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Sonochemical Acetylation Reactions of Tertiary Alkyl Halides

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SONOCHEMICAL ACETYLATION REACTIONS OF TERTIARY ALKYL HALIDES

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ABSTRACT: A simple method for the acetylation of tertiary alkyl halides is described. The reaction was carried out using zinc acetate in presence of a phase transfer catalyst in an ultrasonic bath.

In recent years ultrasonic irradiation has a beneficial role in synthetically useful reactions.[1-7] Sonication will decrease the reaction time and increase the product yield. Metal assisted couplng reactions of alkyl halides and Williamson reactions has been investigated in ultrasonic bath.[8-12]

Nucleophilic substitution at saturated carbon are extensively studied reactions[13,14]. Each type of reaction has its own limitations. When solvolytic substitution is employed for t-alkyl halides, the proportion of elimination product increase with the

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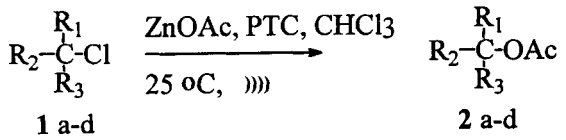
size of these substituents on α-carbon atom. We observed the formation of 30-65% elimination product in the Zn/ROH reaction of ar-curcumyl chloride during our studies on aroma chemicals.[15] Hg^{2+} assisted solvolytic reactions cannot be used for t-alkyl halides since they yield a variety of products. Substitution reactions of t-alkyl halides using zinc salts have good preparative value.

In the present investigation attempts were made to transfer acetate ion from zinc acetate using commercially available phase transfer catalyst such as tetra-n-octyl ammonium bromide. But no significant reaction was observed. We renewed this method by using sonochemical modifications using mild reaction conditions. The applicability of the reaction to some t-alkyl halides were examined.

Compounds **1** a-d were examined, namely t-butyl, t-cumyl, α-terpenyl chloride and ar-curcumene hydrochloride (Scheme 1).

Products **2** a-d were prepared and the percentage yield are given in Table 1.

The results provide evidence that good yields of the expected products can be obtained in short time. Hence the elimination products could be relatively minimised.



1 a-d **2** a-d

1 a; $R_1 = R_2 = R_3 = CH_3$
1 b; $R_1 = R_2 = CH_3$, $R_3 = C_6H_5$
1 c; $R_1 = R_2 = CH_3$, $R_3 = C_6H_9\text{-}CH_3$
1 d; $R_1 = R_2 = CH_3$, $R_3 = CH_3\text{-}C_6H_4\text{-}C_5H_{10}$

Scheme 1

Table 1. Products 2 a-d prepared

Product 2	Reaction time(min)	Yield(%)
a	15	60
b	65	65
c	55	70
d	25	75

The scope of the reaction can be extended further by simply replacing the branching at α-carbon atom.

The process can be utilized for making several perfumery and flavour compounds from terpene hydrocarbons.

EXPERIMENTAL

General Procedure

The reactions were carried out in a Kerry Pulsatron 125

ultrasound cleaning bath at room temperature. In a typical experiment t-alkyl halide (2.5 mmol), tetra n-octyl ammonium bromide (0.25 mmol), zinc acetate (5%,5 ml) potassium carbonate (2.5 mmol) and chloroform (5 ml) were mixed and sonicated. The progress of the reaction was followed by ^{1}H NMR. After the reaction the organic layer was separated, dried over sodium sulphate and purified by passing through a column of silica gel.

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