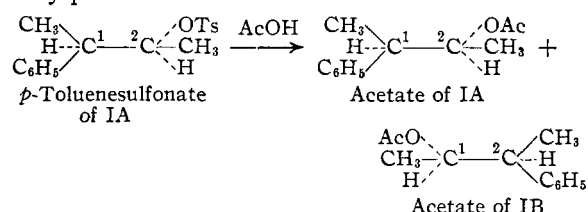


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Studies in Stereochemistry. II. The Preparation and Complete Resolution of 3-Phenyl-2-pentanol and 2-Phenyl-3-pentanol

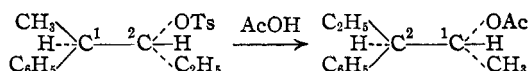
BY DONALD J. CRAM AND ROBERT DAVIS¹

The first paper of this series reported the stereo-specific Wagner-Meerwein rearrangement of the *p*-toluenesulfonates of the stereoisomers of 3-phenyl-2-butanol during acetolysis. Good evidence was provided that the *p*-toluenesulfonate of IA rearranged to I acetate; however, since the *p*-toluenesulfonate of IIA gave the acetate of IIA, there was no concrete proof of any disturbance of the carbon chain even though rearrangement was very probable.



In the similar treatment of the *p*-toluenesulfonate of the isomer of 2-phenyl-3-pentanol that is

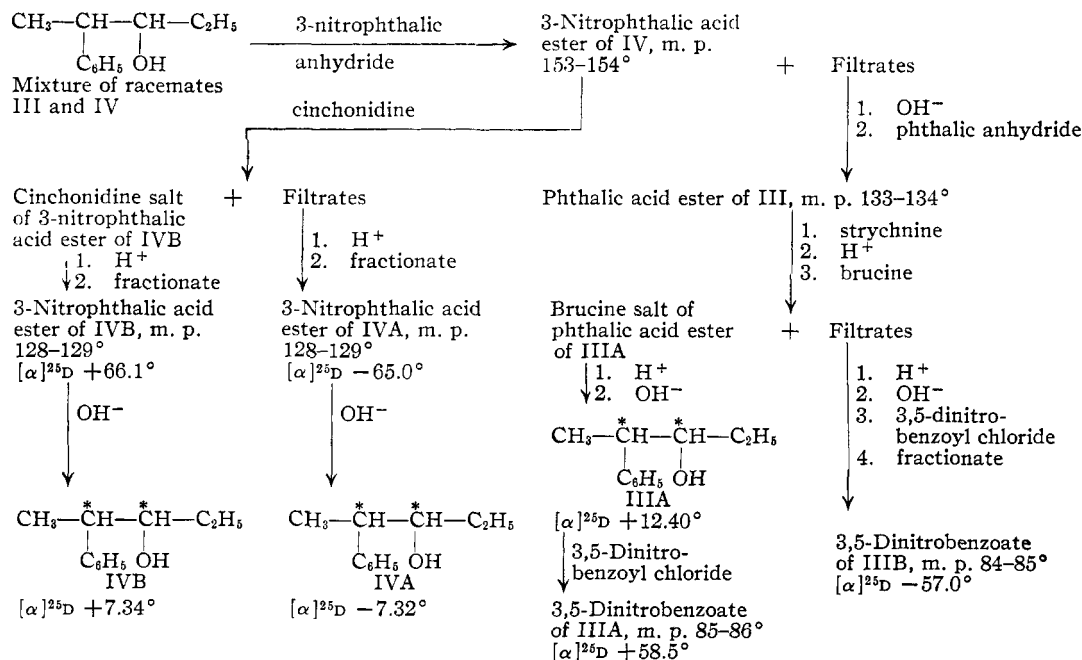
ethyl groups in the product will be reversed, and the substance will be a derivative of 3-phenyl-2-pentanol. This system should also provide additional facts concerning the postulated existence of a cyclic intermediate carbonium ion.



This paper deals with the preparation and resolution of 2-phenyl-3-pentanol and 3-phenyl-2-pentanol into the eight stereoisomers of these two structural isomers, and with a correlation of the probable configuration of these isomers with their physical properties and modes of resolution. Paper III in this series will report the results of the rearrangement studies to which these isomers were submitted.

Results

A mixture of the two racemates of 2-phenyl-3-pentanol was prepared by the treatment of 2-phenylpropionaldehyde² with ethylmagnesium bromide. The method used for the resolution is outlined below.

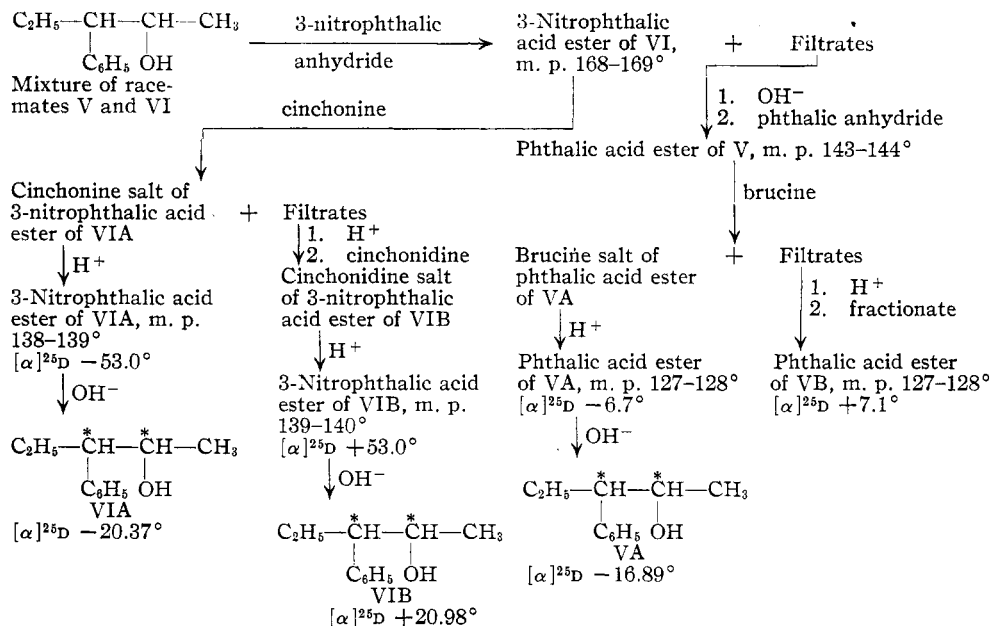


sterically analogous to IIA, if rearrangement occurs, the relative positions of the methyl and

(1) Present address: Medical School, University of California, Los Angeles 24, California.

(2) This compound was prepared by the method that Dutta [*J. Indian Chem. Soc.*, **18**, 233 (1941)] used for the preparation of 2-*p*-tolylpropionaldehyde. Claisen [*Ber.*, **38**, 705 (1905)] prepared 2-phenylpropionaldehyde previously by a different method.

The compound 2-phenylbutyraldehyde³ was prepared by a method analogous to that used for the preparation of 2-phenylpropionaldehyde.² The former substance was treated with methylmagnesium bromide to give a mixture of the two racemates of 3-phenyl-2-pentanol. Resolution of this mixture was affected by the following method.



The magnitude of the rotations and the melting points of the enantiomorphically related substances in the two series are in agreement, which indicates that optical purity was obtained in each case. The acid phthalates of IIIA and IIIB were never obtained in a crystalline condition, and therefore the 3,5-dinitrobenzoate derivative was prepared for identification purposes.

Table I records the physical properties and the yields of the above compounds.

Discussion

The analogy between the methods used for the resolution of 3-phenyl-2-butanol⁴ and the resolutions of 2-phenyl-3-pentanol and 3-phenyl-2-pentanol is so clear cut as to provide a clue to the relative configuration of the isomers of the two latter compounds. In all three cases the two racemates were split through the preparation of the acid phthalate and 3-nitrophthalic acid ester derivatives. In each case the latter derivative was obtained in greater quantity. The racemic mixtures of the acid phthalates of I, III and V were each resolved through the brucine salt, giving in each case a crystalline salt of only one of the enantiomorphs. The racemic mixtures of the 3-nitrophthalic acid esters of II, IV and VI were each resolved through the cinchonidine salts, and in each

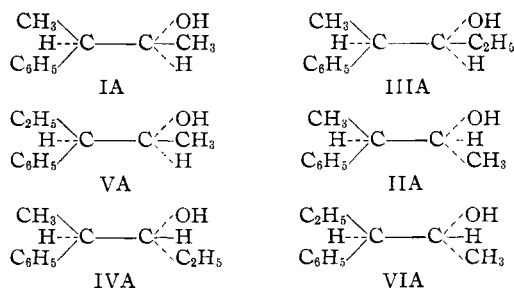
case one of the enantiomorph pair formed a crystalline cinchonidine salt, and in two of the three cases the other member of the enantiomorph pair formed a crystalline cinchonine salt.⁵

A comparison of the melting points of the derivatives of the above alcohols also points to analogous configurational relationships along the lines

suggested above. Thus the acid phthalates of racemates I, III and V melt at 130-131°, 133-134°, 143-144°, and the 3-nitrophthalic acid esters of racemates II, IV and VI melt at 156-157°, 153-154° and 168-169°, respectively.

Finally, comparisons of the specific rotations of the stereoisomers themselves strengthen the analogy. Thus the specific rotation of IA is more positive than that of IIA, IIIA more positive than IVA, and VA is more positive than VIA.

The above argument provides a basis for the following assignments of relative configurations for the stereoisomers of 3-phenyl-2-butanol, 2-phenyl-3-pentanol and 3-phenyl-2-pentanol. Since



(3) This substance has been reported by Stoermer, *Ber.*, **39**, 2300 (1906).

(4) See paper I in this series.

(5) Attempts to form crystalline brucine salts of the acid phthalates of IB, IIIB and VB failed; attempts to form crystalline cinchonine salts of the 3-nitrophthalic acid esters of IIB and VIB failed; attempts to form crystalline cinchonidine salts of IIA and VIA failed. Crystalline cinchonine salts of IVA and IVB and crystalline cinchonidine salts of IVA and IVB were obtained.

TABLE I

PHYSICAL DATA PERTAINING TO THE STEREOISOMERS OF 2-PHENYL-3-PENTANOL, 3-PHENYL-2-PENTANOL AND DERIVATIVES

Compound alcohols	B. p., °C.	Mm.	[α] _D ²⁰ Pure liq.	Formula	Analyses, %				Yields, %
					C	Calcd.	H	Found	
III ^a	127	23	C ₁₁ H ₁₆ O	80.44	9.82	80.49	10.00	93
IV ^b	128	26	C ₁₁ H ₁₆ O	80.44	9.82	80.23	9.97	94
V ^c	125	22	C ₁₁ H ₁₆ O	80.44	9.82	80.09	9.94	94
VI ^d	128	25	C ₁₁ H ₁₆ O	80.44	9.82	80.42	10.00	95
IIIA	125	23	+12.40	C ₁₁ H ₁₆ O	80.44	9.82	80.07	9.99	32 ^e
IVA	123	18	- 7.32	C ₁₁ H ₁₆ O	80.44	9.82	80.14	10.01	90
IVB	123	18	+ 7.34	C ₁₁ H ₁₆ O	80.44	9.82	80.31	10.10	93
VA	120	17	-16.89	C ₁₁ H ₁₆ O	80.44	9.82	80.53	9.94	96
VIA	121	17	-20.37	C ₁₁ H ₁₆ O	80.44	9.82	80.65	9.91	96
VIB	121	17	+20.98	C ₁₁ H ₁₆ O	80.44	9.82	80.08	9.98	93
Acid phthalates	M. p., °C.		[α] _D ²⁰ ($c \cong$ 3% in ethanol)						
III ^f	133-134		C ₁₉ H ₂₀ O	73.06	6.45	72.83	6.79	14
V ^g	143-144		C ₁₉ H ₂₀ O	73.06	6.45	73.06	6.74	18
VA ^g	127-128		- 6.7	C ₁₉ H ₂₀ O	73.06	6.45	72.90	6.76	36
VB ^g	127-128		+ 7.1	C ₁₉ H ₂₀ O	73.06	6.45	73.09	6.62	15
3-Nitro- phthalic acid esters									
IV ^g	153-154		C ₁₉ H ₁₉ NO ₆	63.85	5.36	63.67	5.48	36
VI ^h	168-169		C ₁₉ H ₁₉ NO ₆	63.85	5.36	63.86	5.53	42
IVA ^h	128-129		-65.0	C ₁₉ H ₁₉ NO ₆	63.85	5.36	64.02	5.26	14
IVB ^h	128-129		+66.1	C ₁₉ H ₁₉ NO ₆	63.85	5.36	63.64	5.39	32
VIA ^h	138-139		-53.0	C ₁₉ H ₁₉ NO ₆	63.85	5.36	63.88	5.53	43
VIB ^h	139-140		+53.0	C ₁₉ H ₁₉ NO ₆	63.85	5.36	63.76	5.47	36
3,5-Dinitro- benzoates									
III ^h	83-84		C ₁₈ H ₁₈ N ₂ O ₆	60.33	5.06	60.20	4.90	91
IIIA ^h	85-86		+58.5 ⁱ	C ₁₈ H ₁₈ N ₂ O ₆	60.33	5.06	60.58	5.22	93
IIIB ^h	84-85		-57.0 ⁱ	C ₁₈ H ₁₈ N ₂ O ₆	60.33	5.06	60.33	5.39	0.3 ^e

^a n_D^{25} 1.5113. ^b n_D^{25} 1.5121. ^c n_D^{25} 1.5097. ^d n_D^{25} 1.5106. ^e This yield is based on the acid phthalate of racemic III. ^f Irregular flat needles. ^g Irregular prisms. ^h Fine needles. ⁱ Rotations taken chloroform ($c \cong 3\%$).

the structures of IA and IIA were determined in the first paper of this series, the following assignments can be made. The respective enantiomorphic relationships of the above compounds to IB, IIB, IIIB, IVB, VB and VIB determines the structures of the B series.⁶

The above configurational assignments are consistent with further evidence that is presented in papers III and IV in this series.

Experimental

Preparation and Separation of the Racemates of 2-Phenyl-3-pentanol.—A mixture of 126 g. of 2-phenylpropionaldehyde⁷ and 500 ml. of dry ether was added over a period of an hour to a cooled stirred solution of ethylmagnesium bromide (made from 24.1 g. of magnesium and 110 g. of ethyl bromide) dissolved in 1000 ml. of dry ether. After warming the mixture for one hour, the flask was cooled and the product decomposed by pouring into a mixture of ice and excess 2 *N* sulfuric acid. The two layers that resulted were separated, the organic layer washed with water, dried, and the product distilled to give 130 g. of alcohol, b. p. 123-125° at 18 mm. pressure.

A mixture of this alcohol (130 g.), 155 g. of 3-nitro-

phthalic anhydride and 150 g. of pyridine was heated at 100° for one hour, cooled and shaken with a mixture of excess of 2 *N* sulfuric acid and benzene. The layers were separated and the organic layer was washed with water, dried, evaporated to an oil, and this oil was crystallized from a mixture of three volumes of ethyl acetate and enough low-boiling petroleum ether to make the solution turbid. The crystalline product that separated was recrystallized from ethyl acetate and petroleum ether to give 68 g. of 3-nitrophthalic acid ester of racemate IV, m. p. 153-154° (fine needles).

The combined filtrates were evaporated and hydrolyzed by heating at reflux with a solution of 102 g. of potassium hydroxide in 500 ml. of water for fifteen hours. At the end of this time the mixture was cooled, extracted with petroleum ether, and the organic layer was washed with water, dried, evaporated and the resulting oil distilled, 75 g.

This alcohol (70 g.) was heated at 100° with a mixture of 64 g. of phthalic anhydride and 75 g. of pyridine for one hour. This mixture was then cooled, shaken with a mixture of excess 2 *N* sulfuric acid and benzene, the layers separated and the organic layer washed with water, dried, and evaporated to an oil. This oil was crystallized from two volumes of ethyl acetate and enough petroleum ether to make the solution slightly turbid. The solid that deposited was recrystallized from ethyl acetate and petroleum ether to give 24.7 g. of the acid phthalate of racemate III, m. p. 133-134° (wedge-shaped needles).

The filtrates from the above crystallizations were combined and put through the same cycle as that described above to give 33 g. of additional 3-nitrophthalic acid ester of racemate II, m. p. 153-154°, and 10.5 g. of additional

(6) This type of nomenclature has been adopted until the configuration of one of the two asymmetric carbon atoms of one of these isomers has been related to *D*-glyceraldehyde.

(7) This aldehyde² was prepared by the same procedure described further on for the preparation of 2-phenylbutyraldehyde.

phthalic acid ester of racemate I, m. p. 133–134°. A total of 19 g. of unresolved 2-phenyl-3-pentanol was recovered from these operations.

Preparation of 2-Phenylbutyraldehyde.²—A mixture of 87.2 g. of sodium and 872 ml. of absolute ethanol was refluxed until the sodium disappeared. The solution was cooled and 872 ml. of dry low-boiling petroleum ether was added and the mixture cooled in an ice-bath. To this mixture was added a cooled solution of 410 g. of ethyl chloroacetate and 448 g. of propiophenone, the resulting mixture was stirred to break up all the lumps and then allowed to stand for twenty hours in an ice-bath. At the end of this time the dark solution was brought to reflux and the petroleum ether allowed to gradually escape through the partial condenser over a period of eight hours (this material was collected through the use of a second condenser). The contents of the flask were diluted with sufficient water, ice and ethyl ether to produce two layers which were separated; the water layer was extracted with ether and discarded. The two organic solutions were combined, washed five times with a 1 *N* sodium hydroxide solution, three times with water, dried, and evaporated to an oil which was distilled under reduced pressure. The first fraction, 203.6 g., distilled at about 90° (8 mm.), and the product (a glycidic ester) was collected at 127–133° (5 mm.), weight 314.5 g.

This material was added to a solution of 34.4 g. of sodium which had been decomposed in 560 ml. of 95% ethanol. The mixture formed a red homogeneous solution which was allowed to stand about twenty hours. A white solid formed at first but dissolved when more water was added. This solution was acidified with 330 ml. of 6 *N* hydrochloric acid at a temperature below 10°, and the oil that separated was extracted with ether. The extract was dried, the ether evaporated, and the resulting oil was added to a mixture of 1300 ml. of 6 *N* sulfuric acid and 1300 g. of ice. After standing overnight the mixture was steam distilled until about 2 l. of distillate was obtained. The oily aldehyde was extracted with ether, the resulting solution was washed twice with 3 *N* sodium carbonate solution and twice with water, dried, evaporated to an oil which was distilled to give 165.5 g. of 2-phenylbutyraldehyde, b. p. 97–99° (15 mm.).

Preparation and Separation of the Racemates of 3-Phenyl-2-pentanol.—To a Grignard solution prepared from 30 g. of magnesium, 177 g. of methyl iodide and 500 ml. of ether was added slowly 165.5 g. of 2-phenylbutyraldehyde. The mixture was then refluxed for an hour, cooled, and decomposed on a mixture of ice and excess 2 *N* sulfuric acid. The oil that separated was extracted with ether, the extract was washed with water, dried and evaporated to an oil and distilled to give 142 g. of 3-phenyl-2-pentanol, b. p. 128–131° (30 mm.).

A mixture of 142 g. of this carbinol, 168 g. of 3-nitrophthalic anhydride and 190 g. of dry pyridine was warmed to 100° for one hour, cooled and shaken in a mixture of benzene and excess 2 *N* sulfuric acid. The organic layer was washed first with 2 *N* sulfuric acid, then with water, dried and the benzene was evaporated. The oil crystallized from a mixture of ethyl acetate and petroleum ether and recrystallization of the product from the same solvents gave 96 g. of fine white needles (m. p. 167–168°) of the 3-nitrophthalic acid ester of VI.

The filtrates were combined, the solvent evaporated and the oil held at reflux for twelve hours in a mixture of 40 g. of sodium hydroxide, 40 g. of potassium hydroxide and 400 ml. of water. The resulting mixture was cooled, extracted with petroleum ether and the extract was washed with water, dried, evaporated and the oil distilled to give 70 g. of alcohol. This material was heated to 100° for one hour with 63 g. of phthalic anhydride and 85 ml. of pyridine, cooled, and shaken with a mixture of benzene and excess *N* sulfuric acid. The organic layer was washed, first with 2 *N* sulfuric acid, then with water, the solution was dried, evaporated and the oil crystallized from ethyl acetate and petroleum ether. Recrystallization of the product from the same solvents produced 39 g. of the phthalic acid ester of V, m. p. 143–144° (heavy prisms).

A second cycle similar to that described above produced 33 additional grams of 3-nitrophthalic acid ester of VI, m. p. 167–168°, and 9 additional grams of the phthalic acid ester of V, m. p. 143–144°. A total of 12.5 g. of unresolved alcohol was recovered.

Resolution of the Phthalic Acid Ester of III.—A solution of 13.5 g. of the racemic ester and 10 g. of strychnine in 100 ml. of acetone was brought to boiling and slowly cooled. The solid that separated was collected and shaken with a mixture of ether and excess 2 *N* hydrochloric acid. The organic layer was washed with water, dried, evaporated and the resulting oil was mixed with 7 g. of brucine and 50 ml. of acetone. The material that separated was collected and recrystallized from acetone to give 7.0 g. of salt. The combined filtrates from all the above crystallizations were concentrated and shaken with ether and 2 *N* hydrochloric acid. The organic layer was washed with water, dried, evaporated and crystallized from ethyl acetate and petroleum ether to give 5 g. of racemic starting material. This material was put through the same cycle of operations and an additional 4 g. of recrystallized brucine salt obtained. The combined 11 g. of brucine salt was shaken with excess 2 *N* sulfuric acid and ether, the organic layer washed with water, dried and evaporated to an oil. This oil (4.5 g.) could not be crystallized and was hydrolyzed directly to IIIA by heating at reflux for twelve hours with 3.5 g. of sodium hydroxide and 20 ml. of water. The resulting oil was extracted with petroleum ether, the organic layer was washed with water, dried, evaporated and distilled to give 2.27 g. of IIIA, b. p. 125° (23 mm.).

A small sample of this alcohol was converted to the 3,5-dinitrobenzoate in the usual manner, m. p. 85–86° (needles from ether and petroleum ether).

The combined filtrates from the crystallizations of the brucine salt were concentrated and converted to the acid phthalate of impure IIIB. Crystallization of this oil from ethyl acetate and petroleum ether produced 2.0 g. of the acid phthalate of racemic III. The filtrate from this crystallization was hydrolyzed in the usual manner and the alcohol converted to the 3,5-dinitrobenzoate. Five crystallizations of this material from an ether-petroleum ether mixture produced 400 mg. of the 3,5-dinitrobenzoate of IIIB, m. p. 84–85° (needles from an ether-petroleum ether mixture).

Resolution of the 3-Nitrophthalic Acid Ester of IV.—A mixture of 50 g. of the 3-nitrophthalic acid ester of IV, 41 g. of cinchonidine and 400 ml. of 95% ethanol was heated to reflux temperature and slowly cooled. The material that separated was recrystallized twice from 95% ethanol to give 18 g. of salt which was converted to the 3-nitrophthalic acid ester of IVB by the usual method; weight 8.5 g., m. p. 128–129°, rosettes from ethyl acetate and petroleum ether.⁸

The combined filtrates were concentrated and converted to the 3-nitrophthalic acid ester which crystallized slowly from ethyl acetate and petroleum ether when seeded with racemic 3-nitrophthalic acid ester of IV. A first crop was harvested when about half of the material had crystallized, weight 26 g. (racemic material). This substance was put through the same resolution cycle and an additional 7.5 g. of 3-nitrophthalic acid ester of IVB was obtained, m. p. 128–129°.

The combined filtrates were concentrated and converted to the acid ester and this material was submitted to fractional crystallization (four cycles) from ethyl acetate and petroleum ether, in each case the derivative of IVA crystallizing last. A total of 7.2 g. of the 3-nitrophthalic acid ester of IVA was obtained, m. p. 128–129° (rosettes)⁸ from ethyl acetate and petroleum ether.

Resolution of the Phthalic Acid Ester of V.—A mixture of 30 g. of the phthalic acid ester of V, 25 g. of brucine and 200 ml. of acetone was brought to boiling and cooled slowly. The plates that separated were collected and recrystallized from acetone and the 23 g. obtained was con-

(8) This substance crystallizes in two different forms, needles, which if heated rapidly partially melt at 117°, resolidify and melt at 128–129°, and rosettes, m. p. 128–129°.

verted to the phthalic acid ester of VA; weight 9.2 g., m. p. 127–128° (flakes from ethyl acetate and petroleum ether). The filtrates were combined, concentrated and converted to the acid ester which was allowed to crystallize from ethyl acetate and petroleum ether until about half of the material had appeared. This substance was collected (weight 5 g.) and submitted to the resolution procedure described above to give 1.5 additional grams of acid phthalate of VA.

The combined filtrates were concentrated and converted to the free acid ester which was submitted to a four-cycle fractional crystallization procedure with ethyl acetate and petroleum ether as solvent. In each case the material that first crystallized was rich in racemate. A total of 4.5 g. of the phthalic acid ester of VB was obtained, m. p. 127–128° (flakes).

Resolution of the 3-Nitrophthalic Acid Ester of VI.—A mixture of 100 g. of the 3-nitrophthalic acid ester of VI, 65 g. of cinchonine and 500 ml. of acetone was heated to the boiling point and slowly cooled. The needles that separated were collected and twice recrystallized from a mixture of chloroform and acetone. The salt (55 g.) was converted to the 3-nitrophthalic acid ester of VIA; weight 30 g., m. p. 138–139° (needles from ethyl ether and petroleum ether).

The filtrates were combined, concentrated and converted to the acid ester which was mixed with 50 g. of cinchonidine and 300 ml. of acetone. The needles that separated were recrystallized twice from acetone to give 25 g. of salt which was converted to 13 g. of white needles (from ether and petroleum ether) of the 3-nitrophthalic acid ester of VIB, m. p. 139–140°.

The filtrates were combined, concentrated and converted to the acid ester which was subjected to the resolution pro-

cedure described above to produce 9 additional grams of the 3-nitrophthalic acid ester of VIA (m. p. 139–140°) and 13 additional grams of the 3-nitrophthalic acid ester of VIB, m. p. 139–140°.

Hydrolysis of the Phthalic Acid Esters of III, V and VA to III, V and VA, Respectively, and the 3-Nitrophthalic Acid Esters of IV, VI, IVA, IVB, VIA, and VIB to IV, VI, IVA, IVB, VIA and VIB, Respectively.—The procedure used for the above introconversions is illustrated by the hydrolysis of the 3-nitrophthalic acid ester of VIA to VIA alcohol. A mixture of 36 g. of the ester, 10 g. of potassium hydroxide, 10 g. of sodium hydroxide and 100 ml. of water was heated at reflux for twelve hours. The mixture was then cooled, extracted twice with petroleum ether, the extracts combined and washed with water, dried and evaporated to an oil. This oil was distilled to give 15.6 g. of VIA, b. p. 121° (17 mm.).

Acknowledgment.—The author wishes to express his thanks to Welton Burney, who performed the analysis of the compounds reported in this paper.

Summary

1. The compounds 2-phenyl-3-pentanol and 3-phenyl-2-pentanol have been prepared and completely resolved into the eight optically pure stereoisomers.

2. Tentative stereochemical structures have been assigned to each isomer.

LOS ANGELES, CALIFORNIA RECEIVED MARCH 14, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Studies in Stereochemistry. III. The Wagner-Meerwein Rearrangement in the 2-Phenyl-3-pentanol and 3-Phenyl-2-pentanol Systems¹

BY DONALD J. CRAM

Paper II² of this series reported the primary resolutions of 2-phenyl-3-pentanol into racemates III³ and IV followed by the secondary resolution of each of these racemates into IIIA, IIIB and IVA and IVB, respectively. The structural isomer, 3-phenyl-2-pentanol, was also resolved to give racemates V and VI, and subsequently VA, VB and VIA and VIB, respectively. Tentative assignments of configuration for each of these isomers were suggested. This paper reports the results of an investigation of the acetolyses of the *p*-toluenesulfonates of III, IV, V, VI, IIIA, IVA, VA and VIA.

Results

Table I records the physical properties, analyses and yields of the *p*-toluenesulfonates of III, IV, V, VI, IIIA, IVA, IVB, VA, VIA and VIB. In each case the acetolysis of these substances was conducted at 70° and for thirty hours in anhy-

TABLE I
PHYSICAL AND ANALYTICAL DATA PERTAINING TO THE *p*-TOLUENESULFONATES OF THE ISOMERS OF 2-PHENYL-3-PENTANOL AND 3-PHENYL-2-PENTANOL

Isomer	M. p., °C.	Yield, %	Formula	Analyses, %			
				Caled. C	H	Found C	H
III	90–91 ^a	67	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.82	7.17
IV	67–68	68	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.73	7.18
V	40–41	63	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.98	7.18
VI	Oil ^b	45	C ₁₈ H ₂₂ SO ₃	67.89	6.97	68.02	7.22
IIIA	100–101	71	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.92	7.18
IVA	86–87	66	C ₁₈ H ₂₂ SO ₃	67.89	6.97	68.12	7.06
IVB	86–87	75	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.82	7.17
VA	71–72	85	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.75	6.78
VIA	41–42	69	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.86	7.18
VIB	41–42	68	C ₁₈ H ₂₂ SO ₃	67.89	6.97	67.76	7.25

^a All of the compounds except VI crystallized as needles from low-boiling petroleum ether. ^b This compound was never obtained in a crystalline state. Purification was accomplished through repeated precipitation of the substance from low-boiling petroleum ether at Dry Ice temperature followed by high vacuum drying of the oil at room temperature.

drous glacial acetic acid containing enough potassium acetate to neutralize the *p*-toluenesulfonic acid as it formed. The mixtures of acetate products were hydrolyzed to the corresponding mix-

(1) This paper was presented in part before the Organic Division of the American Chemical Society, San Francisco Meeting, March, 1949.

(2) Cram, *THIS JOURNAL*, **71**, 3871 (1949).

(3) The numbering system has been maintained from paper to paper in this investigation.