The amine oxides, III and VII, could not be isolated, probably because of the facile elimination of oxygen displayed by N-oxides of weakly basic amines.[11]

Experimental

N-Phenylcarbazole.—A cold solution (−5°) of 815 mg. (4.85 mmoles) of 4,5-benzothiadiazol 1,1-dioxide[6] and 857 mg. (8.0 mmoles) of nitrosobenzene in 15 ml. of dry tetrahydrofuran was allowed to warm to room temperature. After removal of solvent, the dark residue was chromatographed on basic alumina. The column was eluted with CCl_4, and the eluate was evaporated to yield N-phenylcarbazole which crystallized as colorless crystals from ethanol–ethyl acetate (267 mg., 45.5%), m.p. 89–90°; picrate, m.p. 129–130° (lit.[12] m.p. 126–129°). The N-phenylcarbazole was identified by means of its mixture melting point with an authentic sample,[13] infrared spectrum, and thin layer chromatography.

3-Bromo-N-phenylcarbazole was prepared from 788 mg. (4.7 mmoles) of 4,5-benzothiazdiazol 1,1-dioxide and 1.49 g. (8.0 mmoles) of *p*-bromonitrosobenzene in 20 ml. of dry tetrahydrofuran by the procedure described above. Elution with CCl_4 yielded 306 mg. (40.5%) of 3-bromo-N-phenylcarbazole which crystallized as colorless crystals from ethanol–ethyl acetate, m.p. 79–80°.

Anal. Calcd. for $C_{18}H_{12}BrN$: C, 67.10; H, 3.75; Br, 24.80; N, 4.35. Found: C, 67.06; H, 3.70; Br, 24.36; N, 4.45.

Further elution with CCl_4–benzene (1:1) gave 420 mg. of 4,4′-dibromoazoxybenzene, which crystallized as yellow needles from ethanol–ethyl acetate, m.p. 169–170° (lit.[14] m.p. 168.5–169.5).[15]

Anal. Calcd. for $C_{12}H_8Br_2N_2O$: C, 40.49; H, 2.27; Br, 44.89; N, 7.87. Found: C, 40.70; H, 2.40; Br, 44.28; N, 7.94.

Reaction of Benzyne and Diphenylhydroxyamine.—A cold solution (−5°) of 737 mg. (4.4 mmoles) of 4,5-benzothiadiazol 1,1-dioxide and 1.48 g. (8.0 mmoles) of freshly prepared diphenylhydroxyamine[10] in 10 ml. of dry tetrahydrofuran was allowed to warm to room temperature. After removal of solvent, chromatography of the dark residue on basic alumina provided 424 mg. (39%) of triphenylamine, which was crystallized from ethanol, m.p. 126–126.5°, identical in all respects with an authentic sample.

Acknowledgment.—G. S. is indebted to the National Academy of Sciences for a postdoctoral research fellowship at the U. S. Army Natick Laboratories. The authors wish to thank Dr. R. W. Hoffmann for helpful suggestions.

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[15] The 4,4′-dibromoazoxybenzene probably was formed by the decomposition of the *p*-bromonitrosobenzene, possibly when it was chromatographed on the basic alumina.

1,3-Diphenyldisiloxanetetrol

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Received May 19, 1964

The crystalline polyol, m.p. 114°, obtained by the hydrolysis of phenyltriacetoxysilane in ether,[1] is of interest as one of the very few partial condensation products of a trifunctional silane hydrolysate to have been isolated as an individual compound. Andrianov and Zhdanov formulated this substance as a trisiloxanepentol,[1] *i.e.*, as the trimeric condensation product of phenylsilanetriol.

We have repeated the preparation of this polyol, and obtained analytical and spectroscopic data which agree more closely with its formulation as a disiloxanetetrol. This was confirmed by the preparation and analysis of two trimethylsilylated derivatives: treatment with an equivalent quantity of trimethylchlorosilane–pyridine gave a pentasiloxanol; with excess trimethylchlorosilane–pyridine a hexasiloxane, the known[2] tetrakis(trimethylsiloxy)diphenyldisiloxane, was obtained.

$$\mathrm{PhSi(OH)_2OSi(OH)_2Ph} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{Me_3SiCl}} \mathrm{PhSi(OSiMe_3)_2OSi(OH)(OSiMe_3)Ph} \xrightarrow[\mathrm{C_5H_5N}]{\mathrm{Me_3SiCl}} \mathrm{PhSi(OSiMe_3)_2OSi(OSiMe_3)_2Ph}$$

The diphenyldisiloxanetetrol resembles the one other known disiloxanetetrol, namely the 1,3-dicyclohexyl derivative,[3] in being a rather reactive intermediate isolatable by conducting the hydrolysis of a trifunctional silane under very mild conditions. Presumably, the silanetriol[4] is formed first and then undergoes partial condensation to the disiloxanetetrol.

$$\mathrm{PhSi(OAc)_3} \xrightarrow{\mathrm{H_2O}} \mathrm{PhSi(OH)_3} \xrightarrow{-\mathrm{H_2O}} \mathrm{Ph(HO)_2SiO(OH)_2Ph}$$

Experimental

1,3-Diphenyldisiloxanetetrol.—A solution of 70 g. (0.25 moles) of phenyltriacetoxysilane in 70 ml. of ether was added slowly with stirring to 250 ml. of an ice–water slurry.[1] After 3 hr., the ethereal layer was separated, washed with ten 25-ml. portions of water, dried over sodium sulfate, and evaporated in a nitrogen stream. The partially crystalline residue was triturated with benzene and the insoluble solid washed and dried *in vacuo*, yielding 3.2 g. (9%), m.p. 114–114.5°. Reprecipitation from ethereal solution with hexane gave the raised m.p. 114.5–115°. The infrared spectrum (in *t*-butyl alcohol *vs.* *t*-butyl alcohol) showed a single ν_aSiOSi band at 1095 cm.$^{-1}$ (in contrast to the doublet seen in trisiloxanes[5]), very strong SiOH absorption around the 915-cm.$^{-1}$ solvent peak, and a weaker SiOH band at 850 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_{14}O_5Si_2$: C, 49.0; H, 4.8; mol. wt., 294. Calcd. for $C_{18}H_{20}O_7Si_3$: C, 50.0; H, 4.6; mol. wt., 432. Reported[1]: C, 49.3; H, 4.9; mol. wt., 433 (dioxane, 11°). Found: C, 49.4; H, 4.9; mol. wt., 301 ± 5% (1.060 g./l. in acetone, 25°).

3,5-Diphenyl-1,1,1,7,7,7-hexamethyl-5-trimethylsiloxytetrasiloxane-3-ol.—To a solution of 0.430 g. (1.46 mmole) of the tetrol in 50 ml. of ether was added 1.0 ml. (7.9 mmole) of trimethylchlorosilane and 1.0 ml. of pyridine. After stirring 1.5 hr., water was added to extract the hydrochloride; the ether layer was then washed with 1% HCl, then with water until neutral, dried over sodium sulfate, and evaporated. Distillation of the residue at 100° (0.02 mm.) yielded 0.400 g. (54%) of a thick liquid. Vapor phase chromatography on a 2-ft. SE-30 column showed 95% of this to be a single compound. An analytical sample of the major constituent was isolated by v.p.c. The infrared spectrum (in CS_2) showed a very strong ν_aSiOSi at 1059 cm.$^{-1}$ (possibly a doublet) with a weak shoulder near 1100 cm.$^{-1}$; the SiOH group gave bands at 3680 and 909 cm.$^{-1}$.

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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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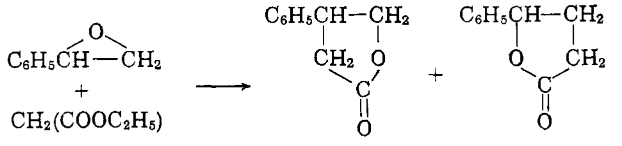
Received April 6, 1964

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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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.

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