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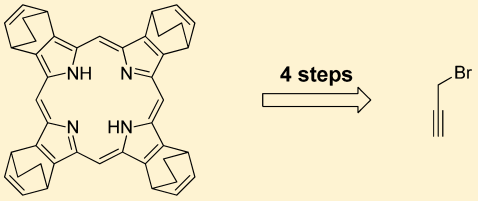
Method for Synthesis of Tetrabenzoporphyrin Precursor for Use in Organic Electronic Devices

Seung-Doo Jeong, Bokki Min, Song Yun Cho, Changjin Lee, Bo Keun Park, Ki-Seok An, and Jongsun Lim*

Division of Advanced Materials, Korea Research Institute of Chemical Technology, P.O. Box 107, 141 Gajeong-Ro, Yuseong-Gu, Daejeon 305-600, Republic of Korea

Supporting Information

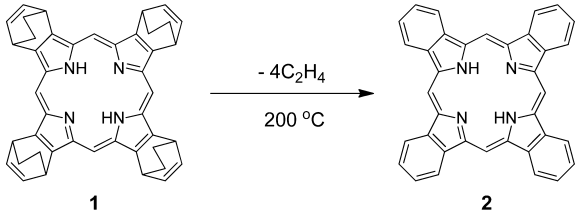
ABSTRACT: We developed a new synthetic method for bicyclo[2.2.2]-octadiene (BCOD)-fused porphyrin (**1**), a tetrabenzoporphyrin (TBP, **2**) precursor that is well-known as a good material for use in organic electronic devices. The newly developed method synthesizes the BCOD-fused pyrrole intermediate (which is the most important intermediate in synthesizing BCOD-fused porphyrin) in a simpler and easier manner than other existing methods, and thus, the new method can efficiently synthesize the TBP precursor.



Benzoporphyrins, the most well-known members of the extended porphyrin family, are among the most widely studied of porphyrin analogues. Among such benzoporphyrins, tetrabenzoporphyrin (TBP, **2**), which has a structure that is very similar to those of phthalocyanines (*Pc*), is known to have very interesting characteristics and various applicabilities.[1] Specifically, it has been proven that TBPs and their metal complexes can be good materials for use in organic electronic devices such as photovoltaic cells (OPVs) and field-effect transistors (OFETs).[2,3] However, difficulties in synthesis and device manufacturing exist because TBPs and their metal complexes have low solubilities due to $\pi-\pi$ stacking. It is known that TBP precursors with improved solubility are used to avoid such difficulties and that the most commonly used precursor is the bicyclo[2.2.2]octadiene-fused TBP precursor (BCOD-fused porphyrin, **1**).

Because **1**, which can dissolve in organic solvents, easily transforms to **2** through the annealing process that accompanies retro-Diels–Alder reaction, it is known to be readily applicable in device manufacturing using solvent processing (Scheme 1). However, unfortunately, the previously known synthetic methods for **1** are complicated because they involve many steps, and consequently, synthesis is not easy (Scheme 2). Therefore, in this study, we developed a new method that can efficiently synthesize **1** by synthesizing BCOD-fused pyrrole (the most important intermediate for the synthesis of **1**) in a simpler and easier manner than existing methods.

Scheme 1. Retro-Diels–Alder Reaction of BCOD-Fused Porphyrin 1



1 **2**

Most reports about the synthesis of **1** have been presented by the Ono group. According to the first reported synthetic method in 1997, a bicyclic compound (**7**) was synthesized through the Diels–Alder reaction between *β*-(phenylsulfonyl)-nitroethylene (**4**) and 1,3-cyclohexadiene (**3**), which were synthesized through processes involving various steps, and subsequently, a BCOD-fused pyrrole (**11**) was synthesized by Barton–Zard pyrrole synthesis using ethyl isocyanoacetate (**10**). The ester function of the synthesized pyrrole **11** was reduced to obtain **12**, which was used to synthesize **1**.[4] A year later, in 1998, *meso*-tetraarylated BCOD-fused porphyrins (**14**) were synthesized by de-ethoxycarbonylation of the above-mentioned synthesized pyrrole's ester and by reacting it with aromatic aldehyde. In addition, it was first reported that TBPs can be easily obtained through a retro-Diels–Alder reaction by heating synthesized **1** or **14** at a high temperature of 200 °C.[5] Later, in 2006, a BCOD-fused porphyrin (**1**) synthetic method using *trans*-1,2-bis(phenylsulfonyl)ethylene (**5**), which is easier to prepare than **4**, was reported, but this method too involved multiple reaction steps.[6] Although a method using tosylacetylene (**6**), which is synthesized in an even shorter step, was reported in the same year, the inconvenience of the reduction and de-ethoxycarbonylation in synthesizing BCOD-fused porphyrins still remained because the method, like other reported methods, includes Barton–Zard pyrrole synthesis, and therefore, the synthesized **11** has an ester function.[7]

We introduce a new method that is significantly simpler than other existing methods for synthesizing BCOD-fused porphyrin (**1**) (Scheme 3). First, we easily synthesized 4-bromo-1,1-diethoxy-2-butyne (**16**) via the reaction between propargyl bromide (**15**) and triethyl orthoformate, using zinc iodide as

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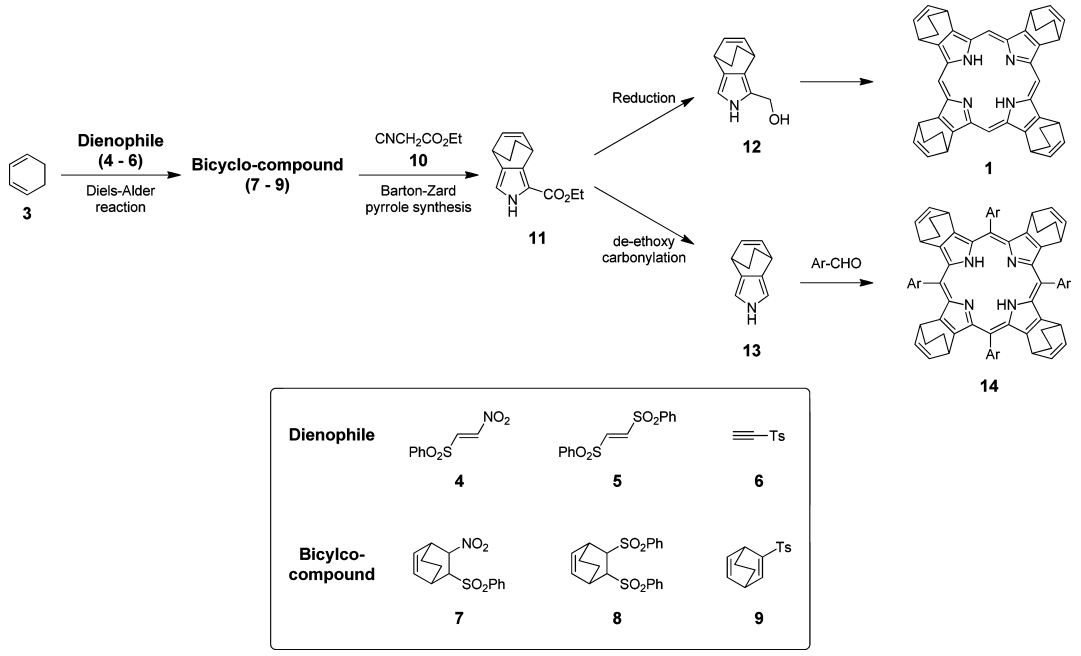
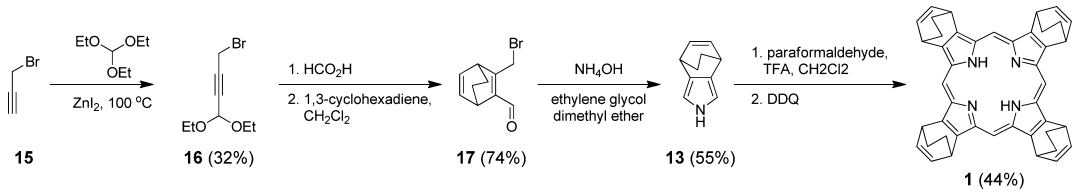
Scheme 2. Previously Known Synthetic Methods for BCOD-Fused Porphyrin (1)



Scheme 3. New Method for Efficiently Synthesizing BCOD-Fused Porphyrin (1)



the catalyst.[8] We substituted the synthesized compound's acetal function with the aldehyde function using formic acid, and immediately proceeded to synthesize a bicyclic compound (**17**) by reacting it with 1,3-cyclohexadiene.[9] Using NH_4OH, we synthesized a pyrrole (**13**) from the synthesized **17** in an extremely simple manner.[10] In addition, in contrast to those synthesized using other existing methods, **13** synthesized this way can be easily reacted with paraformaldehyde without any reduction, to synthesize BCOD-fused porphyrin (**1**),[11] because it does not have an ester function at its α-position. Thus, we synthesized **1** using a new method, which is considerably simpler than existing methods. In addition, various types of BCOD-fused porphyrins can be synthesized without reduction or de-ethoxycarbonylation because the pyrrole (the most significant intermediate in BCOD-fused porphyrins synthesis) synthesized using the new method does not have an ester function at the α-position.

We developed a new synthetic method for BCOD-fused porphyrin (**1**), a TBP (**2**) precursor that is well-known as a good material for use in organic electronic devices. The newly developed method synthesizes the BCOD-fused pyrrole (**13**) intermediate (the most important intermediate in synthesizing BCOD-fused porphyrins) in a simpler and easier manner than other existing methods, and thus, the new method can efficiently synthesize various types of BCOD-fused porphyrins.

EXPERIMENTAL SECTION

4-Bromo-1,1-diethoxy-2-butyne (16). Propargyl bromide solution (80 wt % in toluene, 100 g, 0.84 mol), triethyl orthoformate (100 mL, 0.60 mol), and zinc iodine (4.8 g, 0.015 mol) were combined in a reaction flask under Ar. The mixture was heated to 100−110 °C, and ethanol was removed by slow distillation over 3 h. Then, the mixture was combined with brine and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), and the solvent was removed in vacuo. The remaining oil was purified by column chromatography on silica (CH_2Cl_2) to obtain pure product: yield 42 g (32%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.31 (t, 1H, J = 1.54 Hz), 3.94 (d, 2H, J = 1.54 Hz), 3.75−3.72 (m, 2H), 3.61−3.57 (m, 2H), 1.24 (t, 1H, J = 7.10 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 91.2, 81.9, 80.3, 75.7, 61.0, 15.0, 13.4; EI calcd for $C_8H_{13}BrO_2$ exact mass 220, found 223.

3-(Bromomethyl)bicyclo[2.2.2]octa-2,5-diene-2-carbaldehyde (17). 4-Bromo-1,1-diethoxy-2-butyne (**1**) (42 g, 0.19 mol) was dissolved in formic acid (45 mL) under Ar. The mixture was stirred for 3 h at 45 °C under Ar. Then, CH_2Cl_2 (150 mL) and 1,3-cyclohexadiene (25 mL, 0.26 mol) were added, and the mixture was stirred for an additional 48 h at 45 °C. The mixture was combined with brine and extracted with CH_2Cl_2. The organic layer was washed with aqueous $NaHCO_3$ and water and dried (Na_2SO_4), and the solvent was removed in vacuo. The remaining oil was purified by column chromatography on silica (CH_2Cl_2) to obtain pure product (yellow sticky oil): yield 32 g (74%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.89 (s, 1H), 6.39−6.35 (m, 2H), 4.49 (d, 1H, J = 26.51 Hz), 4.47 (d, 1H, J = 26.51 Hz), 4.31−4.28 (m, 2H), 3.79−3.77 (m, 2H), 1.53−1.39 (m, 3H), 1.35−1.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.3, 158.9, 142.1, 134.7, 132.8, 43.4, 34.2, 26.2, 25.3, 25.2; HRMS m/e $[M]^+$ calcd for $C_{10}H_{11}BrO$ 225.9993, found 225.9994. Anal. Calcd for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88; O, 7.05. Found: C, 52.37; H, 4.71; O, 7.55.

4,7-Dihydro-4,7-ethano-*2H*-isoindole (13). 3-(Bromomethyl)-bicyclo[2.2.2]octa-2,5-diene-2-carbaldehyde (**2**) (27 g, 0.12 mol) was dissolved in ethylene glycol dimethyl ether (100 mL), and NH_4OH

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(50 mL) was added under Ar. The mixture was stirred for 3 h at room temperature. Then, the mixture was combined with brine and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), and the solvent was removed in vacuo. The remaining oil was purified by column chromatography on silica (CH_2Cl_2) to obtain pure product: yield 9.5 g (55%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (br s, 1H), 6.51−6.47 (m, 2H), 6.44 (d, 2H), 3.84−3.82 (m, 2H), 1.57−1.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.3, 129.6, 108.0, 33.2, 27.6; EI calcd for $C_{10}H_{10}N$ exact mass 145, found 145.

Bicyclo[2.2.2]octadiene-Fused Porphyrin (1). 4,7-Dihydro-4,7-ethano-2*H*-isoindole (**3**) (1.45 g, 0.01 mol) and paraformaldehyde (0.3 g, 0.01 mol) were dissolved in CH_2Cl_2 (1 L), and TFA (0.077 mL, 0.001 mol) was added. The mixture was stirred for 12 h at room temperature. Then DDQ (2.5 g, 0.011 mol) was added and the mixture stirred for an additional 1 h. The mixture was chromatographed over alumina (CH_2Cl_2/THF = 19/1), eluting first with to afford the crude mixture. The mixture was purified by column chromatography on silica (CH_2Cl_2/THF = 19/1) to obtain pure product: yield 0.68 g (44%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.40 (t, 4H, J = 3.08 Hz), 7.24−7.16 (m, 8H), 5.78 (s, 8H), 2.24−2.23 (m, 8H), 1.99−1.90 (m, 8H), −4.67 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 136.8, 97.1, 36.4, 27.9; MALDI-TOF MS calcd for $C_{44}H_{38}N_4$ exact mass 622.31, found 623.62.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jslim@krict.re.kr.

Notes

The authors declare no competing financial interest.

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