

## ULTRASOUND IN ORGANIC SYNTHESIS 5<sup>1</sup>.

### PREPARATION AND SOME REACTIONS OF COLLOIDAL POTASSIUM

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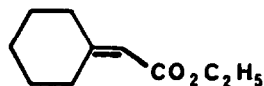
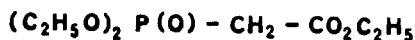
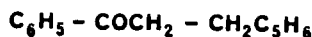
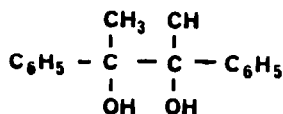
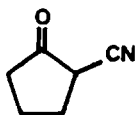
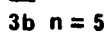
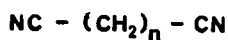
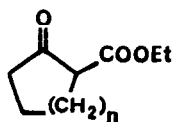
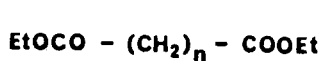
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Summary : colloidal potassium is easily obtained by ultrasonic irradiation in toluene. Some of its reactions with organic substrates are given.

A number of synthetically valuable organic reactions make use of alkali metals. Frequently they react as solutions in various media<sup>2</sup>, as dispersions as a sand<sup>3</sup> or absorbates on solid supports such as alumina<sup>4</sup>, silica<sup>5</sup>, charcoal<sup>6</sup> or graphite<sup>6,7</sup>. However the preparation of these reagents can be hazardous or tedious and a more easily performed method would be desirable.

Colloidal alkali metals have been known for a long time<sup>8</sup>. They can be prepared in various solvents by radiofrequency electric discharges or condensation of metallic vapors. To our knowledge they have not been used in organic synthesis. We wish to report here an extremely easy and rapid method for the formation of colloidal potassium.

When a piece of this metal in dry toluene or xylene under an argon atmosphere is submitted to ultrasonic irradiation<sup>9</sup> at ca. 10°C, a silvery blue color is rapidly developed and after a few minutes the metallic fragment has disappeared. A very fine suspension of potassium is thus obtained, which settles very slowly on standing. In tetrahydrofurane, the same experiment was unsuccessful. Negative results were also observed with lithium in the 3 solvents tested, whereas sodium was dispersed in xylene only. These results seem to indicate that ultrasonic waves interact with the metal by their cavitation effects, which are known to be closely related to some physical constants of the medium (vapor pressure, viscosity, surface tension...)<sup>10</sup>.



When a toluene solution of diethyl adipate 1a is added to colloidal potassium in the same solvent at room temperature, the blue color disappears within a few minutes. Work-up of the mixture and purification gives ethyl 2-oxocyclopentane carboxylate 2a in 83% isolated yield<sup>11</sup>. Under these conditions, the Dieckman condensation is highly favored and much more rapid as by the usual technique. Following the same process, diethyl pimelate 1b, adiponitrile 3a and pimelonitrile 3b yield ethyl 2-oxocyclohexane carboxylate 2b (75%), 2-cyanocyclopentanone 4a (82%) and 2-cyanocyclohexanone 4b (75%). In contrast, diethyl suberate 1c, azelate 1d and sebacate 1e were recovered unaffected after several hours in the presence of the reagent.

Reaction of ketones with alkali metals is a rather complex process<sup>12</sup>. With colloidal potassium, acetophenone gives a pale yellow suspension which is hydrolyzed to afford 82% of starting material and 18% of pinacol 5. Quenching with benzyl bromide instead of water produces 70% of alkylated products among which 46% of compound 6 were identified by VPC. Similarly, 4-*t*-butylcyclo-

hexanone trimethylsilyl enol ether was obtained in 75% yield from reaction of the ketone with K followed by quenching with chlorotrimethylsilane.

Potential synthetic utility of colloidal potassium is further exemplified by the following experiment.

Addition of triethyl phosphonoacetate 7 to colloidal potassium in toluene at room temperature produced an instantaneous evolution of hydrogen and a colorless solution of the expected ylide which gave by reaction with cyclohexanone<sup>13</sup>, a 81% isolated yield of ethyl cyclohexylidene acetate 8. Other synthetic applications of the easily prepared reagent are presently under investigation.

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#### References

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9. A common cleaning bath (Sonoclean, 35 kHz) filled with water and crushed ice was used.
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11. 78 mg of K and 5 mL dry toluene are sonicated for 15 min. 202 mg of diethyl adipate in 2 mL dry toluene are added via a syringe into the colloid. The mixture turns orange with a moderate heat evolution. After 5 min. standing, the mixture is quenched with ethanol then aq.HCl and worked up. Chromatography (SiO<sub>2</sub>) of the crude mixture yields 130 mg of the ketoester (83%). Replacement of colloidal potassium by lithium or sodium sands leaves the starting material unchanged.
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b) Sonication of acetophenone with lithium sand in toluene or THF give the corresponding pinacol 5 in 0% and 74% yield respectively. (unpublished results)
13. Addition of 224 mg (1 mmole) of triethyl phosphonoacetate to 1 meq. colloidal K in dry toluene produces a vigorous hydrogen evolution. The immediately obtained clear solution is reacted at room temperature with 98 mg (1 mmole) cyclohexanone for 2 hrs. Work-up and purification (SiO<sub>2</sub> chromatography) gives 136 mg (81%) of compound 8.

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