NEW POLYYNE DERIVATIVES OF 2,2,6,6-TETRAMETHYLPIPERIDIN-1-OXYL

> V. V. Pavlikov, A. B. Shapiro, and É. G. Rozantsev

The high reactivity of the C \equiv C bond opens up broad possibilities for the synthesis of nitroxyl mono- and polyradicals containing various functional groups. The geometric features of the C \equiv C bond make it possible to construct radicals with a rigid nonspherical structure [1], which are of some interest for molecular biology [2].

At the present time, however, only a small number of stable nitroxyl radicals containing a $C \equiv C$ bond are known [1-6]. In the present work we obtained new radicals with the general formulas



 $\mathbf{H} = \mathbf{C} = \mathbf{C} - \mathbf{p} \cdot \mathbf{C}_{6} \mathbf{H}_{4} - \mathbf{C} = \mathbf{C} \mathbf{H} (\mathbf{I}), (\mathbf{II}); \quad \mathbf{C} = \mathbf{C} - \mathbf{p} \cdot \mathbf{C}_{6} \mathbf{H}_{4} - \mathbf{C} = \mathbf{C} - \mathbf{C} = \mathbf{C} - \mathbf{C}_{6} \mathbf{H}_{5} (\mathbf{III}), (\mathbf{IV})$

and also biradicals of the following type:



The diamine glycol (VIa) is formed during the condensation of p-diethynylbenzene with 4-oxo-2,2,6,6-tetramethylpiperidine under the conditions in [7]:



and the synthesis of the monosubstituted amine (Ia) was therefore realized according to the following scheme:



The radical (I) was obtained by catalytic oxidation of the amine (Ia):

$$(Ia) \xrightarrow{Na_2WO_5} (I)$$

The nitroxyl (III) was synthesized under the conditions of the Chodkiewicz-Cadiot reaction [8]:

$$(I) + Br - C \equiv C - C_6 H_5 \xrightarrow{CuCl, CH_3 NH_2} (III)$$

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Fig. 1. The ESR spectra of the biradicals: a) (VI); b) (VIII); c) (VII) in toluene at 20°C; d) (IX) at 50°C.

The dehydration of (I) and (III) to (II) and (IV) was realized by the action of phosphorus oxychloride in pyridine at $\sim 20^{\circ}$ C. The biradical (VI) was obtained by catalytic oxidation of the corresponding amine (VIb), which was in turn synthesized by dehydration of the glycol (VIa):



The biradicals (V) and (VII) were obtained directly from the monoradicals 4-ethynyl-2,2,6,6-tetramethyl- Δ^3 -piperidin-l-oxyl and (II) by oxidative dimerization according to [9]:



The biradical (V) was synthesized earlier by a different scheme [5]:



The organomercury biradicals (VIII) and (IX) were obtained in the present work by the method in [10]:



The structure of the synthesized compounds was confirmed by elemental analysis and IR and mass spectroscopy.

From the ESR spectra of the new biradicals (VI) and (VIII) (Fig. 1a, b) it can be concluded that there is intramolecular spin—spin exchange in the system of conjugated bonds. The ESR spectra of (VII) and (IX) (Fig. 1c, d) are triplets, and this indicates the absence of spin—spin exchange. The relatively large masses of the molecules of the biradicals (VII, IX) and their rigid nonspherical configuration lead to appreciable anisotropy in the ESR spectra of these biradicals even at room temperature.

EXPERIMENTAL

The mass spectra were recorded on an RMU-6D instrument. The IR spectra were recorded on a UR-20 instrument. The ESR spectra were recorded on an ÉPRV-IKhF spectrometer with a modulation frequency of 100 kHz; the ampuls were evacuated at 10^{-3} torr.

<u>4-Hydroxy-4-(p-ethynylphenylethynyl)-2,2,6,6-tetramethylpiperidine (Ia)</u>. To a suspension of 22.4 g of finely ground potassium hydroxide in 50 ml of absolute THF at -10° C with vigorous stirring we gradually added a solution of 12.6 g of p-diethynylbenzene in 150 ml of THF. After the temperature had been reduced to -40° C a solution of 15.5 g of 4-oxo-2,2,6,6-tetramethylpiperidine in 100 ml of THF was added to the mixture drop by drop over 1.5 h. The mixture was stirred for a further 1 h, and the temperature was gradually raised to -10° C. The reaction mass was poured into ice and saturated with sodium chloride, and the organic layer was separated and evaporated under vacuum until crystals appeared.* After dilution with water the precipitate was filtered off, dried, and washed repeatedly with hexane. After recrystallization from a 3:1 mixture of hexane and chloroform 10.7 g (38%) of (Ia) was obtained in the form of a white crystalline powder; mp 116-117°C. Found %: N 4.88; mol. wt. 281 (mass spectrum). C₁₉H₂₃NO. Calculated %: N 4.98. IR spectrum (v, cm⁻¹): 834 (p-disubstituted benzene), 1507 (C=C aromatic), 2115 w (C=C), 3280 (=CH), 3405 (OH, NH).

<u>4-Hydroxy-4-(p-ethynylphenylethynyl)-2,2,6,6-tetramethylpiperidin-1-oxyl (I)</u>. To a solution of 10 g of (Ia) in 200 ml of methanol we added 2 g of sodium tungstate and 10 ml of 30% hydrogen peroxide. The mixture was left at $\sim 20^{\circ}$ C for 8 days. The mixture was then evaporated by half, diluted with water, saturated with potassium carbonate, and extracted with ether. After drying with potassium carbonate the extract was evaporated under vacuum, and the residue was chromatographed on a column of aluminum oxide of medium activity with chloroform as eluent. We collected the colored fraction with Rf 0.43. We obtained 7.86 g (74.6%) of (I) in the form of light-orange crystals; mp 126-127°C (3:1 hexane-chloroform). Found %: C 76.96; H 7.55; N 4.90. Mol.wt. 296 (mass spectrum). C₁₉H₂₂NO₂. Calculated %: C 77.03; H 7.43; N 4.73. IR spectrum (ν , cm⁻¹): 837 (p-disubstituted benzene), 1510 (C=C aromatic), 2220 w (C=C), 3269 (=CH), 3415 (OH).

 $\frac{4-\text{Hydroxy-4-(phenyl-p-butadiynylphenylethynyl)-2,2,6,6-tetramethylpiperidin-l-oxyl (III)}{\text{To a mixture of 1.43 g of (I), 0.01 g of cuprous chloride, 0.05 g of hydroxylamine hydrochloride, 2 ml of 25% aqueous methylamine, and 10 ml of methanol, while stirring, we added dropwise a solution of 0.9 g of 1-bromo-2-phenylacetylene in 3 ml of methanol. The mixture was stirred at 20°C for 1.5 h, + added to water, and extracted with ether. The extract was dried with potassium carbonate, the solvent was evaporated under vacuum, and the residue was chromatographed on a column of silica gel LS 100/160. The first colored fraction was collected. The eluent was a 28:1:1 mixture of chloroform, methanol, and benzene. We obtained 1.14 g (59.7%) of (III) in the form of a light-orange powder; mp 156-158°C. Rf (Al_2O_3/CHCl_3) 0.25. Found %: C 81.54; H 6.68; N 3.87. Mol. wt. 396 (mass spectrum). C_27H_26NO_2. Calculated %: C 81.82; H 6.57; N 3.54. IR spectrum (<math>\nu$, cm⁻¹): 688, 752 (monosubstituted benzene), 836 (p-disubstituted benzene), 1490, 1505, 1600 (aromatic C=C), 2216 w (C=C), 3405 (OH).

 $\frac{4-(p-\text{Ethynylphenylethynyl})-2,2,6,6-\text{tetramethyl}-\Delta^{3}-\text{piperidin}-1-\text{oxyl} (II). A mixture of 1.48 g of (I), 5 ml of dry pyridine, and 0.5 ml of phosphorus oxychloride was stirred at 20°C for 20 h, diluted with water, and extracted with benzene. The extract was washed repeatedly with dilute hydrochloric acid (pH 2-3) and with water and dried with potassium carbonate. The solvent was evaporated under vacuum, and the residue was chromatographed on aluminum oxide of medium activity (with chloroform as eluent). The first colored fraction with Rf 0.83 was collected. We obtained 0.8 g (57.6%) of (II) in the form of orange crystals; mp 148-148.5°C (from hexane). Found %: C 82.10; H 7.34; N 5.17. Mol. wt. 278 (mass spectrum). C₁₉H₂₀NO. Calculated %: C 82.01; H 7.19; N 5.04. IR spectrum (v, cm⁻¹): 840 (p-disubstituted benzene), 1500 (aromatic C=C), 3228 (≡C-H).$

 $4-(Phenyl-p-butadiynylphenylethynyl)-2,2,6,6-tetramethyl-\Delta^3-piperidin-l-oxyl (IV).$ The compound was obtained from (III) similarly to (II) with a 48.5% yield in the form of light-

^{*}In cases where the precipitate separated at once the procedure for the isolation of the product was simplified.

⁺When the mixture was greatly darkened, hydroxylamine hydrochloride was added until it was light.

orange shiny crystals; mp 184-185°C (2:1 hexane-chloroform). R_{f} (A1₂O₃/CHCl₃) 0.63. Found %: C 85.35; H 6.67; N 4.10. Mol. wt. 378 (mass spectrum). $C_{27}H_{24}NO$. Calculated %: C 85.71; H 6.35; N 3.70. IR spectrum (ν , cm⁻¹): 690, 760 (monosubstituted benzene), 840 (p-disubstituted benzene), 1492 (aromatic C=C), 2150, 2200 (C=C).

Bis(1-oxy1-2,2,6,6-tetramethy1- Δ^3 -4-piperidy1)butadiyne (V). A mixture of 0.89 g of 4-ethyny1-2,2,6,6-tetramethy1- Δ^3 -piperidin-1-oxy1, 5 g of Cu(CH₃COO)₂·H₂O, 10 ml of water, 10 ml of methanol, and 30 ml of pyridine was stirred at 20°C for 3 h and diluted with water. The precipitate was filtered off, washed with water, and dried. We obtained 0.28 g (31.8%) of (V) in the form of orange crystals, which melted with decomposition at 207°C (1:1 hexane-chloroform), cf. [5].

<u>p-Bis(2,2,6,6-tetramethyl- Δ^3 -4-piperidyl)benzene (VIb)</u>. A mixture of 8.7 g of (VIa), 100 ml of dry toluene, and 2 ml of phosphorus oxychloride was boiled for 30 h. The solvent was evaporated under vacuum, and the residue was diluted with water, made alkaline with potassium carbonate, and extracted with chloroform. After drying with sodium sulfate the extract was evaporated, and the residue was sublimed under vacuum. We obtained 3.93 g (49.2%) of (VIb) in the form of white crystals; mp 112-113°C. Found %: N 6.84. Mol. wt. 400 (mass spectrum). C₂₈H₃₆N₂. Calculated %: N 7.00. IR spectrum (ν , cm⁻¹): 840 (pdisubstituted benzene), 1500 (C=C aromatic), 2100, 2200 (C≡C), 3145 (NH).

<u>p-Bis(1-oxyl-2,2,6,6-tetramethyl- Δ^3 -4-piperidylethynyl)benzene (VI)</u>. To a solution of 5 g of (VIb) in 150 ml of methanol we added 2 g of sodium tungstate and 10 ml of 30% hydrogen peroxide. The mixture was left at 20°C for 15 days. It was then diluted with water, saturated with sodium chloride, and extracted with chloroform. The extract was dried with sodium sulfate, the solvent was evaporated under vacuum, and the residue was chromatographed on aluminum oxide of medium activity with chloroform as eluent. The colored fraction with R_f 0.52 was collected. We obtained 1.5 g (27.9%) of (VI) in the form of a yellow powder; mp 220-221°C (decomp.). Found %: C 78.02; H 7.83; N 6.33. Mol.wt. 430 (mass spectrum). $C_{28}H_3AN_2O_2$. Calculated %: C 78.14; H 7.19; N 6.51. IR spectrum (ν , cm⁻¹): 842 (p-disubstituted benzene), 1500 (C=C aromatic), 1640 w (C=C), 2200 (C=C).

<u>Bis(1-oxy1-2,2,6,6-tetramethy1- Δ^3 -4-piperidy1-p-ethyny1pheny1)butadiyne (VII).</u> The compound was obtained from (II) similarly to (V) with a 21.2% yield in the form of a yellow powder poorly soluble in normal organic solvents. Above 225°C it decomposed without melting. Found %: N 4.96. Mol. wt. 554 (mass spectrum). C₃₈H₃₈N₂O₂. Calculated %: N 5.05. IR spectrum (ν , cm⁻¹): 840 (p-disubstituted benzene), 1500 (aromatic C=C), 2200 (C=C).

<u>Bis(1-oxy1-2,2,6,6-tetramethy1- Δ^3 -4-piperidiy1ethyny1)mercury (VIII)</u>. A mixture of 1.65 g of mercuric chloride and 4.05 g of potassium iodide was stirred and gently heated in 4 ml of water until completely dissolved, 3.5 ml of 10% sodium hydroxide solution was added, and at 20°C a solution of 0.9 g of 4-ethyny1-2,2,6,6-tetramethy1- Δ^3 -piperidin-1-oxy1 in 25 ml of ethanol was added drop by drop over 40 min. The precipitate was filtered off and chromatographed on aluminum oxide of medium activity with chloroform as eluent. The fraction with R_f 0.43 was collected. We obtained 0.65 g (46.1%) of (VIII) in the form of orange crystals; mp 203-204°C (from ethanol). Found %: C 47.61; H 5.48; Hg 35.77. Mol. wt. 555 (mass spectrum). C₂₂H₃₀N₂O₂Hg. Calculated %: C 47.57; H 5.41; Hg 36.22. IR spectrum (ν , cm⁻¹): 1640 (C=C), 2148 (C=C).

<u>Bis(1-oxyl-2,2,6,6-tetramethyl- Δ^3 -4-piperidyl-p-ethynylphenylethynyl)mercury (IX).</u> The compound was obtained from (II) similarly to (VIII) with a 41.1% yield in the form of a cream-colored powder; decomp. p. 221-223°C (from ethanol), Rf (Al₂O₃/CHCl₃) 0.48. Found %: C 60.11; H 5.01; Hg 26.54. Mol.wt. 755 (mass spectrum). C₃₈H₃₈N₂O₂Hg. Calculated %: C 60.40; H 5.03; Hg 26.62. IR spectrum (ν , cm⁻¹): 839 (p-disubstituted benzene), 1500 (aromatic C=C), 2142 (C≡C).

CONCLUSIONS

1. New long-chain stable mono- and dinitroxyls with polyyne bonds and biradicals containing mercury atoms were synthesized.

2. Spin conduction through the p-diethynylbenzene and diethynylmercury bridges in the biradicals was established.

3. The ESR spectra of nonviscous solutions of the biradicals with a rigid nonspherical structure possess clearly defined anisotropy.

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SYNTHESIS OF AROMATIC DIISOCYANATES BY

CARBONYLATION OF DINITRO COMPOUNDS WITH

CARBON MONOXIDE ON PALLADIUM CATALYSTS

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The carbonylation of aromatic dinitro compounds to form diisocyanates is catalyzed by Pd compounds activated by organic, organometallic, and inorganic compounds [1]. The oxides $Fe_2O_3 + MoO_3$ and $Fe_2O_3 + V_2O_5$ have an activating effect on PdCl₂ [2, 3].

We have studied the influence of pyridine (Py) and transition-metal oxides, and also the effect of temperature and CO pressure, on the activity of PdCl₂.

At 200°C and 125 atm, PdCl₂ does not catalyze the carbonylation of 2,4-dinitrotoluene (2,4-DNT) (Table 1). When Py is added to the reaction system (PdCl₂:Py molar ratio 1:1), 1-methylbenzene-2,4-diisocyanate is formed in a yield of 24% under the same conditions. Addition of V_2O_5 or MoO_3 to $PdCl_2$ -Py in an amount of 10%, based on 2,4-DNT, increases the yield of the diisocyanate, and a mixture of MoO_3 and Fe_2O_3 (weight ratio 1:2) is even more effective. The oxides of Sc, Mn, Ta, Nb, Cr, and Ni reduce the yield of diisocyanate, giving significant amounts of mononitromonoisocyanates, while CuO and Co_3O_4 inhibit the formation of isocyanates, although the 2,4-DNT is reduced.

Additive	2,4- DNT con- version, øn	1-Methylbenzene- 2,4-diisocyanate yield, %	Mononitro- monoisocya- nate yield, %	Additive	2, 4- DNT con- version, %	1-Methylbenzene- 2,4-diisocyanate yield, %	Mononitro- monoisocya- nate yield, %
None * V ₂ O ₅ MoO ₃ MoO ₃ +Fe ₂ O ₃ Sc ₂ O ₃ MnO ₂ *PdCl ₂ cataly	0 * 100 100 100 100 100 96 rst.	0 24 36 36 58 18 16	0 12 6 0 0 13 25	Ta ₂ O ₅ Nb ₂ O ₅ Cr ₂ O ₃ NiO CuO Co ₃ O ₄	100 100 96 82 88 43	13 11 11 10 0 0	12 15 23 32 8 0

TABLE 1. Effect of Transition-Metal Oxides on Carbonylation of 2,4-DNT in the Presence of a PdCl₂-Py Catalyst (200°C, 125 atm)

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