# Oxidation of Tricyclic Sesquiterpenoids with HBr-DMSO

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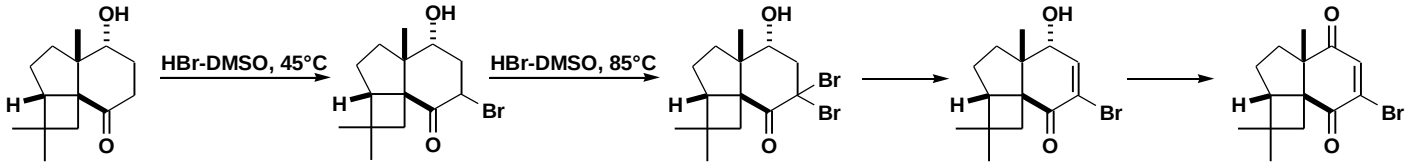
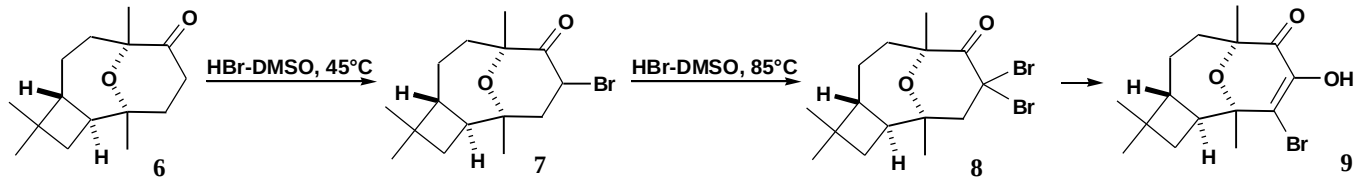
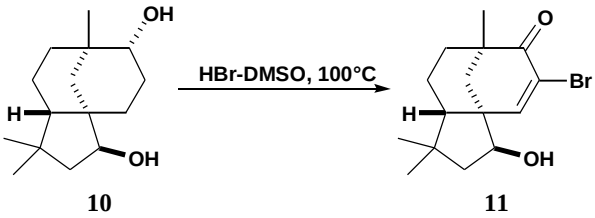
Mixture of aqueous hydrogen bromide and dimethylsulfoxide is known as selective reagent for oxidation of the simplest alkenes, vicinal dibromides and diols, epoxides and ketones to 1,2-diketones. This work demonstrates the use of this reagent in the chemistry of polycyclic terpenic compounds for preparation of different bromo derivatives. Thus, treatment of hydroxyketone **1**, derived from natural *nor*-sesquiterpenoid kobusone, with HBr–DMSO at 45°C results in monobromo derivative **2** in excellent yield. Further heating of the reaction mixture to 85°C and then to 110°C leads consequently to dibromide 3, bromo alkene 4 and finally to unsaturated bromo 1,4-diketone **5**. In the known examples of simple cyclohexane-type derivatives, aromatic compounds are usually the main products of the oxidation. Presence of tertiary carbons in the molecule **1** makes amortization impossible and, in combination with significant steric hindrance, allowed us to observe step-by-step oxidation and isolation of all intermediates that are usually unstable under the reaction conditions.




The first steps of the oxidation of keto ether **6** are similar to the above case and result in monobromo- (**7**) and dibromo- (**8**) derivatives, but the final product **9** is not of the same type:




The role of steric hindrance in the oxidation process is demonstrated by another example shown on the left. In this case, two hydroxyls of clovane diol **10** show different activity to the reagent, and unsaturated bromohydroxy ketone 11 is formed in good yield (76%).

Influence of the reaction conditions to the composition of the reaction mixture, isolation and separation procedures, structure elucidation and spectral data of the new bromo containing sesquiterpenoids are discussed.

***Acknowledgments:*** The research described in this publication was made possible in part by Grant No. 96-03-033054 from the Russian Foundation for Basic Research.