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Chemistry of Sodium Borohydride and Diborane. IV.[1] Reduction of Carboxylic Acids to Alcohols with Sodium Borohydride through Mixed Carbonic-Carboxylic Acid Anhydrides[2]

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Mixed carbonic-carboxylic acid anhydrides, prepared *in situ* from carboxylic acids and ethyl chloroformate, were reduced with sodium borohydride in aqueous tetrahydrofuran to the corresponding alcohols in fair yields. Under the reaction condition examined, it was possible to reduce carboxyl group selectively to hydroxymethyl group in carboxylic acids having functional groups such as nitro-, cyano-, amido-, ester-group, and conjugated double bond. The general procedure for this reaction is given.

Sodium borohydride is one of the most useful reducing agents, and the researches on the elucidation of its chemical reactivities have been a subject of wide investigations.[4] Examinations on the reduction of carboxylic acid esters and amides with sodium borohydride were reported previously,[5,6] and it was recognized[6] that such esters as having primary amino-, hydroxyl-, and halogeno-substituent at α-position to the ester-carbonyl group were reduced with sodium borohydride to the corresponding alcohols in fair yields. These findings seem to suggest that an increase in the electropositivity at the carbonyl carbon atom of carboxylic acid esters facilitates their susceptibility to sodium borohydride reduction. On the basis of this consideration, mixed carbonic-carboxylic acid anhydrides prepared from carboxylic acids and ethyl chloroformate were chosen as substrates for their high reactivity toward nucleophiles,[7] and their reactions with sodium borohydride were examined, with which the present paper is concerned.

It has already been reported that the mixed anhydrides prepared from N-acyl-α-amino acids and ethyl chloroformate are reduced with lithium borohydride in tetrahydrofuran to the corresponding N-acyl-α-amino alcohols.[8] Perron, *et al.* also reported that the mixed anhydride prepared from benzylpenicillinic acid and ethyl chloroformate was reduced with sodium borohydride in tetrahydrofuran to the corresponding alcohol in 94% yield.[9] Application of Perron's procedure to benzoic acid, however, afforded the corres-

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[2] Presented at the 86th Annual Meeting of the Pharmaceutical Society of Japan at Sendai (October, 1966).

[3] Location: *Bunkyo-ku, Tokyo.*

[4] *a*) W. Gerrard, "The Organic Chemistry of Boron," Academic Press, London and New York, 1961. *b*) H.C. Brown, "Hydoboration," W.A. Benhamin Inc., New York, 1962. *c*) H. Steinberg, "Organoboron Chemistry," Vol. 1, Interscience Publ., New York, London and Sydney, 1963. *d*) E. Schenker, *Angew. Chem.*, 73, 81 (1961). *e*) E. Schenker's manuscript entitled "Neuere Methoden der präparativen organischen Chemie. IV. Anwendung von komplexen Borohydriden und von Diboran in der organischen Chemie." The present authors are grateful to Dr. E. Schenker for his courtesy in sending a copy of his manuscript to one of us (S.Y) before publication.

[5] *a*) H. Seki, K. Koga, H. Matsuo, S. Ohki, I. Matsuo, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 13, 995 (1965). *b*) S. Yamada, Y. Kikugawa, and S. Ikegami, *Ibid.*, 13, 394 (1965).

[6] H. Seki, K. Koga, and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 15, 1948 (1967).

[7] *cf.* N.F. Albertson, *Org. Reactions*, 12, 157 (1962).

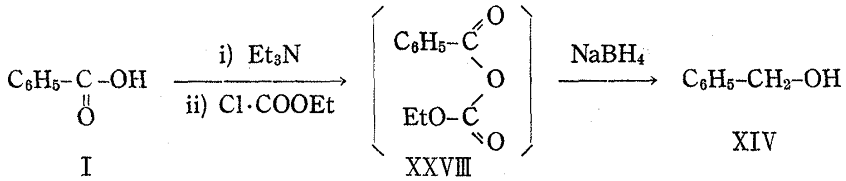
[8] K. Heyns and K. Stange, *Z. Naturforsch.*, **10b**, 252 (1955).

[9] Y.G. Perron, L.B. Crast, J.M. Essery, R.R. Fraser, J.C. Godfrey, C.T. Hodrege, W.F. Minor, M.E. Neubert, R.A. Partyka, and L.C. Cheney, *J. Med. Chem.*, 7, 483 (1964).

ponding benzyl alcohol in a yield below 30%. A similar situation was also encountered in the case of hexanoic acid. As the slight solubility of sodium borohydride in tetrahydrofuran was considered to be responsible for the low yields, efforts were focussed on the reduction condition to give alcohols in better yields, and finally a procedure was devised in which the mixed carbonic–carboxylic acid anhydrides were prepared from carboxylic acids and ethyl chloroformate in the presence of triethylamine in anhydrous tetrahydrofuran, the deposited triethylammonium chloride was filtered off, and the mixed anhydride solution thus obtained was added to a solution of sodium borohydride in water.

Benzoic acid was reduced in this manner with various molar ratios of sodium borohydride in order to examine the amount of this reagent required for this reduction. As shown in Table I, it was revealed that the use of more than 2 molar equivalents of sodium borohydride was sufficient. Therefore, all experiments in this paper were carried out with 2.5 molar equivalents of this reagent. The general procedure is written in the experimental section.

Table I. Reduction of Mixed Anhydride of Benzoic Acid with Various Molar Ratios of Sodium Borohydride



Molar Ratio ($NaBH_4$/Benzoic Acid)	1	2	3
Yield of Benzyl Alcohol (%)	42	73	76

It is also known that the reaction of mixed carbonic–carboxylic acid anhydrides with nucleophiles is accompanied with the evolution of carbon dioxide[7] and that carbon dioxide is reduced with sodium borohydride to formic acid.[10] In the reaction of the mixed anhydride prepared from benzoic acid and ethyl chloroformate with sodium borohydride under this reaction condition, 19% of the theoretical amount of carbon dioxide was trapped as barium carbonate on the acidification of the reaction mixture at the end of the reaction, and the existence of formic acid in the reaction mixture was proved by the isolation of its S–benzylthiouronium salt. These results may explain the necessity of more than 2 molar equivalents of sodium borohydride in this reaction.

As shown in Table II, various kinds of carboxylic acids were converted in this manner to the corresponding alcohols in fair yields. Owing to the mild reaction condition, it was possible to reduce carboxyl function selectively in carboxylic acids having functional groups such as nitro–, cyano–, amido–, ester–group and conjugated double bond. In run 13, however, diol (XXVII) was isolated as a minor product. By the same token, N–carboxy–anhydride of phenylalanine, a kind of mixed carbonic–carboxylic acid anhydride, was also reduced successfully to give 2–amino–3–phenylpropanol (XXX) under the same reaction condition.

For the structural confirmation of the reduction products in run 13, reduction of the half–ester (XIII) with sodium borohydride-lithium bromide in diglyme[11] was performed, and the expected 3,4–dihydroisocoumarin (XXXII) was obtained. It is interesting to note that this lactone(XXXII)was also obtained as a main product in the sodium borohydride reduction of 1,3–isochromandione (XXXI) in isopropanol. Analysis of the reduction product by NMR spectroscopy showed that it is a mixture of 3,4–dihydroisocoumarin (XXXII) and 3–isochromanone (XXVI) in a ratio of 9:1, respectively.

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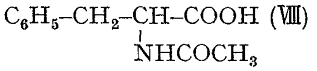
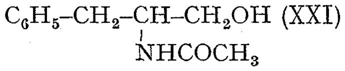
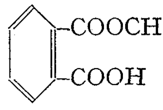
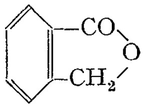
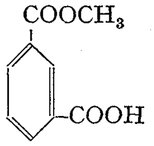
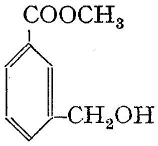
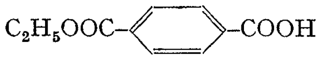
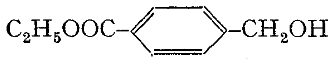
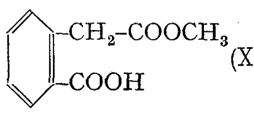
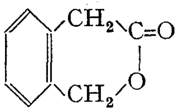
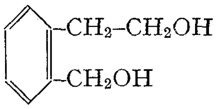
10) Ref. 4*c*) p. 788.

11) H.C. Brown, E.J. Mead, and B.C. Subba Rao, *J. Am. Chem. Soc.*, 77, 6209 (1955).

Table II. Reduction of Mixed Anhydrides derived from Carboxylic Acids with Sodium Borohydride

Run	Carboxylic Acid	Product	Yield
1	C_6H_5-COOH (I)	$C_6H_5-CH_2OH$ (XIV)	77
2	$p-NO_2-C_6H_4-COOH$ (II)	$p-NO_2-C_6H_4-CH_2OH$ (XV)	73
3	$p-NC-C_6H_4-COOH$ (III)	$p-NC-C_6H_4-CH_2OH$ (XVI)	73
4	$p-CH_3O-C_6H_4-COOH$ (IV)	$p-CH_3O-C_6H_4-CH_2OH$ (XVII)	80
5	$CH_3-(CH_2)_4-COOH$ (V)	$CH_3-(CH_2)_4-CH_2OH$ (XVIII)	70
6	$C_6H_5-CH_2-CH_2-COOH$ (VI)	$C_6H_5-CH_2-CH_2-CH_2OH$ (XIX)	71
7	$C_6H_5-CH=CH-COOH$ (VII)	$C_6H_5-CH=CH-CH_2OH$ (XX)	80
8	 $C_6H_5-CH_2-\underset{NHCOCH_3}{CH}-COOH$ (VIII)	 $C_6H_5-CH_2-\underset{NHCOCH_3}{CH}-CH_2OH$ (XXI)	77
9	$C_2H_5OOC-(CH_2)_4-COOH$ (IX)	$C_2H_5OOC-(CH_2)_4-CH_2OH$ (XXII)	75
10	 (X)	 (XXIII)	71
11	 (XI)	 (XXIV)	82
12	 (XII)	 (XXV)	74
13	 (XIII)	 (XXVI)	77
		 (XXVII)	3

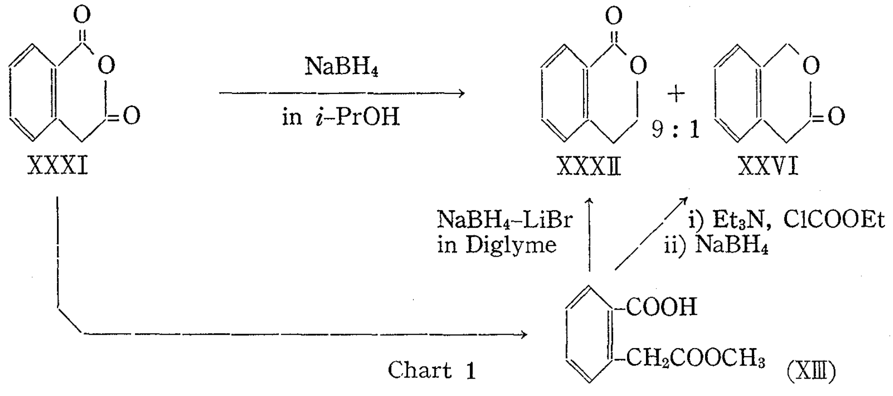


Chart 1

Moreover, phthalic anhydride was reduced to phthalid (XXIII) with sodium borohydride in aqueous tetrahydrofuran. These results may indicate that the reaction of sodium borohydride with anhydrides occurs easily under these conditions, and that the reaction takes place much easier on the aliphatic carbonyl group, as is the case in the reaction of sodium borohydride with acid chlorides.[12]

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[12] S.W. Chaikin and W.G. Brown, *J. Am. Chem. Soc.*, 71, 122 (1949).

Experimental[13]

Materials——$NaBH_4$ was purchased from Kawaken Fine Chemicals Co., Ltd., and dried *in vacuo* before use. The purity was assumed to be about 95%. Authentic samples of reduction products were obtained commercially, unless otherwise stated.

Reductions——Unless otherwise stated, all reductions were carried out in a manner similar to that described in the general procedure.

General Procedure——A solution of ethyl chloroformate (0.02 mole) in tetrahydrofuran (5 ml) was added at $-5°$ to a solution of carboxylic acid (0.02 mole) and triethylamine (0.02 mole) in tetrahydrofuran (30 ml or more to make a clear solution) in the course of 15 to 30 min, and the whole was stirred for 30 min at the same temperature. The white precipitate (triethylammonium chloride) was filtered off, washed with 10 ml of tetrahydrofuran, and the combined filtrate and the washings were added during 30 min to a solution of sodium borohydride (0.05 mole) in water (20 ml) at 10—15° by external cooling. Violent evolution of gas was observed. After the addition was complete, the reaction mixture was stirred at room temperature for 2 to 4 hr, then made acidic with HCl. The reaction mixture separated into two layers. The H_2O-layer was extracted with ether, the combined etheral extracts and the tetrahydrofuran-layer were washed with 10% aq. NaOH, H_2O, and dried over Na_2SO_4. The residue obtained on the evaporation of the solvent was subjected to distillation or recrystallization.

Identification of CO_2 and Formic Acid——A solution of mixed anhydride in tetrahydrofuran (105 ml) prepared *in situ* from benzoic acid (6.15 g, 0.05 mole) as described in the general procedure was added to a solution of $NaBH_4$ (5.0 g, 0.125 mole) in H_2O (50 ml) below 15° under a stream of N_2. The CO_2 generated was trapped by bubbling it into the aq. $Ba(OH)_2$ solution with N_2. Precipitated $BaCO_3$ was not observed during 2 hrs' stirring at room temperature followed by half-an-hour of stirring at 60°. Acidification of the reaction mixture with 30% aq. H_2SO_4 afforded a precipitate of $BaCO_3$, which was collected and dried *in vacuo* to give 1.87 g (19% of the theoretical amount) of $BaCO_3$. The reaction mixture was extracted with ether, and the combined extracts were washed with 10% aq. NaOH to remove the acidic fraction. The ether-layer was washed with H_2O, dried over Na_2SO_4, and the ether was evaporated. The resulting liquid was distilled to give 4.16 g (77% yield) of benzyl alcohol (bp 115—120° (40 mmHg)), identified with the authentic sample. The above 10% aq. NaOH washings were acidified with HCl, and extracted continuously with ether. This ether extract was dried over Na_2SO_4 and distilled under slightly reduced pressure to give 0.48 g of crude formic acid.

S-Benzylthiouronium formate: dp 147—147.2°, identified with the authentic sample of the same dp by IR spectra. *Anal.* Calcd. for $C_9H_{12}O_2N_2S$: C, 50.94; H, 5.70; N, 13.20. Found: C, 50.64; H, 5.44; N, 13.13.

***p*-Nitrobenzyl Alcohol (XV)**——Obtained from *p*-nitrobenzoic acid (II) according to the general procedure as a pale yellow crystalline powder of mp 91—93° (reported[14] mp 93°) in 73% yield, and identified with the authentic sample.

***p*-Cyanobenzyl Alcohol (XVI)**——Obtained from *p*-cyanobenzoic acid (III) as colorless prisms of mp 42—44° (bp 173° (11 mmHg)) (reported[15] mp 41—42°) in 73% yield. IR ν_{max}^{KBr} cm^{-1}: 3330, 2230, 1613, 1031, 1020.

***p*-Methoxybenzyl Alcohol (XVII)**——Obtained from *p*-anisic acid (IV) as a colorless solid of mp 24—25° (reported[16] mp 25°) in 80% yield, and identified with the authentic sample.

1-Hexanol (XVIII)——Obtained from hexanoic acid (V) as a colorless liquid of bp 157° (reported[14] bp 157.5°) in 70% yield, and identified with the authentic sample.

3-Phenylpropanol (XIX)——Obtained from 3-phenylpropionic acid (VI) as a colorless liquid of bp 124° (15 mmHg) (reported[17] bp 105—107° (7 mmHg)) in 71% yield, and identified with the authentic sample.[6]

Cinnamyl Alcohol (XX)——Obtained from cinnamic acid (VII) as a pale yellow solid of mp 32—34° (reported[14] mp 33°) in 80% yield, and identified with the authentic sample.

DL-N-[α-(Hydroxymethyl)phenethyl]acetamide (XXI)——Obtained from DL-N-acetylphenylalanine (VIII) as colorless prisms of mp 92—93° (reported[6] mp 93.5—94.5°) in 77% yield, and identified with the authentic sample.

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13) All melting and boiling points are not corrected. IR spectra were measured with a Koken DS-402G Spectrometer and NMR spectra were measured with a JNM 3H-60 Spectrometer using TMS as an internal standard.

14) N.A. Lange (ed.), "Handbook of Chemistry," 9th ed., Handbook Publ., Sandusky, Ohio, 1956.

15) J.N. Ashley, H.J. Barber, A.J. Ewins, G. Newbery, and A.D.H. Self, *J. Chem. Soc.*, **1942**, 103.

16) E. Späth, *Monatsh.*, **34**, 1965 (1913).

17) J.B. Conant, and W.R. Kirner, *J. Am. Chem. Soc.*, **46**, 232 (1924).

Ethyl 6-Hydroxyhexanoate (XXII)——Obtained from monoethyl adipate (IX) (mp 28.5—30°, reported[18] mp 28—29°) as colorless liquid of bp 134° (16 mmHg) (reported[19] bp 135—140° (16 mmHg)). IR $\nu_{\mathrm{max}}^{\mathrm{Cap}}$ cm^{-1}: 3400, 1740.

Phenylurethane: Colorless pillars of mp 52.5——53.2° from ether. *Anal.* Calcd. for $C_{15}H_{21}O_4N$: C, 64.49; H, 7.58; N, 5.01. Found: C, 64.61; H, 7.45; N, 5.17.

Phthalid (XXIII)——a) Obtained from monomethyl phthalate (X) (prepared according to the known method[20] mp 82—83°) as colorless fine prisms of mp 72.5—73.5° (reported[14] mp 73°) in 71% yield. IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ cm^{-1}: 1754.

b) A solution of phthalic anhydride (4.45 g, 0.03 mole) in tetrahydrofuran (60 ml) was added to a solution of $NaBH_4$ (3.0 g, 0.075 mole) in H_2O (30 ml) at 10°, and the whole was stirred at room temperature for 2 hr. After evaporation of the tetrahydrofuran, the aqueous residue was acidified with HCl, and then extracted with ether. The extracts were washed with sat. aq. $NaHCO_3$, H_2O, and dried over Na_2SO_4. Evaporation of the ether gave 3.08 g (77% yield) of phthalid (XXIII), mp 73—74°, identical with the sample prepared in a).

Methyl *m*-Hydroxymethylbenzoate (XXIV)——Obtained from monomethyl isophthalate (XI) (mp 190—191°, reported[21] mp 193°) as a colorless liquid of bp 166—167° (13 mmHg) in 82% yield. IR $\nu_{\mathrm{max}}^{\mathrm{Cap}}$ cm^{-1}: 3410, 1730.

p-Nitrobenzoate: Colorless fine needles of mp 142.5—143°. IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ cm^{-1}: 1735, 1724, 1524, 1350. *Anal.* Calcd. for $C_{16}H_{13}O_6N$: C, 60.95; H, 4.16; N, 4.44. Found: C, 60.85; H, 3.97; N, 4.39.

m-Hydroxymethylbenzoic acid: Colorless fine needles of mp 115° (reported[22] mp 114.5—115°). *Anal.* Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 62.91; H, 5.12.

Ethyl *p*-Hydroxymethylbenzoate (XXV)——Obtained from monoethyl terephthalate (XII) (mp 168—170°, reported[23] mp 168—170°) as a colorless liquid of bp 145—149° (3.5 mmHg) (reported[24] bp 161—163° (5 mmHg)). IR $\nu_{\mathrm{max}}^{\mathrm{Cap}}$ cm^{-1}: 3450, 1722, 1277.

p-Nitrobenzoate: Pale yellow leaflets of mp 87—88° (reported[24] mp 86°). *Anal.* Calcd. for $C_{17}H_{15}O_6N$: C, 62.00; H, 4.59; N, 4.25. Found: C, 62.31; H, 4.68; N, 4.09.

p-Hydroxymethylbenzoic acid: Colorless leaflets of mp 180—182° (reported[25] mp 179—181°). *Anal.* Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30. Found: C, 63.11; H, 5.33.

3-Isochromanone (XXVI) and *o*-Hydroxymethylphenethyl Alcohol (XXVII)——A solution of mixed anhydride in tetrahydrofuran (30 ml) prepared from methyl (*o*-carboxyphenyl) acetate (XIII) (mp 95.0—96.3°, reported[26] mp 96—97°) (1.95 g, 0.01 mole) as described in the general procedure was added during a period of 10 min to a solution of $NaBH_4$ (0.84 g, 0.021 mole) in H_2O (10 ml) and tetrahydrofuran (5 ml) below 10°, and the whole was stirred at the same temperature for 3 hr. After acidification of the reaction mixture with HCl, the tetrahydrofuran was evaporated *in vacuo*. To the resulting aqueous solution was added 10% aq. NaOH until neutral, followed by the addition of a solution of NaOH (0.6 g, 0.015 mole) in EtOH (30 ml), and the whole was refluxed for 4 hr. After the evaporation of the EtOH, the resulting aqueous solution was extracted with $CHCl_3$. The $CHCl_3$ extracts were dried and evaporated to give 0.05 g (3% yield) of crude *o*-hydroxymethylphenethyl alcohol (XXVII). IR $\nu_{\mathrm{max}}^{\mathrm{Cap}}$ cm^{-1}: 3330, 1043, 1015.

Di-*p*-nitrobenzoate:Fine needles of mp 132—133° (reported[27] mp 134—135°). IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ cm^{-1}: 1716, 1522, 1348, 1265. *Anal.* Calcd. for $C_{23}H_{18}O_8N_2$: C, 61.33; H, 4.03; N, 6.22. Found: C, 61.40; H, 4.30; N, 6.34.

The mother liquor of the $CHCl_3$ extract was made acidic with HCl, and the extraction was made with ether. The extracts were dried and evaporated to give 1.145 g (77% yield) of 3-isochromanone (XXVI) as a colorless solid of mp 78—80.5°. Recrystallization from benzene-petr. ether raised the mp to 82.7—83.2° (reported[28] mp 81—83°). IR $\nu_{\mathrm{max}}^{\mathrm{KBr}}$ cm^{-1}: 1747. NMR (in CCl_4) τ: 6.40 (2H, singlet), 4.78 (2H, singlet), 2.80 (4H, singlet). *Anal.* Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.26; H, 5.66.

3,4-Dihydroisocoumarin (XXXII)——LiBr (0.85 g, 0.01 mole) was added to a solution of $NaBH_4$ (0.40 g, 0.01 mole) in diglyme (15 ml), and the resulting mixture was stirred at room temperature for 30 min. To this was added methyl (*o*-carboxyphenyl) acetate (XIII) (0.97 g, 0.005 mole), and the reaction mixture

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18) G.B. Brown, M.D. Armstrong, A.W. Moyer, W.P. Anslow, Jr., B.R. Baker., M.V. Querry, S. Bernstein, and S.R. Safir, *J. Org. Chem.*, 12, 160 (1947).
19) N. Tokura and R. Oda, *Bull. Inst. Phys. Chem. Research* (Tokyo), 22, 835 (1943).
20) E.L. Eliel and A.W. Burgstahler, *J. Am. Chem. Soc.*, 71, 2251 (1949).
21) A. Wohl, *Ber.*, 43, 3474 (1910).
22) H. Gilman and D.S. Melstrom, *J. Am. Chem. Soc.*, 70, 4177 (1948).
23) J.B. Cohen and H.S. de Pennington, *J. Chem. Soc.*, 113, 57 (1918).
24) F.H. Case, *J. Am. Chem. Soc.*, 47, 1143 (1925).
25) F.H. Case, *J. Am. Chem. Soc.*, 47, 3003 (1925).
26) L.F. Fieser and M.M. Pechet, *J. Am. Chem. Soc.*, 68, 2577 (1946).
27) J.L. Warnell and R.L. Shriner, *J. Am. Chem. Soc.*, 79, 3165 (1957).
28) C.A. Russell, *J. Am. Chem. Soc.*, 78, 1053 (1956).

was stirred at 100° for 3 hr. The solvent was evaporated *in vacuo*, the residue mixed with 10% aq. HCl (5 ml), then a solution of NaOH (1.0 g) in EtOH (15 ml) was added, and the whole was refluxed for 4 hr. The EtOH was evaporated *in vacuo*, the residue was diluted with H_2O (20 ml), and was extracted continuously with ether. Evaporation of the dried etheral extracts gave nothing. The aqueous mother liquor was acidified with HCl, and then extracted with ether. Evaporation of the dried etheral extracts gave a liquid, which was distilled under reduced pressure to give 0.53 g (72% yield) of 3,4-dihydroisocoumarin (XXXII), bp 175° (22 mmHg) (reported29) bp 176° (20 mmHg)). IR $\nu_{\max}^{\text{Cap}}$cm^{-1}: 1727. NMR (in CCl_4) τ: 7.04 (2H, triplet, $J=6$ cps), 5.59 (2H, triplet, $J=6$ cps), 2.1—2.9 (4H, multiplet). *Anal.* Calcd. for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.03; H, 5.59.

Reduction of 1,3-Isochromandione (XXXI) with $NaBH_4$ in iso-PrOH——A mixture of 1,3-isochromandione (XXXI) (3.25 g, 0.02 mole) (mp 140—141°, reported30) mp 140—141°) and $NaBH_4$ (2.0 g, 0.05 mole) in iso-PrOH (100 ml) was stirred at room temperature for 48 hr. Evaporation of the iso-PrOH *in vacuo* gave a residue, which was suspended with 10% aq. HCl, and extracted with ether. The combined etheral extracts were washed with 10% aq. Na_2CO_3, H_2O and dried over Na_2SO_4. Evaporation of the ether gave a liquid weighing 2.75 g (93% yield as a crude mixture). NMR spectrum of this sample in CCl_4 showed two singlet peaks at 6.40 τ and 4.78 τ, two triplet peaks at 7.04 τ and 5.59 τ, and multiplet peaks at 2.1 τ—2.9 τ. Weighing the peaks revealed that the reduction product was a mixture of 3,4-dihydroisocoumarin (XXXII) and 3-isochromanone (XXVI) in a ratio of 9:1, respectively.

DL-2-Amino-3-phenylpropanol (XXX)——A solution of DL-4-benzyl-2,5-oxazolidinedione (XXIX) (mp 126—128°, reported31) mp 127°) (3.8 g, 0.02 mole) in tetrahydrofuran (30 ml) was added to a solution of $NaBH_4$ (2.0 g, 0.05 mole) in H_2O (20 ml) and tetrahydorofuran (10 ml) at 10°, and the reaction mixture was stirred at room temperature for 3 hr. After the acidification of the reaction mixture with HCl, the tetrahydrofuran was removed *in vacuo*, the aqueous residue was extracted with ether. Evaporation of the dried etheral extracts gave a liquid (2.0 g, 66% yield), which crystallized on standing. This sample showed a mp of 62—68.5° (reported32) mp 66—67°), and proved to be identical with the authentic sample32) by IR spectra and mixed melting point test.

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