International Journal of Chemical Studies

P-ISSN2349–8528
E-ISSN 2321–4902
IJCS 2015; 3(2): 70-72

Received: 01-06-2015
Accepted: 05-07-2015

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Investigation and Utilization of the Yu *et al.* protocol for the Synthesis of phenyltriolborates and its derivatives

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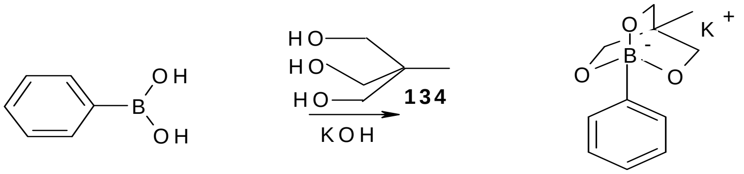
Abstract
The investigation of the Yu *et al.* protocol and its consequent application in the synthesis of phenyl triolborates and its 3-chlorophenyl, 4-bromophenyl and 3-nitrophenyl derivatives is reported. Phenylboronic acid and its 3-chlro, 4-bromo- and 3-nitro derivatives were reacted with trimethylolethane/ trimethylolpropane in a solution of potassium/ lithium hydroxide at room temperature to afford the aryltriolborates. The aryltriolborates thus synthesized were utilized in the synthesis of angular triaza phenoxazinones.

Keywords: Investigation, Utilization, protocol, phenyltriolborates.

1. Introduction

The Yu *et al.* protocol is a method for the synthesis of aryltriolborates from phenylboronic acid, using trimethylolethane in a solution of potassium hydroxide. In this investigation, phenyltriolborates was synthesized, using potassium and lithium hydroxide, trimethylolethane and trimethylolpropane and arylboronic acids. Aryltriolborates have been found to be a good reagent for the coupling reactions involving primary and secondary aliphatic amines

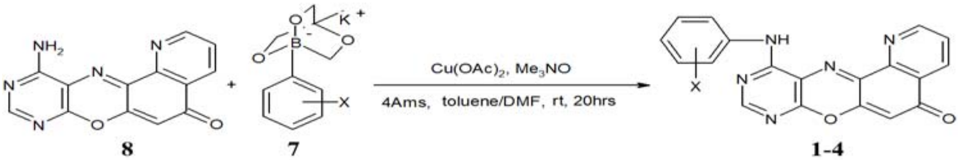


Arylboronic acid **aryltriolborate**

2. Result and Discussion

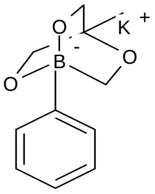
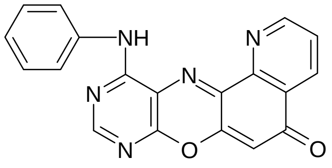
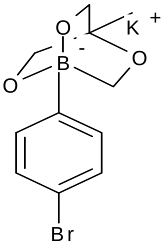
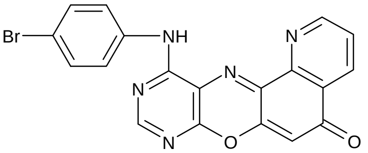
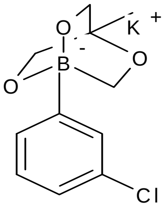
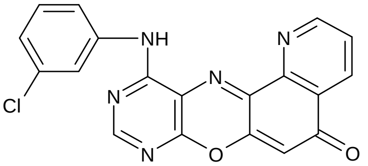
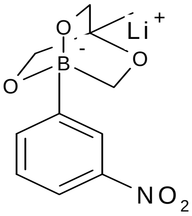
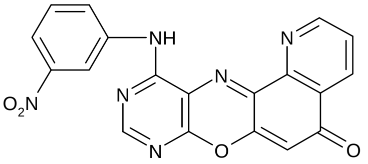
We first started by synthesizing 7-chloro-5, 8-quinolinequinone **5** in a five step reaction beginning from 8-hydroxyquinoline as reported by Petrow and Sturgeon (1954) and substituted potassium/lithium phenyltriolborates **7** using Yu X *et al.* protocol (Yu *et al*. 2008). The reaction of 7-chloro-5, 8-quinolinequinone **5** and 4, 5-diamino-6-hydroxypyrimidine **6** yielded 11-amino-1, 8, 10-triazabenzo[a]phenoxazin-5-one **8.**

The reaction of 11-amino-1, 8, 10-triazabenzo[a]phenoxazin-5-one **8** and substituted potassium/lithium phenyltriolborates **7**, under the catalytic influence of copper (II) acetate in the presence of trimethylamine *N*-oxide, and 4Å molecular sieve, furnished the aminotriazabenzo [a] phenoxazinones in good yields. Elemental analyses and spectroscopy are consistent with the assigned structures.



Ms= molecular sieve.

Table 1: Cu-catalyzed *N*-arylation of 11-amino-1, 8, 10-triazabenzo[a]phenoxazin-5-one. 8[a]

Entry	Substituted aryltriolborate	Product		Yield[b] %
1			1	80
2			2	77
3			3	74
4			4	70

[a]Reactions of 8 (1mmol) with aryltriolborates were performed using $Cu(OAc)_2$ (0.1mmol), Me_3NO (1.1mmol) and 4Å molecular sieve (300mg) at room temperature for 20h.

3. Experimental

3.1 *General*

Melting points were determined using Scott scientific melting point apparatus and are uncorrected. Ultraviolet and visible spectra were recorded on Jenway 6405 UV/Vis spectrophotometer. Absorption maxima are given in nanometer (nm) and (logε**)** in parenthesis. Infrared spectra were obtained on FTIR-8400S and absorption were in wave number (cm^{-1}). ^1H-NMR and ^{13}C-NMR spectra were determined on Variant 200MHz NMR machine and chemical shifts are in parts per million using tetramethylsilane as internal standard. The following abbreviations are used: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet). 7-Chloro-5, 8-quinolinequinone **5** and substituted potassium/lithium phenyltriolborates were synthesized as described. All chemicals were purchased from Zayo-Sigma (local vendor) and used as supplied.

3.2 *General Procedure for Cu-Catalyzed N-Arylation of Compound 8 with Derivatives of Aryltriolborate.*

To a round bottom flask of 100ml, copper acetate (0.1mmol), trimethylamine N-oxide (1.1mmol), 4Å molecular sieve (300mg) and the substituted aryltriolborate (1.5mmol), in toluene (30ml) and DMF (5ml) were stirred for 5 minutes at room temperature; compound **8** (1mmol) was then added. The mixture was stirred for 20hrs at room temperature. After the 20 hrs, the solvents were allowed to evaporate and then the product is washed with ice, filtered, dried and the residue re-crystallized using ethanol.

3.2.1 *11-(Phenylamino)-1, 8, 10-Triazabenzo [A] Phenoxazin-5-One 1*

Brown powder, yield: 80%. UV-VIS (ethanol) λ_{max} (log ε): 206(2.156); 268(1.27); 360(1.117); 426(0.985); 500(0.651) nm. IR (nujol) υ_{max}: 674 and 753cm^{-1} (C-H, out of plane); 1272 cm^{-1} (C-O-C, >N-H ar.) and 3439cm^{-1} (ar. C-H) cm^{-1}. H^1NMR ($DMSO_{-d6}$) δ: 8.40 (d, 2H, C_2 and C_4 protons); 7.90 (d, 2H, C_3 and C_9 protons); 8.0-7.80(m, 5H, monosubstituted benzene); 6.50 (s, 1H, C_6 proton); 3.40(s, b, 1H, >NH). ^{13}CNMR ($DMSO_{-d6}$) ppm: 173.7 (>C=O and C-NH_2); 142.87(>C=C< and >C=N) and 131.40-127.53 (ar. carbon). Anal. Calcd. For $C_{19}H_{11}N_5O_2$; C, 66.86; H, 3.23; N, 20.53. Found: C, 66.70; H, 3.31; N, 20.50.

3.2.2 *11-(4-Bromophenylamino)-1, 8, 10-Triazabenzo [A] Phenoxazin-5-One 2*

Brown powder, yield: 77%. UV-VIS (ethanol) λ_{max} (log ε): 219(2.536); 271(2.176); 360(1.512); 424(1.398); 500(0.921) nm. IR (nujol) υ_{max}: 686, 752cm^{-1} (C-H, out of plane); 1273cm^{-1} (>N-H ar, C-O-C); 1608cm^{-1} (C=O); 3438cm^{-1} (ar. C-H). H^1NMR ($DMSO_{-d6}$) δ: 8.20 (d, 2H, C_2 and C_4 protons); 7.90(d, 2H, C_3 and C_9 protons) 7.30(s, 1H, C_6 proton); 3.40(s, 1H, >NH). ^{13}CNMR ($DMSO_{-d6}$) ppm: 176.38ppm (>C=O and C-NH_2); 142.87(>C=C< and >C=N) and 131.39-127.54(ar.

carbon). Anal. Calcd. For C_{19} H_{10} N_5 $BrO_{2;}$ C, 54.29; H, 2.38; N, 16.67; Br, 19.05. Found: C, 54.30; H, 2.29; N, 16.70; Br, 19.00.

3.2.3 *11-(3-Chlorophenylamino)-1, 8, 10-Triazabenzo [A] Phenoxazin-5-One 3*

Brown powder, yield: 74%. UV-VIS (ethanol) λ_{max} (log ε): 207(2.163); 211(1.933); 217(1.570); 274(1.093); 360(0.853); 499(0.575) nm. IR (nujol) υ_{max}: 675cm^{-1}(C-H, out of plane); 1274cm^{-1}(>N-H ar. C-O-C); 1648cm^{-1}(C=O); 3433cm^{-1}(ar. C-H). H^{1}NMR (DMSO$_{\text{-d6}}$) δ: 8.80(d, 2H, C_2 and C_4 protons); 7.90(d, 2H, C_3 and C_9 protons); 7.60(m, 4H, Ar-H); 3.50(s, b, 1H, >NH). ^{13}CNMR (DMSO$_{\text{-d6}}$) ppm: 140(>C=C< and >C=N) and 132-128(ar. carbon). Anal. Calcd. For C_{19} H_{10} N_5 $ClO_{2;}$ C, 60.72; H, 2.66; N, 18.64; Cl, 9.45. found: C, 60.80; H, 2.59; N, 18.75; Cl, 9.50.

3.2.4 *11-(3-Nitrophenylamino)-1, 8, 10-Triazabenzo [A] Phenoxazin-5-One 4*

Brown powder, yield: 70%. UV-VIS (ethanol) λ_{max} (log ε): 207(2.027); 216(1.777); 245(1.640); 360(1.155); 420(0.865); 498(0.865); 659(0.700) nm. IR (nujol) υ_{max}: 678, 748cm^{-1} (C-H, out of plane); 1273cm^{-1}(>N-H ar. C-O-C); 1644cm^{-1}(C=O); 3462cm^{-1}(ar. C-H). H^1 NMR (DMSO$_{\text{-d6}}$) δ: 8.40(d, b, 2H, C_2 and C_4 protons); 7.80(s, b, 2H, C_3 and C_9 protons); 3.50(s, b, 1H, >NH). ^{13}CNMR (DMSO$_{\text{-d6}}$) ppm: 140 (>C=C< and >C=N) and 132-128(ar. carbon). Anal. Calcd. For C_{19} H_{10} N_6 $O_{4;}$ C, 59.07; H, 2.59; N, 21.76.

4. Conclusion

The Utilization of the Yu *et al*. protocol for the Synthesis of phenyltriolborates and its derivatives is recommended

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