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ZINC SALT ASSISTED SOLVOLYSES OF TERTIARY ALKYL HALIDES

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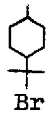
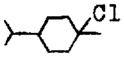
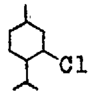
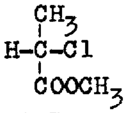
Summary: Tertiary alkyl halides undergo facile substitution reactions under solvolytic conditions in presence of zinc ions yielding alcohols, ethers and esters.

Solvolysis of alkyl halides is a well understood reaction[1]. While primary alkyl halides readily yield substitution products under solvolytic conditions, elimination is a competitive reaction in the case of secondary and, more so, tertiary alkyl halides. Nucleophilic substitution is known to be assisted by salts of silver and mercury, but even under these conditions tertiary and cycloalkyl halides yield mixtures of products and the reaction is unsuitable for preparative purposes[2].

During the course of our work on the preparation of some commercially important terpene esters, we have found that tertiary alkyl halides yield predominantly the substitution products when solvolysis is carried out in presence of the corresponding zinc salts[3]. Thus, α-terpinyl chloride when refluxed in 80% aqueous acetone over zinc oxide gave α-terpineol in over 85% yield. Using alcohols and carboxylic acids as solvents ethers and esters are obtained in excellent yields. The reaction is equally facile with the dissolved zinc salt or zinc oxide, which forms the salt in situ, and is carried out by stirring together 1 mole of the alkyl halide, 0.5 mole of zinc oxide (or the salt) and 5 moles of the solvent. As expected, the the reaction is faster with the bromo compounds and elimination products predominate at higher temperatures. Table 1 shows the reaction conditions and the yields of the products with representative examples of cyclic and acyclic halides and different solvents. Primary and secondary alkyl halides do not react under these conditions even over prolonged periods. The reaction understandably should follow S_N1 mechanism, the initial polarization of the alkyl-halogen bond being assisted by the affinity of the halogens to zinc.

Table 1

Alkyl halide	Solvent	Reaction temperature/time	Product	Yield %
	80% Aq.acetone	reflux/6 hr.	α-terpineol	85
	Acetic acid	25-30°/2 hr.	α-terpinyl acetate	90
	Formic acid(98%)	12-15°/2 hr.	α-terpinyl formate	95
	Methanol	reflux/2 hr.	α-terpinyl methyl ether	95
	Acetic acid	12-15°/30 min.	α-terpinyl acetate	85
	Acetic acid	35-40°/2 hr.	dihydro-β-terpinyl acetate	65
	Formic acid(98%)	12-15°/2 hr.	dihydro-β-terpinyl formate	70
	80% Aq.acetone	reflux/6 days	no reaction	
	Acetic acid	35-40°/6 days	no reaction	
 CH_3 H-C-Cl $COOCH_3$	Acetic acid	35-40°/6 days	no reaction	
n-BuBr	Acetic acid	35-40°/3 days	no reaction	

As tertiary alkyl halides are readily obtainable, the present discovery of substitution reactions at the tertiary center should find considerable synthetic utility. We know of one report[4] of conversion of t-butyl halides to t-butyl acetate using mercuric acetate in diglyme. The applicability of this method to other systems has not been tested; moreover, the well known reactions of mercuric salts with unsaturated systems is a serious limitation.

References and Notes:

1. C.K.Ingold, "Structure and Mechanism in Organic Chemistry", 2nd Ed., Bell, London, 418(1969)
2. A.McKillop and M.E.Ford, Tetrahdron, **30**,2467(1974)
3. A preparative procedure (based on this principle), suitable for the manufacture of some terpenic perfumery and flavouring compounds is being patented in India
4. R.C.Larock, J.Org.Chem., **39**,3721(1974)

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