

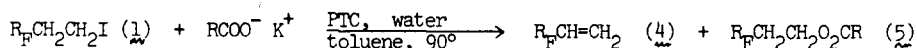
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## SYNTHESIS OF 2-(F-ALKYL)ETHANOLS AND ESTERS BY PHASE TRANSFER CATALYZED S<sub>N</sub>2 REACTIONS OF 2-(F-ALKYL)-1-IODOETHANES

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R<sub>F</sub>CH<sub>2</sub>CH<sub>2</sub>I (1) reacted well with carboxylate ions in liquid/liquid two phase systems. The S<sub>N</sub>2 product, an ester (5) and the E-2 product, an alkene (4) were determined quantitatively in a careful study of several reaction parameters. Conversion of 1 reached 99% in



24 h at 90° and selectivity to ester (5/4) varied with nucleophilicity (basicity) of RCOO<sup>-</sup>. The weaker the base the slower the reaction, and the higher the selectivity. Values of 5/4 were: R = CF<sub>3</sub>, 12; NCCCH<sub>3</sub>, 10; H, 2.3; CH<sub>2</sub>=CH, 1.7. In a series of comparable basicity (K<sub>a</sub> of RCOOH = 1.5 to 2.2 × 10<sup>-3</sup>), the branched ions were superior to short and straight chain substances. 5/4 were: R = CH<sub>3</sub>, 0.6; CH<sub>2</sub>CH=CH, 2.0; n-Bu, 1.3; and i-Bu, 2.76. KOAc vs. KO<sub>2</sub>CHMe<sub>2</sub> and 1 gave isobutyrate/acetate ester of 8.9. In these reactions toluene was better than octane as solvent. Several phase transfer catalysts (PTC) were evaluated.

Reactions run in a dipolar, aprotic solvent gave highly inferior results. 1 with KOAc or with KO<sub>2</sub>CHMe<sub>2</sub> gave varying amounts of reaction, but mostly E-2 product. For KOAc 5/4 was 0.28 to 0.19. Catalysts such as '18-Crown-6' decreased further the selectivity. However, it is believed that phase transfer processes can be improved further.

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## VAPOR PHASE HYDROLYSIS OF BENZAL CHLORIDES HAVING TRIFLUOROMETHYL GROUP ON SOLID ACID CATALYSTS

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Benzaldehydes having trifluoromethyl group (1) were known to be prepared by hydrolysis of the corresponding benzal chlorides (2) with conc. sulfuric acid. However, this method is not favorable for the synthesis of 1 because of the formation of tarry materials and the complexity of the reaction process. In order to overcome these disadvantages, vapor hydrolysis of 2 was investigated in the presence of solid acid catalysts. Metal oxides such as γ-Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> gave 1 but their lives of catalytic activities were not satisfactory. While activated carbon soaked in conc. sulfuric acid yielded 1 with a little amount of phthalic acids, metal chlorides supported on activated carbon gave 1 without hydrolysis of the trifluoromethyl group. Metal chlorides such as Fe(III), Mn(II) and Co(II) were the most effective in these reactions.