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Oxidation of 2-Alkyl-5,10-dihydrophenazines

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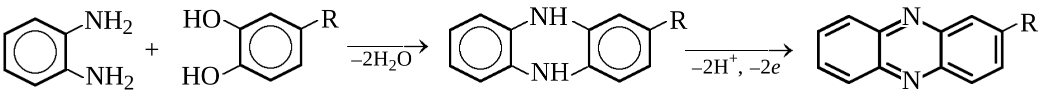
Abstract—Oxidation of 2-alkyl-5,10-dihydrophenazines afforded 1 : 1 molecular complexes of the initial compounds with the corresponding 2-alkylphenazines.

Phenazine derivatives have found wide application as redox indicators. Their formal redox potentials are usually low: they range from 0.05 to 0.30 V [1]. Taking into account the scope of application of these compounds, only water-soluble systems containing hydrophilic substituents in the aromatic ring have been extensively studied. Phenazine derivatives with alkyl substituents in the aromatic ring were not reported. The formal redox potential of alkylphenazine systems is reduced even more strongly due to the presence of electron-donor alkyl groups; in addition, the latter endow such systems with hydrophobic properties, thus making them suitable for redox extraction processes.

We previously developed a procedure for the synthesis of 2-alkyl-5,10-dihydrophenazines [2]. Their oxidation could give rise to the corresponding 2-alkylphenazines. However, the use of conventional oxidation methods resulted in decomposition of these compounds. The present communication describes a procedure for the oxidation of 2-alkyl-5,10-dihydrophenazines **I** to 2-alkylphenazines **II** with an aqueous solution of potassium bromate.



Ia–If **IIa–IIf**

I, II, R = H (**a**), Br (**b**), *t*-Bu (**c**), $MeCH_2CMe_2$ (**d**), $Me(CH_2)_3C(Et)Me$ (**e**), *cyclo*-C_6H_{11} (**f**).

Compounds **II** were isolated as 1 : 1 complexes with initial dihydrophenazines **I**, like that derived from hydroquinone and *p*-benzoquinone. The corresponding complexes were also obtained in the presence of a large excess of the oxidant, as well as on extending the reaction time. In these cases, the fraction of tarry products increased. Stronger oxidants induced decomposition of dihydrophenazines **I**. Presumably, 2-alkylphenazines are less stable than their 5,10-dihydro derivatives, and the formation of complexes with the latter stabilizes the former.

The rate of oxidation of compounds **I** to **II** depends on the alkyl radical structure: it increases with branching of R. In Experimental, the reaction time is given for the oxidation of 2-bromo derivative **Ib** which was oxidized most slowly. The complexes were formed in quantitative yield. Unlike colorless initial compounds **I**, complexes **II** are orange substances.

The IR spectra of initial dihydrophenazines **I** contained absorption bands at 3423–3321 cm^{-1}, typical of stretching vibrations of free and associated NH groups; analogous bands are characteristic of the IR spectra of pyrrole and secondary amines [3]. In the region 1620–1509 cm^{-1} we observed absorption bands due to vibrations of the aromatic rings and NH bending vibrations. Unlike compounds **I**, the NH stretching vibration bands in the IR spectra of complexes **I**–**II** are displaced to 3389–3303 cm^{-1}, and additional absorption bands appear in the region 1633–1504 cm^{-1} due to stretching vibrations of the conjugated C=C and C=N bonds in **II**.

EXPERIMENTAL

The IR spectra were recorded in the range from 4000 to 400 cm^{-1} on an IKS-22 spectrometer from samples pelleted with KBr. Initial compounds **Ia**–**If**

Melting points and elemental analyses of 1:1 complexes of 2-alkylphenazines **II** with 2-alkyl-5,10-dihydrophenazines **I**

Comp. no	mp, °C	Found, %		Formula	Calculated, %	
		C	H		C	H
Ia	88–89	79.31	4.80	$C_{24}H_{18}N_4$	79.54	5.01
Ib	84–85	55.18	2.78	$C_{24}H_{16}Br_2N_4$	55.41	3.10
Ic	101–102	80.77	6.98	$C_{32}H_{34}N_4$	80.98	7.22
Id	99–100	81.03	7.37	$C_{34}H_{38}N_4$	81.24	7.62
Ie	103–104	81.61	8.24	$C_{40}H_{50}N_4$	81.87	8.59
If	86–87	81.79	6.95	$C_{36}H_{38}N_4$	82.09	7.27

were synthesized by the procedure reported in [2], and the corresponding 4-alkyl-1,2-benzenediols were prepared as described in [4].

2-Alkylphenazine–2-alkyl-5,10-dihydrophenazine complexes *(general procedure).* A 4% solution of $KBrO_3$ (25 ml, 6 mmol) was added to 2 mmol of dihydrophenazine **Ia**–**If** (see table), and the mixture was kept for 2 days at room temperature. The originally colorless solution turned persistently orange. The mixture was evaporated at room temperature, and the residue was extracted with three portions of diethyl ether (until colorless extract). The combined extracts were filtered and evaporated on a rotary evaporator, and the product was dried under reduced pressure (water-jet pump). The yields were quantitative. The products were almost pure; the melting points were determined from samples recrystallized from hexane. The complexes were crystalline substances; their melting points and analytical data are given in the table.

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