Heterogenous Catalysis by Solid Superacids; 10[1]. Mercury Impregnated Nafion-H Perfluorinated Resinsulfonic Acid Catalyzed Hydration of Alkynes

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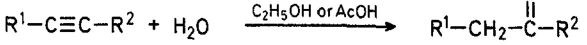
With diminishing hydrocarbon resources, the significance of carbide-based acetylene chemistry can again gain importance. Hydration of alkynes is a convenient method for the preparation of carbonyl compounds. The reaction is usually carried out in diluted sulfuric acid solution. Except for very reactive alkynes, the reaction rates in the absence of mercury(II) salts are low, even when higher acid concentrations are used. One of the serious problems arising from using mercury(II) salts as a catalyst is the formation of precipitate of an inactive sludge consisting of finely divided metallic mercury mixed with insoluble mercury(II)-organic compounds. Apart from the difficulties in the work up stage, this side reaction also causes the loss of the catalyst and environmental problems. Attempts have been made to prevent the reduction to mercury or to regenerate the mercury(II) salt by the addition of oxidizing agents, such as hydrogen peroxide[3,4] and ozone[5] as well as transition metal salts[6].

The catalytic activity of some solid catalysts, as a possible substitute for mercury(II) salts, was investigated[7], showing that phosphates of copper, zinc and cadmium are good catalysts while the phosphates of Ca(II), Be(II), Al(III), Fe(III), Ni(II) and Sr(II) have no catalytic activity. The catalytic activity of ruthenium ions in solution was also studied[8]. However, to affect hydration of alkynes over the solid catalysts, the required operating temperature is 250°–400°. Newman[9] reported the use of mercury-impregnated sulfonated polystyrene for the hydration of alkynes. Long reaction time at reflux temperature was needed to bring the reaction to completion.

In continuation of our studies on the catalytic activity of Nafion-H[1], a superacidic perfluorinated resinsulfonic acid, we report now our results of the convenient hydration of alkynes, using mercury impregnated Nafion-H (Hg/Nafion-H).



$$R^1-C\equiv C-R^2 + H_2O \xrightarrow[C_2H_5OH\ or\ AcOH]{Hg/Nafion-H/} R^1-CH_2-\overset{O}{\overset{\|}{C}}-R^2$$

The advantage of using a heterogenous catalyst is that it can be easily separated from the reaction mixture and reused if the catalytic activity of the solid superacidic catalyst impregnated with mercury will be retained.

Ethanol and acetic acid are the most commonly used solvents for the hydration of alkynes since they dissolve well both of the reagents (water and alkynes). When a solution of the alkyne and water in ethanol is heated under reflux in the presence of Hg/Nafion-H, the conversion of the alkynes to the corresponding carbonyl compounds is completed within 5 min. Although the necessary reaction time is decreased substantially, mercury and mercury(II) complexes are rapidly formed under the reaction conditions. After such deformation, the catalyst is not suitable for reuse. However, when the reaction was carried out at room temperature, it was generally completed within 90 min as followed by G.L.C. The catalyst, filtered off from the reaction mixture, was found to be reuseable with no indication of loss in activity. Further, there is no complication in isolating the products as is usually the case when a fine gray precipitate of mercury and mercury(II) complexes is formed.

The present procedure offers a most convenient improved method for the hydration of alkynes to ketones with retention of the catalytic activity of the catalyst and easy, clean work up. Typical for liquid alkynes is the hydration of 1-heptyne to 2-heptanone, and for gaseous alkynes that of the parent acetylene.

Preparation of Mercury Impregnated Nafion-H Catalyst (Hg/Nafion-H):

To a suspension of mercury(II) oxide (10 g) in deionized water (250 ml) is added sulfuric acid (5 ml). Then Nafion-H (40 g) is stirred with this solution for 5 h at 20°. Subsequently the catalyst is filtered, washed with deionized water (5 × 50 ml) and dried to constant weight (24 h). In the catalyst thus prepared, 25 % of the protons are substituted by mercury(II) ions.

Hydration of 1-Heptyne:

1-Heptyne (1 g, 0.01 mol) and water (0.9 ml, 0.05 mol) are dissolved in ethanol (10 ml). Hg/Nafion-H catalyst (500 mg) is added, and the mixture is stirred at room temperature. Aliquots are taken at time intervals and the reaction is followed using G.L.C. analysis (conditions: 6′ × 1/8″, 5 % SE-30 on Chromosorb W, column temp. 60–70°, carrier gas helium, 30 ml/min) showing that the reaction is completed in ~ 90 min. The mixture is filtered, and the solid catalyst is washed with ethanol (2 × 5 ml) followed by diethyl ether (3 × 10 ml). Water (30 ml) is added and the mixture extracted with ether (2 × 20 ml). The combined ether solution is dried with magnesium sulfate and distilled to give 2-heptanone; yield: 1.05 g (94 %); b.p. 150° (Lit.[11] b.p. 151°).

Hydration of Acetylene:

To a suspension of Hg/Nafion-H (2 g) in ethanol (50 ml) containing water (8 ml) stirred at 20°, acetylene is introduced at a rate of 10 ml/min. After a total of 500 ml (20 mmol) of acetylene is passed through (50 min) at atmospheric pressure, the reaction mixture is stirred for an additional 30 min. The solid catalyst is filtered off, and washed with ethanol until a total filtrate of 100 ml is obtained. A 10 ml sample from that solution is taken and treated with alcoholic 2,4-dinitrophenylhydrazine solution. The precipitate is filtered, and recrystallized from ethanol to give acetaldehyde 2,4-dinitrophenylhydrazone; yield: 296 mg (65 %); m.p. 147°[9].

Table. Hg/Nafion-H Catalyzed Hydration of Alkynes[a]

R^1	R^2	Yield[b] [%]	b.p. or m.p.	Lit.[11] b.p. or m.p.
H	H	65	m.p. 147°[c]	m.p. 147°[9,c]
H	CH_3	67	m.p. 128°[c]	m.p. 128°[c]
H	n-C_5H_{11}	87[d], 94, 92[e]	b.p. 150°	b.p. 151.5°
H	n-C_4H_9	90	b.p. 126°	b.p. 128.0°
H	n-C_3H_7	88	b.p. 101°	b.p. 102.0°
H	*cyclo*-C_6H_{11}	93	b.p. 178°	b.p. 181.0°
C_6H_5	C_6H_5	92[f]	m.p. 52°	m.p. 54°[10]
H	C_6H_5	80	b.p. 199°	b.p. 202°

[a] Reaction time generally 90 min; reactions followed by G.L.C. and product isolated after reaction is complete according to G.L.C.

[b] Yield of isolated product of purity ≥99 % according to G.L.C. analysis.

[c] m.p. of corresponding 2,4-dinitrophenylhydrazones.

[d] 5 min under reflux.

[e] Acetic acid used as reaction solvent.

[f] The solution was heated up to ~40° to afford dissolution of the alkyne.

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[1] For part 9, see: G. A. Olah, D. Meidar, *Synthesis* **1978**, 358.

[2] Post-doctoral research associate.

[3] M. Lucius, *German Patent* 292818 (1914); *C. A.* **11**, 1518 (1917).

[4] T. P. Hilloditch, *British Patent* 125926, J. Crosfield & Sons (1918); *C. A.* **13**, 2218 (1919).

[5] E. Poutermann, *German Patent* 566517 (1930); *C. A.* **27**, 2459 (1937).

[6] I. G. Farbenindustrie, A. E. Johnson, *British Patent* 466569 (1937); *C. A.* **31**, 7892 (1937).

[7] (a) Y. A. Gorin, I. K. Gorn, *Zh. Obshch. Khim.* **28**, 2328 (1958); *C. A.* **53**, 3028 (1959).
(b) Y. A. Gorin, L. P. Bogdanova, *Zh. Obshch. Khim.* **28**, 1146 (1958); *C. A.* **53**, 275 (1959).

[8] J. Halpern, B. R. James, A. L. W. Kemp, *J. Am. Chem. Soc.* **83**, 4097 (1961).

[9] M. S. Newman, *J. Am. Chem. Soc.* **75**, 4740 (1953).

[10] M. Sugii, R. Nakai, *J. Org. Chem.* **21**, 288 (1957).

[11] *Handbook for Chemistry and Physics*, 57th Edit., Chemical Rubber Co. Inc., Cleveland, Ohio, 1976–1977.

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