical intermediate while that of unsaturated hydrocarbons occurs *via* electrophilic addition [5]. However, the direct bromination of the least reactive C–H bonds generally constitutes a limitation toward selective transformations. Various examined reagents included Cl_3CSO_2Br, Et_4NBr, Br_2/HgO, Br_2, CBr_4, NBS, KBr, $BrCCl_3$ and LiBr [6–11]. These reports however showed low selectivity or less amount of desired product. Alkyl bromides are one of the most important synthetic precursors in industrial chemistry. Therefore, the direct bromination is still required for the synthesis of alkyl bromides. Tongkate [12] succeeded in introducing a new and efficient method for the bromination of alcohols with $Br_3CCOCBr_3/PPh_3$. Alkyl bromides can be obtained from alcohols in high yields under mild conditions within 15 min.

Vanadium-catalyzed C–H activation has not much been reported. In previous literatures, Mimoun [13,14] discovered that the oxidation of cycloalkane by $VO(O_2)(pic)LL'$ (pic = pyridine-2-carboxylate; L, L′ = H_2O or MeOH) gave alcohol and ketone products. Shul'pin [15–18] presented several effective oxidovanadium catalyst systems for C–H oxidation. A binuclear oxovanadium(V) complex catalyst with 2-pyrazinecarboxylic acid (PCA) and H_2O_2 also exhibited as competent reagent oxidizes light alkanes in acetonitrile at low temperature [19]. Afterwards, many reports demonstrated that PCA in combination with vanadium catalysts provided efficient and versatile systems for the oxidation of alkanes [20]. The paramagnetic vanadium(IV) monomeric complexes with scorpionate ligand show significant activity toward the peroxidative or aerobic oxidation of cycloalkane to the corresponding alcohols and ketones [21]. Pyrazole vanadium complexes applied as homogeneous catalysts for alkane oxidations. The reactions are usually carried out in CH_3CN, with aqueous H_2O_2 as the oxidizing agent in acidic medium [22]. The highest overall yield (24%) was achieved with high selectivity toward the formation of corresponding alcohol [23]. Peroxo- and oxovanadium(IV) complexes with tridentate *N*-heterocycle ligands were promoted as catalysts in cyclohexane oxidation [24]. Cyclohexanol was achieved as a major product in moderate yield within 5 h. Smirnov [25] reported the bromination of saturated hydrocarbons with CBr_4. Cycloalkanes and alkanes were brominated for 5–10 h in moderate yield at high temperature (150–180 °C). Nishina [26] disclosed the saturated hydrocarbon-bromination through radical reactions induced by LEDs irradiation. Alkyl bromide was produced in low to moderate yield within 24 h. Jiang [27] also revealed the bromination promoted by unactivated MnO_2 at the tertiary carbon. With unsatisfied

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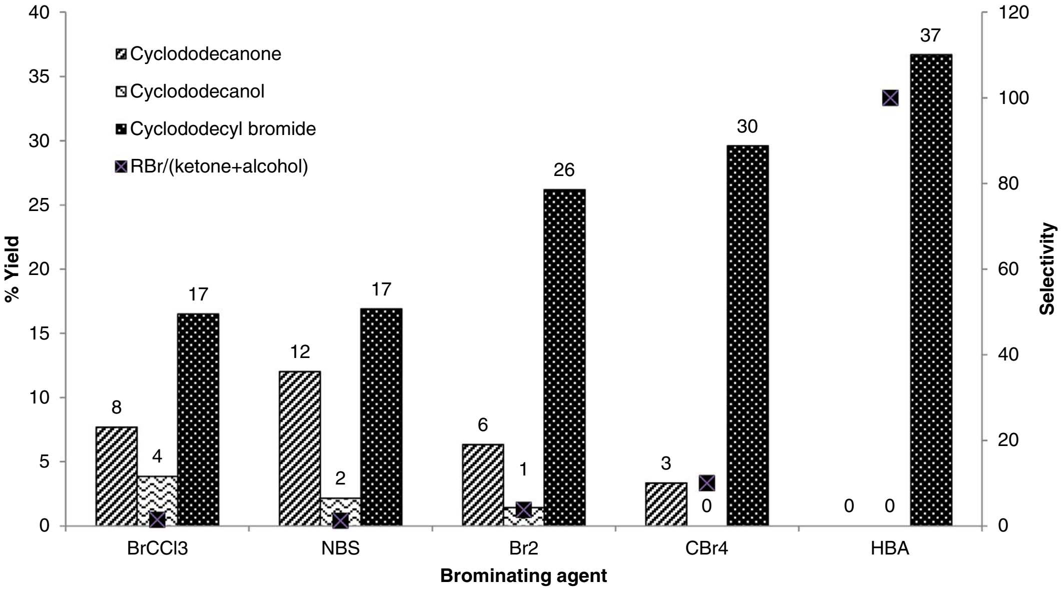

Fig. 1. Effect of brominating agent on cyclododecane bromination.

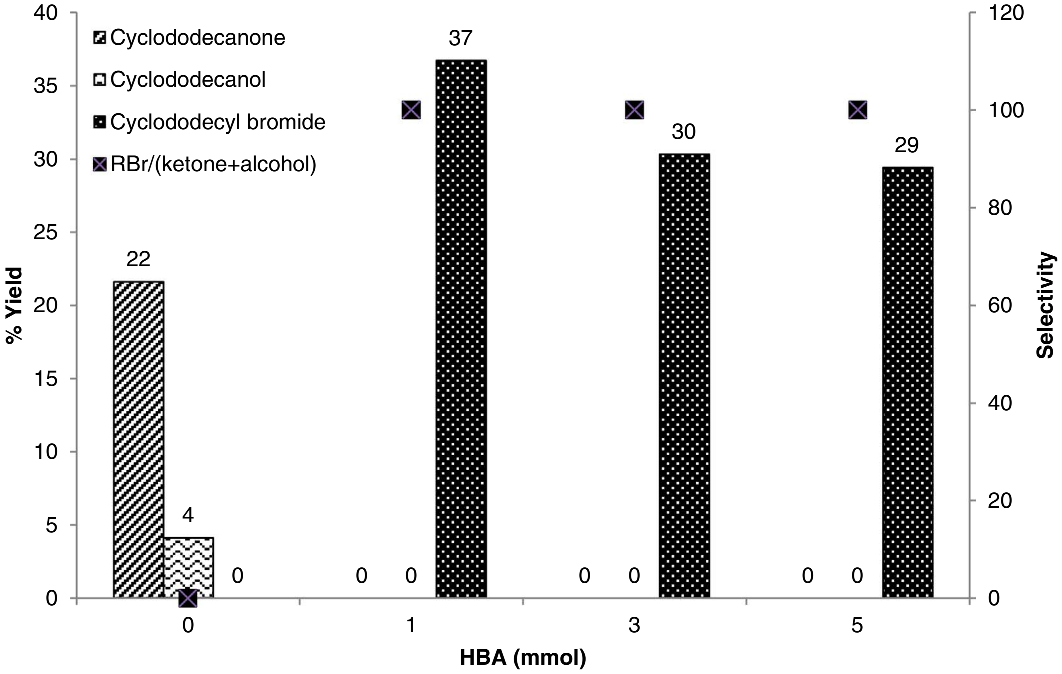

Fig. 2. Effect of HBA on cyclododecane bromination.

yields and selectivities, the catalysis system of reported vanadium catalysts is restricted.

One of the major industrial applications utilizing alkane is the synthesis of derivatives from cyclododecane. These compounds are converted to dodecanedioic acid and lauryl lactam. These two products are intermediates in the production of polyamides for several specialty applications. Cyclododecane was chosen as a model substrate in this study because it could give good mass balance with respect to the hydrocarbon and its products.

We report here the efficient brominating agent-hexabromoacetone (HBA) catalyzed by VO(pic)$_2$ for selective bromination of saturated hydrocarbons using *tert*-butyl hydroperoxide (TBHP) with no competing C—H oxidation.

2. Experimental

2.1. Catalyst preparation

Oxidovanadium(IV) picolinate complex: (VO(pic)$_2$) was prepared from $VOSO_4 \cdot 5H_2O$ and picolinic acid [28]. VO(pic)$_2$ is light blue solid (75%). IR (cm^{-1}): 1630, 1600 and 960. The FT-IR spectra were recorded on a Fourier Transform Infrared Spectrophotometer on Nicolet model 6700.

2.2. Bromination of cyclododecane

Cyclododecane (1 mmol), VO(pic)$_2$ (0.05 mmol), brominating agent (1 mmol), TBHP (10 mmol) and CH_3CN (10 mL) were placed in a round bottom flask. The mixture was refluxed continuously for 6 h. After the