STRUCTURE AND PROPERTIES OF N,N'-DI-(2,2,6,6-TETRAMETHYL-1-OXYL-4-PIPERIDYL)-N-DIETHYLPHOSPHORYLUREA

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N-Phosphorylated ureas, together with other products, are formed in the condensation of carbodiimides with monoesters of phosphoric acid [1]. The N-phosphorylated urea diradical N,N'-di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)-N-diethylphosphorylurea (I) was obtained [2] on reacting isocyanate (II) with the sodium salt of phosphorylaminopiperidine-oxyl (III)



At t \geq 160°C (in the melt) phosphorylurea (I) decomposes with formation of carbodiimide (IV). In solution the thermal decomposition is considerably accelerated by strong bases (NaH)

 $(I) \xrightarrow{\Delta} RN = C = NR + (EtO)_2 PO_2 H$

In this article we describe the determination of the molecular and crystal structures of phosphorylurea (I) by means of x-ray analysis and the investigation of its reactions with strong bases.

Crystallization of compound (I) from cyclohexane yielded light-red, transparent monocrystals of undefined form. The parameters of the elementary units were defined more accurately with a DRON-1 diffractometer.

The main crystallographic data are: $C_{23}H_{45}N_4O_6P$; a = 7.754(2), b = 16.178(4), c = 23.454(6) Å, $\gamma = 102.10(5)^\circ$, V = 2876.8 Å³; M = 504.7; $d_x = 1.166$ g/cm³ for Z = 4, space group $P2_1/b$.

The structure of the molecule in projection on the plane of the atoms $N^{10}P^{10^3}$ is pictured in Fig. 1 [3]. The H atoms (except H⁹) are not shown in Fig. 1; the distance C²-H lies in the interval 0.93-1.17 Å. The six-membered piperidine rings have the chair conformation. Their inflections along the lines $C^{18} \dots C^{20}$, $C^{23} \dots C^{24}$, $C^{14} \dots C^{17}$, and $C^{25} \dots C^{28}$ are 126, 126, 148, and 146°, respectively. The nitrogen atoms of the heterorings have planar surroundings with a slight deformation: the sum of the angles is 356° in both cases. The angle of inclination of the N^8-O^5 ($N^{11}-O^7$) bond* with the plane $C^{14}N^8C^{17}$ ($C^{25}N^{11}C^{28}$) is 21° (22°). This is a consequence of the steric hindrance between the O⁵ (0⁷) atoms and the CH₃ groups, which are located on one side of the N^8 (N^{11}) atoms relative to planes A and B. Consequently, the distances between the atoms O⁵ (0⁷) and C¹², C¹⁶ (C²⁷, C³⁰) are 2.75 and 2.72 Å (2.74 and 2.74 Å), which is 0.2 Å less than the distances to the atoms C¹³, C^{15} (C²⁶, C²⁹), which are 2.93 and 2.96 Å (2.96 and 2.94 Å), respectively. The atoms N⁹

*The data of the second piperidine fragment are given in parentheses.

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Fig. 1. Structure of the molecule in projection on the plane of the atoms $N^{10}P^{1}O^{3}$. The accuracy of the determination of the distances between the nonhydrogen atoms is 0.003-0.008 Å and that of the angles 0.3-0.9°.

and N^{10} occupy equatorial positions at the piperidine rings. The angle between the line N^9C^{19} and plane A (1.5°) is noticeably smaller than the analogous angle between $N^{10}C^{22}$ and plane B (7°). The difference between these angles in combination with the opposite turn around the N-C (heteroring) bond relative to the central part of the molecule points to steric interaction between the "right-hand" 2,2,6,6-tetramethylpiperidine-l-oxyl and the ethoxy groups at the phosphorus atom.

The structure of the central part of the molecule is characterized by the presence of conjugation between the unshared electron pair of the N¹⁰ atom and the phosphorus atom, which manifests itself by enlargement of the distances N¹⁰-C²¹ (1.416 Å) and N¹⁰-C²² (1.503 Å) in comparison with N⁹-C²¹ (1.338 Å) and N⁹-C¹⁹ (1.462 Å). It should be noted that the distance N¹⁰-P (1.664 Å) is 0.2 Å shorter than the sum of the covalent radii.

Another characteristic of the central part is the presence of the six-membered ring that is formed by means of an intramolecular hydrogen bond $(H^9...0^3 = 1.96 \text{ Å})$. The IR spectrum of a CCl₄ solution of urea (I) shows a single absorption band of the NH group, the characteristics of which (\vee 3300 cm⁻¹, ε 190 liters/mole·cm) are independent of the concentration (0.1-0.01 mole/liter). Consequently, at low temperatures, as in the crystalline state, and also in solution an intramolecular hydrogen bond is characteristic of the phosphorylurea group of urea (I).

The atoms H⁹ and O⁶ lie, with an accuracy of 0.006 Å, in the plane N⁹C²¹N¹⁰. At the same time the atoms O³, P¹, and O²² come out of that plane by 0.30, 0.24, and -0.05 Å, respectively, as a result of a minor turn around the C²¹-N¹⁰ bond. Together with the characteristic distortion of the angles (intra- and intercyclic) at the N⁹ and N¹⁰ atoms, this is evidence of a certain strain in the formed ring, which cannot be eliminated by rotation around the P-N¹⁰ bond.

We have also studied the reactions of phosphorylurea (I) with alcoholates and sodium hydride. On reaction of (I) with NaH in dimethoxyethane at 20°C the calculated amount of H_2 is evolved in 6 h, but thin-layer chromatography of the reaction mixture reveals only (I). As a result of subsequent refluxing for 2 h (I) disappears completely and from the mixture obtained carbodiimide (IV) is isolated with a yield of 86%.

On reaction of equimolar amounts of (I) and sodium 2,2,6,6-tetramethyl-1-oxyl-4-piperidolate in dioxane or with sodium ethoxide in alcohol at 20°C, already after 40 min (I) is not detected in the reaction mixture by means of TLC. In both cases amide (V), yield 60-70%, is the common reaction product. In addition to (V) urethanes (VIa, b) are obtained in high yields. Such a result occurs unexpectedly because for known analogs of (I) - RNHC(0)NRP(0). (OR')OH (VII, R = cyclohexyl, 2'- or 3'-adenineribonucleoside) - the capacity to phosphorylate the anion PhCH₂O⁻ with formation of the ester PhCH₂OP(0)(OR')OH was found earlier [1].

$$\begin{array}{cccccccc} & & & & & & \\ & & & & & \\ (I) + R'ONa \rightarrow RNHP(OEt)_2 + RNHCOR' & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ &$$

In contrast to (VII), phosphorylation of alcoholates by urea (I) practically does not take place, as was established with TLC using the specially synthesized references (VIII) and (IX). The fact that under comparable conditions the rate of the reaction of (I) with RO⁻ is ~25 times as fast also points to different mechanisms of this reaction and of the reaction of (VII) with PhCH₂O⁻.

The melting points and IR spectra of compounds (V) and (VIa, b) isolated from the reaction mixtures fully coincide with the melting points and IR spectra of the compounds synthesized by independent methods.

On the basis of the data on the structure of phosphorylurea (I) it may be assumed that during its deprotonation under the action of NaH or alcoholates the original rigidity of the phosphorylurea moiety is lost. The Na⁺ cation can take the place of the proton with the formation of (Ia), but more probable (see diagram) is transfer of the charge to the O atom and conversion of the partially double N⁹-C²¹ bond of (I) to the double bond of (Ib); the formation of (Ib) is completed as the result of rotation around the single C²¹-N¹⁰ bond. At ~20°C the salt (Ib) formed from (I) and NaH is sufficiently stable and manifests itself on TLC as starting compound (I). Decomposition of (Ib) to the carbodiimide and Na⁺(EtO)₂· PO₂⁻ apparently proceeds via (Ic). A similar mechanism is also possible for the thermal decomposition of (I) in the melt.

Reactions of (I) with alcoholates may proceed by two different routes. The electronwithdrawing phosphoryl group of (Ib) shifts the electron density to the phosphorylated N atom, which facilitates heterolysis of the C-N(P) bond with formation of (II) and (III). The equilibrium concentrations of (II) and (III) are very low and detection of these compounds by means of TLC failed. However, in the presence of alcoholates one of the components of the equilibrium mixture, isocyanate (II), is rapidly converted to the urethane, which leads to consumption of starting compound (I). Amide salt (III) gives (V) on contact with moisture.

An alternative mechanism of the reaction of (I) with alcoholates consists of attack of the $R'O^-$ group on the carbonyl group with formation of (Id), in which a shift of the electron density and subsequent heterolysis of the C-N(P) bond lead to the urethane and anion (III).



In contrast to (I), under the action of $PhCH_2O^-$ urea (VII) regenerates the diamion $RNC(O)NRP(OR')O_2^-$, in which the negatively charged phosphoryl group counteracts the transfer of the charge of the same kind to the phosphorylated N atom, and heterolysis of the N-C bond does not occur.

EXPERIMENTAL

The structures of the novel compounds (VIa, b) obtained were confirmed by elemental analyses and spectral methods. Characteristic bands of the IR spectra are given in the experimental part. In the mass spectra there are peaks of the molecular ions M^+ and also peaks of fragmentation ions characteristic of the nitroxyl radicals of the piperidine nucleus: $[M-Me]^+$, $[M-CH_2O]^+$, $[M-NO]^+$, $[M-CH_2=CMe_2]^+$, $[M-MeCH-NO]^+$, and $[M-CH_2=CMe_2-NO]^+$.

The EPR spectra of a dilute benzene solution of diradical (VIb) at ~20°C consists of 13 lines with respective amplitudes of 3:7:100:30:13:36:96:30:16:34:91:5:2; splitting constant $a_{\rm N} = 1.54 \pm 0.01$ mT, and the distances of the symmetrically arranged side lines to the central line in $a_{\rm N}$ units are 0.36, 0.52, 0.64, 1, 1.97, and 2.09. The EPR spectra of urethane (VIb) and starting urea (I) [2] are typical of nitroxyl diradicals with a short rigid bridge between the piperidine rings. It follows from data of x-ray analysis and IR spectra that the rigidity of that bridge in (I) is increased by the formation of an intramolecular bond forming a stable six-membered ring (see Fig. 1). Characteristic of the diradicals under consideration is an indirect spin-exchange mechanism between the nitroxyl groups [4]. In the EPR spectrum of monoradical (VIa) three lines, $a_{\rm N} = 1.53 \pm 0.01$ mT, are observed under the same conditions.

In the UV spectra of the obtained radicals there are two absorption bands of the nitroxyl group at λ_{max} 243 and 455 nm, while the molar absorption coefficient for diradical (VIb) is twice as large as that for monoradical (VIa).

A tom	X	Y	z	Atom	X	Y	Z
<u>р</u> і	5463(1)	2390(2)	6866(3)	H12.1	696(2)	299(4)	1001 (5)
\tilde{O}^2	6252(2)	2047(4)	6318(6)	H ^{12.2}	876(2)	297(4)	986 (5)
Õ3	6738(3)	2948(4)	7223(4)	H12.3	835(2)	242(4)	1039 (5)
Ō4	4003 (4)	2777 (3)	6616(6)	H13.1	542(2)	63(4)	964(5)
Ō5	9747(2)	1314(3)	9991(5)	H13.2	629(2)	97 (4)	1027 (5)
06	4350(3)	450(2)	7870(4)	H13.3	505(2)	137 (4)	998(5)
07	-242(2)	-1089(4)	6095(3)	H15.1	882(2)	-21(4)	950(5)
N^8	8973 (3)	1449(2)	9531 (5)	H ^{15.2}	908 (2)	-25(4)	882(5)
N^9	6078(4)	1731 (3)	8028(6)	H15.3	728(2)	-7(4)	912(5)
N^{10}	4516(5)	1484(2)	7178(4)	H16.1	1162(2)	81(4)	866 (5)
N ¹¹	857 (3)	-527(2)	6377 (5)	H16.2	1199(2)	161 (4)	895(5)
C12	7890(3)	2590(5)	10010 (8)	H ^{18.3}	1168 (2)	83(4)	947 (5)
C ¹³	5929 (4)	1145 (3)	9892(6)	H ^{29.1}	280 (2)	68 (4)	562(5)
C^{14}	7376(3)	1814(4)	9605 (5)	H ^{29.2}	219(2)	-21(4)	534(5)
C15	8478 (5)	18(3)	9111(7)	H ^{29.3}	420(2)	-4(4)	546(5)
C ¹⁶	11323 (5)	1066 (4)	8987(6)	H ^{30.1}	276(2)	-160(4)	589(5)
C^{17}	9342(3)	962(3)	9027 (5)	H ^{30.2}	324(2)	-153(4)	652(5)
C18	6771(3)	2095 (5)	9032(5)	H30.3	460(2)	-97(4)	603(5)
C19	6756(5)	1448(4)	8569 (5)	$H^{26.1}$	49(2)	105(4)	601(5)
C^{20}	8611(4)	1317 (4)	8492(6)	H ^{26.2}	-129(2)	101(4)	640(5)
C ²¹	4961(4)	1183(5)	7714(5)	H ^{26.3}	-128(2)	28(4)	595(5)
C ²²	3215(4)	891(4)	6815(6)	H ^{27.4}	-271(2)	-50(4)	669(5)
C ²³	3926(3)	133(3)	6627 (5)	H ^{27,2}	-202(2)	1(4)	717 (5)
C^{24}	1431(3)	608(4)	7089(6)	$H^{27.3}$	-116(2)	-77(4)	721(5)
C^{25}	77 (3)	112(4)	6678(5)	H ^{32.1}	597(2)	172(4)	524(5)
C ²⁶	-547 (4)	691(5)	6241(7)	H ^{32.2}	801(2)	170(4)	547 (5)
C ²⁷	-1525(4)	-368 (5)	7020(6)	H ^{32.3}	799(2)	264(4)	506(5)
C ²⁸	2720(5)	-405(6)	6191(6)	H ^{34.1}	88(2)	283(4)	680(5)
C ²⁹	2919(3)	-5(4)	5598(5)	H ^{34.2}	195(2)	387 (4)	642(5)
C30	3188(3)	-1276(5)	6160(8)	H ^{34.3}	76(2)	384(4)	691(5)
C**	7103(5)	2593(3)	5868(6)	H ^{31,1}	642(2)	317(4)	582(5)
C**	7065(4)	2095(4)	5353(5)	H31.4	836(2)	288(4)	600(5)
C**	3303(3)	3417 (5)	6922(7)	H33.1	408(2)	390(4)	713(5)
	1681 (3)	3515(5)	6754(8)	H	301(2)	310(4)	137 (5)
H10.1	755(2)	263(4)	891(5)	H44.1	160(2)	30(4)	740(5)
1120 1	555 (Z)	224(4)	907 (5)	H ****	105(2)	111(4)	120(3)
1120 2	869(2)	89(4)	821(5)	H ^{10.1}	590(2)	87(4)	809(5)
	931(Z)	189(4)	839(5) 605(5)	IT 22.4	049(2)	249 (4) 499 (5)	8/7(5)
1123 2	400(2)	-1/(4)	095(5)	LI	308(2)	122(3)	047(3)
n-***	210(2)	30(4)	044(5)				

TABLE 1. Atomic Coordinates ($\cdot 10^4$, hydrogens $\cdot 10^3$)

<u>X-ray structure analysis</u> of (I) was carried out on a DAR-UM diffractometer with Cu K_{α} radiation [5] with an isometric sample with a size of ~0.45 mm. We recorded 2964 independent nonzero reflections (I > 2 σ) with 20 \leq 117°. The structure was determined by the direct method and by refinement with the Roentgen-75 program [6]. Refinement with anisotropic convergence (hydrogens isotropically) using 2587 reflections lead to the final value R = 0.077. Atomic coordinates and their errors are listed in Table 1; the main distances are shown in Fig. 1. Values of the individual temperature parameters can be obtained from the authors.

IR spectra were recorded on a Specord 75-IR spectrophotometer, UV spectra on a Specord UV-VIS spectrophotometer, EPR spectra on an EPA-2A radiospectrometer, and mass spectra on a Finnigan spectrometer at an electron ionization energy of 70 eV and a temperature of the ionization chamber of 250°C. Urea (I), isocyanate (II), carbodiimide (IV), and amide (V) were prepared as described in [2]. 2,2,6,6-Tetramethyl-4-(diethylphosphoryloxy)piperidine-1-oxyl (VIII) was prepared according to [7], and N,N'-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)urea (IX) was prepared from isocyanate (II) and 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl in ether, yield 100%, mp 203-204°C (ethyl acetate), cf. [8]. Reaction products were isolated by means of preparative TLC on silica gel, eluant CHCl₃-MeCN 2:1.

<u>Reaction of N,N'-di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)-N-diethylphosphorylurea</u> (I) with NaH. To a suspension of 30 mg (1.25 mmole) of NaH in 1 ml of dimethoxyethane under a nitrogen atmosphere was added a solution of 504 mg (1 mmole) of (I) in 1.5 ml of dimethoxyethane. The mixture was stirred at ~20°C until hydrogen evolution stopped (6 h). At that moment TLC of the reaction mixture showed only starting compound (I). The mixture was then refluxed for 2 h and the hot solution was filtered. On cooling, 182 mg of carboimide (IV) crystallized out; chromatography of the mother liquor gave an additional 119 mg of (IV). Total yield 301 mg (86%) of (IV); the mp of 175-178°C and the IR spectrum are identical with those of an authentic sample.

<u>Reaction of Phosphorylurea (I) with Alcoholates.</u> a) With sodium 2,2,6,6,-tetramethyl-<u>1-oxyl-4-piperidolate</u>. To a suspension of 29 mg (1.2 mmole) of NaH in 0.5 ml of dry dioxane under a nitrogen stream was added a solution of 172 mg (1 mmole) of the alcohol-radical ROH in 2 ml of dioxane. The mixture was stirred at ~20°C until hydrogen evolution stopped (5 h) and then a solution of 504 mg (1 mmole) of (I) in 1 ml of dioxane was added dropwise. According to TLC all of the starting (I) had reacted after 40 min. Chromatography of the reaction mixture over silica gel yielded 194 mg (63%) of amide (V) and 362 mg (98%) of urethane (VIb).

b) With sodium ethoxide. To a solution of 252 mg (0.5 mmole) of (I) in absolute ethanol was added 1 ml of 1N NaOEt in ethanol. After 40 min 103 mg (67%) of (V) and 177 mg (96%) of (VIa) were isolated by means of preparative TLC.

Melting points and IR spectra of urethanes (VIa, b) prepared from urea (I) are in agreement with those of samples of (VIa, b) synthesized by independent methods (see below).

 $\frac{2,2,6,6-\text{Tetramethyl-4-(ethyloxycarbonylamino)piperidine-1-oxyl (VIa)}{(VIa)}$ A solution of 1 mmole of isocyanate (II) in 1.2 ml of 1N EtONa in alcohol was prepared. TLC showed that the reaction was completed in the time it took to dissolve (II). The solvent was evaporated and the residue extracted with ether. After evaporation of the solvent there remained 240 mg (98%) of (VIa), orange prisms, mp 121-122°C (cyclohexane). Found, %: C 59.08, H 9.66, N 11.46; m/z 243 (M⁺). C₁₂H₂₃N₂O₃. Calculated, %: C 59.23, H 9.53, N 11.51, M 243.33. IR spectrum (CCl₄, v, cm⁻¹): 1723 (C=O) 3348 (N-H bonded), 3450 (N-H free). UV spectrum in alcohol, λ_{max} , nm (ε , liter/mole·cm): 243 (2000), 455 (10.5).

 $\frac{4-[(2,2,6,6-Tetramethyl-1-oxyl-4-piperidyl)oxycarbonylamino]-2,2,6,6-tetramethylpiper$ idine-1-oxyl (VIb). To a solution of 1 mmole of alcohol-radical ROH and 1 mmole of isocyanate (II) in 2 ml of benzene was added 0.1 ml of Et₃N and the mixture was refluxed for 5 hwith exclusion of moisture. Urethane (VIb) was isolated by means of preparative TLC. Yield302 mg (82%) of (VIb), a red glassy substance, melting at >35°C. Found, %: C 61.60, H 9.68,N 11.43; m/z 369 (M⁺). C₁₉H₃₅N₃O₄. Calculated, %: C 61.76, H 9.55, N 11.37; M 369.50. $IR spectrum (CCl₄, <math>\nu$, cm⁻¹): 1723 (C=O), 3342 (N-H bonded), 3448 (N-H free). UV spectrum in alcohol, λ_{max} , nm (ε , liter/mole·cm); 243 (4010), 455 (20.1).

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CONCLUSIONS

1. X-ray structure analysis was carried out with crystals of N,N'-di-(2,2,6,6-tetra-methyl-1-oxyl-4-piperidinyl)-N-diethylphosphorylurea (I). Conjugation of the phosphoryl group with the unshared electron pair of the nitrogen atom disturbs the symmetry of the urea moiety and weakens the C(0)-N(P) bond; reaction of (I) with alcoholates proceeds with rupture of the bond mentioned.

2. In the crystalline state and in solution (I) has an intramolecular NH...O=P hydrogen bond, closing a six-membered ring. After deprotonation under the action of NaH the rigidity of the structure of the urea moiety decreases, which facilitates the thermal decomposition of (I) into carbodiimide (IV) and $(EtO)_2PO_2Na$.

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SYNTHESIS, STRUCTURE, AND PROPERTIES OF DERIVATIVES OF 1,1,2,2-TETRAHALOID-1,2-DIGERMACYCLOBUT-3-ENES — THE FIRST EXAMPLES OF A NEW CLASS OF HETEROCYCLES*

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Investigations of the small germanium heterocycles present interest both from the viewpoint of the evidence of their participation in the reactions of germylenes and digermenes with olefins and acetylenes, and in connection with the general problems of chemical structure and aromaticity, particularly the study of new types of bonds and compounds. Although the first stable silacyclopropenes [2] and 1,2-disilacyclobut-3-enes [3] were described about 10 years ago, their germanium analogs - the germacyclopropenes (germirenes) [4] and 1,2-digermacyclobut-3-enes [1, 5] - were obtained by us comparatively recently. The present work presents detailed information on the synthesis, structure, and chemical properties of the first 1,2-digermacyclobut-3-enes - $\Delta^{1,7}$ -2,2,6,6-tetramethyl-8,8,9,9-tetrachloro-4-thia-8,9-digermabicyclo-[5.2.0]nonene (Ia) and $\Delta^{1,7}$ -2,2,6,6-tetramethyl-8,8,9,9-tetraiodo-4-thia-8,9-digermabicyclo-[5.2.0]nonene (Ib).

The reaction of the dioxane complex of $GeCl_2$ [6] with the heterocyclic acetylene 2,2,6,6-tetramethyl-4-thiacyclohept-l-yne (II) [7] gave the 1,2-digermacyclobutene (Ia).

*For Communication I, see [1].

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