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STRUCTURE OF THE PRODUCTS OF THE OXIDATIVE DEHYDRODIMERIZATION OF 2,4-DIAMINOAZOBENZENES IN THE SYSTEM CuC1-PYRIDINE

Yu. I. Amosov, M. P. Terpugova,

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and I. L. Kotlyarevskii

A feature of the oxidation of diamines of the chrysoidine series (2,4-diamine- (1), 2,4-diamino-5-methyl- (II), and 2,4-diamino-5-butoxyazobenzene (III)) in the presence of CuCl (2-3 moles of CuCl per mole of diamine) in pyridine is that, in addition to polymers, high-melting crystalline solids, provisionally termed oligomers, are obtained. The structures of these compounds have not been established [1].

We here describe the results of an investigation of the oxidation of 2,4-diaminoazobenzenes, and the structures of the products. It has previously been shown [2] that o-aminobenzenes are readily oxidized by oxygen in the presence of the CuCl-pyridine complex with the formation of the benzotriazole ring. It is logical to assume that under oxidative polycondensation conditions the diamines (I), (II), and (III) will give the aminobenzotriazoles as intermediates, which in consequence of the free amino group could undergo further reactions. It was in fact found that oxidation of (I) with a reduced amount of CuCl (1/10 to)1/20 mole of CuCl per mole of diamine) gives 90% of 5-amino-2-phenylbenzotriazole (IV). Similar results were obtianed on oxidation of (II) and (III) [3].



The aminobenzotriazoles obtained (IV), (V), and (VI), did not undergo further oxidation in this system when the amine: CuCl ratios were greater than 10. Considerably increased uptake of oxygen was observed when the temperature was raised to 60°C, and one mole of CuCl was used per mole of aminobenzotriazole, the principal products being compounds similar to the previously obtained "oligomers" [1], together with polymeric products. According to TLC, each oligomer was a mixture of two compounds. The IR spectra of the oligomers did not show absorption for the free NH2 group, but the remaining regions of the spectrum were similar to those of the corresponding aminobenzotriazoles.

Oxidation of aromatic amines with oxygen in the presence of CuCl in pyridine is known to give azo-compounds [4]. In contrast to monocyclic amines, the oxidation of  $\beta$ -naphthylamine under these conditions gives as the main products dibenzophenazine and  $\beta$ ,  $\beta$ '-diamino- $\alpha, \alpha'$ -binaphthyl, the corresponding azo-compound being obtained in trace amounts [5]. In their  $\pi$ -electronic structure, aminobenzotriazoles are isoelectronic with  $\beta$ -naphthylamine, and it would therefore be expected that C-C- and C-N-coupling products would be formed on oxidation of aminobenzotriazoles under similar conditions.

In accordance with the foregoing, the oligomers may be assigned the two structures A and B:

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	•	Benz	tene H		4			Alkyl subst	ituent	
Compound	Solvent	ortho-	meta-, para-	a H		NH <sub>2</sub>	осн <sub>а</sub>	$\operatorname{CH}_2$	CH2	CH3
* (111)	CDC1	7,77 d.d	7,55–7,30 m	7,23 s	5,92 s	5,49 s	4,03 t	1,69 m	1,45 m	0,99 t
(III) * (XIII) * (XIII) * (XII) * (XII)	Dítto "+	8,22 d.d 8,12 d.d 8,52 d.d	7,54–7,37 m 7,39–7,26 m	7,09 s 7,16 s	6,88 s	4,29 s 4,35 s 4,35 s	4,06 t 4,17 t 7 55 t	1,87 m 1,90 m	1,56 m 1,56 m	0,99 t 1,01 t
Ditto	UF,COOH Ditto =	8,20 d.d	7,68–7,55 m	7,61 s 7,68 s 8 s s			4,37 t 4,39 t	13 12 12 12 12 12 12 12 12 12 12 12 12 12	1,62 m 1,62 m	1,06 t
(X1)	D <sub>2</sub> SO <sub>4</sub>	8,63 d.d 8,57 d.d	8,33–8,0 m 7,71–7,68 m	4,30 \$ 8,43 \$ 8,03 \$			4,00 L 5,06 t 4,58 t	2,40 m 2,08 m	1,00 m 2,0 m 1,67 m	1,40 t 1,40 t 1,08 t
(X11)	CF3CUOIL CDCl3 +	8,20 d.d	7,67-7,56 m	7,69 s			4,41 t	$2,07\mathrm{m}$	1,61 m	1,07 t
(XI) Mixture of (IX) and (X)		8,46 <b>d.d</b> 8,58 <b>d.d</b>	7,58-7,45 m 7,69-7,63 m	7,40 s 8,55 s 8,90 s			4,37 t	2,08 m	1,67 m	1,06t 3,15 s 3,75 s
Mixture of (IX) and (X) Mixture of (VII) and (VIII)	D <sub>2</sub> SO <sub>4</sub> CDCl <sub>5</sub> +'	8,10 d.d 8,67	7,85-7,60 m 7,73-7,70 m	8,60 s 8,82 d 8,82 d	8,64 d					3,05 s
Ditto	D <sub>s</sub> SO <sub>4</sub>	8,40-8,12	7,95–7,7 m	9,18 d	8,83 <b>d</b>					
	-			_		_	-	_	_	

%The chemical shifts for the diamine (JII) and aminobenzotriazole (VI) are given for comparison. +Ratio CDCl<sub>3</sub>:CF<sub>3</sub>COOH, 6:1. +Ratio CDCl<sub>3</sub>:CF<sub>3</sub>COOH, 15:1.

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These oligomers are insoluble in most organic solvents, and are moderately soluble only in strong acids (formic, trifluoroacetic, and sulfuric acids). Table 1 shows the PMR spectral data for the oligomers, obtained in  $D_2SO_4$  and  $CDCl_3-CF_3COOH$ . The PMR spectrum (conc.  $D_2SO_4$ ) of the oligomer isolated from the oxidation products (IV) shows, in addition to signals for the benzene ring protons (8.40-7.70 ppm), two doublets (H<sup>a</sup> and H<sup>b</sup>) at 9.20-8.83 ppm with a characteristic o-proton coupling constant of 8.7 Hz.

The PMR spectrum (conc.  $D_2SO_4$ ) of the oligomer obtained on oxidation (V) shows a singlet at 8.60 ppm of unit intensity. The benzene ring proton signals lie at 8.30-7.60 and 3.05 ppm. In the case of the oligomer obtained on oxidation (VI), the PMR spectrum also shows a signal for one proton, which is shifted to even higher field and lies between the signals for the ortho-, meta- and para-protons of the benzene ring. The PMR spectrum of this product shows signals for the protons of the OC<sub>4</sub>H<sub>9</sub> grouping. Such PMR spectra are in accordance with the proposed structures A and B for the oligomeric products, the PMR spectra of each of the isomers being identical in conc.  $D_2SO_4$ .

The PMR spectra of these products obtained in  $CDCl_3-CF_3COOH$  are slightly different. The signals for the H<sup>a</sup> and H<sup>b</sup> protons in the mxiture of products (VII) and (VIII) lie at 8.82-8.64 ppm, and overlap the signals for the ortho-protons of the benzene ring. For the mixture of (IX) and (X), obtained from the oxidation products (V), the PMR spectrum contains two sets of resonance signals. As the concentration of  $CF_3COOH$  is increased, these resonance signals are shifted to lower field. The protons of the methyl group and H<sup>a</sup> of one of the isomers in this mixture are particularly sensitive to this effect.

The PMR spectra of the mixture of isomers (XI) and (XII), isolated from the oxidation products of (III), are identical with that of the corresponding aminobenzotriazole (VI), and also show two sets of resonance signals. The ratio of the isomers in the products of oxidation of (III) is 1:1, whereas the ratio of isomers formed in the oxidation of the benzotriazole (VI) is 2:1. Changes in the concentration of  $CF_3COOH$  have no effect on the isomer ratio, merely shifting the resonance signals to lower field.

The higher solubility of the mixture of isomers (XI) and (XII) enabled them to be separated chromatographically. The isolated isomers have widely differing melting points (211.5 and 299.5°C). The lower melting isomer is appreciably soluble in hot chloroform ( $\sim 10^{-2}$  mole/liter). The solubility of the higher-melting isomer is however less than that of the original mixture. The PMR spectra of these isomers (CDCl<sub>3</sub>-CF<sub>3</sub>COOH) are the same, differing only in the chemical shifts. The signals for the protons of the lower-melting isomer are seen at lower field than those for the higher-melting isomer.

When (VI) was oxidized at 20°C, there was isolated form the reaction products, in addition to (XI) and (XII), a compound which from its elemental analysis, molecular weight, PMR, IR, and UV spectra was (XIII):



TABLE 2.	UV	Spectra	of	the	Oxidative	Dimerization	Products
of Aminob	enzo	otriazole	es				

	- *	$\lambda, \operatorname{nm}(\varepsilon)$		
Product	ethanol	chloroform	ethanol-chlo- roform with added H <sub>2</sub> SO <sub>4</sub>	cyclohexane
(VI) * (XIII) (XI) (XII) Mixture of (IX)and(X) Mixture of (VII) and (VIII)	352,8 (4,20) 347,2 (4,50) 289,1, 306,0, 349,7, 412,5	292,4 (4,83), 309,5 (4,72), 352,1 (4,36) 416,7 (4,01) 328,2 (4,96), 344,8 (5,00), 390,9 (4,10) 285,0 (4,33), 303,8 (4,25), 334,4 (4,41) 281,0 (4,25), 299,8 (4,16), 332,9 (4,06)	332.0 (4.18) 337.8 (4.47) no change disappear no .change -	289,8; 300,0; 348,4; 416,3

\*The UV absorption maxima for the aminobenzotriazole (VI) are given for comparison.

On heating (XIII) in the presence of CuCl-pyridine, oxidation with oxygen takes place at the free amino-groups to give a product with an azo bond, which is identical with the lower-melting isomer (XI). A corresponding intermediate for the higher-melting isomer (XII) was not found, apparently since amines of this type (o-aminodiphenylamines) are oxidized at a greater rate than the starting compounds.

Examination of the UV spectra of the oligomeric products provides conclusive evidence for their relationship with the compounds in question. Table 2 shows the UV absorption maximum values for the aminobenzotriazoles and their oxidative dehydrodimerization products. It will be seen from Table 2 that the UV spectrum of (XIII) is similar to that of (VI). Since the planes of the two benzotriazole rings in (XIII) are rotated relative to each other, its UV spectrum is seen as that of two isolated chromophores, analogs of (VI). The small differences are due to the mutual inductive effects of the benzotriazole rings. The molar extinction coefficient ( $\epsilon$ ) of (XIII) is exactly twice that of (VI).

The UV spectra of isomers (XI) and (XII) differ markedly in their appearance and absorption frequencies. Changing the solvent (from alcohol to cyclohexane) results in little change in the positions of the UV maxima of (XI). A low-intensity band at 416.7 nm is seen as a shoulder which does not possess a clear maximum, and it is therefore difficult to draw any conclusions as to the effect of the solvent upon it. Furthermore, it is known [6] that when two or more nitrogen atoms are present in the molecule, the short-wavelength shift of the n- $\pi^*$  band on changing from a hydrocarbon solvent to alcohol is much less than in the case of pyridine. It was not possible to carry out a similar investigation into (XII) as a result of its inadequate solubility. Addition of acid to a solution of the isomer (XI) (solvent EtOH-CHCl<sub>3</sub>) results in the disappearance of the absorption at 416.7 nm, whereas acidification of a solution of isomer (XII) results in no change in its spectrum. These findings lead to the conclusion that the absorption at 328.9, 344.6, and 390.9 nm for (XII) and 292.4, 309.5, and 352.1 nm for (XI) are due to  $\pi-\pi^*$  transitions, and the absorption at 416.7 nm in the latter is due to the  $n-\pi^*$  transition. In the case of compounds containing several nitrogen atoms (diazines, triazines, diazanaphthalenes, diazaphenanthrenes, etc.), it has been found that the  $n-\pi^*$  absorption wavelength is highly dependent on the relative positions of the nitrogen atoms [6]. In the UV spectra of such compounds, the absorption at longest wavelength is that for the  $n-\pi^*$  transition when the nitrogens are adjacent. The presence of absorption at at 416.7 nm for the  $n-\pi^*$  transition in the UV spectrum of (XI) supports the structure assigned to this compound, which has adjacent nitrogen atoms.

In discussing the UV spectra, it must not be forgotten that the isomer (XII) absorbs at longer wavelength than (XI). Structure B is based on the anthracene system, whereas A is derived from the phenanthrene system, in which the appropriate carbon atoms are replaced by two nitrogens. Bearing in mind the annelation effect [7], it may be concluded that the long wavelength spectrum is attributable to isomer (XII), which has the phenazine structure, and that the other spectrum is due to isomer (XI), which has an angular benzocinnoline structure. This assignment is in accordance with the PMR spectra.

## EXPERIMENTAL

PMR spectra were obtained on Varian A-56/60 A in  $D_2SO_4$  and Varian XL-200 spectrometers, operating at 60 and 200 MHz respectively. The chemical shifts were measured relative to TMS. UV spectra were obtained on a Specord UV-VIS in quartz cells of length 10 mm, at 18  $\pm$  1°C. IR spectra were recorded on a UR-20 spectrometer in KBr disks. Mass spectra were obtained on a Varian MAT-311A mass spectrometer with an ionization field. Melting points were measured on a Koffler block. TLC was carried out on Silufol microplates with silica gel, visualized in CF<sub>3</sub>COOH and iodine vapors, followed by treatment with water, by UV.

Aminobenzotriazoles (IV), (V), and (VI) were obtained as described in [3].

Oxidation of 2,4-Diaminoazobenzene (I). A mixture of 10.6 g (0.05 mole) of (I) and 10 g of CuCl in 200 ml of pyridine was shaken in an atmosphere of oxygen at  $\sim$ 20°C. After 30-40 min, 1390-1420 ml of oxygen had been taken up (not counting the oxygen taken up by the CuCl). The mixture was poured into 100 ml of conc. HCl and 400 ml of water, and the solid which separated was filtered off, washed with dilute (1:4) HCl, water, and aqueous ammonia until Cu and Cl ions were no longer present. There was obtained 10.1 g (97.1%) of product, which was dissolved in DMF, and the insoluble portion filtered off and washed with acetone to give 4.3 g (42.6%) of a mixture of (VII) and (VIII) as fibrous crystals, mp 312-322°C (from pyridine and twice from acetone). Found: C 69.60; H 3.38; N 26.92%. C<sub>24</sub>H<sub>14</sub>N<sub>8</sub>. Calculated: C 69.55; H 3.40; N 27.04%.

Oxidation of 2,4-Diamino-5-methylazobenzene (II). Similarly, from 11.3 g (0.05 mole) of (II) and 10 g of CuCl in 200 ml of pyridine there was obtained 10.8 g (97.3%) of oxidation products, which on treatment with DMF gave 4.18 g (38.7%) of a mixture of (IX) and (X) as crystals, mp 327-362°C (from o-dichlorobenzene). Found: C 70.50; H 4.15; N 25.45%.  $C_{26}H_{18}N_8$ . Calculated: C 70.58; H 4.10; N 25.32%.

Oxidation of 2,4-Diamino-5-butoxyazobenzene (III). Oxidation of 14.2 g (0.05 mole) of (III) and 10 g of CuCl in 200 ml of pyridine gave 13.6 g (97%) of oxidation products containing 5.6 g (41.2%) of DMF-insoluble mixture of (XI) and (XII) as lemon-yellow crytals, mp 217-258°C (tetralin-p-xylene, 1:1). Found: C 68.92; H 5.40; N 20.21%.  $C_{32}H_{30}N_8O_2$ . Calculated: C 68.80; H 5.41; N 20.06%.

The mixture of (XI) and (XII) (1.5 g) was separated chromatographically (heated (40°C) column, 70  $\times$  5 cm, silica gel, eluent heated, alcohol-free chloroform), to give 0.78 g of (XI), mp 211.5°C. (Found: C 68.69; H 5.53; N 20.29%), and 0.64 g (XII), mp 299.5°C. Found: C 68.54; H 5.10; N 20.17%.

Oxidation of 5-Amino-2-phenylbenzotriazole (IV). Oxidation of 2.1 g of (IV) and 2 g of CuCl in 50 ml of pyridine at 60°C gave, following the usual workup procedure, 2.05 g (97.5%) of oxidation products, from which there was obtained 1 g (48.8%) of DMF-insoluble mixture of (VII) and (VIII), mp 309-319°C (o-dichlorobenzene).

Oxidation of 5-Amino-6-methyl-2-phenylbenzotriazole (V). Similarly, 1.9 g of (V) and 2 g of CuCl in 50 ml of pyridine gave 1.87 g (98%) of oxidation products, from which there was isolated 0.87 g (46.5%) of a DMF-insoluble mixture of (IX) and (X), mp 322-352°C (o-dichlorobenzene).

Oxidation of 5-Amino-6-butoxy-2-phenylbenzotriazole (VI). Oxidation of 2.82 g of (VI) and 2.8 g of CuCl in 50 ml of pyridine at 60°C afforded 2.7 g (96.4%) of oxidation products containing 1.2 g (44.4%) of DMF-insoluble mixture of (XI) and (XII).

<u>4,4'-Bis(5-amino-6-butoxy-2-phenylbenzotriazole (XIII)</u>. A mixture of 10 g of (VI) and 5 g of CuCl in 180 ml of pyridine was oxidized with oxygen at 15-20°C (thermostated "duck"), to give 9.6 g of oxidation products, which were dissolved in DMF, the insoluble mixture of (XI) and (XII) (2.8 g) was filtered off, and the filtrate diluted with water, the solid was filtered off, and washed on the filter with acetic acid. There was obtained 2.5 g of acetic acid-insoluble (XIII), mp 249.5-250°C (acetone). Found: C 68.43; H 5.90; N 19.84%.  $C_{32}H_{33}N_8O_2$ . Calculated: C 68.34; H 6.09; N 19.92%. M<sup>+</sup> 562.

A mixture of 2.82 g of (XIII) and 3 g of CuCl in 60 ml of pyridine was oxidized with oxygen at 60°C. After 1 h, 275 ml of oxygen had been taken up (theory 283 ml). The DMF-insoluble portion was dissolved in chloroform and filtered through a layer of silica gel. Removal of the chloroform gave 2.29 g (82%) of (XI), mp 211-211.5°C; M<sup>+</sup> 558.

## CONCLUSIONS

Oxidation of 2,4-diaminoazobenzene and its 5-methyl- and 5-butoxyderivatives with oxygen in the system copper(I) chloride-pyridine gives, in addition to polymers, mixtures of the corresponding bis(2-phenyl-1,2,3-triazolo)[4,5a:4'5'h]phenazines and bis(2-phenyl-1,2,3triazolo)[4,5c:4'5'g]-9,10-diazaphenanthrenes.

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ISOLATION AND INVESTIGATION OF THE THERMAL STABILITY OF THE OZONIDE OF [L(--)-MENTHYL][0-PHENYLENE] PHOSPHITE

V. V. Shereshovets, N. M. Korotaeva, L. V. Spirikhin, V. D. Komissarov, and G. A. Tolstikov UDC 542.91:541.127:542.92:542.943.5:547.558.1

The low-temperature ( $\sim$ 80°C) ozonization of esters of phosphorous acid leads to the ozonides of phosphites (RO)<sub>3</sub>P·O<sub>3</sub> [1]. These compounds are highly effective oxidants [1-4], and are sources of singlet oxygen [5]. There is no information in the literature concerning the isolation of ozonides from optically active phosphites. Moreover, the optically active ozonides may present interest as chiral oxidants.

The aim of the given work is to isolate the optically active ozonide of [L(-)-menthyl] [o-phenylene] phosphite and to study its thermal stability.

## EXPERIMENTAL

The L(-)-menthol having the  $[\alpha]_D^{220}$  of -40.0° (CH<sub>2</sub>Cl<sub>2</sub>) was isolated from menthol oil according to the method of [6]; it was distilled twice *in vacuo*. The CH<sub>2</sub>Cl<sub>2</sub> was purified by passage through a column with Al<sub>2</sub>O<sub>3</sub>, distilled, and dried over a molecular sieve of the 4 Å type.

[L(-)-Menthyl][o-phenylene] Phosphite (I). This was synthesized by the reaction of o-phenylenephosphino chloride with L(-)-menthol by the method analogous to the isolation of ethyl o-phenylene phosphite, having the bp 166-168°C (8 mm) using n-hexane [7] as the solvent [7]. The IR spectrum (v, cm<sup>-1</sup>) was as follows 840 (P-OC aryl), 1245 (P-OC aryl), 2880, 2935, and 2965 (C-H, CH<sub>2</sub>, CH<sub>3</sub>). The PMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm, J, Hz) was as follows: 7.31 m (4H), 3.67 m (CH-O, J  $\approx$  10; 6.5; 4), 1.81-2.25 m (CH-CH<sub>3</sub>, CHO-CH), 1.6 m (CHO-CH<sub>2</sub>, CH(CH<sub>3</sub>)<sub>2</sub>), 0.9-1.27 m (CH<sub>2</sub>, 4H), 0.7, 0.81, and 0.92 d (CH<sub>3</sub>, 9H). The <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>,  $\delta$ , ppm) contains the signals of three methyl groups (15.56; 20.94; 21.98), three methylene groups of the cyclohexane ring (44.04; 33.90; 22.71), four methine carbon atoms of the isopropyl group (25.4) and the cyclohexane ring (31.60; 48.26, J<sub>31P</sub> = 2.93 Hz; 76.89, J<sub>31P</sub>  $\approx$  2 Hz), and the signal of double intensity for the four carbon atoms of the

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