plete in 30 minutes at 140°; in a preliminary run, the mixture turned deep red if heated longer. Evaporation of the solvent left a yellow gum, which was repeatedly triturated with petroleum ether and further evaporated to remove the last traces of decalin. Crystallization from 2 ml. of absolute ethanol in a Dry Ice–methanol-bath gave 0.12 g. of yellow solid, m.p. 43–50°; two more crystallizations gave colorless crystals of pure phenylanthranil, m.p. 53–53.5° (reported[3] 53°). The filtrates and residues gave 0.54 g. (53%) of the colorless mercuric chloride addition product from alcoholic mercuric chloride; m.p. 170–194° dec. Two crystallizations from acetone and one from ethanol raised the m.p. to 195–198° (reported[3] 200°).

α(?)-*o*-**Nitrophenylfuran.**—A suspension of 28 g. of *o*-nitroaniline in 125 ml. of 10% hydrochloric acid was diazotized slowly at 0–5° with a solution of 14.5 g. of sodium nitrite. Furan (400 g.) was then added, followed by the dropwise addition of 80 g. of sodium acetate in 200 ml. of water. After stirring for 3 hours at 0–5° and 72 hours at room temperature, the furan layer was separated, and the alkalized aqueous layer was extracted with ether. After distillation of the furan and ether from the combined extracts, steam was used to remove the slightly volatile reaction product, which was taken up with ether from the large volume of distillate. Evaporation of the dried ether solution left a yellow oil, wt. 5.9 g. (15.5%). Part of this was distilled for analysis at 108–110° (0.8 mm.); it partially crystallized on cooling below room temperature.

*Anal.* Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.73. Found: C, 63.61; H, 3.83.

α(?)-*o*-**Aminophenylfuran.**—α(?)-*o*-Nitrophenylfuran (*ca.* 2 g.) in 100 ml. of boiling methanol was reduced by the dropwise addition of 40 g. of sodium sulfide nonahydrate and 5 g. of sodium bicarbonate in 50 ml. of water dropwise. The filtered solution was concentrated to remove methanol, and then extracted repeatedly with ether. The addition of concd. hydrochloric acid to the combined extracts precipitated 1.10 g. of colorless needles, m.p. 195–210° with sublimation. This substance gave no color with ferric chloride, but could be diazotized to give an orange solution which coupled with β-naphthol to give a scarlet azo dye, m.p. 132–134°.

*Anal.* Calcd. for $C_{10}H_{10}ONCl$: C, 61.37; H, 5.14. Found: C, 61.56; H, 5.16.

The **benzenesulfonyl derivative** formed colorless crystals from aqueous alcohol, m.p. 95–96°.

*Anal.* Calcd. for $C_{16}H_{13}O_3NS$: C, 64.20; H, 4.38. Found: C, 63.98; H, 4.47.

The diazotized amine hydrochloride (0.56 g.) reacted with sodium azide to evolve gas and form a red-brown oil which may have been *o*-azidophenylfuran. Thermal decomposition in decalin at 180° gave a deep red solution, from which by evaporation, treatment with charcoal in methanol, and precipitation with water there was obtained 0.8 g. of a dull red powder, m.p. 105° dec. Recrystallization from hot methanol with the aid of charcoal gave 0.08 g. of pale red powder, m.p. 218–220° dec., which did not appear to be the expected furanoindole.

*Anal.* Found: C, 72.89; H, 4.71.

An attempt to deaminate the aminophenylfuran by the procedure of Kornblum and Iffland[15] gave at first an orange solution, from which only black tar could subsequently be isolated.

*o,o'*-**Diazidobiphenyl.**—*o,o'*-Dinitrobiphenyl[16] (10 g.) in 50 ml. of 95% ethanol was hydrogenated on a Parr shaker at 35 lb. pressure in the presence of 0.2 g. of platinum oxide catalyst. The solution was then filtered, acidified with hydrochloric acid, evaporated *in vacuo* to a turbid, orange residue, and treated with charcoal in water solution. The resulting yellow solution was tetrazotized and treated with sodium azide much as described for *o*-azidodiphenyl ether, giving 8.63 g. (89.5%) of tan crystals, m.p. 70–72°. Recrystallization from alcohol gave 7.94 g. (82.5%) of tan needles, m.p. 72–73°, and 72.5–73.5° after a second crystallization.

*Anal.* Calcd. for $C_{12}H_8N_6$: C, 61.02; H, 3.41. Found: C, 60.67; H, 3.51.

Heating small portions of the azide in 1,2,4-trichlorobenzene, kerosene or tetralin resulted in copious gas evolution, but from the residue after evaporation there was obtained only a dark solid, m.p. indefinite above 200°, which could neither be crystallized nor sublimed. Decomposition of the azide with near ultraviolet radiation gave similar results.

Decomposition of 2.0 g. of the azide in 20 ml. of warm 15% hydrogen bromide in glacial acetic acid[4] proceeded readily. Evaporation left an oily, brown residue which crystallized in part when triturated with ether. Treatment with charcoal in methanol and two crystallizations from methanol gave 0.5 g. of colorless, matted needles, m.p. 113–115°.

*Anal.* Calcd. for $C_{12}H_8Br_2N_4$: C, 39.13; H, 2.16. Found: C, 38.94; H, 2.24.

A primary aromatic amino group was indicated by diazotization and coupling to β-naphthol. When heated above its melting point, the material gave the deflagration characteristic of azides, and with cold, concentrated sulfuric acid it gave a gas and a purple solution. Halogen could be detected by the copper wire flame test, but not by silver nitrate. These results are consistent with the structure **2-amino-3,5-dibromo-2'-azidobiphenyl.**

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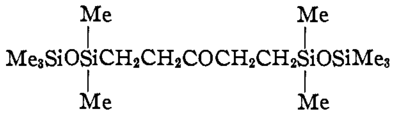
## Aliphatic Organo-functional Siloxanes. II. Diesters with Dimethyl-(β-carboethoxyethyl)-siloxy End Groups[1]

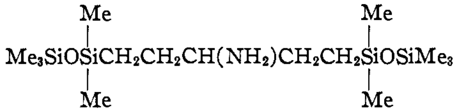
BY LEO H. SOMMER AND RICHARD P. PIOCH

RECEIVED JULY 29, 1953

In the first paper of a series dealing with aliphatic organo-functional siloxanes (organo-siloxanes having functional groups linked to carbon)[2] we reported the synthesis of compounds I and II.



$$Me_3SiO\overset{Me}{\underset{Me}{Si}}CH_2CH_2COCH_2CH_2\overset{Me}{\underset{Me}{Si}}OSiMe_3 \quad (I)$$



$$Me_3SiO\overset{Me}{\underset{Me}{Si}}CH_2CH_2CH(NH_2)CH_2CH_2\overset{Me}{\underset{Me}{Si}}OSiMe_3 \quad (II)$$

Compound I was prepared by equilibration of the appropriate polysiloxane–polyketone with hexamethyldisiloxane using concd. sulfuric acid as the reagent and following a procedure previously used for the preparation of trimethylsiloxy end-blocked dimethylpolysiloxanes.[3] Compound II resulted from equilibration of the appropriate polysiloxane–polyamine with hexamethyldisiloxane using potassium hydroxide in an isopropyl alcohol–water solvent.[4]

In both of the above compounds, the organo-functional polymer unit is difunctional and the monofunctional end-groups are the now conventional trimethylsiloxy units.

We now report the synthesis of *a series of new-type organosiloxanes having ester end-groups and dimethylsiloxy units as the difunctional portion of the*

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[15] N. Kornblum and D. Iffland, THIS JOURNAL, 71, 2137 (1949).

[16] R. C. Fuson and E. A. Cleveland, *Org. Syntheses*, 20, 45 (1940).

(1) Paper 35 in a series on organosilicon chemistry. For Paper 34, see THIS JOURNAL, 75, 3765 (1953).

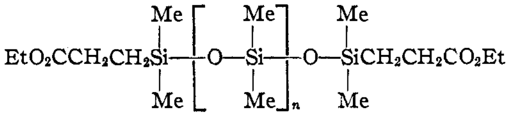
(2) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, 75, 2932 (1953).

(3) W. I. Patnode and D. F. Wilcock, *ibid.*, 68, 361 (1946).

(4) For the use of this reagent in the preparation of trimethysiloxy end-blocked dimethylpolysiloxanes see M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, 68, 2284 (1946).

TABLE I

ORGANOSILOXANE DIESTERS

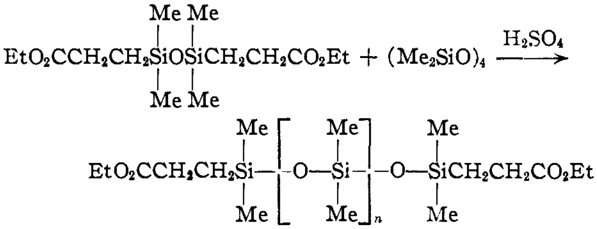


$$\mathrm{EtO_2CCH_2CH_2}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\left[-\mathrm{O}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}-\right]_n\mathrm{O}-\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{CH_2CH_2CO_2Et}$$

| 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° | Viscosity, Centistokes 0° | Viscosity, Centistokes 25° | Viscosity, Centistokes 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.



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

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

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

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## Unsaturated Seven-membered Heterocyclic Rings[1]

BY H. HARRY SZMANT AND RONALD L. LAPINSKI

RECEIVED JUNE 1, 1953

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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(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).