butylphenoxytrimethylgermane (VII), which was identified by comparing its retention time with the retention time of an authentic specimen, which was obtained by treating 2-triphenylsilyl-4-tert-butylphenol with diethyltrimethylgermylamine in CH_3CN. The IR spectrum of (VII) has a band at 1250 cm^{-1}, which is characteristic for $Ph{-}O{-}Ge$. Hydrolysis of the reaction mixture with sodium methoxide gave 2-triphenylsilyl-4-tert-butylphenol, mp 138°. The mixed melting point of the hydrolysis product with the authentic specimen is not depressed.

CONCLUSIONS

1. 2-Triphenylsilyl-4-tert-butyl-6-trimethylgermylphenol was obtained, which when oxidized with potassium ferricyanide in alkaline medium, and also when heated (200°), undergoes rearrangement with a migration of the $(CH_3)_3Ge$ group from the ring to the hydroxyl oxygen.

2. The stability is increased when the $SiMe_3$ group in a mixed phenol that contains both Si and Ge is replaced by $SiPh_3$.

3. The migration ability of the groups in phenoxyl radicals increases in the order: $SiPh_3 < SiMe_3 < GeMe_3$.

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PREPARATION OF 2-CHLOROETHYL ALKYL SULFONES BY THE ADDITION OF ALKANESULFONYL CHLORIDES TO ETHYLENE

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The synthesis of 2-chloroethyl aryl(alkyl) sulfones by the addition of aryl- and alkanesulfonyl chlorides to unsaturated compounds using for initiation the free radicals of oxidation–reduction systems, which include catalysts of the Friedel–Crafts type [1], and also iron [2] and copper [2-5] salts, has been studied quite extensively. However, information is lacking on the addition of the higher alkanesulfonyl chlorides to ethylene. It seemed of interest to determine if this method can be used to synthesize 2-chloroethyl alkyl sulfones of type $RSO_2CH_2CH_2Cl$, where R is a C_4–C_{10} alkyl radical.

We were able to add the higher alkanesulfonyl chlorides to ethylene and obtain the desired 2-chloroethyl alkyl sulfones by using $CuCl_2$, or their mixture, as the catalysts, in the presence of $Et_3N{\cdot}HCl$, and using a mixture of CH_2Cl_2 and CH_3CN as the medium. The reaction was run in an autoclave at 130-160°C and a pressure of 30-45 atm. The composition of the reaction products and their yields were determined by GLC (Tables 1 and 2).

In the presence of Cu_2Cl_2 the synthesis of the 2-chloroethylalkyl sulfone is accomplished by the scheme: (See 1, 2 and 3; next page)

The presence of $Et_3N{\cdot}HCl$ facilitates solution of the copper salts due to the formation of the more soluble complex $([CuCl_4^{2-}]\cdot[Et_3NH^+]_2)$ [6]. Copper salts in this form are more active catalysts, which facilitates the progress of the oxidation–reduction steps (1) and (3).

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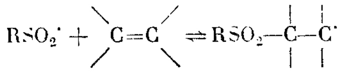
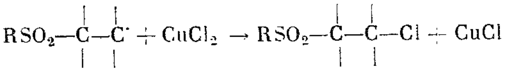
$$RSO_2Cl + CuCl \rightleftharpoons RSO_2^{\cdot} + CuCl_2 \quad (1)$$



$$RSO_2^{\cdot} + \mathrm{>C{=}C<} \rightleftharpoons RSO_2\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}^{\cdot} \quad (2)$$



$$RSO_2\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}^{\cdot} + CuCl_2 \rightarrow RSO_2\text{—}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}\text{—}Cl + CuCl \quad (3)$$

The optimum conditions were selected on the example of the reaction of butanesulfonyl chloride with ethylene. It was found that the character of the copper catalyst ($CuCl_2$, Cu_2Cl_2, or their mixture) has little affect on the process, and the yield of 2-chloroethyl butyl sulfone reaches 90-95% when based on reacted butanesulfonyl chloride (see Table 1), at a 35-40% conversion of the latter. The optimum amount of catalyst is 8 mole % when based on butanesulfonyl chloride taken for reaction (see Table 2), and here the optimum time and temperature are respectively 5-6 h and 140-150°C (see Table 1). The temperature has an important effect on the process. Thus, the alkanesulfonyl chloride does not add to ethylene at 130°C. An increase in the temperature to 170° leads to a decrease in the yield of the desired product, which is associated with the instability of the alkanesulfonyl chloride under these conditions. An increase in the reaction time above 6 h and an increase in the amount of catalyst above 8 mole % have a similar effect on the yield of the desired product. For the quantitative analysis of the higher 2-chloroethyl alkyl sulfones it is expedient to use the smooth dehydrohalogenation reaction, which leads to alkyl vinyl sulfones. The latter are also formed under the conditions of analyzing the higher 2-chloroethyl alkyl sulfones by GLC. In Table 1, on the example of adding butanesulfonyl chloride to ethylene, it was shown that this method gives good agreement with the direct analysis of 2-chloroethyl butyl sulfone by GLC. Under the optimum conditions the higher alkanesulfonyl chlorides also give the 2-chloroethyl alkyl sulfones in 90-95% yield when based on reacted alkanesulfonyl chloride, at a 35-40% conversion of the latter.

TABLE 1. Addition of Butanesulfonyl Chloride to Ethylene (butanesulfonyl chloride: ethylene: copper salt: $Et_3N \cdot HCl = 1:100:8 \cdot 10^{-2}:12 \cdot 10^{-2}$ (moles); molar ratio of $CH_2Cl_2:CH_3CN = 4:1$)

Expt. No.	T., °C	Time, h	Butanesulfonyl chloride conversion, %	Yield of 2-chloroethyl butyl sulfone, %	
				method A*	method B†
			$CuCl_2$ (8 mole %)		
1	130	5	12	0	–
2	140	5	34	31	34
3	140	6	58	44	44
4	150	5	62	41	41
5	160	5	93	53	56
			Cu_2Cl_2 (8 mole %)		
6	130	5	29	0	–
7	140	5	54	26	26
8	140	6	72	23	27
9	150	5	–	35	31
10	160	5	97	39	42
			$CuCl_2 : Cu_2Cl_2 = 1 : 1$ (8 mole %)		
11	130	5	29	0	–
12	140	5	26	25	28
13	140	6	60	38	37
14	150	5	68	41	36
15	160	5	98	42	39

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*Determined directly by GLC.

†Determined by GLC as butyl vinyl sulfone.

TABLE 2. Addition of Alkanesulfonyl Chloride to Ethylene (alkanesulfonyl chloride: ethylene = 0.5:50 (mmoles); 1.5 times excess $Et_3N \cdot HCl$ when based on $CuCl_2$ taken for reaction; 150°; 6 h)

R	$CuCl_2$, mole %	Solvent (mole ratio $\cdot 10^{-3}$)		Yield of 2-chloroethyl alkyl sulfone, %		n	S	Sr
		CH_3CN	CH_2Cl_2	method A	method B			
C_4H_9	2	0.3	8	18	–	2	0.4	2.2
C_4H_9	4	0.3	8	22	–	3	1.2	5.5
C_4H_9	8	0.3	8	42	–	3	0.7	1.7
C_4H_9	8	2	8	43	39	4	2.5	5.8
C_8H_{17}	8	2	8	–	33	3	1.2	3.6
C_9H_{19}	8	2	8	–	28	4	2.1	7.5
$C_{10}H_{21}$	8	2	8	–	38	3	1.4	3.7

Designations: n = no. of repeat experiments; S = standard deviation; Sr = relative standard deviation (%) with a reliability of $\alpha = 0.95$.

EXPERIMENTAL

The alkanesulfonyl chlorides were obtained as described in [7]. The butanesulfonyl chloride was purified by vacuum-distillation. The octane-, nonane-, and decanesulfonyl chlorides were purified by low-temperature crystallization. The 2-chloroethyl alkyl sulfones and alkyl vinyl sulfones were obtained as described in [8]. The reaction products were analyzed by GLC on an LKhM-8MD instrument equipped with a flame-ionization detector. The other conditions were: 1500 × 3 mm column packed with 10% Silicone E-301 deposited on Chromosorb W (60-80 mesh), a temperature of 180-240°, a helium flow rate of 30 ml/min, and pentadecane as the internal standard. The experimental data were processed and the chromatograms were calculated as described in [9].

2-Chloroethyl Butyl Sulfone. A fluoroplastic cassette was placed in a rotated 0.25-liter steel autoclave on four 3.5-ml glass test tubes, into each of which were charged 0.67 ml of a solution, prepared from 14.5 g (0.093 mole) of butanesulfonyl chloride and 4 g of pentadecane in 50 ml of CH_2Cl_2, and 0.12 ml of catalyst, which was obtained by dissolving 0.1 g of $CuCl_2$ and 0.155 g of $Et_3N \cdot HCl$ in 1 ml of CH_3CN. The autoclave was first purged with ethylene, which was then brought up to an initial pressure of 33 atm (butanesulfonyl chloride:ethylene mole ratio ≈ 1:100), and the autoclave was heated for 5 h at 140°. Then the autoclave was cooled, the excess ethylene was removed, and the reaction products in each tube were extracted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and analyzed by GLC (see Table 1, Expt. 2, Method A).

Butyl Vinyl Sulfone. After removal of the CH_2Cl_2, to each of the obtained reaction products were added 1 ml of benzene and 0.28 g (2.8 mmoles) of Et_3N, and the mixture was heated to 45-50° and then kept at this temperature for 0.5 h. After the usual workup, the butyl vinyl sulfone was analyzed by GLC (see Table 1, Method B).

The other 2-chloroethyl alkyl solfones and corresponding alkyl vinyl sulfones were synthesized in a similar manner. Statistical processing as described in [10] disclosed that the relative error of determining the most probable value with a reliability of $\alpha = 0.95$ does not exceed 7.5 rel. % (see Table 2).

CONCLUSIONS

A study was made of the addition of alkanesulfonyl chlorides to ethylene under pressure in the presence of $CuCl_2$, Cu_2Cl_2, and their mixtures, and it was shown that here the corresponding 2-chloroethyl alkyl sulfones are formed in 90-95% yield when based on reacted alkanesulfonyl chloride, with a 35-40% conversion of the latter.

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SYNTHESIS AND STUDY OF DIVALENT PALLADIUM DIETHYLENETRIAMINEPENTAACETATES

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Divalent palladium is capable of complexing with diethylenetriaminepentacetic acid (DTPA, H_5L) to give complexes with a Pd:L ratio = 1:1 [1, 2]. The reaction of Pd(II) with DTPA in solutions containing over 10^{-3} M of Pd(II) has hardly been studied, and the corresponding complexes have not been isolated in the solid state. The complexing of Pd(II) with DTPA in the presence of halide ions has not been studied. The purpose of the present paper is to synthesize and study the complexes of Pd(II) with DTPA.

EXPERIMENTAL

To synthesize $H_3PdL \cdot 5H_2O$, 1.96 g of DTPA was added to a suspension of $Pd(OH)_2$ that had been obtained by treating a solution of 1.65 g of K_2PdCl_4 in 50 ml of water with a solution of 1.1 g of KOH in 10 ml of water, followed by thorough washing to remove the Cl^-. The obtained mixture was heated on the water bath for 1 h. The obtained red solution was filtered and allowed to crystallize at ∿20°C. After 3 h the obtained precipitate (fine yellow plates) was filtered, and washed in succession with water, alcohol, and ether. Yield 93%. The analysis results for the obtained compound are given in Table 1.

To synthesize $H_4PdLCl \cdot 3H_2O$, a solution of 3.93 g of DTPA, obtained by dissolving in 50 ml of hot water, was added to a solution of 3.27 g of K_2PdCl_4 in 50 ml of water. The obtained orange solution was heated on the water bath for 20 min and then cooled. Here a bulky, light yellow flocculent precipitate deposited from solution. The obtained compound (see Table 1)

TABLE 1. Elemental Analysis Results for Complexes of Pd(II) with DTPA

Compound	Found, %				Calculated, %			
	Pd	H	C	Hal	Pd	H	C	Hal
$H_3PdL \cdot 5H_2O$	17.80	5.45	28.88	–	18.10	5,27	28,58	–
$H_4PdLCl \cdot 3H_2O$	18.34	4.81	28.42	6.39	18.09	4.76	28.56	6,02
$H_4PdLBr \cdot 3H_2O$	16.67	4.23	26.97	12.75	16,82	4.43	26,55	12,63

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