Anal. Calcd. for $C_{21}H_{38}O_5Si_5$: C, 49.4; H, 7.5; mol. wt., 511. Found: C, 49.2; H, 7.6; mol. wt., 497 ± 5% (benzene, 25°).

3,5-Diphenyl-1,1,1,7,7,7-hexamethyl-3,5-bis(trimethylsiloxy)-tetrasiloxane.—To a solution of 0.390 g. (1.33 mmole.) of the tetrol in 40 ml. of ether was added 4.0 ml. (31.6 mmoles.) of trimethylchlorosilane and 2.0 ml. of pyridine. Work-up as above yielded 0.422 g. (57%) of distillate which mostly solidified to a waxy solid. Vapor phase chromatography showed this to be about 95% pure; a specimen collected by v.p.c. melted at 85–90° and had an infrared spectrum identical with that of a sample prepared by Simmler's[2] procedure. This spectrum (in CS_2) showed a very strong ν_aSiOSi band near 1062 cm.$^{-1}$ [probably a 1065 (s), 1052 (m) doublet] with a medium shoulder near 1105 cm.$^{-1}$, but no bands of SiOH groups.

Anal. Calcd. for $C_{24}H_{46}O_5Si_6$: C, 49.4; H, 8.0; mol. wt., 583. Found: C, 49.6; H, 8.0; mol. wt., 582 ± 5% (benzene, 25°).

Acknowledgment.—The authors are indebted to Mr. H. W. Middleton and Miss C. L. Harrington for the analyses, to Miss D. V. McClung for the spectra, and to Messrs. E. D. Brown and P. J. Launer of the General Electric Silicone Products Department for the preparation and spectrum of the authentic specimen of the tetrakistrimethylsilylation product.

The Reaction of Diethyl Malonate with Styrene Oxide

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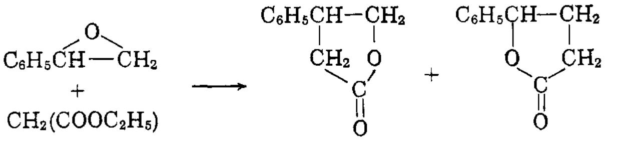
Received April 6, 1964

Russell and VanderWerf have reported[1] that the reaction of styrene oxide with diethyl malonate leads, after hydrolysis and decarboxylation, to γ-phenyl-γ-butyrolactone, which they report to have m.p. 45.5–46°. Other workers have made use of the supposed specificity of this reaction.[2]

In fact, two isomeric γ-lactones, I and II, are formed in this reaction. The compound of m.p. 45–46 is the β-phenyl-γ-lactone I and comprises approximately 60% of the product. The γ-phenyl isomer (II) melts, in agreement with numerous literature references[3] at 37–38°. The two isomers could not be separated by g.p.c. or fractional distillation, but were separable on thin layer or column chromatography using silica gel.



I, m. p. 45–46°, 60%

II, m. p. 37–38°, 40%

Experimental

Reaction of Styrene Oxide with Diethyl Malonate.—In a 5-l. round-bottom flask equipped with a condenser and a mechanical stirrer sodium metal (50 g., 2.2 g.-atoms) was dissolved in 2 l. of dry ethanol and diethyl malonate (325 g., 2.0 moles) was added. The solution was heated to reflux and styrene oxide (240 g., 2.0 moles) was added over a period of 2 hr. After heating for an additional 2 hr. sodium hydroxide (40 g., 1 mole) in 2 l. of water was added and the ethanol was removed by distillation. Concentrated hydrochloric acid (300 ml.) was carefully added and the organic material was extracted with methylene chloride. The methylene chloride was removed and the residue heated at 140° to induce decarboxylation. When the evolution of carbon dioxide ceased the material was distilled to give 200 g. (62% yield) of a mixture of β- and γ-phenyl-γ-butyrolactone, b.p. 103–105 at 0.2 mm. (lit.[1] b.p. 126–126.5 at 0.8 mm.).

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.84; H, 6.15.

β-Phenyl-γ-butyrolactone (I).—In some cases part of the product crystallized giving the lactone reported by Russell and VanderWerf, m.p. 45–46°. The n.m.r. spectrum of this isomer in CCl_4 solution consists of an eight-peak multiplet (AB part of an ABX) centered at δ 2.50, assigned to the methylene group adjacent to the carbonyl group, a doublet of triplets at δ 3.64 (benzylic hydrogen), and a six-peak multiplet (AB part of ABX with coincidental overlaps of two peaks) centered at δ 4.39. This assignment was supported by an experiment in which the reaction product was worked up in D_2O–DCl before decarboxylation. The product from that reaction had no absorption near δ 2.50 and the sextuplet at δ 3.64 had collapsed to a broadened triplet.

γ-Phenyl-γ-butyrolactone.—N.m.r. analysis of the crude, distilled reaction product showed that it contained only about 60% of the β-phenyl lactone and 40% of an isomer. No effective separation of the isomers could be obtained by gas chromatography. They were separated by column chromatography using a 3 ft. × 0.65 in. column and 80–20-mesh silica gel. The lactone mixture (1.5 g.) was added to the column in pentane and eluted with benzene–ethyl acetate (3:1). The β-phenyl lactone was eluted first and then the γ-phenyl-γ-butyrolactone (480 mg. of pure material), m.p. 37–38°. The middle fractions (∽300 mg.) contained a mixture of the two lactones. This lactone had a complex four-proton pattern centered near δ 2.37 and a single, complex peak at δ 5.33 assigned to the benzylic proton also attached to a carbon bearing oxygen.

Acknowledgment.—We are indebted to Maria Wiedemann for the chromatography, and to the National Science Foundation for financial support.

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[1] R. R. Russell and C. A. VanderWerf, *J. Am. Chem. Soc.*, **69**, 11 (1947).

[2] (a) G. Van Zyl and E. E. van Tamelen, *ibid.*, **72**, 1357 (1950); (b) S. J. Cristol and R. F. Helmreich, *ibid.*, **74**, 4083 (1952); (c) E. E. van Tamelen and S. R. Bach, *ibid.*, **77**, 4683 (1955).

[3] (a) R. Fittig and H. W. Jayne, *Ann.*, **216**, 97 (1883); (b) N. H. Cromwell, P. L. Creger, and K. E. Cook, *J. Am. Chem. Soc.*, **78**, 4412 (1956); (c) R. Oda, S. Muneimuja, and M. Okano, *J. Org. Chem.*, **26**, 1341 (1961).

Derivatives of 1,4-Xylene-2,5-diboronic Acid and 1,4-Xylene-2-boronic Acid[1]

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Received April 7, 1964

The remarkable stability toward hydrolytic deboronation of the simple boronolactone, boronophthalide[2] (I), suggests that compounds containing this system be made available for biological testing, for example as possible boron carriers in a proposed method of irradiation therapy.[3] This Note describes experiments on the preparation of the tricyclic diboronolactone (II), which may be named 1,5-dibora-2,6-dioxa-*sym*-hydrindacene-1,5-diol.

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[1] Part of this work was supported by a grant from the U. S. Atomic Energy Commission; Report No. COO-314-9.

[2] H. R. Snyder, *et al.*, *J. Am. Chem. Soc.*, **80**, 835 (1958).

[3] A. H. Soloway, *ibid.*, **82**, 2442 (1960).