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Gas-Phase Reaction of Anisole and Phenol with Tetrachlorogermane in the Presence of Hexachlorodisilane

E. A. Chernyshev, V. G. Bykovchenko, N. G. Komalenko, G. N. Yakovleva, and M. M. Simakina

State Research Institute of Chemistry and Technology of Organoelement Compounds
State Research Center, Moscow, Russia

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Abstract — Gas-phase reaction of anisole with tetrachlorogermane in the presence of hexachlorodisilane was studied. The major reaction products are chloro(phenoxy)silane, trichloro(phenoxy)germane, 1,1,3,3-tetrachloro-1,3-disila-2-oxaindane, and 1,1,3,3-tetrachloro-1,3-digerma-2-oxaindane. The same products are formed with phenol instead of anisole. A mechanism of the reactions of anisole with $GeCl_4$ and Si_2Cl_6 is proposed, that takes account of the formation in the reaction zone of dichlorosilylenes and dichlorogermylenes.

The new field in organometallic synthesis is associated with the use of carbene analogs, dichlorosilylenes and dichlorogermylenes, short-lived active particles [1]. They are widely used in syntheses involving insertion into the C–Cl bond to form trichlorosilyl and trichlorogermyl aromatic compounds [1, 2]. The information concerning insertion of dichlorosilylenes and dichlorogermylenes into the C–O bond is scarce [1, 3]. However, such reactions present interest as a promising synthetic route to a variety of heterocyclic organometallic compounds hardly available by other methods [3].

Here we report the results of our study on the reactions of anisole and phenol with $GeCl_4$ in the presence of Si_2Cl_6. The latter served as a source of dichlorosilylene [4, 5]. Dichlorogermylenes were generated by our developed procedure involving reaction of $GeCl_4$ in the presence of Si_2Cl_6 [2, 6].

Dichlorosilylenes are generated by reaction (1) on pyrolysis of Si_2Cl_6 [4, 5]. Dichlorogermylenes are generated by reactions (1) and (2) [2, 6].

$$Cl_3SiSiCl_3 \longrightarrow :SiCl_2 + SiCl_4, \qquad (1)$$

$$GeCl_4 + SiCl_2 \longrightarrow [Cl_3GeSiCl_3] \longrightarrow :GeCl_2 + SiCl_4. \qquad (2)$$

The reactions of anisole with Si_2Cl_6 in the gas phase at 500 and 550°C gave trichloro(phenoxy)silane (**I**) and 1,1,3,3-tetrachloro-1,3-disila-2-oxaindane (**II**). The yields of products **I** and **II** at 500°C are low (0.4–1.5%), while at 550°C they increase to 27 and 19%, respectively (see table).

The reactions of anisole with $GeCl_4$ in the presence of Si_2Cl_6 at 550 and 600°C form organosilicon products **I** and **II**, as well as organogermaniums: trichloro(phenoxy)germane (**III**) and a heterocyclic compound, 1,1,3,3-tetrachloro-1,3-digerma-2-oxaindane (**IV**) (see table).

A heterocyclic compound containing both silicon and germanium atoms, 1,1,3,3-tetrachloro-1-germa-3-sila-2-oxaindane (**V**), is also formed.

As the temperature is raised from 550 to 600°C, the yield of organosilicon products **I** and **II** changes

Conditions and yields of reactions of anisole and phenol with $GeCl_4$ and Si_2Cl_6 (reaction time 30–40 s)

PhOMe : Si_2Cl_6 : $GeCl_4$ mole ratio	Temperature, °C	Yield[a], %[b]				
		I	**II**	**III**	**IV**	**V**
1 : 1 : 0	500	0.4	1.5	–	–	–
1 : 1 : 0	550	26.6	19.2	–	–	–
2 : 1 : 2	550	23.1	15.4	2.9	13.6	1.6
2 : 1 : 2	600	28.9	14.8	1.1	8.5	1.3
2[c] : 1 : 2	550	0.6	2.1	0.3	1.2	0.5

[a] Per starting Si_2Cl_6. [b] The condensate also contains phenol and diphenyl oxide. [c] Phenol.

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inconsiderable, whereas the yield of organogermanium compounds **III**–**V** decreases, which is probably associated with thermolysis of the latter (see table).

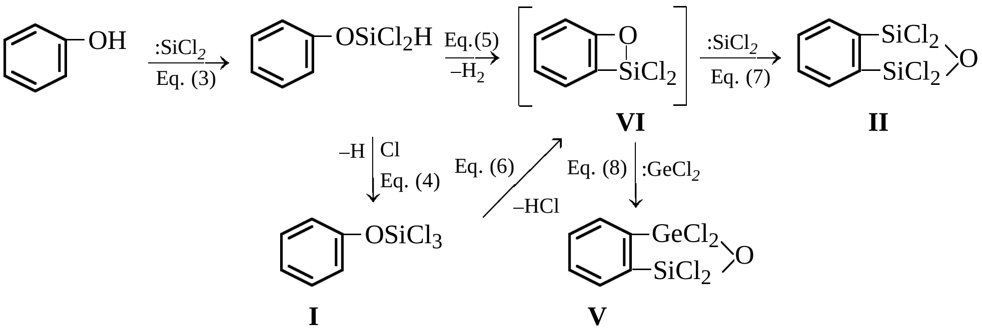
Note that the reactions at 550 and 600°C also afford phenol: The degree of conversion of the starting anisole into phenol is more than 30%.

To find out what is the role of phenol in the process, we performed an experiment at 550°C with phenol, $GeCl_4$, and Si_2Cl_6 as starting reagents (see table). As seen from the table, this reaction gives rise to compounds **I**–**V**, like in the experiment with anisole but in much lower yields.

Among products of the reaction with phenol we found much diphenyl oxide: The degree of conversion of phenol into this product in the reaction at 550°C within 35 s is 35%. Such a conversion of phenol undoubtedly involves liberation of water, and, as a consequence, partial hydrolysis of hexachlorosilane. As a result, reactions (1) and (2) are retarded and produce a little $:SiCl_2$ and $:GeCl_2$, thus decreasing the yield of compounds **I**–**V**.

The formation of compounds **I**, **II**, and **V** is described by reactions (3)–(8) in Scheme 1. The major reactive species are dichlorosilylenes formed by reaction (1). Their reaction with phenol [reaction (3)] provides dichloro(phenoxy)silane that can then convert by reaction (4) into trichloro(phenoxy)silane (**I**) or cyclize with hydrogen evolution into unstable compound **VI** [reaction (5)]. Note that compound **VI** can also be formed by reaction (6) via HCl abstraction from compound **I**. Further on $:SiCl_2$ or $:GeCl_2$ can insert into the C–O bond of unstable compound **VI** to give compound **II** or **V** [reactions (7) and (8)].

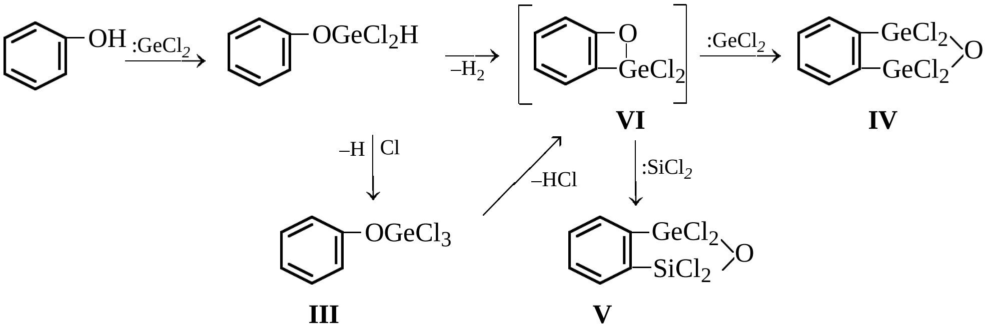
Scheme 1.



It should be noted that reaction (3) has been considered in [7] and reactions (5) and (7), in [3]. It was previously established that compounds comprising SiClH moieties undergo a fairly fast gas-phase conversion into trichlorosilyl derivatives [7] [reaction (4)].

Scheme 2 shows reactions forming compounds **III**–**V**. It is similar to Scheme 1 with the only difference that here the major reactive species are, instead of dichlorosilylenes, dichlorogermylenes formed by reactions (1) and (2).

Scheme 2.



Schemes 1 and 2 fairly describe the formation of compounds **I**–**V** from phenol, $GeCl_4$, and Si_2Cl_6 as starting compounds (see table). With anisole instead of phenol, schemes 1 and 2 are complicated. In this case one should additionally account for anisole pyrolysis reactions.

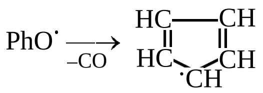
We found no experimental data on pyrolytic transformations of anisole. The only available information concerns bond strengths in this molecule (the PhO–CH_3 and Ph–OCH_3 bond energies are 248 and 403 kJ mol^{-1}, respectively) [8]. Consequently, anisole should primarily cleave by the PhO–CH_3 bond [reaction (9)] that is weaker by 155 kJ mol^{-1} than the Ph–OCH_3 bond.

$$PhOCH_3 \longrightarrow PhO^{\cdot} + {}^{\cdot}CH_3. \qquad (3)$$

This conclusion is nicely consistent with the experimental thermolytic data for the closest analog of anisole, phenetole [9]. Thermolysis of the latter begins with PhO–C_2H_5 bond cleavage [9].

$$PhOC_2H_5 \longrightarrow PhO^{\cdot} + {}^{\cdot}C_2H_5.$$

The phenoxyl radicals formed by reaction (9) can take part in various reactions. Thus, they can decompose with expulsion of CO and formation of the cyclopentadienyl radical [9].



The phenoxyl radicals can also abstract hydrogen from various hydrogen-containing molecules (RH) to form phenol.

$$PhO^{\cdot} + RH \longrightarrow PhOH + {}^{\cdot}R.$$

The reactions of the latter with :$SiCl_2$ and :$GeCl_2$ were considered in Schemes 1 and 2.

Thus, we found out that phenol plays an important role in the formation of organosilicon and organogermanium compounds in the reaction of anisole with $GeCl_4$ in the presence of hexachlorodisilane.

EXPERIMENTAL

The starting compounds and reaction products were analyzed by GLC on an LKhM-80 chromarograph with a thermal conductivity detector, carrier gas helium (30 ml min^{-1}), stainess-steel columns (200 × 0.3 cm) packed with 5% SE-30 on Chromaton N-AW-DMCS (0.25–0.31 mm). The oven temperature was programmed from 30 to 250°C at a rate of 12 deg min^{-1}. Identification was performed by GC–MS on a Kratos MS-890 system, ionizing voltage 70 V. The *m/e* values are given for ^{28}Si, ^{35}Cl, and ^{74}Ge.

Reaction of anisole (VII) with hexachlorodisilane (VIII). A mixture of 15.7 g of compound **VII** and 33.2 g of compound **VIII** was passed through a tubular quartz reactor at 550°C for 30 s. A condensate, 41.8 g, was obtained, whose sublimation gave 18.9 g of tetrachlorosilane. The residue was distilled in a vacuum to obtain 20.5 g of a fraction comprising 6.26 g of compound **VII**, 3.02 g of phenol, 7.43 g of compound **I** [*m/e* 226 ($M^{+\cdot}$), 191 $(M – Cl)^+$], 3.58 g of compound **II** [*m/e* 288 ($M^{+\cdot}$), 253 (*M* – Cl)], and 0.17 g of diphenyl oxide [*m/e* 170($M^{+\cdot}$)]. The still bottom contained 2.4 g of a polymeric residue. The yields of compounds **I** and **II** per starting compound **VIII** were 26.6 and 19.2%, respectively. The reaction of anisole with Si_2Cl_6 at 500°C was performed in a similar way. The resulting data are given in the table.

Reaction of anisole (VII) with tetrachlorogermane (IX) in the presence of hexachlorodisilane (VIII). A mixture of 12.6 g of compound **VII**, 14.6 g of compound **VIII**, and 26.1 g of compound **IX** was passed through a tubular quartz reactor at 550°C for 40 s. A condensate, 43.8 g, was obtained, whose sublimation gave 9.86 g of tetrachlorosilane and 19.1 g of compound **IX**. The residue was distilled in a vacuum to obtain 11.9 g of a fraction containing 2.09 g of compound **VII**, 3.62 g of phenol, 2.83 g of compound **I** [*m/e* 226 ($M^{+\cdot}$), 191 $(M – Cl)^+$], 1.21 g of compound **II** [*m/e* 288 ($M^{+\cdot}$), 253 $(M – Cl)^+$], 0.43 g of compound **III** [*m/e* 272 ($M^{+\cdot}$), 237 $(M – Cl)^+$], 0.16 g of diphenyl oxide [*m/e* 170 ($M^{+\cdot}$)], 1.41 g of compound **IV** [*m/e* 380 ($M^{+\cdot}$), 345 $(M – Cl)^+$], and 0.14 g of compound **V** [*m/e* 334 ($M^{+\cdot}$), 299 $(M – Cl)^+$]. The sill bottom contained 2.9 g of a polymeric residue. The yields of compounds **I**–**V** per starting compound **VIII** were 23.1, 15.4, 2.9, 13.6, and 1.6 %, respectively. The reaction of anisole with $GeCl_4$ in the presence of Si_2Cl_6 at 600°C was performed in a similar way. The resulting data are given in the table.

Reaction of phenol with tetrachlorogermane (IX) in the presence of hexachlorodisilane (VIII). A mixture of 11.4 g of phenol, 15.6 g of compound **VIII**, and 25.2 g of compound **IX** was passed through a tubular quartz reactor at 550°C for 35 s. A condensate, 43.6 g, was obtained, whose sublimation gave 6.59 g of tetrachlorosilane and 20.1 g of compound **IX**. The residue was distilled in a vacuum to obtain 11.8 g of a fraction containing 7.24 g of phenol, 0.08 g of compound **I** [*m/e* 226 ($M^{+\cdot}$), 191 $(M – Cl)^+$], 0.35 g of compound **II** [*m/e* 288 ($M^{+\cdot}$), 253 $(M – Cl)^+$], 0.05 g of compound **III** [*m/e* 272 ($M^{+\cdot}$), 237 $(M - \mathrm{Cl})^+$], 3.65 g of diphenyl oxide [*m/e* 170 ($M^{+\cdot}$)], 0.27 g of compound **IV** [*m/e* 380 ($M^{+\cdot}$), 345 $(M - \mathrm{Cl})^+$], and 0.11 g of compound **V** [*m/e* 334 ($M^{+\cdot}$), 299 $(M - \mathrm{Cl})^+$]. The still bottom contained 5.2 g of a polymeric residue. The yields of compounds **I**–**V** per starting compound **VIII** were 0.6, 2.1, 0.3, 1.2, and 0.5%, respectively.

REFERENCES

1. Nefedov, O.M., Ioffe, A.I., and Menchikov, L.G., *Khimiya karbenov* (Chemistry of Carbenes), Moscow: Khimiya, 1990.
2. Chernyshev, E.A., Komalenkova, N.G., and Bykovchenko, V.G., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, no. 6, p. 1063.
3. Chernyshev, E.A., Komalenkova, N.G., Bashkirova, S.A., Batygina, N.A., and Kisin, A.V., *Zh. Obshch. Khim.*, 1977, vol. 47, no. 5, p. 1196.
4. Chernyshev, E.A., Komalenkova, N.G., and Bashkirova, S.A., *Dokl. Akad. Nauk SSSR*, 1972, vol. 205, no. 4, p. 868.
5. Nefedov, O.M., Mal'tsev, A.K., and Svyatkin, V.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, no. 4, p. 958.
6. Chernyshev, E.A., Komalenkova, N.G., and Yakovleva, G.N., *Dokl. Akad. Nauk SSSR*, 1994, vol. 336, no. 1, p. 69.
7. Chernyshev, E.A., Komalenkova, N.G., and Bashkirova, S.A., *J. Organomet. Chem.*, 1984, vol. 271, nos. 1–2, p. 129.
8. *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Dissociation Energies of Chemical Bonds. Ionization Potentials and Electron Affinity), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1974.
9. Colussi, A.J., Zabel, F., and Benson, S.W., *Int. J. Chem. Kinet.*, 1977, vol. 9, no. 2, p. 161.