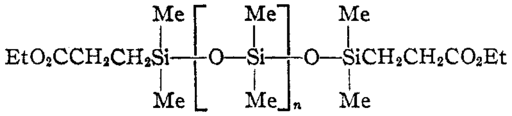
TABLE I

ORGANOSILOXANE DIESTERS

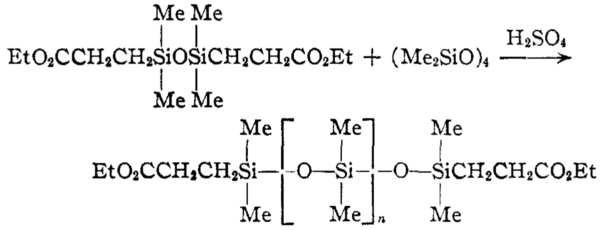


$$EtO_2CCH_2CH_2\overset{Me}{\underset{Me}{Si}}-\left[O-\overset{Me}{\underset{Me}{Si}}-\right]_n O-\overset{Me}{\underset{Me}{Si}}CH_2CH_2CO_2Et$$

Cpd. no.	n	Mol. wt.	B.p., °C.	B.p., Mm.	$n^{20}D$	d^{20}	MR_D Calcd.	MR_D Found	Viscosity, Centistokes −50°	0°	25°	75°	A.S.-T.M.[a] slope	E (visc.),[b] cal./mole
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.



$$EtO_2CCH_2CH_2\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}CH_2CH_2CO_2Et + (Me_2SiO)_4 \xrightarrow{H_2SO_4}$$

$$EtO_2CCH_2CH_2\overset{Me}{\underset{Me}{Si}}-\left[O-\overset{Me}{\underset{Me}{Si}}-\right]_n O-\overset{Me}{\underset{Me}{Si}}CH_2CH_2CO_2Et$$

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-oxanonanedioate (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-oxanonanedioic 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., $n^{20}D$ 1.4340.

Anal. Calcd. for $C_{14}H_{30}Si_2O_5$: Si, 16.7; sapn. equiv., 167. Found: Si, 16.6; sapn. equiv., 168.

Equilibration of Ethyl 4,4,6,6-Tetramethyl-4,6-disila-5-oxanonanedioate 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-oxanonanedioate, 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-oxanonanedioate (III), 103 g., 0.31 mole, 40% recovery. Ethyl 4,4,6,6,8,8-hexamethyl-4,6,8-trisila-5,7-dioxaundecanedioate (IV), 65.2 g., 0.16 mole, 21% yield based on starting disiloxane diester. *Anal.* Calcd. for $C_{16}H_{36}Si_3O_6$: Si, 20.6; sapn. equiv., 204. Found: Si, 20.50; sapn. equiv., 201.

Ethyl 4,4,6,6,8,8,10,10-octamethyl-4,6,8,10-tetrasila-5,7,9-trioxatridecanedioate (V), 38.5 g., 0.08 mole, 11% yield. *Anal.* Calcd. for $C_{18}H_{42}Si_4O_7$: Si, 23.3; sapn. equiv., 241. Found: Si, 23.2; sapn. equiv., 238.

Ethyl 4,4,6,6,8,8,10,10,12,12-decamethyl-4,6,8,10,12-pentasila-5,7,9,11-tetraoxapentadecanedioate (VI), 17.8 g., 0.03 mole, 4.3% yield. *Anal.* Calcd. for $C_{20}H_{48}Si_5O_8$: Si, 25.2; sapn. equiv., 278. Found: Si, 25.7; sapn. equiv., 277.

Acknowledgment.—We are very grateful to Dr. M. J. Hunter and Dr. A. J. Barry for generous help and stimulating discussion.

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Unsaturated Seven-membered Heterocyclic Rings[1]

BY H. HARRY SZMANT AND RONALD L. LAPINSKI

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The limited knowledge of unsaturated seven-membered heterocyclic ring systems was recently pointed out by Brodrick and co-workers[2] 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-

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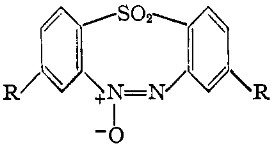
(5) E. M. Bried, H. F. Kidder, C. M. Murphy and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 484 (1947).

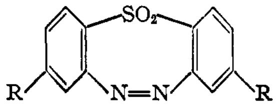
(1) Taken in part from the M.S. thesis of R. L. L., Duquesne University, 1952.

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

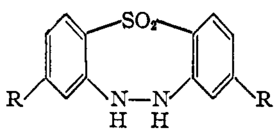
pound (II) which in turn was oxidized with peracetic acid to the azoxy compound I. The hydrazo compound III, or any of its higher oxidation products, could be catalytically hydrogenated or chemically reduced to di-(2-amino-4-trifluoromethylphenyl) sulfone.



I



II



III

(R = CF_3)

It is of interest to note that I and II are thermally quite stable and that they do not show any tendency to lose nitrogen or its oxides at their respective melting points (above 250°) and to produce thereby derivatives of dibenzothiophene. The hydrazo compound, on the other hand, is unstable and decomposes at its melting point (*ca.* 136°) rather violently. The instability of III is not necessarily due to the presence of a seven-membered ring since even simple compounds such as hydrazobenzene are known to decompose on heating.[3]

Experimental[4]

Di-(2-nitro-4-trifluoromethylphenyl) Sulfide. (A).—Potassium ethyl xanthate, 120 g., was added to a mixture of 158 g. of *m*-nitro-*p*-trifluoromethylchlorobenzene and 350 cc. of ethanol. After the initial vigorous reaction subsided the mixture was refluxed for two days. The precipitate was washed and crystallized from acetic acid to give a 40% yield of the desired sulfide, m.p. 146°.

(B).—A solution of 50.5 g. of sodium thiosulfate in 200 cc. of water was added dropwise to a vigorously stirred solution of 45 g. of 4-chloro-3-nitrobenzotrifluoride in 350 cc. of ethanol while the mixture was maintained at constant reflux. After an additional reflux period of six hours the sulfide was filtered, washed with water and ethanol. There was obtained a 61% yield of crude product m.p. 144°.

Anal. Calcd. for $C_{14}H_6O_4N_2SF_6$: C, 40.78; H, 1.47. Found: C, 40.92; H, 1.62.

Di-(2-nitro-4-trifluoromethylphenyl) Sulfone.—The sulfide, 151 g., was dissolved in 1 l. of glacial acetic acid and 50 g. of chromic anhydride was added slowly to the hot solution. The mixture was refluxed for 8 hours, poured on ice and the crude product m.p. 153–155° (86%) was crystallized from acetic acid to a constant melting point of 167–168°.

Anal. Calcd. for $C_{14}H_6O_2N_2SF_6$: C, 37.85; H, 1.36. Found: C, 38.11; H, 1.44.

The Hydrogenation of Di-(2-nitro-4-trifluoromethylphenyl) Sulfone.—A solution of 27 g. of the sulfone in 250 cc. of dioxane was hydrogenated in the presence of Raney nickel[5] until the pressure dropped 22 lb. from the initial pressure of 62.5 lb. The solution was filtered and concentrated and 14.5 g. of the hydrazo compound III separated as a white solid, m.p. 136–137°. This solid was crystallized from benzene and treated with charcoal but on exposure to air it turned yellowish and melted with violent decomposition. In spite of several attempts it could not be preserved in an analytically pure state.

Anal. Calcd. for $C_{14}H_8O_2N_2SF_6$: C, 43.98; H, 2.19. Found: C, 41.69; H, 2.41.

The filtrate from the hydrogenation mixture on further concentration yielded 1 g. of yellow azo compound II, m.p. 247–248° on crystallization from ispropyl alcohol.

Anal. Calcd. for $C_{14}H_6O_2N_2F_6$: C, 44.21; H, 1.59. Found: C, 43.70; H, 2.23.

The hydrazo compound III was also obtained in 37% yield by hydrogenating 5 g. of the sulfone in 200 cc. of isopropyl alcohol (pressure drop from 62.5 to 58.8 lb.).

The azoxy compound I was obtained when a solution of 2 g. of the sulfone in 300 cc. of isopropyl alcohol was hydrogenated in the presence of Raney nickel at atmospheric pressure until 2.8 moles of hydrogen were absorbed. The product (*ca.* 1 g.) on crystallization from isopropyl alcohol gave white crystals, m.p. 267–268°.

Anal. Calcd. for $C_{14}H_6O_3N_2SF_6$: C, 42.42; H, 1.53. Found: C, 42.65; H, 1.93.

Di-(2-amino-4-trifluoromethylphenyl) Sulfone.—The nitro sulfone, 20 g., was dissolved in 250 cc. of benzene and to the stirred solution there was added 100 cc. of water and 20 g. of iron powder. Hydrochloric acid, 2.5 cc. of 20% solution, was added in small portions to the heated mixture and stirring was continued for three hours. The hot mixture was filtered rapidly and from the benzene layer on concentration and cooling there was obtained a 5-g. yield of pure product, m.p. 133–136° after crystallization from benzene.

Anal. Calcd. for $C_{14}H_{10}O_2N_2SF_6$: C, 43.75; H, 2.62. Found: C, 43.77; H, 2.87.

The diamine, 1 g., was also obtained when 2 g. of the azo compound II was hydrogenated in the presence of Raney nickel. The hydrogenation was carried out under 62 lb. of hydrogen pressure and required 24 hours.

The Oxidation of II to I.—The azo compound II, 1 g., was dissolved in 20 cc. of glacial acetic acid and the solution was refluxed with 20 cc. of 40% peracetic acid until the yellow coloration faded. The mixture was poured on ice and upon crystallization from isopropyl alcohol there was isolated 0.7 g. of azoxy compound I, m.p. 267°.

The Oxidation of III to II.—Air was passed into an alcoholic solution of 3 g. of the hydrazo compound III containing a few drops of dilute alkali. After two hours the red solution was concentrated and cooled and there were obtained yellow crystals of the azo compound. After crystallization there was isolated 1.5 g. of product m.p. 247–248° identical with the product obtained from the hydrogenation of the dinitro sulfone.

Acknowledgment.—We wish to thank the Hooker Electrochemical Company for a generous supply of *m*-nitro-*p*-chlorobenzotrifluoride, and the Becco Sales Corporation for the gift of peracetic acid.

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[3] N. V. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford University Press, New York, N. Y., 1942, p. 384.

[4] The melting points are uncorrected. All microanalyses by Mr. George Stragand, University of Pittsburgh.

[5] The catalyst was prepared according to the directions of Covert and Adkins (THIS JOURNAL, **54**, 4116 (1932)), and the dioxane was purified as described by Vogel in "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., p. 175.

Dispiro(5.1.5.1)tetradecane[1]

BY H. M. WALBORSKY AND E. R. BUCHMAN

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Simple dispirane hydrocarbons have not previously been reported. A representative member of this class, dispiro(5.1.5.1)tetradecane (I), was prepared utilizing as starting material dispiro(5.1.5.1)tetradecan-7,14-dione (II) (formed by dimerization of pentamethyleneketene), which was available through the researches of J. R. Johnson and C. M. Hill.[2]

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[1] Presented before the Division of Organic Chemistry, American Chemical Society, at the Philadelphia Meeting, April, 1950. This research received support from the Office of Naval Research.

[2] C. M. Hill, Doctoral thesis, Cornell University, 1941.