Notes A department for short papers of immediate interest.

Simple Preparation of a Very Active Raney Nickel Catalyst

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Received July 6, 1960

After observing the pyrophoric property of the nickel left during the reduction of organic compounds with Raney nickel aluminum alloy, in the presence of an aqueous alkali, according to Papa and co-workers,[1,2] we found this nickel very active as a hydrogenation catalyst. By a slight modification of Papa's procedure, a Raney nickel catalyst (that has been designated as T-1) was obtained. T-1 was found to be more active at low pressures (50–60 p.s.i.) and temperatures (40–60°) and also easier to prepare, than W-6.[3] The studies by Adkins and co-workers[4,5] on improved Raney nickel catalysts, showed that the temperature and alkali concentration acting on the alloy were important factors that might explain the activity of the Raney nickel catalyst T-1.

All the products of the hydrogenation of the α- and β-naphthols, phenol, resorcinol, hydroquinone, D-glucose, heptaldehyde, benzylidenacetone, and coumarin, were identified by their physical constants and their proper derivatives. It was not possible to reduce the β-methoxynaphthol under the experimental conditions.

EXPERIMENTAL

Preparation of the T-1 Raney nickel catalyst. In a 1-l. three necked flask containing 600 ml. of a 10% sodium hydroxide solution, 40 g. of Raney nickel aluminum alloy (50%), was added in small portions (20–30 min.). with mechanical stirring, the temperature being kept during the addition at 90–95°; then the mixture was stirred for 1 hr. The stirring was interrupted, the nickel was allowed to settle, and the solution was decanted. The residue was washed with five 200-ml. portions of water, then five times with 50 ml. of ethanol, in such a way that the nickel was always covered with liquid. Then the catalyst was stored under ethanol, and kept in the refrigerator. The activity of the catalyst did not change after 3 months of storage.

General method of hydrogenation. A low pressure Parr hydrogenator was used. The sample (0.1–0.4 mole) was suspended or dissolved in 30–80 ml. of ethanol, 5–10 g. of the nickel catalyst suspension was added, and then 1–2 ml. of 20% sodium hydroxide solution. The hydrogenations were carried at 40–50° and 40–60 p.s.i. The reduced mixture was filtered and the product was isolated by the usual methods, depending on its physical properties. The results are shown in Table I.

TABLE I

HYDROGENATION PRODUCTS WITH T-1 RANEY NICKEL CATALYST

Starting Material	Moles	Products	Yield, %
α-Naphthol	0.20	1,2,3,4-Tetrahydro-1-naphthol[a]	18
		5,6,7,8-Tetrahydro-1-naphthol[b]	59
β-Naphthol	0.2	5,6,7,8-Tetrahydro-2-naphthol[c]	83
Phenol	0.4	Cyclohexanol[d]	92
Resorcinol	0.4	Cyclohexane-1,3-diol[e]	86.5
Hydroquinone	0.4	Cyclohexane-1,4-diol[f]	77.2
D-Glucose	0.2	D-Sorbitol[g]	94.6
Heptaldehyde	0.3	1-Heptanol[h]	89.3
Benzylidenacetone	0.4	Benzylacetone[i]	75
Coumarin	0.3	3,4-Dihydrocoumarine[j]	83

[a] B.p. 128° (12 mm.), m.p. 31–33°; phenylurethan[6] m.p. 123–125°, lit.[7]: b.p. 130–140° (17 mm.), m.p. 33°, phenylurethan m.p. 121–2°. [b] B.p. 155° (15 mm.), m.p. 70–72°; benzoate[4] m.p. 56–58°; lit.[7]: b.p. 102–104° (2 mm.) m.p. 73–75°, benzoate 56°. [c] B.p. 158° (16 mm.), m.p. 62°; benzoate[6] m.p. 95–97°; lit.[7]: b.p. 148° (12 mm.), m.p. 62°, benzoate m.p. 96°. [d] B.p. 174–176°, n_D^{30} 1.4582; phenylurethan[6] m.p. 81°; lit.[7]: b.p. 176°, n_D^{25} 1.4647 phenylurethan m.p. 82°. [e] M.p. 70–82°, α-naphthylurethan[7] m.p. 245°; lit.[7]: m.p. (*cis*) 86°, (*trans*) 116°, α-naphthylurethan 246°. Oxidation with chromic anhydride gave cyclohexadione-1,3, m.p. 105–106°, lit.[7] m.p. 105°. [f] M.p. 113–114°, benzoate, m.p. 110°; lit.[5]: m.p. (*cis*) 112°. benzoate m.p. 110°. The *trans* isomer was not found. [g] M.p. 106–110°, hexabenzoate[6] 214–216°; lit.[7]: m.p. (anhydrous) 110–112°, hexabenzoate m.p. 216–217°. [h] B.p. 175°, n_D^{25} 1.4224, phenylurethan[6] m.p. 61°; lit[7]: b.p. 176° n_D^{25} 1.4224, phenylurethan, m.p. 60°. [i] B.p. 118° (15 mm.), no. 1.5090, semicarbazone[6] m.p. 141°; lit.[7]: b.p. 235° (760 mm.), n_D^{22} 1.5110, semicarbazone, m.p. 142°. Lit. [j] B.p. 135° (20 mm.), melilotic acid m.p. 81°; lit.[6]: b.p. 272° (760 mm.) melilotic acid m.p. 82°.

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