Palladium-catalyzed amination of dihalobenzenes

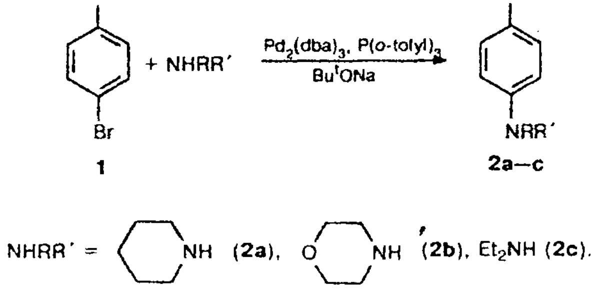
I. P. Beletskaya,[a]* *A. G. Bessmertnykh,*[a] *R. A. Mishechkin,*[a] *and R. Guilard*[b]*

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 939 3618. E-mail: beletska@org.chem.msu.su
[b]*Department of Science, University of Bourgogne,*
21100 Dijon, France.
Fax: 33 (3) 80396117. E-mail: rguilard@satie.u-bourgogne.fr

Amination of arenes as a result of a Pd-catalyzed reaction of amines with aryl halides or aryl triflates is currently an alternative to the Ullman reaction and one of the most interesting fields of metallocomplex catalysis. This is confirmed by the fact that more than 30 papers on this problem have been published over three years.[1—8]

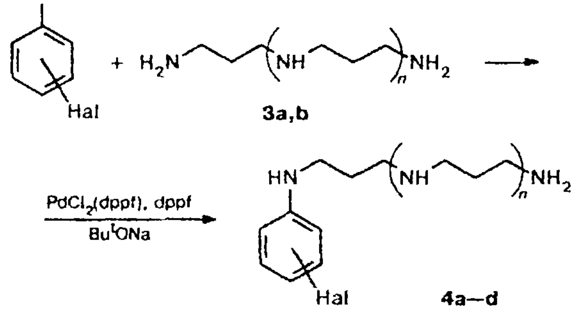
In continuation of our studies in the field of application of this reaction to the synthesis of arylated polyamines,[9] we considered the possibility of amination of dihalobenzenes. Earlier, it was shown that the reaction of dibromobenzenes with secondary cyclic diamines in the presence of $PdCl_2[P(o\text{-tolyl})_3]_2$ and sodium *tert*-butoxide can be used for the preparation of poly(aryleneamines).[10]

We demonstrated that *p*-dibromobenzene can be readily aminated with secondary cyclic amines (Pd_2dba_3 (0.2 mol. %), $P(o\text{-tolyl})_3$ (0.2 mol. %), and $NaOBu^t$; refluxing in dioxane for 20 h). Products of substitution of both bromine atoms (**2a,b**) are formed in high yields (~60%) in the presence of an excess of piperidine or morpholine. Amination of *p*-dibromobenzene with diethylamine, an acyclic secondary amine, proceeds more slowly to give a reaction mixture from which *p*-bis(diethylamino)benzene **2c** was isolated in 24% yield, and *p*-bromo-*N,N*-diethylaniline, a product of monosubstitution, was isolated in 23% yield. The lower reactivity of acyclic secondary amines compared to cyclic ones was noted earlier for amination of aryl halides.[7]



The reaction of *p*-dibromobenzene with 1 equiv. of piperidine results in the formation of a mixture of mono- and disubstituted products in the ratio of 1 : 1, which suggests that the monosubstituted compound is more reactive than the initial dibromide.

Arylation of monohalobenzenes by primary amines is well studied and proceeds with high yields. Our attempts to aminate *o*- and *p*-dibromobenzene and *p*-diiodobenzene with primary amines, *viz.*, butylamine and isopropylamine, under conditions that are optimum for the amination of monohalobenzenes ((dppf)$PdCl_2$ (dppf is 1,1′-bis(diphenylphosphino)ferrocene) (0.1%) and $NaOBu^t$; refluxing in dioxane for 20 h) unexpectedly failed: in all cases, the initial compound was recovered. Primary polyamines were more reactive under these conditions. The reaction of *p*- and *o*-dibromobenzenes with an excess of 1,3-diaminopropane or 3,3′-diaminodipropylamine in the presence of (dppf)$PdCl_2$ and $NaOBu^t$ occurs with substitution of only one bromine atom to give monoarylsubstituted polyamines **4a—d** in high yields. Amination of *p*-diiodobenzene under these conditions leads to similar products but in much lower yields (20—30%).



	4a	**4b**	**4c**	**4d**
Hal	*o*-Br	*o*-Br	*p*-Br	*p*-Br
n	0	1	0	1
Yield (%)	56	48	62	64

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1456—1457, July, 1998.

Thus, we have found the conditions for selective amination of dihalobenzenes with secondary cyclic amines and polyamines. The reactions studied do not cover all synthetic possibilities of the catalyzed amination in the series of polyhaloaromatic compounds. At present, the search for selective conditions of amination of these compounds with different amines is in progress.

References

1. A. S. Guram, R. A. Rennels, and S. L. Buchwald, *Angew. Chem., Int. Ed. Eng.*, 1995, **34**, 1348.
2. M. S. Driver and J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, **118**, 7217.
3. J. Louie, M. S. Driver, B. C. Hamann, and J. F. Hartwig, *J. Org. Chem.*, 1997, **62**, 1268.
4. J.-F. Marcoux, S. Wagar, and S. L. Buchwald, *J. Org. Chem.*, 1997, **62**, 1568.
5. J. P. Wolfe and S. L. Buchwald, *J. Org. Chem.*, 1996, **61**, 1133.
6. S. Wagar, R. A. Rennels, and S. L. Buchwald, *J. Am. Chem. Soc.*, 1997, **119**, 8451.
7. J. P. Wolfe and S. L. Buchwald, *J. Org. Chem.*, 1997, 1264.
8. S.-H. Zhao, A. K. Miller, J. Berger, and L. A. Flippin, *Tetrahedron Lett.*, 1996, **37**, 4463.
9. I. P. Beletskaya, A. G. Bessmertnykh, and R. Guilard, *Tetrahedron Lett.*, 1997, **38**, 2287.
10. T. Kanbara, A. Honma, and K. Hasegawa, *Chem. Lett.*, 1996, 1135.

Received February 6, 1998

Preparation of aqueous solutions of rare-earth element diphthalocyanines

P. N. Moskalev, A. I. Sibilev, and M. A. Sibileva*

B. N. Konstantinov St. Petersburg Nuclear Physics Institute, Russian Academy of Sciences,
188350 Gatchina, Leningrad Region, Russian Federation.
Fax: +7 (812) 713 6025. E-mail: moskalev@hep486.pnpi.spb.ru

Diphthalocyanines of rare-earth elements (REE) PcMPc$^{\cdot}$ (where Pc is the dianion of phthalocyanine $(C_{32}H_{16}N_8)^{2-}$, Pc$^{\cdot}$ is the monoanion-radical of phthalocyanine $(C_{32}H_{16}N_8)^{1-}$, and M is the REE cation in the oxidation state 3+) is characterized by the "sandwich" molecular structure.[1,2] They exhibit various properties and hence can be used in different areas of science and technology.[1,2] However, these compounds are insoluble in water, which restrict their field of application, especially as biologically active substances.[3] We found that complexes of REE diphthalocyanines with polyvinylpyrrolidone (PVP) with a molar ratio of the monomer unit of polyvinylpyrrolidone (—VP—) in PVP to REE diphthalocyanine >25 : 1 are soluble in water without limit, the value of characteristic viscosity in H_2O and D_2O, which is proportional to the specific volume of macromolecules in solutions, being 10% above this value for the initial PVP.

Complexes were synthesized as follows. PcTmPc$^{\cdot}$ powder (0.43 g) obtained according to a known procedure[4] was dissolved in 10 mL of DMF containing 1 vol.% of hydrazine hydrate at 100 °C for 30 min. A prepared solution of monoanion $(PcTmPc)^-$ was added to a solution of PVP (2.1 g, mol. weight 12400—2100) in 2 mL of DMF. The reaction mixture was concentrated in air at 70—80 °C to the consistency of a paste and heated *in vacuo* at 120—130 °C for 1 h. A dark blue friable substance (2.4 g) was obtained with the calculated molar ratio (—VP—) : thulium diphthalocyanine = 50 : 1. The electronic absorption spectrum of its aqueous solution in the range 400—800 nm exhibits a bifurcated Q band characteristic of the monoanion: Q′ (632 nm) and Q″ (710 nm), which is due to the resonance interaction of the equivalent chromophores of two Pc ligands in the diphthalocyanine anion.[2,5] Using this method, we prepared water-soluble complexes of lanthanide (from praseodymium to lutecium, except for promethium), scandium, and yttrium diphthalocyanines with PVP. Depending on the kind of REE in the diphthalocyanine or the solvent type, a weak indication of the state of the PcMPc$^{\cdot}$ radical, characterized by an unsplit Q band of the Pc ligand and poor absorption of the Pc$^{\cdot}$ radical in the range 400—500 nm, appear in the spectra of the complexes.[2,5] This can indicate the presence of the electron transfer state between the REE diphthalocyanine ion and PVP in the water-soluble complexes obtained. An increase in viscosity detected experimentally attests that the hydrodynamic sizes of polymeric molecules

---

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1458—1459, July, 1998.

1066-5285/98/4707-1417 $20.00