Convenient Preparation of 'High-Surface Sodium' in Liquid Ammonia: Use in the Acyloin Reaction

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Abstract. 'Sodium on solid support' (5-20 wt.% of Na on NaCl, glass powder, poly(ethylene) and poly(propylene)) can be conveniently prepared *via* low-temperature (-33°C) deposition of sodium from its solution in liquid ammonia. Use of this reagent in the acyloin reaction of carboxylic esters gave the corresponding products in good yields.

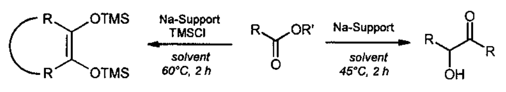
Reagents adsorbed on solid supports are widely used in organic synthesis because they offer some significant advantages such as high activity often connected with better selectivity, simplicity of handling of active reagents, and easy work-up. Among reagents of particular interest is 'high-surface sodium' - metallic sodium deposited on solid support (alumina, titanium dioxide, sodium chloride).[1] This reagent was used *inter alia* for reduction, alkylation and isomerization of organic compounds[2] and preparation of active metals *via* reduction of the corresponding salts.[3] The common methods of preparation of supported sodium consist in vigorous mixing/grinding of the support with melted sodium metal in inert atmosphere at 180-190°C or in boiling solvent (toluene, xylenes).[2] For obvious reasons these procedures are dangerous and inconvenient in laboratory execution.

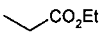
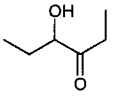
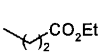
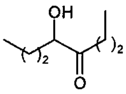
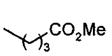
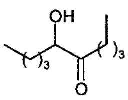
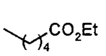
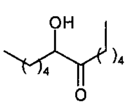
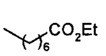
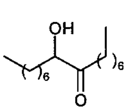
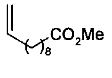
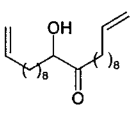
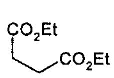
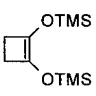
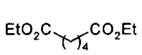
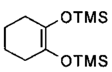
We have found that 'high-surface sodium' can be conveniently prepared *via* deposition of sodium on solid support from its solution in liquid ammonia. In this procedure support materials such as powdered NaCl, glass beads (100 and 200-230 Mesh), as well as poly(ethylene) and poly(propylene), could be used. Evaporation of liquid and removal of traces of ammonia under vacuum leaves a grey, *nonpyrophoric* powder, containing 5-20 wt. % of Na, depending on the ratio of starting materials. We used the acyloin reaction to test the performance of this reagent.

The condensation of carboxylic esters promoted by finely pulverized alkali metal (sodium, less frequently potassium or Na/K alloy) in inert solvent produces α-hydroxyketones (acyloins).[4] The quality of sodium dispersion is essential for the reaction - presence of large particles promotes side reactions and decreases the yield of the desired product.[5] Usually the sodium dispersion is prepared *via* vigorous stirring of molten sodium in boiling toluene or xylene and, when necessary, replacing of the solvent by repeated washing.[6] The *homogeneous* acyloin condensation with sodium naphthalenide or sodium in liquid ammonia-ether proceeds satisfactory in some cases, but is not a general process.[4b]

Since 'sodium on solid support' prepared in liquid ammonia is highly dispersed we expected that it should be an efficient agent promoting the acyloin condensation. Indeed we have found that treatment of a variety of esters with this reagent (in scale of 0.15 to 0.005 mol) resulted in the formation of the expected product in good yields (Table 1).[7]

Table 1. Acyloin Reaction with 'High-Surface Sodium'



Substrate	Product	Support (wt. %)	Sol-vent	Yield (%)[a]	Lit. Yield (%)
		NaCl (10)	THF	34[b]	50-65[4b]
		NaCl (10)	Et_2O[c]	63	50-80[4b]
		NaCl (20)	THF	57	
		NaCl (20)	C_6H_6	65	50[4b]
		NaCl (20)	THF	64	50-80[4b]
		NaCl (20)	C_6H_6	78	53-90[4b]
		NaCl (20)	THF	43	50[4b]
		NaCl (20)	C_6H_6	62	
		PP (10)[d]	C_6H_6	76	
		Glass 100 Mesh (5)	THF	70	65-86[8]
		PE (10)	THF	62	
		NaCl (10)	THF	58	
		PE (16)[e]	Tolu-ene[f]	60	64[9]

[a] Isolated yields. [b] Reaction mixture contains unreacted starting material, ca. 30% by GC. [c] At reflux temperature. [d] PP = Poly(propylene). [e] PE = Poly(ethylene). [f] Addition of substrates (16 h) and reaction (2 h) at 45°C.

In conclusion these results clearly demonstrate that the hazardous and tedious preparation of highly dispersed sodium from the molten metal can be replaced by the simple and convenient low-temperature (-33°C) deposition of sodium from liquid ammonia. Application of the described procedure to preparation of other 'high-surface metals' and its use in organic synthesis is forthcoming.

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References and Notes

(1) The term 'high-surface sodium' was used by National Distillers Chemical Co. to describe films of sodium on various inert solids. See Ref. 2b.

(2) Leading references: a) Shabtai, J., Gil-Av, E. *J. Org. Chem.* **1963**, *28*, 2893. b) Hart, H., Chen, B. L., Peng, C. T. *Tetrahedron Lett.* **1977**, 3121. c) Rienäcker, R., Graefe, J. *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 320. d) Singh, S., Dev, S. *Tetrahedron* **1993**, *49*, 10959. Review: e) Fürstner, A. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley, New York **1995**, 4180.

(3) a) Stadtmüller, H., Greve, B., Lennick, K., Chair, A., Knochel, P. *Synthesis* **1995**, 69. b) Fürstner, A., Seidel, G. *Synthesis* **1995**, 63. c) Fürstner, A., Seidel, G., Gabor, B., Kopiske, C., Krüger, C., Mynott, R. *Tetrahedron* **1995**, *51*, 8875. d) Fürstner, A., Seidel, G., Kopiske, C., Krüger, C., Mynott, R. *Liebigs Ann.* **1996**, 655. e) *Active Metals. Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH, Weincheim, **1996**.

(4) a) McElvain, S. M. *Org. React.* **1948**, *4*, 256. b) Bloomfield, J. J., Owsley, D. C., Nelke, J. M. *Org. React.* **1976**, *23*, 259. c) Rühlmann, K., *Synthesis* **1971**, 236.

(5) Salaün, J., Marguerite, J. *Org. Synth.* **1984**, *63*, 147. The modification of acyloin condensation using chlorotrimethylsilane may be markedly simplified by sonochemical activation. In this case small cubic pieces of sodium can be used. See: Fadel, A., Canet, J.-L., Salaün, J. *Synlett* **1990**, 89.

(6) Snell, J. M., McElvain, S. M. *Org. Synth.* Coll. Vol. II **1943**, 114.

(7) Typical procedure: *12-Hydroxydocosa-1,21-dien-11-one.* Under argon. Sodium (604 mg) was added to a stirred suspension of finely powdered NaCl (2.5 g) in liquid ammonia (30 mL). After 5 min. ammonia was evaporated to dryness. Traces of ammonia were removed under vacuum (1h at 45°C) and the residue was suspended in dry benzene (50 mL). To the stirred suspension methyl undec-10-enoate (2.48 g) was added during 30 min. The reaction mixture was stirred at 45°C for 90 min. and then 2 *M* sol. of HCl (15 mL) was CAREFULLY added. The resulting mixture was extracted with ethyl acetate. The crude product was recrystallized from methanol to give colorless crystals (1.302 g, 62%): mp. 45-46°C (Lit.[4a] 45-48°C).

(8) Bloomfield, J. J., Nelke, J. M. *Org. Synth.* **1977**, *57*, 1.

(9) Hadjiarapoglou, L., Klein, I., Spitzner, D., de Meijere, A. *Synthesis* **1996**, 525.