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POLYMER SUPPORTED REAGENTS. CHROMIC ACID ON ANION EXCHANGE RESIN SYNTHESIS OF ALDEHYDES AND KETONES FROM ALLYLIC AND BENZYLIC HALIDES

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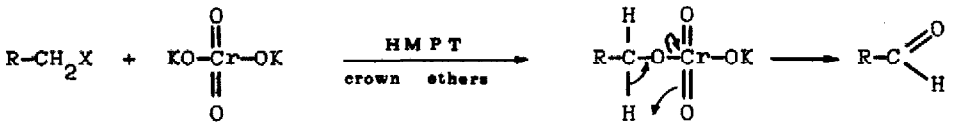
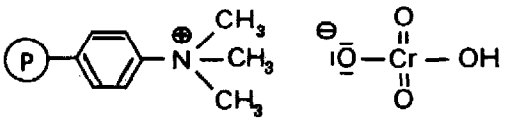
In recent work [1] we reported the reaction between alkyl halides and K_2CrO_4 in HMPT in the presence of crown ethers, to provide an attractive synthetic route to aldehydes in good yields.



Because of the great difficulties encountered to solubilize the chromate ion in the organic solvents, we supported the reagent on insoluble polymer matrix. The polymeric support has moreover the advantage to provide a particular reaction environment capable of enhancing the nucleophilicity of the ion and reducing the working-up to a mere filtration. The use of polymer supported reagents has been already applied in our laboratory for the synthesis of esters and fluorides [2]. We have obtained interesting results in the oxidation of primary and secondary alcohols to carbonyl compounds in good yields using a $HCrO_4^-$ resin [3].



The same reagent has been now used to obtain aldehydes and ketones from allylic and benzylic halides. The table summarizes the results obtained.

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TABLE

HALIDE	REACTION TIME [a]	% CARBONYL COMPOUND [b,c]
Benzyl chloride	75'	95
Benzyl bromide	75'	98
Geranyl bromide	120'	95 [d]
Bromo(diphenyl)-methan	60'	95
9-bromofluoren	120'	97
Ethyl 4-bromo-3-methyl-butenoate	120'	95 [d]

a) Reaction was carried with a 2 : 1 ratio meq resin / mmol substrate in refluxing benzene.

b) Products were characterized by comparison with authentic material by NMR and IR spectra, TLC and GLC analysis (Column: Carbowax 20 M (1/8 in × 6 ft; 10% on 80 - 100 mesh Chromosorb G). Column temperature: program from 50° to 200° at 10°/min. Injection port: 280°. Carrier gas: N_2, 1.0 Kg/cm^2).

c) Yield refers to pure isolated compounds.

d) A mixture of E/Z isomers was recovered in the same ratio as the starting material.

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