mm.). The sublimate weighing 1.6 g. (53% yield) was recrystallized from ether–hexane twice to give 0.5 g. of phthalic anhydride, m.p. and mixed m.p. 127°. Its identity was further confirmed by infrared spectra.

Anal. Calcd. for $C_8H_4O_3$: C, 65.01; H, 2.72. Found: C, 65.21; H, 2.66.

The mother liquid from the above recrystallization was evaporated and the residue recrystallized twice from ether–hexane to give 0.4 g. of 3-ethylphthalic anhydride, m.p. 97–98° (lit.[14] 98°). The infrared absorption band at 14.0 μ characteristic of phthalic anhydride was very faint in its infrared spectrum.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58. Found: C, 68.64; H, 4.41.

4. **4-Ethylphthalic Anhydride (XIX).** a. **2-Ethylbutadiene** was prepared by pyrolysis of 2-ethyl-3-acetoxy-1-butene according to Marvel and Williams.[15] The diene boiled at 66–68.5°, n^{20}_{D} 1.4325 (lit.[15] 65–66°, 1.4325).

b. **Dimethyl 3,6-dihydro-4-ethylphthalate (XVIII)** was prepared from 2-ethylbutadiene as in 3-b in 45% yield. The adduct had b.p. 135–136° (3 mm.), n^{20}_{D} 1.4928, d^{20}_{4} 1.1138 (new compound).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.60; H, 7.20.

c. **Dehydrogenation of the adduct XVIII** was performed as in 3-c, and 4-ethylphthalic anhydride was obtained in 68% yield (new compound), m.p. 76–77°; mixed m.p. with the 3-ethyl isomer, 66–69°. Infrared spectrum showed the absence of phthalic anhydride.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.16; H, 4.58. Found: C, 68.49; H, 4.46.

B. **Apparatus and Procedure. Apparatus.**—The apparatus consisted of a Pyrex reaction tube having a reaction zone of 2.0 cm. outside diameter heated by a thermostatically controlled vertical furnace. The dienes were introduced into the tube, packed with 32 ml. of about 1/8 inch quartz chips in the reaction zone, by means of a motor driven syringe at a rate of 5.6 ml./hr. The lower end of the reaction zone was attached to a liquid receiver, which in turn was attached through Dry Ice–acetone cooled trap to a gas collecting bottle.

Infrared spectra were taken on a Baird double beam recording infrared spectrophotometer having rock salt optics.[16]

Ultraviolet spectra were taken on a Cary model 11 recording quartz spectrophotometer.[17]

Hydrogenations were carried out with a micro-hydrogenation set-up using a platinum oxide catalyst at room temperature and atmospheric pressure.

Vapor phase chromatographic analysis was made on a Podbielniak chromacon.[18] A 6-ft. column packed with 44% of fluorene-picric acid (1:1) on 35–60 mesh fire-brick (density 59 g./100 ml.) was used for analysis of aromatics at 80°. A 12-ft. column packed with 30% of tricresyl phosphate on 35–60 mesh fire-brick (density 59 g./100 ml.) was used for gas analysis. A 6-ft. column of the same kind was used for general purposes. Helium was used as the carrier gas.

Dehydrogenation[19] was done by passing saturated samples over 10 ml. of a platinum-alumina catalyst at 290°.

Reaction with dimethyl acetylenedicarboxylate was done according to Parker and Goldblatt.[7] The gaseous products were analyzed by vapor phase chromatography. The liquid products were converted into phthalic anhydrides and identified by infrared spectra.

---

[15] C. S. Marvel and J. L. R. Williams, THIS JOURNAL, **70**, 3842 (1948).

[16] Baird Associates, Inc., Cambridge, Mass.

[17] Allied Physics Corporation, Pasadena, Calif.

[18] Chromacon, Series 9475, Podbielniak, Inc., Chicago, Ill.

[19] H. Pines and A. W. Shaw, THIS JOURNAL, **79**, 1474 (1957).

EVANSTON, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, KYOTO UNIVERSITY]

The Absolute Configuration of Plant Growth Substances—Partially Hydrogenated 1-Naphthoic Acids[1]

BY KAZUYOSHI KAWAZU, TOSHIO FUJITA AND TETSUO MITSUI

RECEIVED JUNE 2, 1958

It was shown in the previous papers that (–)-1,2,3,4-tetrahydro-1-naphthoic acid (I), (+)-1,4-dihydro-1-naphthoic acid (II) and (+)-1,2-dihydro-1-naphthoic acid (III), having greater plant growth activities than their respective antipodes, possess the same configuration around the asymmetric carbon atom. Recently Westman established the absolute configurations of I and α-phenylglutaric acid (V). The authors have confirmed this by another method: (+)-V has been correlated through (+)-2-phenylpentane (IX) to (+)-α-phenylvaleric acid (X) of known absolute configuration, and (+)-V to (+)-III; (–)-I, (+)-II and (+)-III have been shown to possess the same configuration as the physiologically more active enantiomers of the other plant growth substances. The absolute configurations of the intermediates of the transformations have also been determined.

Optically active α-(3-indole)-propionic acid,[2] reported by Kögl in 1937, provided the first example of a synthetic plant growth substance having an asymmetric carbon atom whose antipodes showed different plant growth activities. Since about 1950 a number of studies on the relationship between plant growth activities of optical antipodes and their configurations have been carried out. It has been found that α-aryloxyalkylcarboxylic acids,[3–5] α-arylalkylcarboxylic acids[5–7] and 1-indancarboxylic acid[8] also show differences between their antipodes, and the physiologically more active enantiomers of these acids possess the same configuration,[8–11] the same arrangement of four substituents around the central asymmetric carbon atom: aromatic ring system, carboxyl group, alkyl chain and hydrogen atom. This arrangement is shown by the projection formula[12]

---

[1] Abstracted partly from the Master Thesis submitted by K. Kawazu, March, 1957, partly reported in *Kagaku-no-Ryoiki* (*J. Japan. Chem.*), **12**, 2 (1958), and presented in the monthly meeting of Kansai Branch of the Agricultural Chemical Society of Japan, Kyoto, April 19, 1958.

[2] F. Kögl, *Naturwissenschaften*, **25**, 465 (1937).

[3] M. S. Smith and R. L. Wain, *Proc. Roy. Soc.* (London), **B139**, 118 (1951).

[4] K. V. Thimann, "Plant Growth Substances," F. Skoog, Ed., Madison, Wisc., 1951, p. 21.

[5] B. Åberg, *Kgl. Lantbruks-Högskol. Ann.*, **20**, 241 (1953).

[6] H. Veldstra and C. van de Westringh, *Rec. trav. chim.*, **70**, 1127 (1951).

[7] K. Kawazu, T. Fujita and T. Mitsui, unpublished.

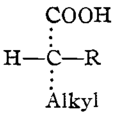
[8] A. Fredga, *Ber.*, **89**, 322 (1956).

[9] K. Pettersson, *Arkiv Kemi*, **9**, 509 (1956).

[10] M. Matell, "Stereochemical Studies on Plant Growth Substances," Diss., Uppsala, 1953, p. 29.

[11] A. Fredga, *Arkiv Kemi*, **7**, 193 (1954).

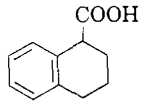
[12] This configuration was assigned to the D-series by Fredga,[11] whether R = O-aryl or aryl. According to the rules proposed by



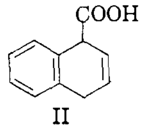
$$\overset{\displaystyle COOH}{\underset{\displaystyle Alkyl}{H-C-R}}$$

R = O-aryl or aryl.

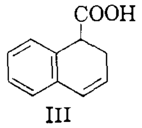
For partially hydrogenated 1-naphthoic acids, *i.e.*, 1,2,3,4-tetrahydro-1-naphthoic acid (I), 1,4-dihydro-1-naphthoic acid (II) and 1,2-dihydro-1-naphthoic acid (III), which have such substituents around the asymmetric carbon atom as α-arylalkylcarboxylic acids and 1-indancarboxylic acid, one of us previously demonstrated that the enantiomers with the greater plant growth activity, (−)-I (+)-II and (+)-III[14,15] belonged to the same steric series by catalytic hydrogenation of the enantiomeric dihydro-acids (II, III) to the tetrahydro-acid (I)[15,16] but the absolute configurations of these acids had not been established. It seems very important to the relationship between plant growth activity and chemical configuration to ascertain whether the enantiomers with the greater activity have the same configurations as those reported previously. The present investigation was therefore undertaken to establish the configurations of these acids by chemical reactions affecting no asymmetric carbon atom.



I



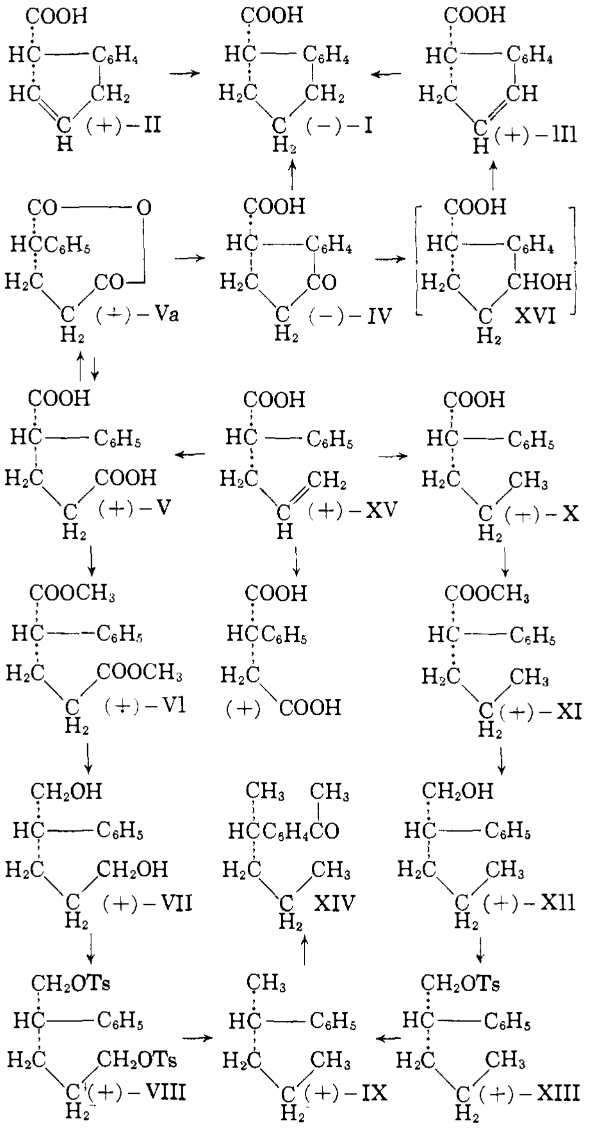
II



III

Recently Westman established the absolute configurations of V[17] and I[18]: he obtained (−)-I by intramolecular acylation and the subsequent reduction of (+)-Va, which was prepared *via* (+)-α-phenyl-δ-bromovaleric acid, (+)-α-phenyl-δ-hydroxyvaleric acid and (+)-V from (+)-α-allylphenylacetic acid (XV) of known configuration.[11]

The authors have converted (+)-Va to (−)-I by the same route as Westman's and further correlated the former to (+)-III by sodium borohydride reduction and subsequent dehydration of (−)-1,2,3,4-tetrahydro-4-oxo-1-naphthoic acid (IV), and correlated (+)-V to (+)-α-phenylvaleric acid (X) of known configuration by reduction of the two acids to the enantiomers of the same hydrocarbon, 2-phenylpentane (IX). The present results are consistent with Westman's, being different from his[17,18] in the route by which the configuration of V is established, and in correlating the configurations of IV and III. It confirms the absolute configurations of I and III, together with his results. Thus all the antipodes of the partially hydrogenated 1-naphthoic acids with greater activity, possess the same configuration as that of the physiologically more active enantiomers of the other synthetic plant growth substances.



Correlation of the Configuration of 1,2,3,4-Tetrahydro-4-oxo-1-naphthoic Acid (IV) and 1,2-Dihydro-1-naphthoic Acid (III).—Sodium borohydride reduction of (±)-1,2,3,4-tetrahydro-4-oxo-1-naphthoic acid (IV), m.p. 94–95°,[19] and (−)-IV, m.p. 85–87°, [α]D −58° (abs. ethanol, ∼90% optical purity)[18] gave viscous oils which seem to be a mixture of *cis* and *trans* isomers of 1,2,3,4-tetrahydro-4-hydroxy-1-naphthoic acid (XVI). Dehydration of each oil by dil. hydrochloric acid yielded (±)-1,2-dihydro-1-naphthoic acid (III), m.p. 98.5–100°, and partially racemized (+)-III, m.p. 81–82°, [α]D +20° (benzene). The racemic form showed no depression in mixed melting point with the authentic sample,[20,21] and the active form had an ultraviolet spectrum identical with that of the racemic form. It has been confirmed that the enantiomeric IV and III with the opposite direction of rotation have the same configuration.

Cahn, Ingold and Prelog,[13] however, when R = O-aryl, this is assigned to the R-configuration, but when R = aryl, to the S-configuration.

[13] R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956).

[14] T. Mitsui, *J. Agr. Chem. Soc. Japan*, **26**, 186 (1952).

[15] M. Inaba and T. Mitsui, *Bull. Agr. Chem. Soc. Japan*, in press.

[16] T. Mitsui, *J. Agr. Chem. Soc. Japan*, **25**, 526 (1952).

[17] L. Westman, *Arkiv Kemi*, **11**, 431 (1957).

[18] L. Westman, *ibid.*, **12**, 161 (1958).

[19] E. C. Horning and A. F. Finelli, THIS JOURNAL, **71**, 3205 (1949).

[20] M. Inaba and T. Mitsui, *Bull. Agr. Chem. Soc. Japan*, **20**, 42 (1956).

[21] K. Alder and K. Triebeneck, *Ber.*, **87**, 237 (1954).

Correlation of the Configuration of α-Phenylglutaric Acid (V) and α-Phenylvaleric Acid (X).—By reduction with lithium aluminum hydride, (±)-α-phenylglutaric acid (V), m.p. 82–84°,[22] and (+)-V, $[\alpha]_D$ +74° (abs. ethanol, ~90% optical purity),[17] were converted to (±)-2-phenylpentane (IX), b.p. 190–193°,[23] and (+)-IX, $[\alpha]_D$ +16° (*n*-hexane), *via* (±)-dimethyl α-phenylglutarate (VI), b.p. 178–180° (20 mm.); and (+)-VI $[\alpha]_D$ +80° (abs. ethanol); (±)-2-phenyl-1,5-pentanediol (VII), m.p. 34–36°; and (+)-VII, m.p. 50–52°, $[\alpha]_D$ +31° (abs. ethanol); and (±)-1,5-ditosyl-2-phenylpentanediol (VIII), 89–90.5°; and (+)-VIII, m.p. 66–67°, $[\alpha]_D$ +10° (acetone), respectively.

In a similar way (±)- and (−)-α-phenylvaleric acid (X), $[\alpha]_D$ −68° (benzene, 85% optical purity) were converted to (±)-IX, b.p. 190–193°,[23] and (−)-IX, $[\alpha]_D$ −17° (*n*-hexane), *via* (±)-methyl α-phenylvalerate (XI), b.p. 123–125° (17 mm.); and (−)-XI, $[\alpha]_D$ −72° (methanol); (±)-2-phenyl-1-pentanol (XII), b.p. 130–135° (17 mm.); and (−)-XII, $[\alpha]_D$ −12° (methanol); and (±)-1-tosyl-2-phenylpentanol (XIII), m.p. 68.5–69.5°; and (−)-XIII, m.p. 42–43.5°, $[\alpha]_D$ −8.0° (acetone), respectively.

The racemic hydrocarbons prepared by the two different routes were identified by infrared spectra and mixed melting points of the corresponding acetophenone semicarbazones, m.p. 174.5–176°.[23] This hydrocarbon might have been accompanied by 1-phenylpentane which could be produced by Wagner–Meerwein rearrangement during reduction of the tosylates. It appears, according to the A.P.I. figures,[24] that the infrared absorption spectra of several *sec*-alkylbenzenes are different from those of the corresponding *n*-alkylbenzenes most distinctly around 750 cm.$^{-1}$, *i.e.* the former exhibit a band at about 760 cm.$^{-1}$ and the latter at about 740 cm.$^{-1}$ This hydrocarbon prepared by reduction of the tosylates exhibited a band at 758 cm.$^{-1}$, the same spectrum as that prepared by Cram[23] in another way where no rearrangement occurs, while 1-phenylpentane[25] exhibited a band at 741 cm.$^{-1}$. Therefore, it is quite adequate to conclude that intramolecular rearrangement[26] did not occur during the reduction of the tosylates.

The transformations described above have confirmed that the enantiomeric V and X with the same direction of optical rotation possess the same configuration.

Experimental[27]

Conversion of 1,2,3,4-Tetrahydro-4-oxo-1-naphthoic Acid (IV) to 1,2-Dihydro-1-naphthoic Acid (III). **(±)-1,2-Dihydro-1-naphthoic Acid (III).**—To a stirred solution of 0.4 g. (0.011 mole) of sodium borohydride in 15 ml. of methanol including a few drops of 2 *N* sodium hydroxide solution was slowly dropped a solution of 1.4 g. (0.0074 mole) of (±)-IV, m.p. 94–95°,[19] in a mixture of 10 ml. of methanol and 1.5 ml. of 5 *N* sodium hydroxide solution, and the reaction mixture was refluxed another hour. After dil. hydrochloric acid was added to decompose the excess of the reagent, methanol was removed *in vacuo*. The residual solution was extracted with ether, the ethereal solution was washed with water, dried and concentrated to yield 0.8 g. of yellow viscous oil. This oil was boiled with 10 ml. of 2 *N* hydrochloric acid for 5 minutes and the mixture was extracted with ether. The ethereal layer was extracted with 2 *N* sodium carbonate solution, the alkali layer acidified with dil. hydrochloric acid and extracted with ether. The usual treatment gave 0.8 g. of crystals. Recrystallization from *n*-hexane yielded 0.6 g. (47.2%) of (±)-III in prisms, m.p. 98–99.5° (lit.[21] 101°), which showed no depression when mixed with the authentic sample, m.p. 98–99°.[20]

Resolution of α-Phenylglutaric Acid (V).[17,28]—It was found that both enantiomers of Va could be obtained by crystallization of the quinine salt; 10.4 g. (0.05 mole) of (±)-V, m.p. 82–84°,[22] and 16 g. (0.05 mole) of quinine were dissolved in a mixture of 100 ml. of ethanol and 100 ml. of water. The solution was left to crystallize, and the salt was purified by repeated crystallization from ethanol. From the last salt fraction, 2.2 g. of the crude (+)-acid, $[\alpha]_D$ +77° (*c* 2.20 in abs. ethanol) was obtained as an oil. It was refluxed with 50 ml. of acetyl chloride for half an hour; after removing the excess of acetyl chloride and acetic acid *in vacuo* the residue was crystallized from benzene to give 0.5 g. of (+)-α-phenylglutaric anhydride (Va), m.p. 114.5–116°, $[\alpha]_D$ +13° (*c* 3.59 in chloroform). Four grams of the acid, $[\alpha]_D$ −66°, obtained from the first filtrate was similarly converted to 0.8 g. of pure (−)-Va, m.p. 114.5–116°, $[\alpha]_D$ −12° (*c* 4.20 in chloroform) (lit.[18] m.p. 118–120°, $[\alpha]^{25}_D$ ±41° (ethyl acetate)).[18]

The free enantiomeric acids were obtained by boiling the anhydrides with water and extracting with ether as oils, $[\alpha]_D$ +84° (*c* 3.10 in abs. ethanol), −82° (*c* 4.72 in abs. ethanol) (lit.[17] m.p. 129–131°, $[\alpha]^{25}_D$ +86.1°, −85.5° (abs. ethanol)).

(+)-1,2-Dihydro-1-naphthoic Acid (III).—Treating (+)-Va with concd. H_2SO_4 gave (−)-IV, m.p. 83–85°, $[\alpha]_D$ −66° (*c* 1.12 in abs. ethanol) (lit.[18] 81–83°, $[\alpha]_D$ −38.3° (ethyl acetate)). A similar reduction and dehydration of 0.5 g. of (−)-rich-IV, m.p. 85–87°, $[\alpha]_D$ −58° (*c* 5.21 in abs. ethanol, ~90% optical purity), gave 50 mg. of (±)-III and 0.1 g. (22.2%) of (+)-rich-III in prisms, m.p. 81–82°, $[\alpha]_D$ +20° (*c* 1.22 in benzene); the latter showed an ultraviolet spectrum identical with that of (±)-III. *Anal.* Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.86; H, 5.68.

Reduction of Acids to Alcohols. **(±)-2-Phenyl-1,5-pentanediol (VII).**—Compound (±)-V (5.4 g., 0.026 mole) was converted to 5.4 g. (89%) of (±)-VI, b.p. 178–180° (20 mm.), with excess of diazomethane in ether. To a stirred solution of 1.3 g. (0.034 mole) of lithium aluminum hydride in 45 ml. of dry ether was added slowly 5.4 g. (0.023 mole) of (±)-VI in dry ether, and the mixture was refluxed with stirring another two hours. After cooling, the excess hydride was decomposed carefully and the hydroxides dissolved in dilute hydrochloric acid. The ethereal layer was separated, the aqueous layer was thoroughly extracted with ether, and the combined ether solution was washed with 2 *N* sodium carbonate solution and water, dried over anhydrous sodium sulfate and concentrated. The residue was distilled *in vacuo* to give 4.0 g. (97%) of (±)-VII, b.p. 150–155° (1 mm.), in a colorless viscous oil which crystallized after standing in a refrigerator for two days. Recrystallization from chloroform–benzene–hexane gave 3.5 g. (85%) of colorless needles, m.p. 34–36°. *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.03; H, 8.89.

(+)-2-Phenyl-1,5-pentanediol (VII).—A similar reduction of 3 g. of (+)-VI, b.p. 179–182° (21 mm.), $[\alpha]_D$ +80° (*c* 5.15 in methanol), prepared from 3.5 g. of (+)-V, $[\alpha]_D$ +74° (*c* 6.48 in abs. ethanol, ~90% optical purity) gave 2.3 g. of colorless viscous oil, b.p. 155–158° (25 mm.), which crystallized after two days cooling. Recrystallization from chloroform–benzene–hexane gave 1.7 g. (74%) of colorless long needles, m.p. 50–52°, $[\alpha]_D$ +31° (*c* 4.38 in abs. etha-

---

[22] M. F. Ansell and D. H. Hey, *J. Chem. Soc.*, 1683 (1950).

[23] D. J. Cram, THIS JOURNAL, **74**, 2154 (1952).

[24] Infrared Spectral Data of the American Petroleum Institute Research Project 44: *n*-propylbenzene, serial no. 313; isopropylbenzene, 314; *n*-butylbenzene, 468; *sec*-butylbenzene, 470; *n*-octylbenzene, 337; 2-phenyloctane, 407; 1-phenyleicosane, 416; 2-phenyleicosane, 417; 3-phenyleicosane, 418.

[25] H. Gilman and J. Robinson, *Org. Syntheses*, **10**, 4 (1930). This hydrocarbon was characterized as the corresponding acetophenone semicarbazone, m.p. 180–181°.

[26] A hydrocarbon, obtained from (±)-VII by treating with phosphorus pentabromide followed by lithium aluminum hydride reduction, exhibited both bands at 741 and 758 cm.$^{-1}$. It is considered that this hydrocarbon involves the rearranged product.

[27] All melting and boiling points are uncorrected and rotation measurements were held at room temperature (13°).

[28] A part of the resolution is by Mr. O. Kimura.

nol). *Anal.* Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.39; H, 8.71.

(±)-2-Phenyl-1-pentanol (XII).—In a procedure similar to the reduction of (±)-VI, 1.9 g. (0.01 mole) of (±)-XI, b.p. 123–125° (17 mm.), prepared from (±)-X,[29] was reduced with 0.3 g. (0.008 mole) of lithium aluminum hydride to give 1.5 g. (94%) of (±)-XII, colorless oil, b.p. 130–135° (17 mm.). *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.21; H, 9.75.

(−)-2-Phenyl-1-pentanol (XII).—A similar reduction of 0.7 g. of (−)-XI, b.p. 123–125° (17 mm.), $[\alpha]_D$ −72° (*c* 2.11 in methanol), prepared from (−)-X, $[\alpha]_D$ −68° (*c* 1.26 in benzene, 85% optical purity), which was obtained by resolution of the (+)-α-phenylethylamine salt,[7,9] gave 0.6 g. (98%) of (−)-XII, b.p. 130–133° (17 mm.), $[\alpha]_D$ −12° (*c* 3.76 in methanol). *Anal.* Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.28; H, 9.61.

Tosylation. (±)-1,5-Ditosyl-2-phenylpentanediol (VIII).—To a solution of 2 g. (0.011 mole) of (±)-VII in 12 ml. of dry pyridine was added 4.5 g. (0.024 mole) of *p*-tosyl chloride at 0°. After standing overnight. the mixture was poured onto ice, and recrystallization of the precipitated material from methanol gave 3.2 g. (65%) of colorless needles, m.p. 89–90.5°. *Anal.* Calcd. for $C_{25}H_{28}S_2O_6$: C, 61.45; H, 5.77. Found: C, 61.31; H, 5.53.

(+)-1,5-Ditosyl-2-phenylpentanediol (VIII).—Compound (+)-VIII, similarly prepared from 1.3 g. of (+)-VII, was obtained in 1.6 g. (46%) of colorless long needles, m.p. 66–67°, $[\alpha]_D$ +10° (*c* 2.92 in acetone), which seems to be pure enantiomer. *Anal.* Calcd. for $C_{25}H_{28}S_2O_6$: C, 61.45; H, 5.77. Found: C, 61.37; H, 5.60.

(±)-1-Tosyl-2-phenylpentanol (XIII).—In a procedure similar to that used for preparation of (±)-VIII, 2 g. of (±)-XIII, colorless needles, m.p. 68.5–69.5°, was obtained from 1.2 g. of (±)-XII; yield 86%. *Anal.* Calcd. for $C_{18}H_{22}SO_3$: C, 67.89; H, 6.96. Found: C, 67.72; H, 7.25.

(−)-1-Tosyl-2-phenylpentanol (XIII).—Compound (−)-XIII (0.9 g.), colorless rods, m.p. 42–43.5°, $[\alpha]_D$ −8.0° (*c* 8.50 in acetone), was similarly prepared in 71% yield from 0.65 g. of (−)-XII. *Anal.* Calcd. for $C_{18}H_{22}SO_3$: C, 67.89; H, 6.96. Found: C, 68.08; H, 6.99.

Reduction of Tosylates to 2-Phenylpentane (IX).[30] **Reduction of (±)-VIII.**—To a solution of 1.7 g. (0.045 mole) of lithium aluminum hydride in 40 ml. of dry ether was dropped with stirring at room temperature a solution of 2.8 g. (0.056 mole) of (±)-VIII in 20 ml. of tetrahydrofuran. The mixture was refluxed under stirring for two hours. After cooling, excess hydride was decomposed carefully with water, and the hydroxides were dissolved in dilute hydrochloric acid. The ethereal layer was separated, washed with 2 *N* sodium carbonate solution and water, dried over anhydrous sodium sulfate and concentrated. Distillation of the residue gave colorless mobile liquid (0.8 g.), b.p. 188–190°. The accompanying unsaturated hydrocarbon was removed by formation of the adduct with 2,4-dinitrobenzenesulfenyl chloride according to Cram.[23] The product free from unsaturated hydrocarbon was distilled twice over a few pieces of metallic sodium to give 0.4 g. (47%) of pure (±)-IX, b.p. 190–193° (lit.[23] 191–193°). The infrared spectrum showed good agreement with that reported by Cram.[23] This hydrocarbon (0.2 g.) was acetylated with acetyl chloride (0.2 g.) in carbon disulfide (5 ml.) in the presence of anhydrous aluminum chloride (0.3 g.) to yield 4-(2′-pentyl)-acetophenone (XIV) (0.15 g.), b.p. 142–147° (21 mm.). The semicarbazone, prepared by the usual procedure, was recrystallized from dilute ethanol in colorless needles, m.p. 175–176.5° (lit.[23] 175–177°). *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.96; H, 8.46.

Reduction of (+)-VIII.—Compound (+)-IX, obtained in 35% yield from (+)-VIII, had b.p. 190–193° (lit.[23] 191–193°), $[\alpha]_D$ +16° (*c* 1.52 in *n*-hexane) (lit.[23] α_D +15.0° homogeneous) and an infrared spectrum identical with that of the racemic form. The corresponding acetophenone semicarbazone had m.p. 170–173.5°. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.97; H, 8.53.

Reduction of (±)-XIII.—In a procedure similar to the reduction of (±)-VIII, reduction of 1.6 g. (0.005 mole) of (±)-XIII with 0.5 g. (0.013 mole) of lithium aluminum hydride in 35 ml. of dry ether and purification with 2,4-dinitrobenzenesulfenyl chloride gave 0.3 g. (50%) of colorless mobile liquid, b.p. 190–193°. The infrared spectrum showed complete correspondence with that of (±)-IX prepared from (±)-VIII and also with that reported by Cram.[23] The corresponding acetophenone semicarbazone was similarly prepared, m.p. 174.5–176°, and showed no depression in melting point when mixed with that prepared from (±)-VIII. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 67.99; H, 8.40.

Reduction of (−)-XIII.—Similar treatment starting with 0.9 g. of (−)-XIII gave 0.2 g. (48%) of (−)-IX, b.p. 191–193°, $[\alpha]_D$ −16.5° (*c* 1.42 in *n*-hexane). Its infrared spectrum was identical with that of the racemic form. The corresponding acetophenone semicarbazone had m.p. 169–173°. *Anal.* Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56. Found: C, 68.02; H, 8.61.

Acknowledgment.—The authors wish to express their sincere thanks to Prof. Sankichi Takei for his constant encouragement, and to Prof. Karl Freudenberg for his suggestive discussions at the Annual Meeting of the Agricultural Chemical Society of Japan, May, 1958. They are also grateful to the Ministry of Education, Japanese Government, for a grant in aid.

KYOTO, JAPAN

---

(29) A. Rossolymo, *Ber.*, **22**, 1235 (1889).

(30) The authors are indebted to Laboratory of Agricultural Chemicals, Kyoto University, for the infrared spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

peri-Substituted Naphthalenes. I. New Rearrangement Reactions of Substituted Naphthopyrans

BY ROBERT L. LETSINGER AND PETER T. LANSBURY[1]

RECEIVED AUGUST 4, 1958

Two new rearrangement reactions were observed in the course of investigating the effect of acids on substituted 1,8-naphthalene compounds: (1) 1-hydroxy-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (II) isomerized to 8-benzhydryl-1-naphthoic acid (VIII) (1,5-hydrogen shift), and (2) 1-methylene-3,3-diphenyl-1H,3H-naphtho[1,8-c,d]pyran (III) rearranged to 3,3-diphenyl-2,3-dihydro-1H-benzonaphthen-1-one (XI). In the presence of acid, 1,8-bis-(phenylhydroxymethyl)-naphthalene (I) dehydrated without rearrangement to give a cyclic ether (IV). The yields in all three reactions were close to quantitative.

The 1,8-disubstituted naphthalene system is particularly well suited for investigations of intramolecular interactions of functional groups. Firstly, the substituents are held firmly in close proximity. The facile conversion of 1,8-bis-bromomethylnaphthalene to acenaphthene by phenyllithium illustrates the ease of bonding across these positions.[2]

---

[1] National Science Foundation Predoctoral Fellow, 1955–1956. Financial assistance for this work was also provided by the du Pont Co. and the Abbott Fund of Northwestern University.

[2] E. Bergmann and J. Szmuszkovicz, THIS JOURNAL, **75**, 2760 (1953).