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Synthesis of some polycyclic aryls by haloaryl coupling with zinc dust – (trialkyl)ammonium formate reagent.

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Abstract. The method for coupling of haloaryls to polycyclic aryls with zinc dust and (trialkyl)ammonium formate in an inert atmosphere was extended for polycyclic haloaryls.

Polycyclic aryls during last decades serves as half-products and desired substances for photoconductive electrophotographic (for example, triphenylbenzene derivatives [1]) and organic electroluminescence (for example, 9,9'-bianthryl derivatives [2]) devices. Usually biaryls are prepared by Ullmann reaction [3]. Plurality of alternative methods also were elaborated (see references in [4, 5]). One of them, elaborated recently, is action of zinc dust and (trialkyl)ammonium formate on haloaryls in methanolic medium and inert atmosphere [4, 5]. We have extended above method for some polycyclic haloaryls.

Ia,b

II

Thus, 4-iodobiphenyl and 4-bromobiphenyl **Ia,b** were coupled with zinc dust and ammonium trialkylformates (R = CH₃, C₂H₅) to p-quaterphenyl **II** with high yield.

III

IV

Similarly, 2-iodofluorene **III** was coupled to correspondent 2,2'-bifluoryl **IV** with zinc dust and ammonium formate (R = H) with some lower yield.

V

VI

5-Bromoacenaphthene **V** was coupled to 1,1',2,2'-tetrahydro-5,5'-biacenaphthyl **VI** with zinc dust and trimethylammonium formate (R = CH₃) with moderate yield.

VII

VIII

Similarly, 9-bromophenanthrene **VII** was coupled to 9,9'-biphenanthryl **VIII** with some lower yield.

IXa,b

X

Coupling of 9-haloanthracenes **IXa,b** with zinc dust and ammonium formates (R = H, C₂H₅) proceeds with low yield of 9,9'-bianthryl **X**.

The results of reduction are summarised in Table.

No. of run	Starting compound	R	Obtained compound	Yield, %	m. p., °C	m.p. [lit]), °C
1	Ia	C ₂ H ₅	II	91	m.p. 316-319	m. p. 320 [3]
2	Ib	CH ₃	II	96	m.p. 317-320	m. p. 320 [3]
3	III	H	IV	90	m.p.316-318	m.p.316.5-318 [6]
4	V	CH ₃	VI	73	m.p. 175-178	m.p. 176-178 [7]
5	VII	CH ₃	VIII	70	m.p. 187-189	m.p. 188-189 [8]
6	IXa	C ₂ H ₅	X	17	m. p. 310-312	m.p. 310-312 [9]

As it was shown, the yield of desired coupling product decreases from high for ortho-unsubstituted to moderate for monoortho-substituted and low for diortho-substituted haloaryls.

Experimental.

General procedure.

To 0.01 mol of aryl halide and 0.01 mol of zinc dust in 50 ml of methanol 0.02 mol of (trialkyl)ammonium formate and 0.01 mol of sodium hydroxide were added. The reaction mixture was stirred and heated with reflux condenser at reflux under N₂ or Ar during 4 hours. After cooling reaction mixture was filtered, residue washed with benzene and water, benzene layer was separated, washed with water and dried over sodium sulphate. After filtration benzene was evaporated on rotatory evaporator under reduced pressure. The residue was subjected for chromatography on silica gel to obtain of pure desired product.

References

1. N. Ito, A. Karasawa, T. Oguchi. (Mitsui Toatsu Chemicals, Inc.). (Diphenylamino)triphenylbenzenes as charge-transporting agents and double-layered photoconductors. **JP 04-233547** (G 03 G 5/06), 21.08.1992; appl. 03-415362, 28.12.1990. (*Chem. Abstr.* 1993, **118**(4), 29997w).
2. C. Hosokawa, H. Ikeda, M. Funahashi. (Idemitsu Kosan, Ltd.). Anthracene derivative and organic electroluminescence device using the derivative. **US 6797848** (C 07 C 13/465), 28.09.2004; appl. 10/610930, 02.07.2003; prior. JP 2000-090644, 29.03.2000.
3. F. Ullmann, G. M. Meyer, O. Loewenthal, E. Gilli. Ueber symmetrische biphenylderivate. *Justus Liebigs Ann. Chem.* 1904, **332**, 38-81.
4. K. Abiraj, G. R. Srinivasa, D. Channe Gowda. Novel and efficient synthesis of symmetrical functionalized biaryls using zinc and triethylammonium formate. *SYNLETT* 2004, (5), 877-879.
5. K. Abiraj, G. R. Srinivasa, D. Channe Gowda. Facile synthesis of symmetrical functionalized biaryls from aryl halides catalyzed by commercial zinc dust using ammonium formate. *Tetrahedron Lett.* 2004, **45**, 2081-2084.
6. M. D. Barnett, G. H. Daub, F. Newton Haues, D. G. Ott. Liquid scintillators. VI. 2-Aryl- and 2,7-diarylfluorenes. *J. Am. Chem. Soc.* 1959, **81**, 4583-4586.
7. L. A. Jones, R. Watson. Acenaphthene. III. Coupling reactions. The preparation of 4,4'-dinaphthalic anhydride and 4',1-naphthyl-naphthalic anhydride. *Can. J. Chem.* 1973, **51**, 1833-1837.
8. A. Zinke, E. Ziegler. Untersuchungen uber perylen und seine derivate. LIII. Synthese des 2.3,10.11-dibenzperylens. *Ber. Deutsch. Chem. Ges.* 1941, **74**, 115-118.
9. A. H. Aly Ismail, Z. M. El-Shafei. The action of Grignard reagents on dianthron-9-ylidene and dianthron-9-yl. *J. Chem. Soc.* 1957, 796-799.