in 72% yield as a colorless liquid, b.p. 94–96° (2 mm.); $n^{20}{}_{\mathrm{D}}$ 1.5425; $d^{20}{}_4$ 1.052; MR_{D} (calcd.)[10] 45.12, MR_{D} (obs.) 44.39; $\lambda_{\max}$ 263 mμ, log ε 3.62; $\lambda_{\min}$ 235 mμ, log ε 3.27.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.01; H, 8.16. Found: C, 80.74; H, 8.03.

The **N-(*p*-bromophenyl)-maleimide adduct** crystallized from methanol in colorless needles, m.p. 198–201°.

Anal. Calcd. for $C_{20}H_{18}O_3NBr$: C, 60.00; H, 4.53; N, 3.50. Found: C, 60.14; H, 4.54; N, 3.57.

BAKER LABORATORY OF CHEMISTRY
CORNELL UNIVERSITY
ITHACA, NEW YORK

Hydroxyalkylcyclosiloxanes

BY MAURICE PROBER

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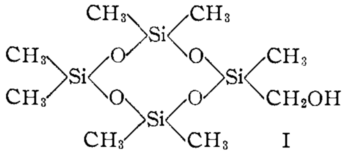
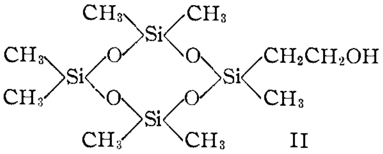
As part of a program on polar silicones, it was of interest to prepare cyclic tetramers containing hydroxyalkyl groups, notably hydroxymethylheptamethylcyclotetrasiloxane (I), and β-hydroxyethylheptamethylcyclotetrasiloxane (II).



I



II

Silicon compounds containing hydroxymethyl groups have been prepared by treating the chloromethyl compound with potassium acetate in acetic acid followed by methanolysis of the acetate.[1] With the chloromethyl cyclic tetramer, the reaction with potassium acetate–acetic acid led to ring opening and formation of polymeric siloxanes.[2] The preparation of I by neutral hydrolysis of the chloromethyl cyclic tetramer was unsuccessful.

Since the Grignard reagent of the chloromethyl cyclic tetramer has been described recently,[3] I was prepared by treating this reagent with oxygen; II was obtained by reaction with formaldehyde. The yields were low in both cases. Although improved yields are often obtained by coöxidizing a Grignard reagent in the presence of isopropylmagnesium bromide,[4] this technique did not increase the yield. Compound I is a crystalline solid, II a somewhat viscous liquid.

I and II were polymerized with ferric chloride and sulfuric acid and cross-linked gels were formed.[5]

Experimental

Hydroxymethylheptamethylcyclotetrasiloxane (I).—Grignard reagents were prepared from 92.1 g. (0.750 mole) of isopropyl bromide in 700 ml. of diethyl ether and 165.3 g. (0.500 mole) of chloromethylheptamethylcyclotetrasiloxane in 700 ml. of diethyl ether. The solutions were mixed and dry oxygen bubbled through the stirred solution for two hours. The solution was allowed to stand overnight and then poured into a 10% ammonium chloride solution containing a trace of sulfuric acid. The ether solution was washed with water, dried and distilled, yielding 78.4 g., b.p. 49–100° at 1.5 mm., with a 59.2-g. residue. Upon rectification of the distillate, there was obtained 24.7 g. of hydroxymethylheptamethylcyclotetrasiloxane, b.p. 55–58° at 0.5 mm., m.p. 52–56°, yield 16%. Recrystallized from Dry Ice-chilled pentane, m.p. 56–57°. Compound I (as a pure solid) exhibited a strong infrared absorption maximum for OH at 2.92 μ.

Anal. Calcd. for $C_8H_{24}O_5Si_4$: C, 30.73; H, 7.74. Found: C, 30.6; H, 7.7.

A 13% yield was obtained in the absence of isopropylmagnesium bromide.

β-Hydroxyethylheptamethylcyclotetrasiloxane (II).—The Grignard reagent was prepared from 264.6 (0.800 mole) of chloromethylheptamethylcyclotetrasiloxane in diethyl ether, the solution chilled to −30 to −40° and 21.0 g. (0.700 mole) of formaldehyde[6] was distilled in. The reaction mixture was stirred overnight, the temperature slowly rising to room temperature, followed by hydrolysis with dilute sulfuric acid. The ether solution was dried and distilled, yielding 190.7 g., b.p. 70–130° at 2.5 mm., and a 56.4-g. residue. Rectification of the distillate gave 28.5 g. of β-hydroxyethylheptamethylcyclotetrasiloxane, b.p. 112–114° at 9 mm., $n^{20}{}_{\mathrm{D}}$ 1.4163, $d^{20}{}_4$ 1.020; MR_{D} (calcd.) 80.96,[7] MR_{D} (obsd.) 80.42; yield 13%. II (as a pure liquid) exhibited a strong infrared absorption maximum for OH at 2.98 μ.

Anal. Calcd. for $C_9H_{26}O_5Si_4$: C, 33.09; H, 8.02. Found: C, 33.2; H, 8.3.

Polymerization.—Anhydrous ferric chloride and concentrated sulfuric acid (0.5% by weight) were used as catalysts.[8] The polymerizations were carried out at 80° except for the room temperature reaction of II and sulfuric acid. The polymers were gels which swelled but did not dissolve in toluene.

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[1] J. L. Speier, B. F. Daubert and R. R. McGregor, THIS JOURNAL, **70**, 1400 (1948); **71**, 1474 (1949).

[2] J. L. Speier, U. S. Patent 2,550, 205 (August 24, 1951).

[3] M. Prober, THIS JOURNAL, **77**, 3224 (1955).

[4] M. S. Kharasch and W. B. Reynolds, *ibid.*, **65**, 50 (1943).

[5] The cross linking is due to etherification or the formation of trifunctional silicon. The latter could result from the interaction of acid and alcohol to form carbonium ions which undergo silicon-carbon bond cleavage: F. C. Whitmore, L. H. Sommer, J. R. Gould and R. E. Van Strien, *ibid.*, **69**, 1551 (1947); L. H. Sommer and F. J. Evans, *ibid.*, **76**, 1186 (1954).

(6) Monomeric formaldehyde was prepared according to J. F. Walker, "Formaldehyde," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1953, p. 14. Although an excess of formaldehyde had been prepared, less than the stoichiometric amount was distilled into the reaction flask because of polymerization in storage at −78°.

(7) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 531 (1952); A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 177 (1954).

(8) J. Marsden and G. F. Roedel, U. S. Patent 2,469,883 (May 10, 1949).

RESEARCH LABORATORY
GENERAL ELECTRIC CO.
SCHENECTADY, NEW YORK

Studies on the Decarboxylation of Radioactive Glucuronolactone by *in vitro* Systems[1-3]

BY JOSEPH L. RABINOWITZ

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A soluble enzyme system from various tissues of the rat has been obtained which is capable of decarboxylating C^{14}-glucuronolactone as well as C^{14}-glucuronic acid. The concentration of this enzyme appeared to be highest in liver and kidney (Table I). Kidney appeared to be more constant in activity than did comparable liver preparations. Active extracts of the enzyme were obtained by treatment of kidney tissues with phosphate buffer at *p*H 7

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(1) The radioactive materials were obtained on allocation from the United States Atomic Energy Commission.

(2) The C^{14}-glucuronolactone uniformly labeled was obtained through the generosity of the Corn Products Refining Company.

(3) Aided by a grant from the Muscular Dystrophy Association of America, Inc.