

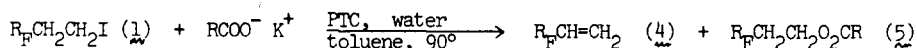
0-69

SYNTHESIS OF 2-(F-ALKYL)ETHANOLS AND ESTERS BY PHASE TRANSFER CATALYZED S_N2 REACTIONS OF 2-(F-ALKYL)-1-IODOETHANES

Neal O. Brace

Wheaton College, Wheaton, IL 60168 (U.S.A.)

R_FCH₂CH₂I (1) reacted well with carboxylate ions in liquid/liquid two phase systems. The S_N2 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⁻. The weaker the base the slower the reaction, and the higher the selectivity. Values of 5/4 were: R = CF₃, 12; NCCH₃, 10; H, 2.3; CH₂=CH, 1.7. In a series of comparable basicity (K_a of RCOOH = 1.5 to 2.2 × 10⁻³), the branched ions were superior to short and straight chain substances. 5/4 were: R = CH₃, 0.6; CH₂CH=CH, 2.0; n-Bu, 1.3; and i-Bu, 2.76. KOAc vs. KO₂CHMe₂ 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 KO₂CHMe₂ 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.

0-70

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

T. Kondow*, K. Okazaki and Y. Katsuhara

Tokyo Research Center, Central Glass Co., Ltd. (Japan)

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-Al₂O₃ and TiO₂ 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.