Chemistry

1958

SovietRxiv

Structural formulas (I)–(XI)

Figure 1: Structural formulas (I)–(XI)

Abstract

Full Text

Chemistry

Z. V. Pushkareva and L. B. Radina

Preparation and Properties of Phenazinium Salts

(On the Question of the Relationship Between Chemical Structure and the Ability to Form Free Nitrogen Radicals)

(Presented by Academician N. I. Nazarov on 20 XI 1956)

Free radicals in which the atom bearing the unpaired electron is nitrogen include diarylnitrogens (1), diarylnitrogen *N*-oxides (2), hydrazyl (3), and certain other radicals (4). Free radicals in the alloxazine (5) and phenazine (6) series also belong to this class of compounds. The free radicals of the latter group have been little studied, but are of great interest because a detailed study of their properties may help to clarify the nature of certain biological oxidation-reduction processes. The literature describes the preparation of a small number of alloxazine and phenazine derivatives possessing the properties of free radicals. These are the so-called phenazyls, of general formula (I) (6), and monoacetylphenazyl (II) (7), the related flavin radicals (III) (5), pyocyanine (IV) (8), and certain others.

Initially we set ourselves the goal of obtaining analogues of (II), containing acyls of different chemical character, in order to determine the influence of the nature of the acyl group on the stability of radicals of this type. Since monoacetylphenazyl (II) was obtained by oxidation of monoacetyldihydrophenazine, a series of monoacyldihydrophenazines (V)–(XI) with various acyl residues was synthesized for the preparation of its analogues. Compounds (V), (VI) are described in the literature (9,10), while compounds (VII)–(XI) were obtained by us for the first time. A brief characterization of their properties is given in Table 1.

Measurement of the dipole moments of individual substances (in benzene at 25°, see Table 1) and calculation of the dipole moments for various configurations of these compounds by the method of vector sums showed that in all cases the experimental dipole moment is close to that calculated for the nonplanar configuration of the dihyd-

Table 1

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{exp} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
1	Monoacetyldihydrophenazine (V)	Fine white crystals from alcohol, m.p. 254–255°		283	4.086	248	3.863
2	Monobenzoyldihydrophenazine (VI)	Slightly yellowish needles from alcohol, m.p. 224–226°Found %: N 9.65; 9.82Calculated %: N 9.79	3.34	281	3.940	258	3.869

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{\text{exp}} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
3	Mono-*p*-nitrobenzoyldihydrophenazine (VII)	Orange plates from alcohol, m.p. 211–213°Found %: N 12.90; 12.78Calculated %: N 12.69	4.90	284	4.230	254	4.111
4	Mono-*p*-dimethylaminobenzoyldihydrophenazine (VIII)	White crystals from alcohol, m.p. 230–231°Found %: N 12.52; 12.89Calculated %: N 12.75		305	4.488	254	3.672

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{\text{exp}} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
5	Mono-*p*-isonicotinyldihydrophenazine (IX)	Pale-yellow needles from alcohol, m.p. 271–272°Found %: N 14.70; 14.59Calculated %: N 14.63	6.18	272	4.119	248	3.929
6	Mono-*p*-cinnamoyldihydrophenazine (X)	Bright-yellow crystals from alcohol, m.p. 223–224°Found %: N 8.77; 8.90Calculated %: N 8.97	2.88	283	4.505	251	4.066

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{exp} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
7	Mono-*o*-chloroacetyldihydrophenazine (XI)	White finely crystalline precipitate from alcohol, m.p. 231–232° Found %: N 11.09; 10.98 Calculated %: N 10.80		278	3.823	254	3.672
8	Diphenylamine			284	4.440	248	3.580

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{\text{exp}} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
9	Product of oxidation of monoacetyldihydrophenazine with anhydrous ferric chloride (XII)	Greenish-orange crystals, m.p. 195–197°Found %: N 9.70; 9.28;Cl 29.79; 28.98Calculated %: N 9.45; Cl 29.71	–	–	–	–	–

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{exp} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
10	“Orange” product (XIII)	Golden-orange crystals from isoamyl alcohol, m.p. 191–193°Found %: N 10.32; 10.48Cl 20.78; 20.76Fe 10.66; 10.38Calculated %: N 10.71Cl 20.38;Fe 10.71		248362	4.8604.530	287	3.498

No.	Name of compounds obtained	Brief characterization of compounds	$\mu_{\text{exp}} \cdot 10^{18}$	Maximum λ_{max}	Maximum $\lg \varepsilon$	Minimum λ_{min}	Minimum $\lg \varepsilon$
11	Hydrochloric acid phenazinium (XIV)	Greenish-yellow crystals from isoamyl alcohol, m.p. 195–197°Found %: N 12.31; 12.52Calculated %: N 12.93		248360	4.7804.180	280	1.000

rophenazine part of the molecule. Moreover, in these compounds, as a rule, the acyl residue is in the trans position with respect to the phenyl rings of the dihydrophenazine part of the molecule and in the cis position with respect to the hydrogen of the NH group, as shown in Fig. 1, which is a photograph of a spherical model of the monobenzoyldihydrophenazine molecule. On this basis, it may be assumed that the acyl residue, which in the presence of such a configuration is removed from conjugation with the phenyl rings, should not exert a substantial influence on the properties of the NH bond in monoacyldihydrophenazines. Experimental confirmation of this assumption is provided by the results obtained in measuring the absorption spectra of monoacyldihydrophenazines in the UV region (Table 1).

As can be seen from the data in Table 1, the spectra of the monoacyldihydrophenazines proved to be very close to one another and very similar to the spectrum of diphenylamine, in which the acyl residue is entirely absent.

The oxidation reaction in the series of monoacyldihydrophenazines had previously been studied only in one example, the oxidation of monoacetyldihy-

Fig. 1

Figure 2: Fig. 1

Fig. 2

Figure 3: Fig. 2

drophenazine with anhydrous

aqueous ferric chloride in chloroform solution ([7]). In this case two products were obtained: violet-black crystals with m.p. 137°, for which the structure of a molecular compound of monoacetyldihydrophenazine (V) with a molecule of monoacetylphenazyl (II) was assumed, and an "orange" substance with m.p. 191–193°, which was regarded as a dimer of monoacetylphenazyl (II). Carrying out the oxidation, with an excess amount of ferric chloride, under analogous conditions of three different monoacyldihydrophenazines (V), (VI), and (VII) unexpectedly led to the formation of one and the same oxidation product with m.p. 195–197°, which, in turn, was converted into a substance identical with the previously known "orange" product with m.p. 191–193°.

Fig. 1

A detailed study of the chemical structure and properties of the oxidation product of monoacetyldihydrophenazines with m.p. 191–193° showed that the substance contains no acetyl groups and, consequently, is a product of oxidative deacylation of monoacetyldihydrophenazine; it is a complex including trivalent iron; it contains chlorine in an amount of 20.78% and nitrogen in an amount of 10.48%. In addition, the compound is strongly paramagnetic ($\chi_g = 24 \cdot 10^{-6}$ m.e.). The ultraviolet spectrum of the "orange" substance is similar to the spectrum of phenazine and is completely unlike the spectrum of monoacetyldihydrophenazine, as is evident from the graph (Fig. 2).

Fig. 2. Absorption spectra: 1 –phenazine, 2 –monoacetyldihydrophenazine, 3 –phenazine hydrochloride, 4 – "orange" product with m.p. 191–193°

Along with this it was observed that the substance formed upon oxidation of monoacetyldihydrophenazine initially possesses the properties of a free radical; for example, it forms dark-green solutions when heated in isoamyl alcohol, but in the process of purification by repeated recrystallization from isoamyl alcohol the compound gradually loses this property, and the "orange" substance with m.p. 191–193° is already completely incapable of dissociating with formation of a green coloration. The "orange" substance, as well as the product initially formed with the properties of a free radical, is very readily hydrolyzed by water, being converted into phenazine.

On the basis of these data, for the oxidation product of monoacetyldihydrophenazine possessing the properties of a free radical, formula (XII) is proposed, which includes two molecules of phenazine hydrochloride (of the type of Weitz ammonium salts), coordinatively bound to a molecule

$FeCl_3$. The "orange" product with m.p. 191-193° is evidently the product of a series of transformations of the phenazinium cation and contains two molecules of phenazine bound in a complex with a molecule of $FeCl_3$ (XIII).

$$[\,2\,\text{phenazine} \cdot \text{FeCl}_3\,]^{++}\ 2\text{Cl}^- \qquad \text{(XII)}$$

$$\text{phenazine}-\text{FeCl}_3-\text{phenazine} \qquad \text{(XIII)}$$

The structure of the latter was confirmed by synthesis from phenazine and ferric chloride.

An attempt was also made to confirm experimentally the formation of the phenazinium cation by obtaining it in the free state, rather than in the form of a complex. Indeed, it was found that phenazine in an anhydrous medium, on interaction with gaseous hydrogen chloride, forms a substance in the form of greenish-yellow crystals with m.p. 195-197°, soluble in isoamyl alcohol with formation of a dark-green coloration. The reaction apparently proceeds according to the scheme:

$$3\,\text{phenazine} + 2\text{HCl} \longrightarrow \text{dihydrophenazine} + 2\,[\,\text{phenazinium}\,]^{++}\ 2\text{Cl}^- \qquad \text{(XIV)}$$

The structure of the product with m.p. 195-197° (XIV) was confirmed by analysis and by determination of the magnetic susceptibility. Substance (XIV) proved to be paramagnetic ($\chi_g = 6.5 \cdot 10^{-6}$ m.e.), which corresponds to the presence of one unpaired electron in the molecule. On repeated heating of solutions, and also under the action of water, it is converted into phenazine (analogously to the way in which (XII) passes into the "orange" substance (XIII)). The absorption spectrum of this compound (Fig. 2, spectrum 3) is identical with the spectrum of phenazine, which also confirms its structure, expressed by formula (XIV).

On the basis of analytical results and the study of the chemical properties of the intermediate "black" product of oxidation of monoacetyldihydrophenazine with m.p. 137°, it was shown that the latter is a complex of one molecule of $FeCl_3$ and the molecular compound of chlorophenazine (XIV) with a molecule of monoacetyldihydrophenazine (V):

$$[\,\text{phenazinium}\,]^{+}\ \text{Cl}^- \cdot \text{monoacetyldihydrophenazine} \cdot \text{FeCl}_3$$

As a result of our work, the ability of phenazine to form free radicals has been demonstrated; these radicals are not analogues of diaryl nitrogen, as had previously been assumed in almost all cases (I-IV), but belong to the type of ammonium salts (phenazinium salts). Phenazinium hydrochloride is paramagnetic in crystals, gives deeply colored solutions in anhydrous but polar organic solvents, shows a tendency to form complexes, and is instantly hydrolyzed by water.

Ural Polytechnic Institute
named after S. M. Kirov

Received
25 X 1956

CITED LITERATURE

1. H. Wieland, *Lieb. Ann.*, **392**, 127 (1912).
2. H. Wieland, M. Offenbacher, *Ber.*, **47**, 2111 (1914).
3. St. Goldschmidt, *Ber.*, **53**, 44 (1920).
4. R. Kuhn, X. Kainer, , No. 17, 39399 (1954).
5. R. Kuhn, K. Schön, *Ber.*, **70**, 753 (1937).
6. H. McIlwarn, *J. Chem. Soc.*, 1937, 1704.
7. Z. V. Pushkareva, I. Ya. Postovskii, *ZhOKh*, **8**, 158 (1938).
8. R. Kuhn, K. Schön, *Ber.*, **68**, 1537 (1935).
9. N. Shcherbina, *ZhRFKhO*, **38**, 623 (1906).
10. J. S. Morley, *J. Chem. Soc.*, 1953, 4008.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.