Homogeneous Hydrogenations of Organic Compounds with Cobalt Complex Ions[1]*. VII. Homogeneous Hydrogenations of Organic Compounds with a Cyano Cobalt Complex as a Catalyst*

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Previous papers[2] from our laboratory have reported various successful reductions of unsaturated groups combined to with such divalent and trivalent cobalt complexes as bis-(pyruvic acid-oximato)-cobalt(II)[3] and phenylpyruvic acid-oximato-bis(propylenediamine)-cobalt(III) carbonate[4] by hydrogenations in an homogeneous solution. We have also reported[2] that the homogeneous hydrogenations were accomplished most effectively when 5∼6 mol. of potassium cyanide were added as a co-catalyst to one mole of cobalt complex ions. In the meantime, Iguchi and his co-workers[5] have reported that, in the presence of sodium hydroxide and potassium chloride, unsaturated compounds (such as cinnamic acid, sorbic acid or nitrobenzene) are successfully reduced by homogeneous hydrogenation with a cyano cobalt(II) complex (pentacyanocobaltate(II)-ion) as a catalyst under atmospheric pressure and at room temperature.

It has been shown by Devries[6] that sorbic acid may be reduced, using pentacyanocobaltate-(II) ions selectively, to γ,δ-hexenoic acid. However, since these reactions were investigated in a small scale, neither the yield nor the separation of the reduction products were clearly shown; therefore, the mechanism of the homogeneous hydrogenations have not been touched upon. Kwiatek and his coworkers[7] reported recently that the homogeneous hydrogenations of unsaturated compounds had been successfully carried out by use of pentacyanocobaltate(II)-ions in an aqueous solution. In an earlier investigation[2], we ourselves reported that the hydrogenation of a cobalt chelate compound, in which the ligand containes unsaturated linkage, in the presence of potassium cyanide and the hydrogenation of an unsaturated compound with pentacyanocobaltate(II)-ions as a catalyst proceed through the entirely different intermediates.

The present paper describes in detail our study on the hydrogenation of an unsaturated compound with a cyano cobalt complex in comparison with other studies; it also presents a new method for the preparation of amino acid from α-keto acid[8].

Results and Discussion

The results of the hydrogenations with a cyano cobalt complex ($CoCl_26H_2O + 5KCN$) as a catalyst under the various conditions in an homogeneous medium are summarized in Table I.

The above findings on the hydrogenation of the oxime of phenylpyruvic acid with a cyano cobalt complex can be summarized as follows (runs 1—7).

(1) When the reaction was carried out under atmospheric pressure and at room temperature, phenylalanine could not be detected among the products, even by the paper chromatographic analysis.

(2) At a hydrogen pressure of 100 kg./cm^2 and at 100°C, phenylalanine was obtained in an about 30% yield, but it was found that the cobalt ions originally in the complex were quantitatively reduced to the metal. It has already been demonstrated that the oxime of phenylpyruvic acid was not reduced by the hydrogenation with a metallic cobalt[2] catalyst. We found that the oxime of phenylpyruvic acid was also reduced to phenylalanine in an about 30% yield by using a cyano cobalt complex which had been exposed to air for 72 hr.

(3) The homogeneous hydrogenation of the oxime of phenylpyruvic acid was carried out at 40∼70°C under a hydrogen pressure of 100

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[1] Part VI: M. Murakami, K. Suzuki and J. W. Kang, presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

[2] M. Murakami, J. W. Kang, H. Itatani, S. Senoh and N. Matsusato, presented at the 12th and 14th Annual Meetings of the Chemical Society of Japan, Kyoto, April, 1959 and Tokyo, April, 1961.

[3] M. Asymaretto, *Gazz. Chim. ital.*, **57**, 648 (1927).

[4] M. Murakami, S. Senoh, N. Matsusato, H. Itatani and J. W. Kang, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 747 (1962).

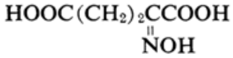
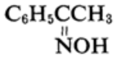
[5] M. Iguchi, M. Takahashi et al., presented at the 9-13th Annual Meetings of the Chemical Society of Japan, Tokyo and Kyoto, April, 1956-1960.

[6] B. Devries, *Koninkle. Ned Akad. Wetenshap. Proc. Sec.*, **B63**, 443 (1960).

[7] J. Kwiatek, I. L. Mador and J. K. Seyler, *J. Am. Chem. Soc.*, **84**, 304 (1962).

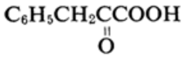
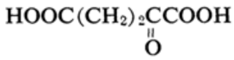
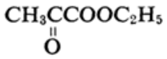
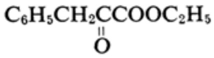
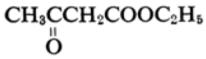
[8] Part V: M. Murakami and J. W. Kang, This Bulletin, **35**, 1243 (1962).

TABLE I. HOMOGENEOUS HYDROGENATIONS OF THE OXIMES OF α-KETO ACIDS AND KETOXIMES USING A CYANO COBALT COMPLEX[a]

Compound	Run	Substrate/ $CoCl_26H_2O$	Temp. °C	Time hr.	Corresponding product, %	Co deposited
 $C_6H_5CH_2\underset{\underset{NOH}{\|}}{C}COOH$	1	1	30	8	—[b]	None
	2	1	40	8	30.0	None
	3	3	60	8	78.3	None
	4	1	70	8	82.0	None
	5	5	70	5	75.2	None
	6	1	100	15	30.0[c]	Much
	7	1	100	15	30.0[d]	Much
 $CH_3\underset{\underset{NOH}{\|}}{C}COOH$	8	2	40	8	20.0	None
	9	2	70	8	63.6	None
 $HOOC(CH_2)_2\underset{\underset{NOH}{\|}}{C}COOH$	10	1.5	70	8	47.5	None
 $CH_3\underset{\underset{NOH}{\|}}{C}CH_3$	11	7.1	70	8	40.0	None
 $C_6H_5\underset{\underset{NOH}{\|}}{C}CH_3$	12	3.5	70	8	57.8	None

a) The reaction was carried out under a hydrogen pressure of 50 kg./cm²
b) Atomospheric pressure
c) A hydrogen pressure of 100 kg./cm²
d) A cyano cobalt(II) complex which had been exposed to air for 72 hr. was employed as a catalyst.

TABLE II. THE REDUCTIVE AMINATIONS OF α-KETO ACIDS AND α- AND β-KETO ESTERS WITH 6% AMMONIUM HYDROXIDE USING A CYANO COBALT COMPLEX AS A CATALYST[a]

Compound	Run	Substrate/ $CoCl_26H_2O$	Temp. °C	Time hr.	Corresponding product, %	Co deposited
 $C_6H_5CH_2\underset{\underset{O}{\|}}{C}COOH$	13	1	30	8	—[b]	None
	14	3	40	8	85.6	None
	15	1	70	5	95.0	None
	16	10	70	5	76.5	None
	17	1	70	5	36.3[c]	None
 $CH_3\underset{\underset{O}{\|}}{C}COOH$	18	3	70	5	84.6	None
	28	1	40	8	73.2	None
 $HOOC(CH_2)_2\underset{\underset{O}{\|}}{C}COOH$	19	1	40	8	36.4	None
 $CH_3\underset{\underset{O}{\|}}{C}COOC_2H_5$	20	1	40	8	68.2	None
 $C_6H_5CH_2\underset{\underset{O}{\|}}{C}COOC_2H_5$	21	1	40	8	76.7	None
 $CH_3\underset{\underset{O}{\|}}{C}CH_2COOC_2H_5$	22	1	40	8	—	None

a) Most of the runs were carried out under the hydrogen pressure of 50 kg./cm².
b) The reaction was carried out under a hydrogen pressure of one atmosphere.
c) Potassium cyanide was not added to the reaction mixture.

kg./cm² to give phenylalanine in 33~82% yield.

These results indicate that the appropriate hydrogen pressure and temperature are necessary in homogeneous hydrogenation with a cyano cobalt complex as a catalyst. The oximes of other α-keto acids were also reduced in a similar method; these results are shown in runs 8—10.

It has been known[9] that reductive amination of an α-keto acid with aqueous ammonia can

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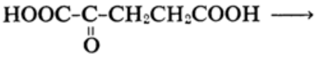
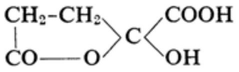
[9] F. Knoop and H. Oesterlin, *Z. Physio. Chem.*, **148**, 294 (1925); **170**, 185 (1927).

be carried out with an active metal such as platinum, palladium or Raney nickel. In the present study, the reductive aminations of the various α-keto acids and their esters with 6% aqueous ammonia could be carried out with a cyano cobalt complex as a catalyst. These results are summarized in Table II. In runs 20 and 21, although esters of α-amino acids were not obtained, free amino acids were obtained in good yields. Perhaps when the ester of α-imino acid is coordinated with cobalt complex ions, the hydrolysis of the ester group takes place more easily than the hydrogenation of the α-imino group. In the reductive amination of α-keto-glutaric acid, a minimum amount of α-hydroxyglutaric acid was obtained as a by-product, together with glutamic acid. This result can be explained by saying that glutamic acid was obtained in a poor yield because α-keto glutaric acid formed the ring structure II in the process of the reductive amination.



$HOOC\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_2CH_2COOH \longrightarrow$

(I)



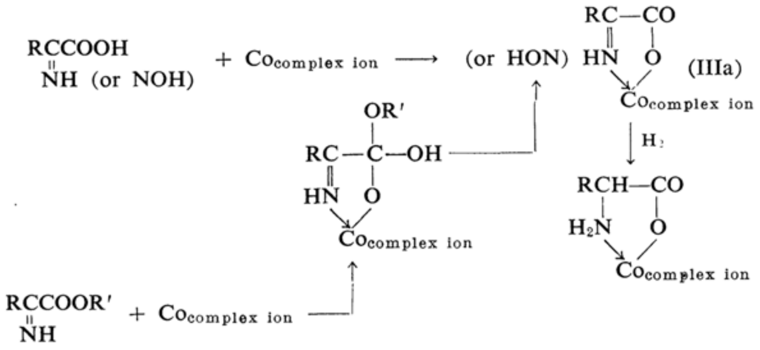
(II)

In the reductive amination of the ester of a β-keto acid, neither the ester of the β-amino acid nor the β-amino acid was formed. The ester of β-keto acid may be more readily hydrolyzed by the action of the cyano cobalt complex ions to yield a stable, enolized compound before the formation of an imino compound. Consequently it can be concluded that the reductive amination of an α-keto acid is carried out smoothly when an α-imino acid is coordinated with cobalt complex ions.

When the reaction was carried out at room temperature under an atmospheric pressure, phenylalanine was not detected among the products, even by the paper chromatographic analysis of these products.

In the run 17, the reductive amination of phenylpyruvic acid was carried out with cobaltous chloride under similar conditions. A comparison of the runs 15 and 17 indicates that the yield of phenylalanine increases appreciably because of the action of potassium cyanide on the reaction mixtuure.

The above results indicate that a cyano cobalt complex serves as a new catalyst for the hydrogenation of an unsaturated compound and for the reductive amination of an α-keto acid with aqueous ammonia in the synthesis of an amino acid. The mechanism of these reactions seems to be as follows: The unstable intermediate, the α-imino acid or the α-isonitroso carboxylic acid, coordinates with cobalt complex ions, and then the complex is reduced. In the case of the ester of an α-keto



Eq. III

TABLE III. THE REDUCTIVE AMINATIONS OF α-KETO ACIDS WITH $[Co(NH_3)_5Cl]Cl_2$ IN AN ALKALINE SOLUTION

Compound	Run	*n*KCN	Keto acid/ complex	Corresponding amino acid, %	Co deposited
$C_6H_5CH_2\underset{\overset{\|}{O}}{C}COOH$	30	0	1	29.6	Little
	31	5	5	53.0	None
	32	5	2	96.4	None
	33	5	1	94.0	None
$CH_3\underset{\overset{\|}{O}}{C}COOH$	34	5	2	85.0	None

TABLE IV. THE HYDROGENATIONS OF UNSATURATED HYDROCARBONS AND UNSATURATED ACIDS WITH A CYANO COBALT COMPLEX

Compound	Run	Substrate/ $CoCl_2 6H_2O$	Reduction product, %	Co deposited
$C_6H_5CH=CHCOOH$	23	3.2	70.0	None
$CH_3CH=CHCH=CHCOOH$	24	4.2	60.0	None
Cyclohexene	25	5.8	—	None
Styrene	26	4.6	—	None

acid, the ester group of the α-imino acid is hydrolyzed and then the product is reduced through the intermediate IIIa (Eq. III).

When α-keto acids were treated with chloropentammine cobalt(III) chloride[10] alone or together with potassium cyanide at 70°C under a hydrogen pressure of 50 kg./cm^2 for five hours in an alkaline solution, α-amino acids were obtained. The results of the reductive aminations with $[Co(NH_3)_5Cl]Cl_2$ are summarized in Table III.

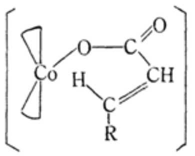
While the reductive amination[8] of phenylpyruvic acid with $[Co(NH_3)_5Cl]Cl_2$ gave phenylalanine in a 29.6% yield, phenylalanine was obtained in a good yield by the addition of five moles of potassium cyanide to the above reaction mixture. The yield of the amino acid decreased with the decrease in the molar ratio of $[Co(NH_3)_5Cl]Cl_2$ to the α-keto acid.

The mechanism of this reaction seems to be similar to that of the reductive amination of an α-keto acid with a cyano cobalt complex.

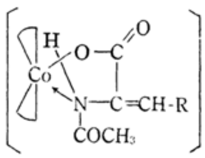
In the hydrogenations at 70°C under a hydrogen pressure of 50 kg./cm^2, cinnamic acid and sorbic acid gave dihydrocinnamic acid in a 70% yield and γ,δ-hexenoic acid in a 60% yield respectively. Runs 11 and 12 revealed that acetoxime and acetophenone oxime were hydrogenated under similar conditions. However, cyclohexene and styrene did not give any reduction product in a similar hydrogenation. This was confirmed by the gas chromatographic analysis (runs 25 and 26).

Table IV indicates that unsaturated hydrocarbons which can not coordinate with cobalt ions are not reduced, while the unsaturated compounds containing functional groups which can coordinate with cobalt ions are readily reduced. These results thus indicate that the homogeneous hydrogenation with a cyano cobalt complex proceeds along a different path from that of the heterogeneous hydrogenation with the metal catalyst. Probably, in the former, hydrogenations are taking place within the molecule of the cobalt complex.

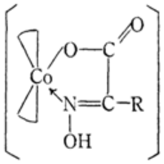
While the α-isonitroso carboxylic acids and the α,β-unsaturated acids were readily hydrogenated with a cyano cobalt complex (Table II, runs 23 and 24), the γ,δ-unsaturated acid was not (run 24). We found, in our previous work[2], that the homogeneous hydrogenations of $[\mathrm{Co\ pn_2\ OCO\underset{NHCOCH_3}{\underset{|}{C}}{=}CHC_6H_5}]\mathrm{Cl_2}$ and $[\mathrm{Co\ pn_2\text{-}OCO\underset{NH_2}{\underset{|}{C}}HCH{=}CHC_6H_5}]\mathrm{Cl_2}$ with six moles of potassium cyanide gave reduction products in a 45.5% and a 3.5% yield respectively. Thus, the hydrogenations of the unsaturated compounds in both cases seem to be carried out through the transition states in which the reducible double bond is fixed in the chelate ring with the cobalt atom (VI and VII) or can come in the same plane (V).



(V)



(VI)



(VII)

A question remains as to the nature of the intermediate in the hydrogenations of the unsaturated compounds with a cyano cobalt complex and in the hydrogenations of the mixed organo-cobalt complexes with potassium cyanide. When the hydrogenation of *N*-acetylaminocinnamic acid with a cyano cobalt complex was carried out at 100°C under a hydrogen pressure of 100 kg./cm^2, the yield of phenylalanine was small. Also, the metallic cobalt quantitatively separated. In the meantime, the mixture of $[\mathrm{Co\ pn_2\ OCO\underset{NHCOCH_3}{\underset{|}{C}}{=}CHC_6H_5}]\mathrm{Cl_2}$ and six moles of potassium cyanide gave phenylalanine in a 45.5% yield under the same conditions. Whereas phenylalanine was obtained in a 55% yield from the hydrogenation of $[\mathrm{Co\ pn_2\ OCO\underset{NO}{\underset{\|}{C}}CH_2C_6H_5}](\mathrm{CO_3})_{1/2}$ with six moles

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[10] B. Inoue, "Mukikagaku Seizo Jickken", Shokabo Co., Tokyo (1949), p. 358.

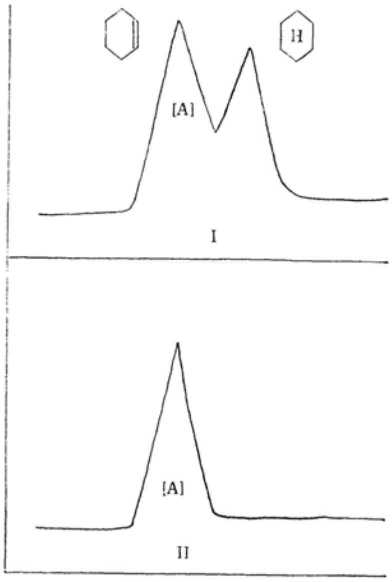

Fig. 1. Gas chromatographic analysis.

I: Standard sample (cyclohexene+cyclohexane), II: The reduction product of cyclohexene. The employed resin is as follows; Silicon grease 30%, Celite 545, 80∼100 mesh.

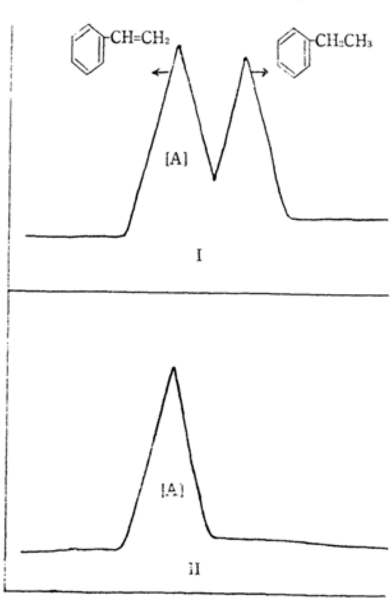

Fig. 2. Gas chromatographic analysis.

I: Standard sample (styrene+ethyl benzene), II: The reduction product of styrene. The employed resin is as follows; Silicon grease 30%, Celite 545, 80∼100 mesh.

of potassium cyanide under a hydrogen pressure 100 kg./cm^2 and 100°C, it was also obtained in a 30% yield from the hydrogenation of the oxime of phenylpyruvic acid with a cyano cobalt complex under the same condition together with the metallic cobalt quantitatively deposited. A comparison of the two reaction enables us to conclude the following points: Whereas the yield of hydrogenation of an unsaturated compound with a cyano cobalt complex was high under mild conditions, the yield of the hydrogenation of the mixed organocomplex with potassium cyanide was low under the similar conditions. Under the drastic conditions, the results were contrary to those observed under the mild conditions.

Consequently, although the two hydrogenations do not seem to proceed through the same intermediate, the unsaturated compound and the cyano group should be combined in the same molecule of the cobalt complex. Accordingly, the homogeneous hydrogenations seems to occur very easily when cyanide and the unsaturated compound are combined with a cobalt ion simultaneously. However, at present we do not known the number of cyano groups which coordinate with a cobalt ion.

Experimental

Apparatus.—Hydrogenations were carried out in a stainless steel autoclave with a capacity of 100 ml.

Hydrogenation of the Oxime of Phenylpyruvic Acid.—To a solution of 0.37 g. (0.0021 mol.) of the oxime of phenylpyruvic acid and 0.082 g. (0.0025 mol.) of sodium hydroxide in 25 ml. of distilled water was added 0.685 g. (0.0105 mol.) of potassium cyanide. After the mixture had been poured into an autoclave, fine crystals of 0.5 g. (0.0021 mol.) of cobaltous chloride were added to the mixture and the autoclave was immediately sealed. The reaction completed at 70°C under a hydrogen pressure of 50 kg./cm^2 in eight hours. The reaction mixture was homogeneous. When 2 ml. of the reaction mixture was treated with the hydrochloric acid solution of 2,4-dinitrophenylhydrazine, only a trace of the hydrazone derivative was detected. The mixture was concentrated to dryness under reduced pressure. The residue was dissolved in the minimum amount of water and the solution was filtered. The filtrate was charged on a column of Ion-Exchange Amberite I. R. 120 (washed with 2 N ammonium hydroxide, water, 2 N hydrochloric acid and water) eluted with water until the elute was shown to be free of halide ions. The amino acid was then eluted with 2 N ammonium hydroxide, and the excess ammonia was evapolated to dryness under reduced pressure to give 0.28 g. (82.1%) of phenylalanine (m. p., 242∼262°C decomp.). After the recrystallization from water-ethanol, it melted at 267∼270°C with decomposition. The identity of the phenylalanine obtained was confirmed by the paper chromatographic analysis and by the mixed melting point determination.

The Reductive Amination of Phenylpyruvic Acid.—To a solution of 1.0 g. (0.0061 mol.) of phenylpyruvic acid in 25 ml. of 6% ammonium hydroxide was added 0.685 g. (0.0105 mol.) of potassium cyanide; the mixture was then poured into an autoclave. Fine crystals of 0.5 g. (0.0021 mol.) of cobaltous chloride were added to the mixture. The reaction completed at 40°C under a hydrogen pressure of 50 kg./cm^2 in eight hours. The reaction mixture was homogeneous. When 2 ml. of the cooled reaction mixture was treated with a hydrochloric acid solution of 2,4-dinitrophenylhydrazine, only a trace of hydrazone derivative was detected. The residual solution was treated with hydrogen sulfide to remove the cobalt ion as its sulfide. The filtrate was concentrated to dryness under reduced pressure. After the residue was treated with a minimum amount of water, the mixture was filtered. The filtrate was then treated in a method similar to that of the previous experiment. The phenylalanine obtained was 0.856 g. (a 85.6% yield); m. p., 248~262°C (decomp.). The identity of the phenylalanine obtained was confirmed by the paper chromatographic analysis and by the mixted melting point determination.

The Reductive Amination of Ethyl Phenylpyruvate.—To a solution of 0.38 g. (0.0019 mol.) of ethyl phenylpyruvate in 25 ml. of 6% ammonium hydroxide was added 0.68 g. of potassium cyanide; the mixture was then poured into an autoclave. Fine crystals of 0.5 g. of cobaltous chloride were added to the mixture. The reaction completed at 40°C under a hydrogen pressure of 50 kg./cm^2 in eight hours. The cooled reaction mixture was repeatedly extracted with ether. When the ether layer was evaporated after dried over anhydrous magnesium sulfate, the ethyl ester of phenylalanine was not obtained. The aqueous layer was treated in a way similar to that above. The phenylalanine obtained was 0.24 g. (a 76.6% yield); m. p., 242~252°C (decomp.). The paper chromatographic analysis of the product proved its identity with the authentic phenylalanine.

The Hydrogenation of Acetoxime.—Into a solution of 1.0 g. (0.0141 mol.) of acetoxime and 0.6 g. (0.0150 mol.) of sodium hydroxide in 25 ml. of water was dissolved 0.685 g. of potassium cyanide. After the mixture had been poured into an autoclave, fine crystals of 0.5 g. of cobaltous chloride were added to the mixture. The reaction was completed under the condition similar to that used in the previous experiment. The cooled reaction mixture was extracted with the ethereal hydrochloric acid solution by means of extraction apparatus. The acidic ether extracts were concentrated to dryness under a reduced pressure, and the residue was dried over sulfuric acid in vacuo. The crude isopropylamine hydrochloride (0.34 g., 40%) melted at 121~138°C. After three additional recrystallizations from ethanol, it was identified with the authentic sample; m. p., 137~139°C.

Found: C, 37.08; H, 10.72; N, 14.05; Cl, 36.89. Calcd. for $C_3H_{10}NCl$: C, 37.48; H, 10.47; N, 14.55; Cl, 37.17%.

The Hydrogenation of Acetophenone Oxime.—A mixture of acetophenone oxime (1.0 g., 0.0074 mol.), sodium hydroxide (0.3 g., 0.0075 mol.), potassium cyanide (0.685 g.) and cobaltous chloride (0.5 g.) in 15 ml. of water was hydrogenated by the method similar to that of the above experiment. The homogeneous solution was repeatedly extracted with ether. After the ethereal extracts had been dried over anhydrous magnesium sulfate, the ether was removed and the product was collected at 81~82°C (16 mmHg). The yield of α-methylbenzylamine was 0.52 g. (57.8%).

Found: C, 79.36; H, 9.01; N, 12.00. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56%.

The Reductive Amination of Phenylpyruvic Acid.—To a solution of 1.0 g. (0.0061 mol.) of phenylpyruvic acid and 0.6 g. (0.015 mol.) of sodium hydroxide in 25 ml. of water was added 0.95 g. (0.0146 mol.) of potassium cyanide. After the mixture had been poured into an autoclave, fine powder of 0.75 g. (0.0030 mol.) of chloro pentammine cobalt(III) chloride was added to the mixture. The reaction completed at 70°C under a hydrogen pressure of 50 kg./cm^2 in five hours. The cooled reaction mixture was concentrated to dryness under a reduced pressure. To the residue was added the minimum amount of water and the mixture was filtered. The filtrate was charged on a column of Ion-Exchange Amberite I. R. 120 and eluted with water until the elute was shown to be free of halide ions. The amino acid was then eluted with 2 N ammonium hydroxide, and the excess ammonia was concentrated to dryness under a reduced pressure to give 0.94 g. (94%) of phenylalanine (m. p., 245~263°C (decomp.)). The identity of the phenylalanine obtained was confirmed by the paper chromatographic analysis.

The Hydrogenation of Cinnamic Acid. — To a solution of 1.0 g. (0.0067 mol.) of cinnamic acid, 0.3 g. (0.0076 mol.) of sodium hydroxide and 0.685 g. of potassium cyanide in 25 ml. of water, 0.5 g. of cobaltous chloride was added. The reaction completed at 70°C under a hydrogen pressure of 50 kg./cm^2 in eight hours. The cooled reaction mixture was acidified with 2 N hydrochloric acid and was repeatedly extracted with ether. After the mixture had been dried with anhydrous magnesium sulfate, the ether was removed to give 0.76 g. of the crystalline product (m. p. 43~65°C). The crude product was dissolved in 5 ml. of ethanol, and the insoluble material was filtered. After the ethanol had been removed, the residue was crystallized from 5 ml. of ligroin. The product weighed 0.7 g. (70%) and melted at 45~46°C. The product was identified with an authentic sample of hydrocinnamic acid.

The Hydrogenation of Sorbic Acid.—A mixture of sorbic acid (1.0 g., 0.0089 mol.), sodium hydroxide (0.36 g., 0.0090 mol.) potassium cyanide (0.685 g.) and cobaltous chloride (0.5 g.) in 25 ml. of water was hydrogenated and was treated in a way similar to that above. γ,δ-Hexenoic acid (0.61 g., 60%) was collected, its b. p. being 101~102°C (12 mmHg). The identify of γ,δ-hexenoic acid was confirmed by its infrared spectrum and by the titrimetric determination of the double bond of the product.

The Hydrogenation of Cyclohexene.—A mixture of cyclohexene (1.0 g., 0.0122 mol.), potassium cyanide (0.685 g.) and cobaltous chloride (0.5 g.) in 15 ml. of water was hydrogenated as above. The cooled reaction mixture was then acidified with 2 N hydrochloric acid and repeatedly extracted with ether. After the mixture had been dried with anhydrous magnesium sulfate, the ether layer was removed and the residue (0.95 g.) was collected at a boiling point of 78∼83°C. It was confirmed by the gas chromatographic analysis that cyclohexane was not present in the product obtained.

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