New Derivatives of 4,4,5,5-Tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-Oxide as Monomers for Polyradicals with Special Magnetic Properties

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Received August 24, 1992

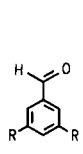
The preparation of new derivatives of 4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide as monomers for purely organic polymers with special magnetic properties is described. 3,5-Diethynylbenzaldehyde and 3,5-bis(trimethylsilylethynyl)benzaldehyde were converted to the corresponding 1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine derivatives which were oxidized to stable nitronyl nitroxide radicals.

J. Heterocyclic Chem., **30**, 425 (1993).

Interest in the preparation of organic materials exhibiting special magnetic properties has increased in recent years because ferromagnetic organic polymers might be used for information storage [1,2]. To the possible candidates for ferromagnetic coupling belong π-conjugated polyradical systems [3,4].

In continuation of our attempts to prepare para- or ferromagnetic substances [5] we synthesized new stable radicals as monomers for stable polyradicals. The radicals synthesized are nitronyl nitroxides, a class of substances first described by Ullmann *et al.* [6]. The advantage of the nitronyl nitroxide groups is their high chemical and thermal stability enabling them to be subjected to boiling temperatures of usual organic solvents without any decomposition [7]. They have already been employed in attempts to prepare magnetic organic compounds [5,8].

The substance groups under consideration are: 3,5-disubstituted benzaldehyde (**1**); 2-phenyl-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine, disubstituted at the phenyl group in position 3 and 5 (**2**); 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, disubstituted at the phenyl group in position 3 and 5 (**3**). The substituents R are **a** = bromine, **b** = trimethylsilylethynyl and **c** = ethynyl.



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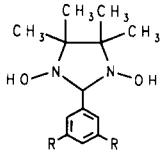

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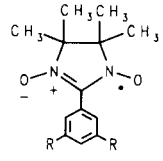

3

1, 2, 3	R
a	–Br
b	–C≡C-Si(CH$_3$)$_3$
c	–C≡CH

The reaction of aromatic halides with ethynyltrimethylsilane, using *in situ* generated palladium(0) as catalyst [9], was applied to the conversion of the dibromine compound **1a** to 3,5-bis(trimethylsilylethynyl)benzaldehyde (**1b**). Subsequent removal of the protecting trimethylsilyl groups of **1b** by use of potassium carbonate in methanol gave 3,5-diethynylbenzaldehyde (**1c**). The workup of the reaction mixture was critical due to the special stability features of **1c**. Evaporation of the solvent led to an exothermic reaction as soon as all solvent was removed; the resulting brown residue was insoluble in organic solvent and no **1c** could be isolated. Concentration of the reaction mixture to a small volume followed by column chromatography through silica gel resulted also in an uncontrolled reaction of **1c**. The diethynyl compound **1c** was eventually isolated by pouring the reaction mixture into distilled water and subsequent extraction with methylene chloride.

The reaction of the aldehydes **1a** and **1c** with 2,3-bis(hydroxyamino)-2,3-dimethylbutane, prepared *in situ* by reaction of 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate with potassium carbonate, gave 2-(3,5-dibromophenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**2a**) and 2-(3,5-diethynylphenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**2c**). Because the Si-C bond is sensitive to the alkaline medium, 2-(3,5-bis(trimethylsilylethynyl)phenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**2b**) was prepared by reaction of the aldehyde **1b** with 2,3-bis(hydroxyamino)-2,3-dimethylbutane in benzene.

The imidazolidines **2a, 2b** and **2c** were converted to the corresponding nitronyl nitroxide radicals 2-(3,5-dibromophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (**3a**), 2-(3,5-bis(trimethylsilylethynyl)phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (**3b**) and 2-(3,5-diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide (**3c**) by oxidation with lead

dioxide [6]. The most interesting product from our point of view was the radical **3c**, and we tried to synthesize the nitronyl nitroxide **3c** with a high yield. The reaction sequence **1b** → **1c** → **2c** → **3c** had an overall yield of 34%. Another possible reaction sequence is **1b** → **2b** → **3b** → **3c**, where the stable radical **3b** is converted to **3c** by deprotection of the ethynyl groups (see Experimental Section); the overall yield here was 29%. The best method for the preparation of **3c** is a "single step" reaction of **1b** with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate and potassium carbonate to **2c**, not isolated, which is oxidized to **3c**; the overall yield (calculated on **1b**) was 43%.

The electron spin resonance (esr) spectra for solutions of the radicals **3a**, **3b** and **3c** in methylene chloride are shown in Figure 1. The two nitrogen atoms give a 2nI + 1 pattern, where I = 1 and n = 2. The g values determined are 2.00667 ± 0.00002 for radical **3a** and 2.00657 ± 0.00002 for the radicals **3b** and **3c**. The value of the hyperfine coupling constant a_N is 7.46 ± 0.06 G for all radicals. The spectra are typical for nitronyl nitroxide monoradicals substituted with a pheny group at C_2 of the imidazole [6,7] and they can be taken as an additional proof of the assumed structure.

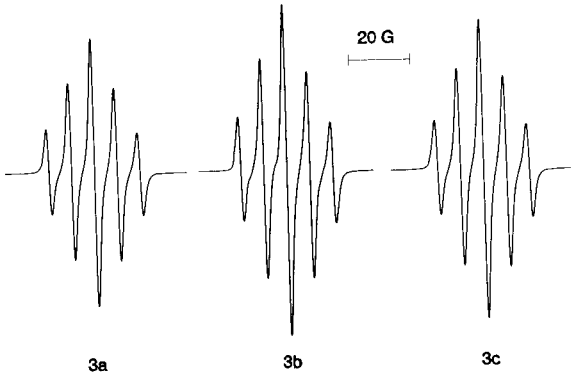

Figure 1. Nitronyl nitroxides dissolved in methylene chloride, esr spectra; (**3a**: c = 1.04 • 10^{-4} mol/l; **3b**: c = 0.88 • 10^{-4} mol/l; **3c**: c = 1.14 • 10^{-4} mol/l).

The radicals **3a**, **3b** and **3c** are suitable for the preparation of polyradicals. For example, radical **3c** can be polymerized by an oxidative coupling reaction of unprotected ethynyl groups [10] to give a π-conjugated polyradical, poly(2-(3,5-diethynylenephenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide) (**4**). The polyradical **4** can be compared with systems calculated by Lahti *et al.* [11]. These calculations demonstrate that ferromagnetic coupling could occur in polydiactylenes with radicals in side groups. The formation and properties of polyradical **4**, exhibiting interesting magnetic properties, will be described in a following paper [12].

EXPERIMENTAL

Instrumental Equipment.

The ^{1}H nmr and ^{13}C nmr spectra were measured in deuteriochloroform or in deuterated dimethyl sulfoxide (DMSO-d_6) on a Bruker MSL 300 spectrometer with tetramethylsilane as standard. The ms spectra were performed on a Finnigan MAT 212 mass spectrometer with direct insertion (DI) of the samples and electron impact (EI) ionization (70 eV). The ir spectra were recorded on a Bomem Michelson 100 FTIR spectrometer using thin films on sodium chloride. Electron spin resonance spectra (esr) were taken on a Bruker ER 200 D X-Band spectrometer; the g values were determined by using Fremy's salt (g = 2.00550 ± 0.00005) as reference.

General and Starting Materials.

All reactions were carried out and all substances were stored under dry argon. Reagents were handled with syringes through septa. The solvents benzene, chloroform, cyclohexane, diethyl ether and triethylamine were distilled from sodium before use. Methanol was dried with magnesium before distillation. Ethyl acetate was dried with phosphorus pentoxide before distillation. Ethynyltrimethylsilane, palladium(II) acetate, triphenylphosphine (all Aldrich Chemical Co.), lead dioxide (Fluka) and 2,3-bis-(hydroxyamino)-2,3-dimethylbutane sulfate (Eastman Kodak Company) were used without further purification. 2,3-Bis(hydroxyamino)-2,3-dimethylbutane was prepared from 2,3-dimethyl-2,3-dinitrobutane (Aldrich Chemical Co.) as described by Lamchen and Mittag [13]. 3,5-Dibromobenzaldehyde was synthesized from 1,3,5-tribromobenzene (Aldrich Chemical Co.) according to Chen *et al.* [14]. The silica gel used for column chromatography (>230 mesh ASTM) was from Merck.

3,5-Bis(trimethylsilylethynyl)benzaldehyde (**1b**).

To a deaerated solution of 10.0 g (37.9 mmoles) **1a**, 12.1 g (123.6 mmoles) of ethynyltrimethylsilane and 400 mg of triphenylphophine in 75 ml of triethylamine were added 150 mg of palladium(II) acetate under argon. The solution was heated to reflux for 3 hours. After cooling to 25° the mixture was filtered. The residue of triethylamine hydrobromide was rinsed twice with 20 ml of triethylamine and dried under reduced pressure (13.71 g triethylamine hydrobromide, 99%). The brown filtrate was evaporated under reduced pressure, mixed with 100 ml of sodium bicarbonate solution (5%), and extracted three times with 100 ml of methylene chloride. The combined organic fractions were dried over sodium sulfate and concentrated to give a brown solid mass. Purification by column chromatography using silica gel and cyclohexane:ethyl acetate (29:1, v/v) gave 8.05 g (75%) of **1b**, mp 68°; ir (sodium chloride): ν 2797 and 2727 (CHO), 2164 (C≡C), 1712 (CO), 1593, 1444, 1252 (Si-C), 1144, 968, 848 (Si-C bending) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.25 (s, 18H, C*H*$_3$), 7.80 (s, 1H, phenyl), 7.88 (s, 2H, phenyl), 9.96 ppm (s, 1H, -C*H*O); ^{13}C nmr (deuteriochloroform): δ 0.02 (-Si(*C*H$_3$)$_3$), 17.6 (≡*C*-Si), 102.8 (Ph-*C*≡), 124.9 (*C*$_3$ phenyl), 132.6 (*C*$_2$ phenyl), 136.7 (*C*$_1$ phenyl), 140.5 (*C*$_4$ phenyl), 190.8 ppm (-*C*HO); ms: (m/z) 298 (M$^+$), 283 (M$^+$ -CH$_3$).

Anal. Calcd. for $C_{17}H_{22}OSi_2$ (298.53): C, 68.40; H, 7.43. Found: C, 68.28; H, 7.38.

3,5-Diethynylbenzaldehyde (**1c**).

Compound **1b** (3.5 g, 11.7 mmoles) was dissolved in 40 ml of methanol at 25° under argon. Anhydrous potassium carbonate (240 mg) was added and the solution was stirred for 1.5 hours. The reaction mixture was poured into 300 ml of distilled water and stirred for 15 minutes. Extraction with methylene chloride (3

x 300 ml) yielded a yellow solution which was dried over sodium sulfate for 12 hours. The solvent was removed by evaporation under reduced pressure. The product was purified by fractional crystallization from diethyl ether giving 1.34 g (74%) of **1c**, mp 115°; ir (sodium chloride): ν 3264 (C≡C-H), 3058, 2953, 2854 and 2850 (CHO), 1707 (CO), 1592, 1287, 1141, 976, 888 cm^{-1}; ^1H nmr (deuteriochloroform): δ 3.20 (s, 2H, ≡C-*H*), 7.80 (s, 1H, phenyl), 7.93 (s, 2H, phenyl), 9.95 ppm (s, 1H, -C*H*O); ^{13}C nmr (deuteriochloroform): δ 79.9 (≡*C*-H), 81.4 (Ph-*C*≡), 124.0 (C_3 phenyl), 133.2 (C_2 phenyl), 136.8 (C_1 phenyl), 140.7 (C_4 phenyl), 190.5 ppm (-*C*HO); ms: (m/z) 154 (M^+), 153 (M^+-H), 125 (M^+-CHO), 100 (M^+-CHO, C≡CH).

Anal. Calcd. for $C_{11}H_6O$ (154.17): C, 85.70; H, 3.92. Found: C, 85.61; H, 3.85.

2-(3,5-Dibromophenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**2a**).

Aldehyde **1a** (1.55 mmoles) was dissolved in 40 ml of methanol at 25° under argon. After the addition of 370 mg (1.5 mmoles) of 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate and 1.0 g of potassium carbonate the dispersion was vigorously stirred for 2 days. The mixture was concentrated by evaporation of the solvent under reduced pressure until it was a solid mass. Purification by column chromatography using silica gel with methylene chloride as eluent gave **2a** in 52% yield. The compound was obtained as white crystalline solid, mp 182°; ir (sodium chloride): ν 3262 (OH), 2984, 2921, 1585, 1559, 1428, 1375 and 1366 (-$C(CH_3)_2$-), 1212, 1142, 1109, 1030 (phenyl-Br), 917, 858, 741 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.06 and 1.12 (2s, 12H, CH_3), 4.56 (s, 1H, -NC*H*RN-), 7.72 (s, 2H, phenyl), 7.77 (s, 1H, phenyl), 8.04 ppm (s, 2H, -O*H*); ^{13}C nmr (DMSO-d_6): δ 17.6 and 24.6 (CH_3), 66.8 (-*C*$(CH_3)_2$-), 89.2 (-N*C*HRN-), 122.2 (C_3 phenyl), 130.4 (C_2 phenyl), 132.4 (C_4 phenyl), 147.3 ppm (C_1 phenyl); ms: (m/z) 394 (M^+).

Anal. Calcd. for $C_{13}H_{18}Br_2N_2O_2$ (394.11): C, 39.6; H, 4.60; N, 7.11. Found: C, 39.47; H, 4.52; N, 7.01.

2-(3,5-Bis(trimethylsilylethynyl)phenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**2b**).

Compound **1b** (910 mg, 3.05 mmoles) and 440 mg (2.97 mmoles) of 2,3-bis(hydroxyamino)-2,3-dimethylbutane were dissolved in 15 ml of benzene at 25° under argon. The mixture was vigorously stirred for 36 hours. The solvent was evaporated under reduced pressure yielding a yellow solid mass. Purification by column chromatography through silica gel using methylene chloride as eluent gave 0.56 g (43%) of **2b**, mp 168°; ir (sodium chloride): ν 3270 (OH), 2961, 2897, 2160 (C≡C), 1594, 1448, 1373 (-$C(CH_3)_2$-), 1253 (Si-C), 1167, 1031, 848 (Si-C bending), 761 cm^{-1}; ^1H nmr (DMSO-d_6): δ 0.28 (s, 18H, -Si(CH_3)$_3$), 1.05 and 1.12 (2s, 12H, -C(CH_3)$_2$-), 4.56 (s, 1H, -NC*H*RN-), 7.45 (s, 1H, phenyl), 7.62 (s, 2H, phenyl), 7.99 ppm (s, 2H, -O*H*); ^{13}C nmr (DMSO-d_6): δ 0.17 (-Si(CH_3)$_3$), 17.6 and 24.6 (-CH_3), 66.7 (-*C*$(CH_3)_2$-), 89.4 (≡*C*-Si), 95.0 (Ph-*C*≡), 104.6 (-N*C*HRN-), 122.5 (C_3 phenyl), 131.9 (C_2 phenyl), 133.6 (C_4 phenyl), 143.7 ppm (C_1 phenyl); ms: (m/z) 428 (M^+), 338 (M^+-Si(CH_3)$_3$, OH).

Anal. Calcd. for $C_{23}H_{36}N_2O_2Si_2$ (428.72): C, 64.44; H, 8.46; N, 6.53. Found: C, 64.29; H, 8.40; N, 6.40.

2-(3,5-Diethynylphenyl)-1,3-dihydroxy-4,4,5,5-tetramethylimidazolidine (**2c**).

The preparation from **1c** was analogous to the method used for imidazolidine **2a**. The yield was 54%. The compound was obtained as white crystalline solid, mp 172°; ir (sodium chloride): ν 3284 (C≡C-H), 3227 (OH), 2982, 2929, 2106 (C≡C), 1589, 1448, 1366 (-$C(CH_3)_2$-), 1241, 1027, 1002, 890, 810 cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.06 and 1.11 (2s, 12H, -CH_3), 4.27 (s, 2H, ≡C-*H*), 4.54 (s, 1H, -NC*H*RN-), 7.50 (s, 1H, phenyl), 7.64 (s, 2H, phenyl), 7.94 ppm (s, 2H, -O*H*); ^{13}C nmr (DMSO-d_6): δ 17.6 and 24.6 (CH_3), 66.7 (-*C*$(CH_3)_2$-), 81.4 (≡*C*-H), 83.0 (Ph-*C*≡), 89.4 (-N*C*HRN-), 122.0 (C_3 phenyl), 132.3 (C_2 phenyl), 133.6 (C_4 phenyl), 143.7 ppm (C_1 phenyl); ms: (m/z) 284 (M^+).

Anal. Calcd. for $C_{17}H_{20}N_2O_2$ (284.34): C, 71.81; H, 7.09; N, 9.85. Found: C, 71.68; H, 6.95; N, 9.71.

2-(3,5-Dibromophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-Oxide (**3a**).

Imidazolidine **2a** (0.51 mmole) was dissolved in 40 ml of chloroform at 25° under argon. Lead dioxide (2.5 g) was added and the dispersion was stirred for 5 minutes (the reaction was monitored by thin layer chromatography; longer oxidation periods led to decomposition of the nitronyl nitroxide). The lead oxides were filtered off and rinsed twice with chloroform (15 ml). The combined organic fractions were evaporated under reduced pressure. The residue was purified by column chromatography through silica gel using methylene chloride as the eluent giving **3a** in 91% yield (181 mg). The compound was isolated in the form of blue crystals, mp 138°; ir (sodium chloride): ν 3095, 2994, 1580, 1542, 1450, 1438, 1384 (N-O), 1361 (-$C(CH_3)_2$-), 1212, 1167, 1137 (N-O), 854, 741, 670 cm^{-1}; ms: (m/z) 391 (M^+).

Anal. Calcd. for $C_{13}H_{15}Br_2N_2O_2$ (391.08): C, 39.93; H, 3.87; N, 7.16. Found: C, 39.85; H, 3.70; N, 7.01.

2-(3,5-Bis(trimethylsilylethynyl)phenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-Oxide (**3b**).

The preparation from **2b** corresponded to that of radical **3a**. Compound **3b** (189 mg, 87%) was isolated in the form of dark blue crystals, mp 82°; ir (sodium chloride): ν 3090, 2958, 2897, 2161 (C≡C), 1582, 1456, 1393 (N-O), 1366 (-$C(CH_3)_2$-), 1253 (Si-C), 1171, 1130 (N-O), 1062, 989, 848 (Si-C bending), 764 cm^{-1}; ms: (m/z) 425 (M^+), 337 (M^+-Si(CH_3)$_3$, CH_3).

Anal. Calcd. for $C_{23}H_{33}N_2O_2Si_2$ (425.70): C, 64.89; H, 7.81; N, 6.58. Found: C, 64.70; H, 7.72; N, 6.46.

2-(3,5-Diethynylphenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-Oxide (**3c**).

Method a).

The compound was prepared from **2c** according to radicals **3a** and **3b**; 122 mg (85%) of **3c** was obtained in form of dark blue crystals, mp 141°; ir (sodium chloride): ν 3302 and 3285 (≡C-H), 3084, 3007, 2980, 2938, 1585, 1453, 1392 (N-O), 1366 (-$C(CH_3)_2$-), 1213, 1172 (N-O), 1146, 1131 (N-O), 885, 864 cm^{-1}; ms: (m/z) 281 (M^+), 282 (M^+ + H).

Anal. Calcd. for $C_{17}H_{17}N_2O_2$ (281.33): C, 72.58; H, 6.09; N, 9.96. Found: C, 72.52; H, 6.04; N, 9.88.

Method b).

The stable nitronyl nitroxide **3b** (165 mg, 0.39 mmoles) was dissolved in 5 ml of methanol at 25° under argon. After addition of 10 mg of anhydrous potassium carbonate the reaction mixture was stirred until thin layer chromatography showed quantitative reaction (45 minutes). The solution was evaporated under reduced pressure and immediately purified by column chromatog-

raphy through silica gel using methylene chloride as the eluent yielding 86.1 mg (78%) of **3c**.

Method c).

Radical **3c** was prepared in a "single step" reaction using **1b** as the starting material. Compound **1b** (1.43 g, 4.80 mmoles) was dissolved in a mixture of 40 ml of chloroform and 40 ml of methanol at 25° under argon. 2,3-Bis(hydroxyamino)-2,3-dimethylbutane sulfate (1.75 g, 7.09 mmoles) and 4.0 g of potassium carbonate was added and the dispersion was stirred for 48 hours. The solvent was evaporated under reduced pressure. The resulting solid mass was dispersed in 120 ml of chloroform. After addition of 7.0 g of lead dioxide the mixture was vigorously stirred for 20 minutes. The lead oxides were filtered off and rinsed twice with chloroform (30 ml). The filtrate was concentrated by evaporation of the solvent. The product was purified by column chromatography using silica gel and methylene chloride as the eluent yielding 564 mg (43%) of **3c**.

Acknowledgements.

The investigations were carried out within a program supported by the Österreichische Nationalbank Jubiläumsfonds (Wien), the Fonds zur Förderung der Wissenschaftlichen Forschung (Wien) and the Max-Buchner-Forschungsstiftung (Frankfurt/Main).

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