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Selective Preparation Of Benzylic Bromides In Dry Media Coupled With Microwave Irradiation.

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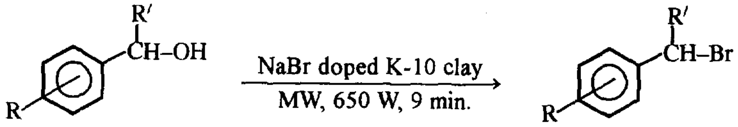
Abstract : Selective and easy synthesis of benzylic bromides in dry media using sodium bromide doped on K-10 clay in an open vessel under microwave irradiation in remarkably reduced reaction times is briefly described. © 1997, Published by Elsevier Science Ltd. All rights reserved.

The use of domestic microwave ovens in organic synthesis in conjunction with solid support is well acknowledged in literature[1]. This easy and environmental friendly technique has several advantages, mainly manifold reduction in reaction times, easy work up and solvent free conditions which are an asset to an organic chemist. Besides, reagents and techniques which are selective towards functional groups of the same class are highly useful for chemical transformations as it overcomes the use of protecting groups.

Benzylic bromides are important precursors in the synthesis of several natural products. Literature records many methods for their preparations and some reagents of choice are 1,1,3,3-tetramethylsiloxane – LiBr[2], N-bromosuccinimide-Me_2S[3], bromo-trimethylsilanes[4] and bromine complex of poly (styrene - co - 4 - vinylpyridine)[5]. Some of these methods[6-8] are selective for conversion of different alcohols (1°, 2°, 3°, allylic and benzylic) into halides. All these methods involve use of expensive reagents and solvents, long reaction times and high temperature.

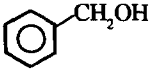
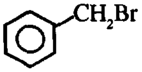
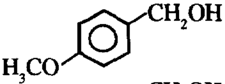
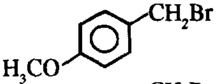
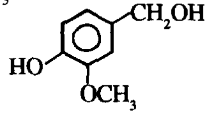
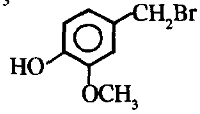
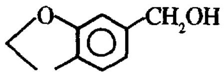
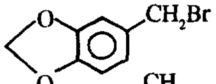
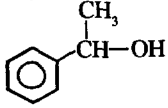
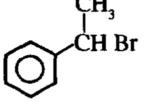
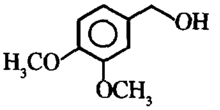
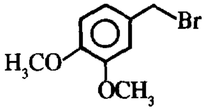
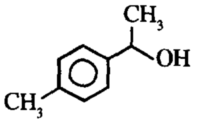
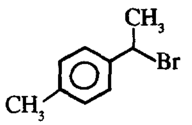
In this paper we report a simple, economical and selective procedure for the preparation of benzylic bromides.



Commercially available anhydrous NaBr (1.02g, 10mmole) was added to activated K-10 clay (1.0g) in a beaker by dissolving in acetone, stirred and the solvent evaporated. To this doped clay was added alcohol (10mmol) in diethylether, stirred for 5 min. and the solvent evaporated. The beaker was covered with a watch glass and exposed to microwave irradiation at 650 W for 9 min., filtered, extracted with diethylether and solvent evaporated in vacuo to give the pure product in excellent yield (60-95%). However, tertiary benzylic alcohols fail to react under these conditions, may be due to steric factors. Under reflux conditions in dry DMF and under microwave irradiation in the absence of clay this transformation was not accomplished. Also, this methods is not applicable to other alcohols e.g. saturated primary, secondary, tertiary and propargylic alcohols. The results of the compounds prepared are enlisted in Table 1.

In conclusion this simple, convenient and efficient method for the selective conversion of benzylic alcohols into benzylic bromides can be useful for the synthesis of natural products.

Table 1 : Preparation of Benzylic Bromides

Substrate	Time/min.	Product	Yield (%)
	9		95
	9		92
	9		79
	9		93
	9		86
	9		60
	6		75

a) Purity of compounds was determined by tlc analysis b) compounds were purified by column chromatography (silica gel; eluent: n-hexane/ether, 9:1). c. All products were characterised by spectral (^1H, IR) and elemental analysis.

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