SOME RULES IN TRANSFORMATIONS
OF GROUP IVB o-SEMIQUINOLATES

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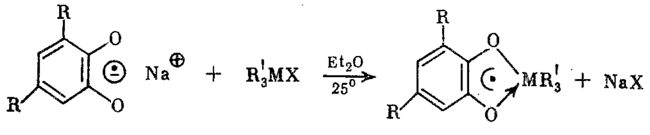
The reactions of metalloorganic compounds (MOC) with o-quinones are convenient models when studying the main rules of one-electron transfer [1-3]. o-Semiquinone derivatives are usually formed as intermediates in these reactions. As was shown previously [4-6], the transformation products of elementoorganic semiquinones can be detected in high yield by reacting o-quinones with some Group IVB bielementoorganic compounds. The mechanism of the process depends on the nature of the elementoorganic fragment of the semiquinone.

In the present paper we studied the transformations of the 3,5-di-tert-butyl-o-benzosemiquinolate complexes of a triorganosilicon, a triorganogermanium, and a triorganotin in order to ascertain some of the rules of the process.

The main method used by us to synthesize the studied semiquinolate complexes was the exchange reaction:


(I) (II)-(IV) (1)

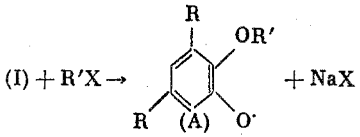
$R = t\text{-Bu}$, $R_3'M = SiMe_3$ (II), $GeEt_3$ (III), $SnEt_3$ (IV).

At room temperature the EPR signal of (II) and (IV) is retained for 10-15 min, while the low intensity of the EPR signal of (III) is retained for several weeks.

Being a general method for the generation of semiquinolate complexes, at the same time the exchange reaction has interest from the standpoint of the mechanism of the reaction of anion-radicals with organic and elementoorganic halides. The last direction was studied very intensely [7, 8]. A scheme was proposed for the reactions of the naphthalene anion-radical with organic halides, which includes the oxidation—reduction step [7].

When reacted with organic halides, (I) behaves as a mixture of quinone and sodium catecholate [8]. We also obtained a similar result for the system (I)—MEt_3SiCl.

Taking the indicated results into account, a general scheme of exchange reaction can be depicted by the following equations: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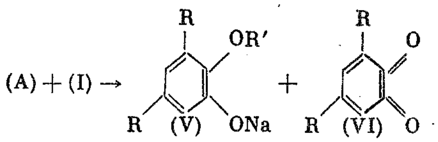
(3)

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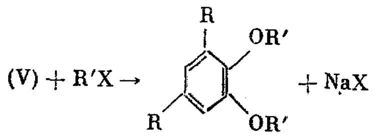
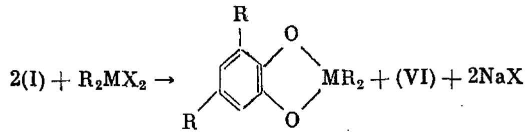


(4)

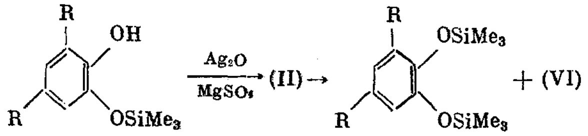
The theoretical possibility of transferring an electron from sodium semiquinolate to the phenoxyl radical [reaction (3)] was shown in [9].

One of the proofs that the given scheme is realized is the reaction of (I) with Me_2SiCl_2 and Et_2GeBr_2. The yields of the reaction products, of the quinone and corresponding catecholate, are close to quantitative.



(5)

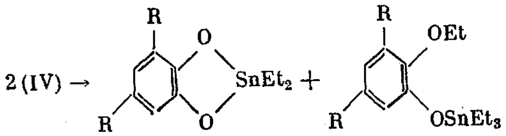
By studying the reaction of (I) with Me_3SiCl and taking into account the ability of silicon to coordinate, it is possible to postulate that the reaction products are formed by the intermolecular coordination of the oxygen on the Si atom. This path is realized in the oxidation of 2-trimethylsiloxy-4,6-di-tert-butylphenol (IX) (in the presence of a drying agent); here the free anion-radical is absent as a reducing agent.



(6)

The discussed mechanisms are not exhaustive in the transformations of the Group IVB semiquinolates. It is known that organotin semiquinolates, in contrast to the Si analogs, eliminate the organic radical from the Sn atom [4].

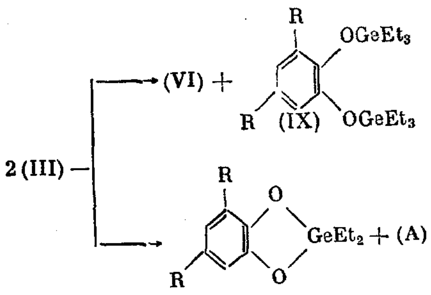
As the study disclosed, the transformation of (IV) is a complex process; the main process is described by the overall equation (7).



(7)

The elimination of the organic substituent from the Sn atom is the consequence of the intramolecular coordination of oxygen on the tin and occurs to vast degree without exit of the kinetically independent ethyl radical into solution. The intermolecular transfer of the alkyl radical is accomplished via reaction of the semiquinone with a second particle, capable of being an acceptor of radicals, for example either the quinone molecule or a second semiquinolate molecule.

The transformation of the triethylgermyl semiquinolates combines the paths discussed for the trimethylsilicon and tin-containing semiquinones. As was reported in [10], (III) mainly disproportionates at 25°C in Et_2O solution. The additional study made by us disclosed that (III) under these conditions undergoes 88% disproportionation and 12% dealkylation.



(8)

The 2-ethoxy-4,6-di-tert-butylphenoxyl is then probably converted to the quinol ether. This process was studied previously [11, 12].

From these facts it follows that with decrease in the energy of the M—C bond in the discussed elementoorganic semiquinones the tendency to cleave the organic radical increases, and here the yield of the bis(triorganoelementoxy)benzenes decreases. The ease with which the latter react with the quinone increases from Si to Sn. Thus, 1,2-bis(trimethylsiloxy)-3,5-di-tert-butylbenzene does not react with the corresponding quinone below 150°, while the analogous organotin derivative reacts with the same quinone at 40°. The weak EPR signal of the germanium semiquinolate, observed for a long time, testifies to the existence of equilibrium (9).

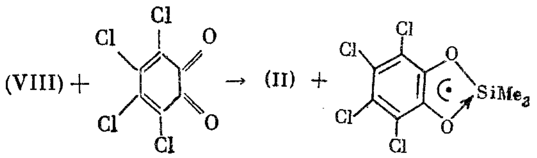
$$(\mathrm{VI}) + (\mathrm{IX}) \rightleftarrows (\mathrm{III}) \qquad (9)$$

An increase in the temperature shifts the equilibrium to the right and increases the probability of dealkylating the organogermanium fragment of the quinone mixture. Due to this, the heating of an authentically prepared mixture of the quinone and (V) at 130° in diamyl ether leads to the disappearance of the quinone and the formation of diethylgermanium catecholate. A stoichiometric ratio of quinone:(V) = 3:1 is observed in the reaction. Previously it was shown [4] that alkylstannylsemiquinones are quantitatively dealkylated by the quinone, and consequently in the reaction of hexaethyldistannane with the quinone the stoichiometric ratio of the reactants is equal to 1:4. Taking into account this quantitative dealkylation, observed in the reaction of the quinone, and Eq. (5), the ratio of the reactants is fully in agreement with the equation.

$$3(\mathrm{VI}) + (\mathrm{III}) \rightarrow 2(\mathrm{X}) + 2(\mathrm{A}) \qquad (10)$$

If the primary step in the reaction of o-quinones with bis(triorganoelementoxy)benzenes is regarded as being the one-electron oxidation of the latter then it must be expected that their reaction will proceed under milder conditions with increase in the polarity of the O—M bond and increase in the oxidation—reduction potential of the o-quinone.

Actually, o-chloranil, which is a stronger electron acceptor than 3,5-di-tert-butyl-1,2-benzoquinone, reacts with 1,2-bis(trimethylsiloxy)-3,5-di-tert-butylbenzene even at room temperature, as can be judged by the disappearance of the o-chloranil color, while at elevated temperature it is possible to observe the EPR signal of (II), which is formed in the reaction.



(11)

EXPERIMENTAL

The EPR spectra were obtained on an RÉ-1301 radiospectrometer. The GLC analysis was run on Tswett-4 and Tswett-129 chromatographs, using helium as the carrier gas and the columns: a) 5% SE-30 deposited on Chromaton, 1 m; b) 5% XE-30 deposited on Chromaton, 1 m; c) 5% OV-17 deposited on Chromaton, 1 m.

The sodium 3,5-di-tert-butyl-o-benzosemiquinolate was obtained by reacting sodium catecholate with an equivalent amount of quinone in diethyl ether. The sodium catecholate was obtained by reacting quinone with Na metal in diethyl ether [13]. All of the reactions were run in evacuated ampuls. Dimethylsilicon catecholate was obtained as described in [14], and (VI) was obtained as described in [15].

Reaction of Et_2GeBr_2 with Sodium Catecholate. A mixture of 2.66 g (0.01 mole) of sodium catecholate, 30 ml of ether, and 2.90 g (0.01 mole) of Et_2GeBr_2 was let stand for 3 h at 20°, and then the NaBr was washed out with water. Evaporation of the water extract gave 1.94 g (95%) of NaBr. The ether was distilled from the organic layer. The residue was recrystallized from acetonitrile to give 3.05 g (87%) of diethylgermanium catecholate, mp 135-136°. Found: C 61.52; H 8.61; Ge 20.37%. $C_{18}H_{30}O_2Ge$. Calculated: C 61.62; H 8.55; Ge 20.69%.

Reaction of Et_2GeBr_2 with (I). A mixture of 2.90 g (0.01 mole) of Et_2GeBr_2, 4.86 g (0.02 mole) of (I), and 50 ml of ether was let stand for 3 h at 20°. The ether was replaced by hexane, and the NaBr was washed out with water. Evaporation of the aqueous extract gave 1.92 g (92%) of NaBr. Based on the GLC data, the reaction product contained 3.1 g (89%) of diethylgermanium catecholate (column a, 180°) and 1.91 g (87%) of quinone (column b, 200°). After distilling off the hexane and recrystallization from acetonitrile we obtained 2.4 g (69%) of diethylgermanium catecholate. The mixed melting point with an authentic specimen was not depressed.

Reaction of Me_2SiCl_2 with (I). A mixture of 1.29 g (0.01 mole) of Me_2SiCl_2, 4.86 g (0.02 mole) of (I), and 50 ml of ether was let stand for 3 h at ∿20°. The ether was replaced by hexane, and the NaCl was separated by centrifuging (1.02 g, 89%). Based on the GLC data, the reaction product contained 2.75 g (99%) of dimethylsilicon catecholate and 1.93 g (88%) of quinone.

Oxidation of 2-Trimethylsiloxy-4,6-di-tert-butylphenol (VII). A mixture of 0.52 g (0.0018 mole) of phenol (VII), 2.00 g of Ag_2O, and 0.50 g of $MgSO_4$ in 10 ml of benzene was stirred for a week at ∿20°. Based on the GLC data, the reaction products contained 0.21 g (57%) of 1,2-bis(trimethylsiloxy)benzene and 0.20 g (∿100%) of quinone.

Reaction of Et_3GeBr with (I). A mixture of 4.76 g (0.02 mole) of Et_3GeBr and 4.86 g (0.02 mole) of (I) was let stand for 3 h at ∿20°. The NaBr (1.90 g, 90%) was washed out with water. After distilling off the ether and recrystallization of the residue from hexane we isolated 1.4 g (63%) of the quinone. Based on the GLC data, the reaction product also contained 4.72 g (88%) of bis(triethylgermyl) catecholate (column c, 180°) and 0.98 g (12%) of diethylgermanium catecholate.

Reaction of (V) with Quinone. A mixture of 2.2 g (0.01 mole) of quinone, 2.70 g (0.005 mole) of (V), and 30 ml of diamyl ether was heated for 5 h at 130°. Analysis by GLC gave 2.13 g (0.0061 mole) (61%) of diethylgermanium catecholate and 1.02 g (0.0019 mole) (38%) of (V).

CONCLUSIONS

1. Disappearance of the free valence in Group IVB semiquinolates, independent of their method of preparation, occurs as the result of their disproportionation into quinone and bis(triorganoelementoxy)benzene derivatives and elimination of the alkyl group from the Group IVB element under the influence of radical acceptors.

2. The concrete ratio of the transformation paths is determined by the nature of the elementoorganic fragment of the semiquinone: the probability of its dealkylation increases with decrease in the energy of the M—C bond.

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SYNTHESIS AND PROPERTIES OF ESTERS AND AMIDO ESTERS OF 1-(2-THIENYL)-2,2,2-TRICHLOROETHYLPHOSPHOROUS ACID

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and F. F. Mertsalova

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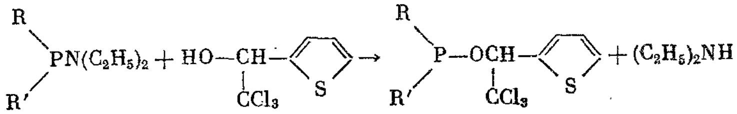
It is known that thiophene derivatives can exhibit biological activity. Thus, for example, some thienylureas are bactericides [1], and some phosphorylated thiophene derivatives are pesticides [2, 3].

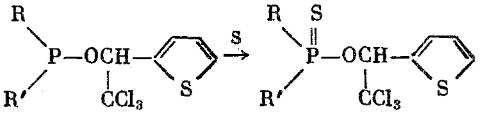
In a search for new pesticides we obtained a number of organophosphorus compounds by the alcoholysis of amidophosphites, diamidophosphites, and triamidophosphites with 1-thienyl-2,2,2-trichloroethanol by the following scheme:



R=AlkO, Alk_2N, R'=AlkO, $(CH_3)_2N$.

Exothermic reaction occurs when the reactants are mixed and leads to the formation of the esters and amides of phosphorous acid in high yield. The obtained products are stable and colorless liquids.

By adding sulfur the 1-(2-thienyl)-2,2,2-trichloroethyl dialkyl phosphites, 1-(2-thienyl)-2,2,2-trichloroethyl alkyl (dimethylamido)phosphites, and also 1-(2-thienyl)-2,2,2-trichloroethyl tetramethyldiamidophosphite were converted to the corresponding thiophosphates.



R=AlkO, $(CH_3)_2N$, R' = AlkO, $(CH_3)_2N$

Some of the 1-(2-thienyl)-2,2,2-trichloroethyl dialkyl phosphites were oxidized to the phosphates. The properties of the obtained products are given in Tables 1-3.

The O-alkyl O-(1-thienyl-2,2,2-trichloroethyl) N-dimethyl phosphites have two asymmetric atoms in their molecule: the P atom and the α-C atom in the 1-(2-thienyl)-2,2,2-trichloroethyl radical. In the synthesis of these compounds four stereoisomers are formed, and specifically two racemates at the phosphorus and at the carbon. The spectra of such compounds are recorded as a mixture of two products. The ^{31}P NMR spectra have doublet signals, which differ by 2-3 ppm. The PMR spectra also have a double set of lines (Fig. 1). The same picture is observed in the spectra of the corresponding phosphates and thiophosphates.

The reaction of the obtained phosphites with CH_3COCl and chloral proceeds with cleavage of the 1-(2-thienyl)-2,2,2-trichloroethyl radical and the respective formation of the dialkyl acetylphosphonate and dialkyl dichlorovinyl phosphate.

The O-(1-thienyl-2,2,2-trichloroethyl) O-alkyl N-dimethylamidothiophosphates exhibit a weak herbicidal activity and suppress the development of plants. However, in activity they are inferior to the standard, the Na salt of 2,4-dichlorophenoxyacetic acid. These compounds lack contact and systemic insectoacaricidal properties.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 182-187, January, 1981. Original article submitted January 15, 1980.

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