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THE FIRST EXAMPLE OF SYNTHESIS OF TETRACYANO DERIVATIVES OF THIANTHRENE AND PHENOXATHIIN WITH USE OF THIOACETAMIDE

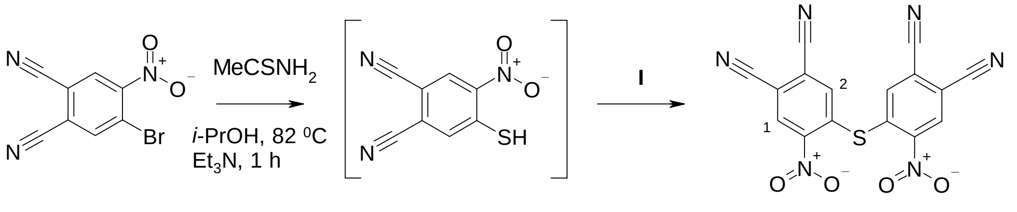
Igor' G. Abramov,* Alexey V. Smirnov, Sergey A. Ivanovsky, Marina B. Abramova, and Vladimir V. Plakhtinskii

Yaroslavl State Technical University, 150023, Yaroslavl, Moscowsky prospekt 88, Russian Federation
E-mail: abramov.orgchem@staff.ystu.yar.ru

Abstract – New cyano derivatives of thianthrene and phenoxathiin have been synthesized by aromatic nucleophilic substitution reaction of the bromine atom and nitro group in 4-bromo-5-nitrophthalonitrile.

We have investigated the interaction of 4-bromo-5-nitrophtalonitrile (**I**) and thioacetamide acting as a nucleophilic agent. Synthesized tetracyano derivatives of thianthrene and phenoxathiin can be used for obtaining polyphthalocyanines,[1] polyhexazocyclanes[2] and other polymers containing isoindole fragments.[2]

In accordance with the agreed-upon theoretical representation the carbon atom connected with the bromine atom in (**I**) is activated by the *ortho*-nitro group. At the same time, two cyano groups activate the carbon atom connected with the nitro group. As a result the high-labile bromine atom primarily and then the nitro group are substituted with *O-,N-,S-* nucleophiles (S_NAr reaction).[3-4] As the *S*-nucleophile in this reaction thioacetamide was used for the first time to react actively with (**I**). This reaction resulted in imidothiol ether formation and then the imidothiol ether was converted to the thiol under the reaction conditions.[5] Thus the obtained 4-mercapto-5-nitrophthalonitrile (**II**) reacts with another molecule of (**I**) in the presence of triethylamine to give the sulfide (**III**) (Scheme 1).



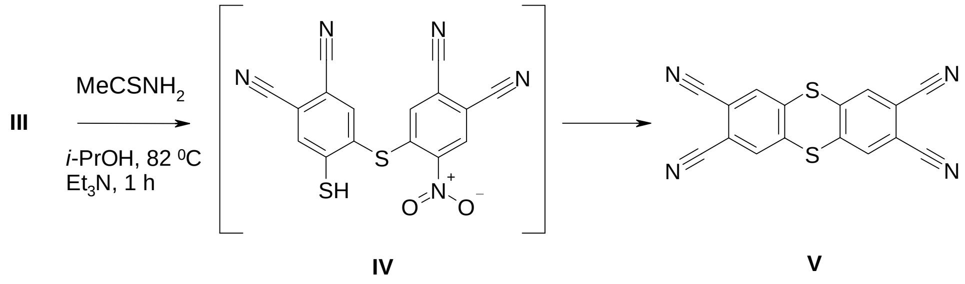
I **II** **III**

Scheme 1

Bis(2-nitro-4,5-dicyanophenyl) sulfide (**III**) has two nitro groups to activate itself sufficiently for further substitution. We used this opportunity for obtaining 2,3,7,8-thianthrenetetracarbonitrile and 2,3,7,8-phenoxathiintetracarbonitrile.

The sulfide (**III**) was heated with the thioacetamide and triethylamine to give the thiol (**IV**) which underwent a cyclization to yield 2,3,7,8-thianthrenetetracarbonitrile (**V**) (Scheme 2).

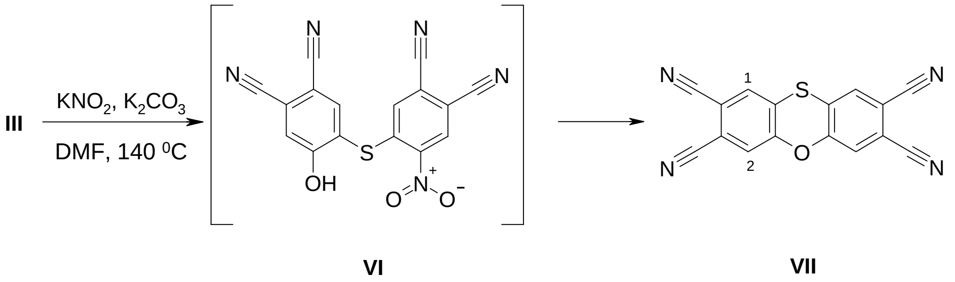
The thianthrene synthesis could be performed without isolation of the intermediate sulfide (**III**) by heating equimolar amounts of (**I**) and thioacetamide. This reaction was accompanied by formation of gas products.



Scheme 2

The thianthrene was also obtained by using thiourea, arylthioamides, thiosemicarbazide, potassium sulphide and ammonium rodanine acting as a nucleophile reagent though in these cases the yield and its purity were low.

The other cyclization reaction of the sulfide (**III**) proceeded at 140 ^{0}C in anhydrous DMF containing K_2CO_3 and KNO_2 to give 2,3,7,8-phenoxathiintetracarbonitrile (**VII**). At the beginning this case one nitro group would be replaced with a nitrosooxy group by nucleophilic substitution of nitrite ion,[6] followed by hydrolysis to give (**VI**) which undergoes the second nitro group intramolecular substitution reaction (Scheme 3). The second reaction is likely to proceed via the Smiles rearrangement.[7]



Scheme 3

EXPERIMENTAL

4-Bromo-5-nitrophthalonitrile is prepared in accordance with the technique described in the paper.[2]

Bis(2-nitro-4,5-dicyanophenyl) sulfide (**III**): 5.0 g (0.02 mol) of **I** and 0.8 g (0.01 mol) of thioacetamide were dissolved and heated in 100 mL of 2-propanol. 2.8 mL (0.02 mol) of triethylamine were added to the prepared solution and the reaction mass was stirred on boiling for 1 h. After cooling, the precipitate was collected by filtration, washed with 50 mL of 2-propanol, and dried to give 6.9 g (92 % from the theory) of compound (**III**) – yellow crystalline powder with mp 237-239 ^{0}C. Anal. Calcd for $C_{16}H_4N_6O_4S$: C, 51.07; H, 1.07; N, 22.33; S, 8.52. Found : C, 50.93; H, 1.13; N, 22.42; S, 8.65; ^{1}H NMR (DMSO - d_6) δ: 8.83 (s, 2H, H-1), 8.47 (s, 2H, H-2); IR ν, cm^{-1}: 2240 (-CN), 1560, 1340 (-NO_2), 650 (-S-); MS *m/z*, 376 (100) [M^+], 344 (32).

2,3,7,8-Thianthrenetetracarbonitrile (**V**): 5.0 g (0.02 mol) of **I** and 1.6 g (0.02 mol) of thioacetamide were dissolved and heated in 100 mL of 2-propanol. 5.5 mL (0.04 mol) of triethylamine were added. Self-boiling reaction mass (intensive foaming) was stirred for 5 min, heated up to 2-propanol boiling temperature, and kept on boiling for 1 h more. After cooling, the settled precipitate was collected by filtration, washed with 50 mL of 2-propanol, and dried to give 5.1 g (81 % from the theory) of compound (**V**) – light yellow crystalline powder with mp > 300 ^{0}C. Anal. Calcd for $C_{16}H_4N_4S$: C, 60.74; H, 1.27; N, 17.71; S, 20.27. Found: C, 60.59; H, 1.36; N, 17.78; S, 20.33; ^{1}H NMR (DMSO - d_6) δ: 8,35 (s, 4H); IR ν, cm^{-1}: 2240 (-CN), 650 (-S-); MS *m/z*, 316 (100) [M^+], 289 (26), 284 (50), 257 (22).

2,3,7,8-Phenoxathiintetracarbonitrile (**VII**): 3.8 g (0.01 mol) of **III**, 2.8 g (0.02 mol) of anhydrous K_2CO_3, 0.085 g (0.001 mol) of KNO_2 and 40 mL of DMF were put into a flask furnished with a mixer, a reflux condenser and a thermometer. The reaction mixture was heated to 140 ^{0}C, kept at this temperature and intensivly stirred for 2 h, cooled to rt and poured into 100 mL of water. The precipitate was collected by filtration, washed with 50 mL of water and crystallized from DMF to give 1.74 g (58 % from the theory) of compound (**VII**) – light yellow crystalline powder with mp > 300 ^{0}C. Anal. Calcd for $C_{16}H_4N_4OS$: C, 63.99; H, 1.34; N, 18.66; S, 10.68. Found: C, 64.12; H, 1.41; N, 18.43; S, 10.82; ^{1}H NMR (DMSO - d_6) δ: 8.10 (s, 2H, H-1), 7.75 (s, 2H, H-2); IR ν, cm^{-1}: 2240 (-CN), 1260 (-O-), 650 (-S-); MS *m/z*, 300 (100) [M^+], 268 (20).

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