

**Brominative Decarboxylation.**—A number of attempts were made to bring about brominative decarboxylation of silver  $\beta$ -methyl- $\gamma$ -phenyl- $\alpha$ -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.),  $n_D^{20}$  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  $\beta$ -methyl- $\gamma$ -phenyl- $\alpha$ -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<sup>6</sup> 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.),  $n_D^{19}$  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.

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

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### Absence of Rearrangement in the Bromination of *sec*-Butyl Alcohol<sup>1a</sup>

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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.<sup>2a,b,c</sup> 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.<sup>3</sup> Neither of these methods was desirable for isotopic synthesis, however, as the former

(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).

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<sup>4a,b</sup> 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.<sup>4a</sup> 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.<sup>2a</sup>

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<sup>a</sup>

	Carbon 1	Carbons 2, 3, 4
<i>sec</i> -Butyl alcohol	2930 $\pm$ 25	17 $\pm$ 41
1- $C^{14}$	2913 $\pm$ 32 <sup>b</sup>	
<i>sec</i> -Butyl bromide	2905 $\pm$ 29	24 $\pm$ 36
1- $C^{14}$		

Percentage rearrangement<sup>c</sup> 0.9  $\pm$  1.9%

<sup>a</sup> All activities are expressed as counts/minute/millimole. <sup>b</sup> Activity of the 3,5-dinitrobenzoate derivative of *sec*-butyl alcohol 1- $C^{14}$ . <sup>c</sup> Rearrangement is expressed by the equation 
$$\frac{\left( \text{act. in labeled position} \right) - \left( \text{act. in same position} \right) \text{ before bromination}}{\left( \text{act. in labeled position} \right) \text{ before bromination}} \times 100$$

### 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<sub>2</sub>O, 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<sub>2</sub>-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-

(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).

perature overnight. A sufficient excess of water was added to form a distinctly separate lower phase of *sec*-butyl bromide. The aqueous layer was pipeted off, and the organic phase washed with several additional 25-ml. portions of water. The yield of the bromide, measured volumetrically, was 7.5 ml. or approximately 85%.

In a calibrated centrifuge tube was placed 1.15 g. of silver nitrate, dissolved in sufficient warm water to make 1.5 ml. of solution. The total volume was brought to 7.0 ml. with warm dioxane, and 0.65 ml. of the undried *sec*-butyl bromide added quickly before the supersaturated silver nitrate solution crystallized. There was an immediate heavy precipitation of silver bromide. The contents of the tube were stirred at 60° for 10 minutes. The silver bromide was then centrifuged down, decanted, washed with two consecutive 12-ml. portions of dioxane, and the supernatant solutions pooled with the original decanted solution. To the dioxane solution was added 5.0 ml. of a 10% NaOH solution. On heating to 60° for 10 minutes, a black solid was formed due to the excess silver. The mixture was treated with the iodine solution as described under the degradation of 2-butanol. The black product dissolved immediately with the formation of silver iodide, which soon dissolved. About 10 ml. of the reagent was required. After the final 2 minutes of heating at 60°, a small amount of inorganic solid was filtered off, and 50 ml. of water added. The iodoform and mother liquors were treated as described for the 2-butanol.

**Isolation of Propionic Acid as the S-Benzyl Pseudothiuronium Salt.**—The mother liquors of the previous degradations were worked up separately. The solution was taken to dryness under a stream of air. A small amount of water was added, followed by acidification with sulfuric acid and treatment with sodium arsenite and silver sulfate, which was in turn followed by steam distillation. The distillate was neutralized with 0.10 *N* NaOH to methyl red, and evaporated to dryness. The resulting sodium propionate was dissolved in a minimum amount of water, and treated with an excess of a saturated solution of S-benzyl pseudothiuronium chloride (prepared from thiourea and benzyl chloride<sup>5</sup>) in water. The curdy salt formed was recrystallized from hot 95% alcohol. The melting point of a typical product was 153–154°, and the mixed melting point with the chloride salt (m.p. 150–151°) was 126–134°.

**Conversion of Iodoform to Barium Carbonate.**—The four samples of radioactive iodoform, from two separate degradation runs on both the 2-butanol and the 2-butyl bromide, were separately converted to carbon dioxide by total oxidation using the wet combustion procedure.<sup>6</sup> The CO<sub>2</sub> was trapped in carbonate-free base, and converted to barium carbonate with BaCl<sub>2</sub> in the usual manner.

(5) S. Veibel and H. Lillelund, *Bull. soc. chim.*, [5] 5, 1153 (1938).

(6) D. D. Van Slyke, J. Folch and J. Plazin, *J. Biol. Chem.*, **136**, 509 (1940).

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### Cyclic Organosilicon Compounds. III. A Four-membered Ring Containing One Silicon Atom<sup>1</sup>

BY ROBERT WEST

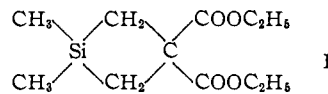
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The preparation of a silicon-containing 4-ring has recently been reported.<sup>2</sup> When this work appeared we had independently completed the synthesis of another silicon-containing four-membered heterocycle by a different sequence of reactions. The ring compound obtained in this work was 3,3-dicarbethoxy-1,1-dimethyl-1-silacyclobutane,<sup>3</sup> compound I. The compound is a colorless liquid; it was obtained

(1) For previous papers in this series see *THIS JOURNAL*, **76**, 6012, 6015 (1954).

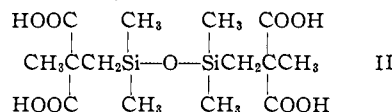
(2) L. H. Sommer and G. A. Baum, *ibid.*, **76**, 5002 (1954).

(3) Or  $\beta,\beta$ -dicarbethoxycyclotrimethylenedimethylsilane, according to the system of nomenclature used in earlier papers.<sup>1</sup>



in a ring closure reaction from bis-(iodomethyl)-dimethylsilane, diethyl malonate and sodium methoxide.

Compound I appears to undergo ring opening readily, as has been reported for 1,1-dimethyl-1-silacyclobutane.<sup>2</sup> When attempts were made to hydrolyze compound I to obtain the free dicarboxylic acid, no material having the composition of the expected diacid could be obtained. Instead, a compound containing additional oxygen was always produced. This product, a water-soluble crystalline solid, was assigned the structure shown as II.



Sommer and Baum<sup>2</sup> attribute the reactivity of silacyclobutane compounds to angular strain in the ring. Since tetraalkylsilanes are not ordinarily cleaved by acids and bases at room temperature, their explanation is doubtless correct. However, the silacyclobutane ring is also much more easily cleaved than the cyclobutane ring. We believe that the total angular strain in the silacyclobutanes is no greater than in cyclobutanes, in spite of the large size of the silicon atom, because the bond angles at a silicon atom appear to be much more easily deformed.<sup>4</sup> Some explanation other than angular strain is therefore required for the rapid cleavage of silacyclobutanes compared to cyclobutanes. In our view the silacyclobutane ring opens more readily because it has available to it mechanisms for ring opening which are not available to cyclobutane.

#### Experimental

##### 3,3-Dicarbethoxy-1,1-dimethyl-1-silacyclobutane<sup>3</sup> (I).

The general procedure used was patterned on that given for cyclobutane-1,1-dicarboxylic acid.<sup>5</sup> Bis-(iodomethyl)-dimethylsilane was prepared as described by Roberts and Dev<sup>6</sup> from 23.5 g. (0.15 mole) of bis-(chloromethyl)-dimethylsilane.<sup>7</sup> The crude (undistilled) product from this preparation was mixed with 21.6 g. (0.135 mole) of diethyl malonate (Eastman practical grade) in a 500-ml. flask fitted with a stirrer, dropping funnel and condenser. A solution of 6.2 g. (0.27 g.-atom) of sodium in 125 ml. of methanol was then added dropwise to the stirred reaction mixture from the dropping funnel. After 15 ml. of the solution had been added, the reaction was initiated by heating. The remainder of the sodium methoxide solution was added over 15 minutes, the heat of reaction serving to keep the temperature of the reaction mixture just below the boiling point. The mixture was then refluxed for three hours, until a test portion added to water was neutral to phenolphthalein.

Methanol was then distilled from the reaction mixture until 85 ml. had been collected. The residual material was partitioned between 200 ml. each of water and petroleum ether, and the organic layer was separated and dried over CaCl<sub>2</sub>. The petroleum ether was then stripped off and the residue was distilled under reduced pressure from a modified Claisen flask. The forerun comprised 21 g. of iodine-containing material distilling at 98–141° (15 mm.). The prod-

(4) Indicated by lower force constants for X-Si-X than for X-C-X bending vibrations. Unpublished infrared studies by M. K. Wilson and S. M. Polo.

(5) G. B. Heisig and F. H. Stodola, *Org. Syntheses*, **23**, 16 (1943).

(6) J. D. Roberts and S. Dev, *THIS JOURNAL*, **73**, 1879 (1951).

(7) Kindly donated by Dr. R. C. Osthoff of the General Electric Company.