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Dedicated to the Full Member of the Russian Academy of Sciences V.A.Tartakovsky on occasion of his 75th birthday

New Procedure for Nucleophilic Sulfonation of Aromatic Nitro Compounds: Destructive Oxidation of S-Arylthioglycolic Acids Esters

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Abstract—A new reaction was discovered: oxidative destruction of sulfides of $ArSCH_2CO_2Me$ type to sulfonic acids $ArSO_3H$ effected by 70% HNO_3. This reaction was used to introduce an SO_3H group instead of aromatic nitro group activated only by *meta*-substituents: At treating with $HSCH_2CO_2Me + K_2CO_3$ the NO_2 group was substituted to form $ArSCH_2CO_2Me$ with subsequent transformation into $ArSO_3H$. *p*-Fluoronitrobenzene behaved similarly (with replacement of the fluorine).

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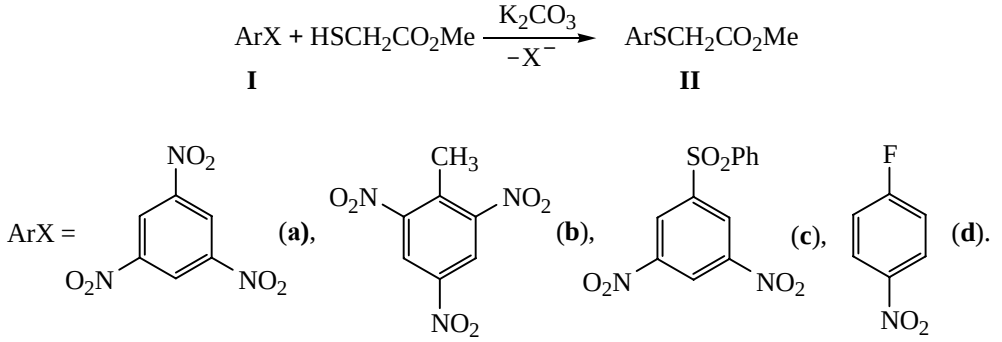
In event the acid (electrophilic) sulfonation of the aromatic ring is hindered by the presence of strong electron-withdrawing substituents (e.g., nitro groups) the sulfonation is performed by nucleophilic substitution of an activated nucleofuge under the action of sulfurous or pyrosulfurous acids salts [1, 2].

However the aromatic nitro group activated only by *meta*-substituents is incapable to be replaced under the treatment with the above salts. We found a new approach for replacement of a weakly activated nitro group by a sulfo group. The procedure is two-stage. In the first stage such a nitro group is substituted by the action of thioglycolic acid ester in the presence of K_2CO_3 in *N*-methylpyrrolidone or DMF giving S-arylthioglycolic acid ester **II** (Scheme 1). The method was demonstrated by examples of 1,3,5-trinitrobenzene (**Ia**) (one of the nitro groups was substituted), 2,4,6-trinitrotoluene (**Ib**) (only the ortho-nitro group was substituted), 3,5-dinitro-1-phenylsulfonylbenzene (**Ic**) (one of the nitro groups was substituted); besides in a similar way a fluorine atom was replaced in *p*-nitrofluorobenzene (**Id**) (Scheme 1)*.

The second stage of the process consists in a conversion of sulfanyl moiety in sulfides **II** into a sulfo group. We discovered a new phenomenon: On heating

Scheme 1.



* Method of converting 2,4,6-trinitrotoluene (**Ib**) into sulfide **IIb** we described previously [3]. Sulfides **IIa, IIc**, and **IId** were obtained similarly from nitro compounds **Ia, Ic**, and **Id** respectively.

S-arylthioglycolic acids esters **II** with 70% HNO_3 in the presence of catalytic quantities of $NaNO_2$ esters **II** underwent an oxidative decomposition leading to the formation of the corresponding nitro-substituted arenesulfonic acids **III** that were isolated in the form of stable potassium salts **IVa–IVd** (Scheme 2).

Among the possible ways of arenesulfonic acids **III** formation from S-arylthioglycolic esters **II** the following one seems the most probable. S-Arylthioglycolic acids at heating with H_2O_2 in diluted mineral acid are known to suffer oxidative cleavage giving arenethiols [4–6]. The reaction proceeds via preliminary oxidation of the initial sulfide into sulfoxide, and the latter in the acid medium undergoes Pummerer type rearrangement followed by hydrolysis to ArSH [6].

Presumably also in our case in keeping with a scheme given in [6] at the oxidation and hydrolysis of the ester first forms arylsulfinylacetic acid **V** (Scheme 3) that in the acid medium rearranges α-hydroxy derivative **VI**. The acid hydrolysis of the latter results in arenethiol **VII** which is oxidized into arenesulfonic acid **III** under the action of boiling 70% HNO_3 and nitrogen oxides vigorously liberated in the course of the reaction (Scheme 3). The second product of hydrolysis of α-hydroxy derivative **VI**, glyoxalic acid (**VIII**), is apparently further oxidized.

It should not be ruled out that the initial S-arylthioglycolic ester is first oxidized to the corresponding sulfone, and just the latter suffers the destructive oxidation. Actually, the beforehand prepared sulfones $ArSO_2CH_2CO_2Me$ under the conditions of the reaction in question give rise to arenesulfonic acids. However alongside these compounds form bis(arylsulfonyl)furoxanes that has not been observed at decomposition of sulfides **II**. The details will be published later.

Thus we demonstrated a possibility to introduce a sulfo group into aromatic nitro compounds through a nucleophilic substitution of the nitro group or a halogen under the treatment with the thioglycolic acid ester followed by destructive oxidation of the arising S-arylthioglycolic ester.

EXPERIMENTAL

^{1}H NMR spectra were registered on a spectrometer Bruker AC-200 in DMSO-d_6. Chemical shifts are reported with respect to TMS. Melting points of compounds obtained were measure by Koeffler method on a Boetius heating block (heating rate 4 deg/min).

Methyl 2-(3,5-dinitrophenylsulfanyl)acetate (IIa). Yield 78%, mp 93–95°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 3.69 s (3H, OCH_3), 4.30 s (2H, CH_2), 8.49 d (2H, ^4J 1.9 Hz), 8.60 t (1H, ^4J 1.9 Hz). Found, %: C 39.48; H 2.79; N 9.96; S 11.49. $C_9H_8N_2O_6S$. Calculated, %: C 39.71; H 2.96; N 10.29; S 11.78.

Methyl 2-[3-nitro-5-(phenylsulfonyl)phenylsulfanyl]acetate (IIc). Yield 70%, oily substance. ^{1}H NMR spectrum, δ, ppm: 3.62 s (3H, OCH_3), 4.25 s (2H, CH_2),

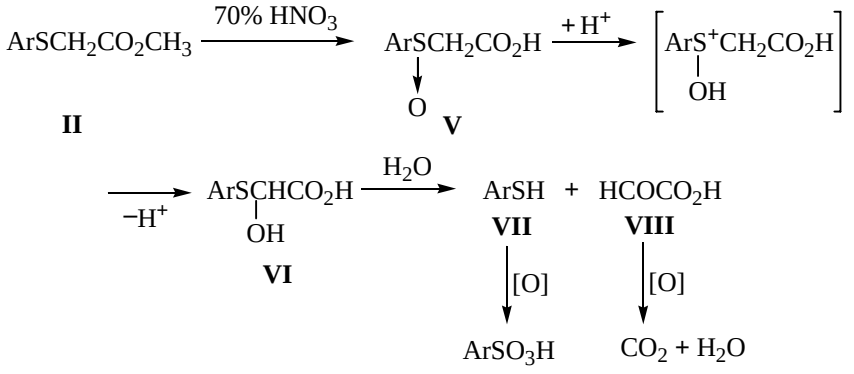
Scheme 2.

$ArSCH_2CO_2CH_3$ (**IIa–IId**) → $ArSO_3H$ (**III**) → $ArSO_3K$

IV, 80% (**a**), 66% (**b**), 52% (**c**), 55% (**d**).

Ar = 3,5-$(NO_2)_2C_6H_3$ (**a**), 2-CH_3-3,5-$(NO_2)_2C_6H_2$ (**b**), 3-NO_2-5-$(PhSO_2)C_6H_3$ (**c**), 4-$NO_2C_6H_4$ (**d**).

Scheme 3.



7.60–7.80 m (3H), 8.08 d (2H, ^3J 5.6 Hz), 8.27 s (1H), 8.37 s(H), 8.38 s (H).

Methyl 2-(4-nitrophenylsulfanyl)acetate (IId). Yield 85%, mp 51–52°C (from MeOH) (50.9– 52.4°C [7]). ^{1}H NMR spectrum, δ, ppm: 3.66 s (3H), 4.15 s (2H), 7.52 d (2H, ^3J 5.8 Hz), 8.15 d (2H, ^3J 5.8 Hz).

Potassium sulfonates. General procedure. A mixture of 1 g of sulfide **IIa–IId** and 5 ml of 70% nitric acid was slowly heated at stirring to boiling and boiled at reflux for 3 h; therewith nitrogen oxides liberated. The reaction mixture was evaporated in a vacuum to dryness, the residue was dissolved in EtOH, and to the cooled solution was added at stirring a solution of KOH in ethanol in an amount equivalent to compound **II**. The separated precipitate was filtered off and dried in air.

Potassium 3,5-dinitrophenylsulfonate (IVa) [8]. Yield 80%, mp 332–334°C (from water). ^{1}H NMR spectrum, δ, ppm: 8.63 d (2H, ^4J 1.9 Hz), 8.79 t (1H, ^4J 1.9 Hz). Found, %: C 25.27; H 1.08; K 13.73; N 9.36; S 10.92. $C_6H_3KN_2O_7S$. Calculated, %: C 25.17; H 1.06; K 13.66; N 9.79; S 11.20.

Potassium 2-methyl-3,5-dinitrophenylsulfonate (IVb). Yield 66%, mp > 360°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 2.71 s (3H), 8.63 d (1H, ^4J 2.1 Hz), 8.78 d (1H, ^4J 2.1 Hz). Found, %: C 28.35; H 1.70; N 9.36; S 10.20; K 13.45. $C_7H_5KN_2O_7S$. Calculated, %: C 28.00; H 1.68; K 13.02; N 9.33; S 10.68.

Potassium 3-nitro-5-(phenylsulfonyl)phenylsulfonate (IVc). Yield 52%, mp > 360°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 7.60–7.85 m (3H), 8.08 d (2H, ^3J 5.6 Hz), 8.38 s (1H), 8.50 s (1H), 8.60 s (1H), Found, %: C 37.49; H 2.31; K 10.63; N 3.83; S 16.41. $C_{12}H_8KNO_7S_2$. Calculated, %: C 37.79; H 2.11; K 10.25; N 3.67; S 16.81.

Potassium 4-nitrophenylsulfonate (IVd). Yield 55%, mp > 360°C (from EtOH) (328°C [9]). ^{1}H NMR spectrum, δ, ppm: 8.21 d (2H, ^3J 6.1 Hz), 7.86 d (2H, ^3J 6.1 Hz). Found, %: C 30.08; H 1.71; K 16.38; N 5.64; S 13.31. $C_6H_4KNO_5S$. Calculated, %: C 29.87; H 1.67; K 16.21; N 5.81; S 13.29.

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