らせん型キノン誘導体とヒドラジンの反応によるジアザ[9]ヘリセン誘導体の合成

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Synthesis of Diaza[9]helicene Derivative by the Reaction of Helical Quinone with Hydrazine
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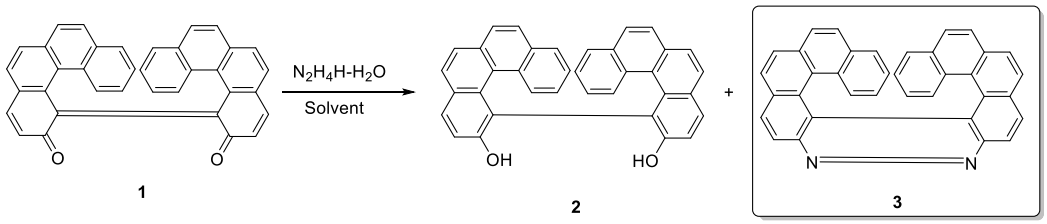
We report that reacting a helical quinone derivative obtained from the oxidative coupling reaction of 2-hydroxybenzo[*c*]phenanthrene[1] with hydrazine yields a reduced bisphenol derivative as the main product.[2] However, we discovered that a diaza[9]helicene derivative is formed as a by-product through a cyclization reaction involving hydrazine. By optimizing the reaction conditions to improve the yield, we also performed optical resolution of the diaza[9]helicene derivative. For both enantiomers, we elucidated their chiral optical properties through measurements such as specific rotation and circular dichroism spectra.
Keywords : Diazaelicene; Bisphenol; Cyclization; Quinone; Optical resolution

2ーヒドロキシベンゾ[*c*]フェナントレンの酸化的カップリング反応で得られるらせん型キノン誘導体(**1**)[1)]とヒドラジンを反応させると、還元された生成物のビスフェノール誘導体(**2**)が得られる事を報告している[2)]。しかし、その副生成物としてヒドラジンを取り込むかたちで環化反応によってジアザ[9]ヘリセン誘導体(**3**)が得られる事を見出した。反応条件を検討して、収率の向上を試みると共に、ジアザ[9]ヘリセン誘導体の光学分割を行い、それら両鏡像異性体について、旋光度や円二色性スペクトルなどでそのキラルな光学特性を明らかにした。



1 2 3

Entry	Reagent/Catalyst(eq.)	Solvent	Temp (°C)	Time (h)	Yield (%)	
					2	**3**
1	N_2H_4-H_2O (2.7)	$CHCl_3$	rt	24	26	4.3
2	N_2H_4-H_2O (6.4)	DMF	rt	24	54	0
3	N_2H_4-H_2O (51)	$CHCl_3$	rt	24	60	19
4	N_2H_4-H_2O (2.0)	$CHCl_3$	60	12	59	16
5	N_2H_4-H_2O (7.3)/$Sc(OTf)_3$(0.2)	$CHCl_3$	rt	24	75	0

1) Synthesis of helical quinone derivatives by oxidative coupling of substituted 2-hydroxybenzo[*c*]phenanthrenes. M. Shahabuddin, A. Akutsu, T. Kimura, M. Karikomi, *SYNTHESIS* **2017**, *49*, 1547.
2) Synthesis of helical shaped 1,1’-bibenzo[*c*]phenanthrene-2,2’-diol (HEBPOL) derivatives by reduction of helical quinones. M. Shahabuddin, K. Ohgoshi, M. S. Hossain, T. Kimura, M. Karikomi, *Tetrahedron Lett.* **2017**, *58*, 3704.