# OXIDATIVE ADDITION PRODUCTS IN REACTIONS OF HETEROORGANIC COMPOUNDS WITH SUBSTITUTED O-QUINONES

G. A. Razuvaev, G. A. Abakumov, E. N. Gladyshev, P. Ya. Bayushkin, and V. A. Tsaryapkin

An early step in the reaction of organosilicon and organogermanium compounds of mercury with di-tert-butylhydroquinones is the one-electron oxidation of the organometallic compound. Intracellular recombination of the initial products affords the product of oxidative 1.4addition of the organometallic compound to the o-quinone. The main products of the reaction of bis(triethylgermyl)- and bis(triethylsilyl)mercury with 3,5-di-tert-butyl-1,2-benzoquinone (I) were mercury and 1,2-bis(triethylgermyloxy)- or 1,2-bis(triethylsilyloxy)-4,6-di-tertbutylbenzene, respectively, showing that the 1,4-addition products had undergone demercurization [1, 2].

When bis(phenyldimethylsilyl)mercury (II) [3] and bis(triisopropylgermyl)mercury (III) [4] reacted with (I) under similar conditions, the 1,4-addition products (IVa, b) were isolated in nearly quantitative yields

> OHgER<sub>3</sub> R' = C(CH<sub>3</sub>)<sub>3</sub>; E R<sub>3</sub> = SiMe<sub>2</sub>Ph (a), Ge(Pr-i)<sub>3</sub> (b) R' OE R3

At room temperature, (IV) is completely stable in the absence of atmospheric oxygen. Its reaction with the quinone (I) occurs at subzero temperatures, with fusion of the reaction mixture accompanied by the appearance of paramagnetic entities in the solution.

The EPR signal obtained during the reaction of (IV) with (I) is composed of the superimposed spectra of the triisopropylgermylmercury hemiquinolate (V) and the triisopropylgermanium aroxyl (VI).

Demercuration of (V) affords (VI), manifested as a decrease in the intensity of the EPR signal for (V) as the temperature of the mixture is raised, the final signal having a doublet structure with the parameters of the aroxyl (VI).

In the analogous reaction of (IVa) with (I), only the EPR spectrum of the silylmercury hemiquinolate (V) was obtained, possibly indicating the decreased stability of the phenyldimethylsilicon aroxyl in comparison with its triisopropylgermanium analog.

These observations show that reactions in the system (IVa) or (IVb)-o-quinone result in the generation of the radicals (VI). In order to study the reactions of the aroxyls (VI), they were also generated by oxidation of the phenols and by the exchange reaction between sodium 3,5-di-tert-buty1-o-benzenehemiquinolate (VII) and silicon and germanium monohalides

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$$(IVb) + (I) \rightarrow \begin{array}{c} R' & R' & 0 \\ \hline (V) & HgER_3 \\ \hline (V) & CV \\ \hline (V)$$

$$\int \frac{\Delta}{-H\sigma} (VI)$$
 (1')

(VII)

It was found that the reactions of the aroxyls (VI) when  $R_3E = PhMe_2Si$  and  $(i-Pr)_3Ge$  were accompanied by the elimination of one of the substituents at the Group IV element

 $(VI) \rightarrow \begin{array}{c} & & \\ & &$ 

When  $R_3E = Et_3Ge$ , the main reaction products were the quinone (I) and 1,2-bis(triethylgermyloxy)-3,6-di-tert-butylbenzene; i.e., in this instance the principal route of reaction of the aroxyl (VI) is disproportionation, similar to that described previously for magnesium hemiquinolates [5, 6]

$$2 \xrightarrow{R'} OGeEt_3 \xrightarrow{R'} O \xrightarrow{R'} OGeEt_3 \xrightarrow{R'} OGeEt_3 \xrightarrow{R'} OGeEt_3 \xrightarrow{R'} OGeEt_3 \xrightarrow{R'} OGeEt_3 \xrightarrow{(5)}$$

This difference in the reaction pathways of the aroxyls (VI), depending on the heteroorganic moiety, can apparently have a considerable effect on the possible formation of products of oxidative 1,4-addition among the reaction products. Thus, with a reactant ratio of 1:1, the reaction between bis(triethylgermyl)mercury and quinone (I) gives, in addition to the oxidative 1,4-addition product, radicals of types (V) and (VI) (followed by EPR spectroscopy). In accordance with schemes (1) and (5), these give rise to significant amounts of the quinone (I). Reaction of the 1,4-addition product with the quinone (I) formed in this way follows scheme (1), and again gives rise to radicals (V) and (VI). This chain of reaction continues until all the oxidative 1,4-addition product has been consumed, the final products being mercury and 1,2-bis(triethylgermyloxy)-4,6-di-tert-butylbenzene.

A different result is obtained when the quinone (I) reacts with bis(phenyldimethylsiloxy)- and bis(triisopropylgermyl)mercury. In this instance, the reactions of the aroxyls (VI) do not give rise to the quinone (I), and when the reactant ratio is 1:1 the contribution of reaction (1) to the overall reaction is small, and the oxidative addition product can be isolated from the reaction mixture.

It is noteworthy that this use of 3,6-di-tert-butyl-1,2-benzoquinone (VIII) as the oxidant makes it possible to determine unambiguously the route of fragmentation of (IVa) and (IVb) in the redox reaction. The EPR signal recorded in the reaction of (IVb) with (VIII) results from superposition of the spectra of the organogermanium aroxyl (VI) (doublet,  $a_{\rm H} = 2.1$  Oe, g = 2.0048) and 3,6-di-tert-butyl-1,2-benzoquinone germylmercury hemiquinolate (triplet,  $a_{\rm H} = 3.4$  Oe,  $a_{\rm Hg} = 11.4$  Oe, g = 1.9980). Similarly, in the reaction of (IVa) with (VIII), the spectrum of 3,6-di-tert-butyl-1,2-benzoquinone silylmercury hemiquinolate is obtained (triplet,  $a_{\rm H} = 3.5$ ,  $a_{\rm Hg} = 10.8$  Oe, g = 1.9968). These findings show that in the course of the redox reaction, fragmentation of (IV) occurs at the O-Hg bond with the formation of the cation <sup>+</sup>HgER<sub>3</sub>, which attaches itself to the anion-radical of the oxidant

$$(IV) \xrightarrow{-e} (VI) + {}^{+}HgER_3$$
(6)



1889

Triphenylchloromethane also reacts with (IVa) under mild conditions. The reaction results in the accumulation in the solution of triphenylmethyl radicals, which is an indication of the one-electron redox nature of the reaction. The presence of mercury and diphenylmercury in the reaction products is evidence that in the stabilization of the phenyldimethylsilicon aroxyl (VI), the phenyl radical becomes attached to mercury. The reaction may be represented as follows:

$$(IVa) + Ph_{3}CCl \rightarrow \begin{bmatrix} R' & 0 & +HgSiMe_{2}Ph \\ 0 & -HgSiMe_{2}Ph \\ R' & OSiMe_{2}Ph & Cl - Ph_{3}C \end{bmatrix}$$
(8)

$$PhMe_{2}SiHg^{+} + Cl^{-} \longrightarrow PhMe_{2}SiCl$$

$$(9)$$

$$Ph \cdot + Hg \rightarrow PhHg \cdot \rightarrow \frac{1}{2}Hg + \frac{1}{2}Ph_{2}Hg$$
(11)

Following oxidation of the triphenylmethyl radical with oxygen, trityl peroxide can be isolated from the reaction mixture in quantitative yield

$$Ph_{3}C \xrightarrow{O_{2}} (Ph_{3}CO)_{2}$$
(12)

The formation of diphenylmercury by attachment of phenyl radicals to mercury is also seen in the reaction of (IVa) with quinone (I), and when 2-phenyldimethylsilyloxy-4,6-ditert-butylphenol (IX) is oxidized with mercuric oxide. Oxidation of this phenol with silver oxide in benzene affords quantitative yields of diphenyl



Compound (IV) is highly reactive towards organomercury halides. Reaction of (IVb) with phenylmercury chloride follows scheme (14), and gives exchange reaction products

$$(IVb) + R''HgCl \rightarrow (i-Pr)_{3}GeCl + Hg + R' OHgR''$$

$$R'' = Et (a), Ph (b)$$

$$(14)$$

Similar reactions of the silicon derivative (IVa) proceed in a more complex manner. The exchange reaction product is not found in the reaction products

$$(IVa) + R''HgCl \rightarrow (X) + PhHgR'' + PhMe_2SiCl + Hg$$
(15)

This difference may be rationalized in terms of the lower stability of the products of the exchange reaction in the case of the silicon derivative as compared with the germanium compound, and its intramolecular breakdown in accordance with scheme (16)

 $\begin{array}{c} R' & \text{OHgR}'' \\ & & \stackrel{\Delta}{\longrightarrow} (X) + PhHgR'' \\ & & \text{OSiMe}_2Ph \end{array} \end{array}$ (16)

However, another explanation is possible, if it is assumed that these reactions are redox in nature, with the intermediate formation of radical species, bearing in mind the differing stabilities of the aroxyls (VI), as noted in the discussion of the reaction of (IV) with the quinone (I). As a result of a one-electron redox reaction followed by fragmentation of the ion-radical species in the reaction cell, two radical and two charged specimens are formed



Reaction of the charged species leads to the formation of a labile organomercury compound, the breakdown of which leads to the appearance in the reaction products of mercury and the heteroorganic halide. Following these reactions, there remain in the reaction cell the aroxyl radical (VI) and the organomercury radical R"Hg., recombination of which gives the exchange reaction product

 $\begin{bmatrix} \mathbf{R}' & \mathbf{O} \cdot \\ & | & \mathbf{O} \cdot \\ & | & \mathbf{O} \mathbf{E} \mathbf{R}_{3} \end{bmatrix} \xrightarrow{\mathbf{R}'} \begin{bmatrix} \mathbf{R}' & \mathbf{O} \mathbf{H} \mathbf{g} \mathbf{R}'' \\ & | & \mathbf{O} \mathbf{E} \mathbf{R}_{3} \end{bmatrix} \xrightarrow{\mathbf{R}'} \begin{bmatrix} \mathbf{O} \mathbf{H} \mathbf{g} \mathbf{R}'' \\ & | & \mathbf{O} \mathbf{E} \mathbf{R}_{3} \end{bmatrix}$ (18)

# $ER_3 = Ge (Pr-i)_3$

In the case of the less stable phenyldimethylsilicon aroxyl (VI), the recombination of the organomercury radical R"Hg• may precede its stabilization, with the production of a phenyl radical and dimethyl(3,5-di-tert-butyl-o-phenylenedioxy)silane. Consequently, the partner of the organomercury radical in the reaction cell becomes the phenyl radical, and the recombination of these gives rise to the organomercury compound R"HgPh

$$\begin{bmatrix} \mathbf{R}' & \mathbf{O} \cdot \mathbf{H} \mathbf{g} \mathbf{R}' \\ \vdots & \mathbf{O} & \mathbf{H} \mathbf{g} \mathbf{R}' \\ \mathbf{R}' & \mathbf{O} \mathbf{S} \mathbf{i} \mathbf{M} \mathbf{e}_2 \mathbf{P} \mathbf{h} \end{bmatrix} \rightarrow \begin{bmatrix} \mathbf{R}' & \mathbf{O} & \mathbf{H} \mathbf{g} \mathbf{R}' \\ \vdots & \mathbf{O} & \mathbf{S} \mathbf{i} \mathbf{M} \mathbf{e}_2 \\ \mathbf{R}' & \mathbf{O} & \mathbf{P} \mathbf{h} \cdot \end{bmatrix} \rightarrow (\mathbf{X}) + \mathbf{R}'' \mathbf{H} \mathbf{g} \mathbf{P} \mathbf{h}$$
(19)

It may be that the formation of R"HgPh occurs without the prior elimination of the phenyl radical, if in the phenyldimethylsilicon aroxyl (VI) there is interaction between the free valence and the d-orbitals of the silicon atom. In this case, attack of R"Hg. on the phenyl nucleus of the organosilicon moiety will lead to the same products



#### EXPERIMENTAL

Reaction of Bis(phenyldimethylsilyl)mercury (II) with 3,5-Di-tert-butyl-1,2-benzoquinone (I). A solution of 4.14 g (8.79 mmole) of (II) in 15 ml of hexane was added with stirring at 20°C to a solution of 1.93 g (8.79 mmole) of (I) in 15 ml of hexane. The reaction mixture became green in color, and the reaction was complete in 20-30 min, when the mixture became colorless. Low-temperature crystallization afforded 5.01 g (7.24 mmole) (82.3%) of 1-phenyldimethylsilyloxy-2-(phenyldimethylsilylmercurioxy)-3,5-di-tert-butylbenzene (IVa) as pale yellow crystals, mp 43-44°C (from pentane). Found: Hg 28.88%. C<sub>30</sub>H<sub>42</sub>O<sub>2</sub>Si<sub>2</sub>Hg. Calculated: Hg 29.01%.

Reaction of 1-Triisopropylgermyloxy-2-(triisopropylgermylmercurioxy)-3,5-di-tert-butylbenzene (IVa) with Phenylmercury Chloride. A solution of 9.96 mmole of (IVb) in 30 ml of toluene was added to a solution of 2.82 g (9 mmole) of phenylmercury chloride in 20 ml of toluene at 20°C. The reaction mixture became green in color. After 1 h, 1.8 g (97.7%) of mercury had separated. The toluene was removed under reduced pressure, and 30 ml of hexane added to the residue. Low-temperature crystallization afforded 5.10 g (81%) of 1-triisopropylgermyloxy-2-phenylmercurioxy-3,5-di-tert-butylbenzene, mp 93-94°C (from hexane). Found: C 50.18; H 7.01; Hg 27.69; Ge 12.27%. C<sub>29</sub>H<sub>46</sub>O<sub>2</sub>GeHg. Calculated: C 49.77; H 6.63; Hg 28.66; Ge 10.37%. Fractionation of the mother liquors afforded 1.46 g (68.3%) of triisopropylchlorogermane (identified by GLC).

Reaction of (IVb) with Quinone (I). To a solution of 4.83 mmole of (IVb) in 30 ml of toluene was added at 20°C a solution of 1.06 g (4.81 mmole) of (I) in 10 ml of toluene. The reaction, which was accompanied by the appearance of a green color, was complete in 3-5 min, the solution becoming colorless. Mercury (0.91 g; 94.2%) separated. The toluene was re-

placed by pentane, and low-temperature crystallization afforded 2.17 g (58.5%) of isopropyl- (3,5-di-tert-butyl-o-phenylenedioxy)germane, mp 115-116°C.

Solutions of quinones (I) and (VIII) were added directly at -40°C to a solution of (IVb) in toluene in the resonator of an RÉ-1301 radiospectrometer. In the case of quinone (I), there was observed superposition of the spectra of the germyl hemiquinolate of quinone (I) (doublet,  $a_{\rm H}$  = 4.0 Oe,  $a_{\rm Hg}$  = 11.3 Oe, g = 1.9981) and 2-triisopropylgermyloxy-4,6-di-tert-butylphenoxyl (doublet,  $a_{\rm H}$  = 2.1 Oe, g = 2.0048). In the case of quinone (VIII), there was observed superposition of signals for the germylmercury hemiquinolate of quinone (VIII) (triplet,  $a_{\rm H}$  = 3.4,  $a_{\rm Hg}$  = 11.4 Oe, g = 1.9980) and 2-triisopropylgermyloxy-4,6-di-tert-butylphenoxyl with the parameters given above.

Reaction of 1-Dimethylphenylsilyloxy-2-(dimethylphenylsilylmercurioxy)-3,5-di-tertbutylbenzene (IVa) with Ethylmercury Chloride. A solution of 6.29 g (9.10 mmole) of (IVa) in 30 ml of toluene was added at  $\sim 20^{\circ}$ C to a solution of 2.41 g (9.09 mmole) of ethylmercury chloride in 10 ml of toluene. The reaction was accompanied by the separation of mercury (1.76 g; 96.4%), and was complete in 15-20 min. The solvent was removed under reduced pressure, and the residue dissolved in 20 ml of hexane. Low-temperature crystallization afforded 2.34 g (92.4%) of dimethyl-(3,5-di-tert-butyl-o-phenylenedioxy)silane (X), mp 95-97°C (from pentane). The mother liquors were treated with dilute HCl (1:1), and from the organic layer by crystallization there was obtained 2.41 g (9.09 mmole) of ethylmercury chloride. Fractionation of the residue gave 1.52 g (97.9%) of phenyldimethylchlorosilane (identified by GLC).

Reaction of (IVa) with Phenylmercury Chloride. A solution of 7.93 mmole of (IVa) in 20 ml of THF was added to 2.35 g (7.50 mmole) of phenylmercury chloride at  $\sim 20^{\circ}$ C. Mercury (1.42 g, 94.3%) separated. The THF was removed under reduced pressure, and to the residue was added 30 ml of hexane. From the hexane solution there was obtained 2.36 g (88.6%) of diphenylmercury, mp 118-119°C. GLC of the mother liquors showed the presence of 2.25 g (8.07 mmole) of (X) and 1.25 g (7.32 mmole) of phenyldimethylchlorosilane.

<u>Reaction of (IVa) with Quinone (I).</u> A solution of 5.76 g (8.33 mmole) of (IVa) in 15 ml of pentane was added at  $\sim 20^{\circ}$ C to a solution of 1.83 g (8.30 mmole) of (I) in 15 ml of pentane. The reaction was accompanied by a green coloration. After 40 min, the mixture became colorless, and crystals of diphenylmercury (2.75 g; 93.4%) separated, mp 121-123°C. Low-temperature crystallization of the mother liquors afforded 4.33 g (93.6%) of (X) (identified by GLC).

To a solution of (IVa) in toluene in the resonator of an EPR radiospectrometer was added at -40°C a solution of the quinone (I) or (VIII). In the case of quinone (I), the spectrum of the silylmercury hemiquinolate of (I) (doublet,  $\alpha_{\rm H}$  = 3.2,  $\alpha_{\rm Hg}$  = 11.6 Oe, g = 1.9982) was obtained. In the case of quinone (VIII), the spectrum of the silylmercury hemiquinolate of quinone (VIII) was obtained (triplet,  $\alpha_{\rm H}$  = 3.5,  $\alpha_{\rm Hg}$  = 10.8 Oe, g = 1.9968). In neither case was the spectrum of the phenyldimethylsilicon aroxyl (VI) obtained.

Reaction of Sodium 3,5-Di-tert-butyl-o-benzohemiquinolate (VII) with Triethylbromogermanium. To a solution of 2.40 g of triethylbromogermane in 5 ml of THF at  $\sim 20^{\circ}$ C was added a solution of 0.01 mole of (VII) in 20 ml of THF. The reaction proceeded as the hemiquinolate was added, with separation of NaBr and the appearance of a reddish-brown color. The THF was removed under reduced pressure, and 15 ml of hexane was added to the residue. The precipitate of NaBr (1.01 g, 98%) was filtered off. Low-temperature crystallization of the hexane solution afforded 0.80 g (36%) of (I). The mother liquors, according to GLC, contained 2.54 g (47%) of 1,2-bis(triethylgermyloxy)-3,5-di-tert-butylbenzene.

Reaction of Hemiquinolate (VII) with Triisopropylchlorogermane. Following the procedure in the preceding experiment, to asolution of 4.82 g of triisopropylchlorogermane in 30 ml of diethyl ether was added 0.02 mole of (VII) in 30 ml of ether. When the reaction was complete, the diethyl ether was replaced by hexane, and 0.016 mole (81%) of NaCl was filtered off. The mixture was evaporated, and low-temperature crystallization of the hexane solution gave 2.45 g (32%) of diisopropyl-(3,5-di-tert-butyl-o-phenylenedioxy)germane, mp 116°C. According to GLC, the mother liquors contained no (I).

Reaction of (IVa) with Triphenylchloromethane. A solution of 14.2 mmole of (IV) in 30 ml of toluene was added at  $\sim 20^{\circ}$ C to 3.95 g (14.16 mmole) of triphenylchloromethane. The exothermic reaction was accompanied by the separation of mercury. After 1 h, 1.39 g (48.8%)

of mercury had separated. Oxygen was passed through the toluene solution for 1 h, and the precipitate of trityl peroxide was filtered off to give 3.58 g (97.4%), mp 180-181°C. The toluene in the mother liquors was replaced by hexane, to give 2.45 g (48.8%) of diphenyl-mercury. GLC of the mother liquors showed the presence of 3.67 g (93%) of (X) and 2.18 g (90.2%) of phenyldimethylchlorosilane.

Oxidation of 2-Phenyldimethylsilyloxy-4,6-di-tert-butylphenol (IX) with Mercuric Oxide. A solution of 2.2 g (6.16 mmole) of (IX) in 20 ml of benzene was added to 3.5 g (16.15 mmole) of HgO. The mixture was shaken for 1 h at 50°C. The solution became green in color. The precipitate was separated by filtration, and GLC of the solution showed the presence of 0.51 g (23.2%) of diphenylmercury.

Oxidation of Phenol (IX) with Silver Oxide. A solution of 0.30 g (0.84 mmole) of (IX) in 5 ml of benzene was added at  $\sim 20^{\circ}$ C to 1.20 g (5.19 mmole) of Ag<sub>2</sub>O. The exothermic reaction was accompanied by the development of a green color, and was complete in 20-30 min. The precipitate was separated by filtration, and GLC showed the presence in the filtrate of 0.05 g (78-1%) of diphenyl.

### CONCLUSIONS

1. The products of the oxidative 1,4-addition formed in the reaction of diheteroorganic compounds with sterically hindered o-quinones react readily with organic oxidants.

2. The types of reactions of o-hemiquinolates of Group IVB elements are determined by the tendency to eliminate alkyl and aryl groups from the heteroatom under the influence of the unpaired electron of the free-radical ligand.

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