

tertiary acetylenic chlorides. Resonance stabilization of this ion by the forms, $\text{H}:\overset{+}{\text{C}}:\overset{-}{\text{C}}::\overset{-}{\text{C}}:\overset{+}{\text{H}} \rightarrow$

$\text{H}:\overset{-}{\text{C}}::\overset{+}{\text{C}}:\overset{-}{\text{C}}:\overset{+}{\text{H}} \leftrightarrow \text{H}:\overset{-}{\text{C}}:\overset{+}{\text{C}}::\overset{-}{\text{C}}:\overset{+}{\text{H}}$, explains how nu-

cleophilic attack by nitrogen (of the phenothiazine ring) can occur at the acetylenic carbon if one assumes either subsequent or simultaneous attack of a proton or sodium ion at the methylenic carbon atom.

EXPERIMENTAL

N-(1-Propynyl)phenothiazine (I). To a stirred suspension of 7.2 g. (0.3 mole) of sodium hydride in 600 ml. of dry dimethylformamide, protected by an atmosphere of dry nitrogen, was added, in portions, 60 g. (0.3 mole) of phenothiazine. After warming at 50° for an additional 2 hr., the reaction mixture was heated to 70° and a solution of 35.7 g. (0.3 mole) of propargyl bromide in 50 ml. of dimethylformamide was added dropwise. After heating for an additional 2 hr. at 70°, the mixture was stirred overnight at room temperature.

Most of the solvent was removed by distillation at reduced pressure, and the residue was poured into cold water. Insoluble product was taken up in ether, washed with water, and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave an oil (52 g.) which solidified on trituration with hexane. Although purification could be accomplished by recrystallization from hexane, it was conveniently found that passing a benzene solution of the product over a column of alumina gave 48 g. of colorless crystals, m.p. 95–96°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{11}\text{NS}$: C, 75.91; H, 4.67; N, 5.90. Found: C, 75.99; H, 4.70; N, 5.85.

Infrared spectrum (μ): 3.3 (w), 3.37 (w), 3.46 (w), 3.55 (vw), 4.48(m), 5.2 (vw), 5.31 (vw), 5.53 (vw), 5.64 (vw), 6.30 (m), 6.39 (m), 6.77 (m), 6.87 (s), 6.96 (s), 7.18 (vw), 7.28 (vw), 7.58 (s), 7.75 (s), 7.83 (m), 7.97 (s), 8.92 (m), 9.31 (w), 9.68 (m), 10.76 (w), 11.01 (w), 11.21 (w).

Substituting *n*-propyl bromide for the propargyl bromide in the above procedure gave a 65% yield of *N*-(*n*-propyl)phenothiazine, b.p. 155–165° (0.8 mm.), m.p. 48–49° (from ethanol) (lit.⁴ reports m.p. 49–50°).

Hydrogenation of I. A solution of 10.5 g. of *N*-(1-propynyl)phenothiazine (I) in 250 ml. of 95% ethanol was treated with 0.53 g. of platinum oxide catalyst and hydrogenated at 30 lb. pressure and room temperature. After 17 hr., hydrogen absorption was 65% complete. The reaction was then warmed to 60° and reaction was complete in 4 hr. After removal of the catalyst by filtration, the filtrate was concentrated to dryness under reduced pressure. Several portions of benzene were distilled from the residue which was then taken up in 25 ml. of warm absolute ethanol. Heating this solution with charcoal followed by filtering, cooling, and seeding gave, after one more recrystallization from absolute ethanol, 4.2 g. of product, m.p. 47–48°, which did not depress the melting point of *N*-(*n*-propyl)phenothiazine. Furthermore, the infrared spectrum of the hydrogenation product was qualitatively identical with that of the known reference compound.

Hydrolysis of I. A mixture of 500 mg. of *N*-(1-propynyl)phenothiazine (I) and 5 ml. of 10% hydrochloric acid was refluxed overnight. However, within 5 min. after the beginning of reflux, the oil turned to a solid. The mixture was

concentrated to dryness; the black, crystalline residue was taken up in benzene and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, the benzene solution was passed through an alumina column (20 × 1 cm.). Concentration of the eluate gave 295 mg. of yellow crystals, m.p. 174–176°. Recrystallization from benzene gave 195 mg., m.p. 177–179°.

Anal. Calcd. for $\text{C}_{12}\text{H}_9\text{NS}$: C, 72.32; H, 4.55; N, 7.03. Found: C, 72.46; H, 4.64; N, 6.95.

The product did not depress the melting point of an authentic sample of phenothiazine.

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Decarboxylation of 2-Vinylcyclopropane-1,1-dicarboxylic Acid to the Lactone of 4-Hydroxy-5-hexenoic Acid

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The synthesis of one of a series of sulfur compounds being prepared in these laboratories involved 3-cyclopentenecarboxylic acid as an intermediate.¹ This acid should readily be obtainable by hydrolysis and decarboxylation of the product of reaction of 1,4-dibromo-2-butene (I) and diethyl disodiummalonate which Skinner *et al.*² have described as diethyl 3-cyclopentene-1,1-dicarboxylate. However, the decarboxylation product obtained by this series of reactions did not possess the properties of the required acid. Its properties and infrared spectrum were in fact those to be expected of a vinyl substituted γ -lactone. Decarboxylation at 200° gave only poor yields of this compound, the majority of the product being a higher boiling material, but heating to 170° under a reduced pressure of nitrogen resulted in considerable improvement in the yields of lactone, presumably due to a decrease in the tendency for polymerization.

In view of the unexpected course of the preparation, a survey of the literature was made and it was then found that Kierstead *et al.*³ had reported that condensation of 1,4-dibromo-2-butene and the monosodio-derivative of diethyl malonate gave diethyl 2-vinylcyclopropane-1,1-dicarboxylate (II). Investigation showed that our condensation product had an infrared spectrum not inconsistent with

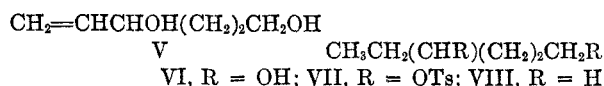
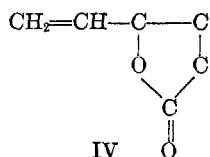
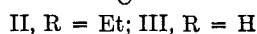
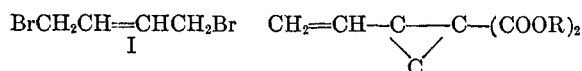
(1) S. F. Birch, R. A. Dean, N. J. Hunter, and E. V. Whitehead, *J. Org. Chem.*, **22**, 1590 (1957).

(2) G. S. Skinner, G. Limperos, and R. H. Pettebone, *J. Am. Chem. Soc.*, **72**, 1648 (1950).

(3) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952).

(4) H. Gilman, R. K. Ingham, J. F. Champaigne, Jr., J. W. Diehl, and R. O. Ranck, *J. Org. Chem.*, **19**, 560 (1954).

its being a vinylcyclopropane diester and that the melting point of the diacid obtained on hydrolysis was in agreement with that quoted³ for III. It was therefore concluded that a process similar to that described by Kierstead *et al.*³ had occurred during our condensation and that the product was not the desired cyclopentene compound, but the diester II. Presumably the 3-cyclopentene-1,1-dicarboxylate described by Skinner *et al.*² is also in fact this cyclopropane compound.



It seemed likely that the cyclopropane ring of the diacid III had undergone fission during the decarboxylation reaction and that the compound⁴ subsequently formed was the lactone of either 4-hydroxy-5-hexenoic acid (IV) or 3-hydroxymethyl-4-pentenoic acid. Examination of the reduction products V–VIII not only confirmed that the cyclopropane ring had been ruptured, but showed that the isolated decarboxylation product was IV, since reduction of the alternative lactone would have given 3-methylpentane instead of *n*-hexane as the final product. It may therefore be concluded that fission of the 3-membered ring occurs in the same position on decarboxylation as on hydrogenation.³

EXPERIMENTAL

Microanalyses by Dr. Ing. A. Schoeller, Kronach/Oberfranken, Bambergerstrasse 20, Germany. All melting points are corrected. Infrared spectra are for the liquid state and were obtained using a Grubb Parsons double beam recording spectrometer.

Condensation of 1,4-dibromo-2-butene and diethyl disodium malonate. 1,4-Dibromo-2-butene (393 g.) was treated (in two batches) with diethyl disodium malonate as described by Skinner *et al.*³ Distillation of the product gave 255 g. (65%) of diester (II) b.p. 102–110°/4.5 mm., n_D^{20} 1.4522. Maxima assignable to vinyl (991 and 917 cm^{-1}) and cyclopropane (1031 and 866 cm^{-1})⁵ groups were observed in the infrared absorption spectrum. Skinner *et al.*³ report b.p. 80–81°/0.5 mm. and n_D^{25} 1.4500 for their material; Kierstead *et al.*³ give b.p. 69–72°/0.5 mm., n_D^{15} 1.4528 for diethyl 2-vinylcyclopropane-1,1-dicarboxylate.

The lactone of 4-hydroxy-5-hexenoic acid (IV). The above diester (254 g.) was refluxed with aqueous ethanolic potash (KOH, 308 g.; EtOH, 1680 ml.; H₂O, 420 ml.) for 6 hr.; the

(4) The sharpness of the melting point indicated that the decarboxylation product was essentially one compound.

(5) J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

ethanol was removed by distillation and the residual liquor acidified with hydrochloric acid (600 ml.) and extracted with ether to give the crude diacid (III) (178 g., 93%). A specimen of this, crystallized twice from benzene, melted at 109.5–110.5°. Kierstead *et al.*³ report m.p. 107–108° for 2-vinylcyclopropane-1,1-dicarboxylic acid.

Anal. Calcd. for C₇H₈O₄: C, 53.8; H, 5.2. Found: C, 54.1; H, 5.3.

A small quantity (11.5 g.) of the crude diacid was heated in an oil bath at 200°. Only 3.0 g. (35%) of distillate (b.p. 62–68°/1.7 mm.) was obtained there being a considerable resinous residue. The remainder of the crude diacid was heated in four batches under a pressure of 100 mm. of nitrogen to only 170°. In each instance, when the rate of evolution of carbon dioxide moderated, the nitrogen pressure was reduced to 24 mm. and the material which distilled at about 114° was collected. On redistillation the combined products (103 g.) gave 77.5 g. (62%) of IV, b.p. 108–112°/20 mm. A mid-cut from this distillation, taken as analytical specimen, had n_D^{20} 1.4601 and m.p. –15.5°. Reported⁶ for the lactone of 4-hydroxy-5-hexenoic acid b.p. 75°/2 mm. and n_D^{25} 1.4603.

Anal. Calcd. for C₆H₈O₂: C, 64.3; H, 7.2. Found: C, 64.0; H, 7.3.

The compound IV could not be esterified by the usual techniques and did not react readily with sodium bicarbonate solution. It rapidly decolorized potassium permanganate solution and bromine water. The infrared spectrum contained bands assignable to a γ -lactone (1779 cm^{-1})⁷ and a vinyl group (990 and 908 cm^{-1}).

1-Hexene-3,6-diol (V). The lactone IV (5 g.) in ether (500 ml.) was reduced with lithium aluminum hydride (3.3 g.) in ether (180 ml.) and the product, b.p. 98–100°/1.8 mm., n_D^{20} 1.4633 was isolated in the usual way;⁸ yield 1.8 g. (35%, extraction not completed). Its infrared spectrum showed absorption peaks at 3378 cm^{-1} (hydroxyl; $k = 0.976$) and at 990 and 920 cm^{-1} (vinyl); comparative group analysis using *n*-propyl alcohol (hydroxyl; $k = 1.04$) as a reference material, indicated the presence of 1.8 hydroxyl groups per molecule.

Anal. Calcd. for C₆H₁₂O₂: C, 62.0; H, 10.4. Found: C, 61.8; H, 10.5.

1,4-Hexanediol (VI). On hydrogenation at room temperature and atmospheric pressure, the diol V (1.32 g.) in ethanol (15 ml.) absorbed 1 molar equivalent of hydrogen and the product (VI), which was isolated in almost theoretical yield, had b.p. 122–124°/10 mm., n_D^{20} 1.4503 and absorption maxima at 3378 cm^{-1} (hydroxyl) and 1379 cm^{-1} (methyl).

Anal. Calcd. for C₆H₁₄O₂: C, 61.0; H, 11.9. Found: C, 60.7; H, 11.8.

Di-*p*-toluenesulfonate of 1,4-hexanediol (VII). The diol VI (0.7 g.) was treated with *p*-toluenesulfonyl chloride and the product VII isolated in the usual way.⁹ The crude product (1.1 g., 43%) was crystallized three times from ethanol to give material (0.4 g.) melting constantly at 33–35°.

Anal. Calcd. for C₂₀H₂₆S₂O₆: C, 56.3; H, 6.1. Found: C, 56.3; H, 6.4.

Reduction of di-*p*-toluenesulfonate of 1,4-hexanediol. An ethereal solution of VII (0.3 g. in 0.75 ml.) was reduced with lithium aluminum hydride (0.12 g.) in ether (0.75 ml.), and water (2 ml.) followed by dilute sulfuric acid (H₂SO₄, 0.3 ml.; H₂O, 1.33 ml.) was added dropwise to the reaction mixture. The ethereal layer was removed by means of a hypodermic syringe, and gas liquid chromatography (*n*-hexatriacontane stationary phase at 78°) indicated that the hydrocarbon component was *n*-hexane (retention volume relative

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(7) L. J. Bellamy, *Infrared Spectra of Complex Molecules*, John Wiley and Sons, N. Y., 1954, p. 159.

(8) S. F. Birch and R. A. Dean, *J. Chem. Soc.*, 2477 (1953).

(9) C. S. Marvel and V. C. Sekera, *Org. Syntheses, Coll. Vol. 3*, 366 (1955).

to *n*-pentane: observed 2.46; determined for *n*-hexane, 2.42 and for 3-methylpentane, 2.12). Several further portions were chromatographed and the hydrocarbon fractions were collected in a liquid nitrogen trap as they emerged from the column. The cracking pattern of this material confirmed that it was *n*-hexane.

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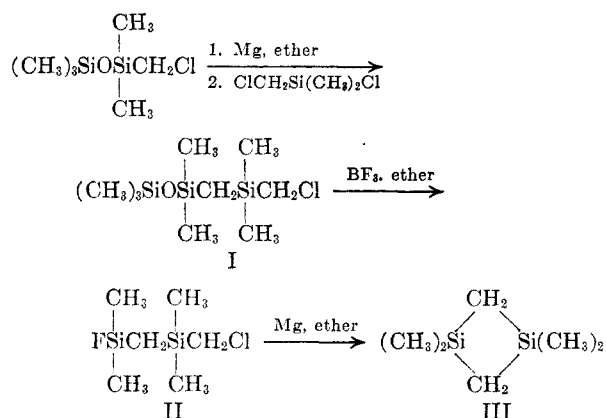
1,1,3,3-Tetramethyl-1,3-disilacyclobutane

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Monosilacyclobutanes have been reported^{1,2} only recently and no cyclobutanes containing more than one silicon atom in the ring have been described. Accordingly, it was of interest to prepare such a compound and to compare its properties with those of the monosilacyclobutanes, particularly in view of the reported ease of ring opening of the latter.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane was synthesized in an over-all yield of 25% by a three-step procedure starting with chloromethylpentamethyldisiloxane. The first step, which proceeded



in 73% yield, is analogous to the reported³ coupling of trimethylsilylmethylmagnesium chloride with

chloromethyldimethylchlorosilane. Cleavage of the siloxane linkage with boron trifluoride ethyl etherate gave a 57% yield of II. Cyclization was accomplished in 60% yield by refluxing a solution of II in ether with magnesium turnings.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane is a mobile liquid boiling at 117–119°. It was characterized by elemental analysis, molecular weight determination, and examination of its proton magnetic resonance spectrum, which is in agreement with the assigned structure. The high reactivity of III was demonstrated by its rapid reduction of silver nitrate in alcohol at room temperature, and by its reaction at room temperature with a solution of bromine in carbon tetrachloride. Similar reactions occur with 1,1-dimethyl-1-silacyclobutane and have been shown to involve ring-opening.⁴

EXPERIMENTAL

1-Chloro-2,2,4,4,6,6-hexamethyl-5-oxa-2,4,6-trisilaheptane (I). A Grignard reagent was prepared from chloromethylpentamethyldisiloxane⁵ (103 g., 0.52 mole) and magnesium (12.8 g., 0.52 mole) in 250 ml. of ether. To this was added chloromethyldimethylchlorosilane (75 g., 0.52 mole). After the addition, the mixture was heated to reflux and stirred overnight. Saturated ammonium chloride solution was added slowly with stirring until the salts separated to leave a clear, supernatant liquid. The mixture was filtered; the salts were washed with ether; and the ether washings were combined with the filtrate. Distillation gave 103.2 g. (0.38 mole, 73%) of I, b.p. 88–89° (8 mm.).

Anal. Calcd. for $\text{C}_9\text{H}_{26}\text{ClOSi}_3$: C, 40.15; H, 9.31. Found: C, 40.66; H, 9.37.

1-Chloro-4-fluoro-2,2,4-trimethyl-2,4-disilapentane (II). The trisilaheptane (I) (125 g., 0.47 mole) and boron trifluoride ethyl etherate (125 g., 1.06 mole) were mixed and immediately distilled until a head temperature of 125° was reached. The distillation residue was extracted with ether and the extracts were combined with the distillate. This solution was distilled to give 52.5 g. (0.26 mole, 57%) of II, b.p. 173–178°.

Anal. Calcd. for $\text{C}_6\text{H}_{16}\text{ClFSi}_2$: C, 36.36; H, 8.07; Cl, 17.93; Neut. Equiv., 199. Found: C, 36.73; H, 8.29; Cl, 17.85; Neut. Equiv., 195.

1,1,3,3-Tetramethyl-1,3-disilacyclobutane (III). Magnesium (7.2 g., 0.30 mole) and 50 ml. of sodium-dried ether were placed in a 500-ml. flask under an atmosphere of nitrogen. A small amount of II was added and the reaction was started by the addition of three drops of methylmagnesium iodide solution. The reaction mixture was heated to reflux temperature. An additional 225 ml. of ether was added and the remainder of a 58 g. (0.29 mole) sample of II was dissolved in 80 ml. of ether and added over a 95-min. period with rapid stirring. After completion of the addition, stirring and refluxing were continued overnight. Decane (200 ml.) was added and the mixture was distilled rapidly until the head temperature was 170°. Redistillation gave 25 g. (0.17 mole, 60%) of III, b.p. 117–119°, n_D^{25} 1.4380.

Anal. Calcd. for $\text{C}_6\text{H}_{16}\text{Si}_2$: C, 50.00; H, 11.11; Si, 39.00; mol. wt., 144. Found: C, 49.98; H, 11.27; Si, 38.29; mol. wt., 133.

The proton magnetic resonance of this material supports the assigned structure. The product decolorized a carbon

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