

# Hydrogenation of 1,1-Diphenyl-4-dimethylamino-2-butyn-1-ol to 1,1-Diphenyl-4-dimethylamino-2-buten-1-ol with a Modified Lindlar Catalyst

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The selective reduction of 1,1-diphenyl-4-dimethylamino-2-butyn-1-ol to 1,1-diphenyl-4-dimethylamino-2-buten-1-ol is described using a modified Lindlar catalyst.

THERE ARE many reports in the literature which claim that selective reduction of acetylenic compounds to the corresponding olefins can be achieved by the use of palladium catalyst. Ott and Schroter (1), for example, obtained selectivity with palladium on carbon catalyst. A better method of accomplishing this is to carry out the hydrogenation in the presence of a lead-poisoned palladium catalyst such as the one described by Lindlar (2). However, such a catalyst at times may be inhibited too strongly by the amount of lead present. This point was well illustrated in an attempt in this laboratory to convert 1,1-diphenyl-4-dimethylamino-2-butyn-1-ol (I) to the corresponding 2-buten-1-ol (II).

The hydrogenation of I with commercial palladium on carbon yielded a mixture of products which consisted of over 50% of recovered I, 34% of II, and about 12% of the saturated compound III. When the author used Lindlar catalyst prepared according to the described directions (2), reduction was slow and incomplete. However, when half the amount of lead acetate was added to poison palladium on calcium carbonate during its preparation successful reduction took place.

## EXPERIMENTAL

Compound III was prepared as a standard for comparison with some of the reduction products of I.

$\alpha$ -(3-Dimethylaminopropyl)benzhydrol (III)—A solution of 2.65 Gm. (0.01 mole) of 1,1-diphenyl-4-dimethylamino-2-butyn-1-ol (I)<sup>2,3</sup> in 75 ml. of absolute ethyl alcohol was hydrogenated in the presence of 0.03 Gm. of platinum oxide under 2 Atm. pressure. Uptake was complete in about 30 min. After filtration from the catalyst the solution was concentrated to dryness and 2.3 Gm. (85%) of III was obtained, m.p. 118–119°, after recrystallization from hexane; hydrochloride salt, m.p. 197°.<sup>3,4</sup>

*Anal.*—Calcd. for C<sub>18</sub>H<sub>23</sub>NO: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.08; H, 8.76; N, 5.14.

1,1-Diphenyl-4-dimethylamino-2-buten-1-ol (II)—A solution of 2.65 Gm. (0.01 mole) of I in 50 ml.

of absolute alcohol was hydrogenated in the presence of 0.27 Gm. of Lindlar catalyst prepared as described (2) but modified by the addition of 50% of the amount of lead acetate used in its preparation. The reaction, conducted at 1.25 Atm. pressure, was complete in about 1 hr. After filtration from the catalyst, concentration of the solution, and recrystallization of the residue from hexane, 1.6 Gm. (60%) was obtained, m.p. 93–94° (the crude product melted at 88–91°; yield, 79%).

*Anal.*—Calcd. for C<sub>18</sub>H<sub>21</sub>NO: C, 80.83; H, 7.91; N, 5.24; O, 6.02. Found: C, 81.01; H, 7.86; N, 5.31; O, 6.03.

A hydrochloride salt of II was prepared. It melted at 177–178°. Mixed melting points with samples of the hydrochloride of III were greatly depressed.

**Hydrogenation of I with Lindlar Catalyst**—When the reduction of 2.65 Gm. of I in ethyl alcohol was carried out in the presence of 0.27 Gm. of Lindlar catalyst, prepared in the exact manner as described (2), hydrogen uptake was 12% in 3 hr. Warming produced little additional uptake. Filtration and addition of 0.54 Gm. of Lindlar catalyst and warming induced further reaction in 3 hr. However, uptake stopped of its own accord at about 35% of 1 mole equivalent.

**Hydrogenation of I with Palladium on Carbon**—The hydrogenation of 0.01 mole of I in alcohol was carried out in the presence of 0.05 Gm. of 5% palladium on carbon and under slight hydrogen pressure, about 0.7 Atm. The low catalyst ratio was resorted to in an effort to keep hydrogen uptake from proceeding beyond 1 mole equivalent. The amount of hydrogen present was only 0.0125 mole, also to prevent overhydrogenation. Uptake was complete in 1 hr. After removal of catalyst, the filtrate was concentrated to dryness. The residual solid was treated with anhydrous ether. The insoluble portion melted between 130–140°. It was shown by infrared examination to be identical to I. The residue, obtained by concentration of the ether filtrate, was recrystallized from pentane. The first crop, 0.3 Gm., melted at 116–120°. It appeared to be a mixture of II and III. Further concentration of the filtrate gave 0.9 Gm. of material melting at 90°. On conversion to the hydrochloride salt, it melted at 166–170°. On recrystallization from alcohol or dry ether the melting point rose to 171–172°. It was odd that when mixed with the hydrochloride salt of III the melting point dropped only to 170°. Nevertheless, on treatment of the salt with aqueous ammonia the base melted at 93–94°, as did the analytical sample of II obtained from the reduction of I with the modified Lindlar catalyst. Elemental analysis of the base, however, showed low carbon, but higher hydrogen values to suggest that it was contaminated with III.

## REFERENCES

- (1) Ott, E., and Schroter, R., *Ber.*, 60, 624 (1927).
- (2) Lindlar, H., *Helv. Chim. Acta*, 35, 446 (1952).

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<sup>2</sup> Preparation described by Libman, N. M., and Kuznetsov, S. G., *Zh. Obshch. Khim.*, 30, 1197 (1960); through *Chem. Abstr.*, 55, 452 (1961).

<sup>3</sup> Footnote 2 by Croxall, W. J., and Dawson, J. W., U. S. pat. 2,584,429 (1952).

<sup>4</sup> Ose, M., and Kaneko, H., Japanese pat. 8316-7 (1959); through *Chem. Abstr.*, 54, 17335 (1960) give 118° for base and 201.5–202° for hydrochloride salt. Croxall and Dawson (see Footnote 3) give 122–123.5°.