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MECHANISM OF HOMOLYSIS OF M-C BONDS IN GROUP IVB ORGANOMETALLIC DERIVATIVES OF o-SEMIQUINONES

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Organometallic derivatives of o-semiquinones with group IVB metals (SQMR<sub>3</sub>) where SQ is 3,5-di-tert-butyl-1,2-benzosemiquinone undergo interconversions in two directions [1-3]:

1. Disproportionation to the quinone (Q) and the corresponding catecholate  $(Cat(MR_3)_2, MR_3=SiMe_3, GeEt_3)$ 



Here and later X = t-Bu.

2. Homolytic rupture of the M-C bond in which the process is formally described by the equation



The mechanism of rupture of the M-C bonds in the process of breakdown of organometallic derivatives of o-semiquinones is discussed in the literature [2-5], in which both mono and bimolecular character were suggested for the transformations. However, up to the present time no clear-cut preference for any one of the indicated pathways is in evidence (for example, see [4]). In our previous works devoted to investigation of group IVB derivatives of o-semi-quinones [1-3, 6] a preference was expressed for the bimolecular character of these processes.

We carried out a kinetic investigation of the breakdown of 3,5-di-tert-butyl-o-benzosemiquinolate of triphenyltin (II). The choice of (II) for investigation was due to its relative stability in the series of group IVB organometallic derivatives of o-semiquinones and a convenient method of synthesis of the radical by the reaction



Institute of Chemistry, Academy of Sciences of the USSR, Gorkii. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, pp. 2098-2105, September, 1984. Original article submitted June 24, 1983. For alkyl-substituted distannates a similar interaction is complicated by secondary processes [1].

It was found that disappearance of the free valence in  $SQSnPh_3$  solutions is described by a second-order kinetic equation with an energy of activation of 17 ± 1 kcal/mole (Fig. 1). On investigation of the reaction indicated above none of the products associated with the reaction of free phenyl radicals (benzene, diphenyl, or dibenzyl when using toluene as solvent) were found. In the absence of free quinone in the system by analogy with  $SQSnEt_3$  [2], the reaction which essentially must take place is



It is interesting to note that the rate constant for the elimination reaction increases with an increase in the donor capability of the solvent (Fig. 2). The influence of the solvent can be linked with a shift in the contact equilibria and separation of ion pairs in the presence of strong bases [4].

It was previously noted that in  $SQGeR_3$  replacement of the triethyl germanyl group by the triisopropyl germanyl group results in complete suppression of the disproportionation reaction [7] whereas products derived from free radical R formation are absent from the solution in both instances. Analogous changes of substituent affect the transformations of silicon derivatives of o-semiquinones. Replacement of a methyl group in  $SQSiMe_3$  by ethyl results in appearance of the free radical elimination products along with the disproportionation products.



From the proportions of products it is evident that the probability of elimination of the  $C_2H_s$  group is about ten times greater than for  $CH_3$ . In itself this fact about elimination of  $CH_3$  groups is evidence of the advantage of the bimolecular process in which the acceptor radical R is a molecule of quinone and it engenders doubt about the crucial role of the M-C bond energy in the elimination reaction.

A still more pronounced change in the reactivity of the silicon-containing radicals is found on replacing one  $CH_3$  group in SQSiMe<sub>3</sub> by phenyl. Oxidation of 2-dimethylphenylsiloxy-4,6-di-tert-butylphenol (III) by silver oxide gives the dimethylphenyl silicon catecholate in 85% yields





Fig. 1. Anamorphisms of kinetic curves (a) and the influence of temperature (b) on the rate constants for the decomposition reaction of SQSnPh<sub>3</sub>: 1) 64.5°C, 2) 61.5°C, 3) 58.5°C, 4) 54.5°C.  $C_0 = 6.0 \cdot 10^{-3}$  mole/liter.



Fig. 2. Anamorphous kinetic curves for the decomposition of  $SQSnPh_3$  in various solvents: 1) touene + pyridine, 2) toluene + DMSO, 3) THF, 4) toluene + acetonitrile, 5) toluene, 6) hexane.  $C = 5 \cdot 10^{-3}$  mole/liter, 59°C. Solvent mixtures contain 75% by volume of toluene.

Replacement of benzene by toluene and cumene in this reaction does not produce any change in the composition of the reaction **products**; dicumyl and dibenzyl are absent in the reaction mix-ture.

In an attempt to fix the phenyl radical in a spin trap (2-methyl-2-nitrosopropane) by the EPR method independently of the solvent the spectrum of phenyl, tertbutyl nitroxide was successfully recorded. It is known that on generating free phenyl radicals in toluene the benzyl radical is always the only one fixed [8]. Consequently, nitrosobutane in this instance is not a "trap" but an acceptor, spontaneously participating in the elimination reaction



Analogously the transformation of  $SQGe(i-Pr)_3$  in the presence of a spin trap leads to the appearance of the EPR signals of the spin adduct of the isopropyl radical. Nitrosobutane also splits off an ethyl radical from  $SQSnEt_3$  [1].

It was previously reported [7] that interaction of equimolar amounts of quinone (I) and bis(phenyldimethylsilyl)mercury leads to the formation of adduct (IV), the reaction of which with a second mole of quinone proceeds nearly quantitatively in the direction



The scheme of the process assumes the formation of  $SQSiMe_2Ph$  and Hg in the course of the reaction [7, 9]. Formation of diphenyl mercury in 48% yield from the phenyl fragment was observed on oxidation of (III) by mercuric oxide.

In accordance with the above explanation it follows that in both these instances the atom of Hg is the acceptor of the phenyl radicals which leads to the formation of the dimethylsilyl catecholate and the phenylmercury radical

$$SQSiMe_2Ph + Hg \rightarrow CatSiMe_2 + PhHg'$$

The phenylmercury radical subsequently either disproportionates to mercury and diphenylmercury, or acts as an acceptor of the phenyl radical from a second molecule.

 $2PhHg \rightarrow Ph_2Hg + Hg$ PhHg  $+ SQSiMe_2Ph \rightarrow CatSiMe_2 + Ph_2Hg$ 

The process described by the latter equation is dominant in the reaction under investigation in that it gives a quantitative yield of diphenylmercury.

Analysis of our experimental data testifies to the unique capability of the phenyldimethylsilyl-o-semiquinone to give up a phenyl radical to an external acceptor. Explanation of this effect must be sought in the interaction of the unpaired electron on the 0 atom of the o-semiquinone and the electron pair of the Si-Ph bond. Coordination of the 0 and Si atoms leading to the formation of a five-membered ring does not directly affect the  $\pi$  system of the radical where the unpaired electron is located. In the formation of the coordinate bond the basic contribution is made by the orbitals of the 0 atom lying in the plane of the ring occupied by electron pairs and  $3d_{x^2-y^2}$  vacant orbitals of the Si atom (the z axis passes through the Si atom perpendicular to the plane of the ring). At the same time, the  $3d_{xz}$  and  $3d_{yz}$  orbitals can interact with the orbitals of the unpaired electron, which permits partial transfer of the spin density to the Si atom (Fig. 3).

It is known that the degree of transfer of the unpaired electron in stable silicon-containing aroxy radicals through the silicon bridge to the methyl substituent is 6.5 times greater than through the carbon [10]. A similar effect can destabilize the Si-C bond. On the other hand, a radical complex of such a type has a structure which is found in the reaction coordinate of the intramolecular  $S_N^2$  elimination, i.e., free radical attack of the 0 atom on Si with removal of the phenyl radical. The driving force of the reaction is the gain of energy for formation of the Si-O bond in comparison with Si-C. However, formation of free radicals is evidently hindered energetically since participation of a molecule of acceptor is still necessary, which binds the Ph<sup>•</sup> and makes a supplementary contribution to the energetics of the reaction.

Evidently the elimination process can be facilitated by replacing the phenyl group in the initial  $SQSiR_3$  by a grouping which give a more stable radical than phenyl as a result of elimination. With this in mind we synthesized the o-semiquinolate of dimethyl(2,4,6-tri-tert-butylphenoxy)silicon by an exchange reaction between the appropriate chlorosilane and SQT1.





Fig. 3. Scheme for intramolecular  ${\rm S}_{\rm N}^2$  elimination of the phenyl radical.

Immediately after mixing the reagents the EPR signals of tri-tert-butylphenoxyl were observed. The yield of products was nearly quantitative. The stability of the fragment split out was illustrated by the fact that the elimination process in this instance was accompanied by formation of radicals as kinetically independent particles and probably proceeds via an intramolecular  $S_N^2$  reaction. It should be noted that in this instance a rare example of homolytic rupture of the Si-O bond takes place which, however, on account of stabilization of the aroxy radical which should be substantially lower in Si-O bond energy compared to aliphatic silox-anes.

With regard to the free radical elimination reaction and the role of the acceptor in it a few peculiarities clearly exist in the procedure for organotin o-semiquinones. In the work mentioned [4] it was noted that in the course of the transformation of organotin o-semiquinones formation of small amounts of SnR4 type compounds was observed



We have previously demonstrated [2, 3] that products of the SnR<sub>4</sub> type are not formed either by reaction of  $R_3SnSnR_3$  with quinones or in the reaction of  $R_3MX$  (M = Si, Ge, Sn) with SQNa in THF, hexane, ether, or toluene. However, formation of SnEt<sub>4</sub> was noted in the reaction of the sodium 3,5-di-tert-butylcatecholate with Et<sub>3</sub>SnCl. In diethyl ether with a 1:2 reagent ratio the reaction proceeds quantitatively with formation of (V)



If the ether is replaced by THF the nature of the reaction changes for the most part. Immediately after mixing the reagents EPR signals for SQNa were observed. In particular the diethyl tin catecholate appears among the products of the reaction (yield 12%) along with tetraethyl tin. DMFA leads to an increase in the intensity of the SQNa signals and an increase in the yield of SnEt<sub>3</sub> to 30%. Special experiments showed that in the THF medium (V) does not decompose to SnEt<sub>4</sub> and CatSnEt<sub>2</sub> even with moderate heating

$$(V) \xrightarrow{\Delta, THF} CatSnEt_2 + SnEt_4$$

The explanation of the results obtained is possible only under the acknowledged condition that in the solvating solvent medium the reaction of the sodium catecholate with  $Et_3SnCl$  does not proceed as an exchange reaction but is accompanied by a redox process

$$CatNa_{2} + Et_{3}SnCl \xrightarrow{THF} [SQNaEt_{3}Sn'] - \bigvee_{X} OSnEt_{3}$$

From the EPR signals SQNa is not formed in this reaction. Inasmuch as the reaction takes place with a 1:2 reagent ratio there is always an excess of  $Et_3SnCl$  in the system. The reaction of the sodium o-semiquinolate with triethyltin chloride may originate during the initial segment of the life of the particle and in the



second segment the SnEt<sub>3</sub> radical can act as an acceptor in free radical elimination in the reaction with SQSnEt<sub>3</sub>.

Thus within the scope of the proposed mechanism tetraethyl tin is a product of radical transformation and its yield can serve as a criterion of the relative contribution of one-electron transfer which changes with variations in the solvating and ionizing capacity of the solvents.

In conclusion it is advisable to display a general scheme of possible products of radical elimination reactions with regard to the series of acceptors known at the present time



Continuing expansion of the scope of Group IVB organometallic derivatives of o-semiquinones should yield the key to more complete understanding of the mechanisms of free radical elimination reactions with respect to the electronic and steric factors of substituents belonging to the group IVB elements. Right now there is interest in a detailed study of the reaction of free radical phenylation with the aid of SQSiMe<sub>2</sub>Ph.

## EXPERIMENTAL

The EPR spectra were recorded on a RÉ-1301 production model radiospectrometer. Chromatographic analyses were carried out on a Tsvet-4 chromatograph. Sodium and thallium semiquinolates were obtained by reacting the Na(T1) catecholates [11, 12] with equivalent amounts of the quinones. All reactions were carried out in evacuated ampuls. The 3,5-di-tert-butyl-o-benzosemiquinolate of triphenyl tin was obtained by reaction of stoichiometric amounts of hexaphenyl stannate and the quinone. Control by the EPR method showed that after 4 h at ~20°C the reaction proceeds quantitatively.

Oxidation of 2-Dimethylphenylsiloxy-4,6-di-tert-butylphenol (III) by  $Ag_2O$  in Cumene. 0.60 g of (III) and 2.0 g  $Ag_2O$  in 10 ml cumene were shaken together at 20°C until the (III) disappeared completely (chromatographic control 2 h). In the final reaction mixture was found 0.12 g (88%) of diphenyl. From the GLC data dicumyl was absent from the mixture.

<u>Reaction of CatNa<sub>2</sub> with Et<sub>3</sub>SnCl in THF.</u> 0.67 g CatNa<sub>2</sub> in 15 ml THF was mixed with 1.20 g Et<sub>3</sub>SnCl. The exothermic reaction was accompanied by deep coloration of the solution, in the EPR spectra the signal appeared for SQNa. The reaction mixture was allowed to stand for 2 h, after which the THF was replaced by hexane. By filtration 0.27 g (96%) of NaCl was isolated. By low temperature crystallization 0.42 g (42%) of CatSnEt<sub>2</sub> was recovered. The mother liquor was treated with 10% HCl. By the GLC method 0.14 g (12%) of SnEt<sub>4</sub>, 0.66 g (54%) of Et<sub>3</sub>SnCl and 0.23 g (42%) of catechol were found.

<u>Reaction of Me<sub>2</sub>EtSiCl with SQNa.</u> A solution of 1.22 g Me<sub>2</sub>EtSiCl in 15 ml abs. ether was mixed at 25°C with a solution of 2.43 g SQNa in 50 ml abs. ether. The reaction mixture was let stand 10 h after which the ether was replaced by hexane. On filtration NaCl was isolated in quantitative yield. By chromatography 0.41 g (19%) of quinone, 1.26 g (32%) of Cat(SiMe<sub>2</sub>-Et)<sub>2</sub>, 0.64 g (23%) of CatSiMe<sub>2</sub> and 0.14 g (5%) of CatSiMeEt were found in the solution.

Synthesis of 3,5-Di-tert-butylcatecholate of Bis(dimethylethyl)silicon. To a solution of 2.66 g of CatNa<sub>2</sub> in 50 ml ether at 25°C was added 2.44 g Me<sub>2</sub>EtSiCl<sub>2</sub>. The mixture was allowed to stand at ~20°C for 2 h then the ether was replaced by hexane and the NaCl filtered off. The solution was fractionated. Recovered 2.81 g (72%) of Cat(SiMe<sub>2</sub>Et)<sub>2</sub>, bp 95-97°C,  $n_{D}^{2^{\circ}}$  1.4880. Found: C 66.04; H 10.61; Si 13.34%. C<sub>22</sub>H<sub>42</sub>SiO<sub>2</sub>. Calculated: C 67.01; H 10.65; Si 14.21%.

Synthesis of 3,5-Di-tert-butylcatecholate of Methylethylsilicon. To a solution of 11.1g 3,5-di-tert-butyl-1,2-catechol and 10.1 g Et<sub>3</sub>N in 100 ml ether was added 7.2 g MeEtSiCl<sub>2</sub> in 70 ml ether, with heating for 1 h at 40°C. The ether was removed by distillation and 150 ml hexane was added to the residue. The NEt<sub>3</sub>•HCl was filtered off and the solution fractionated. Recovered 9.8 g (67%) of CatSiMeEt with a bp of 120-129°C (0.5 mm),  $n_{D}^{2°}$  1.4950. Found: C 68.83; H 9.74; Si 9.25%. C<sub>17</sub>H<sub>28</sub>Si<sub>2</sub>O<sub>2</sub>. Calculated: C 68.86; H 9.59; Si 9.59%. CatSiMeEt hydrolyzes slowly in air.

Reaction of SQT1 with Dimethyl-2,4,6-tri-tert-butylphenoxychlorosilane (VI). A solution of 1.27 g SQT1 in 50 ml of benzene was added at ~20°C to a solution of 1.06 g of (VI) in 10 ml benzene. In the EPR spectrum of the admixture superposition of the signals of SQT1 and the tri-tert-butylphenoxy radical was observed. At the end of the reaction (disappearance of the SQT1 signals) 0.71 g (99%) of TlCl was separated by filtration. Chromatographically there was found 0.81 g (98%) of CatSiMe<sub>2</sub> in the solution. The yield of tri-tert-butylphenoxy radical was estimated to be quantitative by the EPR method.

# CONCLUSIONS

1. Disappearance of the free valence in organometallic derivatives of o-semiquniones with IVB group metals linked with elimination of one of the radicals on the IVB group element, proceeds by a bimolecular mechanism with participation of an external acceptor of the radical. The case in which a stable radical is formed as a result of elimination constitutes an exception.

2. Examples of acceptors contributing to radical elimination are atoms of metals, organometallic and organic radicals, and neutral molecules.

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# ACYLATION OF DICOBALTHEXACARBONYL COMPLEXES OF 1-ETHYNYLCYCLOHEXENE

### AND 1-ETHYNYLCYCLOPENTENE BY ACYLIUM SALTS

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It was previously reported that the dicobalthexacarbonyl (DCHC) complex of isopropenylacetylene (I) reacts with cationoid salts of the type  $E^+BF_4^-$  (where  $E^+$  is alkyl, acyl, thioaryl, and nitronium cation) by a two stage mechanism of electrophilic addition to the olefin with independent variations of the electrophile and nucleophile [1, 2]. However, the question of the generality of the discovered reaction remained open, in particular it was unclear to what extent the presence of the bulky fragment of the DCHC complex\* will influence the ease of carrying out the Ad<sub>E</sub> reaction at the double bond for systems more complex than (I).

In the present work the reactions of certain acylium salts with DCHC complexes of 1-ethynylcyclohexene (II) and 1-ethynylcyclopentene (III) have been studied (preliminary communication [4]).



It was found that the reactions of (II) or (III) with acylium salts of the acetyl tetrafluoroborate (IV) or trans-crotonyl tetrafluoroborate (V) type occur under conditions analogous to those described previously in [1]. The formation of a cationoid intermediate (CI-I) or (CI-II) was evidently the result of addition of the acyl cation at the double bond of (II) or (III). The intermediates were sufficiently stable in solution but were able to be further converted on treatment with water or methanol into the corresponding hydroxy or methoxy adducts (VI)-(XII). The structures of the latter were proved by data of <sup>1</sup>H NMR spectroscopy, the stereochemistry of the products will be considered below. Oxidative decomplexation of (VI)-(VIII) and (X)-(XII) occurred fairly effectively  $(80-95\% \text{ yields})^{\dagger}$  and led to the forma-

\*It is known from [3] that DCHC complexes of acetylenes have a tetrahedral structure, see also data from the present work on the stereochemistry of the obtained adducts.

<sup>†</sup>The assumed conditions proved to be unsuitable for decomplexation of the DCHC complex of the crotonoyloxy adduct (IX) which gave a complex mixture of products under these conditions.

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