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Selective Iodination of Benzylic Alcohols with KI/H_2SO_4 Supported on Natural Kaolinitic Clay Under Microwave Irradiation

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Summary. Benzylic alcohols are selectively converted into their corresponding iodides using KI/H_2SO_4 supported on natural kaolinitic clay and microwaves.

Keywords. Iodination; Benzylic alcohols; Natural kaolinitic clay; Microwaves.

Introduction

Alkyl iodides or bromides are used for ionic or radical carbon–carbon coupling reactions and can also act as intermediates in substitution reactions, eliminations, and rearrangements. Therefore, the conversion of alcohols into alkyl halides is a very important transformation in organic chemistry. Although various methods have been reported to achieve this goal [1–4], some of these require expensive reagents, long reaction times, and tedious work-up. Some methods involve mild conditions and the use of iodo [5] and bromotrimethylsilanes [6], chlorotrimethylsilane-sodium iodide [7], and hexamethyldisilazane-iodine [8] as reagents. More recently, reports have been published regarding the selective conversion of allylic and benzylic and other (primary, secondary, and tertiary) alcohols into halides [9–12].

Heterogenous organic reactions have proven useful in the laboratory as well as in industry. These reactions are effected by reagents immobilized on porous solid supports and have advantages over the conventional solution phase reactions because of good dispersion of active reagent sites and easier work-up. The recyclability of some of these solid supports renders these processes into truly eco-friendly green protocols [13, 14]. A related development that had a profound impact on heterogeneous reactions is the use of the microwave (MW) irradiation technique for the acceleration of organic reactions [15]. The combination of supported reagents and microwave irradiation can be used to carry out a wide range of reactions in short times and with high conversion and selectivity without the need of solvents. This approach can prove beneficial since the recovery of solvents from conventional reaction systems always results in some losses. Recovery of

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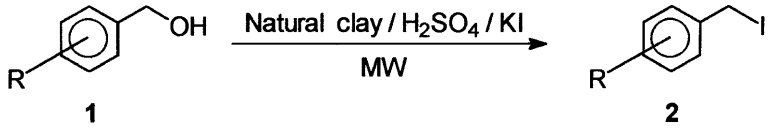


Scheme 1

both products and supported reagent or catalyst is generally possible by simple filtration and evaporation, leading to an efficient and low-waste route to a range of products [15].

We here report on the selective iodination of benzyl alcohols with conc. H_2SO_4 and KI supported on natural kaolinitic clay [16, 17] under pulsed microwave irradiation (Scheme 1).

Results and Discussion

The iodination of various benzylic alcohols is summarized in Table 1. Chemoselective iodination of benzyl alcohols was carried out in the presence of primary, secondary, and tertiary alcohols as well as phenols (Table 2, entries 1–8). Attempts to prepare fluorides, bromides, and chlorides failed when KF, KBr, or KCl and conc. H_2SO_4 supported on natural kaolinitic clay under microwave irradiation were used. It is also important to note that NaI and LiI in the presence of H_2SO_4 supported on natural clay are equally effective reagents for the iodination of benzyl alcohols. Using an alternative conventional heating mode (oil bath) at a temperature of 100°C, trace amounts of benzyl iodide were formed using this supported reagent and benzyl alcohol, thus indicates the importance of microwaves for this transformation.

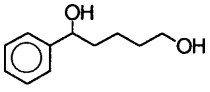
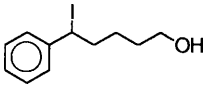
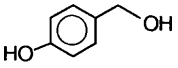
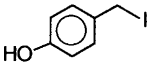
In conclusion, we have developed a simple method for the selective transformation of benzylic alcohols into benzylic iodides using KI and conc. H_2SO_4 supported on natural kaolinitic clay under pulsed microwave irradiation. Fast reactions, high yields, and an inexpensive catalyst are important features of this method.

Table 1. Iodination of benzyl alcohols using KI/H_2SO_4 supported on natural kaolinitic clay under microwave irradiation

Substrate	Product	*R*	Reaction time (min)	Yield[a] (%)
1a	**2a**	H	5	92
1b	**2b**	4-Cl	5	92
1c	**2c**	2,4-Cl_2	4	90
1d	**2d**	4-NO_2	6	91
1e	**2e**	3,4-CH_2O_2	4	93
1f	**2f**	6-Cl,3,4-CH_2O_2	2	93
1g	**2g**	2-Cl,6-F	7	74

[a] Yields of isolated products; products are characterized spectroscopically (IR, ^{1}H NMR) and by comparison with authentic samples [17, 18]

Table 2. Selective synthesis of benzyl iodides

Entry	Hydroxylic compound	Products	t/min	Yield/%[a]
1	4-Nitrobenzyl alcohol	4-Nitrobenzyl iodide		85
	Octadecanol	Octadecyl iodide	7	00
2	Benzyl alcohol	Benzyl iodide		90
	Cyclohexanol	Cyclohexyl iodide	6	00
3	Benzyl alcohol	Benzyl iodide		91
	t-Butyl alcohol	*t*-Butyl iodide	7	00
4	4-Nitrobenzyl alcohol	4-Nitrobenzyl iodide		85
	(-)-Menthol	Menthyl iodide	8	00
5	4-Chlorobenzyl alcohol	4-Chlorobenzyl iodide		87
	t-Butyl alcohol	*t*-Butyl iodide	6	00
6	4-Fluorobenzyl alcohol	4-Fluorobenzyl iodide		82
	4-Chlorophenol	4-Chloro-iodobenzene	5	00
7			4	87
8			5	83

[a] Yields of pure isolated product; products are characterized spectroscopically (IR, ^{1}H NMR) and by comparison with authentic samples [17, 18]

Experimental

The kaolinitic clay was obtained from the Padappakara mine of Quilon District, Kerala, India and was purified, characterized [16, 17], and supplied by Dr. *Lalithambika*, RRL, Trivandrum. Solvents were distilled before use. All chemicals were of analytical grade. IR spectra were recorded on a Bomem MB 104 FT-IR spectrometer. Microwave oven: Kelvinator T-37 model (2450 MHz, 760 W).

General procedure

Natural kaolinitic clay (100 mg) was thoroughly mixed with one drop of conc. H_2SO_4 and 660 mg of KI (4 mmol) and exposed to microwaves for 1 min. This reagent and 5 mmol of 3,4-methylenedioxy benzyl alcohol were thoroughly mixed in a mortar and exposed to microwave irradiation for 10 to 15 s using 100% power. The reaction mixture was cooled to room temperature (1 min) and irradiated again for 10–15 s. After completion of the reaction (TLC), 10 cm^3 of diethyl ether were added to the reaction mixture, and the catalyst was washed with 2×10 cm^3 diethyl ether. The solvent was removed under reduced pressure to afford the product in good yield and in almost pure form. If necessary, products were purified by column chromatography using petroleum ether:ethyl acetate = 9:1 as the eluent.

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