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Solid Phase Oxidation of Alcohols and Benzyl Halides to Carbonyls Using Bromate Exchange Resin

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ABSTRACT

Aromate exchange resin prepared by a simple elution technique and used for the biphasic oxidation of alcohols and benzyi halides to corresponding carbonyl compounds.

Key Words: Bromate exchange resin; Solid phase; Oxidation; Alcohols.

3147

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3148

Sikdar et al.

Ion exchange resin are the earliest known support for reagents and catalysts in organic synthesis.^[1] Among the advantages of supported reagents in organic synthesis are easy work-up procedure, mild reaction condition, site specific reactions, and high turn over. Supported reagents are also environment friendly.^[2–6]

In continuation of our work in the field of ion exchange resin supported reagents in organic synthesis, we had earlier reported the use of bromate exchange resin as an oxidizing agent for the oxidation of aldehyde to the carboxylic acids.^[7] We now report the use of bromate exchange resins for the oxidation of alcohols and benzylhalides to the corresponding carbonyl compounds in biphasic condition. An important observation is that primary alcohols were oxidized only to the aldehydes and overoxidation to the carboxylic acid was not observed.

In our earlier communication, we had reported a method of immobilizing Bromate ion onto ion exchange resin namely Amberlite IRA-400(Cl⁻). The extent of loading of bromate ions was likewise reported to be 0.9 mequivalent per gram of resin.

The bromate exchange resin so obtained was used for the oxidation alcohols and benzyl halides to the corresponding carbonyl compounds. Primary alcohols and halides were oxidized to aldehydes, a transformation which is synthetically useful. The reaction were carried out under biphasic condition in organic solvents. Work-up procedure is simple and involves filtration and removal of solvent. Conversion was found to be as high as 90% in some cases. The products were identified by comparing their m.p., IR, UV, and ¹H NMR spectra with authentic samples. Identification of products were also done by conversion to their 2,4-DNP derivatives and the percentage yield ascertained by this procedure.

EXPERIMENTAL

The anion exchange resin used was AmberliteIRA-400(Cl⁻), 20–50 mesh, according to Rohm and Hass specification obtained from Loba Cheme (India). The resin was washed several times with deionized water and dried. All starting materials were purified before use and sodium bromate was used as a source of bromate ions.

Five grams dry bromate exchange resin was eluted several times with the same volume (100 ml) of 1 M aqueous KCl to ensure complete exchange of BrO_3^- with Cl. The resin was further washed with distilled water. The combined volume of the elutent and washing collected and made up to 250 ml. The bromate present in this solution was estimated by

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Bromate Exchange Resin



Where X = -OH, -Cl, -Br; R = alkyl, aryl; $R_1 = alkyl$, aryl, H

Scheme 1.

Sl. no.	Substrate	Product	Reflux time (h)	Yield ^b (%)	M.p of product (°C) obs. (lit.)	M.p. of 2,4-DNP deriv. (°C) obs. (lit.)
1.	o o o t		8	95	93 (95)	191 (189)
2.	OH	0°0	8	95	50 (48)	238 (238)
3.	ОМ	\bigcirc	10	88	Liquid ^a	248 (255)
4.	ОН	o	10	81	Liquid ^a	160 (160)
5.	MeCHCOOH ' OH	МеССООН О	7	72	Liquid ^a	213 (218)
6.	ОН	Р	12	74	Liquid ^a	236 (240)
7.	X X = -ClBr	Р	12	77, 84	Liquid ^a	236 (240)
8.	OH		8	75	54 (56)	240 (244)
9.	OH Me ,N	Me . N	10	80	72 (74)	Above 270 (320)

Table 1. Oxidation of alcohols to carbonyl compounds.

(continued)

3149

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3150

Sikdar et al.

Table 1	. Con	tinued.

Sl. no.	Substrate	Product	Reflux time (h)	Yield ^b (%)	M.p of product (°C) obs. (lit.)	M.p. of 2,4-DNP deriv. (°C) obs. (lit.)
10.	ОН	CI H	7	80	46 (47)	260 (265)
11.	ОН Н	Мео	8	78	Liquid ^a	250 (253)
12.	ОН		8	88	Liquid ^a	246 (240)
13.	OH		10	88	41 (42)	227 (227)

^aLiquid products directly converted to the hydrazone.

^bYield calculated on the basis of hydrazone obtained. M.p. determined in open capillaries.

a standard procedure according to the reaction

 $BrO_3^- + 6l^- + 6H^+ = Br + 3l_2 + 3H_2O$

The amount of loading was found to be 0.9 mequivalent per gram of resin. $\ensuremath{^{[8]}}$

OXIDATION WITH RESIN IMMOBILIZED BROMATE (GENERAL PROCEDURE)

To 0.01 mole of the substrate dissolved in 100 ml of dioxane was added 15 g of the bromate exchange resin and the solution stirred at reflux temperature. The progress of the reaction was monitored by TLC on silica gel-G plate till complete conversion was observed. The solution was filtered and the product was obtained by removal of solvent by distillation under reduced pressure. The products obtained were converted to their 2,4-DNP derivatives by standard procedures. The results are summarized in Sch. 1 and Table 1. It may also be mentioned that the reaction time can be reduced if 2–3 drops of conc. H_2SO_4 are added to the reaction mixture. This is due to the rapid decomposition of MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

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Bromate Exchange Resin

3151

bromate ions by the action of mineral acid to give oxygen which now acts as the primary oxidant.

The study revealed the versatility of bromate ions for the oxidation of organic substrates provided they were immobilized onto an ion exchange resin. Simplicity of workup procedure is an added advantage. The oxidation of halides and alcohols to aldehydes by this procedure is noteworthy.

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