



Ullmann Reaction Optimization within Bitolyl and Decafluorobiphenyl Synthesis

A. V. KOLOTAEV, A. L. RAZINOV and D. S. KHACHATRYAN*

The Federal State Unitary Enterprise «Institute of Chemical Reagents and High Purity Chemical Substances of National Research Centre «Kurchatov Institute», Bogorodsky val str.3, Moscow, Russia.

*Corresponding author E-mail: derenik-s@yandex.ru

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ABSTRACT

This article describes the investigation of the cross-coupling Ullman's reaction of aryl halides under various conditions to find optimal scalable method of biaryl synthesis and the development of preparative methods of synthesizing 3,3'-bitolyl and perfluorobiphenyl, which are valuable semi-products of organic synthesis.

Keywords: Ullmann reaction, Bitolyl, Decafluorobiphenyl, Polymer materials, Polyarenes, Polyimides.

INTRODUCTION

Previously the authors investigated the aryl halides cross-coupling reaction to produce polyarenes, particularly quaterphenyl derivatives, within the framework of the FTP «Development of methods of producing quaterphenyl derivatives» (Agreement # 16.168.25.2002). Quaterphenyl derivatives are a substances with a high scintillation¹⁻² activity and therefore is promising for use in the detection of low-level radiators for medical research, geological prospecting and environmental monitoring. During the study the

authors thoroughly investigated 3-halotoluene dimerization reaction to produce 3,3'-bitolyl, an intermediate compound within polyarene synthesis.

The process of developing 3,3'-bitolyl was based on reported methods split into three groups:

- Ullmann reaction and its variations
- Cross-coupling reactions with active metals over catalysts
- Cross-coupling reactions between magnesium-organic compounds and 3-halotoluenes over catalysts



As Table 1 shows, given the above-mentioned criteria, the most suitable test methods are those using the combination of active metals and 3-bromotoluene or 3-iodotoluene. The drawback

of the first three methods is using relatively expensive catalysts, while that of the fourth method is using a fire-hazardous reagent.

Table 1: Reported conditions of 3-iodotoluene from literature

Reaction conditions	Output, %
Potassium phosphate, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, palladium-iron complex in dimethylformamide	95 ³
Palladium acetate, potassium carbonate in butanone	76 ⁴
18-crown-6, zinc, Pd/C in water	61 ⁵⁻⁶
Sodium in diethyl ether	7-8
Copper	35 ⁹⁻¹⁰
Copper in dimethylformamide	52 ¹¹

MATERIALS AND METHODS

A series of experiments was conducted to determine the optimal conditions for performing 3,3'-bitolyl and decafluorodiphenyl production reactions. The structure and purity of the products produced were confirmed by NMR and GC methods.

3-Iodotoluene, 3-bromotoluene, perfluorobromobenzene and other chemicals were equipped from Aldrich, Acros and Sigma chemical companies and used without further purification. All chemicals and solvents used in the preparation and characterization were of analytical grade. ¹⁹F-NMR spectra were obtained with a model Bruker AM (283MHz) spectrometer for using CDCl₃ solution in an appropriate deuterated solvent. The chemical shift are reported in ppm using tetramethylsilane (TMS) as the internal reference. Quantitative sample analysis was carried out using gas chromatography (GC), which, in turn, was performed using gas chromatograph «Chromatec Crystal 5000.2», equipped with flame ionization detector and 30-m long fused silica column BP-1 (inner diameter 0.32 mm).

EXPERIMENTAL

Activated copper production

Variation 1

8.1 g copper is mixed in the solution comprising 1.3 g iodine and 80-ml acetone, followed by flushing with concentrated hydrochloric acid in

acetone (20 ml of HCl (36%) per 20 ml of acetone) and 1 h drying in the vacuum oven.

Variation 2

Cold saturated CuSO₄ solution is poured into porcelain cup, followed by portion-wise adding zinc powder (it must contain no impurities non-soluble in 10% HCl) sifted through fine mesh. After 10-g zinc powder has been added, the solution is heated to 80 °C, with further zinc portions being added into hot solution. Adding Zn is stopped when the solution heated to 80 °C is still thin blue (fractured copper powder per 100 ml falls to the bottom as heavy dark red deposit).

Supernatant liquid is drained, while the deposit is probably thoroughly flushed with water by means of decantation. Then, to remove zinc traces, 10% HCl is added to the deposit, accompanied by simultaneous mixing, till the solution stops boiling. The deposits is flushed by means of decantation again, sucked in the Buchner funnel and flushed in the funnel, till flushing water shows neutral reaction, followed by flushing with ethyl alcohol and diethyl ether. The copper produced is vacuum-dried.

Bis-3,3'-bitolyl production using copper

Method A. 10 g 3-iodotoluene and 20 g activated copper powder are mixed in a heat-resistant test tube. The mixture produced is heated to 270 °C, followed by 30 min. dwelling at

this temperature. The reaction mass is treated with boiling heptane thrice. The solution was then decanted and vacuum-stripped, with the residue being vacuum-distilled to collect the fraction of 155-180 °C/ 15-20 mm Hg.

Method B. 10 g 3-iodotoluene and 50 ml dimethylformamide are fed into 100-ml three-head flask equipped with reflux condenser, temperature gauge and magnetic mixer. The solution is heated to the boiling point, followed by adding a single portion (10 g) of copper powder.

The reaction mass is boiled for 40 h, followed by adding another 10 g copper powder and another 40 h boiling. The reaction mass is then cooled down, poured into 200-ml water and filtered out. The deposit is flushed thrice, using 50 ml heptane each time. Water and organic layers are separated. Heptane is stripped, while the deposit is vacuum-distilled through water-jet pump to collect the fraction of 155-180 °C/15-20 mm Hg (lit¹² 153-155 °C/18 mm Hg).

Decafluorobiphenyl production using copper

8.0 g (34.9 mmol) perfluorobromobenzene is dissolved in dry DMF (15 ml), followed by adding 8.6 g (135.2 mmol) activated copper, 5-hour mixing under argon atmosphere at the boiling point (¹⁹F NMR – 100% conversion) and cooling down to room temperature. The deposit is filtered out and flushed with DMF (15 ml). Joint organic fractions are diluted with excessive water (300 ml), while the deposit is filtered out, air-dried and distilled to collect the fraction with the boiling point of 94-95 °C/20 mm Hg, accompanied by simultaneous cooling down of the receiver with ice. The output is 5.4 g (92% of estimated value) of white solid substance with the boiling point of 68.5-69.5 °C. The purity per GC is 99.9%.

¹⁹F NMR (283 MHz, CDCl₃) δ -137.37 (ddd, J = 19.1, 9.2, 5.3 Hz), -149.50 – -150.06 (multiplet), -160.25 (tdd, J = 22.2, 11.1, 5.9 Hz).

Decafluorobiphenyl production using zinc

32.7 g (0.500 mol) zinc powder suspension and 1.00 g (0.006 mol) copper (II) acetate are simultaneously mixed in 120 ml absolute DMF and heated to 140 °C for 40 min,

followed by cooling down to 100 °C and adding 247 g (1.000 mol) bromopentafluorobenzene drop-wise at 2-2.5 ml/min. speed, so the reacting mass would be slowly heated to its boiling point. After adding bromopentafluorobenzene is over, the reacting mixture is boiled for 6 h, cooled down to 60-70 °C and poured into cold water, followed by adding 23-32 ml of concentrated hydrochloric acid. Once two layers have formed, the upper one is decanted, while the lower one is treated with concentrated hydrochloric acid (2x30 ml) and concentrated HNO₃ (3x15 ml), followed by adding hot water (60-70 °C). The oil produced is separated and dwelled for several h in the refrigerator. The solid product is filtered out from unreacted bromopentafluorobenzene and recrystallized from hexane, followed by producing 117 g of decafluorobiphenyl, with its purity of 97-98% (GC data) and T_{boiling} = 68-69 °C. The output is 70%.

¹⁹F NMR (283 MHz, CDCl₃) δ -137.37 (ddd, J = 19.1, 9.2, 5.3 Hz), -149.50 – -150.06 (m), -160.25 (tdd, J = 22.2, 11.1, 5.9 Hz).

Grignard reagent production from 3-bromotoluene

3-Bromotoluene (171.0 g, 1.000 mol) is dissolved in 250 ml THF. The reaction is initiated by adding 2-4 ml of ethylbromide per 1 mol of magnesium (24.3 g) and 15-20 ml of aryl halide's THF solution, accompanied by simultaneous mixing. As the reaction starts, the remaining solution is swiftly added drop-wise to ensure self-maintaining boiling. After adding aryl halide's THF solution is over, the reaction mixture is mixed at the boiling point for 2.5 h, till magnesium is completely dissolved.

Bitolyl production from magnesium-organic derivative, using nickel acetylacetonate

A catalyst, nickel acetylacetonate (1.2 g, 0.0047 mol), is added to bromotoluene (40.0 g, 0.234 mol) solution in tetrahydrofuran (150 ml) under nitrogen atmosphere. Grignard reagent solution, produced from 3-bromotoluene (40.0 g, 0.234 mol) and magnesium (5.9 g, 0.245 mol), in tetrahydrofuran (80 ml) is added drop-wise to the initial mixture at the speed that maintain gentle boiling. The reaction mixture is boiled for three hours, followed by THF stripping and treating the deposit produced with 200 ml water and 300 ml

hexane. To completely dissolve the residue a hydrochloric is added, followed by hexane extraction. Joint extracts are dried over magnesium sulfate. After the solvent has been removed, the residue is vacuum-distilled to collect the fraction with the boiling point of 138-139 °C/5 mm Hg and the output of the target product (34.0 g, colorless oil) of 80%.

Bis-3,3'-bitolyl production from magnesium-organic derivative, using copper (II) chloride

Grignard reagent is produced using 34.2 g (0.200 mol) 3-bromotoluene and 4.9 g magnesium (0.200 mol) in 80 ml anhydrous diethyl ether. 30.0 g (0.220 mol) CuCl₂ suspension in 60 ml diethyl ether is added to the solution produced under ice cooling. The mixture is mixed at the boiling point for 12 hours. The reaction mixture is treated with ice and hydrochloric acid, followed by ether layer separation and drying over sodium sulfate. The product is distilled to collect the fraction with the boiling point of 138-139 °C/5 mm Hg and the output of 11.3 g (62%) colorless oil.

Bis-3,3'-bitolyl production from magnesium-organic derivative, using TEMPO

3-Tolylmagnesium bromide solution (1.54 mmol) is added to TEMPO solution (261 mg, 1.66 mmol, 1.08 eq.) in anhydrous THF (3 ml) at room temperature. The reaction mixture produced is boiled for 5 min, cooled down to room temperature and poured into the mixture of diethyl ether (30 ml) and concentrated aqueous solution of ammonium chloride (10 ml). Once separated, a water layer is extracted twice with diethyl ether (30 ml), and joint organic phases are flushed with saturated salt solution (20 ml) and dried over magnesium sulfate. The product is separated by means of flash-chromatography (SiO₂, size: 60-120 μm, eluent pentane) with the output of 95% (136 mg).

Bis-3,3'-bitolyl production from magnesium-organic compound, using anhydrous iron chloride, oxygen and 2,2'-bipyridine

An anhydrous FeCl₃ (0.12 mmol) and Bipy (0.24 mmol) are dissolved in 3-ml dry THF inside Schlenk tube, followed by adding 3-tolylmagnesium bromide solution (2.0 mmol) under nitrogen atmosphere. The mixture produced is degassed and filled with pure oxygen from the oxygen cushion,

followed by 10 min. mixing of the reaction mixture at room temperature. The end of this reaction is followed by adding 10 ml ethyl acetate and solvent stripping, while the residue is purified by flash-chromatography (SiO₂, size: 60-120 μm, eluent pentane) with the output of 76% (138 mg).

Bis-3,3'-bitolyl production from magnesium-organic derivative, using Tetrakis (triphenylphosphine) palladium

Pd[PPh₃]₄ (8.80 g, 0.007 mol) is added to 3-bromotoluene solution (65.5 g, 0.383 mol) in tetrahydrofuran (200 ml) under argon atmosphere. Grignard solution, produced from 3-bromotoluene (65.5 g, 0.383 mol) and magnesium turnings (9.65 g, 0.402 mol) in 100-ml THF, is added drop-wise to the initial mixture under its gentle boiling and boiled for 1 hour. After the solvent has been stripped, the residue is treated with the mixture of 200 ml water and 300 ml heptane, followed by acidification with hydrochloric acid to completely dissolve the residue. Once an organic layer has been separated, a water layer is extracted with heptane, followed by residue distillation to collect the fraction at 138-139 °C/5 mm Hg and the output of 58.0 g (83 %) of colorless oil.

Grignard reagent production from perfluororomobenzene

28.2 ml (0.222 mol) bromopentafluorobenzene is added drop-wise to 5.40 g (0.222 mol) of magnesium turnings in 150 ml diethyl ether for an hour and at the speed that maintains quiet boiling. The mixture is boiled for another 25 min. till magnesium is completely dissolved.

Decafluorobiphenyl production from magnesium-organic derivative, using nickel acetylacetonate

A catalyst, nickel acetylacetonate (1.1 g, 0.0044 mol), is added to bromopentafluorobenzene (28.2 ml, 0.222 mol) solution in diethyl ether (140 ml) under nitrogen atmosphere. Preliminary produced Grignard reagent solution (0.222 mol) is added drop-wise to the initial mixture at the speed that maintains moderate boiling. The reaction mixture is boiled for three hours, followed by ether stripping and treating the deposit produced with 200 ml water and 300 ml hexane. To completely dissolve the residue a hydrochloric acid is added, followed by hexane extraction. Joint extracts are dried over magnesium sulfate. After the solvent has

been removed, the residue is vacuum-distilled to collect the fraction with the boiling point of 94-95 °C/ 20 mm Hg, accompanied by simultaneous cooling down of the receiver with ice. The output is 22.4 g (61 % of estimated value) of white solid substance with the boiling point of 68.5-69.5 °C.

RESULTS AND DISCUSSION

Method selection criteria were the minimum number of stages, availability and cost of initial reagents, process simplicity and method reproducibility and scalability required for developing process procedure.

Ullmann reaction with 3-iodotoluene over activated copper was conducted in two variations: without solvent (Variation A) and in DMF (Variation B).

Product output of the Variation A ranges between 25 and 42%, while that of the Variation reaches 45 to 60%. The drawback of this method is high cost of initial 3-iodotoluene mostly comprising iodine. Low output of the end product makes this

method difficult to use for producing 3,3'-bitolyl within the process. That is why the authors drew their attention to the Grignard reaction.

Since the discovery of magnesium-organic compounds by Grignard at the start of the 20th century till the present time this reaction has been mainly used for producing symmetrical biaryl derivatives. Various catalysts and method modifications allow to produce high outputs of the products of cross-coupling reaction. At the first stage of this reaction 3-chloro- and 3-bromotoluenes reacted easily to magnesium in tetrahydrofuran or diethyl ether. At the second stage Grignard reacted to aryl halides over different catalysts. The results obtained are shown in Table 2.

The most interesting catalysts are iron salts and complexes. However, the authors did not manage to achieve high output of 3,3'-bitolyl. The best result was achieved when using TEMPO, yet the reaction is poorly scalable due to high cost of the latter. The same drawback is also inherent to tetrakis(triphenyl)palladium.

Table 2: The conditions and results of Grignard reactions of 3-halotoluenes

Initial halide	Catalyst	Specified output, %	Real output, %
3-Br-Tol	Fe(acac) ₃	90 ¹³	12
3-Br-Tol	Fe(OTf) ₃	88 ¹⁴	10
3-Br-Tol	CuCl ₂	64 ¹⁵	62
3-Br-Tol	CoCl ₂	- ¹⁶	48
3-Br-Tol	FeCl ₃ , O ₂ , bipy	80 ¹⁷	76
3-Br-Tol	TEMPO	98 ¹⁸	95
3-Br-Tol	ZnBr ₂	92 ¹³	25
3-BrMgTol/3-Br-Tol	Pd[Ph ₃] ₄	- ¹⁹	82-84
3-ClMgTol/3-Br-Tol	Pd[Ph ₃] ₄	- ¹⁸	78-80
3-BrMgTol/3-Br-Tol	Ni(acac) ₂	- ²⁰	80
3-ClMgTol/3-Br-Tol	Ni(acac) ₂	- ¹⁹	75

The optimal method of producing 3,3'-bitolyl is cross-coupling reaction between 3-tolylmagnesium halide and 3-bromotoluene over nickel salts, since using copper (II) chloride resulted in slightly lower output.

The logical extension of haloarene cross-coupling reaction studies was investigating the conditions of producing decafluorodiphenyl

within the framework of the FTP «Development of simple and environmentally safe technology for producing polymer materials that are flexible over wide temperature range and designed for photosensitive elements» (Code 2016-14-579-009-323). Decafluorodiphenyl is used as initial reagent for producing octafluorobenzidine²¹, a monomer used for polymer synthesis²², particularly fluorinated polyimide²³ films. Aromatic polyimides have been

paid great attention in the microelectronics as interlayer dielectrics due to their properties, including high thermal stability, chemical resistance and good mechanical and electrical properties. In particular, polyimides, which are stable at high temperature, are producing by condensing diamine and pyromellitic²⁴ anhydride.

Decafluorodiphenyl is produced using Ullmann reaction with chloropentafluorobenzene²⁵⁻²⁶ over copper, while slightly raising temperature from 230 to 320-360 °C increases reaction output a little (from 69 % to 73 %). Using bromopentafluorobenzene under the same conditions substantially increase product output²⁷⁻²⁹ (from 87% to 91%), yet replacing copper with activated nickel³⁰, produced by reducing nickel bromide or nickel iodide with lithium naphthalede, is unsuccessful (37-49%).

Noteworthy, in case of iodopentafluorobenzene the last approach leads to quantitative course (according to GC data) of the reaction^{29,31}. This method is difficult to be scaled due to high cost of nickel iodide and aryl iodide and the use of fire-hazardous lithium and dimethoxyethane. Replacing nickel iodide with more available copper (I) chloride leads to slight decrease in the output³² (91%) with the same preparatory drawbacks.

More convenient method is heating iodopentafluorobenzene over copper in the autoclave^{27,33} with the output of 72-87%.

The highest output (96%) of the product was achieved by boiling bromopentafluorobenzene³⁴ in DMF over activated copper. Noteworthy, the other authors³⁵ achieved an output not exceeding 71% under similar conditions (7-hour boiling).

As for Grignard reagents, pentafluorophenyl magnesium chloride³⁶ is turned into decafluorodiphenyl, with its output of 72-84%, over copper (I) iodide, accompanied by producing pentafluorophenyl magnesium iodide (8-11%) as a by-product. In case of pentafluorophenyl magnesium bromide and CoCl_2 , the reaction results in unsatisfactory²⁶⁻²⁷ output, while using CuBr leads to production of tetramer³⁷⁻³⁸ (70% output), which forms perfluorobiphenyl (68% output) when being boiled with copper (II) bromide in hexane.

Pentafluorophenyl bromide is known to be used in the Heck reaction with pentafluorobenzene over dicyclohexyl(2',6'-dimethoxybiphenyl-2-yl) phosphine³⁹ and palladium acetate (83% output). When bromopentafluorobenzene reacts to CuCN⁴⁰, 1-bromo-2,3,4,5-tetrafluorobenzene⁴¹ and 1-chloro-1,2-difluoroethylene⁴², the target product forms as a by-product (9 – 18% output).

Another interesting approach is using pentafluorophenyl iodide in the reaction with potassium perfluorobenzoate⁴³ over copper (I) iodide (80% output).

Recently⁴⁴ pentafluorobenzene dimerization reaction was conducted over palladium acetate and silver carbonate (60% output).

In 2014 a cross-coupling reaction between perfluorophenylboronic⁴⁵ acid and gold complex $[\text{Au}^{\text{III}}(\text{C}_6\text{F}_5)(\text{PPh}_3)\text{Cl}_2]$ (89% output) was published.

As in 3,3'-bitolyl case, the methods of using activated metals and pentafluorophenyl bromide, which is more available comparing to iodo derivatives, turned out to be the most preparatory ones.

Using activated copper under DMF led to the target product's output of 92%. Similarly to 3-tolyl bromide case, the authors produced Grignard reagent, which reacts to the relevant aryl bromide over nickel acetylacetonate and is featured by lower output (61%).

CONCLUSION

As result of investigating various methods of 3-tolylhalides and pentafluorophenyl bromide cross-coupling, it was found that the optimal method was using Grignard reagent over nickel acetylacetonate or activated copper over DMF respectively.

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