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Catalytic Hydrogenation of 1,3-Diphenylpropane-1,2-dione and 2-Hydroxy-1,3-diphenylpropan-1-one

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In the catalytic hydrogenation of 1,3-diphenylpropane-1,2-dione (I) and 1-hydroxy-1,3-diphenylpropan-2-one (II), 1,3-diphenylpropane-1,2-diol (III), mp 65—66°C, was produced by Ruggli and Lutz.[1] Bonner and Raunio[2] considered that the diol must have been *threo*-III, and they speculated that, if I is absorbed on the catalyst surface in such a way as to orient the two polar carbonyl functions and the bulky phenyl and benzyl groups as far apart as possible, the *cis* hydrogenation of the two carbonyl groups would lead to *threo*-III. In the case of the catalytic hydrogenation of benzalacetophenone oxide (IV) over palladium-charcoal containing a small amount of sodium hydroxide, IV was isomerized to the diketone I prior to reduction. The initial main product was II, whose hydrogenation gave *erythro*-III, although it proceeded with great difficulty.

In connection with the stereochemistry of the molecules when absorbed on the catalyst surface, we have undertaken a study of the catalytic hydrogenation of 1,3-diphenylpropane-1,2-dione (I) and 2-hydroxy-1,3-diphenylpropan-1-one (V) in ethanol at an ordinary temperature and at atmospheric pressure. The reduction products were analyzed by gas chromatography and by thin-layer chromatography. The authentic samples, *erythro*- and *threo*-III, were synthesized by the procedure of Bonner and Raunio.[2]

In the catalytic hydrogenation of I over palladium-charcoal, it was found by thin-layer chromatography that two isomeric hydroxy ketones, II and V, were the primary products, in further reduction yielded 1,2-diols, but II, which was not the phenyl ketone, was not hydrogenated under our conditions. In the catalytic hydrogenation of I over palladium-charcoal containing a small amount of sodium hydroxide, II was the main product and the reduction of it did not proceed further. In the catalytic hydrogenation of I over Raney nickel and platinum oxide, the two isomeric ketones, II and V, were produced in almost equal amounts as the primary products, as analyzed by thin-layer chromatography, the 1,2-diols which were rich in the *erythro* form were further products.

The catalytic hydrogenation of V over palladium charcoal, Raney nickel, or platinum oxide, or catalysts containing a small amount of sodium hydroxide, yielded mainly *erythro*-III, which was also the main product of the catalytic hydrogenation of II.

Our results show that the catalytic hydrogenation would not proceed directly in the I→III fashion, so that the isomeric ratio of the 1,2-diols (*erythro*-III *vs.* *threo*-III) must reflect the stereochemistry of the hydroxy ketones, the primarily-desorbed products, on the catalyst surface. As there are many factors which control the orientation, we are now investigating them.

Experimental

1,3-Diphenylpropane-1,2-dione (I). I was prepared by the method of Kohler[3] by the isomerization of benzalacetophenone oxide; bp 132—138°C/1 mmHg, 40% yield.

1,3-Diphenylpropane-1,2-diol (III). *threo*-III was synthesized by the method of Bonner *et al.*[2] by the *cis* hydroxylation of *trans*-1,3-diphenylpropane[4]; mp 62°C, 80% yield, *erythro*-III was prepared by the catalytic hydrogenation of benzalacetophenone oxide

TABLE 1. CATALYTIC HYDROGENATION OF I AND V

Compd.	Catalyst	Additive	Product(III) (%)	
			erythro	*threo*
I	Raney Nickel	—	67	33
I	PtO_2	—	81	19
V	Pd-C	—	79	21
V	Pd-C	NaOH	75	25
V	Raney Nickel	—	63	37
V	Raney Nickel	NaOH	73	21
V	PtO_2	—	82	18
V	PtO_2	NaOH	91	9

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[2] W. A. Bonner and E. K. Raunio, *J. Org. Chem.*, **31**, 291 (1966).

[3] E. P. Kohler and R. P. Barnes, *J. Am. Chem. Soc.*, **56**, 211 (1934).

[4] W. A. Bonner and E. K. Raunio, *J. Org. Chem.*, **31**, 397 (1966).

(IV) over palladium-charcoal; mp 82°C, 62% yield.

2-Hydroxy-1,3-diphenylpropan-1-one (V). V was prepared by the catalytic hydrogenation of benzalacetophenone oxide (IV). IV, palladium-charcoal, and ethanol were stirred with hydrogen at an ordinary temperature and at atmospheric pressure. After one mole of hydrogen had been absorbed, the catalyst was filtered and the product (V) was recrystallized from petroleum benzine containing a small amount of benzene; mp 66°C, 50% yield.

Catalytic Hydrogenation of I or V. I or V (450 mg), the catalyst, and 30 m*l* of ethanol were stirred with hydrogen at an ordinary temperature and at atmospheric pressure. After the hydrogenation was over, the catalyst the filtered, the products were acetylated with acetic anhydride in pyridine, and the acetyl derivatives were analyzed by vapor-phase chromatography. In the course of hydrogenation, the partial reduction products were analyzed by thin-layer chromatography. The results are summarized in Table 1.