Tetrahedron Letters 49 (2008) 6466–6467

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

An unusual fragmentation reaction of substituted 2,3-norbornylhydroquinone with CAN: synthesis of 1,4-naphthoquinone

V. Sridar *, A. Yamuna

Industrial Chemistry Lab, Central Leather Research Institute, Adyar, Chennai 600020, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 30 July 2008
Revised 26 August 2008
Accepted 29 August 2008
Available online 3 September 2008

Keywords:
Fragmentation
Aromatization
2,3-Norbornylhydroquinone
Chlorinated-1,4-naphthoquinone

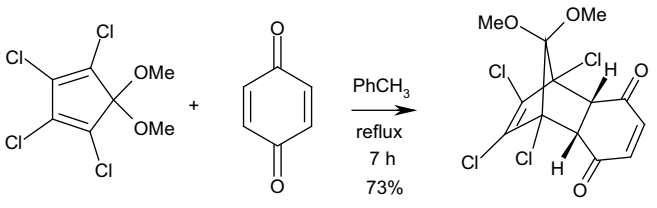
ABSTRACT

When substituted 2,3-norbornylhydroquinone is treated with CAN in acetonitrile or without water, an unusual fragmentation–aromatization reaction occurs which leads to a substituted 1,4-naphthoquinone instead of the desired substituted 2,3-norbornylbenzoquinone.

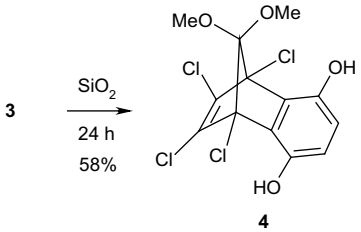
© 2008 Elsevier Ltd. All rights reserved.

RETRACTED

In the pursuit toward hexa- and heptaprismanes, 5,6-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene **1** is a key precursor.[1] Its Diels–Alder adduct **3** from reaction with benzoquinone **2** (Scheme 1) has been subjected to Luche reduction yielding the *exo,exo*-diol.[3] Dailey and co-workers have converted this diol into the *endo,endo*-diol and studied the Diels–Alder reaction with **1**.[4] It has also been reported by Mehta that the unsubstituted 2,3-norbornylbenzoquinone undergoes a Diels–Alder reaction with **1** to furnish *endo,anti* and *endo,syn* adducts in the ratio of 77:23 in good yields. However, the Diels–Alder reaction of the substituted 2,3-norbornylbenzoquinone with **1** has not been reported in the literature. If this reaction could be achieved, it would represent a new direction in synthetic efforts toward hexa- and heptaprismanes.[6] In order to secure, the known Diels–Alder adduct **3** was subjected to reaction with silica gel by impregnation to form the hydroquinone[7] **4** in a yield of 42% over two steps from **1** (Scheme 2).



Scheme 1.



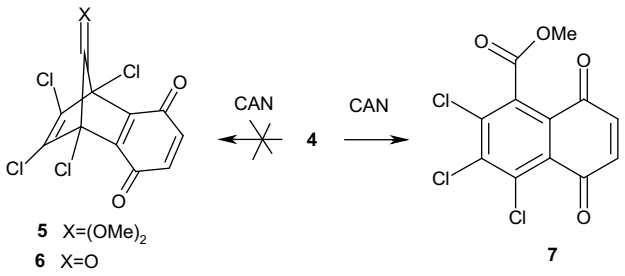
Scheme 2.

We expected a clean oxidation of the hydroquinone with CAN under acetonitrile/water conditions. However, to our surprise, the product obtained was substituted naphthoquinone **7** and none of the desired benzoquinone **5** or its hydrolyzed product **6** (Scheme 3). Obviously, the hydroquinone part of **4** has been converted into the benzoquinone as desired, but, additionally a fragmentation reaction has occurred[8] followed by aromatization leading to 1,4-naphthoquinone **7** in high yield. The structure of **7** was confirmed by proton and carbon NMR spectroscopy.[9] In the proton NMR, an AB quartet at δ 6.94 and δ 7.00 with $J = 10.7$ Hz corresponded to the benzoquinone protons and a singlet at δ 4.04 was due to the methyl ester group. The ^{13}C NMR supports the structure of **7** with two ketone groups at δ 181.74 and δ 181.44 as expected for an unsymmetrical benzoquinone.

As is well known, CAN is a one electron oxidant[10] and it oxidizes the oxygen in the methoxy group leading to an oxygen

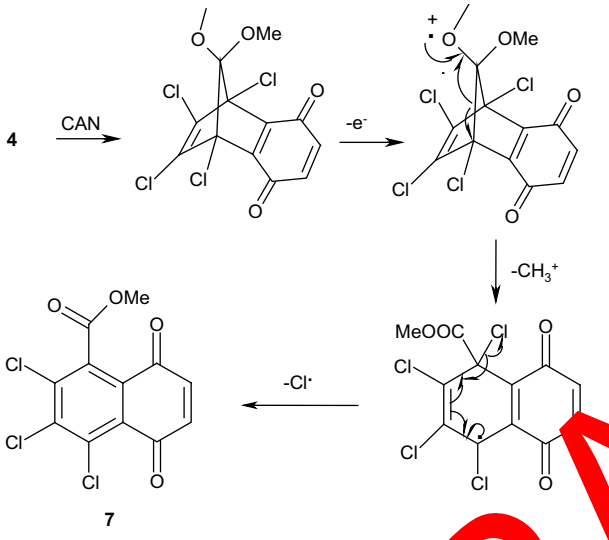
* Corresponding author. Tel.: +91 44 24911386; fax: +91 44 24911589.
E-mail address: svenkates@hotmail.com (V. Sridar).

0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.08.112



5 X=$(OMe)_2$
6 X=O
7

Scheme 3.



7

Scheme 4.

Table 1
Oxidation of hydroquinone **4** with CAN

Entry	Conditions	Oxidant (equiv)	Yield (**7**, %)
1	CAN, CH_3CN/H_2O, 1 h	5.3	78
2	CAN, CH_3CN/H_2O, 4	2.0	82
3	CAN, CH_3CN, 1 h	2.0	76
4	Ag_2O, Na_2SO_4, toluene, 3 h	12.7	47

cation-radical. This cation-radical undergoes a fragmentation reaction followed by aromatization with the leaving group being a chlorine radical (Scheme 4). It is also known in the literature that an acetal is converted into a ketone using CAN.[11] Here, instead of forming a ketone, a fragmentation reaction occurs leading to a substituted 1,4-naphthoquinone[9] in high yield under various conditions (Table 1), including non-aqueous conditions. Since it is also known that silver oxide[5] can oxidize hydroquinone to benzoquinone, we studied these conditions. Here again, we observed the same fragmentation reaction in addition to oxidation of hydroquinone. Using silver oxide, the yield was moderate; however, we did not observe any color change during the reaction as previously reported.[5]

In order to determine that aromatization is the driving force for the above reaction, we subjected Diels–Alder adduct **3** with CAN, wherein aromatization is not possible. In fact, there was no reaction and the substrate was returned in almost quantitative yield. The acetal was not affected by CAN and it is known in the literature that this type of acetal is robust, even under reflux over 48 h in 10% HCl it is not hydrolyzed.[1d] Therefore, one of the oxygens in the dimethyl acetal is oxidized and then cleaved only under aromatization conditions.

In conclusion, we have described a CAN-induced serendipitous reaction leading to a tri-chlorinated 1,4-naphthoquinone in excellent yield which is otherwise difficult to prepare. Work is in progress in our laboratory to form polychlorinated anthraquinone[12] from this product via the above oxidative process of Diels–Alder reaction, hydroquinone formation, and CAN oxidation.

Acknowledgments

The authors thank Dr. A. Mandal, Director, for providing infrastructural facilities and Dr. B. S. Reddy for his support. V.S. thanks the reviewer of this manuscript for useful suggestions. Thanks are due to Mr. K. Madhavan and Mr. S. Nagarajan for providing NMR and MS data, respectively.

References and notes

1. (a) Mehta, G.; Padma, S. *Tetrahedron* **1991**, *47*, 7783; (b) Mehta, G.; Reddy, S. H. K.; Padma, S. *Tetrahedron* **1991**, *47*, 7821. For other unnatural products, see: (c) Khan, F. A.; Das, J. *J. Am. Chem. Soc.* **2002**, *124*, 2424; (d) Khan, F. A.; Dwivedi, J.; Rout, B. *Tetrahedron Lett.* **2007**, *48*, 207.
2. [illegible] and [illegible].; Chou, T.-C. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1948.
3. Marchand, A. P.; LaRoe, W. D.; Sharma, G. V. M.; Suri, S. C.; Reddy, D. S. *J. Org. Chem.* **1986**, *51*, 1622.
4. [illegible]an, M. A.; Dailey, W. P. *J. Org. Chem.* **1993**, *58*, 1501.
5. Mehta, G.; Padma, S.; Karra, S. R.; Gopidas, K. R.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem.* **1989**, *54*, 1342.
6. Golobish, T. D.; Dailey, W. P. *Tetrahedron Lett.* **1996**, *37*, 3239.
7. *Synthesis of hydroquinone* **4**: To a powdered dione **3** (781 mg, 2.1 mmol), silica gel (60–120 mesh, 2 g) was added and thoroughly mixed. This mixture was then loaded onto a column of silica gel (60–120 mesh) in 25% EtOAc/pet. ether and left for 24 h. The column was then eluted using the same solvent mixture to collect the hydroquinone **4** (452 mg, 58%) as a white solid. R_f: 0.21 (25% EtOAc/pet. ether); Mp 156 °C; IR (KBr): 3347, 2981, 1677, 1603, 1488, 1454, 1360 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 8.5 (s, 2H, OH), 6.44 (s, 2H, CH), 3.50 (s, 3H, OCH_3), 3.35 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.68, 135.98, 122.92, 122.55, 119.51, 78.3, 53.18, 52.92; MS (ESI): *m/z* (%): 392 ([M+H_2O], [^{37}Cl, ^{35}Cl], 30), 391 ([M+H_2O+1], [^{37}Cl, ^{35}Cl], 100).
8. Nair, V.; Sheeba, V. *J. Org. Chem.* **1999**, *64*, 6898.
9. *Synthesis of trichlorinated 1,4-naphthoquinone* **7**: To a solution of diol **4** (90 mg, 0.24 mmol) in CH_3CN (2.7 mL), CAN (710 mg, 1.3 mmol) in H_2O (1 mL) was added dropwise with stirring at rt, and the reaction was continued for 1 h. Then, the reaction mixture was treated with H_2O (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layer was dried over Na_2SO_4 and evaporated in vacuo to provide crude naphthoquinone (81.6 mg) which upon column chromatography with 30% EtOAc/pet. ether provided **7** as a dark red solid (60.3 mg, 78%). R_f: 0.39 (25% EtOAc/pet. ether); Mp 148 °C; IR (KBr): 3188, 2937, 1734, 1668, 1620, 1443 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.00, 6.94 (AB q, 2H, J = 10.7 Hz, CH), 4.04 (s, 3H, COOMe); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 181.74, 181.44, 165.44, 141.22, 140.20, 136.95, 136.42, 135.48, 133.38, 129.03, 127.56, 53.48; HRMS calcd for $C_{12}H_5Cl_3O_4$ (M+Na): 340.9151. Found: 340.9144.
10. Nair, V.; Deepthi, A. *Chem. Rev.* **2007**, *107*, 1862.
11. (a) Nair, V.; Nair, L. G.; Balagopal, L.; Rajan, R. *Indian J. Chem.* **1999**, *38B*, 1234; (b) Ates, A.; Gautier, A.; Leroy, B.; Plancher, J. M.; Quesnel, Y.; Vanherk, J. C.; Marko, I. E. *Tetrahedron* **2003**, *59*, 8989; (c) Marko, I. E.; Ates, A.; Augustyns, B.; Gautier, A.; Quesnel, Y.; Turet, L.; Wiaux, M. *Tetrahedron Lett.* **1999**, *40*, 5613.
12. For a recent synthesis of substituted anthraquinones, see: Barluenga, J.; Martinez, S.; Suarez-Sobrino, A. L.; Tomas, M. *Org. Lett.* **2008**, *10*, 677.

RETRACTED