$AgNO_3$ (Silver Nitrate) Test

Functional Group(s): Tertiary and secondary alkyl halides
Known(s): Alkyl bromide starting material; Alkene standard(s) for your reaction

Procedure

Set up a test tube rack containing 3-4 small (75mm X 12mm) test tubes. Label the test tubes 1-3 (or 1-4). Add ~1 ml of the silver nitrate in ethanol reagent to each tube. Add 5-8 drops of the alkyl bromide solution to tube # 1, 5-8 drops of the reaction mixture to tube #2, and 5-8 drops of the alkene solution to tube #3. (If more than one alkene is tested, add an additional tube to the set up). Set a stopwatch. Note the amount of time that elapses from when the solution is added to the reagent and when a result is observable. Observe and record the results immediately, and after 1-3 minutes. If no changes occur at room temperature, vortex the solutions for 20-30 seconds. If still no changes occur, warm the tubes in a ~50°C water bath. To warm the tubes, set a beaker with water in it on the hot plate. Heat the water until just below boiling. Using a test tube clamp, warm each tube in the water for 3-5 minutes. (*Do not set the tubes in the water bath without being clamp. They will fall into the bath and results cannot be evaluated!*). Observe each tube for the formation of a precipitate or color change.

Results

The formation of a precipitate (silver halide salt) is an indication that the tested compound contains a secondary or tertiary alkyl halide, or other alkyl halides capable of forming a "stable" carbocation (i.e., allylic, benzylic). Some cyclic alkyl halides may react very slowly (i.e. cyclohexylchloride). This test is most useful when run alongside the sodium iodide in acetone test, especially to distinguish between primary and tertiary alkyl halides.

Theory

In the presence of ethanolic silver nitrate, alkyl halides that can form "stable" carbocations react, through an SN_1 mechanism to provide a substitution product, in this case, an ether derived from the alkyl halide and the ethanol nucleophile. The silver of the silver nitrate reagent acts as a Lewis acid to promote formation of the carbocation. An insoluble silver halide is formed as a by-product, along with the carbocation. The observed precipitate (the silver halide) indicates a carbocation has formed. Once the carbocation is generated, it reacts with the oxygen atom of ethanol, to first generate an oxonium ion, which rapidly is converted to the ether product.