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Evidence for single electron transfer (SET) pathway in the reaction of primary alkylcadmium reagents with *p*-benzoquinone

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Abstract

The reaction of primary alkylcadmium reagents with *p*-benzoquinone at various conditions was studied. On the basis of our results, reaction proceeds through a SET mechanism that forms loose and tight intermediates, which produce quinole (**1**) and substituted hydroquinone (**2**). In both cases, hydroquinone (**3**) is obtained in different yields. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Single electron transfer; Organocadmium; Benzoquinone

1. Introduction

The organocadmium reagents are known as a very mild and regioselective reagent in organic synthesis [1a]. The most important synthetic application of organocadmium reagents has been in the preparation of ketones in reaction with acyl chlorides [1b,c]. Although this reagent does not react with ketones and esters [2], it reacts with α,β-unsaturated ketones mainly through 1,4-addition [3]. Results obtained from the reaction of Grignard reagents with some ketones and benzoquinone have shown that it proceeds via SET mechanism [4].

On the basis of recent reported results [5], and our studies on the reaction of several organocadmium reagents with benzoquinone [6], we decided to investigate the mechanism of these reactions. We are glad to report the operation of a SET mechanism in the reaction of organocadmium reagents with benzoquinone.

2. Results and discussion

The reaction of several organocadmium reagents with *p*-benzoquinone was carried out at low and high temperatures. Products were identified by the comparison of their spectroscopic data with authentic samples. The results are shown in Tables 1 and 2.

On the basis of our results (Table 1), it seems likely that the quinol formation has arisen via a SET mechanism through the formation of α-complex between the substrate and reagent and subsequent single electron transfer from the reagent to benzoquinone which leads to the formation of cross-conjugated tight intermediate (CCTI) in solvent cage (Scheme 1). The appearance of the deep blue color during the addition of the reagent to benzoquinone supports the SET mechanism [4b]. Moreover, when we carried out the scavenging studies by addition of *p*-dinitrobenzene to the reaction contents, the starting material benzoquinone was recovered

Table 1
Product distribution in reaction of dialkylcadmium reagents with *p*-benzoquinone in tetrahydrofuran (THF) and diethyl ether (DEE) at low temperature

R	Yield (%) of **1** [a]		Yield (%) of **3** [b]	
	THF	DEE	THF	DEE
(a) C_2H_5	80	71	<1	5
(b) C_3H_7	74	60	<1	2
(c) C_4H_9	71	75	2	3

[a] Isolated yields obtained by preparative TLC.
[b] Yields obtained by GC.

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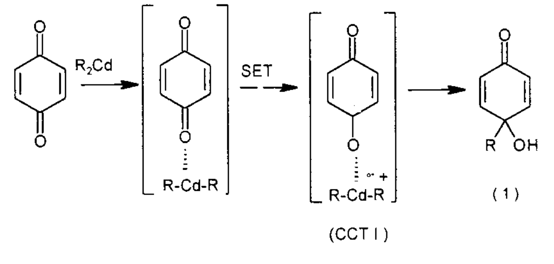
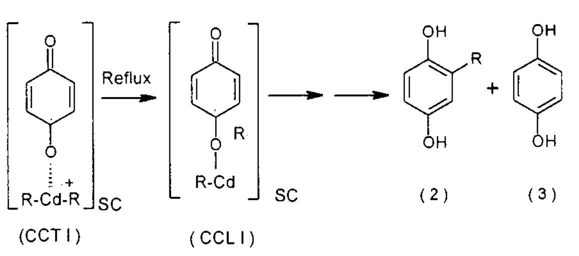
Table 2
Product distribution in reaction of dialkylcadmium reagents with *p*-benzoquinone in tetrahydrofuran (THF) and diethyl ether (DEE) at high temperature

R	Yield (%) of 2 [a]		Yield (%) of 3 [a]	
	THF	DEE	THF	DEE
(a) C_2H_5	18	8	21	25
(b) C_3H_7	15	13	15	18
(c) C_4H_9	15	10	26	22

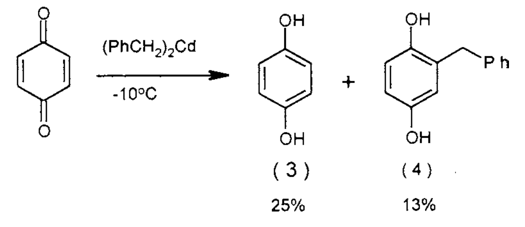
[a] Isolated yields obtained by preparative TLC.



Scheme 1.



Scheme 2.



Scheme 3.

after work up. Similar alkyl–quinone radical ion pairs in low temperature have been described previously in the reaction of alkyl lithiums and Grignard reagents with benzoquinone [4d]. According to this report, there has been a good chance for the intermediate to diffuse out of the solvent cage, hydroquinone is formed in considerable amounts (40%) in the case of butyl magnesium reagent. In our system, under the similar conditions, only 2% of hydroquinone formation was observed.

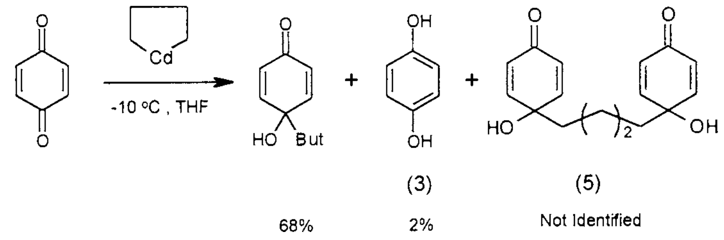
The CCTI is responsible exclusively for the formation of quinol product while the formation of 2% hydroquinone probably resulted from the trace amount of Grignard reagent left in the solution.

Table 2 lists the results of the same reaction under reflux condition. The formation of a considerable amount of substituted hydroquinone (8–18%) and hydroquinone (15–26%) implicates the intermediacy of the cross-conjugated loose intermediate (CCLI) (Scheme 2). On the basis of this mechanism, as soon as the CCTI is formed, it is converted to CCLI under the reflux condition. This in turn collapses either to substituted hydroquinone (**2**) or abstracts hydrogen from solvent molecules and forms hydroquinone.

The different behavior between magnesium and cadmium reagents can be attributed to the higher ionic character of the C–Mg bond and the higher covalent character of C–Cd bond. While the former character encourages the formation of loose intermediate and subsequent formation of hydroquinone in a higher percentage yield even at low temperature, the latter character causes the tight intermediate to have lower tendency toward the formation of loose intermediate and hydroquinone results in trace amounts under the similar conditions.

It should be emphasized that with ethyl, propyl and butyl cadmium reagents, the determining factor in the transformation of tight intermediate to loose intermediate is the covalent character of the C–Cd bond since the stability of the resultant alkyl radical intermediates are similar. When we used dibenzylcadmium reagent, benzylhydroquinone (**4**) and hydroquinone (**3**) were identified as the main products (Scheme 3). These results clearly indicate that when the stability of alkyl radical in the tight ion pair is enhanced, no quinol product is formed in this case.

To demonstrate the activity of one or both groups of alkyl cadmium reagent, we prepared the cadmium cy-



Scheme 4.

clopentane reagent and studied its reaction with benzoquinone under the similar conditions (Scheme 4). The lack of the formation of bisaddition product (**5**) indicates that only one alkyl groups in cadmium reagent is active in these reactions. This result is in contrast to the observed activity of both group in alkylcadmium reagent which previously has been reported [5]. The availability of one group of these reagents can be interpreted on the single electron transfer and the operation of a radical pathway mechanism in these reactions. The free energy equation of the single electron transfer reaction is given in Eq. (1):

$$\Delta G^\circ \text{ (kcal mol}^{-1}) = 23.06[E^\circ(D^{+\bullet}/D) - E^\circ(A/A^{-\bullet})] - \Delta E_{\text{coul}} \qquad (1)$$

where $E^\circ(D^{+\bullet}/D)$ and $E^\circ(A/A^{-\bullet})$ are the standard reduction potentials of the electron donor and acceptor redox couples, respectively, and ΔE_{coul} is the coulombic interaction energy for the two singly charged radical ions formed in the SET process [7]. We suggest that the involvement of two alkyl groups seems to take place in two consecutive steps. Since $E^\circ(A/A^{-\bullet})$ for benzoquinone in both steps is constant, the reduction potential of the alkyl group, $E^\circ(D^{+\bullet}/D)$, should be the effective term in Eq. (1). As soon as the organocadmium reagent is changed from R–Cd–R to R–Cd–X, the $E^\circ(D^{+\bullet}/D)$ of the organocadmium reagent is increased. This itself leads to a higher ΔG° for the second single electron transfer, which means that a less efficient reaction would take place for the transferring of the second alkyl group.

3. Conclusions

From this investigation, it can be concluded that the reaction of the primary alkylcadmium reagent with *p*-benzoquinone proceeds through a SET mechanism. The products and yields are different and depend on the temperature, solvent and the nature of the alkyl group. Reaction at low and high temperature leads to 1,2 and 1,4-addition products, respectively. The yield of the 1,4-addition product is less than the 1,2-addition product, since radical ion pairs diffusing out of the solvent cage is enhanced at higher temperatures. The formation of high percentage yield of hydroquinone at high temperature and in the case of all alkyl groups supports this proposal, as well. Diffusing out of the solvent cage also depends on the viscosity and basicity of the solvent. Comparing the yields of hydroquinone in diethyl ether (DEE) and THF at high temperature shows the increasing yield in DEE, which has, lower basicity and viscosity. The nature of the primary alkyl group is also an important factor in reaction mechanism, since unlike the other primary alkylcadmium reagents, the benzyl cadmium reagent leads to 1,4-addition product even at low temperature.

4. Experimental

4.1. General

^{1}H- and ^{13}C-NMR spectra of $CDCl_3$ solutions were recorded on an 80 MHz Bruker spectrometer. Chemical shifts were expressed as ppm with respect to TMS. Mass spectra were obtained with a GCMS-QP 1000EX, Shimadzu. Reactions were conducted in oven-dried glasswares under a nitrogen stream. Diethyl ether and THF were distilled over Na–benzophenone before use. The structure of products were identified by comparison the spectroscopic data with authentic samples [3,4c,8].

4.2. Preparation of organocadmium reagent

Ethyl, propyl, butyl and benzylcadmium reagents were prepared according to the standard procedure [9]. Cadmium cyclopentane was prepared as follows.

1,4-Dibromobutane (0.02 mol) dissolved in anhydrous THF (150 ml) was added to magnesium turnings (0.05 mol). A small volume of dihalide solution was added dropwise at a rate slow enough to avoid excessive heating (40–50°C). After addition was completed, the clear solution was allowed to stir 1 h at room temperature (r.t). Dried $CdCl_2$ (0.02 mol) was added and the solution was refluxed for 2 h to give a negative test for Grignard reagent.

4.3. Procedure for the addition of cadmiumcyclopentane reagent to benzoquinone at low temperature

The organocadmium reagent solution (0.02 mol) was cooled to -10°C and a solution of benzoquinone (0.01 mol) in THF was added through dropping funnel to cadmium reagent. The reaction mixture was stirred for 1 h. After hydrolysis with saturated aqueous ammonium chloride. The mixture was extracted with CH_2Cl_2 (2×50 ml). The organic phase washed with water (50 ml), and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by PTLC (neutral alumina) eluting with $CHCl_3$–hexane (9:1). The spectral data of resultant quinol, which was obtained as pale yellow oil (68%), are as follows: ^{1}H-NMR 6.8 (2H, d), 6.09 (1H, d), 3.99 (1H, s), 1.73 (2H, m), 1.28 (4H, m), 0.69 (3H, t). ^{13}C-NMR 168.2, 125.5, 127.7, 68.6, 39.6, 25.6, 22.6, 13.6. IR (liquid film, cm^{-1}) 3400, 2956, 1625, 662. MS (EI, *m*/*z*) 166 (M^+), 110 (100%), 81, 71, 55.

4.4. Procedure for addition of cadmiumcyclopentane reagent to benzoquinone at reflux temperature

The organocadmium reagent solution (0.02 mol) was heated to reflux temperature and a solution of benzoquinone (0.02 mol) in THF was added to it. After 3 h, the reaction mixture was hydrolyzed and extracted with ether. The ether layer was separated and the solvent was removed under reduced pressure. The residue was purified by PTLC (silica-gel) eluting by ether–hexane (1:1). The spectral data of resultant butyl hydroquinone, which was obtained as a pale yellow oil (15% yield), are as follow: ^{1}H-NMR 6.63 (3H, m), 5.1 (2H, OH), 2.54 (2H, t), 1.43 (4H, m), 0.92 (3H, t). ^{13}C-NMR 149.97, 148, 130.8, 117.55, 116.9, 113.9, 32.48, 30.37, 23.1, 14.58. IR (liquid film, cm^{-1}) 3355, 1654, 1506, 1456, 1195 MS. (EI, *m*/*z*) 166 (M$^+$), 136 (100%), 123, 107.

Acknowledgements

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