The Stereochemistry of Nucleophilic Substitution Reactions at Tertiary Carbon. II. Solvolysis of 2-Phenyl-2-butyl Chloride

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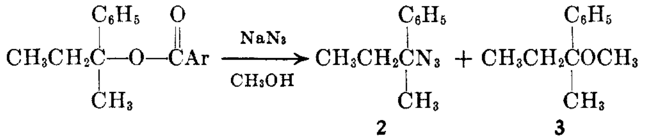
2-Phenyl-2-butyl chloride undergoes solvolysis in aqueous ethanol at a rate independent of the nucleophile present. The stereochemistry is sensitive to the nature of the nucleophile, the reaction with sodium azide being more stereospecific than the reaction with methanol or methoxide ion. A solvolysis scheme is proposed involving rate-determining formation of an asymmetric ion pair which is then attacked by a nucleophile with predominant inversion of configuration.

Recent studies on the solvolysis behavior of optically active hydrogen 2-phenyl-2-butyl phthalate (**1a**) and 2-phenyl-2-butyl *p*-nitrobenzoate (**1b**) revealed a strong stereochemical dependence on nucleophile. The stereochemical results, which are summarized below, provided clear evidence that asymmetric ion pairs or their equivalent are important intermediates in these reactions of the 2-phenyl-2-butyl system.[2]



$$CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}Ar \xrightarrow[CH_3OH]{NaN_3} CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}N_3 + CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}OCH_3$$

2 **3**

1a, Ar = *o*-$CO_2HC_6H_4$ — 62% inversion[3] — 25% inversion

b, Ar = *p*-$NO_2C_6H_4$ — 56% inversion — 14% inversion

Reaction of **1a** with a saturated solution of sodium azide in methanol gave rise to a mixture of 2-methoxy-2-phenylbutane (**3**) and 2-phenyl-2-butyl azide (**2**), the methyl ether being formed with 25% inversion of configuration and the azide with 62% inversion. Similarly, **1b** yielded 2-methoxy-2-phenylbutane which was 14% inverted and 2-phenyl-2-butyl azide which was 56% inverted.

Both the high percentage of inversion observed and the strong stereochemical dependence on nucleophile clearly indicate that a process proceeding through a free carbonium ion is not operating here despite the fact that the carbon center involved is both tertiary and benzylic. In order to obtain a more general picture of the extent and nature of nucleophilic participation in reactions at tertiary carbon, we undertook the study of solvolysis reactions of 2-phenyl-2-butyl chloride with respect to both kinetics and stereochemistry.

Results

Conversion of Optically Active 2-Phenyl-2-butanol to the Chloride.—Optically active 2-phenyl-2-butanol reacted readily under mild conditions with the usual reagents to afford optically active 2-phenyl-2-butyl chloride. The results are summarized in Table I. In all cases the chloride had the same sign of rotation as the alcohol from which it was prepared although smaller in magnitude. Infrared assay showed the chloride to be free of any unconverted carbinol. Thus, the rotation measured was that of the chloride and not that of alcoholic contaminant. Because of its instability,[4,5] the chloride was not further purified but used directly for the solvolysis experiments described below.

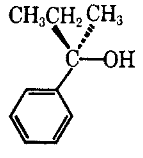
Table I

Conversion of 2-Phenyl-2-Butanol to 2-Phenyl-2-butyl Chloride

Reaction conditions		$[\alpha]_D$ alcohol,[a,b] deg	$[\alpha]_D$ chloride,[a] deg
Reagent	Temp, °C		
Anhydrous hydrogen chloride	0	−13.07	−4.50
Hydrogen chloride in pentane	0	−14.16	−7.27
Hydrogen chloride in pentane	−78	−14.16	−13.90
Phosphorus pentachloride	0	+13.34	+1.52
Phosphorus trichloride	0	+13.34	+6.75
Thionyl chloride	0	+13.34	+3.42

[a] All rotations are for the neat liquids in 1-dm tubes. [b] Optically pure 2-phenyl-2-butanol has a rotation of 17.6°; see H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 3154 (1953).

Before describing the kinetic and stereochemical results, it seems desirable to try to deduce the configurational relationship of (+)-2-phenyl-2-butyl chloride to that of (+)-2-phenyl-2-butanol (**4**), which has been shown to possess the absolute configuration shown below.[6] It may be argued that the reaction of 2-phenyl-2-butanol with thionyl chloride should proceed with predominant *retention* of configuration rather than inversion for the following reasons. First, the gross features of the decomposition of the chlorosulfite intermediates formed from alcohols and thionyl chloride closely resemble the process occurring in amine deaminations in that there is the extrusion of a stable molecule (SO_2 *vs.* N_2) accompanying the formation of an ion pair (eq 1 and 2). While it is recognized that



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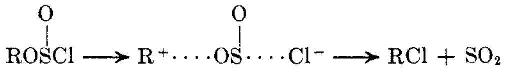

$$RO\overset{O}{\overset{|}{S}}Cl \longrightarrow R^{+}\cdots O\overset{O}{\overset{|}{S}}\cdots Cl^{-} \longrightarrow RCl + SO_2 \qquad (1)$$

$$RN{=}NX \longrightarrow R^{+}\cdots N\equiv N\cdots X^{-} \longrightarrow RX + N_2 \qquad (2)$$

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[1] To whom all correspondence should be addressed at the Department of Chemistry, University of California at Davis, Davis, Calif.

[2] L. H. Sommer and F. A. Carey, *J. Org. Chem.*, **32**, 800 (1967).

[3] Stereospecificities are reported as per cent inversion or retention of configuration with the difference from 100% understood to be racemization.

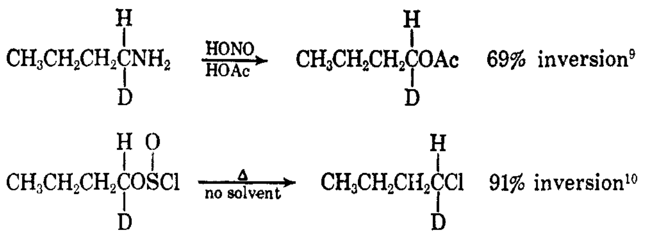
[4] A. Klages, *Ber.*, **35**, 3508 (1902).

[5] D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963).

[6] D. J. Cram and J. Allinger, *ibid.*, **76**, 4518 (1954).

amine deaminations occupy a unique place in carbonium ion chemistry owing to the low energy of the transition state leading to nitrogen evolution,[7,8] the similarity of stereochemical courses to those of chlorosulfite decompositions is striking. Compare the stereochemical courses of the following amine deaminations and chlorosulfite decompositions.

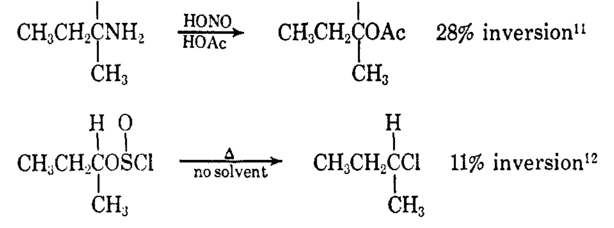
a. At primary carbon



$$\mathrm{CH_3CH_2CH_2\overset{H}{\underset{D}{C}}NH_2} \xrightarrow[\mathrm{HOAc}]{\mathrm{HONO}} \mathrm{CH_3CH_2CH_2\overset{H}{\underset{D}{C}}OAc} \quad \text{69\% inversion[9]}$$

$$\mathrm{CH_3CH_2CH_2\overset{H}{\underset{D}{C}}\overset{O}{S}OCl} \xrightarrow[\text{no solvent}]{\Delta} \mathrm{CH_3CH_2CH_2\overset{H}{\underset{D}{C}}Cl} \quad \text{91\% inversion[10]}$$

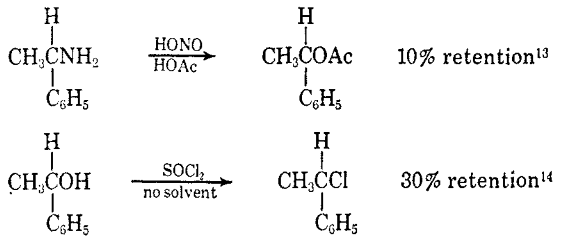
b. At secondary carbon



$$\mathrm{CH_3CH_2\overset{H}{\underset{CH_3}{C}}NH_2} \xrightarrow[\mathrm{HOAc}]{\mathrm{HONO}} \mathrm{CH_3CH_2\overset{H}{\underset{CH_3}{C}}OAc} \quad \text{28\% inversion[11]}$$

$$\mathrm{CH_3CH_2\overset{H}{\underset{CH_3}{C}}O\overset{O}{S}Cl} \xrightarrow[\text{no solvent}]{\Delta} \mathrm{CH_3CH_2\overset{H}{\underset{CH_3}{C}}Cl} \quad \text{11\% inversion[12]}$$

c. At a secondary benzylic carbon atom

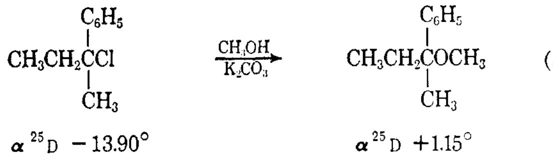


$$\mathrm{CH_3\overset{H}{\underset{C_6H_5}{C}}NH_2} \xrightarrow[\mathrm{HOAc}]{\mathrm{HONO}} \mathrm{CH_3\overset{H}{\underset{C_6H_5}{C}}OAc} \quad \text{10\% retention[13]}$$

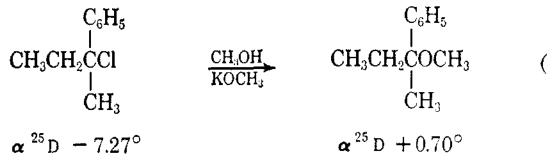
$$\mathrm{CH_3\overset{H}{\underset{C_6H_5}{C}}OH} \xrightarrow[\text{no solvent}]{\mathrm{SOCl_2}} \mathrm{CH_3\overset{H}{\underset{C_6H_5}{C}}Cl} \quad \text{30\% retention[14]}$$

Since deamination of optically active 2-phenyl-2-butylamine in acetic acid proceeds with 24% retention of configuration,[15] it is not unreasonable to conclude that retention of configuration is also preferred in reaction of the alcohol with thionyl chloride. Having previously observed that the reactions of 2-phenyl-2-butyl *p*-nitrobenzoate and hydrogen 2-phenyl-2-butyl phthalate with sodium azide proceeded with high inversion of configuration,[2] it seemed likely that the reaction of the chloride with azide, though not necessarily as stereospecific, should also follow an inversion path. Therefore the solvolytic stereochemical studies described below provide not only an index of nucleophilic participation in the product-formation stage of reactions at tertiary carbon, but also serve as a check on our assumption that 2-phenyl-2-butanol and 2-phenyl-2-butyl chloride of the same sign of rotation have the same configuration.

Methanolysis of 2-Phenyl-2-butyl Chloride.—Treatment of optically active 2-phenyl-2-butyl chloride with methanol at 25° in the presence of potassium carbonate afforded 2-methoxy-2-phenylbutane (eq 3) in 86% yield by gas chromatography along with 14% 2-phenylbutenes.[16] Changing the solvent system to methanol containing 0.18 *M* potassium methoxide gave a similar product mixture (82% 2-methoxy-2-phenylbutane and 18% olefins) (eq 4). The stereochemical outcome was not appreciably altered. Since 2-phenyl-2-butanol and 2-methoxy-2-phenylbutane of the same sign of rotation have the same configuration,[17] assignment of the same configuration to (−)-2-phenyl-2-butyl chloride and (−)-2-phenyl-2-butanol indicates that the above methanolysis reactions proceed with predominant inversion of configuration, a result in accord with previous findings[2] for compounds **1a** and **1b**.

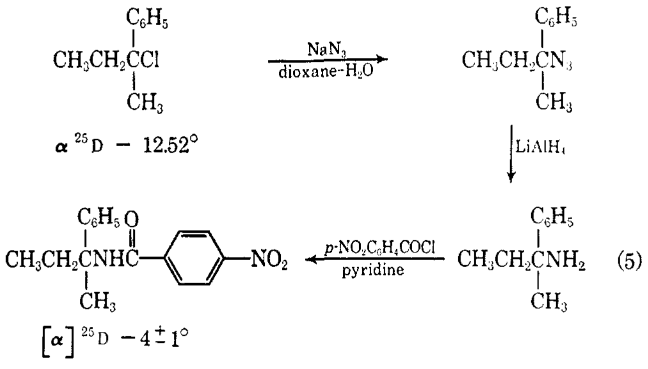


$$\underset{\alpha^{25}\mathrm{D}\ -13.90^\circ}{\mathrm{CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}Cl}} \xrightarrow[\mathrm{K_2CO_3}]{\mathrm{CH_3OH}} \underset{\alpha^{25}\mathrm{D}\ +1.15^\circ}{\mathrm{CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}OCH_3}} \qquad (3)$$



$$\underset{\alpha^{25}\mathrm{D}\ -7.27^\circ}{\mathrm{CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}Cl}} \xrightarrow[\mathrm{KOCH_3}]{\mathrm{CH_3OH}} \underset{\alpha^{25}\mathrm{D}\ +0.70^\circ}{\mathrm{CH_3CH_2\overset{C_6H_5}{\underset{CH_3}{C}}OCH_3}} \qquad (4)$$

Reaction with Sodium Azide.—Solvolysis of the chloride with sodium azide in 75% aqueous dioxane afforded, after chromatographing the crude reaction product, 2-phenyl-2-butyl azide which was reduced to 2-phenyl-2-butylamine with lithium aluminum hydride in ether and characterized as its *p*-nitrobenzamide (eq 5). Since the (−)-*p*-nitrobenzamide has been configurationally related to (+)-2-phenyl-2-butanol,[2] the over-all stereochemical course is one of inversion of configuration, in accord with previous findings for compounds **1a** and **1b**, and serves to confirm our original assignment of configuration to the chloride.



Kinetic Studies.—Rate data for several solvolysis reactions provided quantitative information regarding the reactivity of 2-phenyl-2-butyl chloride and indicated

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[7] H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp 93–101, 123–136.

[8] A. Streitwieser, Jr., *J. Org. Chem.*, **22**, 861 (1957).

[9] A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).

[10] A. Streitwieser, Jr., *ibid.*, **79**, 379 (1957).

[11] K. B. Wiberg, dissertation, Columbia University, July 1950.

[12] E. S. Lewis and C. E. Boozer, *J. Am. Chem Soc.*, **74**, 308 (1952).

[13] R. Huisgen and C. Ruchardt, *Ann. Chem.*, **601**, 21 (1956).

[14] E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937).

[15] E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, **85**, 2168 (1963); F. A. Carey, Ph.D. Thesis, The Pennsylvania State University, 1963.

[16] The olefin fraction is a mixture of *cis*-2-phenyl-2-butene, *trans*-2-phenyl-2-butene, and 2-phenyl-1-butene. Elimination reactions in the 2-phenyl-2-butyl system have been the subject of a thorough study by Cram and Sahyun.[5]

[17] See footnote *b* of Table I.

that we were dealing with a classical limiting unimolecular nucleophilic substitution (see Tables II and III).

TABLE II

SOLVOLYSIS RATES OF CHLORIDES IN ETHANOL AT 25.0°

Chloride	Rate constant, sec^{-1}	Relative rate
t-Butyl[a]	9.7×10^{-8}	1
α-Phenylethyl[b]	2.9×10^{-7}	30
Benzhydryl[c]	5.75×10^{-5}	594
2-Phenyl-2-butyl	9.66×10^{-5}	995

[a] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948). [b] E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1201 (1937). [c] E. D. Hughes, C. K. Ingold, and N. Taber, *ibid.*, 949 (1940).

TABLE III

EFFECT OF NUCLEOPHILE ON RATE OF SOLVOLYSIS OF 2-PHENYL-2-BUTYL CHLORIDE IN 80% ETHANOL AT 0°

Added nucleophile	k, sec$^{-1} \times 10^4$
None	2.28
0.034 *M* KOH	2.26
0.10 *M* NaN_3	2.93
0.10 *M* $NaClO_4$	3.26

It is apparent that the nature of the nucleophile has little effect on the rate of reaction, in full accord with the classical S$_N$1 mechanism for the solvolysis of tertiary halides. The approximately 28% increase in rate in the presence of sodium azide is ascribable to a salt effect since the nonnucleophilic perchlorate ion gives an even larger rate increase.

Discussion

Since the optical activity of optically pure 2-phenyl-2-butyl chloride is unknown at the present time,[18,19] we are unable to determine the absolute stereospecificities of the nucleophilic substitutions described here. However we can determine the relative stereospecificities using as a basis the most optically active chloride obtained, $\alpha^{25}\mathrm{D}$ −13.90° from 80.4% optically pure 2-phenyl-2-butanol. On these grounds the minimum stereospecificities are as given in Table IV.

TABLE IV

STEREOCHEMICAL COURSE OF SOLVOLYSIS OF 2-PHENYL-2-BUTYL CHLORIDE

Reaction conditions			
Reagent	Temp, °C	Inversion (min), %	Product
Potassium carbonate in methanol	25	3.4 ± 0.1[a]	2-Methoxy-2-phenylbutane
Potassium methoxide in methanol	28	4.0 ± 0.3	2-Methoxy-2-phenylbutane
Sodium azide in 75% aqueous dioxane		17 ± 4	2-Phenyl-2-butyl azide

[a] The uncertainties represent that involved in measuring the rotations of the optically active products.

It is apparent that stereochemical outcome for reactions of the 2-phenyl-2-butyl chloride system is dependent on nucleophile in exactly the same manner as in the solvolyses of 2-phenyl-2-butyl *p*-nitrobenzoate and hydrogen phthalate. That is, reaction with sodium azide is some three to five times more stereospecific than reaction with methanol or methoxide ion.[20,21] This implies the presence of intermediates of similar selectivities and therefore of similar energies for reactions of all three systems. This stereochemical dependence and kinetic independence on nucleophilicity indicate that the solvolysis reactions at this tertiary center proceed by way of a rate-determining formation of an asymmetric ion pair which is attacked by nucleophile (product-determining step) with predominant inversion of configuration. It is clear from Table IV that, relative to methoxide ion and methanol, attack on the asymmetric ion pair by the more nucleophilic azide ion is better able to compete with processes leading to racemic product.

It is interesting to compare the present stereochemical results for the 2-phenyl-2-butyl chloride system with those reported for some studies of optically active secondary systems. Treatment of optically active 2-octyl methanesulfonate with sodium azide in 25% aqueous dioxane gave 2-octyl azide with predominant inversion of configuration and having 80% optical purity.[22] Furthermore, in the same highly aqueous solvent, the rate of reaction of the 2-octyl mesylate was unaffected by added sodium azide, even at 0.0462 *M* salt, which gave a 31% yield of alkyl azide.[23] These results clearly implicate an asymmetric secondary ion pair which undergoes attack by azide ion with predominant inversion of configuration.[24]

Experimental Section

Instruments used were a Beckman IR-5A infrared spectrophotometer, an O.C. Rudolph precision optical polarimeter, and an Aerograph A-90-P gas chromatograph equipped with a 10 ft × 0.25 in. 20% Ucon Polar on Chromosorb column. 2-Phenyl-2-butanol was resolved by the method of Zeiss.[17]

Conversion of 2-Phenyl-2-butanol to 2-Phenyl-2-butyl Chloride. With Hydrogen Chloride at 0°.—The method used by Brown[25] to prepare *t*-cumyl chlorides was investigated. Anhydrous hydrogen chloride was passed over 2.00 g (13.3 mmoles) of (−)-2-phenyl-2-butanol, $\alpha^{25}\mathrm{D}$ −13.07° (length 1 dm, neat), for 0.75 hr while cooling in an ice bath. The lower layer was then withdrawn with a capillary, several pieces of calcium chloride were added to the upper layer, and the product was simultaneously dried and freed of hydrogen chloride at 25° (1 mm). The crude chloride weighed 1.98 g (92% yield) and was shown to be free of unconverted alcohol by its infrared spectrum which was void of absorbance in the 2.8–3-μ region and lacked the bands at 10.9 and 11.1 μ found in the spectrum of 2-phenyl-2-butanol. A new band appeared at 15.35 μ[26] and also a medium-strength doublet at 9.3–9.4 μ. The product had $[\alpha]^{22}\mathrm{D}$ −4.50° (*c* 20, pentane).

With Hydrogen Chloride in Pentane at 0°.—A solution of 1.50 g (10 mmoles) of (−)-2-phenyl-2-butanol, $\alpha^{25}\mathrm{D}$ −14.16° (length 1 dm, neat), in 25 ml of pentane was cooled to 0° and anhydrous

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[18] Coupling of the chloride with the pyrrole Grignard reagent followed by oxidation gave racemic 2-methyl-2-phenylbutanoic acid. This reaction sequence which proceeds with clean inversion in secondary systems has been proposed as a means of relating configurations of halides to carboxylic acids of known configuration.[19]

[19] P. S. Skell and G. P. Bean, *J. Am. Chem. Soc.*, **84**, 4660 (1962).

[20] This cannot be a solvent effect since 75% aqueous dioxane is a better ionizing solvent than methanol as measured by *Y* values.[21]

[21] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); W. H. Cropper, F. Spieth, and A. R. Olson, *ibid.*, **76**, 6248 (1954).

[22] H. Weiner and R. A. Sneen, *ibid.*, **87**, 287 (1965).

[23] H. Weiner and R. A. Sneen, *ibid.*, **87**, 292 (1965).

[24] For other recent data on the involvement of ion pairs in displacements on secondary carbon centers, see A. Streitwieser, Jr., and T. D. Walsh, *ibid.*, **87**, 3686 (1965).

[25] H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Am. Chem. Soc.*, **79**, 1899 (1957).

[26] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 329, gives 12.5–16.7 μ as the range for the C–Cl stretching frequency.

hydrogen chloride passed through for 8 min. The solution was then washed with 15 ml of water and two 10-ml portions of 5% potassium carbonate solution and dried over sodium sulfate. The solvent was removed to afford 1.37 g (81%) of (−)-2-phenyl-2-butyl chloride, α^{27}_{D} −7.27° (length 1 dm, neat).

With Hydrogen Chloride in Pentane at −78°.—Anhydrous hydrogen chloride was passed into a solution of 1.50 g (10 mmoles) of (−)-2-phenyl-2-butanol, α^{25}_{D} −14.16° (length 1 dm, neat), in 25 ml of pentane for 15 min while cooling in a Dry Ice–acetone bath. The solution was washed with 10 ml of water and two 10-ml portions of 5% potassium carbonate solution and dried over sodium sulfate. Evaporation of the pentane yielded 1.32 g (78%) of (−)-2-chloro-2-phenylbutane, α^{28}_{D} −13.90° (length 1 dm, neat).

With Phosphorus Pentachloride.—(+)-2-Phenyl-2-butanol (3 g, 20 mmoles), α^{25}_{D} +13.34° (length 1 dm, neat), was added by drops with swirling to 5.0 g (24 mmoles) of phosphorus pentachloride while cooling in an ice bath. Hydrogen chloride was evolved and a homogeneous solution resulted. After 5 min, the reaction mixture was poured into ice water and extracted with 50 ml of pentane followed by a 25-ml portion of pentane. The extracts were combined, washed with 25 ml of cold water, 10% potassium carbonate solution, and water, and dried over sodium sulfate. Removal of the pentane gave 3.3 g (99%) of (+)-2-chloro-2-phenylbutane, $[\alpha]^{30}_{\mathrm{D}}$ +1.25° (*c* 27, pentane).

With Phosphorus Trichloride.—Phosphorus trichloride (9.0 g, 65.5 mmoles) was cooled to 0° and 3.0 g (20 mmoles) of (+)-2-phenyl-2-butanol, α^{25}_{D} +13.34° (length 1 dm, neat), added slowly with stirring. After 10 min, 30 ml of ice water was added and the solution extracted with 50 ml of pentane followed by 25 ml of pentane. The organic layers were combined and washed with potassium carbonate solution, dried (sodium sulfate), and evaporated to leave 2.60 g (75%) of 2-phenyl-2-butyl chloride, $[\alpha]^{25}_{\mathrm{D}}$ +6.75° (*c* 26, pentane).

With Thionyl Chloride.—(+)-2-Phenyl-2-butanol (3.0 g, 20 mmoles), α^{25}_{D} +13.34° (length 1 dm, neat), was added slowly while cooling in an ice bath to 9.0 g (75 mmoles) of thionyl chloride. An immediated exothermic reaction occurred accompanied by gas evolution. After 8 min the solution was poured into 30 ml of water and extracted with 50 ml of pentane. The organic layer was washed three times with 30-ml portions of cold water and once with 30 ml of 20% potassium carbonate solution. After washing again with water and drying over sodium sulfate, the pentane was removed to give 2.85 g (85%) of 2-chloro-2-phenylbutane, α^{25}_{D} +3.42° (length 1 dm, neat).

Methanolysis of (−)-2-Phenyl-2-butyl Chloride. In the Presence of Potassium Carbonate.—A solution of 1.05 g (6.2 mmoles) of (−)-2-phenyl-2-butyl chloride, α^{25}_{D} −13.90° (length 1 dm, neat), in 50 ml of anhydrous methanol was stirred with 2.0 g of anhydrous potassium carbonate for 2.5 hr at 25°. The reaction mixture was poured into 200 ml of water and extracted with three 50-ml portions of pentane. The pentane extracts were combined, washed with 20 ml of water and 20 ml of 10% potassium carbonate solution, and dried over anhydrous potassium carbonate. After removal of the pentane by distilling through a short column, 0.84 g of residue was obtained, having α^{25}_{D} +1.01 ± 0.03° (length 1 dm, neat). Analysis by gas chromatography revealed a composition of 86% 2-methoxy-2-phenylbutane and 14% 2-phenylbutenes, requiring a rotation of 1.15 ± 0.03° for the methyl ether.

In the Presence of Potassium Methoxide.—(−)-2-Phenyl-2-butyl chloride (1.19 g, 7.1 mmoles), α^{28}_{D} −7.27° (length 1 dm, neat), was dissolved in 50 ml of a methanol solution which was 0.18 *M* in potassium methoxide and allowed to stand for 1 hr at 28°. Potassium chloride precipitated in a short time. The solution was poured into 200 ml of water and extracted with three 50-ml portions of pentane. The pentane extracts were combined and washed with two 10-ml portions of water and dried over sodium sulfate. The pentane was distilled through a short column to give 1.00 g of product having α^{28}_{D} +0.57 ± 0.04° (length 1 dm, neat). Analysis by vapor phase chromatography revealed a composition of 82% 2-methoxy-2-phenylbutane and 18% 2-phenylbutene. The methyl ether therefore had α^{28}_{D} +0.70 ± 0.05° (length 1 dm, neat).

Reaction of 2-Phenyl-2-butyl Chloride with Sodium Azide.—To a flask containing a solution of 45 ml of purified dioxane, 15 ml of water, and 1.30 g (20 mmoles) of sodium azide was added 1.24 g (7.4 mmoles) of (−)-2-phenyl-2-butyl chloride, α^{27}_{D} −12.52° (length 1 dm, neat). After 18 hr at 25° the solution was poured into 100 ml of water and extracted with three 50-ml portions of pentane. The pentane extracts were combined and washed with three 20-ml portions of water, dried over sodium sulfate, and percolated through 100 g of alumina. The column was washed with 200 ml of pentane and the solvent removed to afford 0.31 g of product. The infrared spectrum indicated that this material was a mixture of 2-phenyl-2-butyl azide (strong band at 4.8 μ) and isomeric 2-phenylbutenes. In order to effect separation and configurational relationships, the product was added to a stirred slurry of 0.5 g of lithium aluminum hydride in 25 ml of anhydrous ether to convert the azide portion of the product to 2-phenyl-2-butylamine. After stirring overnight the excess reducing agent was decomposed with water and the ether solution decanted from the inorganic salts and the salts rinsed with a small portion of ether. The ether solutions were washed with 5 ml of water and dried over sodium sulfate.

In view of the small quantity of amine to be realized from this process, it was isolated as its *p*-nitrobenzamide. The ether was removed on the steam bath and the amine taken up in 5 ml of chloroform containing 0.5 g of freshly recrystallized *p*-nitrobenzoyl chloride and shaken with 20 ml of 5% potassium hydroxide solution. After 1 hr the layers were separated and the aqueous layer was extracted with 5 ml of chloroform. The chloroform extracts were combined, washed with 3 ml of water, and dried over sodium sulfate. Concentration and chromatography on 50 g of alumina afforded, after elution with 50% ether–50% pentane, 107 mg of N-2-phenyl-2-butyl-*p*-nitrobenzamide. Its infrared spectrum was identical with that of authentic material.[2] The optical activity of this derivative was $[\alpha]^{26}_{\mathrm{D}}$ −4.0 ± 1.0° (*c* 1.0, chloroform) corresponding to a minimum stereospecificity of 17 ± 4%.

Kinetic Measurements.—To 50 ml of the appropriate solvent mixture cooled in a well-mixed slurry of ice and water was added *ca.* 0.5 g of 2-phenyl-2-butyl chloride and the flask shaken several times. A 5.00-ml aliquot was removed and added to 20 ml of ice-cold acetone to quench the reaction. Zero time was taken when one-half of the first aliquot was added to the acetone. The acetone solution was then titrated as rapidly as possible with 0.0237 *N* potassium hydroxide solution to the bromothymol blue end point. Aliquots (5 ml) were removed periodically, quenched, and titrated in the same manner. Infinity titers were determined by adding the aliquot to 20 ml of water to accelerate the reaction and titrating the liberated hydrochloric acid after approximately 3 hr. Solvolysis in the presence of 0.034 *M* KOH was followed by titrating with 0.0141 *M* hydrochloric acid. The chloride used in the rate studies was prepared from the alcohol and hydrogen chloride in a pentane solvent at −78°.

Registry No.—(−)-2-Phenyl-2-butyl chloride, 13144-95-1; (+)-2-phenyl-2-butyl chloride, 13144-96-2; 2-methoxy-2-phenylbutane, 1007-66-5; N-2-phenyl-2-butyl-*p*-nitrobenzamide, 10181-69-8.

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