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.

Acknowledgment. The authors wish to thank the Chairman and Directors of The British Petroleum Company Limited for permission to publish this paper and Messrs. N.G. McTaggart and A.R. West for the determination of the spectroscopic data.

THE RESEARCH STATION
THE BRITISH PETROLEUM COMPANY LIMITED
SUNBURY-ON-THAMES
ENGLAND

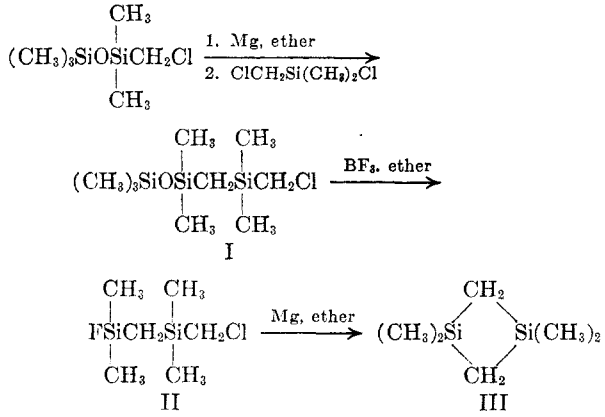
1,1,3,3-Tetramethyl-1,3-disilacyclobutane

W. H. KNOTH, JR., AND R. V. LINDSEY, JR.

Received March 26, 1958

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 reported[3] 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 chloromethylpentamethyldisiloxane[5] (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 $C_9H_{25}ClOSi_3$: 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 $C_6H_{16}ClFSi_2$: 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^{27} 1.4380.

Anal. Calcd. for $C_6H_{16}Si_2$: 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

(1) L. H. Sommer and G. A. Baum, *J. Am. Chem. Soc.*, **76**, 5002 (1954).
(2) R. West, *J. Am. Chem. Soc.*, **77**, 2339 (1955).
(3) L. H. Sommer, G. M. Goldberg, J. Gold, and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 980 (1947); L. H. Sommer, F. A. Mitch, and G. M. Goldberg, *J. Am. Chem. Soc.*, **71**, 2746 (1949).
(4) L. H. Sommer, private communication.
(5) R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, **67**, 1810 (1945).

tetrachloride solution of bromine slowly, and reduced alcoholic silver nitrate rapidly as evidenced by the formation of a silver mirror.

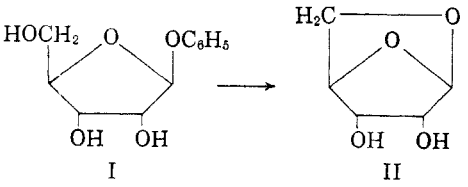
CONTRIBUTION NO. 467 FROM THE CENTRAL RESEARCH DEPARTMENT
EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS & CO., INC.
WILMINGTON 98, DEL.

1,5-Anhydro-β-D-ribofuranose from Phenyl β-D-Ribofuranoside

ERIK VIS[1] AND HEWITT G. FLETCHER, JR.

Received April 7, 1958

While the action of strong alkali on aryl glycopyranosides represents a familiar procedure for the synthesis of 1,5-anhydroglycopyranoses[2] and other analogous substances containing this ring system, similar treatment of aryl glycofuranosides has not, to our knowledge, been reported to yield 1,5-anhydroglycofuranoses. In a recent paper,[3] indeed, we stated that an attempt to synthesize 1,5-anhydro-β-D-ribofuranose (II, 1,4-anhydro-α-D-ribopyranose) from phenyl β-D-ribofuranoside (I) had



I II

failed to yield a crystalline product. Subsequent work has now shown, however, that I is converted to II (albeit in low yield) through the action of sodium isopropoxide in 2-propanol.

EXPERIMENTAL[4]

Phenyl β-D-ribofuranoside (158 mg.), prepared as described earlier,[3] was dissolved in 10 ml. of 2-propanol and the solution treated with 6 ml. of 2-propanol in which 32.5 mg. of sodium had been dissolved. The reaction mixture was boiled under reflux for 90 hr., cooled, diluted with a few drops of water and neutralized with carbon dioxide. Solvent was removed *in vacuo* and the residue extracted with acetone. Toluene was added to the extract and the solution concentrated *in vacuo* to a sirup which was freed of the remaining phenol by repeated extraction with benzene. Attempts to crystallize the residue failed and it was therefore benzoylated in the usual fashion to yield a sirup which was partially purified by precipitation from benzene with pentane and then from ethanol with water. On standing for several months at −8° in aqueous ethanol a small deposit of crystalline material was obtained. Recrystallized from methanol this product (*ca.* 15 mg., 6%) showed a double melting point: 132–133° and 146–147°. We reported earlier[3] that 1,5-anhydro-2,3-di-*O*-benzoyl-β-D-ribofuranose melts at 132–133°. Reexamination of the authentic material now reveals that it too shows the double melting point just quoted; a mixture of samples of the compound from the two sources shows the same two melting points. Upon appropriate seeding, either the form with the double melting point or one with the higher melting point only could be obtained from solution.

(1) Chemical Foundation Fellow 1956–58. Present address: Quartermaster Research and Development Center, Natick, Mass.

(2) *Cf.* L. C. Stewart, E. Zissis, and N. K. Richtmyer, *Chem. Ber.*, **89**, 535 (1956).

(3) E. Vis and H. G. Fletcher, Jr., *J. Am. Chem. Soc.*, **79**, **1182** (1957).

(4) Melting points are corrected.

NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES
NATIONAL INSTITUTES OF HEALTH
PUBLIC HEALTH SERVICE
U. S. DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
BETHESDA 14, MD.

Reciprocal Resolution of DL-Tryptophan and DL-α-Phenylethylamine

LACY R. OVERBY

Received April 11, 1958

Our interests in producing large quantities of L-tryptophan from the DL-form by economically feasible methods prompted a study of known methods and a search for new methods of resolution. The availability of *N*-acetyl-DL-tryptophan as an intermediate in commercial synthesis and the ease of racemization of the undesired D-form[1] indicated that this would be the desirable starting compound. Published methods[1–6] for resolving *N*-acetyl-DL-tryptophan suffer from one or more of the usual disadvantages of resolutions; such as, low yields, time consuming and tedious crystallizations, expensive resolving agents, or handling of large volumes. The method of du Vigneaud and Sealock[1] appeared to offer possibilities for attainment of maximum antipodal purity and for large scale use. The main disadvantage was the scarcity of the desired active form of α-phenylethylamine. DL-α-Phenylethylamine is readily available. If one were able to resolve this with the active forms of acetyltryptophan it would be possible to build up large supplies of optically active acid and base by repetition of the reciprocal resolution.

When one mole of *N*-acetyl-DL-tryptophan was combined with 0.5 mole of (−)- α-phenylethylamine and 0.5 mole of potassium hydroxide in ethanol the sparingly soluble diastereoisomeric salt [LA(−)B]

(1) V. du Vigneaud and R. R. Sealock, *J. Biol. Chem.*, **96**, 511 (1932).

(2) C. P. Berg, *J. Biol. Chem.*, **100**, 79 (1933).

(3) A. C. Shabica, *J. Am. Chem. Soc.*, **71**, 3251 (1949).

(4) Usines Chemiques des Laboratoires Francais, Brit. Patent **745,097**, Feb. 22, 1956; U. S. Patent **2,797,226**, June 25, 1957.

(5) C. Neuberg and I. Mandl, U.S. Patent **2,511,867** (Interchemical Corp.) June 20, 1950.

(6) D. G. Doherty and E. A. Popenoe, Jr., *J. Biol. Chem.*, **189**, 447 (1951).