

Catalytic Hydrogenation of Acetophenone

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The low pressure hydrogenation of acetophenone to 1-phenylethanol in the presence of some nickel and noble metal catalysts is described. The effects of each are noted. While palladium-on-carbon appears to be the catalyst of choice, others can be used under proper conditions. Only rhodium causes enough side reaction to discourage its use.

THE HYDROGENATION of acetophenone (I) to 1-phenylethanol (II) has been studied before. Delepine and Horeau (1) carried out the reduction¹ with Raney nickel which was promoted with alkali. They obtained II but reported no yield. Theilacker and Drossler (2) used platinum and palladium blacks from the freshly prepared corresponding oxides. A third group (3), in what was essentially a rate study, described the effect of platinum metal catalysts on the conversion of I to II.

In the reduction of I to II, competing reactions can and do take place. Other by-products are ethylbenzene (III), 1-cyclohexylethanol (IV), and ethylcyclohexane (V). Breitner and her associates (3) suggested from their work that two or more competing reactions occur concurrently or at

Platinum oxide,³ Raney nickel,⁴ and a reduced and stabilized nickel⁵ also were tried. The last named was only effective at a high ratio when promoted with sodium hydroxide (1).

EXPERIMENTAL

The following preparation is typical of those carried out with the various catalysts, except for the addition of 0.5 ml. of 20% sodium hydroxide solution in the two runs with nickel.

A solution of 30 Gm. (0.25 mole) of acetophenone in 100 ml. of ethyl alcohol was hydrogenated in the presence of 3.0 Gm. of 5% palladium-on-carbon. When one equivalent of hydrogen was absorbed, the solution was filtered from the catalyst and examined. (See Table I for results.)

TABLE I.—RESULTS

Catalyst ^a	Ratio, %	Reaction Time, Hr.	Products of Reaction, %				
			I ^f	II ^h	III ^h	IV ^h	V ^h
A	1	2	10.24	90.5	0.2
B	10	5-6	Trace	99.9	0.1
C	10	0.5 to 0.75 ^c	6.28	75.9	...	16.4	2.6
			33.4	50.3	0.3	12.5	3.0
D	15 ^e	1.5	1.09 ^f	99.0	0.1
E	40 ^{e, d}	12-15	0.2	99.3	0.5

^a A, platinum oxide; B, 5% palladium-on-carbon; C, 5% rhodium on alumina; D, Raney nickel; E, G-69 nickel. ^b The ratio is based on grams of catalyst (total weight) per 100 Gm. of compound. ^c One-half milliliter of 20% sodium hydroxide solution was added. ^d When a 20% catalyst ratio was used, no uptake occurred with or without sodium hydroxide. ^e Over hydrogenation occurred; uptake was more than theoretical. ^f Determined by comparison with the ultraviolet spectrum of I. ^g After distillation, less than 1% was observed. ^h Determined by gas chromatography with available pure standards.

nearly similar rates. It is our opinion that this is due to the rather high catalyst ratios that were used by this group.

Since there was a need in this laboratory for a substantial amount of II, it gave us an opportunity to reinvestigate the reaction. It was our aim to carry out the reductions at low pressure in alcoholic solution in the presence of modest ratios of commercially available catalysts and to identify the products of reaction by gas chromatography² and ultraviolet spectroscopy.

The results seen in the table indicate that, of those used for the reductions, 5% palladium-on-carbon³ is indeed the best catalyst (3). They also show that the competing reactions of II to III and of II to IV do not occur concurrently with the conversion of I to II. It is likely that the rates are energy dependent and that side reaction can be easily controlled, except with 5% rhodium on alumina.³ It is of interest that IV was still formed with the rhodium catalyst at a 3% ratio. Its propensity toward ring reduction precludes its use for the preparation of II.

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¹ These authors found that the reduction was accelerated by the addition of sodium hydroxide.

² Gas phase chromatography was carried out with a Barber-Colman unit, model 10, modified with a thermal conductivity detector.

³ Available from Engelhard Industries, Newark, N. J.

1-Phenylethanol.—This was used as one of the standards for gas chromatography and was prepared by hydrogenation of acetophenone in alcoholic solution at 125° and 1900 p.s.i. in the presence of barium promoted copper chromite catalyst. The product was distilled and redistilled over a column 30 cm. long packed with glass helices, b.p. 123°/55 mm. (4), reported 118°, 40 mm. and 198°, atmospheric pressure. Its ultraviolet spectrum indicated a maximum of 0.3% of acetophenone. Gas phase chromatography showed only traces of impurities.

1-Cyclohexylethanol.—Sixty grams of acetophenone was hydrogenated in the presence of 0.6 Gm. of ruthenium dioxide³ at 100° and 1000 p.s.i. (1 hour). Distillation of the residual oil after removal of the catalyst gave a product which boiled at 188° at atmospheric pressure, n_D^{20} 1.4635 (5); yield, 88%. (Reported 189.4 to 189.8°, 761 mm., n_D^{20} 1.4677.)

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- ⁴ Supplied in a water suspension by the Harshaw Chemical Co., Cleveland, Ohio.
⁵ Designated as Girdler G-69, Chemical Products Division, Chemetron Corp., Louisville, Ky.