

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).

DIVISION OF BIOCHEMISTRY  
SCHOOL OF MEDICINE  
UNIVERSITY OF CALIFORNIA  
BERKELEY 4, CALIFORNIA

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

BY ROBERT WEST

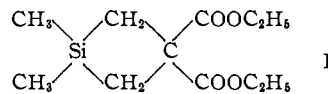
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The preparation of a silicon-containing 4-ring has recently been reported.<sup>2</sup> When this work appeared we had independently completed the synthesis of another silicon-containing four-membered heterocycle by a different sequence of reactions. 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).

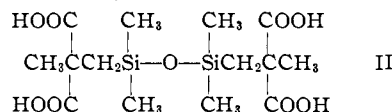
(2) L. H. Sommer and G. A. Baum, *ibid.*, **76**, 5002 (1954).

(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.

uct came over at 141–143° (15 mm.).<sup>8</sup> The yield was 16.2 g. (50%) of a colorless oil with a faint pleasant odor, having  $n_D^{25}$  1.4318 and  $d_4^{25}$  0.997.

*Anal.* Calcd. for  $C_{11}H_{20}O_4Si$ : C, 54.06; H, 8.25; Si, 11.5; mol. wt., 244; molecular refraction<sup>9</sup> 64.1. Found: C, 54.23; H, 8.65; Si, 11.0; mol. wt. 216; molecular refraction, 63.6; I, absent.

**Symmetrical Bis-(2,2-dicarboxypropyl)-tetramethyldisiloxane (II).**—To a solution of 3.0 g. of KOH in 50 ml. of ethanol was added 5.0 g. (0.020 mole) of compound I. The mixture was refluxed for two hours, during which time a white precipitate of the potassium salt of II formed. The precipitate was removed by filtration and the filtrate was discarded. The crude potassium salt was dissolved in 10 ml. of warm water and made just acid with HCl. The solution was extracted with four 30-ml. portions of diethyl ether, and the extracts were combined and dried over  $MgSO_4$ . The product was obtained by allowing the ether to evaporate, taking up the residue in ethyl acetate, and precipitating with petroleum ether. The yield was 2.2 g. (55%). After one more reprecipitation, the product was quite pure. (Analytical results were the same for material prepared in slightly different ways and crystallized from different solvents.)

*Anal.* Calcd. for  $C_{14}H_{26}O_8Si_2$ : C, 42.62; H, 6.64; neut. equiv., 98.6. Found: C, 42.79; H, 6.59; neut. equiv., 98.2.

The compound crystallized as small diamond-shaped prisms, soluble in water, alcohols, ethyl acetate and acetone, but only sparingly soluble in benzene and petroleum ether; m.p. 141–142° dec. When titrated with alkali, compound II gave a  $pH$  curve resembling that for a dibasic acid such as malonic acid. If the proposed structure is correct, the hydrogens must therefore ionize in pairs, presumably in a symmetrical fashion about the disiloxane group. The acidic dissociation constants were estimated to be  $K_{I,II} = 10^{-3}$  and  $K_{III,IV} = 5 \times 10^{-7}$  from the  $pH$  titration curve. The aqueous solution gave a white precipitate with  $Pb^{++}$ , but gave no precipitate with  $Na^+$ ,  $K^+$ ,  $Ag^+$ ,  $Ca^{++}$  or  $Ba^{++}$ . The lead salt was filtered off, washed with water and dried at 120°.

*Anal.* Calcd. for  $C_{14}H_{22}O_8Si_2Pb_2$ : Pb, 51.5. Found: Pb, 51.9.

**Decarboxylation of II.**—In a typical experiment 0.2112 g. of II was heated to 160° for five minutes in a test-tube. The product, a viscous oil, was not purified. The yield was 0.156 g. The product had a neutralization equivalent of 150; that calculated for the diacid expected from the decarboxylation of II is 153.

(8) 2-Ethylbutane-1,1-dicarboxylic acid diethyl ester, a carbon compound of similar molecular weight, has b.p. 130° at 13 mm.: F. Fichter, A. Kiefer and W. Bernoulli, *Ber.*, **42**, 4712 (1909).

(9) E. L. Warrick, *THIS JOURNAL*, **68**, 2455 (1946).

DEPARTMENT OF CHEMISTRY  
LEHIGH UNIVERSITY  
BETHLEHEM, PENNSYLVANIA

## 2-Pyrones. XIV.<sup>1</sup> The Hydrogenation of 2-Pyrones

By RICHARD H. WILEY AND ALBERT J. HART

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Although the hydrogenation and hydrogenolysis of unsaturated  $\delta$ -lactones (2-pyrones) to saturated  $\delta$ -lactones and open chain derivatives have been used as significant facets of the proof of structure of many naturally occurring and synthetic compounds,<sup>2</sup> there has been no reported study of the

(1) Previous paper in this series: R. H. Wiley and L. H. Knabeschuh, *THIS JOURNAL*, **77**, 1615 (1955).

(2) M. Bergmann, L. Zervas and E. Silberkweit, *Ber.*, **64B**, 2428 (1931); T. W. Campbell, *THIS JOURNAL*, **73**, 4190 (1951); J. Fried and R. C. Elderfield, *J. Org. Chem.*, **6**, 577 (1941); R. Malachowski, *Bull. intern. acad. Polonaise*, 265A (1929); R. Malachowski and T. Wancziera, *ibid.*, 547A (1933); J. Meinwald, *THIS JOURNAL*, **76**, 4571 (1954); E. B. Reid and J. R. Siegel, *ibid.*, **76**, 938 (1954); A. Stoll, A. Hofmann and N. Kreis, *Helv. Chim. Acta*, **17**, 1334 (1934); R.

hydrogenation of the simple, readily available 2-pyrones. This is particularly striking in view of the variety of catalysts and conditions which have been used in structural studies and the apparent ease with which hydrogenolysis of certain structures occurs with some catalysts. The present study was undertaken to develop a satisfactory procedure for conversion of 2-pyrones to saturated  $\delta$ -lactones and to provide additional information on this important reaction.

The addition of hydrogen to 2-pyrones is known to take place readily over platinum oxide or various palladium catalysts.<sup>2</sup> Experiments recorded here show that with a commercially available 5% palladium-on-charcoal catalyst, absorption of two moles of hydrogen per mole of 2-pyrone is complete within 45 minutes to 5 hours at 15 pounds pressure of hydrogen and in methanol or ether. Under these conditions coumalic acid reacted most rapidly absorbing in excess (122–129%) of two moles of hydrogen per mole of compound in less than 45 minutes. Isodehydroacetic acid absorbed two moles of hydrogen in five hours. The yields of isolated tetrahydro-2-pyrone varied from very low with coumalic acid to 37% for isodehydroacetic acid and to 82–85% with other 2-pyrones. The low yields were obtained in attempts to isolate pure solid products from the two acids—coumalic and isodehydroacetic. These isolations were difficult because the crude solid consists of mixtures of stereoisomers. The yields of the crude solid are considerably greater than those recorded for the recrystallized, analytical sample.

The hydrogenation of coumalic acid is not only more rapid than that of the other types but it is also accompanied by hydrogenolysis.  $\alpha$ -Methylglutaric acid was identified as the chief constituent in a benzene-soluble fraction of the product, and tetrahydrocoumalic acid was separated in poor yield from the benzene-insoluble fraction. The formation of  $\beta$ -methylglutaric acid by hydrogenolysis of methyl coumalate has been noted before.<sup>2</sup> This behavior of coumalic acid and its ester is obviously exceptional and confirms previous observations<sup>3</sup> as to the anomalous character of coumalic acid and its derivatives.

The product from the reduction of methyl 2-pyrone-6-carboxylate is very soluble in water, is very hygroscopic, and is acidic to moist test paper. Ultimate analysis indicates the addition of a mole of water, presumably during isolation, as well as two moles of hydrogen, on which basis the compound is taken to be a hydrate. Its behavior toward alkali on titration indicates that the lactone structure is intact.

**Acknowledgment.**—The authors wish to thank the Damon Runyon Memorial Fund for a grant in support of this study.

### Experimental<sup>4</sup>

All of the hydrogenations were run in a Parr hydrogenation apparatus under an initial hydrogen pressure of 50–60 lb. using 5% palladium-on-carbon catalyst.

Tschesche and H. A. Offe, *Ber.*, **69B**, 2361 (1936); H. Wieland, G. Hesse and H. Meyer, *Ann.*, **493**, 272 (1932); F. G. Young, *THIS JOURNAL*, **71**, 1346 (1949).

(3) R. H. Wiley and L. H. Knabeschuh, *ibid.*, **77**, 1615 (1955).

(4) Analyses by Micro Tech Laboratories.