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Phthalocyanines and Related Compounds: XLVIII.[1] Stepwise Nucleophilic Substitution in Tetrachlorophthalonitrile: Synthesis of Polysubstituted Phthalonitriles

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Abstract—Chlorine-containing products of incomplete nucleophilic substitution in tetrachlorophthalonitrile were subjected to further reaction with nucleophiles. The nature of the nucleophiles and the order of their introduction into stepwise nucleophilic substitution in tetrachlorophthalonitrile were shown to be of principal importance for selective synthesis on this basis of phthalonitrile derivatives with various substituents.

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The overwhelming majority of presently known substituted phthalocyanines is represented by various tetra- and octa-substituted phthalocyanines generally obtained by tetramerization of respective mono- and disubstituted phthalonitriles [2]. The latter were commonly synthesized by nucleophilic substitution of halogen atoms or nitro groups in phthalonitrile precursors, that include widely known commercially available 3- and 4-nitrophthalonitriles [3], 4,5-dichloro- [4], 3,5-dinitro- [5], 4-bromo-5-nitrophthalonitriles [6] and some others.

Phthalocyanines containing in their macrocycle sixteen substituents are much less known, because the development of studies in this direction is hindered by the limited accessibility of respective tetrasubstituted phthalonitriles. The latter are represented mainly by tetrafluoro- and tetrachlorophthalonitriles and by some products of halogen substitution in the tetrahalides. First of all, this relates to tetrafluorophthalonitrile that was introduced into nucleophilic substitution with O- (alcohols, phenols) [7–16], S- (thiols) [7, 15–18], N- (amines) [7, 13, 19], C- (malonic ester) [20], and P-nucleophiles (diethylphosphine) [7]. Tetrachlorophthalonitrile was rarely used as a precursor for the synthesis of substituted phthalonitriles. It was subjected to O- [21–23], C- and N-substitution in reactions with the sterically hindered 2,6-di-*tert*-butylphenol and 3,5-di-*tert*-butyl-4-hydroxyaniline, respectively [24].

Unlike complete substitution products [7, 9–14, 19, 21], the products of partial substitution contain substituents of two types: remaining halogen atom(s) and other one [7, 13, 20–24], two [7, 13, 21, 22] or three identical groups [18, 21] which are the fragments of the nucleophile. Theoretically, acting on a tetrahalophthalonitrile consecutively by different nucleophiles one can obtain phthalonitriles even with four different substituents. However, in practice, this synthetic possibility was realized only partially. The examples include consecutive disubstitution to prepare 3,6-difluoro-5-phenoxy-4-phenylsulfanylphthalonitrile [16], trisubstitution to prepare 4,5-bis(2-chlorophenylsulfanyl)-3-(2,6-dimethylphenoxy)-6-fluorophthalonitrile [18] and several tris(aryloxy)chloro(fluoro) phthalonitriles with different aryloxy groups [22], and tetrasubstitution to prepare bis(aryloxy)bis(alkoxy) phthalonitriles [22].

The last example is represented by one publication only, where halogen-free tetrasubstituted phthalo-

[1] For communication XLVII, see [1].

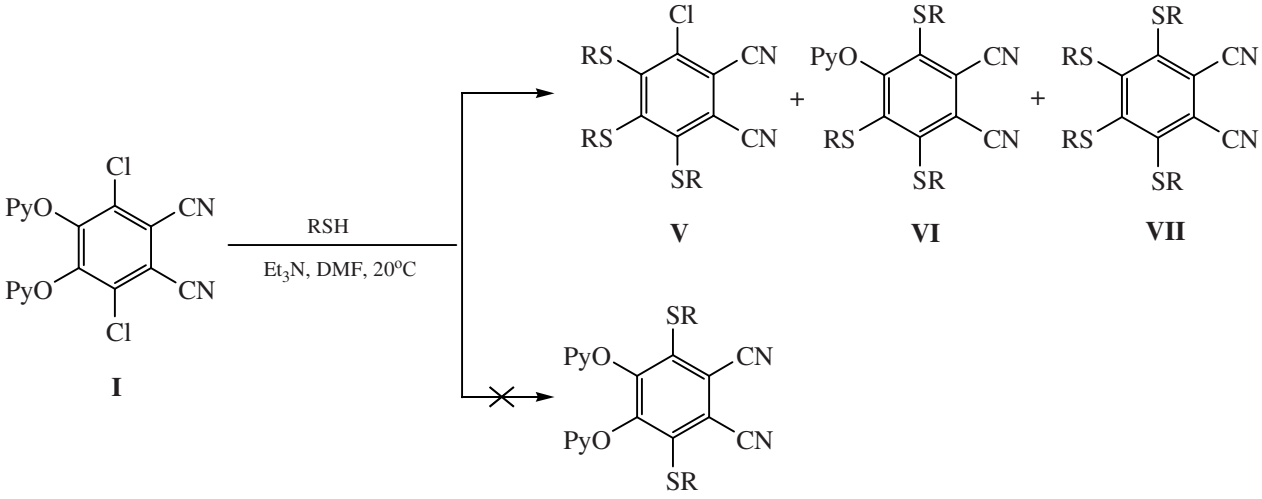
nitriles with more than one sort of substituents were obtained by substitution in tetrafluorophthalonitrile. Several such phthalonitriles were obtained by other methods: 4,5-Bis(phenylsulfanyl)-3,6-dialkoxyphthalonitriles were prepared from 2,3-dichloroo-5,6-dicyano-1,4-benzoquinone by its reduction followed by alkylation [25], and dialkyldialkoxyphthalonitriles were prepared by the Rosemund–Brown reaction from corresponding substituted *o*-dibromobenzenes [26–30].

For enhancing the synthetic potential of tetrachlorophthalonitrile and proceeding with our studies on the regularities of chlorine substitution in this compound under the action of various nucleophiles [1, 31, 32], we involved tetrachlorophthalonitrile into consequtive reactions with two different nucleophiles.

In previous works we determined conditions for the synthesis of a series of chlorine-containing compounds from tetrachlorophthalonitrile under the action of the first nucleophile. Now we involved some of them, namely, 3,6-dichloro-4,5-bis(pyridin-3-yloxy)- (**I**) [32], 3,6-dichloro-4,5-bis(phenylsulfanyl)- (**II**) [31], 3,5,6-trichloro-4-phenylamino- (**III**), and 4,5-bis-(alkylamino)-3,6-dichlorophthalonitriles (**IV**) [1] in further reactions with nucleophiles.

Initially we attempted to replace the chlorine atoms in phthalonitrile **I** by sulfanyl groups to obtain new symmetrical dinitriles with two different substituents (aryloxy and sulfanyl), but the reactions with two or four mol of a thiol (thiophenol, butanethiol) at room temperature in the presence of an equimolar amount of triethylamine as a base afforded, instead of the expected product of substitution of two chlorine atoms, a mixture of three other phthalonitriles (Scheme 1, Tables 1, 2).

Scheme 1.

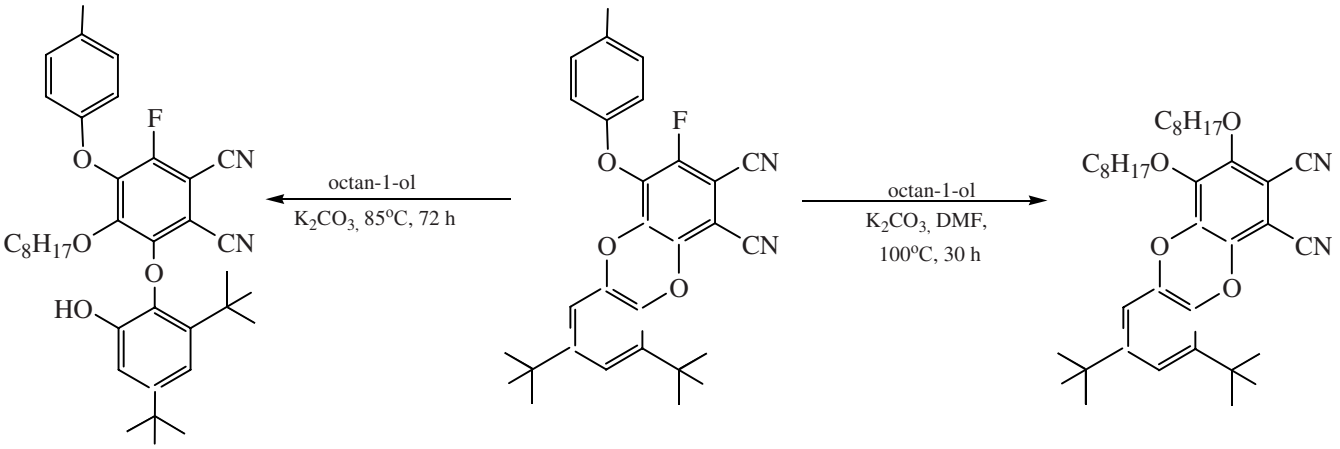


R = Ph (**Va–VIIa**), Bu (**Vb–VIIb**). Py = pyridine-3-yl.

The products included tetrasulfanyl-substituted dinitriles **VII** indentical to those we obtained and characterized earlier [31]. Two other products were trisulfanyl-substituted phthalonitriles **V** and **VI**; one of them, compound **Va**, was also prepared by us earlier [31]. It should be noted that all the final products contain more sulfanyl groups (three or four) than might be expected at the 1:2 stoichiometric reagent ratio we used. This result can be explained by initial substitution of the pyridyloxy group in dinitrile **I**. The intermediate dinitrile formed by sulfanyl substitution for the pyridyloxy group should be more susceptible to further nucleophilic attack than parent dinitrile **I** in view of the fact that the sulfanyl group is a weaker π-donor compared to the aryloxy group; as a result, tri- and tetrasulfanyl-substituted dinitriles (**V, VI,** and **VII**, respectively) are formed.

Such a preferable substitution of the pyridyloxy group in the 4 position compared with the chlorine atom in the 3 position is consistent with the data of Wang et al. [22] who described the substitution of the aryloxy group in preference to fluorine in 3,4,5-tris-(aryloxy)-6-fluorophthalonitrile under the action of alkoxide ion (Scheme 2).

Scheme 2.



Under more rigid conditions (reagent ratio 1:4, temperature 70°C), both the pyridyloxy groups and chlorine atoms in phthalonitrile **I** can be replaced by sulfanyl groups to prepare tetrasulfanyl-substituted phthalonitriles **VII** in high yields (70–75%).

As a result, the aryloxy groups introduced in the first step in the 4 and 5 positions of tetrachlorophthalonitrile to form 4,5-bis(aryloxy)-3,6-dichlorophthalonitriles were substituted in the second step by a stronger nucleophile (thiolate anion). Hence, consecutive action on tetrachlorophthalonitrile of O- and then S-nucleophiles holds little promise in terms of selective synthesis of polysubstituted phthalonitriles.

Dinitrile **II** is formed at a 1:2 tetrachlorophthalonitrile:thiophenol under mild conditions with nearly quantitative yield [31]. We expected to obtain symmetrical tetrasubstituted phthalonitrile **VIII** with two different sulfanyl groups by reacting dinitrile **II** with another thiol Actually, the reaction of phthalonitrile **II** with decanethiol in a 1:2 ratio at room temperature in the presence of triethylamine afforded expected compound **VIII** (Scheme 3, Tables 2 and 3) but in a low yield (17%). Along with this compound, we isolated from the resulting reaction mixture four other phthalonitriles. Two of them, **IX** and **X,** like dinitriles **V** and **VI** in the preceding experiment, are formed by substitution of three of the four existing groups and were isolated in a total yield of 15%. Therewith, one or both phenylsulfanyl groups of the parent compound were substituted, and this is the first example for phthalonitriles, when sulfanyl is a leaving group.

Table 1. Reaction of thiols with phthalonitrile **I**

RSH	Dinitrile **I** : RSH molar ratio	*T*, °C	Yield, %[a]		
			V	**VI**	**VII**
Ph (a)	1:2	20	2.0	14.1	13.7
	1:4	20	17.7	26.7	24.6
		70	1.7	1.3	74.7
Bu (b)	1:2	20	2.3	31.6	16.0
	1:4	20	12.3	31.5	16.9
		70	1.5	0.6	72.2

[a] Yield after column chromatography (sorbent silica gel, eluent benzene).

Two other additional products, phthalonitriles **XI** and **VIIa**, isolated with yields of 5.5 and 12.3%, respectively, contain more phenylsulfanyl groups than parent phthalonitrile **II** (three and four, respectively). This can be explained by the fact that the phenylthiolate anion generated in the course of formation of compounds **IX** and **X** compares in nucleophilicity with the decyl analog and takes part in further nucleophilic attack; as a result, more diverse substitution products are formed.

It becomes obvious that using S-nucleophiles in the second step of chlorine substitution in tetrachloro–phthalonitrile after using either O- or another S-nucleophile in the first step does not lead to selective synthesis of polysubstituted phthalonitriles.

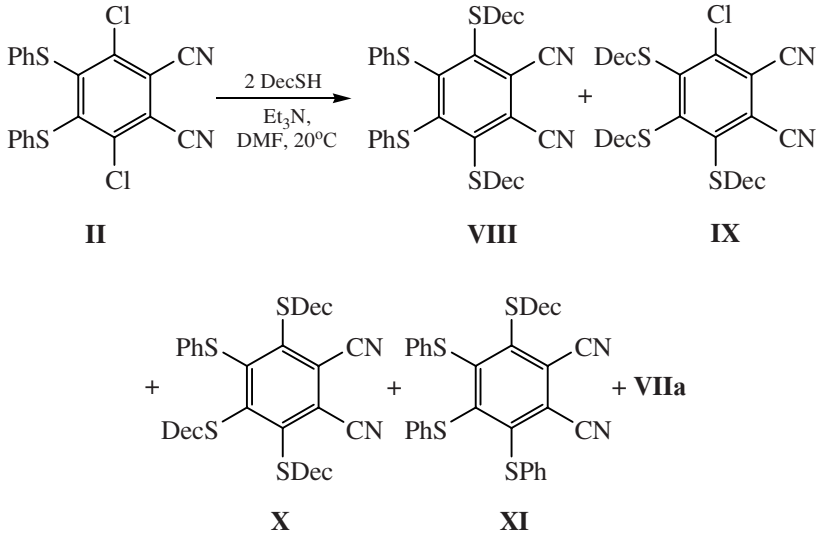
In a further experiment we assumed that the 4- and 5-phenylsulfanyl groups in dinitrile **II** would resist to

Table 2. Melting points, elemental analyses, and IR and mass spectra of the obtained phthalonitriles

Comp. no.[a]	Yield,[b] %	mp,[c] °C	Elemental analysis data											ν_{CN}, cm^{-1}	M^+
			Found, %					Formula	Calculated, %						
			C	H	Cl	N	S		C	H	Cl	N	S		
Vb	12.3	[d]	56.16 56.33	6.37 6.43	8.21 8.37	6.43 6.61	22.42 22.62	$C_{20}H_{27}ClN_2S_3$	56.25	6.37	8.30	6.56	22.52	2233	426
VIa	26.7	122–123	68.12 68.34	3.47 3.55	–	7.62 7.78	17.55 17.71	$C_{31}H_{19}N_3OS_3$	68.23	3.51	–	7.70	17.63	2232	545
VIb	31.6	[d]	61.74 61.90	6.36 6.44	–	8.60 8.75	19.72 19.87	$C_{25}H_{31}N_3OS_3$	61.82	6.43	–	8.65	19.80	2230	485
VIII	17.0	[d]	69.62 69.79	7.53 7.58	–	3.88 3.94	18.47 18.56	$C_{40}H_{52}N_2S_4$	69.72	7.61	–	4.07	18.61	2236	688
IX	6.3	[d]	67.04 67.20	9.37 9.40	5.09 5.18	4.10 4.26	14.07 14.27	$C_{38}H_{63}ClN_2S_3$	67.16	9.34	5.22	4.12	14.15	2241	678
X	8.8	[d]	69.98 70.21	9.04 9.11	–	3.62 3.79	16.93 17.14	$C_{44}H_{68}N_2S_4$	70.16	9.10	–	3.72	17.02	2239	752
XI	5.5	99–102	69.06 69.25	5.75 5.78	–	4.40 4.62	20.41 20.58	$C_{36}H_{36}N_2S_4$	69.19	5.81	–	4.48	20.52	2238	624
XII	22.3	163–165	72.62 72.75	3.85 3.88	–	5.18 5.35	11.97 12.22	$C_{30}H_{18}N_4O_2S_2$	72.70	3.81	–	5.30	12.13	2242	530
XIII	6.1													2240	471
XIV	2.4													2237	545
XVa	61.7	212–214	60.50 60.65	2.74 2.80	17.76 17.97	10.48 10.62	7.96 8.18	$C_{20}H_{11}Cl_2N_3S$	60.62	2.80	17.89	10.60	8.09	2235	395
XVb	63.3	85–87	57.33 57.52	3.97 4.06	18.72 18.93	11.09 11.24	8.43 8.65	$C_{18}H_{15}Cl_2N_3S$	57.45	4.03	18.84	11.17	8.52	2236	375
XVIa	68.9	187–189	66.27 66.41	3.40 3.47	7.43 7.60	8.79 8.88	13.53 13.75	$C_{26}H_{16}ClN_3S_2$	66.44	3.43	7.54	8.94	13.64	2232	469
XVIb	64.6	[d]	61.33 61.54	5.61 5.66	8.11 8.30	9.65 9.87	14.83 15.02	$C_{22}H_{24}ClN_3S_2$	61.45	5.63	8.24	9.77	14.91	2232	429
XVIIa	68.3	163–165	70.57 70.74	3.81 3.87	–	7.78 7.86	17.54 17.76	$C_{32}H_{21}N_3S_3$	70.69	3.89	–	7.73	17.69	2233	543
XVIIb	65.7	[d]	64.45 64.62	6.81 6.85	–	8.54 8.77	19.73 19.91	$C_{26}H_{33}N_3S_3$	64.56	6.88	–	8.69	19.88	2236	483
XVIIIa	74.2	202–205	65.26 65.42	5.00 5.06	–	10.76 10.98	12.31 12.54	$C_{28}H_{26}N_4O_2S_2$	65.35	5.09	–	10.89	12.46	2230	514
XVIIIb	75.0	211–213	70.44 70.62	5.94 5.99	–	10.88 11.07	12.37 12.60	$C_{30}H_{30}N_4S_2$	70.55	5.92	–	10.97	12.55	2228	510
XIX	72.4	270–272	55.52 55.73	1.61 1.64	23.37 23.55	13.81 13.95	–	$C_{14}H_5Cl_2N_3O$	55.66	1.67	23.47	13.91	–	2231	301

[a] Compounds **Va, VIIa** and **VIIb** have been characterized in [31]. [b] Yields of products after separation of mixtures by preparative column chromatography [sorbent silica gel; eluents: benzene (**V–XIV**), toluene (**XV–XVII**), or ethyl acetate (**XVIII**, **XIX**)]. [c] From ethanol. [d] Yellow oil crystallizing on storage.

Scheme 3.



Dec = n-$C_{10}H_{21}$.

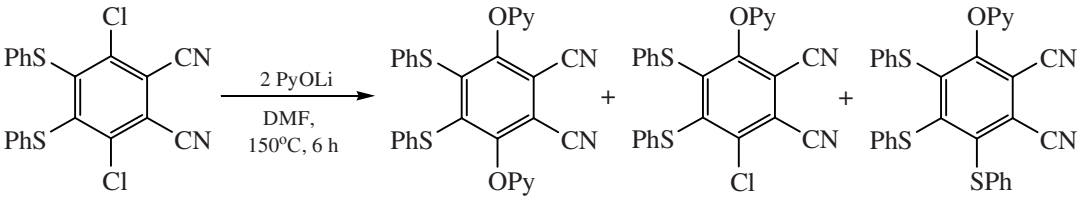
substitution by a weaker nucleophile (pyridinolate anion). As would be expected [32], the reaction of dinitrile **II** with lithium pyridin-3-olate in a 1:2 ratio proceeds at an elevated temperature, but even within 6 h at 150°C only half of the substrate is involved in substitution. The expected symmetrical 4,5-bis-(phenylsulfanyl)-3,6-bis(pyridin-3-yloxy)phthalonitrile (**XII**) was obtained (accounting for the conversion of the parent dinitrile) in a fairly good yield of 43% and could be easily isolated from the reaction mixture by chromatography. We also isolated trace amounts of two others phthalonitriles (Scheme 4, Tables 1, 2). One of them, compound **XIII,** results from phenoxy substitution for one chlorine atom only. The formation of the other product, tris(phenylsulfanyl)-substituted dinitrile **XIV,** provides evidence showing that the pyridin-3-olate still attacks the 4 and 5 positions to substitute the phenylsulfanyl groups. Such substitution is also confirmed by the appearance of a typical thiophenol odor upon acidification of the reaction mixture.

This, the of an S-nucleophile in the first step and of an O-nucleophile in the second step can lead to selective formation of symmetrical aryloxy(sulfanyl)-substituted phthalonitriles from tetrachlorophthalonitrile.

Table 3. ^{13}C NMR spectra of certain obtained phthalonitriles (DMSO-d_6)

Product	δ_C, ppm
VIII	147.9 (C_{Ar}–S), 137.8 (C_{Ar}–S'), 134.5 ($C_{Ar'}$–S), 129.8 ($C_{Ar'}$–H), 129.6 ($C_{Ar'}$–H), 127.7 ($C_{Ar'}$–H), 124.7 (C_{Ar}–CN), 114.8 (CN), 37.0 (CH_2–S'), 32.0, 29.8, 29.6, 29.4, 29.2, 28.7, 28.5, 22.8 (CH_2), 14.7 (CH_3)
XII	154.7 (C_{Ar}–O), 153.6 ($C_{Ar'}$–O), 145.6 ($C_{Ar''}$–H), 142.2 ($C_{Ar''}$–H), 138.6 (C_{Ar}–S), 134.0 ($C_{Ar'}$–H), 130.2 ($C_{Ar'}$–S), 129.7 ($C_{Ar'}$–H), 128.5 ($C_{Ar''}$–H), 125.2 ($C_{Ar''}$–H), 123.5 ($C_{Ar''}$–H), 113.2 (C_{Ar}–CN), 112.7 (CN)
XVIIIa	155.9 (C_{Ar}–N), 148.2 (C_{Ar}–S), 135.7 ($C_{Ar'}$–S), 129.5 ($C_{Ar'}$–H), 127.3 ($C_{Ar'}$–H), 125.7 ($C_{Ar'}$–H), 114.1 (C_{Ar}–CN), 112.4 (CN), 67.6 (CH_2–O), 51.0 (CH_2–N)
XVIIIb	156.8 (C_{Ar}–N), 148.3 (C_{Ar}–S), 135.7 ($C_{Ar'}$–S), 129.3 ($C_{Ar'}$–H), 127.2 ($C_{Ar'}$–H), 125.9 ($C_{Ar'}$–H), 114.0 (C_{Ar}–CN), 112.1 (CN) 52.4 (CH_2–N), 25.7(CH_2), 23.5 (CH_2)
XIX	146.4 ($C_{Ar'}$–O), 141.3 (C_{Ar}–O), 136.7 (C_{Ar}–N), 133.9 (C_{Ar}–Cl), 132.1 (C_{Ar}–Cl), 127.6 ($C_{Ar'}$–N), 125.6 ($C_{Ar'}$–H), 123.9 ($C_{Ar'}$–H), 116.0 ($C_{Ar'}$–H), 115.3 ($C_{Ar'}$–H), 113. 8 (C_{Ar}–CN), 111.9 (C_{Ar}–CN), 109.7 (CN), 108.0 (CN)

Scheme 4.

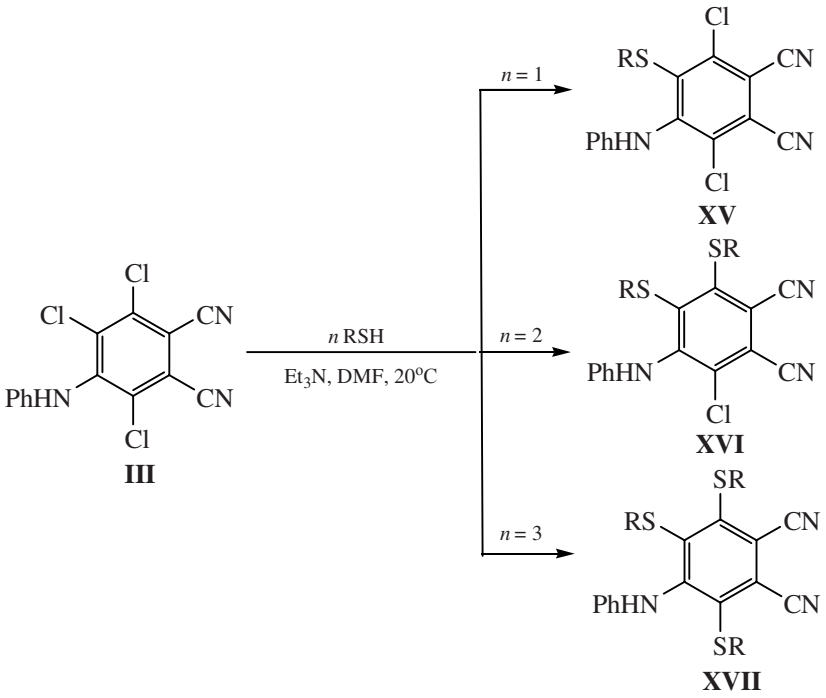


II **XII** **XIII** **XIV**

Py = pyridine-3-yl.

Amino-substituted phthalonitriles obtained from tetrachlorophthalonitrile by substitution in the first step [1] proved to be ever more attractive substrates for the synthesis of variously substituted phthalonitriles. The model 3,4,6-trichloro-5-(phenylamino)phthalonitrile (**III**) did not enter into further nucleophilic substitution with aryloxides even at an elevated temperature (100°C) but reacted with thiols already at room temperature. In this case, by contrast with the three preceding ones, we observed exclusive substitution of one (**XV**), two (**XVI**), or three (**XVII**) chlorine atoms by phenylsulfanyl groups, depending on the stoichiometric ratio of the substarte and nucleophile (Scheme 5, Table 2).

Scheme 5.



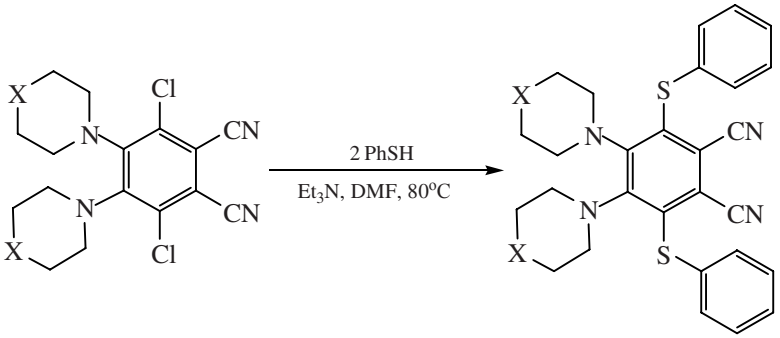
R = Ph (**XVa–XVIIa**), Bu (**XVb–XVIIb**).

The same reaction but at an elevated temperature (80°C) proceeds smoothly with diaminodichloro-substituted phthalonitriles **IV** and leads to symmetrical 4,5-diamino-3,6-disulfanyl-substituted phthalonitriles **XVIII** in ~75% yield (Scheme 6, Tables 2 and 3).

The last two experiments show that the use of amines in the first step of nucleophilic substitution in tetrachlorophthalonitrile is suitable not only for synthesis of aminochloro-substituted-phthalonitriles [1], but also for further synthesis from them of amino (sulfanyl)- substituted phthalonitriles.

We also attempted to prepare polyfunctional phthalonitriles directly from tetrachlorophthalonitriles in one

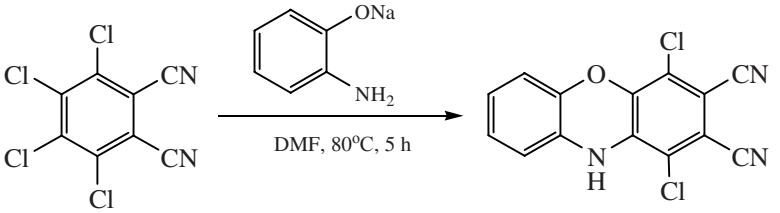
Scheme 6.



IV **XVIII**

X = O (**IVa, XVIIIa**), CH_2 (**IVb, XVIIIb**).

Scheme 7.



XIX

step, using a bifunctional nucleophile (Scheme 7, Tables 2, 3). The use of such nucleophile as *o*-aminophenoxide anion in a 1:1 molar ratio with tetrachlorophthalonitrile at 80°C for 5 h allows to synthesize in one step in high yield (~72%) tetrasubstituted phthalonitrile **XIX** containing substituents of three different types.

Thus, by consecutive action of different nucleophiles on tetrachlorophthalonitrile we synthesized a wide series of tetrasubstituted phthalonitriles and showed that the nature and sequence of introducing nucleophiles into such stepwise nucleophilic substitution are of key importance for selective synthesis of phthalonitriles with substituents of different types.

EXPERIMENTAL

Elemental analyses were carried out on a Hewlett-Packard HP□185B C,H,N-analyzer. The IR spectra were taken from KBr pellets on a FSM 1201 FT–IR spectrometer. The mass spectra were measured on an MKh-1321 instrument (ionizing electron energy 70 eV). The ^{13}C NMR spectra were obtained on a Bruker AM-300 instrument from solutions in DMSO-d_6, internal reference TMS. The composition of the reaction mixtures and the individuality of the obtained substances were monitored by TLC on Silufol UV-254 plates.

Reaction of phthalonitriles I–IV with thiols (*general procedure*). To a solution of 5.0 mmol of phthalonitrile **I–IV** and corresponding amount of a thiol (10.0 and 20.0 mmol with **I**, 10.0 mmol with **II**; 5.0, 10.0, and 15.0 mmol with **III;** and 10.0 mmol with **IV**) in 20 ml of DMF we added dropwise at 20°C under stirring an equimolar amount of triethylamine. The reaction mixture was kept at room temperature (**I–III**) or at 70 (**I**) or 80°C (**IV**) for 45 min and then poured to a saturated solution of NaCl and extracted with ethyl acetate. The organic layer was washed with two portions of water, dried over anhydrous Na_2SO_4, and the solvent was removed under a vacuum. The residue was subjected to chromatography on silica gel (eluent benzene, toluene, and ethyl acetate for the reactions with **I** and **II**, **III**, and **IV,** respectively). The resulting crystalline substances were recrystallized from ethanol.

Reaction of phthalonitrile II with lithium pyridin-3-olate. A solution of 0.50 g of phthalonitrile **II** and 0.245 g of lithium pyridine-3-olate in 20 ml of DMF was heated at 150°C for 6 h, cooled to room temperature, poured to a saturated solution of NaCl, and extracted with ethyl acetate. The organic layer was then washed with two portions of water, dried over anhydrous Na_2SO_4, the solvent was evaporated under a vacuum, and the residue was subjected to chromatography on silica gel (eluent benzene) to isolate 0.28 g of parent dinitrile **II**, 0.22 g (22.3 or 43.1% with account for conversion) of dinitrile **XII**, 0.035 g (6.1%) of dinitrile **XIII,** and 0.016 g (2.4%) of dinitrile **XIV**. Dinitrile **XII** was recrystallized from ethanol.

Reaction of tetrachlorophthalonitrile with *ortho*-aminophenol. A solution of 1.33 g of tetrachlorophthalonitrile and 0.65 g of *ortho*-aminophenol sodium salt in 20 ml of DMF was heated to 80°C and kept at that temperature for 5 h. Then the reaction mixture was cooled to room temperature, and 120 ml of water was added to it. The precipitate formed was filtered off, washed on the filter with hot water, dried, dissolved in ethyl acetate, and subjected to chromatography on silica gel (eluent ethyl acetate). Recrystallization from ethanol gave 1.09 g (72.4%) of compound **XIX**.

ACKNOWLEDGMENTS

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