Phenylsubstituted Porphyrins. 2. Synthesis of 5–Arylporphyrins[⊗]

Ekaterina A. Kolodina,[a] Tatiana V. Lubimova,[b] Sergei A. Syrbu,[a @] and Alexander S. Semeikin[a]

[a]*Ivanovo State University of Chemistry and Technology, Ivanovo, 153000, Russia*
[b]*Institute of Solution Chemistry, Russian Academy of Science, 153045, Ivanovo, Russia*
[@]*Corresponding author E-mail: syrbu@isuct.ru*

The condensation of biladiene-a,c dihydrobromides with benzaldehyde gives 5-phenylporphyrins. The reaction conditions have been studied and optimized; it is shown that synthesis of biladiene-a,c dihydrobromides can be combined with their following condensation with benzaldehyde.

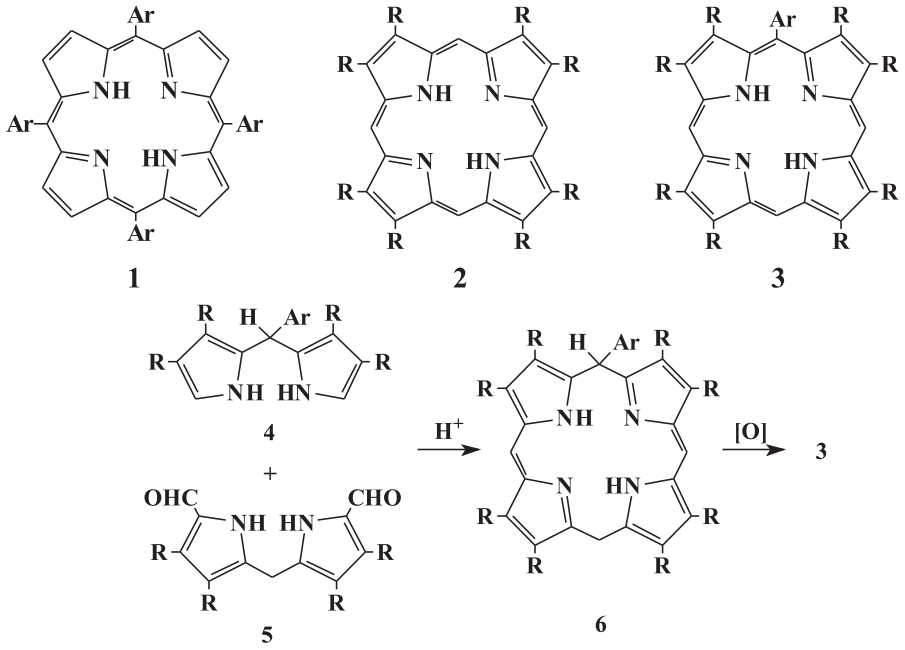
Keywords: 5-Arylporphyrins, biladiene-*a,c* dihydrobromides, benzaldehyde, condensation reaction.

Introduction

Investigation of porphyrins, that are widely present in the nature, is often carried out with the use of their synthetic analogs as model compounds. *meso*-Tetraarylporphyrins **1** containing different substituents on the phenyl rings can be easily prepared by condensation reaction of pyrrole with corresponding benzaldehydes in the acidic media.[1-3] Unlike natural species, *meso*-tetraarylporphyrins don't have any alkyl or pseudoalkyl substituents in the β-positions of porphyrin macrocycle but, oppositely, have aryl rings in the *meso*-positions which can contain different active substituents allowing their further structural modification. On the other hand, β-octaalkylporphyrins **2**, being also available, contain no active groups what makes difficult their modification. That's why the porphyrins, combining the advantages of these two classes of porphyrins (*i.e.* 5-aryloctaalkylporphyrins **3**) are of great interest.

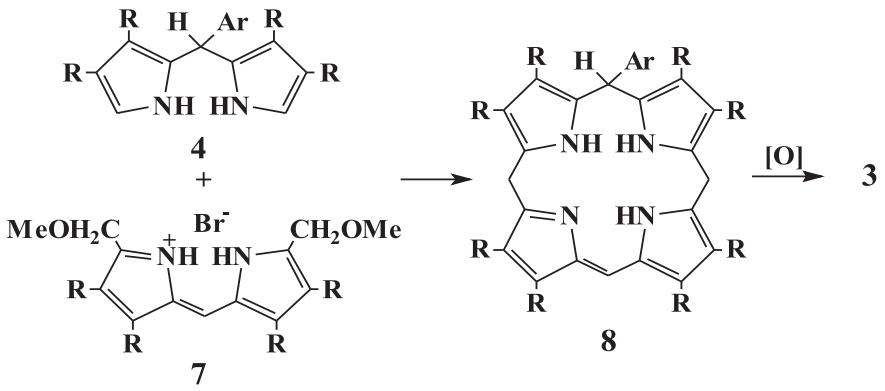
Presently several synthetic methods for 5-aryloctaalkylporphyrins **3** are known. One of the approaches is condensation of *meso*-aryl-3,3',4,4'-tetraalkyldipyrrolylmethanes **4** with 5,5'-diformyl-3,3',4,4'- tetraalkyldipyrrolylmethanes **5** in CH_3OH or CH_2Cl_2 under the action of strong acids (HI, $HClO_4$ or *p*-toluenesulfonic acid)[4-9] (Scheme 1). In this reaction atmospheric oxygen or derivatives of benzoquinone with electron-withdrawing substituents (*p*- or *o*-chloranil, 2,3-dichloro-5,6-dicyanobensoquinone (DDQ)) act as oxidizers of the intermediate porphodimethene **6**.

In a similar manner 5-aryloctaalkylporphyrins can be obtained by condensation of *meso*-aryl substituted dipyrrolylmethanes **4** with hydrobromides of 5,5'-dimethoxymethyl-3,3',4,4'-tetraalkyldipyrrolylmethenes **7** in refluxing benzene with following oxidation of the intermediate product **8** by benzoquinone derivatives (Scheme 2).[10]



Scheme 1.

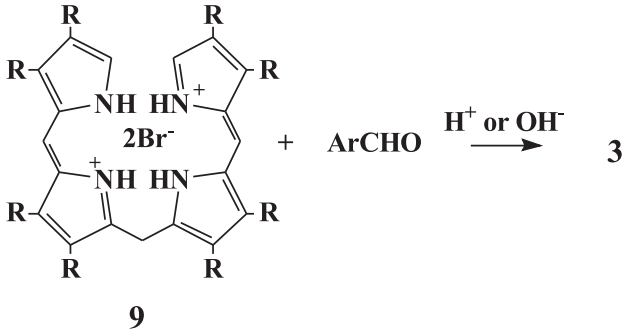
[⊗] Paper 1. Syrbu S.A., Lubimova T.V., Semeikin A.S. *Khim. Geterotsikl. Soedin.* **2004**, 1464-1472.



Scheme 2.

However this method is complicated by the formation of rather great quantity of octaalkylporphyrins unsubstituted in *meso*-positions.[10]

Another method widely used in the synthesis of 5-aryloctaalkylporphyrins **3** is the condensation reaction of benzaldehydes with 1,19-unsubstituted biladienes-*a,c* in alcholols catalized by acids[9, 11-14] or bases[15] (Scheme 3).



Scheme 3.

The goal of the present work was optimization of syntesis of 5-aryloctaalkylporphyrins **3** by condensation of biladienes-*a,c* **9** with benzaldehydes. The condensation reaction of dihydrobromides of 2,3,7,13,17,18-hexamethyl-8,12-diethylbiladienes-*a,c* **12** (R = R_1 = Me; R_2 = Et) and 8,12-dibuthyl-2,3,7,13,17,18-hexamethylbiladienes-*a,c* **12** (R = R_1 = Me; R_2 = Bu) with benzaldehydes was chosen as a model reaction (Scheme 4).

Experimental part

The UV-vis spectra were recorded on Lambda 20 spectrophotometer. ^{1}H NMR spectra were measured in $CDCl_3$ on Bruker AC-200 spectrometer. The purity and individuality of substances were established by thin layer chromotography (Silufol). The data of elemental analyses corresponded closely to the calculated values.

Syntheses

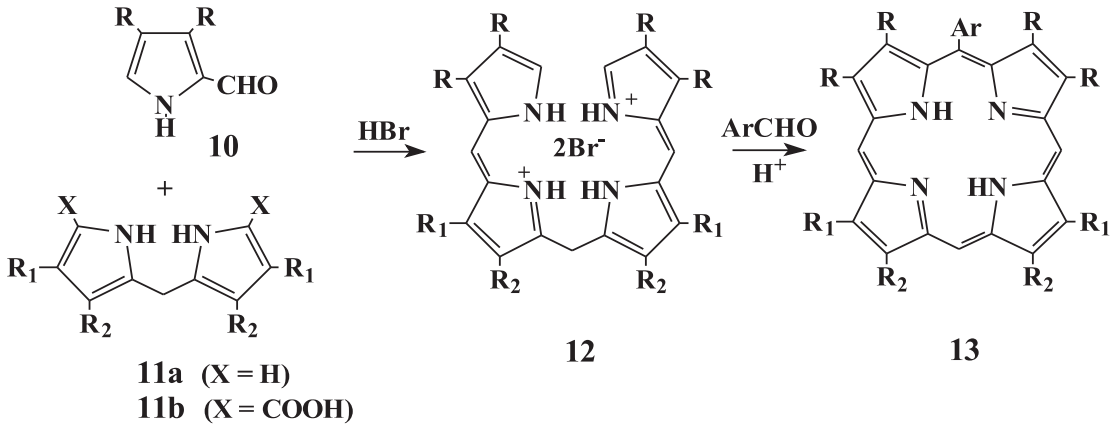
3,3'4,4'-Tetraalkyldipyrrolylmethanes ***11a***.

3,3'-Dimethyl-4,4'-diethyldipyrrolylmethane ***11a*** (R_1 = Me; R_2 = Et). The mixture of 5,5'-dicarbethoxy-3,3'-dimethyl-4,4'-diethyldipyrrolylmethane[16] (5 g, 13.4 mmol), KOH (5 g, 89.3 mmol) and ethylene glycol (50 ml) was refluxed during 1 hour. Then the solution was poured into 200 ml of water; the precipitate was filtered, washed with water and dried at room temperature. Yield 2.7 g (88%).

3,3',4,4'-Tetramethyldipyrrolylmethane ***11a*** (R_1 = R_2 = Me) and *4,4'-dibutyl-3,3'-dimethyl-dipyrrolylmethane* ***11a*** (R_1 = Me; R_2 = Bu) were prepared in the same way using 5,5'-dicarbethoxy-3,3',4,4'-tetramethyldipyrrolylmethane[16] (yield 89%) and 5,5'-dicarbethoxy-4,4'-dibutyl-3,3'-dimethyldipyrrolylmethane[16] (yield 91%), correspondingly.

5,5'-Dicarboxy-3,3'4,4'-tetraalkyldipyrrolylmethanes ***11b***.

5,5'-Dicarboxy-3,3'-dimethyl-4,4'-diethyldipyrrolylmethane ***11b*** (R_1 = Me; R_2 = Et) The solution of 5,5'-dicarbethoxy-3,3'-dimethyl-4,4'-diethyldipyrromethane[16] (5 g, 13.4 mmol) and potassium hydroxide (5 g, 89.3 mmol) in MeOH was refluxed during



Scheme 4.

4 hours. Then the mixture was poured into 200 ml of water and slightly acidified by 5% HCl. The precipitate was filtered, washed by water and dried at room temperature. Yield 3.8 g (89%).

5,5'-Dicarboxy-3,3',4,4'-tetramethyldipyrrolyl-methane ***11b*** (R_1 = R_2 = Me) and *5,5'-dicarboxy-4,4'-dibutyl-3,3'-dimethyldipyrrolylmethane* ***11b*** (R_1 = Me; R_2 = Bu) were obtained in a similar way using 5,5'-dicarbethoxy-3,3',4,4'-tetramethyldipyrrolylmethane[16] (yield 92%) and 5,5'-dicarbethoxy-4,4'-dibuthyl-3,3',4,4'-tetramethyldipyrrolylmethane[16] (yield 87%), correspondingly.

2,3,7,8,12,13,17,18-Octaalkylbiladiene-a,c dihydrobromides ***12***.

Method A.

2,3,7,13,17,18-Hexamethyl-8,12-diethylbiladiene-a,c dihydrobromide ***12*** (R = Me; R_1 = Me; R_2 = Et). Concentrated HBr (2 ml) was added into solution of 5,5'-dicarboxy-3,3'-dimethyl-4,4'-diethyldipyrromethane (3 g, 9.43 mmol) and 2-formyl-3,4-dimethylpyrrole[17] (2.3 g, 18.9 mmol) in MeOH (50 ml) and the mixture was stirred 1 hour. The dark-violet crystal precipitate was washed with MeOH, ether and dried at room temperature. Yield 5.1 g (90%).

The same procedure was carried out for the syntheses of *7,8,12,13-tetramethylbiladiene-a,c dihydrobromide* ***12*** (R = H; R_1 = R_2 = Me) from 5,5'-dicarboxy-3,3',4,4'-tetramethyldipyrrolylmethane and 2-formylpyrrole (90% yield);

7,13-dimethyl-8,12-diethylbiladiene-a,c dihydrobromide ***12*** (R = H; R_1 = Me; R_2 = Et) from 5,5'-dicarboxy-3,3'-dimethyl-4,4'-diethyldipyrromethane and 2-formylpyrrole (87%);

2,3,7,8,12,13,17,18-octamethylbiladiene-a,c dihydrobromide ***12*** (R = R_1 = R_2 = Me) from 5,5'-dicarboxy-3,3',4,4'-tetramethyldipyrrolylmethane and 2-formyl-3,4-dimethylpyrrole (70%);

8,12-dibutyl-2,3,7,13,17,18-hexamethylbiladiene-a,c dihydrobromide ***12*** (R = R_1 = Me; R_2 = Bu) from 5,5'-dicarboxy-3,3'-dibutyl-4,4'-dimethylpyrrolyl-methane and 2-formyl-3,4-dimethylpyrrole (85%).

Method B.

2,3,7,13,17,18-Hexamethyl-8,12-diethylbiladiene-a,c dihydrobromide ***12*** (R = Me; R_1 = Me; R_2 = Et). 4,4'-Dimethyl-3,3'-diethyldipyrrolylmethane (2.6 g, 11.3 mmol) and 2-formyl-3,4-dimethylpyrrole (2.8 g, 22.8 mmol) were dissolved in 70 ml MeOH at stirring, then conc. HBr (3.5 ml) was added. The mixture was stirred for 1 hour at room temperature. The precipitate, containing biladiene, was filtered, washed with MeOH and ether and dried. Yield 6.2 g (91%). UV-vis λ_{max} ($CHCl_3$) nm (lgε): 451 (4.77), 521 (5.15).

The same procedure was carried out for the syntheses of *8,12-dibutyl-7,13-dimethylbiladiene-a,c dihydrobromide* ***12*** (R = H; R_1 = Me; R_2 = Bu) using 4,4'-dibutyl-3,3'-dimethyldipyrrolylmethane and 2-formylpyrrole (yield 71%);

2,3,7,8,12,13,17,18-octamethylbiladiene-a,c dihydrobromide ***12*** (R = R_1 = R_2 = Me) from 3,3',4,4'-tetramethyldipyrrolylmethane and 2-formyl-3,4-dimethylpyrrole (72%);

8,12-dibutyl-2,3,7,13,17,18-hexamethylbiladiene-a,c dihydrobromide ***12*** (R = R_1 = Me; R_2 = Bu) from 3,3'-dibuthyl-4,4'-dimethyldipyrrolylmethane and 2-formyl-3,4-dimethylpyrrole (84%). UV-vis λ_{max} ($CHCl_3$) nm (lgε): 452 (4.79); 522 (5.10).

5-Phenyl-2,3,7,8,12,18-hexamethyl-13,17-diethylporphyn ***13*** (Ar = Ph; R = R_1 = Me; R_2 = Et)

Method A. The mixture of biladiene **12** (R = R_1 = Me; R_2 = Et) (0.25 g, 0.415 mmol), benzaldehyde (0.5 ml, 4.5 mmol), HBr (0.5 ml) and MeOH (50 ml) was refluxed with stirring during 4 hours. Then iodine (0.05 g, 0.20 mmol) was added and the mixture was refluxed for 15 min. The solution was poured into 200 ml of cold water and neutralized by aqueous NH_3 solution. The precipitate was filtered, washed with water and dried at 70°C. The product was purified by column chromotography on Al_2O_3 (Brockmann III degree, eluent-$CHCl_3$). The first fraction containing porphyrin was collected and its volume was reduced to 5 ml solution, and the porphyrin was precipitated by methanol (30 ml). Yield 113 mg (52%).

Method B. To the solution of 4,4'-dimethyl-3,3'-diethyldipyrrolylmethane (1.1 g, 4.78 mmol) and 2-formyl-3,4-dimethylpyrrole (1.2 g, 9.76 mmol) in MeOH (50 ml) conc. HBr (3 ml) was added at stirring. The mixture was stirred at room temperatrure for 1 hour, then benzaldehyde (5.8 ml, 57.4 mmol) was added. The resulting solution was heated and refluxed for 4 hours. After cooling aqueou NH_3 solution (3 ml) was added. The precipitate was filtered, dried, dissolved in $CHCl_3$ and purified by chromotography on Al_2O_3 (Brockmann II degree). The porphyrin fraction was concentrated and the product was precipitated by MeOH. Yield 1.2 g (48%).

The other porphyrins with electron-donating substituents were prepared analogously (Table 1).

5-(4'-Nitrophenyl)-2,3,7,8,12,18-hexamethyl-13,17-diethylporphin ***13*** (Ar = 4-$PhNO_2$; R = R_1 = Me; R_2 = Et).

Method A. The mixture of biladiene **12** (R = R_1 = Me; R_2 = Et) (0.25 g, 0.415 mmol), 4-nitrobenzaldehyde (0.75 g, 5 mmol), HBr (0.5 ml) and BuOH (50 ml) was refluxed for 4 hours; then iodine (0.05 g, 0.20 mmol) was added and the mixture was allowed to reflux for 15 min more. Then the mixture was poured into 200 ml of water, BuOH was distilled away with water steam. The precipitate formed was filtered, washed with water and dried at 70°C. Dry product was dissolved in $CHCl_3$ and purified by column chromotography on Al_2O_3 (Brockmann III degree, eluent-$CHCl_3$). The first porphyrin containing fraction was collected, reduced to 5 ml solution and the porphyrin was precipitated by 30 ml of MeOH. Yield 90 mg (38%).

Method B. To the solution of 4,4'-dimethyl-3,3'-diethyldipyrrolylmethane (0.6 g, 2.6 mmol) and 2-formyl-3,4-dimethylpyrrole (0.64 g, 5.2 mmol) in 30 ml of BuOH conc. HBr (3.0 ml) was added at stirring (the precipitate of biladiene has been formed). After 40 min 4-nitrobenzaldehide (2.0 g, 13.2 mmol) was added and the resulting mixture was refluxed for 4 hours. Then the mixture was cooled, diluted with water, and BuOH was distilled away with water steam. The precipitate was filtered, washed with water, dried on air at 70°C. The product was dissolved in $CHCl_3$ and purified by column chromotography on Al_2O_3 (Brockmann II degree, eluent-$CHCl_3$). The eluate was evaporated and the porphyrin was precipitated by MeOH, filtered and washed with MeOH and dried on the air at 70°C. Yield 0.52 g (35%).

The other porphyrins with electron-withdrawing substituents were prepared analogously (Table 1).

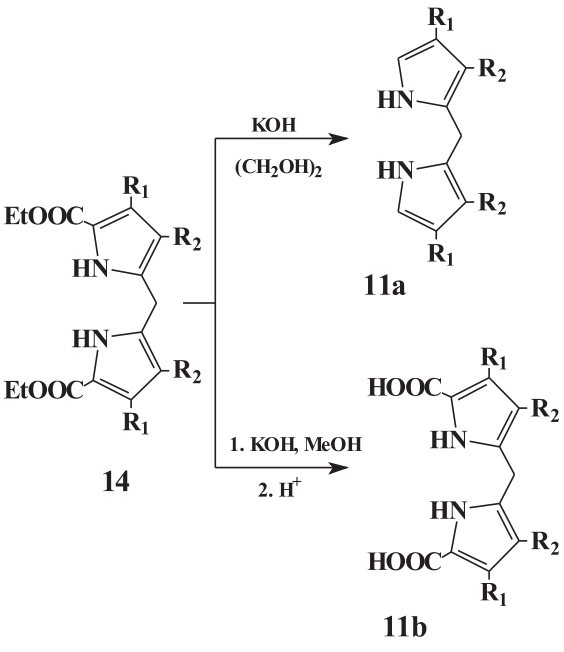
Results and Discussion

The initial biladienes-*a,c* **12** (R = R_1 = Me; R_2 = Et) and **12** (R = R_1 = Me; R_2 = Bu) were obtained by condensation of α-unsubstituted dipyrrolylmethanes **11a** (X = H) or their 5,5'-dicarboxy derivatives **11b** (X = COOH) with 2-formyl-3,4-dimethylpyrrole **10** (R = Me) in CH_3OH in the presence of HBr as an acidic catalyst. 5,5'-Dicarboxydipyrrolylmethanes **11b** were previously obtained by hydrolysis of 5,5'-dicarbethoxydipyrrolylmethanes **14** in KOH-CH_3OH solution; and 5,5'-unsubstituted dipyrrolylmethanes **11a** were prepared by hydrolysis of **14** accompanied by decarboxylation in solution of KOH in ethylene glycol (Scheme 5). The both derivatives give biladienes-*a,c* with practically the same yield. It should be noted that the carboxy derivatives **11b** are quite stable and can be stored for some

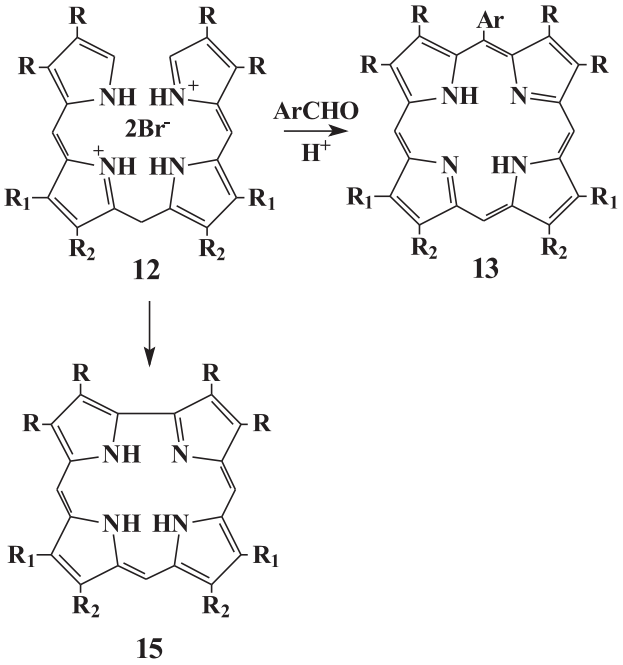
Table 1. Influence of the reaction conditions on the yield of 5-phenyloctaalkylporphyrins **13** (R = R_1 = Me; R_2 = Bu)

Ar	solvent	catalyst	oxidizer	yield (%)
4-methoxyphenyl	EtOH	-	-	51.2
	EtOH	-	iodine	57.0
	EtOH	Py	iodine	22.7*
	EtOH	HBr	iodine	60.1
	MeOH	HBr	iodine	63.2
	MeOH	HBr	*o*-chloranil	55.9
	BuOH	Py	-	16.7*
	BuOH	HBr	-	29.7
	BuOH	HBr	iodine	53.3
	acetic acid	-	iodine	6.3
	$CHCl_3$	HBr	*o*-chloranil	6.5
	DMSO (100^0)	-	-	0
2-methoxyphenyl	MeOH	HBr	iodine	45.9
4-nitrophenyl	MeOH	HBr	iodine	15.4*
	EtOH	HBr	iodine	17.0*
	PrOH	HBr	iodine	26.7*
	BuOH	-	-	13.6*
	BuOH	Py	-	19.3*
	BuOH	HBr	-	20.0*
	BuOH	HBr	iodine	25.3*
	pentanol	HBr	-	19.4*
	pentanol	HBr	iodine	33.2*
	acetic acid	-	-	19.8*
	Py	-	-	16.2*
	xylene	$ClCH_2COOH$	-	11.3*
	DMSO(100^0)	-	-	10.9*
3- nitrophenyl	BuOH	HBr	iodine	16.5*
2- nitrophenyl	BuOH	HBr	iodine	18.0*

* - the parallel formation of corrole **15** (R = R_1 = Me; R_2 = Bu)



Scheme 5.



Scheme 6.

time unlike to unstable α-unsubstituted dipyrrolylmethanes **11a**, which should be used immediately after their synthesis. However, the preparation of the latter is more simple to execute experimentally**.**

We have found, that condensation of biladienes-*a,c* **12** with benzaldehydes proceeds with best results in alcohols (Table 1). The addition of mineral acid (HBr), which should suppress the porphyrin formation, on the contrary, increases the yield of 5-arylporphyrins **13**, whereas the presence of the base (pyridine) decreases the porphyrin yield and the corresponding corrole **15** is always formed (Scheme 6). The ratio of porphyrin and corrole yields seems to be determined by relative rates of these competitive reactions. The proceeding of the reaction in acetic acid, as well as in chloroform, decreases drastically the porphyrin yield. In the highly polar solvent such as DMSO no porphyrin formation is observed. The addition of oxidizer agent to the reaction mixture influences the yield of the product as well.

The study of the conditions of condensation reaction of **12** (R = R_1 = Me; R_2 = Et) with *p*-anisaldehyde (Scheme 4) has shown that the yield of porphyrin **13** (R = R_1 = Me; R_2 = Et; Ar = 4-methoxyphenyl) is increased with the reaction duration; but after the 4 hours the yield is diminished possibly due to the oxidation processes which begin to dominate over the porphyrin formation (Figure 1).

It was found that the highest yield of porphyrin **13** is observed when 12-fold excess of benzaldehyde over biladiene-*a,c* **12** is used (Figure 2). So, the large excess of benzaldehyde is needed to suppress the formation of corrole **15** (R = R_1 = Me; R_2 = Et).

So, the optimal conditions for the synthesis of porphyrin **13** is condensation of biladiene-*a,c* **12** with 12-fold excess of benzaldehyde in MeOH during 4 hours in the presence of HBr addition and the equimolar quantity of iodine as oxidizing agent.

We have also studied the influence of position and electronic effects of the substituents in the benzaldehydes on the yield of porphyrin **13.** It was found that the highest yield is observed in the case of *p*-substituted benzaldehydes. The decreasing of yield, when *o*-substituted benzaldehydes are used, is explained by the steric factors of *o*-substituents in the condensation reaction. The decreasing of the porphyrin **13** yield in the case of some *m*-substituted species is still not fully clear (Tables 1, 2). The use of benzaldehydes with electron-withdrawing substituents results in drastic decreasing of the porphyrin **13** yields and formation of corroles **15** as by-products. However, the reaction in more highly boiling butanol enhances the yield and allows to avoid formation of corroles.

Using the methods devised we have also synthesized the porphyrins containing four alkyl substituents in the β-positions of the porphyrin macrocycle **13** (R = H) (Scheme 4). The yields of these porphyrins is much more lower then of their octaalkyl analogs **13** (R = Me), which can be connected with the decreasing of the electron-donating influence of alkyl groups.

The yields and some properties of the obtained porphyrins **13** are presented in Tables 2 and 3.

The long-wave shift of *ca.* 4-5 nm of all bands and considerable decreasing of intensity of I and III bands are observed in the UV-vis spectra of porphyrins **13** (Table 2) if compared with that of octaalkylporphyrins unsubstituted on *meso*-positions. This can be caused by electron-withdrawing influence of aryl substituent or porphyrin macrocycle distortion owing to aryl substituent.

Since synthesis of dihydrobromides of biladienes-*a,c* and their following condensation proceed in the similar conditions using alcohol as the solvent, we have carried out the one-pot synthesis of porphyrins **13** using dipyrrolylmethanes and formylpyrroles without isolation of intermediate biladienes-*a,c*. This approach allows simplification of the synthetic procedure and reduces the reaction time with practically the same yields relative to the initial reagents.

Acknowledgements. This work was supported by Russian Foundation of Basic Research (Grant 07-03-00818) and Program for leading scientific schools.

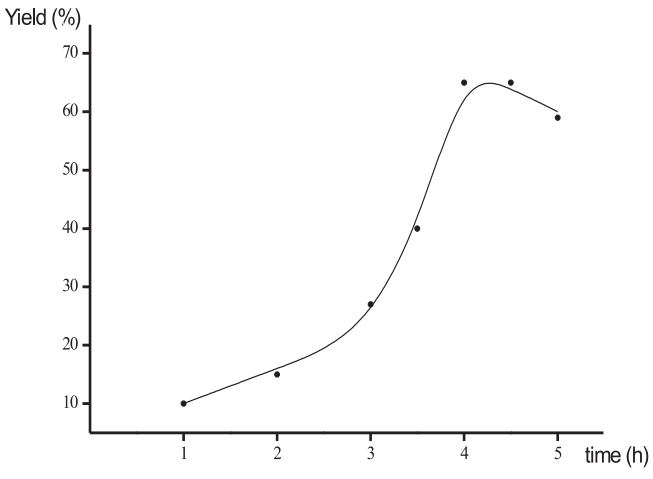


Figure 1. The dependence of porphyrin **13** (R = R_1 = Me; R_2 = Et; Ar = 4-methoxyphenyl) yield on the duration of condensation of biladiene-*a,c* dihydrobromide **12** (R = R_1 = Me; R_2 = Et) in 10-fold excess of anisaldehyde in MeOH.

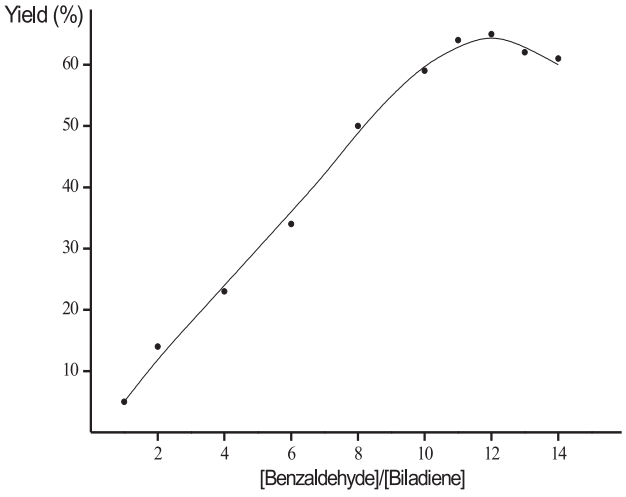


Figure 2. The dependence of the yield of porphyrin **13** (R = R_1 = Me; R_2 = Et; Ar = 4-methoxyphenyl) on the concentration ratio of anisaldehyde and dihydrobromide of biladiene-*a,c* **12** (R = R_1 = Me; R_2 = Et) in MeOH during 4 hours reaction.

Table 2. The yields and some properties of porphyrins **13.**

Nr.	Porphyrin **13**					
	Ar	R	R_1	R_2	Yield (%)*	R_f** Silufol
1	H	H	Me	Me	7.2	0.26 (benzene-heptane 2:1)
2	phenyl	H	Me	Me	14.0	0.78 ($CHCl_3$) 0.15 (benzene-heptane 2:1)
3	H	H	Me	Et	6.8	
4	phenyl	H	Me	Et	11.0(10.6)	
5	4-methoxyphenyl	H	Me	Et	13.0(13.8)	
6	3-nitrophenyl	H	Me	Et	11.0(14.9)**	
7	H	H	Me	Bu	13.5	
8	phenyl	H	Me	Bu	27.0	
9	2-methoxyphenyl	H	Me	Bu	25.0	0.19 (benzene-heptane 2:1)
10	4-methoxyphenyl	H	Me	Bu	43.0	0.75 ($CHCl_3$)
11	2-nitrophenyl	H	Me	Bu	7.6**	0.34 ($CHCl_3$)
12	3-nitrophenyl	H	Me	Bu	16.0**	0.80 ($CHCl_3$)
13	4-nitrophenyl	H	Me	Bu	14.0**	0.30 (benzene-heptane; 2:1)
14	4-pyridyl	H	Me	Bu	10.3	0.20 ($CHCl_3$)
15	phenyl	Me	Me	Me	56.2	0.27 ($CHCl_3$) 0.65 (benzene)
16	H	Me	Me	Me	18.0	
17	4-methoxyphenyl	Me	Me	Me	35.0	
18	4-nitrophenyl	Me	Me	Me	17.0	0.24 (benzene)
19	H	Me	Me	Et	22.3	
20	phenyl	Me	Me	Et	52.0	0.30 (benzene)
21	2-methoxyphenyl	Me	Me	Et	65.0	0.40 (benzene)
22	3-methoxyphenyl	Me	Me	Et	48.0	0.48 (benzene)
23	4-methoxyphenyl	Me	Me	Et	74.0(65.6)	0.45 (benzene)
24	2-nitrophenyl	Me	Me	Et	17.0	0.27 (benzene)
25	3-nitrophenyl	Me	Me	Et	27.0(35.0)**	0.42 (benzene)
26	4-nitrophenyl	Me	Me	Et	38.0(35.0)**	0.41 (benzene)
27	4-pyridyl	Me	Me	Et	20.0(27.7)**	
28	H	Me	Me	Bu	38.2	0.87 ($CHCl_3$) 0.37 (benzene-heptane; 2:1)
29	phenyl	Me	Me	Bu	43.5	0.81 ($CHCl_3$) 0.32 (benzene-heptane; 2:1)
30	2-methoxyphenyl	Me	Me	Bu	47.7	0.29 ($CHCl_3$)
31	3-methoxyphenyl	Me	Me	Bu	20.2	0.67 ($CHCl_3$)
32	4-methoxyphenyl	Me	Me	Bu	60.6	0.89 ($CHCl_3$)
33	2-nitrophenyl	Me	Me	Bu	25.5**	0.66 ($CHCl_3$)
34	3-nitrophenyl	Me	Me	Bu	51.0**	0.53 ($CHCl_3$)
35	4-nitrophenyl	Me	Me	Bu	48.0**	0.81 ($CHCl_3$)
36	4-pyridyl	Me	Me	Bu	12.6**	0.95 ($CHCl_3$-CH_3OH; 5:1)
37***	-	H	Me	Bu		
38***	-	Me	Me	Me		0.45 ($CHCl_3$)
39***	-	Me	Me	Et		
40***	-	Me	Me	Bu		0.28 ($CHCl_3$)

* - the yield in brackets is given for synthesis without isolation of intermediate biladiene
** - the reaction was carried out in BuOH

UV-vis spectra in $CHCl_3$: λ_{max}/nm (lgε)				
I	**II**	**III**	**IV**	**Soret**
616(3.20)	564(3.56)	528(3.54)	495(3.91)	397(5.08)
623(3.20)	570(3.80)	532(3.63)	501(4.20)	404(5.39)
621(3.39)	569(3.86)	531(3.73)	499(4.24)	403(5.38)
621(3.21)	570(3.80)	531(3.63)	501(4.20)	405(5.36)
622(3.32)	570(3.81)	533(3.69)	501(4.19)	404(5.26)
618(3.24)	564(3.57)	530(3.54)	496(4.00)	398(5.16)
623(3.18)	570(3.79)	534(3.62)	501(4.20)	404(5.39)
623(3.30)	570(3.85)	534(3.71)	501(4.26)	405(5.44)
623(3.23)	571(3.83)	534(3.65)	502(4.24)	406(5.43)
624(3.36)	571(3.83)	535(3.72)	503(4.21)	405(5.33)
623(3.32)	570(3.84)	535(3.72)	502(4.23)	406(5.32)
624(3.36)	571(3.83)	537(3.76)	504(4.21)	405(5.26)
623(3.34)	570(3.82)	534(3.72)	502(4.20)	404(5.38)
624(3.45)	571(3.81)	537(3.85)	504(4.16)	404(5.26)
620(3.65)	568(3.68)	535(3.96)	500(4.60)	400(5.61)****
623(3.56)	571(3.84)	538(3.86)	504(4.21)	405(5.28)
624(3.57)	572(3.81)	537(3.85)	504(4.11)	402(5.15)
620(3.73)	568(3.81)	533(3.96)	498(4.10)	398(5.12)
623(3.51)	571(3.83)	536(3.86)	502(4.15)	403(5.22)
624(3.54)	571(3.85)	537(3.89)	504(4.19)	404(5.28)
623(3.52)	571(3.86)	537(3.90)	504(4.19)	404(5.28)
623(3.47)	571(3.83)	537(3.86)	503(4.17)	404(5.33)
627(3.48)	574(3.81)	539(3.81)	506(4.19)	404(5.21)
624(3.56)	573(3.87)	538(3.94)	505(4.20)	403(5.22)
624(3.50)	573(3.82)	537(3.87)	505(4.15)	403(5.18)
623(3.65)	571(3.92)	536(3.98)	503(4.25)	403(5.33)
620(3.78)	566(3.87)	533(4.04)	498(4.17)	398 (5.22)
624(3.51)	571(3.85)	538(3.89)	504(4.20)	404(5.29)
624(3.54)	571(3.85)	537(3.90)	504(4.18)	405(5.27)
624(3.48)	571(3.85)	538(3.88)	505(4.20)	406(5.30)
627(3.49)	574(3.74)	539(3.79)	506(4.06)	404(5.09)
626(3.57)	573(3.86)	539(3.94)	506(4.20)	404(5.22)
624(3.54)	573(3.86)	538(3.90)	506(4.20)	404(5.22)
624(3.56)	573(3.86)	538(3.93)	504(4.20)	404(5.29)
595(4.23)	550(4.17)	-	-	397(5.13)
593(4.14)	549(4.11)	539(4.13)	shoulder	396(5.06)
593(4.06)	shoulder	537(4.04)	shoulder	397(4.99)
593(4.29)	550(4.22)	537(4.23)	shoulder	397(5.16)

*** - corroles **15**
**** - trichloroethylene

Table 3. The data of ^{1}H NMR spectra of porphyrins **13**, δ, ppm ($CDCl_3$).

Nr.	Ar	R	R_1	R_2	*meso*-CH	NH
2	8.18m (2H) *o*-H 7.74m (3H) *m,p*-H	8.96d (2H) 9.20d (2H)	3.48s (12H)	3.48s (12H)	10.02s (2H) 9.83s (1H)	-3.45bs (2H)
4	8.25m (2H) *o*-H 7.78m (2H) *m,p*-H	9.29d (2H) 9.04d (2H)	3.62s (6H)	4.04q (4H) CH_2 1.89t (6H) CH_3	10.16s (2H) 10.03s (1H)	-3.37bs (2H)
8	8.25m (2H) *o*-H 7.79m (3H) *m,p*-H	9.02d (2H) 9.29d (2H)	3.61s (6H)	4.04q (4H) CH_2 2.28qv (4H) CH_2 1.75sc (4H) CH_2 1.13t (6H) CH_3	10.14s (2H) 10.01s (1H)	-3.38bs (2H)
9	8.01d (1H) 6-H 7.78t (1H) 5-H 7.37t (2H) 3,4-H	8.95d (2H) 9.26d (2H)	3.60s (6H)	4.04t (4H) CH_2 2.28qv (4H) CH_2 1.75sc (4H) CH_2 1.12t (6H) CH_3	10.12s (2H) 10.00s (1H)	-3.39bs (2H)
11	8.42m (1H) 6H 8.29m (1H) 5-H 7.96m (2H) 3,4-H	8.81d (2H) 9.28d (2H)	3.59s (6H)	4.04t (4H) CH_2 2.28qv (4H) CH_2 1.74sc (4H) CH_2 1.12t (6H) CH_3	10.14s (2H) 10.04s (1H)	-3.39bs (2H)
13	8.62d (2H) *o*-H 8.42d (2H) *m*-H	8.91d (2H) 9.33d (2H)	3.60s (6H)	4.03t (4H) CH_2 2.28qv (4H) CH_2 1.79sc (4H) CH_2 1.13t (6H) CH_3	10.12s (2H) 10.05s (1H)	-3.46bs (2H)
15	8.03m (2H) *o*-H 7.76m (3H) *m,p*-H	2.46s (6H) 3.51s (6H)	3.58s (6H)	3.61s (6H)	10.13s (2H) 9.92s (1H)	-3.20bs (1H) -3.30bs (1H)
17*	8.96d (2H) *o*-H 8.51d (2H) *m*-H 4.12s (3H) OCH_3	2.03s (6H) 3.14s(12H)	3.14s (12H)	3.19s (6H)	10.09s (2H) 9,90s (1H)	-2.85bs (4H)
20	8.03d (2H) *o*-H 7.75m (3H) *m,p*-H	2.43s (6H) 3.52s (6H)	3.63s (6H)	4.04q (4H) CH_2 1.86t (6H) CH_3	10.15s (2H) 9.94s (1H)	-3.28bs (2H)
25	8.99s (1H) 2-H 8.64d (1H) 4-H 8.48d (1H) 6-H 7.93t (1H) 5-H	2.40s (6H) 3.53s (6H)	3.64s (6H)	4.12q (4H) CH_2 1.88t (6H) CH_3	10.18s (2H) 9.99s (1H)	-3.33bs (2H)
32*	8.15d (2H) *o*-H 7.42d (2H) *m*-H 4.10s (3H) OCH_3	2.20s (6H) 3.19s (6H)	3.48s (6H)	3.92t (4H) CH_2 2.05qv (4H)CH_2 1.62sc (4H)CH_2 1.02t (6H) CH_3	10.22s (2H) 10.05s (1H)	-1.34s (2H) -2.72s (2H)
33	8.37d (2H) *o*-H 7.94m (3H) *m,p*-H	2.43s (6H) 3.51s (6H)	3.60s (6H)	4.02t (4H) CH_2 2.25qv (4H) CH_2 1.76sc (4H) CH_2 1.10t (6H) CH_3	10.13s (2H) 9.94s (1H)	-3.23bs (2H)
34	8.98s (1H) *o*-H 8.67d (1H) *p*-H 8.36d (1H) *o*-H 7.90t (1H) *m*-H	2.39s (6H) 3.52s (6H)	3.62s (6H)	4.03t (4H) CH_2 2.27qv (4H) CH_2 1.78sc (4H) CH_2 1.12t (6H) CH_3	10.16s (2H) 9.97s (1H)	-3.25bs(2H)
35*	8.73d (2H) *o*-H 8.57d (2H) *m*-H	2.18s (6H) 3.22s (6H)	3.50s (6H)	3.94t (4H) CH_2 2.04qv (4H) CH_2 1.58sc (4H) CH_2 1.00t (6H) CH_3	10.31s (2H) 10.17s (1H)	-1.53s (2H) -2.79s 5(2H)
40**	-	3,14s (6H) 3,25s (6H)	3.35s (6H)	3.80t (4H) CH_2 2.17qv (4H) CH_2 1.74sc (4H) CH_2 1.14t (6H) CH_3	8.98s (3H)	-3.96bs (3H)

* - in $CDCl_3$+5% trifluoroacetic acid
** - for corrole **15** (R = R_1 = Me; R_2 = Bu)

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