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Unusual nucleophilic substitution in the nitrophthalimide series

E. V. Kudrik,* M. A. Zharnikova, E. A. Deryabkina, and G. P. Shaposhnikov

Ivanovo State Academy of Chemistry and Technology,
7 prosp. Engelsa, 153460 Ivanovo.
Tel.: +7 (093 2) 30 3339. Fax: +7 (093 2) 41 7995. E-mail: isl@icti.ivanovo.su

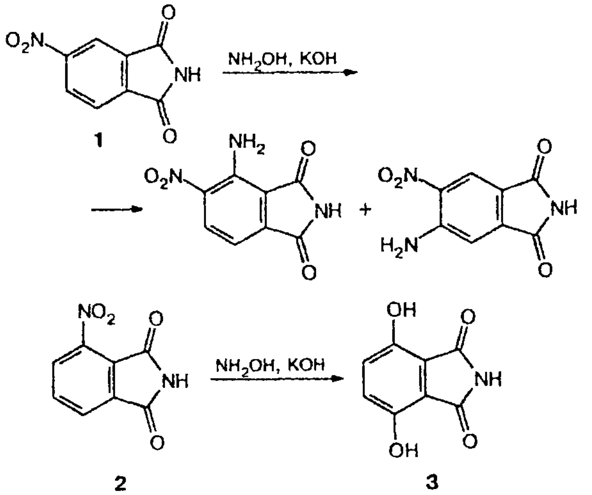
The reactions of 3- and 4-nitrophthalimides with hydroxylamine in aqueous alcohol media were studied. A mixture of 3-amino-4-nitro- and 4-amino-5-nitrophthalimides is formed in the case of 4-nitrosubstituted derivative, whereas 3,6-dihydroxyphthalimide is unexpectedly found to be the main product of the reaction of 4-nitrosubstituted derivative. A possible mechanism of the transformation was suggested.

Key words: phthalimide, hydroxylamine, nucleophilic substitution, 3,6-dihydroxyphthalimide.

Many works, summarized in the monograph,[1] are devoted to the chemistry of hydroxylamine. These studies showed that hydroxylamine is a convenient aminating reagent, which allows amino groups to be inserted in electron-deficient heterocycles, for example, in nitrosubstituted derivatives of quinoline.[2] Aromatic compounds activated by electron-withdrawing substituents also react sufficiently readily, for example, *m*-dinitrobenzene affords 2,4-dinitroaniline in high yield.[2]

Substituted phthalimides are the starting compounds in the synthesis of the corresponding phthalonitriles,[3] phthalocyanines, and tetrabenzoporphines, which are of unambiguous practical interest as mesomorphic[4] and nonlinear-optic[5] materials, dyes and pigments, whose properties are mainly dependent on the number and nature of substituents in the macrocycle periphery.[4]

In order to obtain isomeric nitroaminophthalimides, we studied the reactions of hydroxylamine with 4- and 3-nitrophthalimide (**1** and **2**) in aqueous-alcohol media in the presence of KOH.



In the presence of 4-nitrophthalimide, as should be expected, we obtained a mixture of 3-amino-4-nitro- and 5-amino-4-nitrophthalimides with a ~60 : 40 isomer ratio (according to the ^{1}H NMR spectroscopic data). The presence of the nitro and amino groups in the

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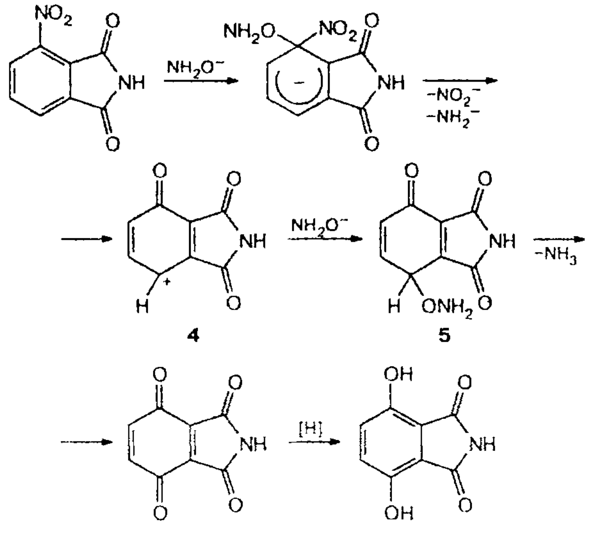
compounds obtained is confirmed by the data of elemental analysis and IR and ^{1}H NMR spectroscopy. The compounds obtained are capable of diazotization by nitrosylsulfuric acid and of coupling with β-naphthol to give a red pigment.

However, the compound formed from 3-nitrophthalimide under the same conditions did not give the qualitative reaction of the primary amino group and was identified, according to the data of elemental analysis and mass, ^{1}H, and IR spectroscopies, as 3,6-dihydroxyphthalimide (**3**). After single recrystallization from water, imide **3**, according to the ^{1}H NMR spectroscopic data, contained almost no noticeable amounts of admixtures. The IR spectrum of **3** exhibited bands assigned to stretching vibrations of C—H, O—H, N—H, C=O, and C—O bonds, and the band corresponding to stretching vibrations of O—H bonds was substantially broadened and shifted to the low-frequency region, which indicates that hydrogen atoms of hydroxyl groups participate in the formation of the intramolecular hydrogen bond.[6]

It is sufficiently difficult to explain the formation of compound **3** on the basis of traditional concepts on the mechanism of nucleophilic addition reactions. The published data[7] show that hydroxylamine and its derivatives can react as *O*-nucleophiles rather than *N*-nucleophiles. In particular, the reaction of *N*-methylhydroxylamine with ethyl ester of cinnamic acid in the presence of bases was studied.[8] It is shown that in this case, the MeNHO$^-$ anion is the reacting particle, which reacts with the substrate (Michael addition) only at the oxygen atom of hydroxylamine.

The formation of **3** cannot occur as the successive introduction of two OH groups, because the electron donor that has already reacted deactivates substantially the *para*-position thus preventing the second act of the transformation. We believe that the formation of **3** can occur through intermediate **4** of the quinoid type according to the following scheme:



The scheme suggested explains satisfactorily the observed experimental facts. For example, it is established that the mixture gains a red color during the reaction and decolorizes only after some time. This can be due to the formation of a sufficiently stable intermediate of the quinoid type. No admixture of the 3,4-isomer was found in the reaction mass, which can be explained by the high stability of the intermediate **5** compared to an isomeric complex, which could be formed during the nucleophilic attack at position 4. In the case of 4-nitrophthalimide, the formation of intermediate similar to **4** is impossible, and the reaction occurs *via* the traditional mechanism of nucleophilic substitution.[9]

Experimental

Mass spectra were recorded on an LKB 9000S instrument. ^{1}H NMR spectra were recorded on a Tesla 587 FT instrument with a working frequency of 80 MHz, and IR spectra were recorded on a Bio-Rad FTS instrument.

3,6-Dihydroxyphthalimide (3). 3-Nitrophthalimide (5 g) obtained from 3-nitrophthalic acid (chemically pure grade) according to the known procedure[10] and pre-powdered hydroxylamine sulfate (11 g) were successively added to propan-2-ol (90 mL). The mixture was thoroughly stirred, and KOH (6 g) in water (5 mL) was added as one portion. The reaction mass gained a red color, and its temperature increased spontaneously to 40 °C. The solution obtained was stirred for 30 min. Then the precipitate formed was filtered off, twice recrystallized from water, and dried at 80 °C to obtain **3** as crystal hydrate (1.4 g) in the form of yellowish needles with m.p. 225—227 °C. After drying *in vacuo* (0.1 Pa) at 120 °C, we obtained **3** (1.12 g, 24%) as a yellowish powder with m.p. 270—273 °C. Found (%): N, 8.05. $C_8H_5NO_4$. Calculated (%): N, 7.82. IR (KBr), ν/cm^{-1}: 3403 (N—H); 3147 (O—H); 2928 (C—H); 1713 (C=O); 1465 (C=C); 1187 (C—N); 1136 (C—C); 1014 (C—O). ^{1}H NMR (DMSO-d$_6$), δ: 10.02 (s, 1 H, N—H); 7.84 (s, 2 H, C—H$_{\text{arom}}$). MS (EI, 70 eV, 130 °C), *m/z* (I_{rel} (%)): 179 [M]$^+$ (4.3), 178 [M-1]$^+$ (25.8), 163 [M-16]$^+$ (100), 146 [M-33]$^+$ (40), 132 [M-47]$^+$ (68.8), 119 [M-60]$^+$ (10.7), 104 [M-75]$^+$ (100), 89 [M-90]$^+$ (12.9), 76 [M-103]$^+$ (36.6), 75 [M-104]$^+$ (81.7).

Amination of 4-nitrophthalimide. 4-Nitronaphthalimide (5 g) and pre-powdered hydroxylamine sulfate (11 g) were placed in propan-2-ol (90 mL). The mixture was thoroughly stirred, and KOH (6 g) in water (5 mL) was added as one portion. The reaction mass gained a red color, and its temperature increased spontaneously to 30 °C. The solution obtained was stirred for 30 min. The precipitate formed was filtered off, washed with water and propan-2-ol, and dried at 120 °C. A mixture (3.9 g, 72.4%) of 3-amino-4-nitro- and 5-amino-4-nitrophthalimides in the form of yellowish powder with m.p. 260—263 °C was obtained. Found (%): N, 18.70. $C_8H_5N_3O_2$. Calculated (%): N, 20.30. IR (KBr), ν/cm^{-1}: 3432 (N—H); 1784 (C=O); 1752 (C=O); 1568 (N=O); 1344 (N=O). ^{1}H NMR (DMSO-d$_6$), δ: 10.1 (s, 1 H, N—H); 8.0—6.0 (m, 2 H, C—H$_{\text{arom}}$); 3.8—4.4 (br.s, 2 H, NH$_2$).

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Synthesis of $9\text{-}C_6H_5\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$ by cross-coupling reaction of $9\text{-}I\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$ with C_6H_5ZnCl catalyzed by palladium complexes

L. I. Zakharkin, G. G. Zhigareva, and E. V. Balagurova*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The cross-coupling reaction of $9\text{-}I\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$ with organozinc compounds catalyzed by palladium complexes was used to synthesize the first representative of B-phenyl-substituted carboranes, $9\text{-}C_6H_5\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$.

Key word: π-cyclopentadienyl-3,1,2-dicarbollylcobalt, catalysis, cross-coupling.

No B-phenyl derivatives of π-cyclopentadienyl-3,1,2-dicarbollylcobalt have been prepared to date.[1] Recently,[2] the salt $[MePPh_3]^+[\pi\text{-}C_2B_9H_8(CH_3)_3]_2Co^-$ was synthesized by cross-coupling reaction of $[MePPh_3]^+[\pi\text{-}C_2B_9H_8I_3]_2Co^-$ with CH_3I catalyzed by palladium complexes[2] using the reaction we found in 1982,[3] *i.e.*, replacement of iodine atom with an organic group in B-iodocarboranes under the action of organomagnesium compounds in the presence of metallocomplex catalysts. This reaction cannot be used in the case of B-iodo-substituted derivatives of $3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}I$ since organomagnesium compounds react with the $\pi\text{-}C_5H_5$-group of $3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{11}$ to replace a hydrogen atom with the organic group.[4]

In this connection, we studied the cross-coupling reaction of $9\text{-}I\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$ (**1**) with organozinc compounds in the presence of $(Ph_3P)_4Pd$ taking C_6H_5ZnCl as an example. We found that this reaction occurs with the replacement of the iodine atom with the phenyl group and with the formation of $9\text{-}C_6H_5\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}$ (**2**) in a high yield analogously to reactions with other B-iodocarboranes.[5] In this case, the $\pi\text{-}C_5H_5$ group does not enter into the substitution reaction under the action of C_6H_5ZnCl. The reaction occurs by the following scheme:

Scheme 1

$$\underset{\mathbf{1}}{9\text{-}I\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}} + C_6H_5ZnCl \xrightarrow[\text{THF}]{(Ph_3P)_4Pd^0} \underset{\mathbf{2}}{9\text{-}C_6H_5\text{-}3\text{-}(\pi\text{-}C_5H_5)\text{-}3,1,2\text{-}CoC_2B_9H_{10}}$$

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