Letters to the Editor

Substitution of nitro groups in 1,3,5-trinitrobenzene and 2,4,6-trinitrotoluene under the action of thiophenols and their heterocyclic analogs

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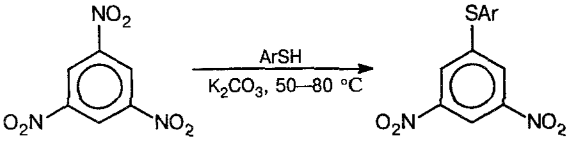
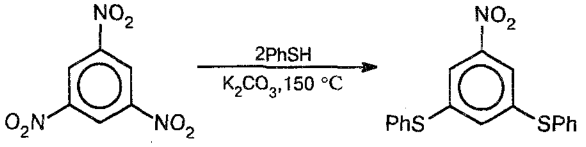
3,5-Dinitrophenylaryl (or -hetaryl) sulfides have not hitherto been known.* We established with a series of examples that they could be obtained in the reaction of 1,3,5-trinitrobenzene (TNB) with thiophenols and their heterocyclic analogs in dipolar aprotic solvents of amide type (*N*-methylpyrrolidone, *N*,*N*-dimethylacetamide, tetramethylurea, *etc.*), preferably in the first, in the presence of an equimolar amount of K_2CO_3 at 50—80 °C for several hours. Aprotic dipolar solvents of non-amide type, *e.g.*, DMSO and acetonitrile, are of low effectiveness. Substitution of a nitro group in TNB and in 2,4,6-trinitrotoluene (TNT) under the action of thiophenols has not been shown so far.



15—90 %

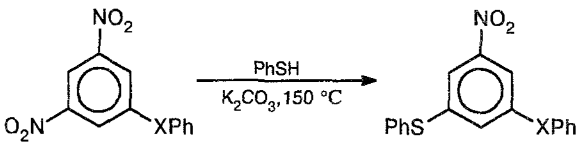
Ar (m.p./°C) = Ph (97—98), 3-MeC_6H_4 (99—100), 2-pyridyl (118—119), 2-benzothiazolyl (141—142), 2-benzimidazolyl (242—243)

Under more drastic conditions (150 °C), when 2 equiv. of thiophenol are used, two nitro groups in TNB are substituted to give 5-nitro-1,3-bis(phenylthio)benzene (**1**).



60 %
1, m.p. 111—112 °C

Compound **1** can also be obtained from the product of substitution of one nitro group in TNB by a PhS fragment (**2**). 3,5-Dinitro-1-phenoxybenzene (**3**) reacts with thiophenol analogously.



2, 3
X = S (**2**), O (**3**)

56 %
X = S (**1**),
O (m.p. 66—67 °C)

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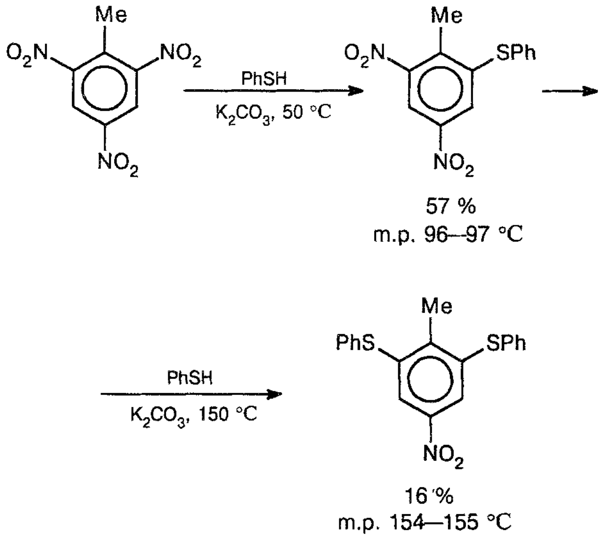
* It is understood that a 3,5-dinitrophenyl fragment does not have substituents other than nitro groups.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2528—2529, December, 1995.

1066-5285/95/4412-2424 $12.50



It has been shown with thiophenol as an example that TNT also enters into a similar reaction, *ortho*-nitro groups being substituted in succession. Phenol does not substitute nitro groups in TNT under these conditions, but can substitute them in TNB.[1]

The compounds obtained are new; they were characterized by ^1H, ^{13}C, and $^{14(15)}N$ NMR, IR, and mass spectra as well as by elemental analysis data.

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Received July 3, 1995

Oxidation of ferrocene with ozone and chemiluminescence

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It is known that ferrocene (**1**) is resistant to oxygen,[1] but information about its interaction with ozone is lacking.

We have found that it is oxidized by gaseous ozone both in crystalline state and in a solution in CCl_4. In both cases, chemiluminescence (CL) is registered (in the form of a fast-dropping curve: 90 % in 2—3 min at $[Cp_2Fe]_0 = 10^{-2}$ mol L^{-1}, $w = 1$ g of O_3 h^{-1}, $I_{max} = (0.7–1.2) \cdot 10^7$ photon s^{-1} mL^{-1}). The CL spectrum correlates well with the phosphorescence spectra of the oxidation products, ketones,[2] which were synthesized in an independent way. An absorption band at 1720 cm^{-1}, which is characteristic of cyclopentadienones, appears in the IR spectrum of **1** following its oxidation in a solution, and an oscillation band of the Fe—C bond at 478 nm disappears. Thus, triplet-excited ketones derived from the cyclopentadiene cycle are the most probable emitters of CL.

The initial act of oxidation of **1** with ozone is the electron transfer from the Fe^{II} ion to a molecule of O_3 according to the reaction:

$$Cp_2Fe + O_3 \longrightarrow [Cp_2Fe]^+ + O_3^{\dot{-}}.$$

The formation of ferricinium cation was confirmed by the absorption spectrum of an oxidized solution ($\lambda_{max} = 625$ nm) and by the appearance of a characteristic blue-green color of a product on oxidation of crystalline **1**. On deeper oxidation of **1**, the specimen turns grayish brown, which is connected with the formation of products of complex composition, which include an organic part (a $C_{10}H_8O_8$ fragment) and metal-oxide groups Fe_xO_y.

References

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2. R. G. Bulgakov, S. P. Kuleshov, V. N. Khandozhko, I. P. Beletskaya, G. A. Tolstikov, and V. P. Kazakov, *Dokl. Akad. Nauk SSSR*, 1989, **304**, 114 [*Dokl. Chem.*, 1989, **304** (Engl. Transl.)].

Received July 21, 1995

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2529—2530, December, 1995.