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Functional Group Transformations of Diols, Cyclic Ethers, and Lactones Using Aqueous Hydrobromic Acid and Phase Transfer Catalyst under Microwave Irradiation

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Abstract:

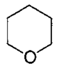
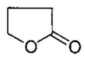
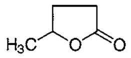
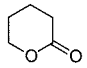
Synthesis of bromoalkanols has been achieved from diols, ethers, and lactones using aq HBr (48%) and tetrabutylammonium iodide/bromide as phase transfer catalyst under microwave irradiation. This environmentally benign route provides enhanced yields of products and does away with the use of benzene as compared to existing conventional methods.

Discussion

Bromoalkanols and bromocarboxylic acids are important intermediates in the synthesis of insect pheromones and other naturally occurring products, as they provide two reactive sites for further reaction. After suitable protection of alcoholic/acidic groups, these compounds can be important precursors for the formation of C−C bonds[1−3] and conversion to Wittig[4] or to a Grignard reagent.[5]

Various methods have been reported in the literature to achieve this goal; however, they require reaction of diols with aqueous hydrogen bromide using a continuous extraction apparatus employing nonpolar solvents such as cyclohexane[5] (72 h) or toluene[6] (16 h). Kang *et al.*[7] have prepared bromoalkanols by refluxing a mixture of diols with 48% aq HBr in benzene in 40−90% yield; dibromide (13%) and unreacted diol (2%) were also present.

Table 1. [a]

S. No.	Substrate	Product	Yield (%)
1.		$HO(CH_2)_4Br$	81
2.		$HO(CH_2)_5Br$	78
3.		$Br(CH_2)_3COOH$	87
4.		$Br(CH_3)(CH_2)_3COOH$	87.5
5.		$Br(CH_2)_4COOH$	85
6.	$HO(CH_2)_3OH$	$HO(CH_2)_3Br$	75
7.	$HO(CH_2)_4OH$	$HO(CH_2)_4Br$	77.4
8.	$HO(CH_2)_5OH$	$HO(CH_2)_5Br$	80.4
9.	$HO(CH_2)_6OH$	$HO(CH_2)_6Br$	75
10.	$HO(CH_2)_7OH$	$HO(CH_2)_7Br$	79
11.	$HO(CH_2)_8OH$	$HO(CH_2)_8Br$	78.7
12.	$HO(CH_2)_9OH$	$HO(CH_2)_9Br$	79.4
13.	$HO(CH_2)_{10}OH$	$HO(CH_2)_{10}Br$	80

[a] Analysis was carried out using ^{1}H NMR and IR spectral data.

Now, microwave energy has been used in a wide variety of reactions,[8−12] owing to their high heating efficiencies with remarkable rate enhancement and dramatic reduction in reaction times. In continuation to our work on chemoselective studies in organic synthesis using microwave irradiation,[13−15] we report a simple and ecofriendly method for the formation of bromoalkanols and bromoacids. On treatment with 48% aqueous hydrogen bromide and tetrabutylammonium iodide/bromide (PTC), diols and ethers provided bromoalcohols in

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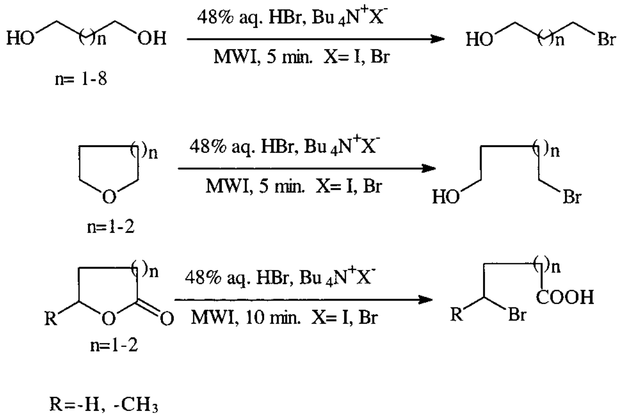
75−80% yield along with dibromide (∼8−10%) on microwave irradiation for 5 min, whereas lactones furnished the corresponding bromoacids. No transformation took place when a mixture of 1,6-hexanediol and aqueous HBr was stirred for 12 h or refluxed in dichloromethane for 12 h with or without tetrabutylammonium iodide/bromide. The use of 20 mol % of the PTC gave best results; the increase of PTC to 30 mol % lead to charring of the reaction mixture and reduced yields of ∼50%. The decreased PTC concentrations of 15 mol % and 10 mol % resulted in reduced yields. Heating the diols with 48% aq HBr in the presence of phase transfer catalyst in an oil bath (100°) for 2.5 h resulted in the formation of monobromoalkanol (60%) and 1,6-dibromohexane (25%); however, in the absence of phase transfer catalyst, no reaction occurred. About a 10% yield of monobromoalkanols was formed when diols and 48% aq HBr were irradiated with microwave energy, without PTC, indicating that microwaves as well as tetrabutylammonium iodide/bromide play an important role for the conversion.



Experimental Section

Microwave assisted reactions were carried out in a BPL BMO 700T (640W) domestic microwave oven. Unless otherwise stated, all organic extracts were dried over anhydrous sodium sulphate. Silica gel (ASC, Mumbai) impregnated with calcium sulphate was used for TLC.

A mixture of 1,6-hexanediol (0.5 g, 4.23 mmol), 48% aq hydrogen bromide (0.74 g, 9.13 mmol), and tetrabutylammonium iodide/bromide (0.84 mmol) was taken in a 100 mL borosil beaker. The beaker was covered with a watch glass and exposed to microwave irradiation. (For low boiling substrates, the beaker was placed in an ice bath. Table 1, entries 1 and 2.) After 5 min of irradiation, the reaction mixture was cooled, extracted with dichloromethane (3 × 10 mL), and washed with saturated sodium bicarbonate solution (2 × 5 mL), 10% aq sodium thiosulphate (2 × 5 mL) (in case of tetrabutylammonium iodide), water (2 × 5 mL), and brine, and the extract was dried over anhydrous $CaCl_2$. Evaporation of solvent in vacuo followed by silica gel chromatography eluting with *n*-hexane/ethyl acetate mixture (8:2) furnished pure 6-bromo-1-hexanol (0.57 g, 75%).

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