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SHORT COMMUNICATION

OXIDATION OF ORGANIC COMPOUNDS BY POLYMER-SUPPORTED BROMATE ION

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ABSTRACT

Aromatic aldehydes, secondary alcohols and thiophenol have been oxidized by polymer-supported bromate ion under mild reaction conditions to give the oxidized products in high yields and purities.

Polymer-supported ionic reagents have been used in the past to oxidize organic compounds. Polymer-supported acid chromate oxidizes alcohols (1) and allylic or benzylic halides (2) in benzene to aldehydes and ketones. Polymer-supported periodate in methylene chloride smoothly oxidizes quinols and sulphides (3). Polymer-supported iodate effects the same oxidations but the reactions are slower and it could not oxidize sulphides (3).

Potassium bromate has long been used as an oxidant for many organic compounds such as secondary alcohols (4), alpha-hydroxy acids (5) and aliphatic saturated aldehydes (6). In many of these methods, mercuric acetate is used to remove HBr formed.

In continuation of work (7 - 9) on polymer-supported reagents, we now report a simple method for the oxidation of the above compounds by bromate supported on Amberlyst A-26 in acetic acid. The concentration of acid was kept constant. Oxidations of some of the compounds (5, 6, 11) reported here have not previously been carried out under classical conditions. Oxidations of aromatic aldehydes, secondary alcohols and thiophenol with A-26 supported bromate ion gave the corresponding acids, ketones and dithiodiphenyl respectively.

The usual advantages of polymer-supported reactions (such as high yield , purity of product and easy work-up) apply to the present reaction also. HBr is taken up by the resin so that mercuric acetate is not needed. The bromide form of the resin obtained in the reaction can be re-used. The products obtained in high yield were essentially pure and were characterized by N.M.R., I.R. and comparison with authentic samples; volatile ketones were also characterized by their 2:4 D.N.P. derivatives.

Typical Procedure. The chloride form of Amberlyst A-26 (5 g) was stirred for 6 h with potassium bromate (5 g) in 50 ml of water. The resin was then filtered and washed successively with water, ethanol and ether and finally dried overnight at 50° in vacuum over P_2O_5. The capacity of the resin was calculated as follows. 0.3 g of Amberlyst A-26 bromate resin was washed with 50 ml of 0.2M KI and the washings diluted to 100 ml. The diluted solution was titrated iodometrically. The capacity of the resin was found to be 3.2 mmol of bromate/g.

To the above polymer-supported bromate ion dry resin (5 g) in 20 ml of 50% acetic acid was added 5 mmol of the substrate; the mixture was heated for 1 to 5 h. The resin was filtered off. The filtrate was distilled under vacuum to remove acetic acid and water. The solid products obtained in high yield were essentially pure. In the case of volatile ketone as product, the filtrate was fractionally distilled to obtain the required product. 2:4 D.N.P. reagent was then used to give a derivative which was characterized by the usual method.

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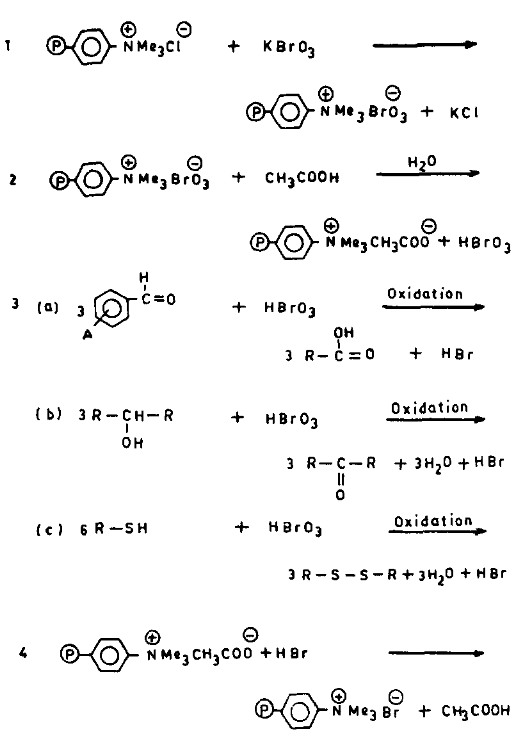
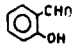
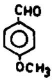
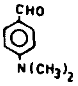
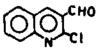
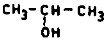
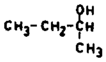
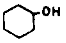
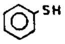
Reaction



TABLE

Sr. No.	Substrate	Reaction Time in hour	Reaction Temp. °C	Yield %
1		5	100	90
2		5	100	90
3		3	80	92
4		4	80	90
5		5	100	85
6		3	100	80
7	 $CH_3-\underset{OH}{CH}-CH_3$	1	80	95
8	 $CH_3-CH_2-\underset{CH_3}{\overset{OH}{CH}}$	1	80	92
9		2	85	88
10		3	85	80

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