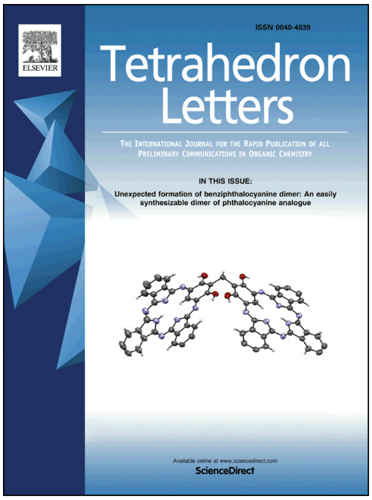


Synthesis of 1,2-Naphthalenediol Derivatives by Rh-catalyzed Intermolecular O-H Insertion Reaction of 1,2-Diazonaphthoquinones with Water and Alcohols

Mitsuru Kitamura, Kota Otsuka, Shuhei Takahashi, Tatsuo Okauchi

PII: S0040-4039(17)30948-6
DOI: http://dx.doi.org/10.1016/j.tetlet.2017.07.084
Reference: TETL 49166

To appear in: *Tetrahedron Letters*

Received Date: 5 June 2017
Revised Date: 19 July 2017
Accepted Date: 25 July 2017

Please cite this article as: Kitamura, M., Otsuka, K., Takahashi, S., Okauchi, T., Synthesis of 1,2-Naphthalenediol Derivatives by Rh-catalyzed Intermolecular O-H Insertion Reaction of 1,2-Diazonaphthoquinones with Water and Alcohols, *Tetrahedron Letters* (2017), doi: http://dx.doi.org/10.1016/j.tetlet.2017.07.084

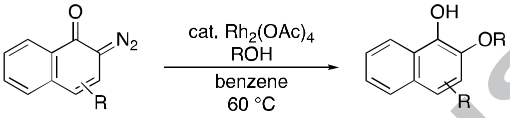
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Synthesis of 1,2-Naphthalenediol Derivatives by Rh-catalyzed Intermolecular O-H Insertion Reaction of 1,2-Diazonaphthoquinones with Water and Alcohols

Leave this area blank for abstract info.

Mitsuru Kitamura,* Kota Otsuka, Shuhei Takahashi, Tatsuo Okauchi



Tetrahedron Letters
journal homepage: www.elsevier.com

Synthesis of 1,2-Naphthalenediol Derivatives by Rh-catalyzed Intermolecular O-H Insertion Reaction of 1,2-Diazonaphthoquinones with Water and Alcohols

Mitsuru Kitamura,* Kota Otsuka, Shuhei Takahashi, and Tatsuo Okauchi

Department of Applied Chemistry, Graduate School of Engineering, Kyushu Institute of Technology, 1-1 Sensuicho, Tobata, Kitakyushu, 804-8550 Japan

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

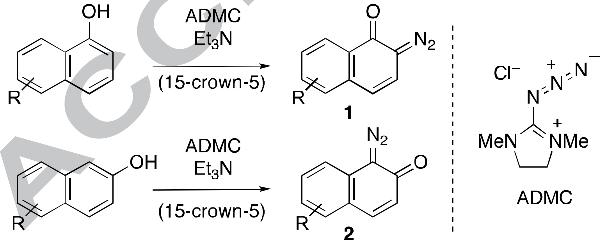
Keywords:
diazonaphthoquinones
naphthalenediol
O-H insertion
rhodium

ABSTRACT

Rh(II)-catalyzed O-H insertion reaction of diazonaphthoquinones with water or alocohols proceeded to yield 1,2-naphthalenediol derivatives.

Similar to catechol derivatives, 1,2-naphthalenediols are attractive possible aromatic functional materials (or their building blocks), such as solar cells, metal ligands, and anti-oxidants.[1] However, there are only a few reports regarding the synthesis of 1,2-naphthalenediols.[2]

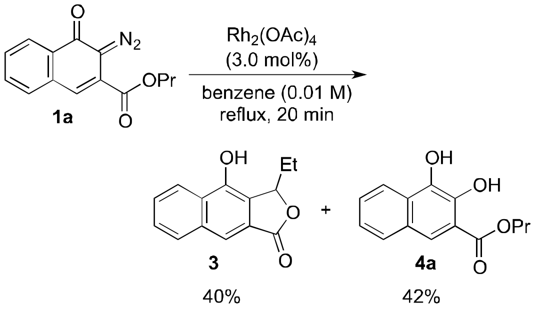
Recently, we developed an easy method of synthesis of diazonaphthoquinones (DNQ) from corresponding naphthols by diazo-transfer reaction using azidoimidazolinium salt (ADMC) (Scheme 1).[3,4] By the reaction of 1-naphthol or 2-naphthol with ADMC, 2-diazotized DNQ **1** or 1-diazotized DNQ **2** was selectively obtained, respectively.



Scheme 1. Synthesis of diazonaphthoquinones by the reaction of naphthol with azidoimidazolinium salt (ADMC).

DNQs have been used exclusively as photoresists such as novolak-DNQ resist,[5] and we are addressing the development of poly-substituted aromatic compounds from the DNQs.[6,7]

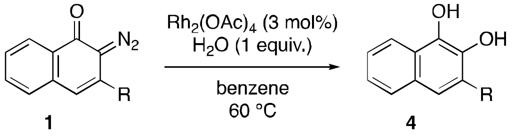
During the course our study of Rh(II)-catalyzed reaction[8] of propyloxycaroonyl-2-diazotized DNQ **1a** expecting the preparation of **3** by intramolecular C–H insertion reaction, we found the formation of naphthalenediol **4a**, which would be formed by the intermolecular O–H insertion of contaminated water in solvent (Scheme 2).[9] Inspired by the result, we considered that 1,2-naphthalenediols could be synthesized by the Rh(II)-catalyzed intermolecular O–H insertion reaction between 1,2-DNQs and water and started to examine the consideration.[10] Furthermore, we examined the O–H insertion reaction with alcohol. In this letter, we report the results in detail.



Scheme 2. Rh-catalyzed reaction of 3-propyloxycarbonyldiazonaphthoquinone **1a**.

As shown in Table 1, naphthalenediols **4** were obtained by the Rh(II)-catalyzed reaction of DNQs in the presence of water. When a mixture of DNQ **1a** in benzene was heated at 60 °C for 7 h in the presence of 3 mol% $Rh_2(OAc)_4$ and 1 equiv. of water, naphthalenediol **4a** was obtained quantitatively (run 1). Various 3-carbonylgroup substituted DNQs, such as ester **1a**–**e** and aldehyde **1f** gave corresponding O–H insertion products **4a**–**f** in good yields. When 3-unsubstituted **1h** and 3-methyl-substituted **1i** were employed for the reaction, DNQs were consumed within 1 hour. However, expected O–H insertion products were not obtained at all. 3-Alkoxycarbonyl DNQs **1** were found to be more stable than 3-unsubstituted and 3-alkyl-substituted DNQs like **1h** and **1i**. Therefore, some of the reasons of the no yield of O–H insertion products form **1h** and **1i** were attributed to the stability of DNQ under the reaction conditions and reactivity of its Rh carbene complex. However, we presume the main reason instability of the expected products, 1,2-naphthalenediols **4h** and **4i**, under the reaction conditions. Because, we confirmed the decomposition of **4h** under the reaction conditions. In addition, we also confirmed that Rh-catalyzed O-H insertion reaction of alcohol with same DNQ **1h** and **1i** proceeded to afford mono alkyl ethers of 1,2-naphthalenediol which were not decomposed under the reaction conditions (vide infra, Table 2 runs 20-22).[11] This result suggested DNQ **1h** and **1i** and its Rh carbenes have adequate life-time for the O-H insertion reaction in the reaction conditions.

Table 1. Rh-catalyzed O–H insertion reaction of 3-alkoxycarbonyl-1,2-diazonaphthoquinone **1**.[a]



Run	R	1	4	Time (h)	Yield (%)
1	CO_2Pr	**1a**	**4a**	7	quant.
2	CO_2Me	**1b**	**4b**	5.5	quant.
3	CO_2Et	**1c**	**4c**	5	78
4	CO_2Allyl	**1d**	**4d**	8	64
5	CO_2Bn	**1e**	**4e**	9	84
6	CHO	**1f**	**4f**	7	76
7	CONHPh	**1g**	**4g**	6.5	73
8	H	**1h**	**4h**	1	0
9	Me	**1i**	**4i**	1	0

[a] Reaction conditions: 3.0 mol% $Rh_2(OAc)_4$ in benzene (0.01 M for **1**) at 60 °C.

Next, we examined the Rh-catalyzed reaction with alcohol (Table 2). In the reaction mixture, molecular sieve 4A was added to avoid the formation of diol formed by the reaction with contaminated water.

In runs 1–10 the results of the reaction of 3-methoxycarbonyl DNQ **1b** and alcohols are shown. Various alcohols, such as methanol, benzyl alcohol, *tert*-butyl alcohol, phenol, and glycolic acid ester reacted with **1b** to afford corresponding naphthalenediol derivatives **5** in good to high yields (runs 1–7). In the reaction with allylic alcohol, the reaction mixture became complex, but the expected diol derivative **5h** was isolated in 40% yield (run 8). Interestingly, tricyclic compound **6a** was obtained primarily in the reaction with propargyl alcohol (run 9).

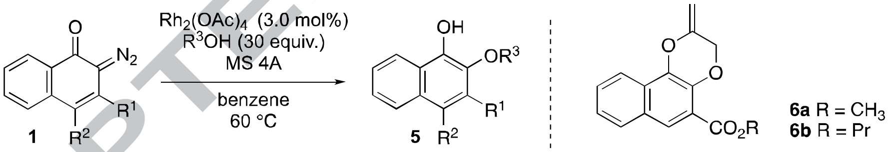
Similarly, various 3-carbonyl group substituted DNQ reacted with alcohol to give O–H insertion reaction as shown in runs 11–19. Introduction of methyl group or phenylgroup at C-4 positions did not drag down for the O–H insertion reaction (runs 18 and 19).

In contrast to the reaction with water, O–H insertion products were obtained in high yields by reacting 3-unsubstituted/3-alkyl group substituted DNQs and alcohol (Table 2, runs 20–25 versus Table 1, runs 7 and 8).

The O–H insertion reaction is also examined for 1-diazotized DNQ **2** (Table 3).

In case of the reaction with water, O–H insertion products were not obtained from 3-unsubstituted and 3-trifluoromethanesulfonyl DNQ **2a** and **2b** (runs 1 and 2), while naphthalenediol **4b** was obtained from 3-methoxylcarbonyl DNQ **2c** (run 3). By the reaction with methanol with DNQ **2a**-**c**, O–H insertion product was obtained in high yields (runs 4–6). O-H insertion product **7d** was also formed by the reaction with propargyl alcohol (run 7).

Table 2. Rh-catalyzed O-H insertion reaction of 1,2-diazonaphthoquinones **1** with various alcohol.[a]



Run	R^1	R^2	1	R^3OH (equiv.)	time (h)	5	yield (%)
1	CO_2Me	H	**1b**	MeOH (30)	8	**5a**	88
2	CO_2Me	H	**1b**	EtOH(30)	9	**5b**	88
3	CO_2Me	H	**1b**	PrOH(30)	7.5	**5c**	92
4	CO_2Me	H	**1b**	BnOH (5)	8	**5d**	86
5	CO_2Me	H	**1b**	*t*-BuOH (5)	9.5	**5e**	72
6	CO_2Me	H	**1b**	PhOH (1)	15.5	**5f**	72
7	CO_2Me	H	**1b**	$MeCO_2CH_2OH$ (5)	10.5	**5g**	60
8	CO_2Me	H	**1b**	$CH_2=CHCH_2OH$ (30)	21	**5h**	40
9	CO_2Me	H	**1b**	$HC\equiv CCH_2OH$ (30)	8	**5i**	20[b]
10[c]	CO_2Me	H	**1b**	$(CH_2OH)_2$ (5)	14	**5j**	63
11	CO_2Pr	H	**1a**	MeOH (30)	10	**5k**	88
12	CO_2Pr	H	**1a**	BnOH(5)	8	**5l**	95
13	CO_2Pr	H	**1a**	$HC\equiv CCH_2OH$ (30)	9.5	**5m**	2[d]
14	CO_2Bn	H	**1e**	MeOH(30)	6.5	**5n**	94
15	CO_2Ph	H	**1j**	MeOH (30)	9.5	**5o**	72
16	CHO	H	**1f**	MeOH (30)	7	**5p**	83
17	CONHPh	H	**1g**	MeOH (30)	12	**5q**	99
18	CO_2Me	Me	**1k**	MeOH (30)	5.5	**5r**	79
19	CO_2Me	Ph	**1l**	MeOH (30)	8	**5s**	77
20	H	H	**1h**	MeOH(30)	4.5	**5t**	78
21	Me	H	**1i**	MeOH (30)	11	**5u**	85
22	Me	H	**1i**	BnOH(5)	4.5	**5v**	97
23	*i*-Pr	H	**1m**	MeOH (30)	7	**5w**	95
24	CH_2OTBS	H	**1n**	MeOH (30)	4	**5x**	88
25	CH_2OTBS	H	**1n**	BnOH(5)	4.5	**5y**	quant.

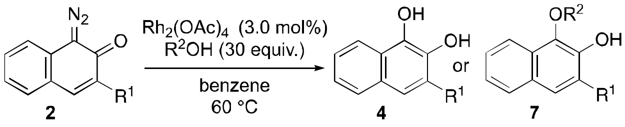
[a] Reaction conditions: 3.0 mol% $Rh_2(OAc)_4$ in benzene (0.01 M for **1**) at 60 °C.

[b] **6a** was obtained in 72% yield.

[c] Reaction mixture was 0.02 M.

[d] **6b** was obtained in 76% yield.

Table 3. Rh-catalyzed O–H insertion reaction of 3-alkoxycarbonyl-1,2-diazonaphthoquinone **2a**.

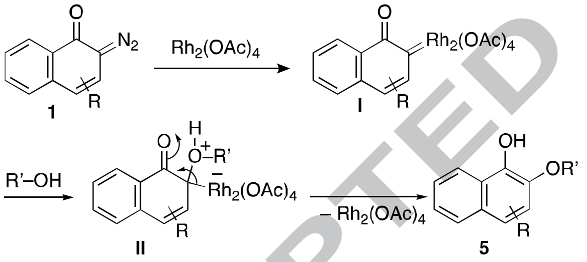


Run	R^1	**2**	R^2	time (h)	product	yield (%)
1	H	**2a**	H	0.5	**4h**	0
2	OTf	**2b**	H	2.5	**4j**	0
3	CO_2Me	**2c**	H	1	**4b**	67
4	H	**2a**	Me	3	**7a**	86
5	OTf	**2b**	Me	3	**7b**	86
6	CO_2Me	**2c**	Me	1	**7c**	97
7	CO_2Me	**2c**	$HC\equiv CCH_2$ [b]	3	**7d**	91

[a] Reaction conditions: 3.0 mol% $Rh_2(OAc)_4$ in benzene (0.01 M for **2**) at 60 °C.

[b] MS 4A was added in reaction mixture.

In Scheme 3, possible reaction mechanism is depicted for the $Rh_2(OAc)_4$-catalyzed formation of naphthalenediol derivatives from DNQ **1** by reaction with alcohol. We confirmed that the O–H insertion reaction did not proceed in the absence of Rh(II) catalyst, and the reaction was not affected strongly in the presence of radical-trap reagent such as TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl).[12] Therefore, we suppose this O–H insertion reaction proceeds via Rh(II) carbene as intermediate. First, $Rh_2(OAc)_4$ reacts with DNQ **1** to form Rh(II) carbene complex **I**. Nucleophilic attack of alcohol on carbene complex **I** proceeds to form oxonium ylide **II**, and then aromatization and deprotonation proceeds to form **5** with releasing $Rh_2(OAc)_4$.



Scheme 3. Plausible reaction mechanism.

In conclusion, we developed the $Rh_2(OAc)_4$-catalyzed synthesis of 1,2-naphthalenediol derivatives by the reaction of DNQs with water/alcohol.

Acknowledgments

This work was supported by JSPS KAKENHI Grant Number 26410054.

References and notes

1. (a) Stahl P, Kissau L, Mazitschek R, Huwe A, Furet P, Giannis A, Waldmann H. *J. Am. Chem. Soc*. 2001; 123: 11586;
   (b) Lu T, Shao P, Mathew L, Sand A, Sun W. *J. Am. Chem. Soc.* 2008; 130: 15782;
   (c) Madan S, Cheng C. *J. Org. Chem.* 2006; 71: 8312.
2. (a) Platt KL, Oesch F. *J. Org. Chem.* 1983; 48: 265;
   (b) Zambrao JL, Dorta R. *Synlett* 2003; 1545
   (c) Crandall JK, Zucco M, Kircch RS, Coppert DM. *Tetrahedron Lett.* 1991; 32: 5441.
3. For reviews, see: (a) Kitamura M. *J. Synth. Org. Chem., Jpn.* 2014; 72: 14;
   (b) Kitamura M. *Chem. Rec.* DOI: 10.1002/tcr.201600118;
   (c) Othman DIA, Kitamura M. *Heterocycles*, 2016; 92: 1761.
4. (a) Kitamura M, Tashiro N, Sakata R, Okauchi T. *Synlett* 2010; 2503;
   (b) Kitamura M, Sakata R, Tashiro N, Ikegami A, Okauchi T. *Bull. Chem. Soc. Jpn*., 2015; 88: 824.
5. (a) Reiser A, Shilh HY, Yeh TF, Huang JP. *Angew. Chem.* Int. Ed, 1996; 35: 2428;
   (b) Reiser A, Huang JP, He X, Yeh TF, Jha S, Shih HY, Kim MS, Han YK, Yan K. *Eur. Polym. J.* 2002; 38: 619;
   (c) Fukukawa K-i, Ueda M. *Polym. J.* 2008; 40: 281.
6. (a) Kitamura M, Sakata R, Okauchi T. *Tetrahedron Lett.* 2011; 52: 1931;
   (b) Kitamura M, Kisanuki M, Sakata R, Okauchi T. *Chem. Lett*. 2011; 40: 1129;
   (c) Kitamura M, Kisanuki M, Okauchi T. *Eur. J. Org. Chem.* 2012; 905;
   (d) Kitamura M, Araki K, Matsuzaki H, Okauchi T. *Eur. J. Org. Chem.* 2013; 5045: 35;
   (e) Kitamura M, Kubo K, Yoshinaga S, Matsuzaki H, Ezaki K, Matsuura T, Matsuura D, Fukuzumi N, Araki K, Narasaki M. *Tetrahedron Lett.* 2014; 55: 1653;
   (f) Kitamura M, Kisanuki M, Kanemura K, Okauchi T. *Org. Lett*. 2014; 16: 1554;
   (g) Kitamura M, Takahashi S, Okauchi T. *J. Org. Chem.* 2015; 80: 8406;
7. Recent reaction of diazonaphthoquinone by other groups, see: (a) Bahadur K, Magar S, Lee YR. *Org. Lett.* 2013; 15: 4288.
   (b) Baral EKR, LeeYR, Kim SH. *Adv. Synth. Catal.* 2015; 357: 2883;
   (c) Baral EKR, Lee YR, Kim SH, Wee YJ. *Synthesis* 2016; 48, 579.
8. For reviews of metal-catalyzed reaction of diazo compounds, see: (a) Padwa A, Krumpe KE. *Tetrahedron* 1992; 48: 5385;
   (b) Ye T, McKervey MA. *Chem. Rev.* 1994; 94: 1091;
   (c) Doyle M. P.; Ye, T.; McKervey, M. A. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; John Wiley & Sons: New York, 1998;
   (d) Davies HML, Beckwith RE. *J. Chem. Rev.* 2003; 103: 2861;
   (e) Zhang Z, Wang J. *Tetrahedron* 2008; 64: 6577;
   (f) Doyle MP, Duffy R, Ratnikov M, Zhou L. *Chem. Rev.* 2010; 110: 704.
9. Rh-catalyzed O–H insertion reaction of diazocarbonyl compounds with water or alcohols, see: (a) Paulissen R, Reimlinger H, Hayez E, Hubert AJ, Teyssié P. *Tetrahedron Lett.* 1973; 2233;
   (b) Noels AF, Demonceau A, Petiniot N, Hubert AJ, Teyssié P. *Tetrahedron* 1982; 38: 2733;
   (c) Bulugahapitiya P, Landais. Y, Parra-Rapado L, Planchenault D, Weber V. *J. Org. Chem.* 1997; 62: 1630.
10. We reported several methods for the synthesis of protected 1,2-naphthalenediols by metal-catalyzed reaction of diazonaphthoquinones: see ref. 6b,c,f.
11. Stability of naphthalenediols and naphthols, see:
    (a) Foti, MC, Johnson ER, Vinqvist MR, Wright JS, Barclay LRC, Ingold, KU. *J. Org. Chem.* 2002; 67: 5190;
    (b) Pino E, Aspée A, López-Alarcón C, Lissi E. *J. Phys. Org. Chem.* 2006; 19: 867.
12. When 1 equiv. of TEMPO was added in the same reaction conditions of Table 2, Run 2, O-H insertion product **5a** was obtained in 81% and DNQ **1b** was recovered in 7 % after stirring for 11 h.

Supplementary Material

Supplementary data associated with this article can be found, in the online version.

1,2-Napthalendiols were synthesized from diazonaphthoquinone.

1,2-Napthalendiol mono-protected alcohols were selectively synthesized.

Various alcohols and water were used as the reactants.