REACTION OF 2,3-DICHLOROBENZO[b]THIOPHENE 1,1-DIOXIDE WITH 3-AMINOPROPYLSILANES, 3-AMINOPROPYLSILOXANES, AND 3-AMINOPROPYLSILATRANE

V. É. Udre and É. Ya. Lukevits

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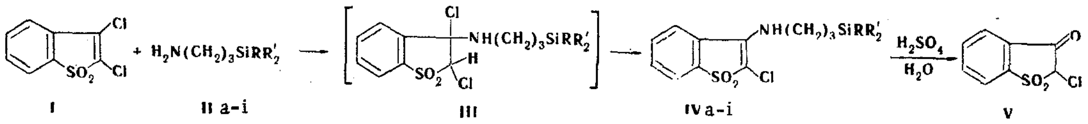
2-Chloro-3-[γ-(organosilyl)propylamine]benzo[b]thiophene 1,1-dioxides are formed in the reaction of 2,3-dichlorobenzo[b]thiophene 1,1-dioxide with 3-aminopropylsilanes, 3-aminopropylsiloxanes, and 3-aminopropylsilatrane.

Continuing our investigation of nucleophilic addition to 2,3-dichlorobenzo[b]thiophene 1,1-dioxide (I) [1], which is an effective fungicide [2, 3], we decided to study the reaction of I with 3-aminopropylsilanes, which display antimicrobial activity [4, 5], in order to obtain organosilicon derivatives of benzo[b]thiophene and to determine the fungistatic activity of the compounds obtained.

When I is refluxed with trialkyl(3-aminopropyl)silanes, heptamethyl-3-(γ-aminopropyl)trisiloxane, 3-aminopropyltriethoxysilane, and 1-(γ-aminopropyl)silatrane (in a molar ratio of 1 : 3) in benzene for 3 h, 2-chloro-3-[γ-(organosilyl)propylamino]benzo[b]thiophene 1,1-dioxides (IV) and the hydrochlorides of the corresponding 3-aminopropylsilanes or 3-aminopropylsilatrane (Table 1) are formed in yields of 60-70%:



We were unable to obtain the assumed intermediate (III). Lowering of the temperature from 80 to 20°C and changing the molar ratio of the reagents to 1 : 1 led only to a considerable decrease in the yield of IV. Addition of the aminoalkylsilanes and dehydrochlorination apparently proceed simultaneously.

The structure of IV was established by their acid hydrolysis to 3-oxo-2-chloro-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (V) and was confirmed by the IR spectra, which contain the following absorption bands: $\nu_{=CN}$ at 1275-1285 cm^{-1}, ν_{NH} at 3360-3390 cm^{-1}, ν_{SO_2} at 1335-1340 and 1160 cm^{-1}, and δ_{CHSi} at 1260-1270 cm^{-1}. The absorption band at 578 cm^{-1} for IVi can be assigned to the stretching vibrations of the Si ← N bond [6].

Compound V was also formed in an attempt to obtain the hydrochlorides of IV by the action of alcoholic hydrogen chloride.

Compound I and all of the aminoalkylsilanes (IIa-h) used suppress the growth of the pathogenic fungi Candida albicans 17/846, Epidermophyton Kaufmann-Wolf 41, and Trichophyton gypseum 4/3. The minimum concentration that suppresses the growth of the fungi is 55.6, 3.5, and 6.9 μg/ml for I, respectively, and 7.8, 15.6, and 7.8 μg/ml for diethylamyl derivative IIg. However, the introduction of an aminopropylsilyl grouping (in place of the 3-aminopropyltriethoxysilyl grouping) into the I molecule deprives it of its fungistatic activity.

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Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 493-494, April, 1973. Original article submitted March 29, 1972.

TABLE 1. 2-Chloro-3-[γ-(organosilyl)propylamino]benzo[b]thiophene 1,1-Dioxides (IVa-i)

Compound	R	R′	mp, °C	Empirical formula	Found, %			Calc., %			
					C	H	N	C	H	N	
IVa	CH_3	C_4H_9	149	$C_{20}H_{32}ClNO_2SSi$	57,8	8,0	3,4	58,0	7,8	3,4	57
IVb	CH_3	$(CH_3)_3SiO$	152	$C_{18}H_{32}ClNO_4SSi_3$	46,5	6,9	3,0	46,7	6,7	2,9	58
IVc	C_2H_5	C_5H_{11}	129	$C_{23}H_{38}ClNO_2SSi$	60,8	8,6	3,1	60,6	8,4	3,1	68
IVd	C_2H_5	C_2H_5	178	$C_{17}H_{26}ClNO_2SSi$	54,9	7,3	3,8	54,9	7,1	3,8	73
IVf	C_3H_7	C_2H_5	172	$C_{18}H_{28}ClNO_2SSi$	56,3	7,4	3,5	56,0	7,3	3,6	70
IVg	C_4H_9	C_2H_5	163	$C_{19}H_{30}ClNO_2SSi$	56,5	7,5	3,5	57,1	7,6	3,5	70
IVh	C_5H_{11}	C_2H_5	145	$C_{20}H_{32}ClNO_2SSi$	58,0	7,9	3,0	58,0	7,8	3,3	68
IVi	C_2H_5O	C_2H_5O	137	$C_{17}H_{26}ClNO_5SSi$	48,8	6,3	3,2	48,6	6,2	3,3	56
IVj	$(OCH_2CH_2)_3N$		226—228	$C_{17}H_{23}ClN_2O_5SSi$	47,6	5,3	6,6	47,4	5,4	6,5	79

EXPERIMENTAL

2-Chloro-3-[γ-(organosilyl)propylamino]benzo[b]thiophene 1,1-Dioxides (IVa-h) (see Table 1). A solution of 4 mmole of I [7] and 12 mmole of II in 15 ml of dry benzene was refluxed for 3 h, after which it was filtered and the solvent was partially removed by distillation. The precipitated IV was washed with hexane and recrystallized from benzene–hexane.

2-Chloro-3-[γ-(1-silatranyl)propylamino]benzo[b] thiophene 1,1-Dioxide (IVi). A solution of 4 mmole of I and 12 mmole of IIi [8] in 20 ml of dry benzene was refluxed for 3 h, after which the precipitate was removed by filtration, washed with water, and recrystallized from dimethylformamide.

3-Oxo-2-chloro-2,3-dihydrobenzo[b]thiophene 1,1-Dioxide. This compound was obtained by hydrolysis of IV with 6 N H_2SO_4 [1] and had mp 154-155° and ν_{CO} 1740 cm^{-1}.

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