Comparison of Nickel Catalysts in the Hydrogenation of β -Naphthol

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The partial hydrogenation of β -naphthol over nickel catalysts may give predominantly either the alcohol, 1,2,3,4-tetrahydro-2-naphthol or the phenol, 5,6,7,8-tetrahydro-2-naphthol. In this Laboratory Musser¹ obtained the alcohol in a 55% yield, while Schultz² prepared the phenol in 70% yield. Stork³ obtained the phenol in 55% or the alcohol in 66% yield depending upon the alkalinity of the reaction mixture. With copper-chromium oxide as the catalyst the alcohol is produced to the exclusion of the phenol.¹

Musser used Raney nickel (W-1) prepared by the Covert process.⁴ Schultz and Stork used Raney nickel (W-2), prepared by the Mozingo procedure,⁵ under a pressure of about 200 atmospheres. Schultz completed the reaction in less than thirty minutes at 120° while Stork did the hydrogenation in two to three hours at 85°. Musser used a lower pressure of about 100 atmospheres and somewhat more drastic conditions, *i. e.*, six hours at 140°, in forcing the hydrogenation to completion so that decalols and decalin were also produced.

It seemed worth while to test different nickel

TABLE I

Comparison	OF	Raney	Nickel	CATALYSTS	IN	Hydro-			
GENATION OF β -NAPHTHOL									

Catalyst	°C.	minutes	Alcohol	n, % Phenol					
Commercial	90	260	7	86					
Commercial	120	25	11	75					
W-1'	140	160	8	83					
W-1	140	24 0	9	72					
W-2	65	245	6	81					
W-2	90	180	6	84					
W-2	140	15	7	82					
W-4	65	120	9	87					
U. O. P.	130	30	21	65					
W-1ª	140	240	48	31					
W-4 ^b	65	90	65	19					
W-4°	65	90	23	61					
W-4 ^d	65	90	22	59					
U. O. P.	130	30	68	8					
W-6 ^g	65	30	18	73					

• 0.02 g. sodium hydroxide. • 0.24 g. sodium hydroxide. • 0.02 g. sodium hydroxide. • 0.6 ml. triethylamine. • 0.24 g. sodium hydroxide. / Washed by Pavlic method. • test by Harry Billica with a Raney nickel W-6 catalyst described in a forthcoming paper.

(2) Harry Schultz, unpublished report (1943).

(3) Stork, This Journal, 69, 576 (1947).

(4) Covert and Adkins, ibid., 59, 416 (1932).

(5) Mozingo, "Organic Syntheses," 21, 14 (1941).

catalysts for activity in the hydrogenation of β naphthol. There is recorded in Table I the temperature and time required for the addition of two moles of hydrogen per mole of β -naphthol over various catalysts and the yields of the alcohol and the phenol obtained. The hydrogenations were on 36 g. of β -naphthol in 50 ml. of ethanol with 1 g. of catalyst at 3600 to 4000 p. s. i. The results given are the average of two runs. The catalysts could not be compared at the same temperature because the activity of a Raney nickel catalyst is so dependent upon the procedure followed in preparing it from the nickel aluminum alloy. The catalyst W-4 gave a more rapid hydrogenation at 65° than did the W-1 catalyst at 140°. The data show that in the order of increasing activity the Raney nickel catalysts are: W-1 as prepared by the Covert process; commercial Raney nickel catalyst as supplied by the Gilman Paint and Varnish Co., Chattanooga, Tenn.; W-2 as prepared by the Mozingo procedures; and W-4 as prepared by the Pavlic procedure.6 The W-6 Raney nickel, described in a paper submitted for publication, is even more active than W-4. Catalysts W-1 and W-2 were somewhat more active if the procedure for washing the catalyst described in the Pavlic process was used.

All of the catalysts referred to above except W-6 gave 6 to 11% yields of the alcohol and yields of the order of 80% of the phenol. The addition of small amounts of sodium hydroxide or of triethylamine to the hydrogenation mixture changed the proportion of the products so that with the W-4 catalyst, for example, the yield of alcohol was increased almost eight-fold with a corresponding decrease in the yield of the phenol. In no case did the addition of sodium hydroxide, in the quantities used, decrease the rate of hydrogenation.

The nickel on kieselguhr catalyst sold by the Universal Oil Products Co. was also tested for the hydrogenation of β -naphthol. It was similar in rate of reaction to the commercial Raney nickel but gave a higher yield of alcohol and a lower yield of the phenol than did any of the Raney nickel catalysts. The U.O.P. catalyst, for a similar rate of hydrogenation, must be used at a temperature 50 or 60° higher than that required by a Raney nickel catalyst prepared by the preferred procedure. The addition of a small amount of sodium hydroxide to the U.O.P. catalyst had the same effect in shifting the course of the hydrogenation to the production of the alcohol as with Raney nickel catalysts.

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(6) Pavlic and Adkins, THIS JOURNAL, 68, 1471 (1946).

⁽¹⁾ Musser and Adkins, THIS JOURNAL, 60, 664 (1938).