

Synthesis of Conjugated Materials for Organic Photovoltaics and Luminescence

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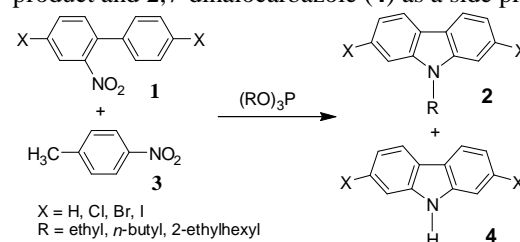
The conjugated organic polymers, polyelectrolytes and copolymers have become the theme of significant scientific and industrial research in recent years because of their application in organic electronics, such as organic light-emitting diodes, solar cells, and field-effect transistors. The synthesis of such polymers requires, among others, the organic syntheses and characterization of convenient monomers. In this contribution we report about our improvements in the preparation of monomers which are necessary in the syntheses of conjugated organic materials/polymers. From this point of view we will show and discuss several recently prepared materials in our laboratory, such as 2,7-dibromocarbazole or 3,8-dibromo-1,10-phenanthroline derivatives, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-bis(2-ethylhexyl)dibenzosilole, 9-(2,7-dibromocarbazol-9-yl)nonan-2,4-dionato-bis(2-phenylpyridine)iridium (III) complex-monomer, or 3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)dibenzothiophene-5,5-dioxide etc. New results will be presented and compared with those published recently.¹⁻³

As an example we developed new efficient synthesis of *N*-alkyl-2,7-dihalocarbazoles by simultaneous carbazole ring closure and *N*-alkylation. The *N*-alkyl-2,7-dihalocarbazole (**2**) as the main product was formed by the reaction of 4,4'-dihalo-2-nitrobiphenyl (**1**) with aromatic nitro compound (**3**) and trialkyl phosphite (**Table 1**). The presence and crucial role of aromatic nitro compound causes simultaneous carbazole ring closure and *N*-alkylation unlike the Cadogan ring closure where non-alkylated carbazole (**4**) is formed as a main product. In addition, the mixture of aromatic nitro compound and trialkyl phosphite was found to be a possible *N*-alkylating agent for heterocycles such as carbazole or indole. The prepared new materials **2a-m** were characterized by TLC, elemental analysis, melting point, ¹H and ¹³C NMR and FT IR. The non-alkylated carbazole derivatives **4** were identified by means of separately prepared 2,7-diiodocarbazole (**4a-c**), 2,7-dibromocarbazole (**4d-f**), 2,7-dichlorocarbazole (**4g-i**), and carbazole (**4j-m**). The yields of *N*-alkyl-2,7-dihalocarbazole varied between 40 – 80% depending on the alkyl phosphite and X-substituent. In the case of heavy halogen substituent (X = Br, I), the yield of **2** increases with a size of alkyl in the used alkyl phosphite (ethyl < butyl < 2-ethylhexyl). On the other hand, for relatively lightweight chlorine or hydrogen as substituents (X = Cl, H) the tendency seems to be opposite. Just the results gained with 2-nitrobiphenyl (X = H) indicate that the yields are more likely connected with the weight of X rather than with its electronegativity. The isolated yields of the side product **4** were found to be low (1 – 6%) and one could say negligible. Except the case of R = 2-ethylhexyl and X = Cl or H, where the yields for **4i** and **4m** were determined as 24 and 35%, respectively. It is not clear now why we recovered the 2,7-dihalocarbazole more efficiently just in these two cases although the reaction time here was even increased from 5

to 17 hours (**Table 1**). The 4,4'-dihalo-2-nitrobiphenyl and 4-nitrotoluene were mixed in molar ratio 1:1.5 for the best yield. More nitro compound did not increase the yield and moreover caused the problem in column chromatography. The trialkyl phosphite was used in 5 mol excess per both reaction components. It was more than theoretical value 3.5 mol (2 mols for ring closure + 1.5 mol for nitro compound) and adequate for reaction workup. More trialkyl phosphite caused problem in the next chromatographic separation and did not increase the yield. The excess of triethyl or tributyl phosphites was removed by vacuum distillation before chromatography. In the case of tris(2-ethylhexyl) phosphite (b.p. 446 °C) it was difficult and the reaction mixture had to be chromatographed without vacuum distillation. In the similar way we will report about new improvements in the organic synthesis of 3,8-dibromo-1,10-phenanthroline derivatives or iridium (III) complex-monomer.

Table 1.

Simultaneous carbazole ring closure and *N*-alkylation yielding the *N*-alkyl-2,7-dihalocarbazole (**2**) as a main product and 2,7-dihalocarbazole (**4**) as a side product



entry ^a	R	X	Yield (%) ^b	
			2	4
a	ethyl	I	38	1
b	<i>n</i> -butyl	I	44	1
c	2-ethylhexyl	I	60	5
d	ethyl	Br	57	3
e	<i>n</i> -butyl	Br	63	1
f	2-ethylhexyl	Br	70	6
g	ethyl	Cl	74	1
h	<i>n</i> -butyl	Cl	73	1
i	2-ethylhexyl	Cl	62	24
j	ethyl	H	81	2
k	<i>n</i> -butyl	H	82	2
m	2-ethylhexyl	H	48	35

^a Reaction condition: The 4,4'-dihalo-2-nitrobiphenyl and 4-nitrotoluene (1:1.5 by mol) were mixed under argon in trialkyl phosphite (5 mol excess per both reaction components) and heated at 160 °C for 5 h (**a-h**, **j**, **k**) or 17 h (**i**, **m**), and then chromatographed (Silica gel 60) in toluene/heptane (1:1 by vol.). ^b Isolated yields by column chromatography.

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