

Reaction of Electron-Rich Quadricyclane with *p*-Benzoquinone Derivatives

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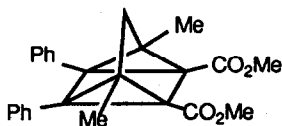
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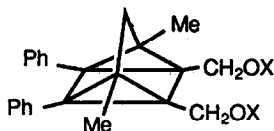
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Abstract: Preparation of electron-rich quadricyclane (3) with low half-wave oxidation potential and its reactions with some *p*-benzoquinones are presented. Electron transfer mechanisms are presented for these reactions.

Valence isomerization between norbornadiene and quadricyclane derivatives has been thought to be an attractive system for light energy conversion.¹ Though the concerted thermal reaction of quadricyclane to norbornadiene is forbidden by the Woodward-Hoffmann rules,² the reaction using various catalysts has been extensively studied.³ In 1978, the very low oxidation potential ($E_{1/2}$ vs. SCE = 0.91V) of quadricyclane was reported by Gassman.⁴ This finding stimulated the studies on the reversion of quadricyclane to norbornadiene through electron transfer processes.⁶ It was also shown that quadricyclane and *p*-benzoquinone derivatives, typical organic oxidizing

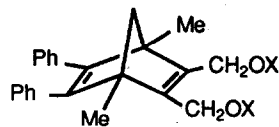


1



2 X=H

3 X=Me



4 X=H

5 X=Me

agents, formed electron donor-acceptor complexes.⁵ Thus, it is expected that *p*-benzoquinones initiate the reversion of quadricyclane to norbornadiene. Actually, the isomerization of quadricyclane to norbornadiene by chloranil has been reported to take place under photo-

chemical conditions.⁷ However, the thermal reaction of quadricyclane to norbornadiene by *p*-benzoquinone derivatives has not been known, but the cycloaddition between quadricyclane and *p*-benzoquinones was reported to occur exclusively.⁸ Therefore, it became of interest to examine the effect of electron donating groups on the reactivities of quadricyclane, which may cause a decrease in the half-wave oxidation potential of the quadricyclane skeleton. We now wish to report the synthesis of electron rich quadricyclane (**3**), its oxidation potential, and also its reactivities toward some quinones.

The conversion of **1**⁹ into **3** was conducted in the usual manner.¹⁰ The half-wave oxidation potential for **3** in CH₃CN, which contained 0.1 mol dm⁻³ lithium perchlorate and 1.6 x 10⁻⁴ mol dm⁻³ **3**, was 0.83 V versus a saturated calomel electrode (SCE).⁴ The value was obtained on a PAR Model 173 potentiostat equipped with a PAR model 175 function generator and platinum electrodes (sweep rate 50 mVs⁻¹).

When the benzene-*d*₆ solutions of **3** and *p*-benzoquinone or chloranil were reacted at 50.0±0.1°C, norbornadiene **5** was an only product and possible adducts of **3** with quinones or other decomposition compounds could not be detected by means of ¹H-NMR. As shown in the Table, chloranil is a more effective reagent than *p*-benzoquinone for the reaction. Both reactions under these conditions do not go to completion within 6.5 h.

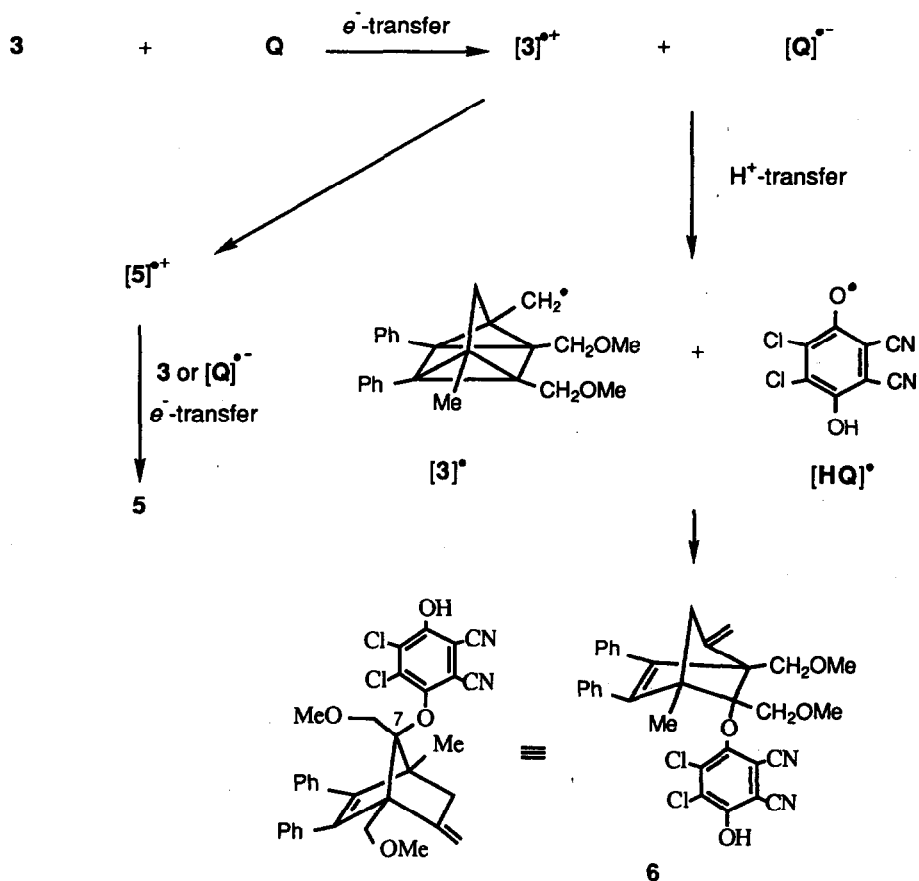
Table. The Reversion of **3** into **5***

Time/h	<i>p</i> -Benzoquinone		Chloranil	
	3	5	3	5
1.0	19	1	8	1
6.5	11	1	2	1

*The solutions were analyzed for unreacted **3** and produced **5** by ¹H-NMR analysis (270 MHz).

If the reaction starts with the transfer of an electron from **3** to the benzoquinones, DDQ is expected to be more effective for the cycloreversion of **3** than *p*-benzoquinone and chloranil because of its high reduction potential.¹¹ Actually the reaction of **3** with DDQ in benzene completed at room temperature, but an additional product **6** (48%) was obtained along with **5** (45%). The structure of **6** was determined by the following spectral data. Only one methyl group attached to the quaternary carbon at δ 1.30 (s, 3H) and a pair of exocyclic methylene protons at δ 4.81 (s, 1H) and 4.94 (s, 1H) were observed in its ¹H NMR spectrum (270 MHz, DMSO-*d*₆). NOEs between two protons (δ 4.32 and 4.42) of the methoxymethylene group substituted at C-7 and phenyl protons (4.3 and 2.2%, respectively) provided proof for the stereochemistry of **6** depicted in the Scheme. And the absorptions at 1650 and 900 cm⁻¹ in the IR spectrum of **6** also show the presence of the exocyclic olefin structure.

On the basis of the amphoteric redox nature of quinones,¹² possible mechanisms for the reaction of **3** with the quinones (**Q**) can be described by the following scheme. For the formation of the norbornadiene (**5**) the reaction may proceed via two electron transfer processes. In the first step, quinones oxidize **3** to form the radical cation $[3]^{+\bullet}$. The transformation of the radical cation $[3]^{+\bullet}$ to the another radical cation $[5]^{+\bullet}$ is a well established process.^{6,13} Next, the second electron transfer from **3** or $[Q]^{-\bullet}$ to $[5]^{+\bullet}$ yields **5**. The formation of **6** can be explained by the radical coupling between $[3]^\bullet$ and $[HQ]^\bullet$ which are formed by the proton transfer from $[3]^{+\bullet}$ to $[Q]^{-\bullet}$. This tentative mechanism accounts nicely for the reaction, and we are actively engaged in obtaining the further evidence providing the conclusion.



Scheme. Possible mechanisms for the reactions of **3** with quinones.

References and Notes

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10. (i) LAH reduction of the diester (1) in ether gave 2 (m.p. 142-145°C, 87%). In this reaction, a small amount of norbornadiene derivative (4) formed.; (ii) The diol (2) was methylated with MeI and NaH in DMF giving 3 (m.p. 93-95°C, 70%).
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