tion of the first crop from acetone–water afforded colorless needles, m.p. 118.5–120.5°.

Anal. Calcd. for $C_{21}H_{21}NO_3S$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.5; H, 6.18; N, 3.88.

N-(β-Hydroxy-β-phenethyl)-*p*-toluenesulfonamide (II).—A solution of *p*-toluenesulfonamide (17.1 g., 0.10 mole) and Triton B (1.0 ml.) in styrene oxide (12.0 g., 0.10 mole) was heated on a steam-cone for 2 hours. Crystallization of the resulting oil from 50 ml. of toluene afforded 17.0 g. (58.5%) of colorless needles, m.p. 95–110°. To remove traces of III present, the crude product was dissolved in 5% aqueous sodium hydroxide, the solution was filtered and acidified with concentrated hydrochloric acid. The crystalline precipitate was collected and recrystallized from methanol–water to yield colorless needles of m.p. 112.5–113° (reported m.p. 113°).[3]

N,N-Bis-(β-hydroxy-β-phenethyl)-*p*-toluenesulfonamide (III).—Styrene oxide (24.0 g., 0.20 mole) and *p*-toluenesulfonamide (17.1 g., 0.10 mole) were heated with Triton B (1.0 ml.) on a steam-cone for 2 hours. The crystalline mass which separated during this time was dissolved in 50 ml. of hot toluene. On cooling, there was deposited 14.9 g. (36.3%) of colorless needles, m.p. 166–174°. Several recrystallizations from toluene yielded an analytical sample, m.p. 178.5–179.5°.

Anal. Calcd. for $C_{23}H_{25}NO_4S$: C, 67.14; H, 6.12; N, 7.78. Found: C, 67.1; H, 6.14; N, 7.71.

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(3) M. S. Kharasch and H. M. Priestley, THIS JOURNAL, **61**, 3425 (1939).

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Attempted Preparation of 1-Phenyl-2-methyl-3-Bromohexane by Brominative Decarboxylation[1]

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RECEIVED OCTOBER 11, 1954

In the course of some work on another problem it was necessary to prepare 1-phenyl-2-methyl-3-bromohexane. It is a well-known fact that this type alkyl halide cannot be prepared from the alcohol,[3] nor will addition of hydrogen bromide to an olefin produce the desired compound. Since brominative decarboxylation has not been investigated previously for the preparation of such bromides, we proposed to carry through the sequence of reactions given in Fig. 1.

In order to prove the structure of the bromide which was obtained in low yield, the following reactions were studied. Qualitative tests with sodium iodide in acetone and silver nitrate in alcohol indicated that the bromide was secondary and not tertiary. The carbon–hydrogen analysis confirmed the empirical formula given. Although a Grignard reagent was obtained in low yield, carbonation gave no acidic material. An unsaturated compound was recovered from this process but no structure proof was attempted. Due to this lack of success in carbonating the Grignard and the low yield of bromide obtained, this procedure was of no value to the investigation at hand and further work was discontinued. Thus no definite structure assignment can be made for the bromide.

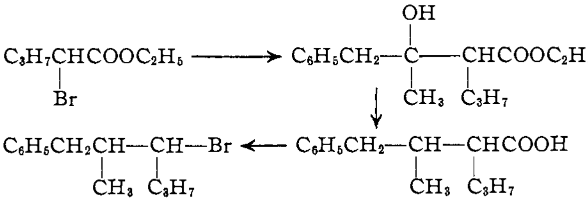

Fig. 1.

Experimental

Ethyl β-Hydroxy-β-methyl-γ-phenyl-α-propylbutyrate.—A mixture of 43.0 g. (0.321 mole) of phenylacetone and 63.0 g. (0.30 mole) of ethyl α-bromo-*n*-valerate dissolved in 120 ml. of benzene and 105 ml. of toluene was added dropwise to 21.0 g. (0.321 mole) of 40-mesh zinc. The reaction was initiated by heating with a steam-bath, and then the solution was added at a rate which kept the reaction mixture gently boiling. After the addition had been completed the reaction mixture was heated for two hours. After cooling, the reaction mixture was decomposed with dilute sulfuric acid, the organic layer separated and dried over sodium sulfate. The product was isolated by distillation, b.p. 110–113° (0.1 mm.), as a colorless liquid in a yield of 60%, $n^{22}D$ 1.4970.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.62; H, 9.13.

Ethyl β-Methyl-γ-phenyl-α-propylcrotonate.—Dehydration of the above hydroxyester was attempted by the Hibbert[4] method and by the use of 90% formic acid,[5] but both methods proved unsuccessful.

A solution containing 57.4 g. (0.217 mole) of the above hydroxyester dissolved in 200 ml. of anhydrous benzene was heated under reflux for four hours with 40.0 g. (0.282 mole) of phosphorus pentoxide. The inorganic materials were taken up in ice water, the organic layer separated and dried. An 84% yield of colorless ester, b.p. 93–94° (0.1 mm.), $n^{27}D$ 1.5043, was obtained.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.36; H, 9.04.

β-Methyl-γ-phenyl-α-propylcrotonic Acid.—A solution containing 27.0 g. (0.11 mole) of the above ester and 18.4 g. (0.328 mole) of potassium hydroxide in 100 ml. of 30% ethanol was heated under reflux for 12 hours. The solvent was removed by evaporation and the solid residue dissolved in a minimum of cold water. This solution was made distinctly acid and the organic product extracted with ether. Distillation gave 16.6 g. (69%) of a colorless oil, b.p. 130–131° (0.1 mm.), $n^{28}D$ 1.5286.

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.0; H, 8.32; neut. equiv., 218.1. Found: C, 77.29; H, 8.41; neut. equiv., 217.0.

β-Methyl-γ-phenyl-α-propylbutyric Acid.—A sample, 16.5 g. (0.076 mole), of the unsaturated acid was dissolved in 50 ml. of glacial acetic acid and hydrogenated over 100 mg. of platinum oxide at room temperature using three atmospheres hydrogen pressure. Separation of the catalyst and distillation gave 15.0 g. (90%) of the saturated acid, b.p. 125–130° (0.1–0.15 mm.), $n^{20}D$ 1.5088.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15; neut. equiv., 220.3. Found: C, 76.28; H, 8.96; neut. equiv., 222.4.

Silver β-Methyl-γ-phenyl-α-propylbutyrate.—A solution of 7.72 g. (0.0454 mole) of $AgNO_3$ in 60 ml. of distilled water was added to 120 ml. of a solution containing 10 g. (0.0454 mole) of the acid and 2.55 g. (0.0454 mole) of potassium hydroxide. The voluminous white precipitate that formed was removed by filtration, washed with cold water, methanol and dried in a vacuum oven at 60° for six hours. Storage even in the dark caused this salt to darken slightly.

Anal. Calcd. for $C_{14}H_{19}O_2Ag$: C, 51.39; H, 5.85. Found: C, 51.29; H, 5.97.

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[1] This work was supported by the Atomic Energy Commission under contract with Oregon State College. Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 266, School of Science, Department of Chemistry.

[2] This article is based on a thesis submitted by Norman R. Odell in partial fulfillment of the requirements for the Doctor of Philosophy degree at Oregon State College.

(3) Frank C. Whitmore and Franklin Johnston, THIS JOURNAL, **60**, 2265 (1938).

(4) H. Hibbert, *ibid.*, **37**, 1748 (1915).

(5) H. Rupe, H. Steiger and F. Fielder, *Ber.*, **47**, 63 (1914).

Brominative Decarboxylation.—A number of attempts were made to bring about brominative decarboxylation of silver β-methyl-γ-phenyl-α-propylbutyrate using bromine in carbon tetrachloride or petroleum ether at high and low temperatures, but low yields of an unidentified bromide were obtained in all cases. The following procedure is typical.

Dry bromine, 17.4 g. (0.109 mole), was added to a vigorously stirred suspension of 35.0 g. (0.107 mole) of the silver salt in 150 ml. of anhydrous carbon tetrachloride as rapidly as the gas evolution would permit. After the addition the mixture was heated on a steam-bath for an hour, cooled and the precipitated silver bromide removed by filtration. The filtrate was washed with sodium bicarbonate solution, sodium bisulfite solution and water. The product was isolated by distillation, b.p. 84–85° (0.1 mm.), $n^{20}\text{D}$ 1.5240, yield 18%.

Anal. Calcd. for $C_{13}H_{19}Br$: C, 61.18; H, 7.50. Found: C, 61.30; H, 7.47.

2-Propyl-3-methyl-1-tetralone.—When efforts to secure conventional derivatives of β-methyl-γ-phenyl-α-propylbutyric acid failed, the acid was cyclized for purposes of structure proof.

Twenty grams (0.09 mole) of the acid and 150 g. of polyphosphoric acid[6] were heated at 70° for 45 minutes. After cooling the mixture was poured over ice and the organic material extracted with ether. The product boiled at 90–96° (0.15–0.2 mm.), $n^{19}\text{D}$ 1.5349, and was obtained in 71% yield.

Anal. Calcd. for $C_{14}H_{18}P$: C, 83.12; H, 8.97. Found: C, 83.26; H, 8.77.

A **2,4-dinitrophenylhydrazone** of the above ketone was prepared and melted at 162–164°.

Anal. Calcd. for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80. Found: C, 62.80; H, 5.73.

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(6) Sample kindly supplied by Victor Chemical Company, Chicago, Ill.

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Absence of Rearrangement in the Bromination of *sec*-Butyl Alcohol[1a]

BY ALEXANDER T. SHULGIN[1b]

RECEIVED OCTOBER 18, 1954

It generally has been accepted that a pure secondary bromide cannot be obtained from the corresponding alcohol by the usual bromination methods (HBr, HBr and H_2SO_4, PBr_3) when an isomeric secondary bromide is structurally possible. In the course of the synthesis of chain-labeled isoleucine it was necessary to investigate this point, for if there was migration the labeled isoleucine formed from 2-butyl bromide would not be unique in its labeled position.

The best studied case of this migration is the preparation of 2-bromopentane and 3-bromopentane from the corresponding amyl alcohols.[2a,b,c] Pure secondary alkyl bromides have been made from the corresponding secondary carboxylic acid silver salts by means of bromine, or from the *p*-toluenesulfonate esters by treatment with inorganic bromide ion.[3] Neither of these methods was desirable for isotopic synthesis, however, as the former entailed several additional steps and the latter provided low yields of the alkyl halide.

In the conversion of *sec*-butyl alcohol to the bromide, one would be led to predict extensive rearrangement, as the isomeric carbonium ions are chemically identical. The involvement of an ethyleneprotonium ion[4a,b] between the two adjacent secondary carbon atoms would require complete randomization. The ethyleneprotonium ion has been shown to be of minor importance in the hydrolysis of 2-butyl *p*-toluenesulfonate.[4a] The involvement of this ion to any appreciable extent in the course of the bromination of secondary alcohols seems unlikely, for otherwise the isomeric mixture obtained from either 2- or 3-amyl alcohol should have the same composition, and this was not the case.[2a]

It was found, however, that the bromination of 2-butanol-1-C^{14} with PBr_3 produced 2-bromobutane-1-C^{14} in a good yield with less than 3% rearrangement to the isomeric 2-bromobutane-4-C^{14} (see Table I).

TABLE I

DISTRIBUTION OF RADIOACTIVITY IN THE CONVERSION OF 2-BUTANOL-1-C^{14} TO *sec*-BUTYL BROMIDE[a]

	Carbon 1	Carbons 2, 3, 4
sec-Butyl alcohol 1-C^{14}	2930 ± 25 2913 ± 32[b]	17 ± 41
sec-Butyl bromide 1-C^{14}	2905 ± 29	24 ± 36
Percentage rearrangement[c]		0.9 ± 1.9%

[a] All activities are expressed as counts/minute/millimole. [b] Activity of the 3,5-dinitrobenzoate derivative of *sec*-butyl alcohol 1-C^{14}. [c] Rearrangement is expressed by the equation

$$\frac{\begin{pmatrix}\text{act. in labeled position}\\ \text{before bromination}\end{pmatrix} - \begin{pmatrix}\text{act. in same position}\\ \text{after bromination}\end{pmatrix}}{\begin{pmatrix}\text{act. in labeled position}\\ \text{before bromination}\end{pmatrix}} \times 100$$

Experimental

Degradation of 2-Butanol-1-C^{14}.—A small sample of 2-butanol-1-C^{14}, the product of the Grignard reaction between methyl iodide C^{14} and propionaldehyde, was diluted with sufficient inert 2-butanol to allow purification by fractional distillation. The fraction boiling at 98–101°, weighing 7.8 g., was divided into three portions for conversion to the 3,5-dinitrobenzoate ester, to iodoform and propionic acid directly, and to the 2-butyl bromide with subsequent conversion to iodoform and propionic acid.

A 1.0-g. portion of the above described 2-butanol-1-C^{14} was divided into two parts, and each was individually degraded as follows: To a solution of 0.5 g. of 2-butyl alcohol in 25 ml. of dioxane (Eastman Kodak Co. histological dioxane was used) there was added 5 ml. of 10% NaOH. To this mixture there was added, portionwise, sufficient I_2 in KI solution ($1:2:8::I_2:KI:H_2O$, w./w./v.) until the iodine color remained even after vigorous shaking. The reaction mixture was heated and shaken at 60° for several minutes and more iodine solution added if necessary. The excess color now was removed by 1 or 2 additional drops of the NaOH solution. To the light yellow solution there was added 50 ml. of water and the iodoform was allowed to aggregate for an hour. The yellow iodoform (0.24 g.) was filtered off, washed well with CO_2-free water, dried briefly and kept in a tightly stoppered vial. The mother liquors were saved for propionic acid isolation.

Degradation of 2-Bromobutane-1-C^{14}.—To a 6.0-g. portion of the labeled 2-butanol-1-C^{14} which was cooled to −20° in an ice–concd. HCl bath, there was added cautiously 8.0 g. of PBr_3. The reaction was allowed to come to room tem-

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[1] (a) This work was supported in part by a U.S.P.H. grant to David M. Greenberg. (b) Bio-Rad Laboratories, 800 Delaware Street, Berkeley 2, Calif.

[2] (a) H. Pines, A. Rudin, and V. N. Ipatieff, THIS JOURNAL, **74**, 4063 (1952); (b) J. Cason and R. H. Mills, *ibid.*, **73**, 1354 (1951); (c) W. M. Lauer and F. H. Stodola, *ibid.*, **56**, 1215 (1934).

[3] A. J. H. Houssa, J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1700 (1929).

[4] (a) J. D. Roberts, W. Bennett, R. E. McMahon and E. W. Holroyd, Jr., THIS JOURNAL, **74**, 4283 (1952); (b) D. J. Cram, *ibid.*, **74**, 2137 (1952).