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ONE-ELECTRON TRANSFER IN REACTIONS OF ORGANOMERCURY COMPOUNDS WITH DI-tert-BUTYL-SUBSTITUTED *o*-QUINONE

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Summary

The reaction of bis(triethylgermyl)mercury with 3,5-di-tert-butyl-1,2-benzoquinone has been investigated. It has been shown by means of ESR spectroscopy that the primary reaction step is a one-electron transfer from a germylmercurial compound to quinone, the paramagnetic species observed being *o*-semiquinone derivatives. The adduct, 3,5-di-tert-butyl-1,2-bis(triethylgermyloxy)benzene, is formed via the recombination of an ion-radical pair in the solvent cage. Partial exit of triethylgermyl radicals from the cage leads to the generation of hexaethyldigermane as one of the reaction products.

Under more drastic temperature conditions, the same quinone reacts with diethylmercury via a one-electron transfer stap. The observed ESR spectrum has been attributed to a mercury-containing chelate of 3,5-di-tert-butyl-1,2-benzosemiquinone.

Introduction

Bimetallic organometallic compounds containing Si—Hg, Ge—Hg and Sn—Hg bonds have been studied extensively [1 - 3]. Such compounds have already found quite considerable application in the syntheses of new types of organometallic compounds and have often been used in the solution of a variety of theoretical problems. The studies of Neumann et al. [4 - 8] and of Eaborn et al. [9 - 12] have been particularly successful in this respect.

Recently we have shown that electron transfer is the main step in the reaction of bis(triethylgermyl)mercury with tetracyanoethylene [13]. In this case, the ESR signal obtained demonstrated that a germylmercurial acts as an electron donor. The 1,4-addition of bis(trimethylsilyl)mercury to benzyl, PhCOCOPh, also involves an anion-radical as an intermediate [4].

A radical mechanism has also been suggested [4,12,14] for the exothermal addition of bis(trimethylsilyl)mercury to benzoquinone and related compounds. On the other hand, an alternative multicentre polar mechanism has been assumed in the case of benzoquinone [4] as the nature of the solvent has a considerable influence on the rate. In these reactions, an ESR signal was only observed in the case of anthraquinone but the authors were unable to interpret the ESR spectrum [4].

In our opinion it was interesting to check the possibility that one-electron transfer mechanism applies in the reaction of bis(triethylgermyl)mercury with di-tert-butyl substituted *o*-quinone, the latter compound being chosen on account of its high reactivity and the relative stability of the intermediate radicals generated.

Results and discussion

The compound 3,5-di-tert-butyl-*o*-benzoquinone (I) reacts readily with bis(triethylgermyl)mercury (II) in toluene even upon melting the mixture, which becomes intensely green in colour. On warming the mixture for 15-20 min to room temperature, the formation of metallic mercury (93%), 1,2-bis-(triethylgermyloxy)-3,5-di-tert-butylbenzene (III) (83%) and hexaethyldigermane (12%) occurred. The structure of compound (III) was confirmed by elemental analysis, and IR and PMR spectral analysis.

For the ESR study, equimolar amounts of the reagents were mixed in toluene at −80°. Immediately after mixing, an ESR signal (see Fig. 1) due to superposition of the spectra of the two radicals was observed. The upfield signal (g 1.9989) consists of a doublet with h.f. constant a(H) 3.5 Oe. Additional lines are observed at the sides of this signal due to coupling of the unpaired electron with the magnetic isotopes of mercury, $a(^{199}\mathrm{Hg})$ 11.7 Oe (J 1/2). The

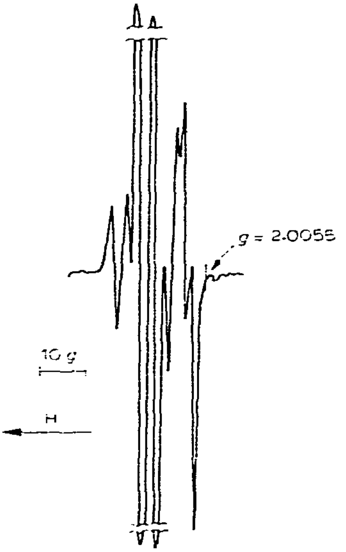
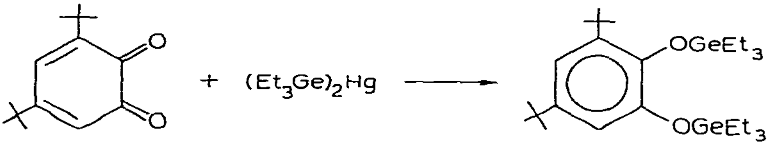


Fig. 1. ESR spectrum obtained during the reaction of (I) with bis(triethylgermyl)mercury at −40° in toluene.

downfield signal also consists of a doublet whose constant is equal to 1.6 Oe and with a *g* factor of 2.0046.

On increasing the temperature, line narrowing is observed and the mercury satellites are clearly resolved. At −20°, the signal with *g* 1.9989 rapidly disappears, the intensity of the downfield doublet increases and additional lines appear at the sides of the signal (both upfield and downfield). At room temperature, the signal with *g* 2.0046 slowly loses its intensity while the additional lines rapidly disappear. The final spectrum (doublet with a h.f. coupling constant of 1.6 Oe) was observed after several hours.

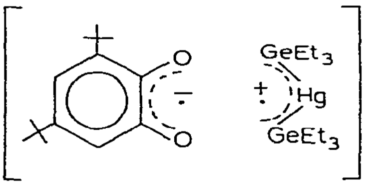
As far as the composition of the final product is concerned, reaction of (I) and (II) generally occurs with precipitation of mercury and addition of Et_3Ge groups to the quinone oxygens.



(1)

(I) (II) (III)

The ESR signal observed during the course of the reaction at low temperature demonstrates unequivocally that the first step in the reaction occurs by means of a one-electron transfer. The determination of the direction of the electron transfer in the system poses no problem since (i) *o*-quinones exhibit distinct acceptor properties, (ii) from the nature of the h.f. couplings, the ESR spectra may be assigned to *o*-semiquinones or to their chelate complexes [15 - 17], and (iii) recently, bis(triethylgermyl)mercury has been found to behave as a one-electron donor in reactions involving strong electron acceptors [13,18,19]. Thus the first reaction step is initiated through the generation of the ion-radical pair (IV).



(IV)

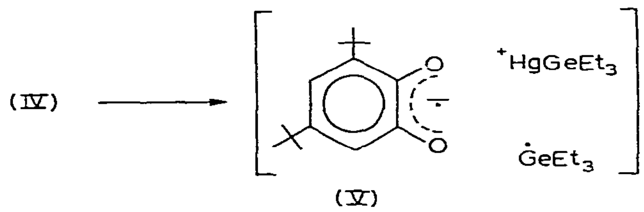
The germylmercury cation-radical is not stabilized by its internal charge and electron delocalization and hence it decomposes:

$$[(C_2H_5)_3Ge]_2Hg^{\overset{+}{\cdot}} \rightarrow (C_2H_5)_3Ge\cdot + {}^{+}HgGe(C_2H_5)_3 \qquad (2)$$

Hence, three particles are produced in the solvent cage (two of them being charged) (eqn. 3).

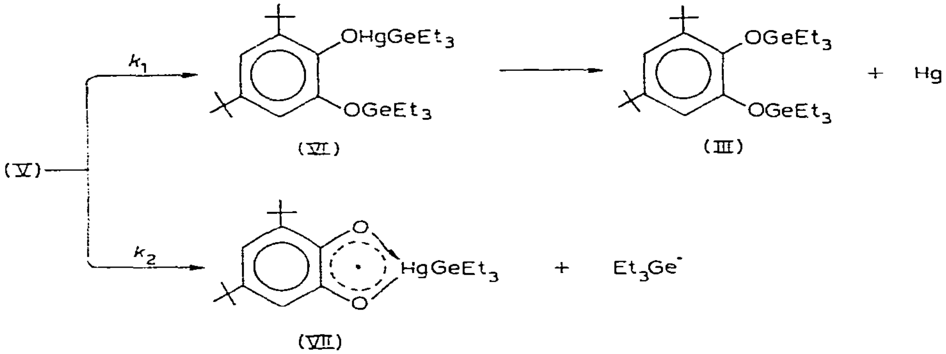
Further transformation of system (V) depends on the relative importance of the two processes shown in eqn. 4.

The constant k_1 specifies the rate of formation of a diamagnetic intermediate compound (VI) as a result of the recombination of the ion pair and



(3)

radicals in the solvent cage. Subsequent demercuration of (VI) leads to (III). The constant k_2 determines the rate of exit of the more labile Et_3Ge radical



(4)

from the reaction cage. This process leads to hexaethyldigermane amongst the products and also to the generation of a considerable concentration of stable radicals during the course of the reaction.

The two ESR signals observed directly after mixing the reagents indicate that the spectrum with the lower *g* factor is due to the radical (VII). The main reasons for this assignment are as follows:

(i) Splitting of the main doublet with a constant *a*(H) 3.5 Oe provides evidence in the favour of a complex chelate structure for *o*-semiquinone [16]. The satellites observed at the sides of spectrum may be attributed to splitting at ^{199}Hg nuclei (*J* 1/2) and the ^{201}Hg nuclei (*J* 3/2). The ratio of the magnetic moments of the isotopes [20] shows that the mercury multiplet should contain five highfield components if $a(H) = a(^{201}Hg)$ (see the pattern of the spectrum given in Fig. 2). Calculations show that the intensity of the edge satellite should be 16.8% of the value of the main doublet line. In the actual spectrum, the value calculated from the amplitudes of the first derivatives is considerably lower than this (ca. 10%) which may be attributed to a different line width.

(ii) The considerable deviation of the *g* factor obtained from the ESR signal from the purely spin value may be readily explained by assuming participation of the vacant 6*p* mercury orbital in the delocalization of the unpaired electron. Excitation of the unpaired electron into this orbital should decrease the *g* factor by a value proportional to $\lambda/\Delta\epsilon$ where λ is the spin-orbital coupling constant of mercury and $\Delta\epsilon$ is the difference in energies between the vacant mercury orbital and the orbital of the unpaired electron.

The ESR spectrum obtained at lower field strengths has been assumed to be that of 2-(triethylgermyloxy)-4,6-di-tert-butylphenoxyl (VIII) which is gene-

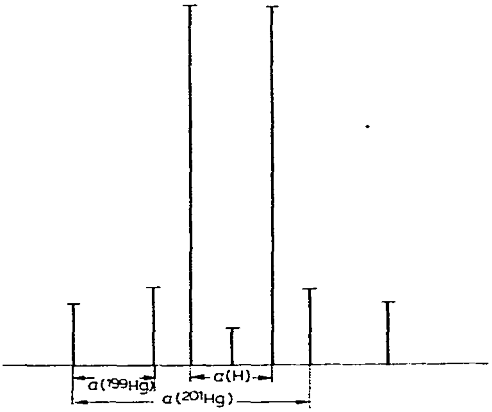
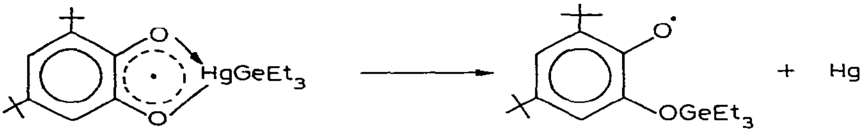
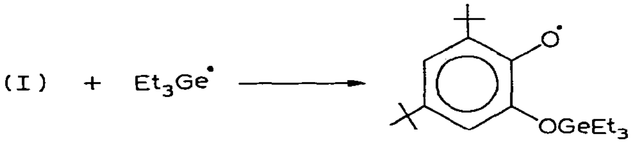


Fig. 2. Theoretical ESR spectrum for radical (VII).

rated during the demercuration of the radical (VII) as depicted in eqn. (5) and/or by attachment of a triethylgermyl radical on to quinone (I) [eqn. (6)].



(VII) (VIII) (5)



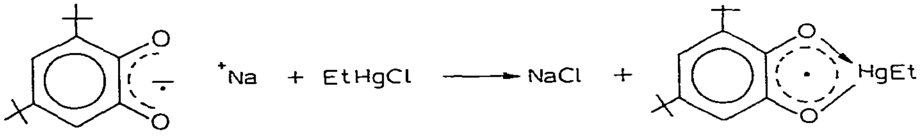
(6)

(VIII)

It is well known that asymmetric germylmercury compounds, Et_3GeHgR, having an electron-attractive substituent R are all labile and may be readily demercurated to give mercury and Et_3GeR [21] [cf. eqn. (5)].

If a chelate structure is assumed for radical (VII), the mercury atom should possess a coordination number of 3. In spite of this unusual value for a Group II element there are convincing literature data [22] supporting this value for alkaline-earth elements in chelate complexes with an anion-radical. Moreover, recently, a bridged structure has been postulated [23] for phenylmercury alkoxide complexes in which the mercury atom has a coordination number of 3.

An interesting confirmation of the existence of stable complexes of radicals of type (VII) is provided by the following reaction:



(7)

(IX)

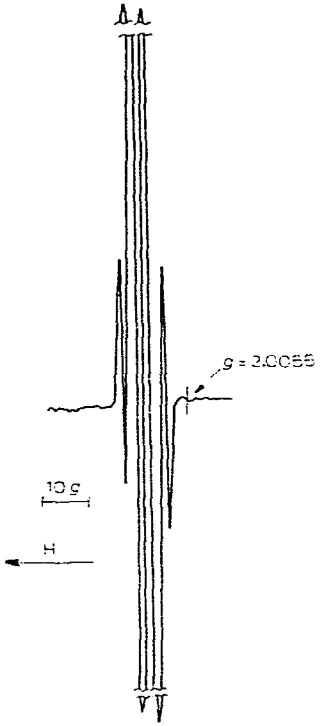
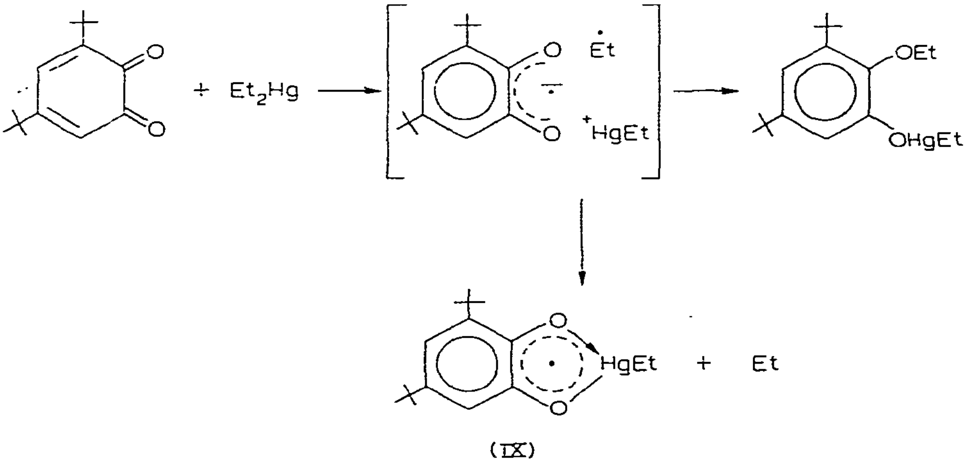


Fig. 3. ESR spectrum of radical (IX) in toluene.

The resulting green solution of radical (IX) is quite stable at room temperature in the absence of oxygen and moisture. The ESR spectrum (Fig. 3) consists of a doublet [*a*(H) 2.8 Oe, *g* 1.9996] with satellites at the sides of the spectrum being attributed to splitting of the magnetic isotopes of mercury ($a(^{199}\text{Hg})$ is 6.7 Oe). The low *g* factor, the splitting involving mercury iso-



(8)

(IX)

topes, the high value of the high-field proton constant and the solubility of the radical in non-polar solvents support a chelate structure (IX) for the radical. The formation of (IX) as an intermediate in the reaction of (I) with diethylmercury in toluene has also been observed. This reaction is slow at room temperature, but at 40-50° the solution rapidly becomes bluish-green in colour and the ESR spectrum specific to radical (IX) is observed. It is not unreasonable to assume that diethylmercury in a similar manner to bis(triethylgermyl)mercury transfers an electron to *o*-quinone, although in this case the donor properties of the latter are much less pronounced.

ESR signals have also been observed in reactions of (II) with such electron acceptors as *o*-chloranyl and 2,4,6-tri-tert-butyl-4-bromo-2,5-cyclohexadienone. The spectrum in the first case is due to the formation of the *o*-chloranyl semiquinone derivative, and in the second case to formation of the 2,4,6-tri-tert-butylphenoxyl radical. The results of these studies will be published at a later date.

Experimental

4,6-Di-tert-butyl-1,2-benzoquinone (I) was prepared by a previously described method [24]. Quinone sodium-semiquinolate was obtained by reaction of (I) with metallic sodium in THF [15].

ESR spectra

All ESR spectral measurements were performed on a RE-1301 X-region spectrometer with magnetic field modulation at 975 kHz. The reagent solutions (1 - 5×10^{-2} mol/l) were mixed in a double-necked ampoule at −80° in vacuo. The mixture was then transfered to a soldered glass tube (4 mm in diameter) which was placed in the resonator of the spectrometer which was thermostatted by means of a TC-1 IKhF thermoblock. The ESR spectra were registered at −80° to 0°C. The g factors and the h.f. coupling constants were measured relative to an aqueous Fremi salt solution as a standard [a(N) 13.07 Oe, g_{iso} 2.005500] [25].

The reaction of bis(triethylgermyl)mercury with (I) in toluene

(I) (5.46 g, 10.50 mmole) in 20 ml of toluene was added to 2.20 g (10.00 mmole) of (II) in 20 ml of toluene at liquid-nitrogen temperatures.

The mixture was heated to ca. 20° for 15-20 min when the solution became green in colour. Metallic mercury (1.86 g, 92.7%) was isolated. The solvent was removed at low pressure and the residue fractionated in vacuo. 1,2-Bis(triethylgermyloxy)-4,6-di-tert-butylbenzene (4.50 g, 8.34 mmole, 83.4%) was obtained, b.p. 163-165°/1 mm, n_D^{20} 1.5122. (Found: C, 58.10; H, 9.46; Ge, 26.51. $C_{26}H_{50}Ge_2O_2$ calcd.: C, 57.86; H, 9.33; Ge, 26.86%.) GLC analysis of the distillated revealed the presence of 1.21 mmole (11.5%) of hexaethyldigermane. All yields were computed on the basis of the quantity of initial $(Et_3Ge)_2Hg$ used.

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