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NEW "GREEN" METHOD OF BROMINATION OF (–)-NOPINONE AND (+)-*CIS*-VERBANONE

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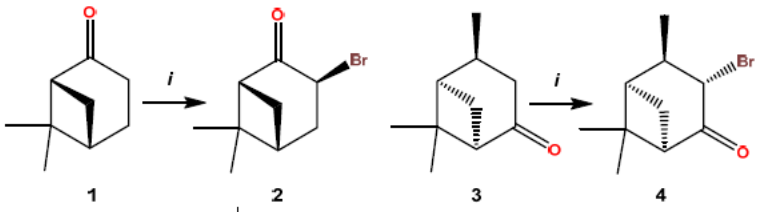
Abstract. Bromination of ketones is one of the simplest and widespread methods of the obtaining of bromoketones. They, in turn, serve as valuable intermediates in the synthesis of heterocyclic compounds, including pharmaceuticals[1]. Direct bromination of monoterpene ketones is nonselective process. For example, the interaction of (–)-nopinone **1** with *N*-bromosuccinimide (NBS) in the presence of benzoyl peroxide proceeds with the formation of a mixture of di- and monobromonopinones[2]. (+)-*Cis*-verbanone **3** is brominated with Meldrum's acid dibromide, resulting in the formation of a single bromoverbanone[3].



i. NBS (5 equiv.), KH_2PO_4 (10 mol%), EtOH, reflux, 72 h.

In 2015, a group of Indian scientists proposed and successfully implemented a new "green" method for bromination of aralkyl ketones in the presence of potassium dihydrophosphate (KH_2PO_4)[4].

We applied this approach to the bromination of (–)-nopinone **1** and (+)-*cis*-verbanone **3**. In the presence of a "green" catalyst KH_2PO_4 the interaction of ketones with NBS proceeds selectively with the formation of the only products **2** and **4** with yields 48 and 47%, respectively.

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