(IIa) in 50 ml of DMSO was added dropwise with ice-cooling 20 ml of 20% aqueous sodium acetate, followed by 50 ml of water. The solid which separated was filtered off, and washed with water and methanol. Recrystallization from dioxane gave 0.6 g of the solvate of (III) with dioxane, mp 227°C.

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SYNTHESIS OF TETRAORGANO-SUBSTITUTED SILANES WITH THE

BENZO[b]THIOPHENE MOIETY

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Catalytic dehydrocyclization of dimethyl(o-tolyl)- and dimethyl-4-(m-xylyl)-(benzo[b]thien-2-yl)silanes has given 11,11-dimethyl and 8,11,11-trimethyl-6,11-dihydro-11-silabenzo[b]naphtho[2,3-d]thiophenes, which were oxidized to the ketones. Previously unknown diorganobis(benzo[b]thien-2-yl)silanes have been obtained.

Organosilylated benzo[b]thiophenes have received little attention [1-4]. The availability of the starting benzo[b]thiophene, obtained in high yield from ethylbenzene and hydrogen sulfide over a chromium catalyst [5], has permitted silicon-containing compounds of this type, which are novel with respect to the nature of the substitution at the silicon atom, to be examined.

It has previously been shown possible [6] to carry out the catalyzed dehydrocyclization of organo-substituted silanes over chromic oxide catalysts. We here report the catalytic synthesis of some representatives of this new class of heterocyclic compounds containing the benzo[b]thiophene fragment (I) and a silicon atom in the ring. X-ray crystal

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Fig. 1. Molecular structure of (V).

studies of monocrystals have shown that the compounds obtained are 11,11-dimethyl- and 8, 11,11-trimethyl-6,11-dihydro-11-silabenzo[b]naphtho[2,3-d]thiophenes (IV, V). The formation of (IV) and (V) under the reaction conditions used is unexpected, and probably involves rearrangement of the starting (benzo[b]thien-2-yl)silanes (II) and (III) over the oxide catalyst. The assumption that this rearrangement resulted from thermal treatment was not confirmed in a control experiment. In the absence of a catalyst at 550-560°C, only small amounts (<5%) of cracking products (benzo[b]thiophene and silanes of unknown structure) were formed, the structure of the starting material remaining unchanged.



The molecular structure of (V) (Fig. 1) was determined directly using the MULTAN program, and refined in full-matrix anisotropic mode. Hydrogen atoms were localized from the Fourier synthesis, and refined in isotropic approximation. The elementary cell parameters were: a = 7.556 (1), b = 17.177 (2), c = 12.324 (1) Å. Space group Pbc2<sub>1</sub>, Z = 4.

The dehydrocyclization was carried out in a quartz tube in a flow system, the yields of liquid catalyzate being 75-80% and the content of target product being 30-35% according to GLC. The silanes (II) and (III) required for dehydrocyclization were obtained by successive treatment of benzo[b]thiophene (I) with n-butyllithium and dimethyl(o-tolyl)- or dimethyl-4-(m-xylyl)chlorosilane.

The methylene group in the dihydrosilanaphthalene fragment was readily oxidized by potassium permanganate in acetone to give the ketones (VI) and (VII) in high yields. Absorption for stretching vibrations of the -C=0 group were seen in the IR spectrum at 1630 cm<sup>-1</sup>.

Similarly, 2-Li-benzo[b]thiophene and the appropriate diorganodichlorosilanes gave the diorganobis(benzo[b]thien-2-y1)silanes (VIII-X). Compounds (VIII-X) were oxidized to the sulfones by 30% hydrogen peroxide in glacial acetic acid.



The IR spectra of the sulfones (XI-XIII) showed strong absorption for stretching vibrations of the  $SO_2$  group at 1300 and 1150 cm<sup>-1</sup>.

## EXPERIMENTAL

PMR spectra were obtained on a Bruker WM-250 in  $\text{CDCl}_3$ , internal standard TMS, mass spectra on a Hitachi M-80A, and IR spectra on a UR-20 spectrometer in KBr. Monocrystals were examined on an SAD-4 automatic four-circle diffractometer, with Mo Kaı irradiation, graphite monochromator, and w-scanning. TLC was carried out on Silufol UV-254 plates.

Com- pound	Empirical formula	mp,°C	М-	R <sub>j</sub> *	δ, ppm (without benzene ring protons**)	Yield, %
II	C <sub>17</sub> H <sub>18</sub> SSi	_	282	0,27	0,73 (s, 6H, SiCH <sub>3</sub> ); 2,42 (s, 3H.	85
111	C18H20SSi	6768	296	0,25	(1, 1) (\$, 6H, SiCH <sub>3</sub> ); 2,37 (d, 6H, CH); 2,37 (d, 6H)	72
IV	C17H16SSi	121 122	280	0,24	$(0.58(s, 6H, SiCH_3); 4.53(s, 2H, CH_3);$	20***
V	C <sub>18</sub> H <sub>18</sub> SSi	112 113	294	0,21	$(0.57 (s, 6H, SiCH_3); 2.40 (s, 3H, CH); 2.40 (s, 3H, CH); 2.40 (s, 3H, CH); 3.40 (s, 3H); 3.40 (s$	20
VI	C17H14OSSi	132 133	294	0,48	$(CH_3)$ ; 7,18 (S,111, 7-H) 0,65 (S, 6H, SiCH <sub>3</sub> ); 8,50 (m, 1H,	95
VII	C <sub>18</sub> H <sub>16</sub> OSSi	174 175	308	0,45	(7-H) $(0,62 (s, 6H, SiCH_3); 2,50 (s, 3H, CH_3); 7,66 (d, 1H, 10-H); 8,30 (s, 1H,$	95
VIII	C <sub>18</sub> H <sub>16</sub> S <sub>2</sub> Si	83 83,5	324	0,69	(1R, 7-R) 0.82 (s, 6H, SiCH <sub>3</sub> ); 7,64 (d, 2H,	67
IX X	C <sub>28</sub> H <sub>20</sub> S <sub>2</sub> Si C <sub>19</sub> H <sub>16</sub> S <sub>2</sub> Si	152 153 71 72	448 336	0,77 0,85	7,70 (d, 2H, 3·H, 3'-H) 7,70 (d, 2H, 3·H, 3'-H) 0,90 (s, 3H, SiCH <sub>3</sub> ); $6,056.68$ (m, 3H, CH=CH <sub>2</sub> ); $7,68$ (s, 2H, 3·H, 3-H)	63 60
XI	C <sub>18</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub> Si	241 242	388	—	3-H) 0.82 ( <b>s</b> , 6H, SiCH <sub>3</sub> ); 7.37 ( <b>m</b> , 2H, 7-H, 7'-H); 7.58 ( <b>m</b> , 2H, 3'-H); 7.72 ( <b>m</b> , 2H, 4'H)	90
XII	$C_{28}H_{20}O_4S_2Si$	285 286	512	—	7,38 (m, 2H, 4-H, 4-H); 7,67 (s, 2H, 2H, 7'-H); 7,67 (s, 2H, 4'-H); 7,67 (s, 2H, 4'	95
XIII	C <sub>19</sub> H <sub>16</sub> O <sub>4</sub> S <sub>2</sub> Si	187 188	400		(3-H), $(3-H)$ ; $(7,3 (M)$ , $2H$ , $4-H$ , $4-H$ ) $(9,2)$ (s, $3H$ , $SiCH_3$ ); $(6,17, 6.62 (M)$ , $3H$ , $CH=CH_2$ ); $(7,38 (M)$ , $2H$ , $7-H$ , (7'-H); $(7,62 (S)$ , $2H$ , $3-H$ , $3'-H$ ); $(7,75 (M)$ , $2H$ , $4-H$ , $4'-H$ )	85

TABLE 1. Physicochemical Characteristics of Products

\*Compounds (II-V) in hexane, (VI-VII) in 2:1 hexane—ethyl acetate, and (VIII-X) in 5:1 hexane—ethyl acetate. \*\*Multiplets at 7.20-7.95. \*\*\*Yields on silanes (II) and (III) reacting.

Liquid catalysis products were examined by GLC in a stream of helium on a chromatograph type LKhM-8MD (Special Construction Department, Institute of Organic Chemistry, Academy of Sciences of the USSR) with a catharometer, on a 3 m  $\times$  2 mm steel column packed with Chromatone N-DMCS with 5% SE, with temperature programming from 210-280°C at 20°C/min.

The properties of the products are given in Table 1. The elemental analyses of compounds (II-XIII) were in agreement with the calculated values for C, H, S, and Si.

<u>Dimethyl(o-tolyl)(benzo[b]thien-2-yl)silane (II).</u> To a solution of 10.9 g (81 mmole) of (I) in 150 ml of dry ether was added under dry argon a solution of 5.2 g (81 mmole) of butyllithium in 80 ml of hexane at -10 to -15°C over 30 min. The mixture was stirred at this temperature for 30 min, then cooled to -70°C and a solution of 16.7 g (90 mmole) of dimethyl(o-tolyl)chlorosilane in 20 ml of ether added. The mixture was stirred for 5 h, the temperature being gradually raised to 20°C, then kept for 12 h at 20°C and decomposed with 50 ml of saturated aqueous ammonium chloride. The ether layer was separated, dried over magnesium sulfate, and the residue after removal of the ether fractionated to give 19.5 g of the silane (II) as a colorless liquid, bp 156-157°C (3 mm),  $n_D^{2^\circ}$  1.6140.

<u>Dimethyl-4-(m-xylyl)(benzo[b]thien-2-yl)silane (III)</u> was obtained as for (II), by reacting 2-Li-benzo[b]thiophene with dimethyl-4-(m-xylyl)chlorosilane. bp 172-174°C (3 mm). Recrystallization from alcohol gave colorless crystals.

<u>11,11-Dimethyl-</u> and 8,11,11-Trimethyl-6,11-dihydro-11-silabenzo[b]naphtho[2,3-d]thiophenes (IV) and (V). A solution of 3.5 g (12.5 mmole) of the silane (II or III) in 20 ml of benzene was passed over the catalyst at a velocity  $v_{mass} = 0.5-0.7 h^{-1}$  at 550-560°C. When the reaction was complete, 10 ml of benzene was passed through. The residue (2.8 g) after removal of benzene from the catalyst was crystallized from alcohol to give 0.7 g of (IV) [or (V)] as colorless crystals.

 $\frac{11,11-\text{Dimethyl-} \text{ and } 8,11,11-\text{Trimethyl-}11-\text{silabenzo[b]naphtho[}2,3-d]\text{thiophen-}6-\text{ones}}{(\text{VI}) \text{ and }(\text{VII})}$ . To a solution of 0.5 g (1.8 mmole) of (IV) or (V) in 50 ml of acetone was added in small portions KMnO<sub>4</sub> until a persistent pink coloration was obtained. The

precipitated  $MnO_2$  was filtered off, the acetone removed, and the residue crystallized from alcohol to give 0.5 g of the ketone (VI) or (VII) as colorless crystals.

<u>Dimethyl-, diphenyl-, and methylvinylbis(benzo[b]thien-2-yl)silanes (VIII-X)</u> were obtained as for (II), by reacting 2-Li-benzo[b]thiophene with the appropriate diorganodichlorosilanes. Obtained as colorless crystals by recrystallization from alcohol.

Dimethyl-, diphenyl-, and methylvinylbis(benzo[b]thien-2-yl)silane S,S,S',S'-tetraoxides (XI-XIII). To a solution of 2 mmole of the diorganobis(benzo[b]thien-2-yl)silane in 15 ml of glacial acetic acid was added portionwise 6 ml of 30% hydrogen peroxide. The mixture was stirred for 5 h at 100°C, then cooled, the solid filtered off, washed with water, and crystallized from a 5:1 mixture of alcohol and benzene to give colorless crystals.

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