SYNTHESIS AND SPECTRAL PROPERTIES OF PORPHYRINQUINONE DERIVATIVES BASED ON DEUTEROPORPHYRIN IX

V. V. Borovkov, E. I. Filippovich
and R. P. Evstigneeva

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A series of diquinone derivatives of deuteroporphyrin IX, having different bond lengths between the chromophores, have been prepared. Deuteroporphyrin IX was condensed with modified hydroxyl-containing quinones by the mixed anhydride method. PMR spectroscopy was used to show that the magnetic anisotropy of the porphyrin ring has a strong effect on the chemical shift of the protons of the quinone ring and its neighboring substituents.

Photosynthesis is one of the most important biological processes, in the first stage of which the photoinduced separation of charges takes place [1]. Various types of reaction centers exist in photosynthetic systems. However, in spite of differences, inherent in all these centers is the presence of a chromophore (X), which absorbs solar energy, linked to an electron donor (D) and an electron acceptor (A). The chromophore in photosynthesis is usually the chlorophyll molecule; while the chemical nature of D and A differ, in the majority of cases A has a quinone structure [2]. The mechanism of charge separation on absorption of a photon is as follows:

$$DXA \xrightarrow{h\nu} DX^*A \longrightarrow DX^+A^- \longrightarrow D^+XA^-$$

The state of D^+XA^- is further stabilized by processes involving fast secondary electron transfer. The extreme complexity of studying this process in vivo makes it necessary to create synthetic models, which make it possible to examine the process of electron transfer from light-excited pigments to specific acceptors. Porphyrin structures are most often used as model compounds for chromophores because they have an electronic structure which is similar to that of chlorophyll but more stable. Recently, a series of models was synthesized in which the electron acceptors – quinones – are covalently bonded to the electron donors – porphyrins [3-11].

We have synthesized some model diquinone derivatives of deuteroporphyrin IX (Xa-f) to study primary electron transfer in photosynthesis. In contrast to previously synthesized models of the system, the derivatives which we have prepared are based on a natural porphyrin, coupled by means of a quinone ester bond. In addition, in these models the quinone structure is directly bonded to a heteroatom (nitrogen or sulfur), depending on the method of synthesis, and can be used to study the effect of the heteroatom on the course of the photoreaction of electron transfer and of the dark reaction of recombination of charges. The quinone and porphyrin parts are separated by 7-8 covalent bonds. The extent of the reaction between the donor and the acceptor, and the effect on the photoinduced separation of charges, can be determined from measurements of the distance between the chromophores. It has been shown that lengthening the chain increases the life of the separated charges, and hinders the reverse recombination [10, 11].

Our synthesis program consisted mainly of modifying the quinone part of the molecule and condensing it with porphyrin; we were able to use unsaturated quinones, which reduced the overall number of steps in the reaction, and thus simplified the preparation of the porphyrin derivatives.

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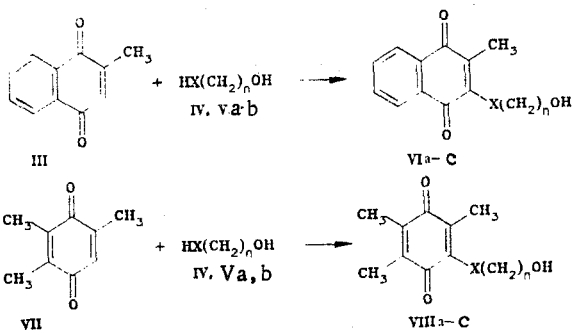
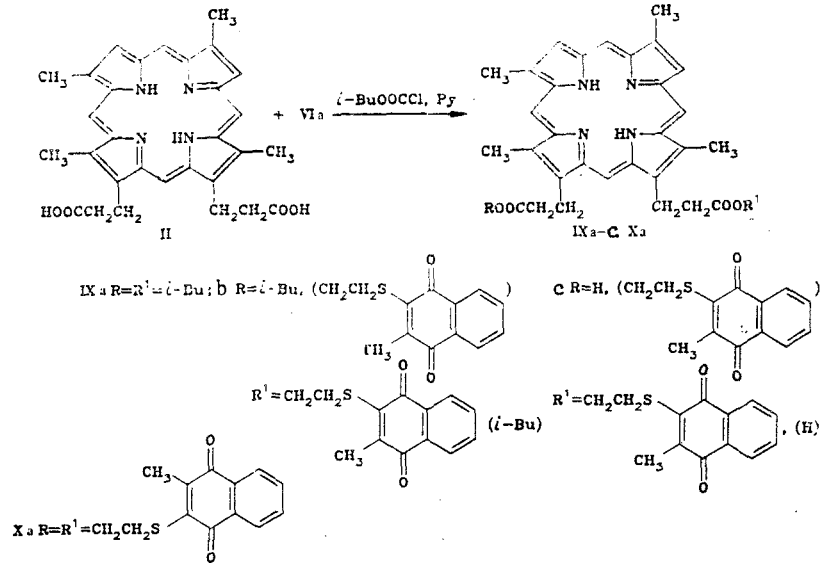


IV, VIa, VIIIa X=S, n=2; Va, VIb, VIIIb X=NH, n=2; Vb, VIc, VIIIc X=NH, n=3

Deuteroporphyrin IX (II), obtained from protohemin IX [12], was used for the synthesis of the derivatives Xa-f.



As starting quinones were chosen 2-methylnaphthoquinone (III) and 2,3,5-trimethylbenzoquinone (VII); these have different oxidation-reduction potentials so that the quinone which is the most suitable acceptor for model porphyrin systems can be determined. There was only one available position on the quinone ring, so that directed introduction of the substituent containing the hydroxyl group was possible. Combining 2-mercaptoethanol (IV) and 2-aminoethanol (Va) with the starting quinones III and VII gave hydroxy-containing quinone derivatives (VIa, b, and VIIA, b) [13, 14]; using 3-aminopropanol (Vb), the chain length was increased by one methyl group. The reaction of the heteroalcohols IV, Va, b and the quinones III, VII gave the corresponding hydroxyquinones, which were oxidized by the starting quinone molecule to give the substituted derivatives VIa-c, and VIIIa-c. Additional oxidation of the reaction mixture with a solution of $CuSO_4$ increased the yields to 91.2% (VIa) and 55.4% (VIIIa). The reaction with the aminoalcohols Va, b under the same conditions did not proceed in such a straightforward manner. After purification by chromatography on aluminum oxide and recrystallization from a mixture of chloroform and hexane (1:3) yields of the compounds were: VIb, 24.8%; VIc, 24.3%; VIIb, 14.3%; VIIC, 8%. Yields could not be increased by additional oxidation of the reaction mixture. PMR spectroscopic data showed that the main byproducts were dimers. The modified quinones VIa-c and VIIIa-c were characterized by TLC.

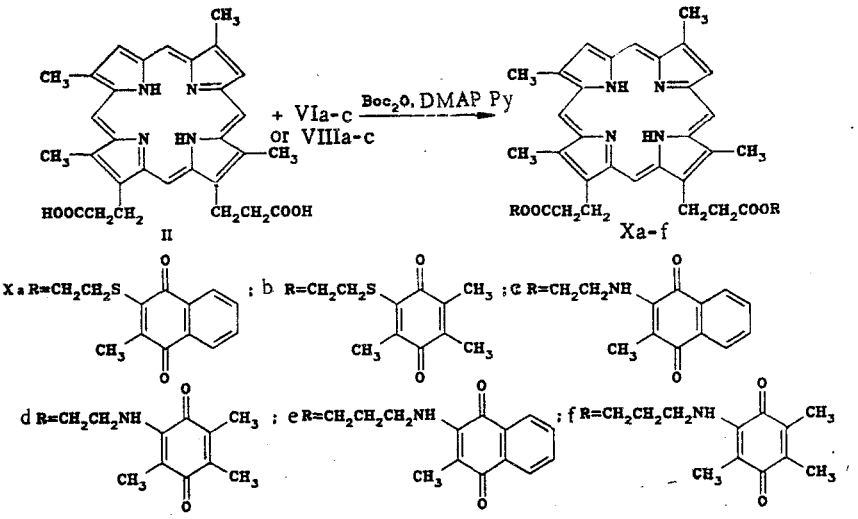
The prophyrin quinone esters Xa-f were synthesized by the method of mixed anhydrides. Pivaloyl chloride (PivCl), isobutylchloroformate (iso-BuOCOCl), and tert-butylpyrocarbonate (Boc_2O) were used as activating agents. The direction of the reaction depended strongly on the method of activation. Pivaloyl chloride in dry THF with pyridine (Py) as base at −10°C gave a mixture of the monoderivative IVc (68%) and the diderivative Xa (5%). Even a fourfold excess of the quinone VIa gave mainly the monosubstituted compounds IXc, probably because of steric factors. Purification was carried out by column chromatography on Kieselgel (Merck). Using iso-BuOCOCl under similar conditions, followed by column chromatography and preparative TLC on silica gel, we isolated and identified the di-isobutylester IXa (6%), a

TABLE 1. Yields (%) of Compound Xa and Other Reaction Products Obtained with Different Activation Methods

Compound	Yields for different methods		
	Piv Cl+Py	*iso*-BuOCOCl+Py	Boc_2O+Py+DMAP
Diquinone derivative Xa	5	53	78,8
Monoquinone derivative IXc	68	9	~1—2
By-products*	<1	17	<1

*Total yield of all by-products.

mixture of the isomers 6- and 7-position isobutylquinone diester IXb (11%), monoderivative IXc (9%), and the desired product (53%).



When the diquinone derivatives Xa-f were prepared from Boc_2O in the presence of Py and a catalytic amount of 4-dimethylamino pyridine (DMAP) [15] at 0°C, it was shown (TLC) that at first the monoester was formed, but after an hour the disubstituted compounds Xa-f were formed. Purification was carried out by column chromatography on Kieselgel (Merck). Yields of 76.3-89.3% of products Xa-f were obtained, considerably higher than when other activating reagents were used (Table 1).

Of the three methods used to activate the carboxyl group, the most promising is activation with Boc_2O, which is highly selective and gives a quantitative yield of desired product; moreover, the reaction takes place under milder conditions and at a faster rate.

The UV spectra of all the quinones were taken in methanol. For the substituted quinones VIa-c and VIIIa-c the presence of the heteroatom linked to the quinone structure leads to redistribution of the electron density in the molecules, and this is reflected in their spectra. In addition to changes in the UV region, with compounds VIa-c and VIIIa-c there is a new long-wave band at 412-510 nm (412 nm for VIa, 470 nm for VIb, 474 nm for VIc, 427 nm for VIIa, 504 nm for VIIb and 510 nm for VIIIc), which is not present in the unsubstituted quinones III and VII and may be due to the transfer of charge from the heteroatom to the quinone structure. From UV spectroscopic data it can be seen that the long-wave absorption band undergoes a bathochromic shift of 15-36 nm on going from the naphthoquinone to the benzoquinone structure, and of 58-77 nm on going from sulfur-containing to nitrogen-containing quinone; there is also an insignificant shift (4-6 nm) on increasing the chain length by one methylene group.

The position of the absorption band of the diquinone derivatives Xa-f, the monoderivative IXb, and the porphyrin structures IXa and b correspond to that of the dimethyl ester of deuteroporphyrin IX (DMEDP IX). This indicates that there is essentially no reaction between chromophores in the main structure. It is reported in the literature that in the spectra of porphyrinquinone derivatives, the absorption bands due to the porphyrin part of

TABLE 2. Infrared Data for Compounds Synthesized (in mineral oil)

Compound	Characteristic absorption bands, ν, cm^{-1}				
	C=C	C=O quinone	C=O ester	NH	OH
VIa	1554, 1587	1654	—	—	3524
VIb	1545, 1600	1675	—	3320	3388
VIc	1565, 1597	1665	—	3313	3400
VIIIa	1570	1650	—	—	3350
VIIIb	1590	1636	—	3335	3400
VIIIc	1600	1636	—	3239	3370
Xa	1560, 1591	1661	1729	3307	—
Xb	1580	1645	1730	3300	—
Xc	1564, 1591	1660	1730	3300	—
Xd	1580	1640	1733	3300	—
Xe	1564, 1600	1660	1723	3307	—
Xf	1582	1638	1725	3310	—
IXa	—	—	1725	3302	—
IXb	1560, 1590	1661	1726	3306	—
IXc*	1560, 1591	1660	1728	3305	—

*Absorption band for carboxyl C=O ν 1707 cm^{-1}.

the molecule do not change in relation to the starting porphyrin, and the spectrum as a whole is the sum of the spectra of the porphyrin and the quinone [3-5].

The IR spectra of the synthesized compounds correspond to their structures (Table 2). Compounds VIa-c and VIIIa-c absorb at a frequency characteristic of intramolecular hydrogen bonding, possibly between the hydroxyl group and one of the quinone carbonyl groups. In addition, the sulfur-containing quinones VIa, VIIIa, and also the porphyrins IXb and c, and Xa and b show a weak absorption at 655-659 cm^{-1}, which may be associated with the stretching vibrations of the S–C bond.

An analysis of the IR spectra of the iso-BuOCOCl reaction products showed a relationship between the intensity of the stretching vibrations of the quinone carbonyls and the ester carbonyl groups, which depends on the quinone group. Thus for monosulfur-containing porphyrins IXb and c, the intensity of the absorption of the ester carbonyl is greater than that of the quinone, but for the diquinone derivative Xa this relationship is reversed.

PMR spectroscopic data confirms the structures of the synthesized compounds, and gives some preliminary information on the relative orientation of the porphyrin and quinone groups Xa-f.

Depending on the nature of the heteroatom, the chemical shift (CS) also changes; thus, signals from the aromatic protons in the sulfur-containing compound VIa are downfield from those from the nitrogen-containing analog VIb; signals from the methylene groups of compound VIa are shifted by 0.3 ppm in the upfield direction relative to the quinone VIb and c, and by 0.04-0.23 ppm for compound VIIIa relative to compounds VIIIb and c (Table 3). Lengthening the chain by one methylene group did not affect the change in the PMR spectrum of the quinone derivatives, but the quinones VIIc and VIIIc had additional peaks with coupling constants J = 6.25 Hz and 6.5 Hz respectively, due to the β-CH_2 group of the propionyl chain. Small changes in the signals for the α-CH_2 of the ethyl and propionyl groups were observed. For compounds VIa and VIIIa, these signals, as expected, are triplets; for quinones VIb and VIIIb splitting occurs not only because of the neighboring β-CH_2 group, but also because of the NH group, which gives rise to multiplets. When the chain length is increased to propionyl, in compounds VIc and VIIIc, the multiplets become well-resolved quadruplets with J = 6.5 Hz in both cases. Signals from the NH group of the quinones VIb and c, and VIIIb and c are split into broad singlets, while for the naphthoquinone structures VIb and c, they are shifted by 0.33 ppm downfield relative to the benzoquinones.

For the diquinones Xa-f, there is a considerable shift in the downfield direction for the protons of the quinone groups compared with the quinones VIa-c and VIIa-c (Table 3). Signals from the aromatic protons of compound Xa are shifted by 0.46-0.47 ppm, and for the nitrogen-containing compounds Vc and e, by 0.37-0.39 ppm and 0.23-0.24 ppm respectively. Singlets from the quinone methyl groups of Xa-f are shifted upfield compared with the quinones VIa-c and VIIIa-c; by 0.86-1.04 ppm for compounds Xa, by 0.35-0.50 ppm for Xb, by

TABLE 3. PMR Spectra of Quinones and Quinone Groups in Porphyrin Derivatives

Compound	Chemical shift, δ, ppm						
	C–H arom (m)	CH_3 (s)	NH–CH_2	NHCH_2CH_2	SCH_2CH_2 (t)	CH_2CH_2O	$CH_2CH_2CH_2$
VIa	7,66—8,13 (4H)	2,44 (3H)	—	—	3,37 (2H)	3,83 (t, 2H)	—
VIb	7,47—8,03 (4H)	2,14 (3H)	5,99 (br s, 1H)	3,70 (m, 2H)	—	3,83 (t, 2H)	—
VIc	7,52—8,08 (4H)	2,22 (3H)	5,98 (m, 1H)	3,73 (q, 2H)	—	3,83 (m, 2H)	1,90 (q, 2H)
VIIIa	—	2,01 (6H); 22,4 (3H)	—	—	3,17 (2H)	3,71 (t, 2H)	—
VIIIb	—	1,92; 1,98; 2,01 (to 3H)	5,66 (br s, 1H)	3,58 (m, 2H)	—	3,78 (t, 2H)	—
VIIIc	—	1,97; 2,02; 2,08 (to 3H)	5,65 (m, 1H)	3,61 (q, 2H)	—	3,79 (m, 2H)	1,86 (q, 2H)
Xa	7,20—7,66 (8H)	1,40; 1,58 (to 3H)	—	—	2,93; 2,97 (to 2H)	4,16 (t, 4H)	—
Xb	—	1,66; 1,69; 1,74 (to 6H)	—	—	2,92 (4H)	4,13 (t, 4H)	—
Xc	7,08—7,66 (8H)	0,94; 1,17 (to 3H)	4,66; 4,73 (t, to 1H)	2,79; 2,94 (q to 2H)	—	3,95; 3,99 (t, to 2H)	—
Xd	—	1,14; 1,20; 1,29; 1,35; 1,63; 1,66 (to 3H)	4,63 (m, 2H)	2,96 (m, 4H)	—	4,01 (t, 4H)	—
Xe	7,29—7,84 (8H)	0,79; 0,83 (to 3H)	4,37 (t, 2H)	1,89 (q, 4H)	—	3,85 (t, 4H)	1,12 (q, 4H)
Xf	—	0,97; 1,00 (to 3H); 1,60 (6H); 1,79; 1,81 (to 3H)	4,43 (t, 2H)	2,12—2,25 (m, 4H)	—	3,92; 3,94 (t, to 2H)	1,57—1,62 (m, 4H)

TABLE 4. PMR Spectra of Porphyrin Part of Porphyrin Derivatives and DMEDP IX

Compound	Chemical shift, δ, ppm				
	meso-H (s)	β-H (s)	CH_3 (s)	CH_2CH_2CO (t)	CH_2CH_2CO (t)
DMEDP IX	9,83 (1H); 9,86 (2H); 9,87 (1H)	8,92 (2H)	3,63; 3,64 (to 6H)	4,30; 4.29 (to 2H)	3,20; 3,21 (to 2H)
Xa	9,87 (1H); 9,90 (2H); 9,94 (1H)	8,95; 9.02 (to 1H)	3,55 (6H); 3,66; 3,68 (to 3H)	4,34 (4H)	3,19; 3,21 (to 2H)
Xb	9,96 (1H); 10.02 (2H); 10,08 (1H)	9.06; 9.08 (to 1H)	3,61; 3,63; 3,72; 3,74 (to 3H)	4,41 (4H)	3,28 (4H)
Xc	9,82; 9,88; 9,95; 10,06 (to 1H)	8,91; 8,94 (to 1H)	3,62; 3,63; 3,65; 3,67 (to 3H)	4,46 (4H)	3,37 (4H)
Xd	9,97; 10,03 (to 1H); 10,10 (2H)	9,06; 9.08 (to 1H)	3,65; 3,68; 3,73; 3,76 (to 3H)	4,47 (4H)	3,36 (4H)
Xe	9,78; 9,89; 9,96; 10,03 (to 1H)	8,86; 8.89 (to 1H)	3,59; 3,62 (to 3H); 3,63 (6H)	4,44 (4H)	3,35 (4H)
Xf	9,98; 10,00; 10,07; 10,10 (to 1H)	9,06 (2H)	3,64; 3,67; 3,71; 3,74 (to 3H)	4,46 (4H)	3,34 (4H)

0.97-1.20 ppm for Xc, by 0.35-0.78 ppm for Xd, by 1.39-1.43 ppm for Xe, and by 0.27-1.00 ppm for Xf. Moreover, the nonequivalence of the quinone substituents at positions 6 and 7 of porphyrin gives rise to the appearance of two, instead of one, singlets from the methyl group of compounds Xa, c, and e. The methyl-group protons of Xd give rise to six singlets, Xf to five singlets, and Xb to three singlets. Signals from the NH group protons in compounds Xc-f are shifted towards the higher-field region by 1.26-1.33 ppm for Xc, by 1.03 ppm for Xd, by 1.61 ppm for Xe, and by 1.22 ppm for Xf; they occur as two broad triples for the porphyrinquinone Xc, one broad triplet for derivatives Xe and f, and a multiplet for compound Xd. Signals from the quinone α-CH_2 group of compounds Xa-f were also shifted in the upfield direction; for the porphyrinquinones Xe and f with increased chain-length this effect is much more marked than for the derivatives Xc and d (Table 3). The position of the signals from the porphyrin ring protons of compounds Xa-f were either essentially unchanged in comparison with DMEDP IX, or showed an insignificant downfield shift (Table 4).

Changes in the PMR spectra of the porphyrinquinone derivatives with flexible bonds were due to the effect of magnetic anisotropy of the porphyrin nucleus and could be explained by

assuming that the quinone was located over the plane of this nucleus [5, 8, 9]. However, for compounds of this type, and also for derivatives Xa-f, it is difficult to determine the relative orientation of the chromophore in space and the degree of overlapping of the ring, because of the flexibility of the covalent bridge. The effect of the magnetic anisotropy of the porphyrin ring exerts an influence on both acceptors, but to a different extent, indicating that the quinone groups are in nonequivalent positions with respect to the plane of the porphyrin ring.

The structure of the monoquinone derivatives IXb and c was confirmed with PMR spectroscopy; it was also shown that compounds IXb and c exist as isomers (at positions 6 and 7 of the porphyrin ring) which are present in a 1:1 ratio.

EXPERIMENTAL

Condensations were carried out in anhydrous solvents. The compounds were identified and the course of the reaction was followed by TLC using the following systems: (1) Silufol UV-254 (Kavalier), chloroform–methanol, 15:1, (2) Kieselgel F-254 (Merck), chloroform–methanol 15:1, (3) chloroform–methanol 30:1, (4) Alufol (Kavalier), chloroform. IR spectra were taken on a Shimadzu IR-435 spectrophotometer, and UV spectra on Shimadzu UV-240 and Beckman DU-8B spectrophotometers. PMR spectra were recorded in $CDCl_3$ on a Bruker WP-250 (250 MHz), internal standard HMDS.

2-(2-Hydroxyethyl)thio-3-methylnaphthoquinone (VIa). To a solution of 1 g (5.81 mmole) of 2-methylnaphthoquinone III in a mixture of 100 ml of methanol and 80 ml of isopropanol was added 1.5 ml (21.39 mmole) of 2-mercaptoethanol. The reaction mixture was stirred for 24 hours at 20°C, poured into 300 ml of water, and extracted with ether (3 × 300 ml). The extract was washed with a 10% $CuSO_4$ solution, then water (3 × 300 ml), and dried over Na_2SO_4. The solvent was removed by evaporation, and the residue recrystallized from a 1:2 chloroform–hexane mixture. The crystals were dried in vacuum over P_2O_5 and paraffin to give 1.86 g (91.2%) of product with mp 79-80°C and R_f 0.48 (1), 0.65 (2), 0.39 (4). Found: C 60.7; H 4.9; S 12.8%. $C_{13}H_{12}O_3S \cdot 0.5H_2O$. Calculated: C 60.7; H 5.1; S 12.5%.

2-(2-Hydroxyethyl)thio-3,5,6-trimethylbenzoquinone (VIIIa) was synthesized by the same method as VIa from 580 mg (3.86 mmole) of 2,3,5-trimethylbenzoquinone (VII). Yield 483 mg (55.4%), mp 55.5-56.5°C, R_f 0.46 (1), 0.64 (2), 0.48 (4). Found: C 58.8; H 6.1; S 14.0%. $C_{11}H_{14}O_3S$. Calculated: C 58.4; H 6.2; S 14.2%.

2-(2-Hydroxyethyl)amino-3-methylnaphthoquinone (VIb). To a solution of 1 g (5.81 mmole) of compound III in a mixture of 100 ml of methanol and 80 ml of isopropanol was added 2 ml (33.14 mmole) of 2-aminoethanol. The reaction mixture was stirred for 24 hours at 20°C, the solvent removed, the residue dissolved in 200 ml of chloroform, washed with 0.5% hydrochloric acid (3 × 100 ml), and water (3 × 300 ml), and dried over Na_2SO_4. The solvent was distilled off, the residue chromatographed on a column (3.8 × 10 cm) packed with aluminum oxide (activity grade 2), eluting with a 1:1 mixture of chloroform and petroleum ether. The red band was collected, the solvent evaporated, and the oil that remained crystallized from a 1:3 mixture of chloroform and hexane. The crystals were dried in vacuum over P_2O_5 and paraffin to give 333 mg (24.8%), mp 108.5-109.5°C and R_f 0.20 (1), 0.38 (2), 0.20 (4). Found: C 67.5; H 5.5; N 5.6%. $C_{13}H_{13}NO_3$. Calculated: C 67.5; H 5.7; N 6.1%.

2-(2-Hydroxyethyl)amino-3,5,6-trimethylbenzoquinone (VIIIb) was synthesized in the same way as VIb from 1.5 g (9.98 mmole) of compound VII, to give 297 mg (14.3%) with mp 91-92.5°C and R_f 0.21 (1), 0.41 (2), 0.26 (4). Found: C 62.8; H 7.4; N 6.6%. $C_{11}H_{15}NO_3$. Calculated: C 63.1; H 7.2; N 6.7%.

2-(3-Hydroxypropyl)amino-3-methylnaphthoquinone (VIc) was obtained by the same method as VIb from 1 g (5.81 mmole) of III. Yield 346 mg (24.3%), mp 85-86°C, R_f 0.17 (1), 0.39 (2), 0.23 (4). Found: C 68.3; H 6.2; N 5.5%. $C_{14}H_{15}NO_3$. Calculated: C 68.6; H 6.2; N 5.7%.

2-(3-Hydroxypropyl)amino-3,5,6-trimethylbenzoquinone (VIIIc) was synthesized in the same way as VIb from 1.5 g (9.98 mmole) of compound VII. Yield 178 mg (8%) mp 64-65°C, R_f 0.18 (1), 0.43 (2), 0.27 (4). Found: C 64.4; H 7.8; N 6.3%. $C_{12}H_{17}NO_3$. Calculated: C 64.6; H 7.7; N 6.3%.

1,3,5,8-Tetramethyl-6,7-di[2-(2-(3-methyl-1,4-naphthoquinone-2-yl)thioethyl)hydroxycarbonylethyl]porphyrin (Xa). A. To a solution of 296 mg (0.58 mmole) of compound II in 20 ml of THF was added 140 µl (1 mmole) of Et_3N and 164 µl (2 mmole) of pyridine. After cooling to −15°C, 262 µl (2.02 mmole) of iso-butylchloroformate was added, and after 20 minutes 537

mg (2.16 mmole) of compound VIa. The reaction mixture was then warmed to room temperature, stirred for 10 hours, poured into 200 ml of water, and extracted with 200 ml of chloroform. The chloroform solution was washed with water (3 × 250 ml) and dried over Na_2SO_4. The solvent was evaporated, and the residue chromatographed on a column (3.8 × 20 cm) packed with silica gel L 40/100 in chloroform. The fraction containing impurities was purified by preparative TLC on plates (20 × 20 cm) of silica gel L 5/40 in a 3:2 mixture of chloroform and hexane. The solvent was evaporated, the residue crystallized from a 1:2 mixture of chloroform and pentane, and the crystals dried in vacuum over P_2O_5 and paraffin to give 298 mg (53%).

B. To a solution of 67 mg (0.13 mmole) of compound II in 10 ml of THF was added 31.7 μl (0.23 mmole) of Et_3N and 37.1 μl (0.45 mmole) of pyridine. The reaction mixture was cooled to −15°C and 56.3 μl (0.46 mmole) of pivaloyl chloride added. After 20 minutes 123 mg (0.49 mmole) of VIa was added, the mixture allowed to warm to 20°C and stirred for 20 h. The mixture was poured into 300 ml of water, extracted with 50 ml of chloroform, washed with water (3 × 300 ml) and dried over Na_2SO_4. The solvent was removed and the residue chromatographed on a column (1.8 × 21 cm) packed with 0.08 mm Kieselgel (Merck), eluting with a 100:1 mixture of chloroform and methanol. The solvent was evaporated, the residue crystallized from a 1:2 mixture of chloroform and pentane, and dried in vacuum over P_2O_5 and paraffin to give 6.4 mg (5%).

C. To a solution of 60 mg (0.11 mmole) of compound II in a mixture of 20 ml of chloroform and 3 ml of pyridine was added 55 mg (0.22 mmole) of VIa. The mixture was cooled to 0°C, 55 mg (0.25 mmole) of tert-butylpyrocarbonate added and after 10 minutes 5 mg (0.04 mmole) of 4-dimethylaminopyridine. After mixing for 2 hours at 0°C, the reaction mixture was poured into 300 ml of 2% hydrochloric acid, extracted with 50 ml of chloroform, washed with water (3 × 300 ml) and dried over Na_2SO_4. The solvent was evaporated, the residue chromatographed on a column (1.8 × 25 cm) packed with 0.08 mm Kieselgel (Merck), eluting with chloroform. The solvent was evaporated and the residue crystallized from a 1:2 mixture of chloroform and pentane. The crystals were dried in vacuum over P_2O_5 and paraffin to give 104.9 mg (78.8%) with mp 64-65°C and R_f 0.81 (1), 0.85 (3), 0.82 (4). UV spectrum (in chloroform), λ_{max} (log ε): 620 (3.57), 566.7 (3.76), 530 (3.88) 497 (4.12), 400 nm (5.21) (Soret). Found: C 69.3; H 5.1; N 5.7; S 6.5%. $C_{56}H_{50}N_4O_8S_2$. Calculated: C 69.3; H 5.2; N 5.8; S 6.6%.

1,3,5,8-Tetramethyl-6,7-di[2-(2-(3,5,6-trimethyl-1,4-benzoquinone-2-yl)thioethyl)hydroxycarbonylethyl]porphyrin (Xb) was synthesized by method C above from 70 mg (0.13 mmole) of compound II. Yield 107.9 mg (84.9%), mp 59-60°C, R_f 0.82 (1), 0.86 (3), 0.86 (4). UV spectrum (in chloroform), λ_{max} (log ε): 620 (3.64), 565.8 (3.83), 530 (3.98), 497.5 (4.21), 399.2 nm (5.22) (Soret). Found: C 67.6; H 5.8; N 6.3; S 6.5%. $C_{52}H_{54}N_4O_8S_2$. Calculated: C 67.4; H 5.9; N 6.0; S 6.9%.

1,3,5,8-Tetramethyl-6,7-di[2-(2-(3-methyl-1,4-naphthoquinone-2-yl)aminoethyl)hydroxycarbonylethyl]porphyrin (Xc) was synthesized by method C above from 70 mg (0.13 mmole) of compound II. Yield 98 mg (76.3%), mp 78-79.5°C, R_f 0.46 (1), 0.78 (3), 0.59 (4). UV spectrum (in chloroform), λ_{max} (log ε): 620.8 (3.58), 568.3 (3.79), 530 (3.95), 497.5 (4.21), 400 nm (5.17) (Soret). Found: C 71.7; H 5.4; N 8.6%. $C_{56}H_{52}N_6O_8$. Calculated: C 71.8; H 5.6; N 9.0%.

1,3,5,8-Tetramethyl-6,7-di[2-(2-(3,5,6-trimethyl-1,4-benzoquinone-2-yl)aminoethyl)hydroxycarbonylethyl]porphyrin (Xd) was obtained by method C above from 70 mg (0.13 mmole) of II. Yield 102.7 mg (89.3%), mp 94-95°C, R_f 0.51 (1), 0.81 (3), 0.68 (4). UV spectrum (in chloroform), λ_{max} (log ε): 620 (3.62), 566.7 (3.86), 530 (4.01), 497.5 (4.22), 400 nm (5.17) (Soret). Found: C 69.7; H 6.1; N 9.2%. $C_{52}H_{56}N_6O_8$. Calculated: C 69.9; H 6.3; N 9.4%.

1,3,5,8-Tetramethyl-6,7-di[2-(3-(3-(methyl-1,4-naphthoquinone-2-yl)aminopropyl)hydroxycarbonylethyl]porphyrin (Xe) was synthesized by method C above from 60 mg (0.11 mmole) of II. Yield 86 mg (75.8%), mp 64-65°C, R_f 0.39 (1), 0.78 (3), 0.60 (4). UV spectrum (in chloroform), λ_{max} (log ε): 620.8 (3.50), 568.3 (3.74), 530 (3.90), 497.5 (4.17), 399.2 nm (5.16) (Soret). Found: C 72.0; H 5.9; N 8.7%. $C_{58}H_{56}N_6O_8$. Calculated: C 72.2; N 5.9; N 8.7%.

1,3,5,8-Tetramethyl-6,7-di[2-(3-(3,5,6-trimethyl-1,4-benzoquinone-2-yl)aminopropyl)hydroxycarbonylethylporphyrin (Xf) was synthesized by method C above from 60 mg 0.11 mmole) of II. Yield 84.3 mg (78%), mp 69-70°C, R_f 0.43 (1), 0.81 (3), 0.68 (4). UV spectrum (in chloroform), λ_{max} (log ε): 620 (3.61), 567.5 (3.89), 530 (4.02), 497.5 (4.22), 399.2 nm (5.20)

(Soret). Found: C 70.2; H 6.8; N 9.0%. $C_{54}H_{60}N_6O_8$. Calculated: C 70.4; H 6.6; N 9.1%.

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SYNTHESIS OF CARBAZOLE UNDER CONDITIONS FOR THE CATALYTIC DEHYDROGENATION OF CYCLOHEXYLAMINE

V. A. Tarasevich, O. A. Stefanovich, and N. S. Kozlov

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The dehydrogenation of cyclohexylamine on platinum catalysts is investigated. In addition to aniline and diphenylamine, significant amounts of carbazole are formed. A possible mechanism for its formation is proposed.

Carbazole, I, is formed in small amounts as a by-product of such catalytic reactions as the preparation of diphenylamine by the deamination of aniline, as well as in the amination of phenol with aniline on oxide catalysts [1, 2], and the dehydrogenation of N-cyclohexylideneaniline on nickel/oxide catalysts [3]. In studying the deamination and dehydrogenation of cyclohexylamine on Ni/Al_2O_3 catalysts, we found that carbazole was formed in addition to the primary products, diphenylamine and aniline. The yield of carbazole increased significantly when aluminoplatinum catalysts were used.

The formation of carbazole in the dehydrogenation of diphenylamine and dicyclohexylamine was first observed by N. D. Zelinskii on Pt/carbon catalysts [4]. Despite the difference in the mechanisms of carbazole formation from the products named on acid-base type catalysts and of hydrogenation-dehydrogenation, a common step uniting these reactions is possible. The presence in the reaction mixtures of the same products through which the cyclization reaction probably occurs, is evidence in favor of this supposition. To elucidate the possible mechanism of formation of compound I from cyclohexylamine, we studied the transformation of the latter on platinum-containing catalysts under the conditions for dehydrogenation. The dependence of the percent yield of carbazole on the use of catalysts of aluminoplatinum and

Institute of Physical Organic Chemistry, Academy of Sciences of the Belorussian SSR, Minsk 220603.

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