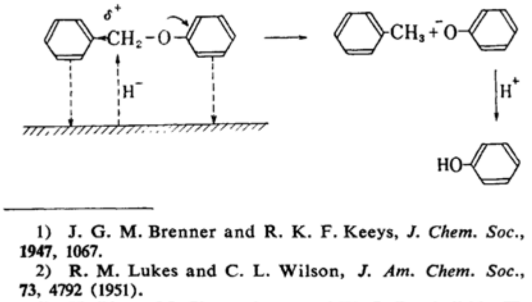
Stereochemistry and Mechanisms of Catalytic Hydrogenolysis and Hydrogenation. I. Catalytic Hydrogenolysis of Optically Active Compounds with Raney Nickel

By Sekio MITSUI and Shin IMAIZUMI

(Received August 15, 1960)

There have been only a few investigations on the mechanisms of catalytic hydrogenolysis taking the action of catalysis into consideration. Brenner and Keeys[1] presumed that the furyl carbonium ion was produced at an intermediate stage of the course of catalytic hydrogenolysis reaction of furfuryl alcohol, which yielded methylfuran, and this concept was supported by Lukes[2]. Pines et al.[3] presumed that the dehydroxylation reaction of alcohols at high temperature and pressure takes place via the carbonium ion. On the other hand, Mitsui et al.[4] presented papers reporting as follows: in the case of catalytic hydrogenolysis of phenyl benzyl ethers, these substances are adsorbed on the catalyst surface and the electron density between C–O bond decreases, and also the carbon of benzyl group becomes δ^+, and the hydrogen adsorbed on the catalyst surface dissociates into H^- and H^+. This hydride is presumed to attack δ^+ carbon.



The above mentioned mechanism elucidates clearly the cases of various benzyl ether and benzylamine derivatives[5]. The question as to the mechanism by which the reaction takes place, may be clearly elucidated upon catalytic hydrogenolysis of optically active compounds with tertiary carbon. That is, if carbonium ion is formed, optically inactive compounds would be produced and if attacking reaction of hydride ion occurs, optically active compounds must be produced. Ott et al.[6], already reported that (+)-α-phenylpropionic acid was obtained when (−)-α-phenyl-α-chloropropionic acid was subjected to catalytic hydrogenolysis using palladium-charcoal as a catalyst and that (−)-α-phenylpropionic acid was obtained when (−)-α-phenyl-α-chloropropionic acid was reduced with zinc and acetic acid. Bonner[7,8] performed catalytic hydrogenolysis of several atrolactic acid derivatives I and III with excess of Raney nickel in boiling alcohol. The results were as follows: in cases of phenyl thioether (I, $X=SC_6H_5$) and of α-phenyl-α-benzenesulfinylpropionamide (I, $X=SOC_6H_5$), racemic α-phenylpropionamide (II) was produced. However, in cases of α-phenyl-α-benzenesulfonylpropionamide (I, $X=SO_2C_6H_5$) and of ethyl α-phenyl-α-benzenesulfonylpropionate (III, $X=SO_2C_6H_5$), II or

---

1) J. G. M. Brenner and R. K. F. Keeys, *J. Chem. Soc.*, **1947**, 1067.

2) R. M. Lukes and C. L. Wilson, *J. Am. Chem. Soc.*, **73**, 4792 (1951).

3) H. Pines, M. Shamarieger and W. S. Postl, ibid., **77**, 5099 (1955); H. Pines, J. Marechal and W. S. Postl, ibid., **77**, 6390 (1955).

4) S. Mitsui, N. Inoue and A. Kasahara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **71**, 203 (1951); *Chem. Abstr.*, **46**, 8102 i (1952).

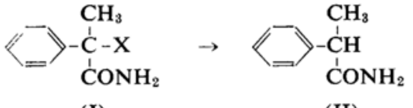
5) S. Mitsui and N. Kiseki, ibid., **70**, 203 (1950); *Chem. Abstr.* **45**, 6631 g (1951); S. Mitsui, A. Kasahara and N. Endo, ibid., **75**, 234 (1954); *Chem. Abstr.*, **49**, 10210 d (1955); S. Mitsui and S. Imaizumi, ibid., **75**, 974 (1954); *Chem. Abstr.*, **51**, 14608 i (1957); S. Mitsui, S. Imaizumi and J. Kusume, ibid., **75**, 1065 (1954); *Chem. Abstr.*, **51**, 14609 c (1957).

6) E. Ott and K. Krömer, *Ber.*, **68**, 1655 (1935).

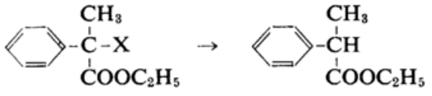
7) W. A. Bonner, *J. Am. Chem. Soc.*, **74**, 1034 (1952).

8) W. A. Bonner, ibid., **74**, 5089 (1952).

ethyl α-phenylpropionate (IV), with only 10% recemization, was obtained, and it was definitely evidenced that Walden inversion accompanied this occasion. Thus he presented the mechanisms of these reactions. Developing this investigation, Bonner et al.[9,10] obtained ethyl D(+)-α-phenylpropionate (IV) with 79% of retention of configuration from ethyl D(−)-atrolactate (III, X=OH) and methyl D(+)-α-phenylpropionate with 72% of retention of configuration from methyl D(+)-α-phenyl-α-methoxypropionate, respectively. Cram et al.[11] obtained (+)-2-phenylbutane with 64% retention of optical activity from (+)-2-hydroxy-2-phenylbutane over excess of Raney nickel by means of boiling in alcohol. Barnes et al.[12] conducted catalytic hydrogenation of L(−)-1,2-diphenyl-1,2-propanediol over copper-chromium oxide catalyst at 200°C with hydrogen at 1400 p. s. i. and obtained L(+)-1,2-diphenylpropane with 22.3% retention of optical activity (61.2% retention of configuration).



(I) (II)



(III) (IV)

The results indicate that optically active hydrogenolyzed products are obtained exclusive of poisonous compounds such as thioether and sulfinyl compounds. This fact seems to support the present author's concept described earlier.

The author et al. have conducted many investigations on catalytic hydrogenolysis of optically active derivatives of atrolactic acid in order to elucidate more clearly the mechanism of catalytic hydrogenolysis by which the mechanism of catalytic hydrogenation may be explained. One of the present authors, Imaizumi[13], already performed catalytic hydrogenation of ethyl L(+)-atrolactate (III, X=OH), $[\alpha]^{8}_{D}$ +25.30° (92.4% optical purity), over Raney nickel catalyst at ordinary temperature and pressure and obtained ethyl L(−)-α-phenylpropionate (IV)*, $[\alpha]^{9}_{D}$ −54.82°, which upon hydrolysis gave L(−)-α-phenylpropionic acid (V), $[\alpha]^{7}_{D}$ −73.2° (82.2% optical purity), with 89% retention of optical activity. Upon catalytic hydrogenation of ethyl L(+)-α-phenyl-α-chloropropionate (III, X=Cl), $[\alpha]^{21}_{D}$ +2.36° (42.1% optical purity), over 7.7% palladium-charcoal, L(−)-IV, $[\alpha]^{19}_{D}$ −4.97° (L(−)-V, $[\alpha]^{18}_{D}$ −7.20°, 7.6% optical purity), was obtained with 18% of optical activity. However, ethyl L(−)-α-phenyl-α-phenoxypropionate (III, X=OC_6H_5), $[\alpha]^{15}_{D}$ −2.10° (35.9% optical purity), gave D(+)-IV, $[\alpha]^{14}_{D}$ +23.3° (D(+)-V, $[\alpha]^{13}_{D}$ +30.5°, 34.2% optical purity), and ethyl D(+)-α-phenyl-α-phenoxypropionate, $[\alpha]^{15}_{D}$ +1.02° (18.4% optical purity), gave L(−)-IV, $[\alpha]^{16}_{D}$ −11.61° (L(−)-V, $[\alpha]^{15}_{D}$ −16.10°, 17.1% optical purity), with 95% and 93% retention of optical activity. It was evident that the Walden inversion accompanied this process simultaneously. An optically inactive product IV resulted from the hydrogenolysis of ethyl D(+)-α-phenyl-α-ethylmercaptopropionate (III, X=SC_2H_5), $[\alpha]^{20}_{D}$ +4.11°, and ethyl D(−)-α-phenyl-α-phenylmercaptopropionate (III, X=SC_6H_5), $[\alpha]^{29}_{D}$ −31.3° [14]. Accordingly, in the case of thioethers, nearly perfect racemization is observed to occur, which is in accord with the result of Bonner's experiments.

Considering the results of catalytic hydrogenolysis of these optically active ethylatrolactate derivatives, the authors[15] proposed to classify them into the following four kinds (or six kinds) of mechanisms of catalytic hydrogenolysis, according to both chemical constitution of compounds and stereochemical constitution of compounds. Explained in detail, in the case of strong catalytic poisonous compounds like thioether (III, X=SC_2H_5, SC_6H_5), the carbon-sulfur bond cleaves to radicals because three groups, carboethoxy, phenyl and sulfur atom, of the molecules may be adsorbed and chemisorption of the sulfur atom occurs strongly, and then hydrogen is incorporated with the radicals (radical cleavage reaction 1). Accordingly racemization ensues. If groups, incorporated into the asymmetric carbon atom, are not chemisorption groups such as carboethoxy or phenyl but are like alkyl groups, which do not cause chemisorption —if they cause any, it is an extremely weak one—, these groups probably act as electron releasing groups, and accordingly they cleave both to carbonium ion and to sulfide anion and then hydrogen is incorporated, ensuing on this occasion racemization too (S_N1 reaction,

---

9) W. A. Bonner, J. A. Zderic and G. A. Casaletto, ibid., 74, 5086 (1952).

10) W. A. Bonner and J. A. Zderic, ibid., 78, 3218 (1956).

11) D. J. Cram and J. Allinger, ibid., 76, 4516 (1954).

12) R. A. Barnes and B. R. Juriano, ibid., 81, 6462 (1959).

13) S. Imaizumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 77, 1511 (1956); *Chem. Abstr.*, 53, 5179 g. (1959).

* D(−) Atrolactic acid has been correlated in two independent ways with D(+) α-phenylpropionic acid by E. L. Eliel and J. P. Freeman [*J. Am. Chem. Soc.*, 74, 923 (1952)] and Bonner[9]. Rotations of the acid and its ethyl ester have the same sign.

14) S. Imaizumi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 1396 (1957); *Chem. Abstr.*, 54, 1403 h (1960).

15) S. Mitsui and S. Imaizumi, ibid., 77, 1516 (1956); *Chem. Abstr.*, 53, 5180 e (1959).

reaction 2). However, in the case of oxygen compounds like ethyl atrolactate (III, X=OH) and its phenyl ether (III, $X=OC_6H_5$), cleavage does not occur by the adsorption on the catalyst surface because chemisorption of the oxygen atom proceeds comparatively weakly. By the chemisorption of phenyl, carboethoxy and OR groups, the asymmetric carbon atom bears a positive charge (δ^+), to which electron and proton or electrons and proton are transferred from the catalyst to produce ·OR radical or :OR anion and thereupon the reaction completes itself with the incorporation of electron and proton or proton to hold optical activity. On this occasion, if carboethoxy, phenyl and OR groups are adsorbed on the same catalyst surface, and the electron is transferred from the same catalyst surface, the reaction is the retention of configuration which we have designated as S_Ni type reaction on catalyst (reactions 3 and 4). In the case of ethyl atrolactate, since carboethoxy, phenyl and hydroxy groups can be easily adsorbed on the same surface of the catalyst without any steric hindrance, the S_Ni type reaction with retention of configuration occurs (Fig. 1). In the case of phenoxy compound (III, $X=OC_6H_5$), owing to the plane structure of the phenoxy group, when this plane is adsorbed on a catalyst surface, three groups, carboethoxy, phenyl and phenoxy, of the compound can not be so easily adsorbed on the same catalyst surface because of steric hindrance among these groups. However, when the phenoxy group is adsorbed on one catalyst surface and carboethoxy and phenyl groups are adsorbed on another catalyst surface, adsorption proceeds easily on the catalyst surfaces as there occurs no steric hindrance (Fig. 2). Then the asymmetric carbon atom is drawn near to the latter surface and the electron or electrons are transferred from the latter surface pushing out the phenoxy group to another catalyst surface and thereupon Walden inversion occurs. We have designated this reaction as S_N2 type reaction on catalyst (reactions 5 and 6).

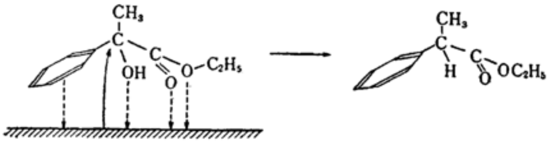


Fig. 1

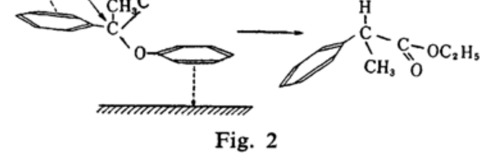
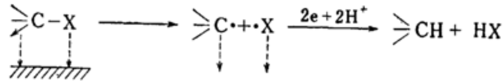


Fig. 2

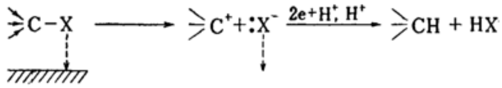
In the case of ethyl α-phenyl-α-chloropropionate (III, X=Cl), palladium-charcoal was used as the catalyst and because of comparatively strong chemisorption of chlorine, radical cleavage reaction 1 occurred predominantly. Besides this reaction, S_Ni type reactions 3 and 4 proceeded as well, which led us to consider that retention of optical activity seemed to be scanty.

i) Radical cleavage reaction on catalyst



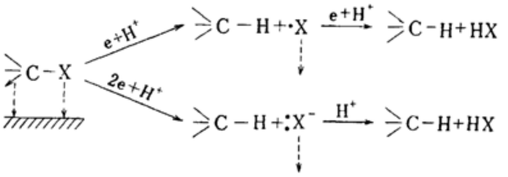
(1)

ii) S_N1 type reaction on catalyst



(2)

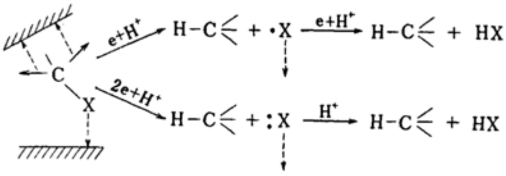
iii) S_Ni type reaction on catalyst



(3)

(4)

iv) S_N2 type reaction on catalyst



(5)

(6)

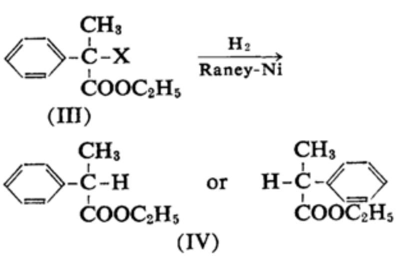
To verify the previously presented mechanisms of catalytic hydrogenolysis, investigations on catalytic hydrogenolysis of various optically active derivatives of ethyl atrolactate over Raney nickel were conducted, First, from ethyl L(−)-α-phenyl-α-ethoxypropionate (III, $X=OC_2H_5$), $[\alpha]^{17}_{D}-31.93°$ (82.4% optical purity), which is presumed to undergo chemisorption in a similar manner as that of ethyl atrolactate, ethyl (−)L-α-phenylpropionate (IV), $[\alpha]^{18}_{D}-53.4°$ (74.1% optical purity), was obtained with retention of configurations, as was expected, and the retention of optical activity was 90%. As for methyl α-phenyl-α-methoxypropionate, Bonner et al.[10] reported as mentioned before and the present authors investigated the matter also to obtain D(+)-IV, $[\alpha]^{16}_{D}+53.7°$ (74.4% optical purity), from ethyl D(+)-α-phenyl-α-methoxypropionate (III,

$X=OCH_3$), $[\alpha]_D^{15}+47.96°$ (88.6% optical purity), with 83% retention of optical activity. Secondly, from several aryloxy compounds (III, $X=OAr$) which are presumed to undergo chemisorption over Raney nickel in a similar manner as that of phenoxy compound (III, $X=OC_6H_5$), IV with Walden inversion was obtained with more than 90% retention of optical activity.

These facts can be explained as follows: ethyl α-phenyl-α-aryloxypropionate is adsorbed on both sides of the surface of Raney nickel catalyst to react readily and react with difficulty when adsorbed on one side of the surface. In the case of ethyl α-phenyl-α-alkyloxypropionate, as there exists no steric hindrance, it is adsorbed on one side of the surface to react. Thus, the previously presented conception is verified as correct and also indicates that Raney nickel catalyst has such a surface structure that ethyl α-phenyl-α-aryloxypropionate is easily adsorbed on both sides of its surface. This fact elucidates the fact that when palladium-charcoal or palladium-alumina is used as catalyst, ethyl α-phenylpropionate produced in the catalytic hydrogenolysis of optically active ethyl α-phenyl-α-phenoxypropionate accompanies retention of configuration if palladium concentration is dilute against carrier, and Walden inversion if palladium concentration is dense. According to the structure of catalyst surface, either retention of configuration or Walden inversion occurs, the fact concerning which will be reported in the next paper.

In Table I are shown the results of investigations of catalytic hydrogenolysis of optically active ethyl atrolactate derivatives over Raney nickel, which have been carried out so far.

TABLE I



	X	Maintained optical activity %[a]		Configuration
1	O-H	89[13]	79[9,10]	rentention
2	$O-CH_3$	83	72[b,10]	〃
3	$O-C_2H_5$	90		〃
4	$O-CH_2-C_6H_5$	87[16]		〃
5	$O-C_6H_5$	95[13]		inversion
6	$O-C_6H_4-CH_3(o)$	96		〃
7	〃 (p)	92		〃
8	$O-C_6H_4-OCH_3(o)$	94		〃
9	〃 (p)	92		〃
10	$O-C_{10}H_7(\beta)$	91		〃
11	$SO_2-C_6H_5$	81[16]	90[7]	〃
12	$SO_2-C_6H_4-CH_3(p)$	75[16]		〃
13	$S-C_2H_5$	0[14]		racemization
14	$S-C_6H_5$	0[14]		〃
15	$S-C_6H_4-CH_3(p)$	0[16]		〃
16	Cl	0[c]		〃
17	$O-COCH_3$	67[16]		inversion
18	$O-COC_2H_5$	82[16]		〃
19	$O-COC_6H_5$	34[16]		〃

a) Author's % = (optical activity of IV/optical activity of III) × 100 = 2 × Bonner's % − 100. Bonner's % = 50 + author's %/2.

b) Methyl ester.

c) In case of 7.7% palladium charcoal catalyst, which maintained optical activity of resulting IV was 18% with retention of configuration[13]. However, in case of Raney nickel catalyst, the resulting IV was almost completely racemic (cf. Experimental).

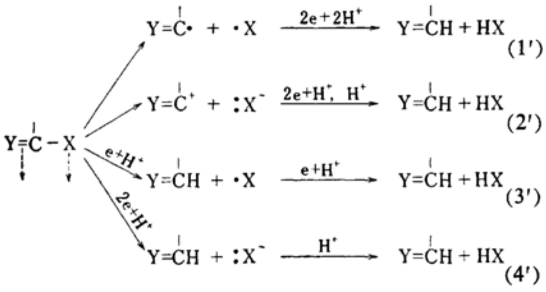
Ethyl α-phenylpropionate was produced with Walden inversion from acyloxy compounds (III, $X=OCOR$) which is prevented from being adsorbed on one side of the surface because of steric hindrance as in the case of aryloxy compounds. However, in the case of benzoyloxy compound (III, $X=OCOC_6H_5$) retention of optical activity is as small as 34%. These results lead us to presume that these phenomena occur because radical cleavage reaction and/or S_N1 type reaction and/or S_Ni type reaction partially occur with S_N2 type reaction in the case of benzoyloxy compound owing to their benzoyloxy group's strong power of adsorption. We will report about this mechanism at a later date.

The above-mentioned mechanism may clarify not only catalytic hydrogenolysis of benzyl-, aralkyl-, and allyl-compounds but also hydrogenolysis of compounds of aromatic ring, hetero-aromatic ring and unsaturated bond to which are combined halogens, OR, SR, CN etc., directly. In these cases, however, there exists $Y=C-X$ on the same plane and it is scarcely possible for adsorption on both sides to occur. Accordingly S_N2 type reaction is not supposed to occur. If adsorption of double bond occurs, production of carbonium ion is least probable. But when this adsorption of X is strong, 2′ reaction might occur. In the case of strong adsorption of X (catalytic poisonous compounds), mainly 1′ reaction would proceed. When adsorption of X is comparatively weak and temperature is comparatively low, mainly 3′ or 4′ reaction proceeds. If temperature is high, 1′ reaction proceeds. Also the dehydroxylation reaction

---

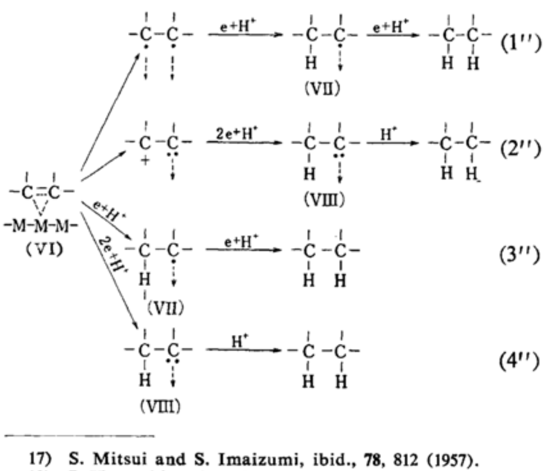
16) S. Imaizumi, ibid., 81, 625, 631, 633 (1960).

of saturated alcohol at high temperature is presumed to be the type of 2′.



The hydrogenolysis of such bonds as $\ddot{N}$–$\ddot{N}$ and $\ddot{N}$–$\ddot{O}$ which have lone pairs is presumed to undergo exactly the same mechanism[17].

On the basis of this mechanism of catalytic hydrogenolysis, when the mechanism of catalytic hydrogenation is speculated upon, the following may be indicated. π-Electrons of unsaturated linkage transfer into d-band vacancy of the catalyst metal surface to form π-complex VI. Then, according to the kinds of catalyst and to the reaction condition, the unsaturated linkage cleaves to radicals or to carbonium ion and to anion to which $e+H^+$ or $2e+H^+$ transfers to become the half-hydrogenated state[18], VII or VIII. To this $e+H^+$ or H^+ transfers and the reaction is completed (1″, 2″ reactions). Otherwise by forming π-complex, carbon becomes δ^+, to which transfers $e+H^+$ or $2e+H^+$ from catalyst and the reaction is completed via half-hydrogenated state VII or VIII (3″ and 4″ reactions). At comparatively low temperature, the reaction is of mainly 3″ or 4″ type, and at high temperature, 1″ or 2″ type reaction may occur.



Experimental

Optically Active Ethyl Atrolactate (III_1).—Atrolactic acid was resolved according to the procedure of Smith[19] and converted to the ethyl ester III_1[20]. The value for the rotation of optically pure ester III_1 is 27.38° (neat)[13].

Optically Active Ethyl α-Phenyl-α-chloropropionate (III_{16}).—This chloride was prepared from the above optically active ester III_1 and thionyl chloride by the method of McKenzie and Clough[20]. This reaction has been demonstrated to occur with the retention of configuration[20]. For the rotation of optically pure chloride III_{16}, we adopted the greatest value, $[\alpha]_D+5.6°$(neat)[20], reported hitherto for the chloride.

Optically Active Ethyl α-Phenyl-α-aryloxypropionate (III_{6-10}).—Related phenol (0.05 mol.) was dissolved in a solution of sodium (0.05 mol.) in absolute ethanol (50 ml.). The above optically active chloride III_{16} (0.05 mol.) was added to the alcoholic solution, and the mixture was boiled under reflux for 15 hr. The reaction mixture was freed of solvent by distillation, and after being cooled poured into water. The mixture was extracted twice with ether, and the extract was washed twice with 5% sodium hydroxide solution, and twice with water. The extract was then dried over anhydrous sodium sulfate, and the solvent was distilled. The residual oil was distilled thrice at reduced pressure to give 20~40% yield of arylethers III_{6-10}. This reaction has been demonstrated to occur with inversion of configuration in other systems[21]. Considering the stereochemical results of catalytic hydrogenolysis of these arylethers, the reaction of these arylethers formation took place with almost complete retention of optical activity. Therefore, optical activities of these arylethers were taken from the optical activity of chloride III_{16}.

Ethyl D(−)-*α-Phenyl-α-(o-cresoxy)propionate(III_6).*—B. p. 145~146°C/3 mmHg, $[\alpha]^7_D-7.3°$ (c 5.6, absolute ethanol), 45.2% optical purity.

Found: C, 75.85; H, 7.23. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

Ethyl L(+)-*α-Phenyl-α-(p-cresoxy)propionate(III_7).*—B. p. 143~145°C/0.5 mmHg, $[\alpha]^3_D+3.5°$ (c 5.4, absolute ethanol), 37.5% optical purity.

Found: C, 76.16; H, 7.36. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

Ethyl L(+)-*α-Phenyl-α-(o-anisoxy)propionate(III_8).*—B. p. 158~160°C/2 mmHg, $[\alpha]^5_D+13.6°$ (c 4.2, absolute ethanol), 52.5% optical purity.

Found: C, 72.21; H, 6.99. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

Ethyl D(−)-*α-Phenyl-α-(p-anisoxy)propionate(III_9).*—B. p. 170~172°C/3 mmHg, $[\alpha]^4_D-8.4°$ (c 5.3, absolute ethanol), 45.2% optical purity.

Found: C, 71.95; H, 6.64. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

Ethyl D(+)-*α-Phenyl-α-(β-naphthoxy)propionate (III_{10}).*—B. p. 190~191°C/1 mmHg, m. p. 65~66°C, $[\alpha]^8_D+4.8°$ (c 7.3, absolute ethanol), 45.2% optical purity.

---

[17] S. Mitsui and S. Imaizumi, ibid., **78**, 812 (1957).

[18] J. Horiuchi and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[19] L. Smith, *J. Prakt. Chem.*, [2] **84**, 738 (1911).

[20] A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **97**, 2564 (1910).

[21] H. Hart and H. S. Eluterio, *J. Am. Chem. Soc.*, **76**, 519 (1954).

Found: C, 78.74; H, 6.56. Calcd. for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29%.

Optically Active Ethyl α-Phenyl-α-alkyloxypropionate (III$_{2-3}$).—The following preparation is an adaptation of the methods of Freudenberg[22] and Bonner[10]. A mixture of alkyl halide (6 ml.), silver oxide (6 g.) and optically active ethyl atrolactate (6 g.) was stirred at room temperature for 5 days, whereupon it was treated with ether and filtered. The filter cake was washed thrice with ether, and the filtrate and washings were freed of solvent. The residual oil was distilled at reduced pressure, and the specific rotation of the oil was examined, and then the oil was retreated in the above manner six additional times. The specific rotation and boiling point of the six treated materials were compared with seven treated ones. The final oil was distilled at reduced pressure to give optically active alkylether III$_{2-3}$. It is clear that the reaction proceeds without modification of configuration.

Ethyl D(+)-*α-Phenyl-α-methoxypropionate (III$_2$).*—B. p. 128∼129°C/14 mmHg, d^{15}_{4} 1.047, $[\alpha]^{5}_{D}+47.96°$ (neat). On the basis of the ethyl D(−)-atrolactate (III$_1$) ($[\alpha]^{21}_{D}-24.27°$ (neat)) used, the methyl ether appears to be 88.6% optically pure.

Found: C, 69.54; H, 7.82. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.74%.

Ethyl L(−)-*α-Phenyl-α-ethoxypropionate (III$_3$).*—B. p. 130∼131°C/13 mmHg, d^{17}_{4} 1.041, $[\alpha]^{17}_{D}-31.93°$ (neat). On the basis of the ethyl L(+)-atrolactate (III$_1$) ($[\alpha]^{9}_{D}+22.56°$ (neat)) used, the ethyl ether appears to be 82.4% optically pure.

Found: C, 70.33; H, 8.15. Calcd. for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16%.

Catalytic Hydrogenation of Optically Active Ethyl α-Phenyl-α-aryloxypropionate (III$_{6-10}$).—A mixture of 1.5 g. of optically active arylether III$_{6-10}$, 50 ml. of absolute ethanol and 1.5 g. of W-5 Raney nickel was shaken under hydrogen at ordinary temperature and pressure for 5 hr. The catalyst was filtered and rinsed with ethanol, and the solvent was distilled. The residual oil was taken up in ether, and extracted with 5% sodium hydroxide solution. The alkali-insoluble material was dried over anhydrous sodium sulfate, and the solvent was removed. The residual oil was distilled at reduced pressure to give ethyl α-phenylpropionate (IV). The specific rotation of optically pure IV is 67.5° (neat) and 72.2° (absolute ethanol)[14].

The alkaline extract was acidified with hydrochloric acid, and the resulting oil was taken up in ether, dried, and the solvent was removed by distillation and the residue was converted into a solid derivative. These results were as follows.

D(−)-III$_6$ (45.2% optical purity) gave L(−)-IV (b. p. 101∼102°C/10 mmHg, $[\alpha]^{7}_{D}-31.2°$ (*c* 6.4, absolute ethanol), 43.2% optical purity) and *o*-cresol (its tosylate, m. p. 54∼55°C[23]).

L(+)-III$_7$ (37.5% optical purity) gave D(+)-IV (b. p. 103∼104°C/12 mmHg, $[\alpha]^{2}_{D}+23.3°$ (*c* 8.6, absolute ethanol), 34.5% optical purity) and *p*-cresol (its tosylate, m. p. 69∼70°C[23]).

L(+)-III$_8$ (52.5% optical purity) gave D(+)-IV (b. p. 101∼102°C/10 mmHg, $[\alpha]^{3}_{D}+34.2°$ (*c* 8.1, absolute ethanol), 47.4% optical purity) and guaiacol (*o*-anisoxyacetic acid, m. p. 126∼127°C[24]).

D(−)-III$_9$ (45.2% optical purity) gave L(−)-IV (b. p. 103∼104°C/12 mmHg, $[\alpha]^{7}_{D}-28.20°$ (neat), $[\alpha]^{4}_{D}-30.1°$ (*c* 7.0, absolute ethanol), 41.7% optical purity) and *p*-methoxyphenol (m. p. 52∼53°C).

D(+)-III$_{10}$ (45.2% optical purity) gave L(−)-IV (b. p. 103°C/11 mmHg, $[\alpha]^{12}_{D}-29.6°$ (*c* 9.1, absolute ethanol), 41.0% optical purity), 1,2,3,4-tetrahydro-β-naphthol (its phenylurethane, m. p. 98∼99°C[25]) and 5,6,7,8-tetrahydro-β-naphthol (m. p. 57∼59°C).

It is calculated from the above results that the percentages of retention of optical activity in the catalytic hydrogenolysis of III$_{6-10}$ to IV on Raney nickel, accompanied by inversion of configuration, are 96, 92, 94, 92 and 91%, respectively.

Catalytic Hydrogenation of Ethyl D(+)-α-Phenyl-α-methoxypropionate (III$_2$).—A mixture of 1 g. of D(+)-III$_2$ (88.6% optical purity), 30 ml. of absolute ethanol and 10 g. of W-5 Raney nickel was shaken under hydrogen at ordinary temperature and pressure for 3 days. The catalyst was filtered and rinsed with ethanol, and then the solvent was removed. The residual oil was distilled at 110∼112°C (17 mmHg) to give 0.4 g. of D(+)-IV, $[\alpha]^{16}_{D}+53.6°$ (*c* 6.7, absolute ethanol), 74.4% optical purity. The percentage of retention of optical activity in IV is calculated to be 83% with retention of configuration.

The above mixture was shaken for 6 days in the same condition. The usual processing yielded 0.6 g. of D(+)-IV, $[\alpha]^{18}_{D}+34.5°$ (*c* 7.0, absolute ethanol), 47.8% optical purity. In this case, partial racemization of the IV produced appears to take place in the prolonged reaction time.

Catalytic Hydrogenation of Ethyl L(−)-α-Phenyl-α-ethoxypropionate (III$_3$)—A mixture of 1 g. of L(−)-III$_3$ (82.4% optical purity), 30 ml. of absolute ethanol and 10 g. of W-5 Raney nickel was shaken under hydrogen at ordinary temperature and pressure for 3 days. The catalyst was filtered and rinsed with ethanol, and then the solvent was removed. The residual oil was distilled at 110∼111°C (16 mmHg) to give 0.3 g. of L(−)-IV, $[\alpha]^{18}_{D}-53.4°$ (*c* 5.2, absolute ethanol), 74.1% optical purity. The percentage of retension of optical activity in IV is calculated to be 90% with retention of configuration.

The above mixture was shaken under hydrogen at about 70°C for 20 hr. The customary work-up gave 0.5 g. of oil, b. p. 110∼120°C/17 mmHg, $[\alpha]^{17}_{D}+13.5°$ (*c* 5.0, absolute ethanol). The product could not be identified, but seems to be a mixture of IV and cyclohexyl derivatives of III$_3$ and/or IV.

Catalytic Hydrogenation of Ethyl L(+)-α-Phenyl-α-chloropropionate (III$_{16}$).—A mixture of 2.1 g. of L(+)-III$_{16}$ ($[\alpha]^{12}_{D}+3.40°$ (neat), 60.7% optical purity), 50 ml. of absolute ethanol and 6 g. of W-5 Raney nickel was shaken under hydrogen at ordinary themperature and pressure for 2 hr. The catalyst was filtered and rinsed with ethanol and the solvent was distilled. The residual oil was taken up in ether, and extracted with 5% sodium

---

22) K. Freudenberg, J. Todd and R. Seidler, *Ann.*, **501**, 199 (1933).

23) F. Beverdin and P. Crépieux, *Ber.*, **35**, 1439 (1902).

24) O. Behaghel, *J. prakt. Chem.*, **114**, 296 (1926).

25) F. Straus and A. Rohrbacher, *Ber.*, **54**, 55 (1921).

carbonate solution. The alkali-insoluble material was dried over anhydrous sodium sulfate, and the solvent was removed. The residual oil was distilled at 108~110°C (14 mmHg) to give 1.2 g. of IV, $[\alpha]^{18}_{D}+0.49^{\circ}$ (neat), 0.7% optical purity. The percentage of retention of optical activity in IV is calculated to be 1% with inversion of configuration. Therefore, in the hydrogenolysis, almost complete racemization occurred.

Department of Applied Science
Faculty of Engineering
Tohoku University, Sendai