ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 10, pp. 1474–1481. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.M. Andrievskii, M.V. Gorelik, R.V. Linko, M.K. Grachev, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 10, pp. 1496–1502.

Bromination of Deactivated Polycyclic Aromatic Nitro Compounds

A. M. Andrievskii[a], M. V. Gorelik[a], R. V. Linko[b], and M. K. Grachev[c]

[a] *State Scientific Center "Research Institute of Organic Intermediate Products and Dyes," ul. Bol'shaya Sadovaya 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 November 10, 2012

Abstract—Bromination of 2,7-dinitro-9,10-phenanthrenequinone, 2,5-dinitro-9,10-phenanthrenequinone, and 2,4,7-trinitrofluorenone with bromine in concentrated sulfuric acid in the presence of acetic acid gave, respectively, 4-bromo-2,7-dinitro-9,10-phenanthrenequinone, 2-bromo-4,7-dinitro-9,10-phenanthrenequinone, and 5-bromo-2,4,7-trinitrofluorenone. No bromination occurred in the absence of nitric acid. The same brominated polynitro compounds can be obtained under analogous conditions directly from unsubstituted 9,10-phenanthrenequinone and fluorenone.

DOI: 10.1134/S1070428013100126

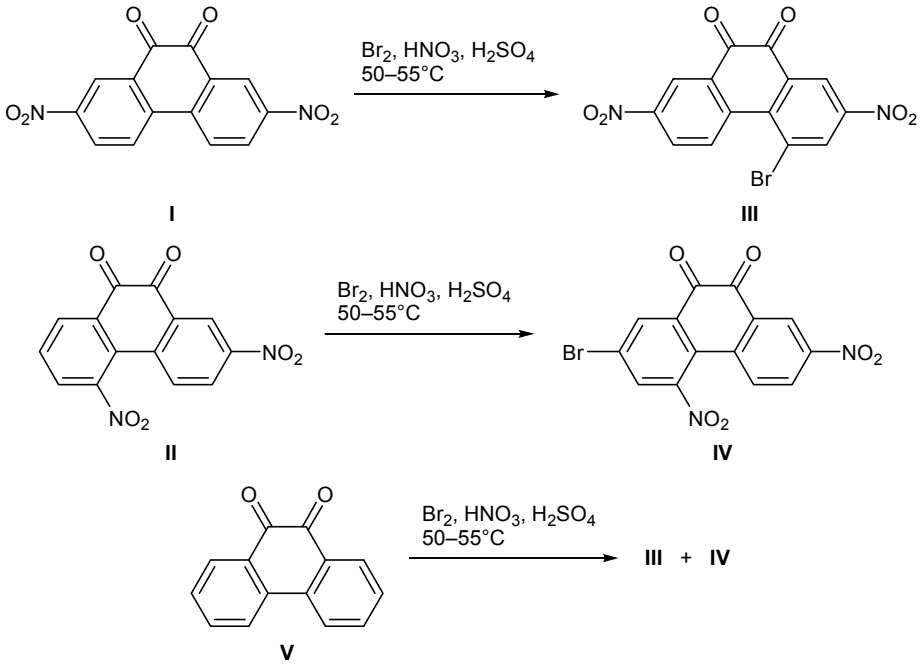
Aromatic bromo derivatives [1] are important for organic synthesis as intermediate products capable of entering into a number of bromine exchange reactions. The significance of bromoaromatics considerably increased in the past decades due to development of cross-coupling reactions catalyzed by palladium compounds [2, 3]. Therefore, studies in the field of synthesis of bromoarenes are quite urgent. The main method for introduction of a bromine atom into aromatic ring is based on substitution of hydrogen by electrophilic brominating agent [4]. Electrophilic bromination readily occurs if an aromatic ring contains activating electron-donating groups. The presence of electron-withdrawing substituents that deactivate aromatic system requires special bromination procedures [5].

We previously developed [6] a new procedure for the bromination of deactivated aromatic compounds with bromine in sulfuric acid in the presence of nitric acid and examined its applicability to compounds of the benzene series [7]. In the present work the developed procedure was tested on deactivated polycyclic aromatic systems, nitro-substituted 9,10-phenanthrenequinones and fluorenone.

As substrates we selected 2,7- and 2,5-dinitro-9,10-phenanthrenequinones **I** and **II**. The nitration of phenanthrenequinone with boiling 65% nitric acid gave 2- and 4-nitrophenanthrenequinones, whereas treatment of the same compound with 65% HNO_3 in 98% H_2SO_4 at 50°C afforded a mixture of 2,7- and 2,5-dinitro derivatives [8]. The bromination of 2-nitro-9,10-phenanthrenequinone with bromine in acetic acid at 140°C under pressure or in nitrobenzene under photochemical initiation in the presence of benzoyl peroxide was reported to produce 3-bromo-7-nitro-9,10-phenanthrenequinone [9]. 4-Nitro-, 2,7-dinitro-, and 2,5-dinitro-9,10-phenanthrenequinones failed to undergo bromination under the above conditions. No other methods for bromination of nitro-substituted 9,10-phenanthrenequinones have been reported so far.

By heating 2,7-dinitro-9,10-phenanthrenequinone (**I**) and 2,5-dinitro-9,10-phenanthrenequinone (**II**) with bromine and nitric acid in concentrated sulfuric acid at 50–55°C we obtained 4-bromo-2,7-dinitro-9,10-phenanthrenequinone (**III**) and 2-bromo-4,7-dinitro-9,10-phenanthrenequinone (**IV**), respectively (Scheme 1). A mixture of compounds **III** and **IV** was also formed in analogous reaction with unsubstituted 9,10-phenanthrenequinone (**V**). These findings suggest that a combination of brominating and nitrating agents promotes nitration of phenanthrenequinone and mononitrophenanthrenequinones derived therefrom and that the resulting dinitrophenanthrenequinones **I** and **II** undergo

Scheme 1.



bromination. 2,4,7-Trinitro-9,10-phenanthrenequinone remained unchanged under analogous conditions.

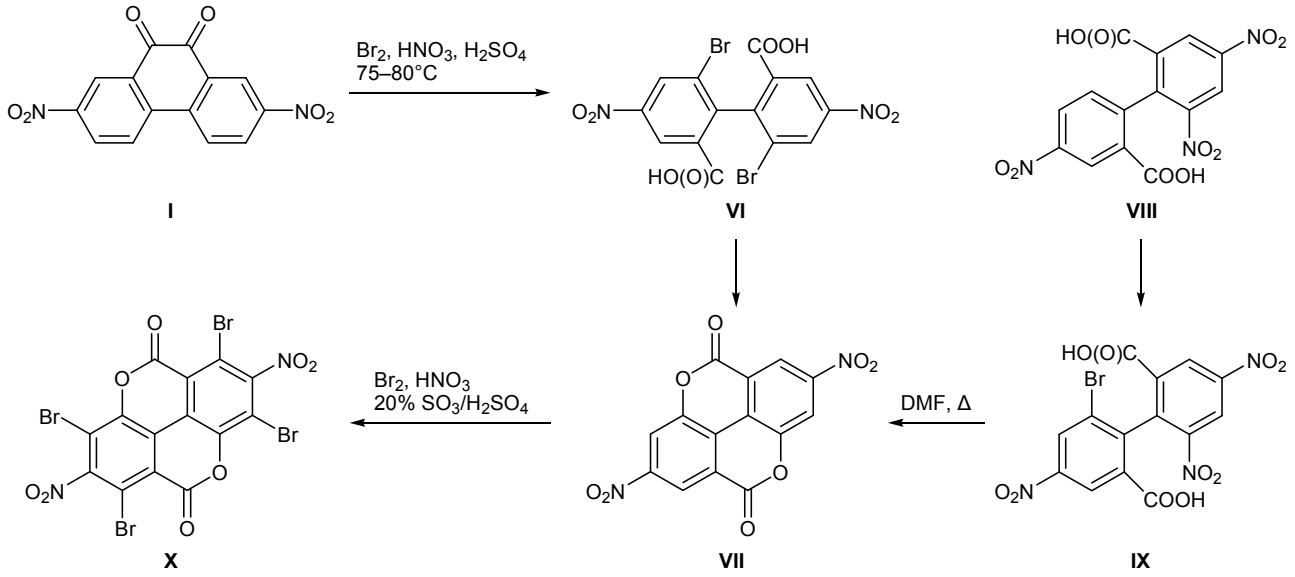
The position of the bromine atom in molecule **III** was determined by X-ray analysis of its solvate with H_2O and DMF [10], and the structure of **IV** was proved by ^{1}H NMR. The ^{1}H NMR spectrum of **IV** contained three doublets at δ 8.83 (8-H), 8.60 (6-H), and 7.85 ppm (5-H). Analogous signals were observed from protons in positions *1*, *3*, and *4* of 2,5-dinitro-9,10-phenanthrenequinone (**II**). The latter also displayed a triplet at δ 7.92 ppm (7-H), which was absent in the spectrum of **IV**. Two doublets at δ 8.50 (1-H) and 8.44 ppm (3-H) in the spectrum of **IV** appeared in a weaker field relative to the 8-H and 6-H signals of **II** (δ 8.43 and 8.22 ppm, respectively). Thus the position of signals, their intensity and multiplicity, and coupling constants indicated the presence of substituents in positions *2*, *4*, and *7*.

Treatment of 2,7-dinitro-9,10-phenanthrenequinone (**I**) with bromine and nitric acid in sulfuric acid under more severe conditions (75–80°C, 3 h) lead to the formation of 6,6′-dibromo-4,4′-dinitrobiphenyl-2,2′-dicarboxylic acid (**VI**) and 2,7-dinitrochromeno-[5,4,3-*cde*]chromene-5,10-dione (**VII**) (Scheme 2). Compound **VI** was also synthesized by bromination of 4,4′-dinitrobiphenyl-2,2′-dicarboxylic acid. Bis-lactone **VII** was described previously [11]; it was prepared by bromination of 4,4′,6-trinitrobiphenyl-2,2′-dicarboxylic acid (**VIII**), followed by heating 6-bromo-4,4′,6′-trinitrobiphenyl-2,2′-dicarboxylic acid (**IX**) in boiling dimethylformamide. Apart from compounds **VI** and **VII**, the reaction mixture obtained from **I** contained three more products, assumingly resulting from mono-, di-, and tribromination of **VII**. The bromination of **VII** with bromine in the presence of nitric acid in 20% oleum at 80–100°C gave 1,3,6,8-tetrabromo-2,7-dinitrochromeno[5,4,3-*cde*]chromene-5,10-dione (**X**) in 52% yield.

Most probably, 2,7-dinitro-9,10-phenanthrenequinone (**I**) is initially converted into 4-bromo derivative **III** which is oxidized to 6-bromo-4,4′-dinitrobiphenyl-2,2′-dicarboxylic acid, and bromination of the latter yields compound **VI**. The reverse reaction sequence, i.e., dibromination of **I** followed by oxidation, is hardly possible, for introduction of two substituents into positions *4* and *5* of phenanthrenequinone is hindered for steric reasons. The subsequent cyclization of **VI** leads to dinitrodioxapyrene **VII**.

We also examined bromination of 2,7-dinitro- and 2,4,7-trinitrofluorenones. The nitration of fluorenone (**XV**) with concentrated nitric acid at room temperature gives 2-nitrofluorenone, while the reaction at the boiling point leads to 2,7-dinitrofluorenone [12]. The nitration of **XV** with a mixture of fuming nitric acid and concentrated sulfuric acid on heating for 2 h produces 2,4,7-trinitrofluorenone [13], while 2,4,5,7-tetranitrofluorenone is formed on prolonged heating (8.5 h) [14].

Scheme 2.

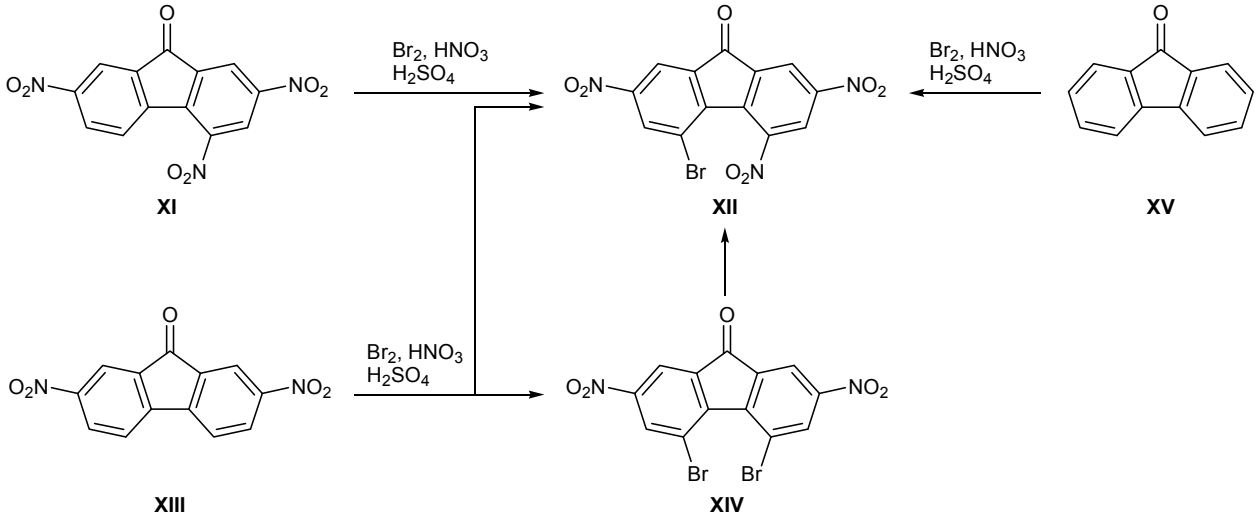


By heating 2,4,7-trinitrofluorenone (**XI**) with bromine and nitric acid in concentrated sulfuric acid at 80–85°C we obtained 5-bromo-2,4,7-trinitrofluorenone (**XII**) in 96% yield (Scheme 3). Compound **XII** was synthesized previously by nitration of 4-bromofluorenone with fuming nitric acid in a mixture of sulfuric and acetic acids [15]. Perepichka et al. [16] modified our procedure described in [7]; initially, fluorenone was nitrated with a nitrating mixture, and the resulting 2,4,7-trinitrofluorenone (**XI**) without isolation was treated with bromine on heating for 2 h at 55–60°C; as a result, 5-bromo-2,4,7-trinitroflurenone (**XII**) was obtained in 91% yield.

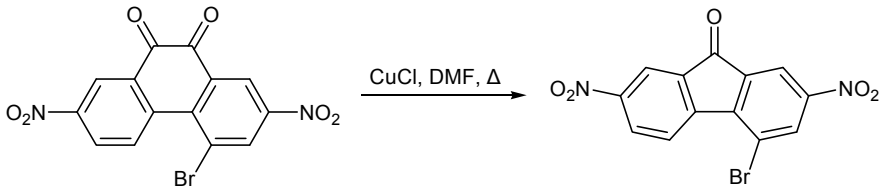
2,4,5,7-Tetranitrofluorenone (**XVI**) remained unchanged under the conditions of bromination of trinitrofluorenone (**XI**), while cleavage of the fluorenone ring system occurred under more severe conditions. In the latter case, apart from unreacted tetranitrofluorenone **XVI**, 6′-bromo-2′,4,4′,6-tetranitrobiphenyl-2-carboxylic acid (**XVII**) was isolated from the reaction mixture. Acid **XVII** was also synthesized from 2′,4,4′,6-tetranitrobiphenyl-2-carboxylic acid (**XVIII**) by the action of bromine in a nitrating mixture.

2,7-Dinitrofluorenone (**XIII**) as less deactivated substrate than 2,4,7-trinitrofluorenone (**XI**) underwent simultaneous nitration and bromination. When the reaction mixture was heated at 60–65°C, we isolated 60% of 5-bromo-2,4,7-trinitrofluorenone (**XII**) and 20% of 4,5-dibromo-2,7-dinitrofluorenone (**XIV**) (Scheme 3). Monitoring of the reaction course by TLC

Scheme 3.



Scheme 4.



III **XIX**

and ^{1}H NMR revealed the presence of 4-bromo-2,7-dinitrofluorenone and 2,4,7-trinitrofluorenone in the initial period, and these compounds were then converted into 4,5-dibromo-2,7-dinitrofluorenone (**XIV**) and 5-bromo-2,4,7-trinitroflurenone (**XII**). The latter became the only reaction product after prolonged heating. Thus 5-bromo-2,4,7-trinitroflurenone (**XII**) can be synthesized directly from unsubstituted fluorenone (**XV**) by treatment with bromine and nitric acid in sulfuric acid until disappearance of 4,5-dibromo-2,7-dinitrofluorenone (**XIV**). The transformation of **XIV** into **XII** under the bromination conditions was confirmed by special experiment with preliminarily isolated 4,5-dibromo-2,7-dinitrofluorenone. Obviously, this transformation involves elimination of bromine from the 4-position (hydrodebromination) and subsequent nitration. Hydrodebromination was also observed in the nitration of 2-bromophenanthridinone [17].

4,5-Dibromo-2,7-dinitrofluorenone (**XIV**) and 4-bromo-2,7-dinitrofluorenone (**XIX**) were synthesized previously by bromination of 2,7-dinitrofluorenone in concentrated sulfuric acid in the presence of silver sulfate [18, 19]. We also prepared 4-bromo-2,7-dinitrofluorenone (**XIX**) by rearrangement of 4-bromo-2,7-dinitro-9,10-phenanthrenequinone (**III**) on heating in DMF in the presence of CuCl by analogy with the rearrangement of 2,4,7-trinitro-9,10-phenanthrenequinone into 2,4,7-trinitrofluorenone [20] (Scheme 4).

Thus, as in the benzene series [7], the action of bromine and nitric acid in concentrated sulfuric acid on moderately deactivated polycyclic aromatic compounds initially brings about their nitration, and the resulting strongly deactivated compounds undergo bromination. The question arises as to the nature of the brominating agent. The presence of nitric acid is essential for the bromination, otherwise no reaction occurs. The concentration of sulfuric acid is also important. The brominating power of the system in ~90% sulfuric acid is considerably lower, and it disappears completely in going to 85% sulfuric acid [7]. Insofar as nitric acid in ≥90% sulfuric acid exists as nitronium salt [21], the key step in the formation of brominating agent is likely to be the reaction of nitronium cation with bromine. The overall bromination stoichiometry corresponds to consumption of 0.5 mol of Br_2 per 1 mole of aromatic substrate in the reduction of nitronium ion to nitrosonium [7] (Scheme 5).

Scheme 5.

$$2\,ArH + Br_2 + NO_2^+HSO_4^- \longrightarrow 2\,ArBr + NO^+HSO_4^- + H_2O$$

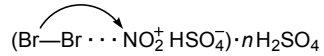
Prevalence of nitration over bromination for moderately deactivated aromatic compounds is not related to the low rate of generation of brominating agent. Prolonged keeping of a mixture of bromine with nitric and sulfuric acids before addition of aromatic substrate does not favor bromination instead of nitration.

The fact that the brominating agent is less reactive than nitrating agent toward moderately deactivated compounds but is more reactive toward strongly deactivated substrates may be rationalized by its lower sensitivity to electronic structure of substrates. Introduction of electron-withdrawing substituents into substrate molecule hinders nitration to a considerably greater extent as compared to bromination, i.e., the substrate selectivity in the bromination is lower than in the nitration. As the number of electron-withdrawing nitro groups in a substrate molecule increases, at some step of structural variations the substrate becomes deactivated toward electrophilic attack by nitronium ion more strongly than toward attack by brominating agent. As a result, the ratio of the nitration and bromination rates changes to the opposite, and the bromination becomes the dominant process.

The sensitivity of a reaction to variation of the substrate structure is quantitatively characterized by the ρ value [22, 23]. The nitration in sulfuric acid is generally highly sensitive to electronic effects of substituents (ρ = –9.7 for benzene derivatives [24]). Insofar as there are no corresponding kinetic data, the reduction of the reactivity toward nitration may be assessed qualitatively by comparing the experimental conditions. Mononitro phenanthrenequinones are converted into dinitro derivatives by the action of 65%

HNO_3 in concd. H_2SO_4 in 30 min at 50°C, whereas the transformation of 2,7-dinitrophenanthrenequinone into 2,4,7-trinitro derivative requires prolonged (14.5 h) heating with fuming HNO_3 in concd. H_2SO_4 at 100°C, 16% of the initial dinitro compound remaining unchanged [8].

The high sensitivity to structural variation in the substrate upon nitration with nitronium ion is determined by the formation of a polar transition state whose structure is similar to an ionic σ complex bearing a whole positive charge [23]. The lower sensitivity of the bromination to electronic properties of substituents indicates that the corresponding transition state is less polar and that it results from attack by less polar reagent. The reaction of bromine with nitronium ion is unlikely to involve complete electron transfer with formation of a solvated species like bromonium hydrogen sulfate but it is limited to polarization of bromine molecule due to association. The brominating agent may be represented as complex **A** of bromine molecule with nitronium ion, which is stabilized by solvation with sulfuric acid. The electron-deficient bromine atom in the polarized Br–Br fragment of complex **A** acts as electrophilic species, and further transformations occur with participation of the substrate. However, special studies are necessary to identify elementary steps of the examined process.



A

The concept of complex **A** as brominating agent allows us to understand the lack of correlation between the oxidizing power (which is given by standard redox potential) and bromination efficiency [7]. The oxidation potential E^{ox} measured electrochemically relative to standard hydrogen electrode does not reflect the ability of oxidant to donor–acceptor interaction with bromine, which determines generation of brominating agent. Nitronium ion activates bromine molecule making the latter electrophilic Lewis acid, and it acts as oxidant in some further steps.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Jeol ECX-400 spectrometer at 400.13 MHz using DMSO-d_6 as solvent; the chemical shifts are given relative to tetramethylsilane. The IR spectra were obtained in KCl on a Perkin Elmer 598 instrument. 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 mixture of solutions of $SnCl_2$ and 4-dimethylaminobenzaldehyde in aqueous ethanol acidified with HCl. Silicagel L (40–100 μm, Chemapol, Czechia) was used for preparative column chromatography. The melting points were determined on a Boetius micro hot stage. The mass spectra were recorded on an MKh-1320 mass spectrometer.

4-Bromo-2,7-dinitro-9,10-phenanthrenequinone (III). *a*. Compound **I**, 10 g (34 mmol), was dissolved in 120 ml of H_2SO_4 (d = 1.84), 12.4 g (80 mmol) of bromine and 4.0 ml of HNO_3 (d = 1.51) were added, and the mixture was heated to 50–55°C and stirred for 2 h at that temperature. The mixture was cooled and poured onto ice, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 8.0 g (63%), yellow crystals, R_f 0.45 (benzene–acetone, 7:1), mp >300°C (decomp., from AcOH–dioxane, 2:1). IR spectrum, ν, cm^{-1}: 1700 (C=O); 1515, 1340 (NO_2). Found, %: C 44.29; H 1.58; Br 21.32; N 7.62. $C_{14}H_5BrN_2O_6$. Calculated, %: C 44.59; H 1.34; Br 21.19; N 7.43.

2-Bromo-4,7-dinitro-9,10-phenanthrenequinone (IV). *a*. Compound **II**, 8.0 g (27 mmol), was dissolved in 100 ml of H_2SO_4 (d = 1.84), 12.4 g (80 mmol) of bromine was added, the mixture was heated to 40–45°C, 2.0 ml (45 mmol) of HNO_3 (d = 1.51) was added, and the mixture was heated to 55°C and stirred for 30 min at that temperature. The mixture was cooled and poured onto ice, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 5.4 g (53%), yellow crystals, R_f 0.60 (benzene–acetone, 7:1), mp 253.5–254.5°C (from AcOH). IR spectrum, ν, cm^{-1}: 1685 (C=O); 1525, 1350 (NO_2). ^{1}H NMR spectrum, δ, ppm: 7.85 d (1H, 5-H, ^3J = 8.2 Hz), 8.43 d (1H, 3-H, ^4J = 2.0 Hz), 8.52d (1H, 1-H, ^4J = 2.0 Hz), 8.60 d.d (1H, 6-H, ^3J = 8.2, ^4J = 1.8 Hz), 8.84 d (1H, 8-H, ^4J = 1.8 Hz). Found, %: C 44.39; H 1.90; Br 20.92; N 7.40. $C_{14}H_5BrN_2O_6$. Calculated, %: C 44.59; H 1.34; Br 21.19; N 7.43.

b. 9,10-Phenanthrenequinone, 2.08 g (10 mmol), was treated as described above in *a*. The precipitate was dissolved in a mixture of 160 ml of benzene and 20 ml of acetone, and isomers **III** and **IV** were separated by column chromatography on silica gel using benzene–acetone (8:1) as eluent. From the first fraction we isolated 0.98 g (26%) of **IV**, and from the second, 1.47 g (39%) of **III**.

6,6′-Dibromo-4,4′-dinitrobiphenyl-2,2′-dicarboxylic acid (VI) and 2,7-dinitrochromeno[5,4,3-*cde*]-

chromene-5,10-dione (VII). *a*. Compound **I**, 1.05 g (3.5 mmol), was dissolved in 20 ml of H_2SO_4 (d = 1.84), 2 ml (40 mmol) of bromine and 1 ml of HNO_3 (d = 1.51) were added, and the mixture was heated to 55–60°C and stirred for 1.5 h at that temperature. The mixture was then heated to 75–80°C, stirred for 3 h, cooled, and poured onto 100 g of ice. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield of **VII** 0.38 g (33%), yellow crystals, R_f 0.36 (benzene), mp 333–335°C (decomp., from AcOH); published data [11]: mp 331–332°C (decomp.). IR spectrum, ν, cm^{-1}: 1770 (C=O); 1544, 1358 (NO_2). Mass spectrum: m/z 328 $[M]^+$. Found, %: C 51.18; H 1.19; N 8.45. $C_{14}H_4N_2O_8$. Calculated, %: C 51.24; H 1.23; N 8.54.

The mother liquor was diluted with water, and the precipitate was filtered off, washed with water, dried, and recrystallized from benzene. Yield of **VI** 0.14 g (8%), colorless crystals, R_f 0.83 (25% aq. ammonia–dioxane, 1:3), mp 303–304°C (in a sealed capillary; from benzene). IR spectrum, ν, cm^{-1}: 3200–2400 (OH); 1710 (C=O); 1534, 1346 (NO_2). Found, %: C 34.23; H 1.23; Br 32.27; N 5.89. m/z 488/490/492 $[M]^+$. $C_{14}H_6Br_2N_2O_8$. Calculated, %: C 34.29; H 1.23; Br 32.61; N 5.72.

b. 4,4′-Dinitrobiphenyl-2,2′-dicarboxylic acid, 1.65 g (5 mmol), was dissolved in 15 ml of H_2SO_4 (d = 1.84), 2 ml (40 mmol) of bromine and 2 ml of HNO_3 (d = 1.51) were added, and the mixture was heated to 50°C and stirred for 1 h at that temperature. The mixture was then heated to 65°C, stirred for 2 h, cooled, and poured onto 100 g of ice. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield of **VI** 1.8 g (73%). The product was identical to a sample isolated as described in *a* in the IR spectrum, melting point, and R_f value.

A mixture of 0.2 g of compound **VI** or **IX** and 6 ml of DMF was heated for 3 h under reflux. The solution was cooled to room temperature and poured into 200 ml of water acidified with hydrochloric acid to pH 1–2. The precipitate of compound **VII** was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 82% (from **VI**), 83% (from **IX**).

6-Bpomo-4,4′,6′-trinitrobiphenyl-2,2′-dicarboxylic acid (IX) was synthesized in a similar way from compound **VIII**. Yield 1.4 g (77%), light yellow needles, R_f 0.76 (25% aq. ammonia–dioxane, 1:3), mp 284–285°C (in a sealed capillary; from 10% aqueous acetic acid). IR spectrum, ν, cm^{-1}: 3200–2400 (OH); 1712 (C=O); 1536, 1346 (NO_2). Found, %: C 36.60; H 1.48; Br 17.83; N 8.88. m/z 455/457 $[M]^+$. $C_{14}H_6BrN_3O_{10}$. Calculated, %: C 36.84; H 1.33; Br 17.52; N 9.21.

1,3,6,8-Tetrabromo-2,7-dinitrochromeno-[5,4,3-*cde*]chromene-5,10-dione (X). Compound **VII**, 3.0 g (9 mmol), was dissolved in 100 ml of 20% oleum, 6 ml (116 mmol) of bromine and 15 ml of HNO_3 (d = 1.51) were added, and the mixture was heated to 95–100°C and stirred for 15 h at that temperature. By the end of the reaction strong foaming was observed, and a solid precipitated. The mixture was cooled to room temperature, and the precipitate was filtered off through a glass filter, washed with water, dried, and recrystallized from DMSO. Yield 3.1 g (53%), colorless crystals, R_f 0.87 (benzene), mp 350°C (from DMSO). IR spectrum, ν, cm^{-1}: 1755 (C=O); 1558, 1377 (NO_2). Found, %: C 26.26; Br 49.42; N 4.23. m/z 640/642/644/646/648 $[M]^+$. $C_{14}Br_4N_2O_8$. Calculated, %: C 26.12; Br 49.65; N 4.35.

5-Bromo-2,4,7-trinitrofluorenone (XII). *a*. 2,4,7-Trinitrofluorenone (**XI**), 3.15 g (10 mmol), was dissolved in 60 ml of H_2SO_4 (d = 1.84), 10 ml of HNO_3 (d = 1.51) and 1 ml of bromine were added, and the mixture was heated for 2 h at 80–85°C. The mixture was cooled and poured onto 200 g of ice, and the precipitate was filtered off, washed with water, dried, and recrystallized from ethanol. Yield 3.78 g (96%), light yellow crystals, R_f 0.6 (benzene), mp 192–193°C (from EtOH); published data [15]: mp 191–192°C. IR spectrum, ν, cm^{-1}: 1729 (C=O); 1533, 1343 (NO_2). ^1H NMR spectrum, δ, ppm: 8.15 d (1H, 8-H, $^4J_{8,6}$ = 1.3 Hz), 8.62 d (1H, 1-H, $^4J_{1,3}$ = 1.4 Hz), 8.75 d (1H, 6-H, $^4J_{6,8}$ = 1.3 Hz), 9.80 d (1H, 3-H, $^4J_{3,1}$ = 1.4 Hz). ^{13}C NMR spectrum, δ, ppm: 118.4 (C^8), 121.0 (C^5), 122.0 (C^1), 126.1 (C^3), 135.6 (C^6), 149.6 (C^7), 150.1 (C^2); 138.9, 139.7, 139.8, 144.6, 146.1 (C^4, C^{4a}, C^{4b}, C^{8a}, C^{9a}); 185.3 (C^9). Found, %: C 39.58; H 1.05; Br 20.26; N 10.35. $C_{13}H_4BrN_3O_7$. Calculated, %: C 39.62; H 1.02; Br 20.28; N 10.66.

b. Compound **XV**, 2.14 g (5 mmol), was dissolved in 60 ml of H_2SO_4 (d = 1.84), 10 ml of HNO_3 (d = 1.51) and 1 ml of Br_2 were added, and the mixture was treated as described above in *a*. Yield 1.38 g (70%).

c. A mixture of 2.14 g (5 mmol) of 4,5-dibromo-2,7-dinitrofluorenone (**XIV**), 60 ml of H_2SO_4 (d = 1.84), 10 ml of HNO_3 (d = 1.51), and 1 ml of bromine was heated for 4 h at 60–65°C until the initial compound disappeared (TLC). The mixture was poured onto ice, and the precipitate was filtered off and recrystallized to isolate 1.18 g (60%) of **XII**.

d. Compound **XIII**, 2.7 g (10 mmol), was dissolved in 60 ml of H_2SO_4 (d = 1.84), 10 ml of HNO_3 (d = 1.51) and 1 ml of bromine were added, and the mixture was heated for 4 h at 60–65°C. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 2.36 g (60%).

4,5-Dibromo-2,7-dinitrofluorenone (XIV). The filtrate obtained after separation of compound **XII** was poured onto 200 g of ice, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 0.86 g (20%), yellow crystals, R_f 0.7 (benzene), mp 228–229°C (from AcOH); published data [19]: mp 226–227°C. IR spectrum, ν, cm^{-1}: 1739 (C=O); 1533, 1344 (NO_2). ^{1}H NMR spectrum, δ, ppm: 8.35 d (2H, 1-H, 8-H, ^4J = 1.8 Hz), 8.72 d (2H, 3-H, 6-H, ^4J = 1.8 Hz). Found, %: C 36.58; H 1.08; Br 37.42; N 6.35. $C_{13}H_4Br_2N_2O_5$. Calculated, %: C 36.48; H 0.94; Br 37.34; N 6.55.

4-Bromo-2,7-dinitrofluorenone (XIX). Copper(I) chloride, 0.2 g (2 mmol), was added to a solution of 0.20 g (0.53 mmol) of compound **III** in 8 ml of DMF, and the mixture was heated to 90–95°C and stirred for 4 h at that temperature. The mixture was then filtered, the filtrate was poured into 50 ml of water acidified with hydrochloric acid to pH 1–2, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 0.10 g (54%), light brown needles, R_f 0.7 (benzene), mp 262–264°C (from AcOH). IR spectrum, ν, cm^{-1}: 1735 (C=O), 1520 (NO_2, asym.), 1344 (NO_2, sym.). ^{1}H NMR spectrum, δ, ppm: 8.32 d (1H, 1-H, $^4J_{1,3}$ = 2.1 Hz), 8.37 d (1H, 8-H, $^4J_{8,6}$ = 2.3 Hz), 8.63 d.d (1H, 6-H, $^3J_{6,5}$ = 8.2, $^4J_{6,8}$ = 2.3 Hz), 8.69 d (1H, 5-H, $^3J_{5,6}$ = 8.2 Hz), 8.72 d (1H, 3-H, $^4J_{3,1}$ = 2.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 118.5 (C^1), 118.8 (C^4), 119.5 (C^8), 125.6 (C^6), 131.1 (C^5), 135.1 (C^3); 136.4, 138.2, 145.6, 146.9 (C^{4a}, C^{4b}, C^{8a}, C^{9a}); 149.7, 149.9 (C^5, C^7); 187.6 (C^9). Found, %: C 44.59; H 1.48; Br 23.07; N 8.35. $C_{13}H_5BrN_2O_5$. Calculated, %: C 44.73; H 1.44; Br 22.89; N 8.02.

6′-Bromo-2′,4,4′,6-tetranitrobiphenyl-2-carboxylic acid (XVII). *a*. 2,4,5,7-Tetranitrofluorenone **XVI**, 3.60 g (10 mmol), was dissolved in 60 ml of 60% oleum, 10 ml of HNO_3 (d 1.51) and 1 ml of bromine were added under stirring, and the mixture was heated for 3 h at 85°C. The mixture was cooled and poured onto 200 g of ice, and the precipitate was filtered off, washed with water, dried, treated with 50 ml of a 10% solution of $NaHCO_3$, and filtered off again. The filtrate was acidified to pH 4–5 by adding dropwise under stirring concentrated aqueous HCl, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 0.70 g (15%), light yellow crystals, R_f 0.26 (benzene–acetone, 10:1), mp 123–125°C (from AcOH). ^{1}H NMR spectrum, δ, ppm: 8.96 d (1H, 5′-H, ^4J = 2.3 Hz), 8.98 d (1H, 3′-H, ^4J = 2.3 Hz), 9.00 d (1H, 3-H, ^4J = 2.3 Hz), 9.17 d (1H, 5-H, ^4J = 2.3 Hz), 12.5 br.s (1H, COOH). ^{13}C NMR spectrum, δ_C, ppm: 119.7 ($C^{5'}$), 124.0 ($C^{3'}$), 124.7 ($C^{6'}$), 130.0 (C^3), 132.5 (C^5), 134.2 (C^2), 136.5 ($C^{1'}$), 137.7 (C^1); 148.5, 148.5, 148.6, 148.7 (C^4, C^6, $C^{2'}$, $C^{4'}$); 163.4 (C=O). Found, %: C 33.95; H 1.15; Br 17.47; N 12.05. $C_{13}H_5BrN_4O_{10}$. Calculated, %: C 34.16; H 1.10; Br 17.48; N 12.26.

The residue obtained after treatment of the product with a solution of $NaHCO_3$ was washed with water and dried. We thus isolated 3.02 g (84%) of unreacted 2,4,5,7-tetranitrofluorenone (**XVI**).

b. 2′,4,4′,6-Tetranitrobiphenyl-2-carboxylic acid (**XVIII**), 3.78 g (10 mmol), was dissolved in 60 ml of concentrated sulfuric acid, 10 ml of HNO_3 (d = 1.51) and 1 ml of bromine were added, and the mixture was heated to 65°C and stirred for 2 h at that temperature. The mixture was cooled to room temperature and poured onto 200 g of ice, and the precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid. Yield 3.38 g (74%); the product was identical to a sample of **XVII** prepared as described in *a*.

REFERENCES

1. Ioffe, D. and Kampf, A., *Kirk–Othmer Encyclopedia of Chemical Technology*, Hoboken: Wiley, 2007, 5th ed., vol. 4, p. 340.
2. *Metal-Catalyzed Cross-Coupling Reactions*, de Meijere, A. and Diederich, F., Eds., Weinheim: Wiley-VCH, 2004, 2nd ed.
3. Afanas'ev, V.V., Bespalova, N.B., and Beletskaya, I.P., *Ross. Khim. Zh.*, 2006, vol. 50, p. 81.
4. Andrievskii, A.M. and Gorelik, M.V., *Usp. Khim.*, 2011, vol. 80, p. 443.
5. Stanforth, S.P., *Comprehensive Organic Functional Group Transformations II*, Katritzky, A.R. and Taylor, R.J.K., Eds., San Diego: Elsevier, 2005, vol. 2, p. 561.
6. Andrievsky, A.M., Gorelik, M.V., Avidon, S.V., Nikonov, V.V., Vorozhtsov, G.N., Linko, R.V., Chelysheva, O.V., Poplavsky, A.N., and Djumaev, K.M., Int. Patent Appl. no. WO 9007479; *Chem. Abstr.*, 1990, vol. 129, no. 211867.
7. Andrievskii, A.M., Gorelik, M.V., Avidon, S.V., and Al'tman, E.Sh., *Zh. Org. Khim.*, 1993, vol. 29, p. 1828.

8. Kato, S., Maezawa, M., Hirano, S., Ishigaku, S., and Nitratio, *Yûki Gosei Kagaku Kyôkai Shi*, 1957, vol. 15, p. 29; *Chem. Abstr*., 1957, vol. 51, p. 10462.
9. Bhatt, M.V., *Tetrahedron*, 1964, vol. 20, p. 803.
10. Gridunova, G.V., Struchkov, Yu.T., Linko, R.V., Andrievskii, A.M., and Zaitsev, B.E., *Izv. Akad. Nauk, Ser. Khim*., 1992, p. 910.
11. Migachev, G.I., Andrievskii, A.M., and Dokunikhin, N.S., *Zh. Org. Khim*., 1977, vol. 13, p. 463.
12. Schmidt, J. and Bauer, K., *Ber*., 1905, vol. 38, p. 3737; Schmidt, J., Retzlaff, F., and Haid, A., *Justus Liebigs Ann. Chem*., 1912, vol. 390, p. 210.
13. Orchin, M. and Woolfolk, E.O., *J. Am. Chem. Soc*., 1946, vol. 68, p. 1727.
14. Newman, M.S. and Lutz, W.B., *J. Am. Chem. Soc*., 1956, vol. 78, p. 2469.
15. Newman, M.S. and Blum, J., *J. Am. Chem. Soc*., 1964, vol. 86, p. 5600.
16. Perepichka, D.F., Bryce, M.R., Perepichka, I.F., Lyubchik, S.B., Christensen, C.A., Godbert, N., Batsanov, A.S., Levillain, E., McInnes, E.J.L., and Zhao, J.P., *J. Am. Chem. Soc*., 2002, vol. 124, p. 14227.
17. Andrievskii, A.M., Chelysheva, O.V., Poplavskii, A.N., Nikonov, V.V., Chetkina, L.A., Bel'skii, V.K., Zavodnik, V.E., Perov, A.A., Andronova, N.A., and Dyumaev, K.M., *Khim. Geterotsikl. Soedin*., 1990, p. 789.
18. Tagaki, T. and Sasaki, O., JPN Patent Appl. no. 63-122263, 1988.
19. Hellwinkel, D. and Haas, G., *Justus Liebigs Ann. Chem*., 1978, p. 1913.
20. Andrievskii, A.M., Linko, R.V., and Grachev, M.K., *Russ. J. Org. Chem*., 2013, vol. 49, p. 1025.
21. Schofield, K., *Aromatic Nitration*, Cambridge: Cambridge Univ., 1980, p. 33.
22. Hammett, L., *Physical Organic Chemistry*, New York: McGraw–Hill, 1970, 2nd ed. Translated under the title *Osnovy fizicheskoi organicheskoi khimii*, Moscow: Mir, 1972, p. 460.
23. Johnson, C.D., *The Hammett Equation*, Cambridge: Cambridge Univ., 1973. Translated under the title *Uravnenie Gammeta*, Moscow: Mir, 1977, p. 20.
24. Katritzky, A.R., Clementi, S., and Tarhan, H.O., *J. Chem. Soc., Perkin Trans. 2*, 1975, p. 1624.