ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 7, pp. 1025–1030. © Pleiades Publishing, Ltd., 2013. Original Russian Text © A.M. Andrievskii, R.V. Linko, M.K. Grachev, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 7, pp. 1041–1045.

Synthesis and Reactions of Trinitro-9,10-phenanthrenequinone Derivatives

A. M. Andrievskii^a, R. V. Linko^b, and M. K. Grachev^c

^a Research Institute of Organic Intermediate Products and Dyes, Bol'shaya Sadovaya ul. 1-4, Moscow, 123995 Russia e-mail: info@cemess.ru

^b Peoples' Friendship University of Russia, Moscow, Russia

^c Moscow State Pedagogical University, Moscow, Russia

Received August 30, 2012

Abstract—The reaction of 2,4,7-trinitro-9,10-phenanthrenequinone with CuCl in aqueous dimethylformamide or dimethyl sulfoxide at room temperature, followed by acidification, gave a stable red complex of 2,4,7-trinitro-9,10-dihydroxyphenanthrene with a solvent molecule. On heating in a polar aprotic solvent in the presence of CuCl or other metal salt, 2,4,7-trinitro-9,10-phenanthrenequinone underwent benzilic acid rearrangement with formation of 2,4,7-trinitrofluorenone. The nitration of 9,10-sulfuryldioxyphenanthrene and subsequent decomposition of cyclic sulfates afforded previously unknown 1,3,6-trinitro- and 1,8-dinitro-9,10-phenanthrenequinones.

DOI: 10.1134/S1070428013070117

Nitro derivatives of 9,10-phenanthrenequinone tend to react with nucleophiles at the carbonyl groups [1, 2]. 2,4,7-Trinitro-9,10-phenanthrenequinone (I) in polar aprotic solvents undergoes hydration at the carbonyl groups via addition of one or two water molecules, depending on the solvent nature. In DMF or DMSO, the addition of one water molecule gives 2,4,7-trinitro-10,10-dihydroxy-9,10-dihydrophenanthren-9-one solvates II and III with two solvent molecules [3] (Scheme 1).

After addition of CuCl to a solution of 2,4,7-trinitro-9,10-phenanthrenequinone (I) in aqueous DMF or DMSO at room temperature and subsequent acidification, a red solid separated almost immediately. According to the elemental analysis data, the product contained no metal and the phenanthrene fragment was bound to one solvent molecule. The product displayed in the IR spectrum a strong band in the region 3200-3300 cm⁻¹, which may be assigned to stretching vibrations of hydroxy groups involved in hydrogen bond. Treatment of both compounds with acetic anhydride led to the formation of 9,10-diacetoxy-2,4,7-trinitrophenanthrene (VI). Therefore, they were assigned the structure of 1:1 2,4,7-trinitro-9,10-dihydroxyphenanthrene solvates with DMF (IV) and DMSO (V). Thus the quinone is selectively reduced to hydroquinone, the

nitro groups remaining intact. 2,7-Dinitro-9,10-phenanthrenequinone was not reduced under analogous conditions.

No reaction occurred in anhydrous DMF or DMSO. Presumably, the presence of water weakens solvation by aprotic solvent, and the equilibrium between quinone I and solvate II or III is displaced toward the former. The reduction of I yields hydroquinone which is stabilized as complex IV or V. These complexes are stronger than solvates II and III. Unlike hydrated quinone solvates II and III, the H-chelate ring in hydroquinone solvate complexes IV and V lies in the phenanthrene ring plane, which ensures conjugation with the aromatic system. Electronic interaction between the chelated hydroxy groups and the aromatic phenanthrene core bearing three nitro groups is responsible for the color-determining absorption band $(\lambda_{max} 465 \text{ nm})$ in the electronic absorption spectrum, which is likely to be a charge-transfer band. In the electronic spectra of solutions of IV and V in an inert solvent, the absorption intensity in the visible region gradually decreases due to decomposition of the solvate structure and oxidation of hydroquinone with atmospheric oxygen. The spectra of IV and V in acetonitrile become identical to the spectrum of the initial quinone approximately in one hour.





 $M = Cu(I), Cu(II), Ni, Cr, Al; X = Hlg_n (n = 1-3).$

Heating of 2,4,7-trinitro-9,10-phenanthrenequinone (I) in DMF in the presence of CuCl gave 2,4,7-trinitrofluorenone (VII) in 76% yield, obviously as a result of benzilic acid rearrangement [4] (Scheme 1). No fluorenone VII was detected in the absence of copper salt, whereas only traces of VII were formed in ethanol or acetonitrile. Copper(I) salt can be replaced by salts of other metals, such as copper(II), nickel, chromium, or aluminum.

Conventional mechanism of benzilic acid rearrangement of 1,2-diketones involves addition of hydroxide ion to carbonyl group, which induces valence electron transfer with formation of α -hydroxy carboxylic acid. In our case, the transferred electron pair is supplied not by the anionic center but by the bond formed by the hydroxy group of hydrate molecule **II** with metal ion in reaction complex **A**. Decarboxylation of intermediate 9-hydroxyfluorene-9-carboxylic acid yields 9-hydroxyfluorene which is oxidized to fluorenone **VII** with atmospheric oxygen.

The presence of three nitro groups in molecule **I** is a significant factor determining its ability to undergo hydration at the carbonyl groups, reduction to hydroquinone complex, and benzilic acid rearrangement under atypical conditions. 2,7-Dinitro-9,10-phenanthrenequinone does not undergo analogous transformations.

2,4,7-Trinitro-9,10-phenanthrenequinone (I) is the only known phenanthrenequinone derivative containng more than two nitro groups. We made an attempt to



synthesize new polynitro-substituted phenanthrenequinones according to the procedure proposed in [5], starting from 9,10-sulfuryldioxyphenanthrene (VIII). Schenck and Schmidt-Thomée [5] prepared cyclic sulfate VIII by photochemical reaction of phenanthrenequinone with sulfur dioxide, and the nitration of VIII, followed by thermal decomposition of the nitration products gave 3-nitro- and 3,6-dinitro-9,10-phenanthrenequinones. Judging by the electronic absorption spectra of the corresponding charge-transfer complexes and polarographic reduction potentials, 3,6-dinitro-9,10-phenanthrenequinone is superior to its 2,7and 2,5-dinitro isomers in acceptor power [6].

By heating a suspension of sulfate VIII in HNO₃ $(d = 1.40 \text{ g/cm}^3)$ at the boiling point for 3 min we obtained a mixture of dinitro derivatives, which was

heated to $200-250^{\circ}$ C; by fractional crystallization we isolated 3,6-dinitro-9,10-phenanthrenequinone (IX) and 1,8-dinitro-9,10-phenanthrenequinone (X) in 24 and 6% yield, respectively (Scheme 2).

The position of nitro groups in molecules IX and X was determined on the basis of the ¹H NMR data. The ¹H NMR spectrum of IX contained a doublet at δ 8.23 ppm (1-H, 8-H), a doublet of doublets at δ 8.43 ppm (2-H, 7-H), and a doublet at δ 9.22 ppm (4-H, 5-H) with coupling constants typical of 3,6-dinitro-9,10-phenanthrenequinone (IX), and the melting point of IX coincided with that given in [5]. Compound X had the same elemental composition, and it displayed in the ¹H NMR spectrum doublets of doublets at δ 7.73 (4-H, 5-H), 8.09 ppm (3-H, 6-H), and 8.68 ppm (2-H, 7-H); the coupling constants were

typical of 1,8-dinitro derivative. The formation of 4,5-dinitro-9,10-phenanthrenequinone can be ruled out for steric reasons. Thus the ¹H NMR spectrum conformed to the structure of previously unknown 1,8-dinitro-9,10-phenanthrenequinone (\mathbf{X}).

With a view to introduce more than two nitro groups into 9,10-phenanthrenequinone molecule, a suspension of VIII in concentrated nitric acid (d = 1.51) was heated for 10 min at the boiling point. The solid product separated from the reaction mixture by filtration contained four nitro groups and a sulfur atom (according to the elemental analysis data) and was identified as tetranitro-9,10-sulfuryldioxyphenanthrene (XI). Its mass spectrum lacked molecular ion peak, but a ion peak with m/z 388 $[M - SO_2]^+$ was observed, which was assigned to tetranitro-9,10-phenanthrenequinone. No carbonyl absorption was present in the IR spectrum of XI. The bands at 1436 and 1226 cm⁻¹ were assigned to $v_s(SO_2)$ and $v_{as}(SO_2)$, respectively, indicating cyclic sulfate structure. These bands appeared at higher frequencies relative to the corresponding bands in the spectrum of sulfate VIII, which may be due to strong acceptor effect of the nitro groups. Antisymmetric and symmetric stretching vibrations of the nitro groups were observed at 1546, 1538, and 1346 cm⁻¹, and the doublet character of the $v_{as}(NO_2)$ band indicated nonequivalence of the nitro groups. These findings, as well as the results of electrophilic substitution in molecule VIII with formation of dinitro derivatives, allowed us to assign the structure of 1,3,6,8-tetranitro-9,10-sulfuryldioxyphenanthrene to product XI. However, we failed to isolate 1,3,6,8-tetranitro-9,10-phenanthrenequinone: thermal decomposition of XI led to the formation of a complex mixture of products which were difficult to separate.

After separation of XI, we isolated from the filtrate a yellow-orange substance which showed in the IR spectrum a carbonyl absorption band at 1688 cm⁻¹ and absorption bands at 1564, 1532, and 1352 cm⁻¹ due to stretching vibrations of nitro groups. In keeping with the elemental composition and mass spectrum (m/z 343) $[M]^+$), the product was identified as trinitro derivative of 9,10-phenanthrenequinone. Its ¹H NMR spectrum contained a doublet at δ 8.32 ppm (8-H), a doublet of doublets at δ 8.52 ppm (7-H), a doublet at δ 8.68 ppm (3-H), a doublet at δ 9.34 ppm (5-H), and a doublet at δ 9.50 ppm (4-H). The position of signals, their multiplicities and intensity ratio, and the coupling constants allowed us to conclude that the nitro groups occupy positions 1, 3, and 6 of the phenanthrene core. Thus the product was assigned the structure of 1,3,6-trinitro9,10-phenanthrenequinone (XII); obviously, it was formed via thermal decomposition of the corresponding cyclic sulfate during the nitration process. The yield of XII was about ~50%, which makes 1,3,6-trinitro-9,10-phenanthrenequinone an accessible substrate for further study.

EXPERIMENTAL

The ¹H NMR spectra were recorded on a Jeol ECX-400 spectrometer at 400.13 MHz from solutions in acetone- d_6 ; the chemical shifts were determined relative to tetramethylsilane. The IR spectra were obtained on a Perkin Elmer 598 spectrometer from samples prepared as KCl pellets. The mass spectra were recorded on an MKh-1320 instrument. The melting points were measured on a Boetius melting point apparatus. The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; spots were visualized by treatment with a solution of SnCl₂ and 4-dimethylaminobenzaldehyde in aqueous ethanol acidified with HCl. Silicagel L (40– 100 and 100–160 µm; Chemapol, Czechia) was used for preparative column chromatography.

2,4,7-Trinitro-10,10-dihydroxy-9,10-dihydrophenanthren-9-one–DMF solvate (II). A solution of 1.0 g (2.9 mmol) of 2,4,7-trinitro-9,10-phenanthrenequinone (**I**) in 5 ml of DMF was left to stand in an open beaker. After two weeks, the crystals were filtered off and washed with DMF and CCl₄. Light yellow crystals, mp 89–90°C. IR spectrum, v, cm⁻¹: 3200–2600 (OH), 1740 (C=O), 1660 (N–C=O), 1526 (NO₂), 1350 (NO₂). Found, %: C 47.41; H 4.12; N 13.77. C₁₄H₇N₃O₉·2C₃H₇NO. Calculated, %: C 47.34; H 4.14; N 13.81.

2,4,7-Trinitro-10,10-dihydroxy-9,10-dihydrophenanthren-9-one–DMSO solvate (III). A solution of 0.5 g (1.45 mmol) of compound I in 5 ml of DMSO was left to stand for 3 weeks in an open beaker. The light orange crystals were filtered off, washed with CCl₄, and dried in air. mp 94–96°C. IR spectrum, v, cm⁻¹: 3350–2600 (OH), 1736 (C=O), 1526 (NO₂), 1350 (NO₂), 1008. Found, %: C 42.05; H 3.46; N 8.36; S 11.98. C₁₄H₇N₃O₉·2 C₂H₆OS. Calculated, %: C 41.78; H 3.68; N.12; S 12.38.

2,4,7-Trinitro-9,10-dihydroxyphenanthrene– DMF complex (IV). A solution of 0.2 g (0.06 mmol) of compound I in 10 ml of aqueous DMF (3:1) was added under stirring at room temperature to a solution of 0.3 g (3.0 mmol) of copper(I) chloride in 30 ml of aqueous DMF (2:1) acidified with concentrated aqueous HCl to pH 1–2. After 1 h, the precipitate was filtered off, washed with water, dried in a vacuum desiccator over P₂O₅, and reprecipitated from DMF. Yield 0.19 g (78%), red crystals, mp 173–174°C (decomp.), R_f 0.21 (benzene–acetone, 8:1). IR spectrum, v, cm⁻¹: 3306 (OH), 3100 (CH), 1662 (N–C=O), 1620 (C=C), 1512 (NO₂), 1344 (NO₂). Found, %: C 49.10; H 3.55; N 13.19. C₁₄H₇N₃O₈·C₃H₇NO. Calculated, %: C 48.80; H 3.34; N 13.40.

2,4,7-Trinitro-9,10-dihydroxyphenanthrene– DMSO complex (V). A solution of 0.35 g (3.5 mmol) of copper(I) chloride in 20 ml of aqueous DMSO (1:1) acidified with concentrated aqueous HCl to pH 1–2 was mixed with a solution of 0.24 g (0.07 mmol) of compound I in 20 ml of aqueous DMSO (1:1). After 1 h, the precipitate was filtered off, washed with water, dried over P₂O₅, and reprecipitated from DMSO. Yield 0.25 g (84%), red crystals, mp 191–193°C (decomp., sealed capillary), $R_{\rm f}$ 0.21 (benzene–acetone, 8:1). IR spectrum, v, cm⁻¹: 3226 (OH), 3102 (CH), 1624 (C=C), 1514 (NO₂), 1346 (NO₂), 1000 (S=O). Found, %: C 45.19; H 3.32; N 10.54; S 7.30. C₁₄H₇N₃O₈· C₂H₆OS. Calculated, %: C 45.39; H 3.07; N 9.93; S 7.57.

2,4,7-Trinitrophenanthrene-9,10-diyl diacetate (VI). Complex **IV** or **V**, 0.1 g (0.2 mmol), was dissolved in 5 ml of acetic anhydride, and the solution was heated for 1 h at 90°C and cooled to room temperature. The precipitate was filtered off and dried under reduced pressure. Yield 85–88%, thin yellow needles, mp 255–257°C (decomp.), R_f 0.86 (benzene-acetone, 8:1). IR spectrum, v, cm⁻¹: 3092 (CH), 1782 (C=O), 1616 (C=C), 1524 (NO₂), 1348 (NO₂). Found, %: C 50.14; H 2.58; N 9.49. C₁₈H₁₁N₃O₁₀. Calculated, %: C 50.35; H 2.56; N 9.79.

2,4,7-Trinitrofluorenone (VII). Compound I, 0.31 g (0.09 mmol), was dissolved in 20 ml of DMF, 0.6 g (6 mmol) of copper(I) chloride was added, and the mixture was heated for 5 h on a boiling water bath. The mixture was filtered, and the filtrate was poured into 150 ml of water acidified with aqueous HCl to pH 1–2. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 0.22 g (76%), yellow needles, mp 173–174°C, R_f 0.75 (benzene–acetone, 30:1). The product showed no depression of the melting point on mixing with a sample of **VII** synthesized by nitration of fluorenone [7]. ¹H NMR spectrum, δ , ppm: 8.17 d (1H, 5-H, ³J = 8.7 Hz), 8.41 d (1H, 8-H, ⁴J = 1.8 Hz), 8.59 d (1H, 1-H, ⁴J = 2.3 Hz), 8.60 d.d (1H, 6-H, ³J = 8.7, ⁴J = 1.4 Hz)

1.8 Hz), 8.97 d (1H, 3-H, ${}^{4}J$ = 2.3 Hz). ${}^{13}C$ NMR spectrum (DMSO- d_6), δ_C , ppm: 119.7 (C⁸), 122.6 (C¹), 126.6 (C³), 128.4 (C⁵), 131.2 (C⁶), 136.7 (C⁷), 138.4 (C⁴), 139.5 (C²); 143.9, 145.6, 149.4, 150.2 (C^{4a}, C^{4b}, C^{8a}, C^{9a}); 186.7 (C⁹).

When the reaction was carried out under analogous conditions in the presence of copper(II) nitrate instead of CuCl, the yield of **VII** was 51%.

3,6-Dinitro-9,10-phenanthrenequinone (IX) and **1,8-dinitro-9,10-phenanthrenequinone (X).** 9,10-Sulfuryldioxyphenanthrene (VIII) [5], 0.6 g (2.2 mmol), was added to 25 ml of nitric acid (d = 1.4) heated to 120°C, and the mixture was quickly heated to the boiling point, kept boiling for 3 min, and cooled to room temperature. The precipitate was filtered off, washed with 5 ml of nitric acid (d = 1.4) and water, dried over P₂O₅, and treated with boiling chloroform (2×10 ml). The product was filtered off, dried, and heated to 240–250°C under stirring for 20 min (thermal decomposition). Fractional crystallization from acetic acid gave compounds IX and X.

Compound **IX**. Yield 0.16 g (24%), yellow-orange crystals, mp 290–292°C (from AcOH); published data [4]: mp 293–295°C; R_f 0.67 (benzene–acetone, 8:1). IR spectrum, v, cm⁻¹: 1688 (C=O), 1528 (NO₂), 1354 (NO₂). ¹H NMR spectrum, δ , ppm: 8.23 d (2H, 1-H, 8-H, ³J = 8.7 Hz), 8.43 d.d (2H, 2-H, 7-H, ³J = 8.7, ⁴J = 1.8 Hz), 9.22 d (2H, 4-H, 5-H, ⁴J = 1.8 Hz). Mass spectrum: m/z 298 $[M]^+$. Found, %: C 56.77; H 2.16; N 9.26. C₁₄H₆N₂O₆. Calculated, %: C 56.37; H 2.01; N 9.40.

Compound X. Yield 0.04 g (6%), yellow-green crystals, mp 355-357°C (from AcOH), R_f 0.21 (benzene-acetone, 8:1). IR spectrum, v, cm⁻¹: 1702 (C=O), 1544 (NO₂), 1370 (NO₂). ¹H NMR spectrum, δ , ppm: 7.73 d.d (2H, 4-H, 5-H, ³J = 8.6, ⁴J = 1.8 Hz), 8.09 d.d (2H, 3-H, 6-H, ³J = 8.7 Hz), 8.68 d.d (2H, 2-H, 7-H, ³J = 8.6, ⁴J = 1.8 Hz). Mass spectrum: m/z 298 $[M]^+$. Found, %: C 56.66; H 2.22; N 9.74. C₁₄H₆N₂O₆. Calculated, %: C 56.37; H 2.01; N 9.40.

1,3,6,8-Tetranitro-9,10-sulfuryldioxyphenanthrene (XI) and 1,3,6-trinitro-9,10-phenanthrenequinone (XII). Compound VIII, 0.6 g (2.2 mmol), was added to 25 ml of nitric acid (d = 1.51) heated to 75°C, and the mixture was quickly heated to the boiling point, kept boiling for 8 min, and cooled. The precipitate of XI was filtered off, washed with 5 ml of nitric acid (d = 1.4) and water, dried, and recrystallized from acetic acid–dioxane (2:1). The filtrate was poured onto 100 g of ice, and the precipitate of XII was filtered off, washed with water, dried, and recrystallized from acetic acid.

Compound XI. Yield (27%), white crystals, mp >300°C (decomp.), R_f 0.79 (benzene–acetone, 8:1). IR spectrum, v, cm⁻¹: 1538 (NO₂), 1436 (SO₂), 1343 (NO₂), 1226 (SO₂). Mass spectrum: m/z 388 $[M - SO_2]^+$. Found, %: C 36.91; H 1.09; N.35; S 7.45. C₁₄H₄N₄O₁₂S. Calculated, %: C 37.17; H 0.88; N 12.39; S 7.08.

Compound **XII**. Yield 0.36 g (48%), yellow-orange crystals, mp 261–263°C, $R_{\rm f}$ 0.53 (benzene-acetone, 8 : 1). IR spectrum, v, cm⁻¹: 1688 (C=O), 1532 (v_{as}NO₂), 1352 (v_sNO₂). ¹H NMR spectrum, δ , ppm: 8.32 d (1H, 8-H, ³J = 8.7 Hz), 8.52 d.d (1H, 7-H, ³J = 8.7, ⁴J = 1.8 Hz), 8.68 d (1H, 3-H, ⁴J = 1.8 Hz), 9.34 d (1H, 5-H, ⁴J = 1.8 Hz), 9.50 d (1H, 4-H, ⁴J = 1.8 Hz). Mass spectrum: m/z 343 $[M]^+$. Found, %: C 49.25; H 1.42; N 12.34. C₁₄H₅N₃O₈. Calculated, %: C 48.98; H 1.46; N 12.24.

REFERENCES

- 1. Gridunova, G.V., Struchkov, Yu.T., Linko, R.V., Andrievskii, A.M., and Zaitsev, B.E., *Izv. Akad. Nauk, Ser. Khim.*, 1992, p. 1575.
- Linko, R.V., Bel'skii, V.K., Varlamov, A.V., Zaitsev, B.E., and Chernyshev, A.I., *Izv. Akad. Nauk, Ser. Khim.*, 2001, p. 1548.
- Gridunova, G.V., Struchkov, Yu.T., Linko, R.V., Andrievskii, A.M., and Zaitsev, B.E., *Izv. Akad. Nauk, Ser. Khim.*, 1992, p. 910.
- Kumar, R.R. and Balasubramanian, M., Name Reactions for Homologations, Li, J.J. and Corey, E.J., Hoboken, NJ: Wiley, 2009, vol. 2, p. 395.
- 5. Schenck, G.O. and Schmidt-Thomée, G.A., Justus Liebigs Ann. Chem., 1953, vol. 584, p. 199.
- 6. Mukherjee, T.K., J. Phys. Chem., 1976, vol. 71, p. 2277.
- Woolfolk, E.O. and Orchin, M., Organic Syntheses, Horning, E.C., Ed., New York: Wiley, 1955, collect. vol. 3, p. 837.