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The Catalytic Hydrogenation of 2,5-Diphenylfuran

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The reductions of *trans*-1,2-dibenzoylethylene and its derivatives have been studied, and the reaction mechanisms have been discussed.[1]

In the following experiment, the hydrogenation of 2,5-diphenylfuran, which was often obtained by these reductions, was carried out over several kinds of catalysts.

Experimental

2,5-Diphenylfuran (I). I was prepared from *trans*-1,2-dibenzoylethylene or 1,2-dibenzoylethylene oxide by the method of Lutz and Rowlett[2] or by that of the present author.[1]

Catalysts. The catalysts used were palladium-charcoal-A (5%), palladium-charcoal-B (5%), Raney nickel W-5, and Adams' platinum oxide, all of which were prepared by known methods.[3-6]

Solvents. When Raney nickel was the catalyst, ethanol was used as the solvent, while in the case of the other catalysts, glacial acetic acid was used. One milliliter of concentrated hydrochloric acid or 0.05 g of sodium hydroxide was used as the additive.

Hydrogenation. I (1.1 g, 1/200 mol) was dissolved in 100 m*l* of a solvent, and reduction was then carried out over a catalyst (0.5 g, of Pd–C, 0.1 g of platinum oxide, or 0.5—1.5 g of Raney nickel) under atmospheric hydrogen pressure and at room temperature. After the reduction had been completed and the catalyst had been filtered out, the solvent was distilled off under reduced pressure. The residue was then recrystallized from 15 m*l* of ethanol. After the filtration of I, which was recovered as crystals, the filtrate was condensed to about 5 m*l*; the solution was subsequently kept below 0°C. After the substance, mp 54—55°C, had crystallized, it was filtered and the solvent of the filtrate was distilled off completely. This residue was recrystallized from *n*-hexane. A substance with a mp of 48—49°C was thus obtained. When platinum oxide was used as a catalyst, the raw reduction product was recrystallized from *n*-hexane after the filtration of the catalyst and the complete distillation of the solvent. The crystals thus obtained melted at 82—83°C. When the hydrogen uptake was stopped at less than 8 mol over platinum oxide, an oily substance, perhaps be a mixture of several intermediates, was produced.

1,4-Diphenyl-1-butanol (II) and 1,4-diphenyl-1-butanone (III), which had been prepared by the method of Stoemer and Schenck,[7,8] were also reduced by the

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[1] Y. Inamura, *Nippon Kagaku Zasshi*, **85**, 905 (1964); *ibid.*, **88**, 648 (1967); *ibid.*, **87**, 734 (1966); *ibid.*, **89**, 208 (1968).

[2] R. E. Lutz and R. J. Rowlett, Jr., *J. Amer. Chem. Soc.*, **70**, 1359 (1948).

[3] R. Mozingo, "Organic Syntheses," Vol. 26, p. 77. (1964),

[4] S. Mitsui and H. Saito, *Nippon Kagaku Zasshi*, **83**, 390 (1961).

[5] H. Adkins and H. R. Billica, *J. Amer. Chem. Soc.*, **70**, 695 (1948).

[6] R. Adams, V. Voorhees and R. L. Schriner, "Organic Syntheses," Coll. Vol. 1, 2nd Ed., p. 463 (1948),

[7] R. Stoemer and Fr. Schenck, *Ber.*, **61**, 2320 (1928).

[8] H. Rupe and J. Bürgin, *ibid.*, **43**, 172 (1910).

same method as that described above.

Results

The results of the experiments are shown in Tables 1, 2, and 3. In the reduction of I, the maximum quantity of absorbed hydrogen was 3 mol when palladium-charcoal or Raney nickel was the catalyst, and 9 mol when Adams' platinum oxide was used. No effect was observed on the reduction products by the addition of an acid or an alkaline substance.

The substance (mp 48—49°C) yielded by the reaction of I with 2—3 mol of hydrogen with palladium-charcoal-B or Raney nickel as a catalyst was identified by a mixed-melting-point determination with 1,4-diphenyl-1-butanol, an authentic sample which had been synthesized by the method described in previous papers.[7,8] The IR spectrum of this substance showed an absorption at 3300 cm^{-1}.

Table 1. The yields of products in the hydrogenation of I (%)

Catalyst	Additive	Quantity of absorbed hydrogen (mol/mol)	Recovered (I)	(II)	(IV)	(V)
Pd-C-A	—	1	91	—	—	—
Pd-C-A	—	2	23	—	19	—
Pd-C-A	—	3	—	—	41	—
Pd-C-A	HCl	3	—	—	46	—
Pd-C-B	—	1	67	—	—	—
Pd-C-B	—	2	41	5	—	—
Pd-C-B	—	3	—	—	62	—
Pd-C-B	HCl	3	—	—	50	—
Raney Ni	—	1	78	5	—	—
Raney Ni	—	2	32	14	—	—
Raney Ni	—	3	—	14	28	—
Raney Ni	NaOH	1.5	50	14	—	—
PtO_2	—	9	—	—	—	55
PtO_2	HCl	9	—	—	—	30

Table 2. The yields of products in the hydrogenation of II (%)

Catalyst	Quantity of absorbed hydrogen (mol/mol)	Recovered (II)	(IV)
Pd-C-A	1	12	55
Pd-C-B	1	—	55
Raney Ni	1	32	19

Table 3. The yields of products in the hydrogenation of III (%)

Catalyst	Quantity of absorbed hydrogen (mol/mol)	Recovered (II)	(IV)
Pd-C-A	1	14	48
Pd-C-A	2	—	80
Pd-C-B	1	64	—
Pd-C-B	2	—	50
Raney Ni	1	69	—
Raney Ni	2	32	19

The IR spectrum of the substance (mp 54—55°C) yielded by the reaction of I of 2 or 3 mol of hydrogen with palladium-charcoal-A, or that of the substance yielded by the reaction of 3 mol of hydrogen with palladium-charcoal-B or Raney nickel, showed no absorption of the hydroxyl group or the carbonyl group. The mixed-melting-point determination confirmed that this substance was 1,4-diphenylbutane (IV). The authentic sample of IV was prepared by the method of Freund[9] or by the hydrogenation of *trans*-1,2-dibenzoylethylene with 5 mol of hydrogen.[10]

The IR spectrum of the substance (mp 82—83°C) obtained in the hydrogenation of I over the Adams' platinum oxide catalyst showed an absorption at 3400 cm^{-1}. The chromic anhydride oxidation of this compound in glacial acetic acid gave an oily substance. The 2,4-dinitrophenylhydrazone made from it melted at 80—81°C. Moreover, the data of the elementary analysis of this substance (mp 82—83°C) proved it to be 1,4-dicyclohexyl-1-butanol (V).

Found: C, 80.51; H, 12.73%. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68%.

The ketone III was not obtained under any of the following conditions: that is, when large quantities of I were used, when the absorption period was shortened, when a small quantity of hydrogen was absorbed, or when the solvents were changed.

Discussion

The hydrogenation of furan derivatives has been well examined,[11] and the reductions of 2-phenylfuran and 2-phenyltetrahydrofuran have been reported on by Mitsui and his co-workers.[12] These reports indicate that hydrogenation mainly occurs when palladium-charcoal or Raney nickel is used as the catalyst, while hydrogenation and hydrogenolysis occur competitively over the platinum oxide catalyst.

The present results show that 2,5-diphenylfuran also undergoes hydrogenolysis to give II and IV

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9) M. Freund and P. Immerwahr, *Ber.*, **23**, 2845 (1890).

10) Y. Inamura, *Nippon Kagaku Zasshi*, **84**, 416 (1963).

11) H. A. Smith and J. F. Fuzeck, *J. Amer. Chem. Soc.*, **71**, 415 (1949); H. A. Smith, J. B. Conley and W. H. King, *ibid.*, **73**, 4633 (1951).

12) S. Mitsui, Y. Ishikawa, Y. Takeuchi, H. Saito and H. Mamuro, *Nippon Kagaku Zasshi*, **81**, 286 (1960); S. Mitsui and H. Saito, *ibid.*, **81**, 289 (1960).

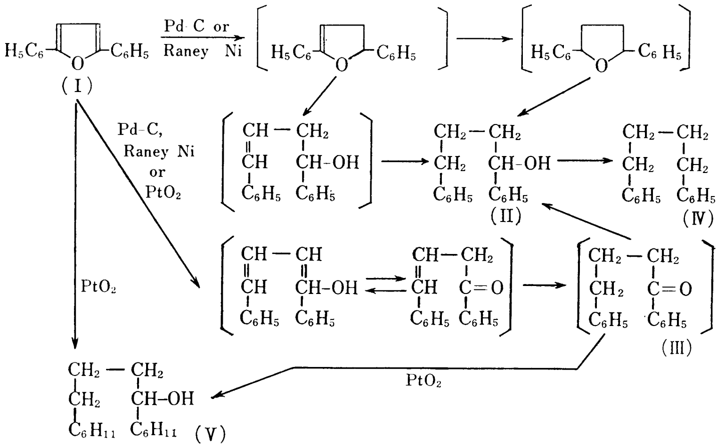

Fig. 1

over the palladium-charcoal or the Raney nickel catalyst.

Some possible courses of the reduction of I are shown in Fig. 1. The hydrogenation of I over Raney nickel gave more II than that over the palladium-charcoal catalyst. The results presented above and those of Table 2 show that the hydrogenation of I took the course: I→II→IV and that the II→IV course was more difficult over the Raney nickel catalyst than over the palladium-charcoal catalyst.

It is well known that the benzene ring is hydrogenated over the platinum catalyst.[13] In the present experiment, too, after the cleavage of the furan ring and the saturation of the benzene ring of I, V was produced. Though III easily gave II and IV, as is shown in Table 3, III was not obtained at all in the reduction of I.

The compounds described in brackets in Fig. 1 were not isolated; therefore, it is uncertain which course of those shown in Fig. 1 is mainly taken in this reaction. However, from the fact that III which, if present, is expected to crystallize easily, was not obtained under any of the conditions described above, and from the fact that 2-aryltetrahydrofuran is easily hydrogenated,[12] it can be said that the hydrogenation of I seems to take the reaction course of, first, the reduction of the furan ring, and then the reaction II→IV.

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[13] R. H. Baker and R. D. Schuetz, *J. Amer. Chem. Soc.*, **69**, 1259 (1947).