# The Stereochemistry and Mechanisms of Catalytic Hydrogenation and Catalytic Hydrogenolysis. II[1]. The Catalytic Hydrogenolysis of Optically-active Ethyl α-Phenyl-α-aryloxypropionates over Palladium and Nickel Catalysts[2]

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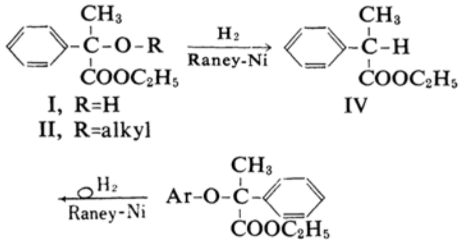
(Received March 30, 1963)

In order to clarify the mechanisms of catalytic hydrogenolysis, hydrogenation, and the exchange reaction of hydrogen on the surface of the catalyst, we have carried out an investigation of the catalytic hydrogenolysis over Raney nickel of optically-active ethyl atrolactate and its derivatives[3] and suggested the mechanisms of both catalytic hydrogenolysis and hydrogenation[1,4].

In the catalytic hydrogenolysis of ethyl atrolactate (I) and its alkyl (II) and aryl ethers (III) over Raney nickel, optically-active ethyl α-phenylpropionate (IV) was obtained with a 90% retention of optical activity. While I and II were hydrogenolyzed with retention of their configurations, III, underwent an apparent Walden inversion.



I, R=H
II, R=alkyl
IV

III Ar=aryl
$III_1$ Ar=$C_6H_5$-
$III_2$ Ar=$p$-$CH_3C_6H_4$-
$III_3$ Ar=$o$-$CH_3C_6H_4$-
$III_4$ Ar=$p$-$CH_3OC_6H_4$-
$III_5$ Ar=$o$-$CH_3OC_6H_4$-

In view of these results, we have suggested the following explanation[1,4]. In the cases of I and II, the phenyl, carboethoxy and hydroxy (alkoxy) groups, which are the chemisorption groups on Raney nickel, can be easily adsorbed on the catalyst surface without any steric hindrance (Fig. 1), and the electron or electrons and the proton are transferred from the catalyst surface to the asymmetric carbon of the molecule; accordingly, there results a retention of the configuration ($S_{Ni}$ type mechanism on the catalyst). However, owing to steric hindrance by a planar structure of the aryloxy group in III, the three chemisorption groups (phenyl, carboethoxy and aryloxy) can not be so easily adsorbed on the same catalyst surface. Therefore, the aryloxy group is adsorbed on one side of the catalyst surface and the carboethoxy and phenyl groups on the other, thus avoiding steric hindrance and allowing adsorption to proceed smoothly on the catalyst surface (Fig. 2). The asymmetric carbon is then drawn near to the catalyst surface and the electron or electrons and the proton are transferred from the latter, pushing out the aryloxy groups to another catalyst surface (that is, there is a concerted reaction), thereupon allowing the Walden inversion to take place (an $S_N2$ type reaction on the catalyst).

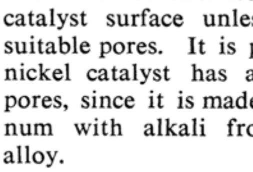


Fig. 1.

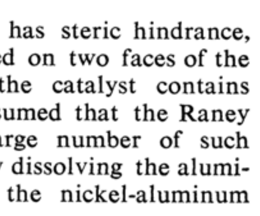


Fig. 2.

Although a molecule has steric hindrance, it can not be chemisorbed on two faces of the catalyst surface unless the catalyst contains suitable pores. It is presumed that the Raney nickel catalyst has a large number of such pores, since it is made by dissolving the aluminum with alkali from the nickel-aluminum alloy.

From the stereochemical viewpoint, it seemed pertinent to investigate hydrogenolysis using a catalyst other than Raney nickel. Therefore, the present paper reports observations on the hydrogenolysis of ethyl α-phenyl-α-aryloxypropionates (III) using palladium and nickel catalysts on some carriers.

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[1] Part I in this series: S. Mitsui and S. Imaizumi, This Bulletin, **34**, 774 (1961).

[2] Presented at the 8th and 9th Symposiums on Catalysis of The Chemical Society of Japan, Osaka, March, 1959 and Tokyo, April, 1960.

[3] S. Imaizumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1511 (1956); **78**, 1396 (1957); **80**, 336 (1959); **81**, 627, 631, 633 (1960).

[4] S. Mitsui and S. Imaizumi, ibid., **77**, 1516 (1956); *Chem. Abstr.*, **53**, 5179 g (1959).

TABLE I. STEREOCHEMICAL RELATIONSHIPS IN THE CATALYTIC HYDROGENOLYSIS OF ETHYL $\alpha$-PHENYL-$\alpha$-ARYLOXYPROPIONATE OVER 5% PALLADIUM ON CHARCOAL AND RANEY NICKEL CATALYSTS

| Aryl ether (III) -Ar | | Catalyst | Maintained optical activity of IV % | Configuration |
|---|---|---|---|---|
| $-C_6H_5$ | ($III_1$) | 5% Pd-C | 47 | Retention |
| $-C_6H_5$ | ($III_1$) | Raney-Ni | 90 | Inversion |
| $-C_6H_4CH_3(p)$ | ($III_2$) | 5% Pd-C | 52 | Retention |
| $-C_6H_4CH_3(p)$ | ($III_2$) | Raney-Ni | 92 | Inversion |
| $-C_6H_4CH_3(o)$ | ($III_3$) | 5% Pd-C | 48 | Retention |
| $-C_6H_4CH_3(o)$ | ($III_3$) | Raney-Ni | 88 | Inversion |
| $-C_6H_4OCH_3(p)$ | ($III_4$) | 5% Pd-C | 64 | Inversion |
| $-C_6H_4OCH_3(p)$ | ($III_4$) | Raney-Ni | 94 | Inversion |
| $-C_6H_4OCH_3(o)$ | ($III_5$) | 5% Pd-C | 49 | Inversion |
| $-C_6H_4OCH_3(o)$ | ($III_5$) | Raney-Ni | 95 | Inversion |

TABLE II. STEREOCHEMICAL RELATIONSHIPS IN THE CATALYTIC HYDROGENOLYSIS OF ETHYL L(+)-$\alpha$-PHENYL-$\alpha$-PHENOXYPROPIONATE ($III_1$) OVER VARIOUS AMOUNTS OF 5% PALLADIUM ON CHARCOAL CATALYST

Weight of $III_1$ used, 1.4 g.; Optical rotation, absolute configuration and optical purity of $III_1$, $[\alpha]^6_D$ +6.2° ($c$ 9.0, absolute ethanol), L, 44.6%; Solvent, absolute ethanol 50~100 ml.

| Weight of catalyst g. | Reaction time hr. | Yield % | IV | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Optical rotation a) | | | A. C. b) | Optical purity, % c) | Maintained optical activity % d) |
| | | | $[\alpha]^t_D$ | $t$, °C | $c$ | | | |
| 0.1 | 48 | 60 | −12.5° | 12 | 7.7 | L | 17.4 | 39 |
| 1.0 | 5 | 100 | −15.0° | 7 | 8.0 | L | 20.9 | 47 |
| 7.0 | 2 | 100 | − 9.7° | 8 | 5.1 | L | 13.3 | 30 |
| 15.0 | 4 | 100 | −14.6° | 10 | 10.0 | L | 20.2 | 45 |

a) Solvent is absolute ethanol.
b) Absolute configuration
c) Calculated by (optical rotation of IV/optically pure rotation of IV) ×100. The rotation of optically pure IV is 72.2° (absolute ethanol)[2).
d) Calculated by (optical purity of IV/optical purity of III) ×100.

TABLE III. STEREOCHEMICAL RELATIONSHIPS IN THE CATALYTIC HYDROGENOLYSIS OF ETHYL L(+)-$\alpha$-PHENYL-$\alpha$-PHENOXYPROPIONATE ($III_1$) OVER PALLADIUM ON CHARCOAL CATALYSTS

Weight of $III_1$ used, 1.4 g.; Optical rotations, absolute configration and optical purity of $III_1$, $[\alpha]^6_D$ +6.2° ($c$ 9.0, absolute ethanol), L, 44.6%; Solvent, absolute ethanol 50 ml.

| Catalyst | g. | Reaction time hr. | Yield % | IV | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Optical rotation a) | | | A. C. b) | Optical purity % c) | Maintained optical activity % d) |
| | | | | $[\alpha]^t_D$ | $t$, °C | $c$ | | | |
| 1% Pd-C | 3.0 | 2 | 100 | −20.8° | 7 | 9.4 | L | 28.8 | 65 |
| 5% Pd-C | 1.0 | 5 | 100 | +15.1° | 7 | 8.0 | L | 20.9 | 47 |
| 10% Pd-C | 1.0 | 5 | 90 | + 2.0° | 4 | 9.8 | D | 2.8 | 6 |
| 25% Pd-C | 1.0 | 6 | 75 | + 5.9° | 4 | 7.0 | D | 8.2 | 18 |
| 50% Pd-C | 0.5 | 20 | 80 | + 9.5° | 7 | 9.2 | D | 13.2 | 30 |
| 75% Pd-C | 0.5 | 48 | 80 | +15.9° | 5 | 8.5 | D | 22.0 | 49 |
| 90% Pd-C | 0.5 | 48 | 50 | +24.8° | 7 | 8.5 | D | 34.3 | 77 |
| Pd | 1.0 | 48 | 25 | +13.9° | 6 | 5.6 | D | 19.4 | 44 |
| 5% Pd-$BaSO_4$ | 1.0 | 24 | 75 | +14.2° | 6 | 9.0 | D | 19.7 | 44 |

Notation a—d) refer to the footnotes of Table II.

Optically-active ethyl α-phenyl-α-aryloxypropionates (III) were prepared according to the process described in the preceding paper[1] and were shaken with 5% palladium on a charcoal catalyst at an ordinary temperature and under hydrogen pressure. These aryl ethers III were hydrogenolyzed to ethyl α-phenylpropionate (IV) and related phenols. As may be seen in Table I, the retention of optical activity and the configuration of IV varied with the structure of the aryl group attached to III. In another series of experiments, ethyl α-phenyl-α-phenoxypropionate ($III_1$) was hydrogenated by employing various amounts of 5% palladium on a charcoal catalyst. The effects of various amounts of catalyst did not produce appreciable differences in the results, as is shown in Table II. The phenyl ether, $III_1$, was then hydrogenated over palladium on charcoal catalyst of different palladium concentrations. The configurations of IV produced in each case are shown in Table III.

It may be seen that, with concentrations of palladium on charcoal of 1 and 5%, the retentions of the optical activity of ethyl α-phenylpropionate (IV) with retention of configuration were 65 and 47% respectively. When the palladium concentration on charcoal was increased to 10, 25, 50, 75 and 90%, the retentions of the optical activity of IV with the inversion of the configuration were 6, 18, 30, 49 and 77% respectively. These results show that the percentage of Walden inversion in catalytic hydrogenolysis increases in an orderly fashion with an increase in the concentration of palladium on charcoal. When palladium was used without a carrier, the amount of Walden inversion in the catalytic hydrogenolysis was about the same as that produced with 5% palladium on barium sulfate, but much less than that produced with 75 and 90% palladium on charcoal.

These results lead to the conclusion that, when the palladium concentration on charcoal is low, the catalytic surfaces on which the phenyl ether $III_1$ can be chemisorbed on the two faces of the catalyst are comparatively small, because the palladium is deposited thinly on the carrier surface, but with an increase in the palladium concentration, the crystals of palladium are deposited on charcoal in such a manner that they create rugged surfaces so that the phenyl ether $III_1$ can be chemisorbed on the two faces of the catalyst. Thus, the occurrence of the two face-chemisorption of the phenyl ether $III_1$ is increased, and the proportion of the inverted product IV is likewise increase, because the palladium catalysts are capable of causing a catalytic hydrogenolysis of the phenyl ether $III_1$ even in a one face-chemisorption state on the catalysts, the proportion of D- and L-forms of IV is principally determined by the quantity of suitable pores in which phenyl ether $III_1$ can be chemisorbed on the two faces of the catalysts. Of course, besides this fact, the proportion is also related to the reaction rates of both the one face-chemisorption state and the two face-chemisorption state of phenyl ether $III_1$.

The palladium catalyst without the carrier acted less stereospecifically than 90% palladium on charcoal. This fact seems to account for the existence of fewer suitable pores on the catalyst because of its massive state. Moreover, 5% palladium on barium sulfate acted in the same manner as the palladium catalyst without the carrier. This result may be because the barium sulfate acted merely as a dispersing agent of the palladium, since the adsorptive power of the carrier is comparatively weak.

When alumina instead of charcoal was used as the carrier of the palladium catalyst, the stereospecific hydrogenolysis of the phenyl ether $III_1$ gave results qualitatively similar to these observed during the course of hydrogenolysis over the palladium on charcoal catalysts, as is shown in Table IV. In the case of palladium on alumina catalysts, however, the extent of the inverted product IV was high, even when 2% palladium on alumina was employed. The reason for this may be that the surface area of alumina is smaller than that of charcoal.

The *p*-anisyl ether $III_4$ was hydrogenolyzed in the same manner as the phenyl ether $III_1$ using palladium on charcoal and palladium on alumina catalysts. In these cases, however, the proportion of inverted IV was high, even when 1% palladium on charcoal and 0.2% palladium on alumina catalysts were used, as Table V shows. Therefore, it may be conceived that the hydrogenolysis of the *p*-anisyl ether $III_4$ in the one face-chemisorption state on the catalyst surface presents some difficulty, since the steric hindrance of the *p*-anisyl ether $III_4$ in the one face-chemisorption state is more predominant than the corresponding steric hindrance of the phenyl ether $III_1$, because of a greater chemisorption of the *p*-methoxy group.

The above results prove that not only a small difference in the chemical structure of a molecule but also in the surface structure of the catalyst alters the steric structure of the hydrogenolyzed product. That is, the steric state of a molecule which is being chemisorbed on the catalyst surface is the most important factor in the stereochemistry of the hydrogenolysis.

TABLE IV. STEREOCHEMICAL RELATIONSHIPS IN THE CATALYTIC HYDROGENOLYSIS OF ETHYL D(−)-α-PHENYL-α-PHENOXYPROPIONATE ($III_1$) OVER PALLADIUM ON ALUMINA CATALYSTS

Weight of $III_1$ used, 1.4 g.; Optical rotation, absolute configuration and optical purity of $III_1$, $[\alpha]^{27}_{D}$ −7.0° (*c* 9.0, absolute ethanol), D, 49.5%; Solvent, absolute ethanol 50 ml.,

| Catalyst | g. | Reaction time hr. | Yield % | IV | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Optical rotation[a] | | | A. C.[b] | Optical purity %[c] | Maintained optical activity %[d] |
| | | | | $[\alpha]^t_D$ | *t*, °C | *c* | | | |
| 0.2% Pd-$Al_2O_3$ | 12.5 | 10 | 100 | +11.2° | 28 | 10.0 | D | 15.5 | 31 |
| 0.5% Pd-$Al_2O_3$ | 10.0 | 4 | 100 | + 5.2° | 25 | 9.3 | D | 7.3 | 15 |
| 1% Pd-$Al_2O_3$ | 5.0 | 10 | 100 | + 1.1° | 25 | 9.3 | D | 1.5 | 3 |
| 2% Pd-$Al_2O_3$ | 5.0 | 10 | 100 | − 5.9° | 25 | 11.0 | L | 8.1 | 16 |
| 5% Pd-$Al_2O_3$ | 1.0 | 24 | 80 | −25.4° | 23 | 5.3 | L | 35.1 | 71 |
| 10% Pd-$Al_2O_3$ | 1.5 | 24 | 100 | −27.1° | 23 | 9.5 | L | 37.1 | 76 |

Notations a—d) refer to the footnotes of Table II.

TABLE V. STEREOCHEMICAL RELATIONSHIPS IN THE CATALYTIC HYDROGENOLYSIS OF ETHYL L(+)-α-PHENYL-α-(*p*-ANISOXY)PROPIONATE ($III_4$) OVER PALLADIUM ON CHARCOAL AND PALLADIUM ON ALUMINA CATALYSTS

Weight of $III_4$ used, 1.5 g.; Optical rotation, absolute configuration and optical purity of $III_4$, $[\alpha]^{7}_{D}$ +10.9° (*c* 8.7, absolute ethanol), L, 50.3%; Solvent, absolute ethanol 50 ml.

| Catalyst | g. | Reaction time hr. | Yield % | IV | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Optical rotation[a] | | | A. C.[b] | Optical purity %[c] | Maintained optical activity %[d] |
| | | | | $[\alpha]^t_D$ | *t*, °C | *c* | | | |
| 1% Pd-C | 3.0 | 24 | 90 | +19.3° | 6 | 8.1 | D | 26.8 | 53 |
| 5% Pd-C | 2.0 | 24 | 90 | +23.2° | 9 | 9.6 | D | 32.1 | 64 |
| 50% Pd-C | 1.0 | 24 | 70 | +27.8° | 5 | 8.9 | D | 38.5 | 77 |
| 0.2% Pd-$Al_2O_3$ | 12.5 | 10 | 40 | +29.5° | 15 | 9.5 | D | 4.09 | 81 |
| 1% Pd-$Al_2O_3$ | 10.0 | 5 | 50 | +28.1° | 18 | 8.5 | D | 38.9 | 77 |
| 5% Pd-$Al_2O_3$ | 3.0 | 7 | 50 | +27.6° | 18 | 8.9 | D | 38.2 | 76 |

Notations a—d) refer to the footnotes of Table II.

TABLE VI. STEREOCHEMICAL RELATIONSHIPS IN THE CATALYTIC HYDROGENOLYSIS OF ETHYL L(+)-α-PHENYL-α-PHENOXYPROPIONATE ($III_1$) OVER VARIOUS NICKEL CATALYSTS

Weight of $III_1$ used, 1.4 g.; Optical rotation, absolute configuration and optical purity of $III_1$, $[\alpha]^{6}_{D}$ +6.2° (*c* 9.0, absolute ethanol), L, 44.6%; Solvent, absolute ethanol 50 ml.

| Catalyst | g. | Reaction time hr. | Yield % | IV | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Optical rotation | | | A. C.[b] | Optical purity %[c] | Maintained optical activity %[d] |
| | | | | $[\alpha]^t_D$ | *t*, °C | *c* | | | |
| Catalyst VI[e] | 5.0 | 48 | 65 | +31.1° | 7 | 7.6 | D | 43.1 | 97 |
| Catalyst VIII[f] | 2.5 | 48 | 65 | +31.6° | 24 | 9.0 | D | 43.8 | 98 |
| Catalyst X[e] | 5.0 | 48 | 50 | +31.9° | 24 | 9.2 | D | 44.2 | 99 |
| Catalyst FC[e] | 10.0 | 24 | 70 | +31.7° | 11 | 8.2 | D | 43.9 | 98 |
| Catalyst FD[e] | 10.0 | 24 | 80 | +31.8° | 7 | 8.7 | D | 44.1 | 99 |
| U-Ni-B[g] | 0.5(Ni) | 48 | 50 | +32.1° | 9 | 8.7 | D | 44.5 | 100 |

Notations a—d) refer to the footnotes of Table II.

e) Stabilized nickel on kieselguhr catalyst (Ni, about 50%); cf. T. Yamanaka et al., *J. Sci. Res. Inst.*, **51**, 168 (1957); **52**, 143 (1958).

f) Stabilized Raney nickel catalyst: cf. ibid.

g) Urushibara nickel-B catalyst: cf. Y. Urushibara and S. Nishimura, This Bulletin, **27**, 480 (1954).

Attention was next paid to the hydrogenolysis of the phenyl ether III$_1$ over nickel catalysts which had been prepared by different methods. In the cases of these catalysts, the retention of the optical activity of the product IV produced with an inversion of the configuration was almost 100%, as is shown in Table VI.

Since it is not likely that these catalysts, have more pores than are found in an ordinary Raney nickel catalyst, it is presumed to be scarcely possible to hydrogenolyze the phenyl ether III$_1$ in the one face-chemisorption state. This concept is supported by the fact that larger amounts of these catalysts are essential to complete the hydrogenolysis of the phenyl ether III$_1$.

## Experimental

**Optically-active Ethyl $\alpha$-Phenyl-$\alpha$-aryloxypropionate (III).**—The procedure for preparing the aryl ethers III and their optical purities were reported in the experimental part of the preceding paper[1].

**The Catalytic Hydrogenation of Optically-active Ethyl $\alpha$-Phenyl-$\alpha$-aryloxypropionate (III).**—A mixture of the aryl ether III, 50 ml. of absolute ethanol, and a catalyst was shaken under hydrogen at an ordinary temperature and pressure until the catalyst hydrogen was no longer adsorbed. The catalyst was filtered and rinsed with ethanol, and the solvent was distilled. The residual oil was taken up in ether and extracted with a 5% sodium hydroxide solution. The alkaline insoluble material was dried over anhydrous sodium sulfate, and the solvent was removed. The residual oil was distilled at reduced pressure to give ethyl $\alpha$-phenylpropionate (IV) (b. p., 103~104°C/12 mmHg).

The alkaline extract was acidified with hydrochloric acid. In the case of phenyl ether III$_1$, bromine was added to the acidified solution to give tribromophenol (m. p., 94~95°C). The yield was calculated from the weight of the tribromophenol. In the cases of other aryl ethers (III$_{2-5}$), the resulting oil in the acidified solution was taken up in ether and dried; the solvent was removed by distillation, and the residue was converted to a solid derivative.

It has been established in previous papers[1,3] that (+)-III (absolute ethanol solution) and (−)-IV (neat or absolute ethanol solution) have the same L-form.

These results are described in Tables II–VI and are as follows: Ethyl L(+)-$\alpha$-phenyl-$\alpha$-phenoxypropionate (III$_1$) (b. p., 142~143°C/2.5 mmHg, $[\alpha]^{6}_{D}$ +6.2° ($c$ 9.0, ethanol), 44.6% optical purity) gave ethyl L-(−)-$\alpha$-phenylpropionate (IV) ($[\alpha]^{7}_{D}$ −15.1° ($c$ 8.0, ethanol), 20.9% optical purity) and phenol over 5% palladium on a charcoal catalyst[5], while if gave D(+)-IV ($[\alpha]^{9}_{D}$ +29.0° ($c$ 5.0, ethanol), 40.2% optical purity) and phenol over a Raney nickel catalyst[6].

Ethyl L(+)-$\alpha$-phenyl-$\alpha$-($p$-cresoxy)propionate (III$_2$) (b. p., 143~145°C/0.5 mmHg, $[\alpha]^{3}_{D}$ +3.5° ($c$ 5.4, ethanol), 37.5% optical purity) gave L(−)-IV ($[\alpha]^{5}_{D}$ −14.3° ($c$ 7.6, ethanol), 19.5% optical purity) and $p$-cresol (its tosylate; m. p., 69~70°C) over 5% palladium on a charcoal catalyst, while it gave D(+)-IV ($[\alpha]^{8}_{D}$ +23.3° ($c$ 8.8, ethanol), 34.5% optical purity) and $p$-cresol over a Raney nickel catalyst.

Ethyl D(−)-$\alpha$-phenyl-$\alpha$-($o$-cresoxy)propionate (III$_3$) (b. p., 145~146°C/3 mmHg, $[\alpha]^{7}_{D}$ −7.3° ($c$ 5.6, ethanol), 45.2% optical purity) gave D(+)-IV ($[\alpha]^{6}_{D}$ +15.7° ($c$ 9.1, ethanol), 21.7% optical purity) and $o$-cresol (its tosylate; m. p., 54~55°C) over 5% palladium on a charcoal catalyst, while it gave L(−)-IV ($[\alpha]^{7}_{D}$ −28.7° ($c$ 8.7, ethanol), 39.8% optical purity) and $o$-cresol over a Raney nickel catalyst.

Ethyl L(+)-$\alpha$-phenyl-$\alpha$-($p$-anisoxy)propionate (III$_4$) (b. p., 170~172°C/3 mmHg, $[\alpha]^{7}_{D}$ +10.9° ($c$ 8.7, ethanol), 50.3% optical purity) gave D(+)-IV ($[\alpha]^{9}_{D}$ +23.2° ($c$ 9.6, ethanol), 32.1% optical purity) and $p$-methoxyphenol (m. p., 52~53°C) over 5% palladium on a charcoal catalyst, while it gave D(+)-IV ($[\alpha]^{8}_{D}$ +34.0° ($c$ 7.4, ethanol), 47.2% optical purity) and $p$-methoxyphenol over a Raney nickel catalyst.

Ethyl L(+)-$\alpha$-phenyl-$\alpha$-($o$-anisoxy)propionate (III$_5$) (b. p., 158~160°C/2 mmHg, $[\alpha]^{5}_{D}$ +13.6° ($c$ 4.2, ethanol), 52.5% optical purity) gave D(+)-IV ($[\alpha]^{6}_{D}$ +18.5° ($c$ 8.5, ethanol), 25.7% optical purity) and guaiacol ($o$-anisoxyacetic acid; m. p., 126~127°C) over 5% palladium on a charcoal catalyst, while it gave D(+)-IV ($[\alpha]^{5}_{D}$ +36.0° ($c$ 9.2, ethanol), 49.8% optical purity) and guaiacol over a Raney nickel catalyst.

The stereochemical results calculated from the above results are shown in Table I.

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[5] H. Adkins and J. P. Carnahan, "Organic Syntheses", Vol. 26, p. 78, Method C.

[6] W-4 Raney nicke; H. Adkins and A. A. Pavlic, *J. Am. Chem. Soc.*, **69**, 3039 (1947).