REACTIONS OF BIS(DUROQUINONE)NICKEL WITH NUCLEOPHILIC REAGENTS AND REDUCING AGENTS

A. N. Nesmeyanov, L. S. Isaeva,

UDC 542.957:547.257.1:547.567

T. A. Peganova, and A. A. Slinkin

A very limited number of papers is known up to now that are devoted to a study of the properties of the quinone π -complexes of nickel and, in particular, of bis(duroquinone)nickel (I). The papers deal mainly with the reactions for the replacement of the duroquinone by an olefinic ligand [1, 2] and trialkyl phosphite [3]. A new method was proposed in a previous paper for the synthesis of (I) [4], which made it possible to undertake a study of the reactivity of the latter.

The reaction of (I) with an acidified alcohol solution of p-nitrophenylhydrazine at $\sim 20^{\circ}$ C gave 4'-nitro-4-hydroxy-2,3,5,6-tetramethylazobenzene in 54% yield

$$(DQ)_{2}Ni + p \cdot NO_{2} - C_{6}H_{4} - NHNH_{2} \xrightarrow{HO_{1}} \rightarrow H_{3}C \qquad CH_{3}$$

$$\rightarrow HO - - N = N - NO_{2} + NiCl_{2} + H_{2}O \qquad (1)$$

$$H_{3}C \qquad CH_{3}$$

$$DQ \text{ is duroquinone}$$

uai

The reaction also proceeds in a similar manner with the free duroquinone [5]. If (I) is reacted with a neutral solution of p-nitrophenylhydrazine, then, the same as in the case of the uncoordinated duroquinone [6], only durohydroquinone can be isolated in 20% yield or less. Apparently, either initial attack at the carbonyl group of the ligand occurs in this case, which leads to a change in its quinoid structure and cleavage of the metal—ligand bond, or else this reagent first attacks the metal atom with a destruction of the π -complex bond and the formation of the free quinone, which then reacts with the p-nitrophenylhydrazine in the usual manner.

The reaction of (I) with electron donors, like sodium amalgam, anion-radicals and carbanions, proved to be especially interesting. As a rule, the vigorous stirring of a suspension of (I) in THF with either one or two equivalents of the reducing agent leads to the formation of highly colored solids that are stable only in an inert gas atmosphere (Table 1). These crystalline compounds were separated by filtration, in which connection their mother liquors were practically devoid of either duroquinone or durohydroquinone, which indicates that (I) is not decomposed. The reaction of (I) with electron donors can be depicted by the scheme:

$$(I) + \vec{e} \longrightarrow [(DQ)_2 Ni]^{-}$$
(2)

As will be shown below, apparently more profound reduction is possible if excess reducing agent is used, with the formation of the bis(duroquinone)nickel dianion.

A study of these compounds disclosed that they possess paramagnetic properties. The EPR spectrum of the solid material is shown in Fig. 1a. However, the fine structure of the EPR spectra of these compounds could not be obtained, since they are insoluble in most organic solvents. Destruction of the π -complex bond apparently occurs when they are dissolved in either absolute alcohol or DMF, and, according to the EPR data, the durosemiquinone anion is present in the solution (Fig. 1b). Compound (I) is regenerated when these compounds are treated with dilute acids.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 158-164, January, 1974. Original article submitted June 20, 1973.

• 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.

No.	Reducing agent	Ratio of reactants (DQ) ₂ Ni : R*	Reaction time, h	Reaction tempera- ture, °C	Solor of product	Specific mag- netic suscepti- bility, χ · 10 ⁶
1 2 3 4 5 6	1% Na/Hg C10HaNa C10HsNa (C6Hs)2CNa (C6Hs)2CNa CC4Hs)2CNa	1:4 1:1 1:2 1:1 1:1	27716	20 20 20 35 35 20	Dark blue "" Dark violet The same	1,3 1,8
7 8 9	C5H5Na (C2H5OCO)2CHNa C6H6FeC5H5	1 : 2 1 : 2 1 : 1	1,5 3 3,5	20 50 0	The same Blue Dark brown	5,6 2,0
*R =	reducing agent,	•	· .	I	1	1

TABLE 1. Reaction of Bis(duroquinone)nickel with Reducing Agents (Solvent = THF, and Toluene for $(C_2H_5OCO)_2CHNa)$

When (I) is reacted with the electroneutral benzenecyclopentadienyliron [7] the reduction of (I) to the anion-radical is accompanied by the oxidation of $C_6H_6FeC_5H_5$ to the cation.*

 $(I) + C_6 H_6 FeC_5 H_5 \rightarrow [(DQ)_2 Ni]^{-} [C_6 H_6 FeC_5 H_5]^+$ (3)

In the solid state the formed salt $[(DQ)_2Ni]^{-} \cdot [C_6H_6FeC_5H_5]^+$ possesses paramagnetic properties (see Fig. 1a), while its treatment with aqueous NaBF₄ solution leads to (I), which deposits as a crystalline precipitate, and to benzenecyclopentadienyliron fluoborate, which remains in solution. The latter was identified as the difficultly soluble benzenecyclopentadienyliron tetraphenylborate.

Thus, the reaction of sodium naphthalene or triphenylmethylsodium with duroquinone in THF leads to the rapid precipitation of the Na salt of durosemiquinone, which is recorded by the EPR method after dissolving in absolute alcohol (see Fig. 1b).

The reaction of duroquinone with sodiomalonic ester in toluene proceeds in a different manner, as a result of which the coumarin derivative is formed in 60% yield [8].

 $DQ + NaCH(COOC_2H_5)_2 \rightarrow \underbrace{H_3C}_{NaO} \underbrace{CH_3}_{COOC_2H_5} O \tag{4}$

When the course of this reaction was checked by EPR it was shown that the reaction mixture fails to contain any paramagnetic particles. Consequently, weak electron donors, like sodiomalonic ester, reduce (I), but are incapable of transferring electrons to the free duroquinone. Consequently, (I) is a stronger oxidizing agent than the free duroquinone.

Next we ran the reaction of the reverse oxidation of the obtained bis(duroquinone)nickel anion-radicals by treatment with an electron acceptor like triphenylchloromethane [9]. The oxidation with triphenylchloromethane was run in THF solution at $\sim 20^{\circ}$ in an argon atmosphere. Compound (I) is precipitated during the reaction process, while, employing EPR, we were able to detect the triphenylmethyl radical in the mother liquor (Fig. 1c).

$$[(DQ)_2Ni]^{-} + (C_6H_5)_3CCI \rightarrow (I) + (C_6H_5)_3C' + CI^{-}$$
(5)

It should be mentioned that the amount of isolated substances is strongly dependent on the extent of the reduction of (I), which, in turn, is determined by the nature of the reducing agent and its relative amount.

If the bis(duroquinone)nickel anion-radicals were obtained when treatment was with one equivalent of either sodium naphthalene or sodium cyclopentadienyl, two equivalents of sodiomalonic ester, and either one or two equivalents of triphenylmethylsodium, then the removal of an electron from the anion-radical leads to the formation of (I) (61-87% yield), triphenylmethyl peroxide (51-67% yield), triphenylmethane (9-19% yield), benzhydryltetraphenylmethane (3-9% yield), and duroquinone ($\leq 9\%$ yield). This shows that when (I) is treated with the above enumerated reagents the reduction goes to the extent of 70-80%.

* The reaction was run in collaboration with N. A. Vol'kenau and V. A. Petrakova.

149



Fig. 1. EPR spectra: a) reduction products of bis(duroquinone) nickel; b) durosemiquinone anion-radical; c) triphenylmethyl radical.

However, if the bis(duroquinone)nickel anion-radical was obtained by starting with either two equivalents of sodium naphthalene or sodium cyclopentadienyl, then two equivalents of triphenylchloromethane is required for the complete transition of this anion to (I). Apparently, (I) is reduced to the dianion in this case. In the experiments after treatment of the reduction products with triphenylchloromethane the yield of (I) is a total of 28-26%, 16-23% for triphenylmethyl peroxide, 29% for triphenylmethane, 6% for benzhydryltetraphenylmethane, and 35% for duroquinone. In a similar manner, the yields of (I) decrease by a matter of 1.5-2 times when the reduction products, obtained using two equivalents of the reducing agent, are treated with dilute acids.

Together with a study of the obtained complexes by the EPR method, it seemed of interest to measure their magnetic susceptibility. The static magnetic susceptibility of a number of compounds was measured by the Faraday method in an inert gas (N_2) atmosphere at 20° and a magnetic field strength ranging from 800 to 3500 Oe. For sample 3^* the temperature dependence of χ was studied in the range 77-293°K. For complex 3 the dependence of χ on the temperature obeys the Curie–Weiss law, with the value of the magnetic moment $\mu_{eff} = 1.3 M_{B}$ and the Weiss constant Δ = $-100 \mathrm{K}.~$ The large value of Δ is probably due to the presence of strong exchange reactions in the system, which leads to a low value of μ_{eff} when compared with the value that is characteristic for one unpaired electron $(1.7 M_{\rm B})$. Taking into account the values of μ and Δ for compound 3, we calculated the theoretical value of the specific magnetic susceptibility (per gram of complex), on the assumption that each complex bears one unpaired electron, by means of the equation

$$\chi = \frac{N}{M} \frac{\mu_{\rm B}^2 M_{\rm B}^2}{3k \left(T + \Delta\right)}$$

where N is Avogadro's number, M is the molecular weight of the complex, μ_B is the magnetic moment of the complex, M_B , M_B is the Bohr magneton, k is the Bohrzmann constant, T is the absolute temperature, and Δ is the Weiss constant, K.

The value $\chi = 8.7 \cdot 10^{-6}$ was obtained as a result. The experimental value is $\chi = 1.3 \cdot 10^{-6}$, i.e. approximately 20% of the molecules of the complex have an unpaired electron. When two unpaired electrons are localized on a molecule of the complex the amount of paramagnetic molecules drops to 10%. The values of χ for the other studied complexes are also smaller than the theoretical values of χ . This is possibly due to the peculiarities of the topochemical reaction for the preparation of the complexes, which make it impossible to obtain a quantitative yield of the radicals.

EXPERIMENTAL METHOD

All of the reactions were run in an argon atmosphere and in absolute solvents, which had been distilled immediately before experiment. For all of the paramagnetic compounds the EPR spectra were taken on a Varian E-12 radiospectrometer.

Reaction of Bis(duroquinone)nickel with Sodium Amalgam. To 23 g of 1% (10 mmoles) of sodium amalgam in THF was added 0.84 g (2.5 mmoles) of (I), and the mixture was stirred at $\sim 20^{\circ}$ for 2 h. The end of reaction was determined by the change in the color of the reaction mixture from red to dark blue. The dark blue precipitate was separated from the mercury, repeatedly washed with absolute ether, and dried in argon. The EPR spectrum of this compound is shown in Fig. 1a.

*The complex was obtained by the reduction of bis(duroquinone)nickel with two equivalents of sodium naph-thalene (see Table 1).

The obtained reduction product was treated with dilute HCl solution (1:5), and the obtained red precipitate was filtered, and then washed with alcohol and ether. We obtained 0.35 g (42%) of (I), mp ~ 205° (decompn.) [10].

Reaction of Bis(duroquinone)nickel with Sodium Naphthalene. A suspension of 1 g (2.6 mmoles) of (I) was stirred at $\sim 20^{\circ}$ for 7 h with 24 ml of a 0.11 N (2.6 mmoles) THF solution of sodium naphthalene. The obtained dark blue precipitate was filtered, washed with ether, and dried in argon. We obtained 1.05 g ($\sim 100\%$) of substance. The EPR spectrum of the solid sample is shown in Fig. 1a.

To 0.40 g of the obtained dark blue substance was added 15 ml of CH_3COOH (1:3). We isolated 0.19 g (50%) of (I) as a result.

To 0.53 g (1.3 mmoles) of the reduction product was added a solution of 0.36 g (1.3 mmoles) of triphenylchloromethane in 30 ml of THF, and the mixture was stirred at $\sim 20^{\circ}$ for 6 h. The obtained precipitate was filtered, and washed in succession with water, alcohol and ether. We obtained 0.41 g (82%) of (I).

Triphenylmethyl radicals were detected in the mother liquor by means of the EPR spectrum. After evaporation of the solvent the dry residue was treated with ether, and subsequent chromatographing on Al_2O_3 led to the isolation of 0.20 g (60%) of triphenylmethyl peroxide, mp 178-182° [11], 0.03 g (9%) of triphenylmethane, mp 93° [12], 0.01 g (3%) of benzhydryltetraphenylmethane, mp 220° [13], 0.02 g (5%) of duroquinone, mp 110° [14], and 0.08 g (24%) of triphenylcarbinol [15].

The reaction of (I) with triphenylmethylsodium, sodium cyclopentadienyl and sodiomalonic ester were run in a similar manner (see Table 1). In each case the obtained reduction products of (I) were treated with triphenylchloromethane (Table 2).

Reaction of Bis(duroquinone)nickel with Benzenecyclopentadienyliron. To 0.40 g (1 mmole) of (I) was added a THF solution that contained 0.20 g (1 mmole) of benzenecyclopentadienyliron. The reaction mixture was stirred at 0° for 3.5 h, and at $\sim 20^{\circ}$ for 2 h, until the green color of the solution, characteristic for benzenecyclopentadienyliron, had disappeared completely. Then the dark brown precipitate was filtered, and washed with THF and ether. We obtained 0.49 g of substance, the EPR spectrum of which is shown in Fig. 1a.

Aqueous NaBF_4 solution was added to 0.42 g of the reduction product, and the residual precipitate was filtered and then washed with alcohol and ether. After drying in the air we obtained 0.25 g (73%) of (I).

To the aqueous mother liquor, which contained benzenecyclopentadienyliron fluoborate, was added an aqueous solution of tetraphenylboronsodium. The obtained precipitate of $[C_6H_6FeC_5H_5]^+[B(C_6H_5)_4]^-$ was filtered and reprecipitated from nitromethane solution with ether. We obtained 0.07 g (16%) of benzenecyclopentadienyliron tetraphenylborate, mp 250-251° (decompn.) [16].

<u>Reactions of Duroquinone with Reducing Agents</u>. To a THF solution, containing 0.60 g (3.6 mmoles) of duroquinone, was added 150 ml of a 0.024 N (3.6 mmoles) THF solution of sodium naphthalene. The obtained amorphous precipitate of durosemiquinonesodium was filtered immediately, washed with ether, and dried in argon. The EPR spectrum of an alcohol solution of the obtained compound is shown in Fig. 1b. It corresponds to the EPR spectrum of durosemiquinone [17]. The reaction of duroquinone with triphenyl-methylsodium was run in a similar manner.

(DQ) ₂ Ni reduction product		Relative	Yield,%					
reducing - agent (R)	ratio of re- actants (DQ) ₂ Ni : R	$(C_6H_5)_3$ CC1, equiv.	(DQ)2Ní	triphenyl- methyl peroxide	triphenyl- methane	benzhy- dryltetra- phenyl- methane	рд	triphenyl- carbinol
$C_{10}H_8Na$ $C_{10}H_8Na$ $(C_6H_5)_3CNa$ $(C_6H_5)_3CNa$ C_6H_5Na C_6H_5Na C_6H_5Na	1:1 1:2 1:1 1:2 1:2 1:1 1:2 1:2	$ \begin{array}{c} 1 \\ 2,6 \\ 1 \\ 1 \\ 2,6 \\ 4 \end{array} $	82 28 82 87 61 28 70	60 16 67 51 34 23 54	9 29 14 19 32 29	3 7 8 16 9 5	5 34 8 7 18 35 8	24 16 12 15 20 23 24

TABLE 2. Reaction of Reduction Products of Bis(duroquinone)nickel with Triphenylchloromethane

The treatment of 0.50 g (2.7 mmoles) of durosemiquinonesodium with 0.75 g (2.7 mmoles) of triphenylchloromethane gave 0.33 g (47%) of triphenylmethyl peroxide, 0.04 g (6%) of triphenylmethane, 0.05 g (8%) of benzhydryltetraphenylmethane, 0.35 g (80%) of duroquinone, and 0.14 g (20%) of triphenylcarbinol.

<u>Reaction of Duroquinone with Sodiomalonic Ester</u>. A solution of 0.58 g (3.2 mmoles) of sodiomalonic ester in 25 ml of toluene was added to 0.50 g (3 mmoles) of duroquinone. The reaction mixture was refluxed for 54 h. Then it was cooled and 30 ml of CH_3COOH (1:1) was added to it. The obtained yellow precipitate was filtered, and then washed in succession with water, alcohol and ether. We obtained 0.25 g (60%) of 3-carbethoxy-5,7,8-trimethyl-6-hydroxycoumarin with mp 184-184.5° [8].

Reaction of Bis(duroquinone)nickel with p-Nitrophenylhydrazine. a) To an alcohol solution, containing 0.84 g (5.5 mmoles) of p-nitrophenylhydrazine, was added 3.7 ml of 24.5% (11 mmoles) H_2SO_4 solution. The obtained mixture was added carefully to 0.5 g (1.3 mmoles) of (I) in chloroform. The reaction mixture was stirred at ~20° for 2 h. The obtained precipitate of p-nitrophenylhydrazine sulfate was filtered, while the mother liquor was evaporated to dryness. The solid residue was dissolved in hot alcohol. Then water was added to the alcohol solution to precipitate the 4'-nitro-4-hydroxy-2,3,5,6-tetramethylazobenzene. The yield was 0.41 g (54%), mp 174° (decompn.) [5].

b) An alcohol solution of 0.29 g (6 mmoles) of p-nitrophenylhydrazine was added to a chloroform solution of 0.5 g (1.3 mmoles) of (I). The reaction mixture was refluxed for 1.5 h. The obtained precipitate of nickel metal was filtered, while from the mother liquor we isolated 0.09 g (20%) of hydroduroquinone, mp 212-216° [14].

The authors express their gratitude to N. N. Bubnov and S. P. Solodovnikov for taking the EPR spectra and their discussion.

CONCLUSIONS

1. The effect of nucleophilic reagents (sodium amalgam, sodium naphthalene, sodium cyclopentadienyl, sodiomalonic ester, triphenylmethylsodium) on bis(duroquinone)nickel was studied and it was shown that the transfer of an electron from the reducing agent to the bis(duroquinone)nickel is observed in all cases, with the formation of anion-radicals.

2. The EPR spectra were taken for the obtained reduction products, the specific magnetic susceptibility was measured, and they were reacted with triphenylchloromethane.

3. A comparison of the reactivity of the free and complex-bound quinone ligand disclosed that bis-(duroquinone)nickel is a stronger oxidizing agent than duroquinone.

LITERATURE CITED

- 1. G. N. Schrauzer and H. Thyret, Z. Naturforsch., <u>16b</u>, 353 (1961).
- 2. G. N. Schrauzer and H. Thyret, Z. Naturforsch., <u>17b</u>, 73 (1962).
- 3. A. Pidcock and G. G. Roberts, J. Chem. Soc., A, 2922 (1970).
- 4. A. N. Nesmeyanov, L. S. Isaeva, L. N. Lorens, A. M. Vainberg, and Yu. S. Nekrasov, Dokl. Akad. Nauk SSSR, <u>205</u>, 1362 (1972).
- 5. L. I. Smith and W. B. Irwin, J. Am. Chem. Soc., <u>63</u>, 1036 (1941).
- 6. R. Otte and H. von Pechmann, Ber., 22, 2116 (1889).
- 7. A. N. Nesmeyanov, N. M. Vol'kenau, and V. A. Petrakova, Abstracts of Papers Delivered at International Congress on Organometallic Chemistry [in Russian], Vol. 2, VINITI, Moscow (1971), p. 339.
- 8. L. I. Smith and F. J. Dobrovolny, J. Am. Chem. Soc., <u>48</u>, 1693 (1926).
- 9. Z. V. Todres, N. T. Ioffe, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., 1968, 523.
- 10. G. N. Schrauzer and H. Thyret, J. Am. Chem. Soc., <u>82</u>, 6420 (1960).
- 11. M. Gomberg, Ber., 33, 3150 (1900).
- 12. L. I. Smith and F. J. Dobrovolny, J. Am. Chem. Soc., <u>48</u>, 1420 (1926).
- 13. W. R. Orndorff, R. C. Gibbs, S. A. McNulty, and C. N. Shapiro, J. Am. Chem. Soc., <u>49</u>, 1541 (1927).
- 14. Z. Schmid and R. Falke, Monatsh., <u>60</u>, 295 (1932).
- 15. D. Stadnikoff, Ber., <u>47</u>, 2133 (1914).
- 16. A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesova, Dokl. Akad. Nauk SSSR, 149, 615 (1963).
- 17. B. Venkataraman and G. K. Fraenkel, J. Am. Chem. Soc., 77, 2707 (1955).