Use of Different Alkali Carbonates in the Methylation of Acetylacetone

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In 1894, Claisen [1] reported that Fette had prepared methylacetylacetone by alkylation of acetylacetone with methyl iodide and potassium carbonate in alcohol or ether solution, but he did not give any detailed procedure.

In recent years this method has been of some importance in preparing alkylated β-ketoesters [2,3]. In these cases ketones have been used as solvents.

Fette [1,4] stated that potassium derivatives of β-diketones were markedly more reactive than the sodium derivatives. In order to confirm this and to work out a practical method for the synthesis of alkylated β-diketones, a kinetic study of the methylation of acetylacetone with the aid of methyl iodide and an alkali carbonate has been carried out.

The reaction appears to be of the first order and the reaction velocity is directly proportional to the concentration of methyl iodide. The monomethylation process proceeds about ten times as fast as that of the dimethylation. The monomethylation reaction constant with potassium carbonate is of the order of 1.8×10^{-3} min^{-1} at 769 mm and reflux temperature.

The reaction constants with the other alkali carbonates are: *sodium* carbonate about a fiftieth, *rubidium* carbonate seven times, and *cesium* carbonate ten times that with *potassium* carbonate. This very great difference is perhaps due to the solubility of the carbonate and the acetylacetonate in the reaction medium.

The use of rubidium and cesium carbonate in alkylation processes is therefore very advantageous when the reaction proceeds slowly with potassium carbonate. The disadvantage of the relative high costs of these carbonates can be overcome as they can be readily recovered.

Experimental. Long necked, thin walled, round bottomed micro flasks were made from 15 cm lengths of Pyrex tubing with an external diameter of 6 mm and an internal diameter of 3 mm. The diameters of the completed flasks were 14 mm.

Pyrex wool and a carbonate (23 mg of sodium, 30 mg of potassium, 50 mg of rubidium, or 70 mg of cesium carbonate) were placed in a number of these micro flasks. Small jackets, for reflux condensers, were placed on the necks of the flasks, and the necks were scratched immediately under the condensers. 0.200 ml of an acetone solution, containing 10.00 mg of acetylacetone and 40.000 mg of methyl iodide, were added to each flask with cooling in an ice bath. The mixture was then refluxed by immersing the flasks in a bath at 65°, while alcohol at — 15° was circulated through the condensers. At fixed intervals the neck of a flask was broken, the flask washed, wipped off with a piece of filtering paper and then broken. The contents were washed into an Erlenmeyer flask with 2 per cent acetic acid and the iodide ions formed titrated with silver nitrate using eosine as indicator.

1. Claisen, L. *Ber.* **27** (1894) 3184.
2. Stenhagen, S., and E. *Arkiv Kemi, Mineral. Geol.* **A 19** (1945) no. 1.
3. Hunsdiecker, H. *Ber.* **75** (1942) 1190.
4. Fette, A. *Diss.* München (1894).

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tions for this substance, but it should be noted, that it could be formed by oxygen atoms by a side reaction leading to phenyl- and hydroxyl-radicals or by a ternary reaction between one oxygen atom and two benzene molecules.

1. Merz, J. H., and Waters, W. A. *J. Chem. Soc.* (1949) 2427.
2. Andersen, V.S. *Acta Chem.Scand.* **2** (1948) 1.

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