A Modified Procedure for the Synthesis of tert-Butylacetic Acid

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In order to investigate steric effects in enamines we needed a series of neopentyl ketones and to prepare these ketones substantial amounts of 3,3-dimethylbutanoic acid (tert-butylacetic acid) were needed. 3,3-Dimethylbutanoic acid is accessible by several routes, e.g., haloform cleavage of neopentyl methyl ketone, \(^1\) via conjugate addition of methyl Grignard reagents to ethyl isopropylidenedicyanacetate \(^2,3\) and by the Willgerodt reaction of pinacolone. \(^4\) Recently a method using the boron trifluoride catalyzed addition of tert-butyl chloride to 1,1-dichloroethylene appeared. \(^5\)

We now report that this method can be modified by replacing gaseous boron trifluoride by the more easily handled and less expensive boron trifluoride dihydride. The yields of 3,3-dimethylbutanoic acid by the modified procedure were in the range of 79 – 81 % of isolated, distilled product in 1 mol runs to compare with the reported yield, 79 %, by the original procedure. \(^5\)

Experimental. Synthesis of 3,3-dimethylbutanoic acid. A typical procedure was: To a stirred solution of 33 ml of boron trifluoride dihydride (pract. Fluka AG) in 200 ml of concentrated sulfuric acid was added dropwise over a period of 3 h a mixture of 92.5 g (1 mol) tert-butyl chloride (puriss. KEBO) and 146 g (1.5 mol) of 1,1-dichloroethylene (p.a. KEBO). The temperature of the reaction mixture was maintained between 5 – 15 °C during addition. The mixture was then stirred at 10 °C for an additional 0.5 h, whereafter the mixture was poured onto crushed ice. The aqueous solution was saturated with sodium chloride and extracted several times with ether. Drying (MgSO\(_4\)), removal of solvent and distilling the crude product under reduced pressure afforded 94.0 g (81 %) of pure (≥ 98 %, \(^1\)H NMR) 3,3-dimethylbutanoic acid, b.p. 91 – 93 °C/20 mmHg (litt. \(^6\) 96 °C/26 mmHg).


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