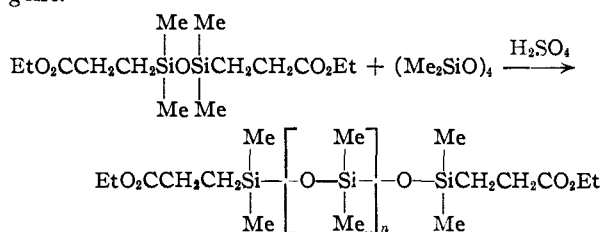


TABLE I

Cpd. no.	n	Mol. wt.	B.p., °C.		n _D ²⁰	d ₄ ²⁰	Calcd. MR _D	Found	Viscosity, Centistokes				A.S.-T.M. ^a slope	E (visc.), ^b cal./mole
			mm.						-50°	0°	25°	75°		
III	0	334.6	150	7	1.4340	0.9788	89.26	89.00	99.3	8.93	4.27	1.78	0.780	5540
IV	1	408.6	174	7	1.4288	.9787	108.1	107.7	82.9	8.89	4.77	2.11	.665	5020
V	2	482.8	186	7	1.4257	.9797	126.8	126.3	84.2	9.24	4.94	2.18	.655	5000
VI	3	556.8	190	4	1.4255	.9807	145.4	145.0	90.6	11.10	6.21	2.70	.600	4715

^a Slope on A.S.T.M. Standard Viscosity-Temperature Chart, Chart D, using centistoke viscosity data 32°F. to 167°F.; ^b E (visc.), energy of activation of viscous flow over the temperature range -50 to 25° with viscosities in centistokes, see ref. 4 for comparable data on linear dimethylsiloxanes with trimethylsiloxy end-groups.

siloxane chain. These substances were prepared by equilibration of a disiloxane diester with octamethylcyclotetrasiloxane (as the source of dimethylsiloxy units^{3,4}) using concd. sulfuric acid as the reagent.



It seems desirable to delay any extensive discussion of the physical properties of aliphatic organofunctional siloxanes until additional data on a wider variety of these substances can be accumulated. These data should furnish a more extensive and valid basis for comparison with physical properties of the polymethylpolysiloxanes on the one hand and purely organic compounds on the other.

However, even a brief examination of Table I gives clear indication of the interesting effects on physical properties produced by the inclusion of dimethylsiloxy units into an organic structure such as a diester. The decrease in refractive index with an increase in molecular weight and the almost constant density, when compounds III, IV, V and VI are compared, are two examples of these effects. The decrease in energy of activation for viscous flow, E (visc.), with increasing molecular weight, and the A.S.T.M. slope of compound VI which is lower than that of conventional purely organic diesters,⁵ are further indication that the diesters here reported are indeed new-type hybrid substances.

Experimental

Synthesis of Ethyl 4,4,6,6-Tetramethyl-4,6-disila-5-oxanonedioate (III).—In a 2-liter distillation flask were placed 375.6 g., 1.35 moles, of 4,4,6,6-tetramethyl-4,6-disila-5-oxanonedioic acid, 2 liters of absolute alcohol and 25 ml. of concd. hydrochloric acid. The flask was then placed under a fractionating column and the reaction mixture refluxed for 18 hours. The water-alcohol azeotrope was then slowly distilled during 20 hours. Fractionation of the residual material gave 407 g., 90.2% yield of the desired product, b.p. 153° at 6 mm., n_D²⁰ 1.4340.

Anal. Calcd. for C₁₄H₂₀Si₂O₅: Si, 16.7; sapon. equiv., 167. Found: Si, 16.6; sapon. equiv., 168.

Equilibration of Ethyl 4,4,6,6-Tetramethyl-4,6-disila-5-oxanonedioate with Octamethylcyclotetrasiloxane.—In a

500-ml. 3-necked flask fitted with a mercury-sealed stirrer and a Gilman sulfuric acid trap there were placed 258.5 g., 0.77 mole, of ethyl 4,4,6,6-tetramethyl-4,6-disila-5-oxanonedioate, 58.5 g., 0.198 mole, of octamethylcyclotetrasiloxane and 7.5 ml. of concd. sulfuric acid. The homogeneous reaction mixture was stirred for 15.5 hours at room temperature, 25 ml. of water was added and the contents of the flask stirred for 15 minutes. The aqueous layer, 34 ml., was separated and the organic layer was washed with 25 ml. each of 5% sodium bicarbonate solution and water. The product was partially dried with Drierite, 150 ml. of benzene was added and the remaining water was removed as water-benzene azeotrope. Fractionation gave: Ethyl 4,4,6,6-tetramethyl-4,6-disila-5-oxanonedioate (III), 103 g., 0.31 mole, 40% recovery. Ethyl 4,4,6,6,8,8-hexamethyl-4,6,8-trisila-5,7-dioxadecanedioate (IV), 65.2 g., 0.16 mole, 21% yield based on starting disiloxane diester. *Anal.* Calcd. for C₁₈H₂₆Si₃O₆: Si, 20.6; sapon. equiv., 204. Found: Si, 20.50; sapon. equiv., 201.

Ethyl 4,4,6,6,8,8,10,10-octamethyl-4,6,8,10-tetrasiloxane-5,7,9-trioxa-tridecanedioate (V), 38.5 g., 0.08 mole, 11% yield. *Anal.* Calcd. for C₁₈H₂₆Si₄O₇: Si, 23.3; sapon. equiv., 241. Found: Si, 23.2; sapon. equiv., 238.

Ethyl 4,4,6,6,8,8,10,10,12,12-decamethyl-4,6,8,10,12-pentasiloxane-5,7,9,11-tetraoxapentadecanedioate (VI), 17.8 g., 0.03 mole, 4.3% yield. *Anal.* Calcd. for C₂₀H₂₈Si₅O₈: Si, 25.2; sapon. equiv., 278. Found: Si, 25.7; sapon. equiv., 277.

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Unsaturated Seven-membered Heterocyclic Rings¹

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The limited knowledge of unsaturated seven-membered heterocyclic ring systems was recently pointed out by Brodrick and co-workers² who also described the preparation of derivatives of 1-oxa-4-azacyclohepta-2,4,6-triene.

In the course of the study of the reduction of di-(2-nitro-4-trifluoromethylphenyl) sulfone there were obtained three derivatives (I-III) of the ring system 1-thia-4,5-diazacyclohepta-2,4,6-triene. Of these three products the hydrazo compound III was difficult to purify because it seems to oxidize partially on exposure to air. The oxidation of III with air in the presence of alkali gave the azo com-

(1) Taken in part from the M.S. thesis of R. L. L., Duquesne University, 1952.

(2) C. I. Brodrick, M. L. Donaldson, J. S. Nicholson, W. F. Short and D. G. Wibberley, *J. Chem. Soc.*, 1079 (1953).

(5) E. M. Bried, H. F. Kidder, C. M. Murphy and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 484 (1947).

