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Experimental and semiemprical studies of chemical reactivity of dialkylcadmium reagents addition to α,β-enones

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Abstract

Experimental and semiempirical calculations were carried out to study the reactivity of dialkylcadmium reagents addition to α,β-enones. It was demonstrated that α,β-enone such as benzoquinone with low lying LUMO energy reacts via single electron transfer (SET) mechanism with the formation of the 1,2 or 1,4-type alkyl addition product depending on the reaction temperature and substrate structure. Site and chemoselectivity in unsymmetrical benzoquinone derivatives are determined by the stability of the cadmium coordinated semienone complex intermediates and the carbon spin densities of these reactive species respectively. On the other hand, by increasing the LUMO energy of α,β-enone system, the reaction mechanism changes from SET to polar addition affording the 1,4-type alkyl addition product. The establishment of a correlation scale between substrate LUMO energies and reaction mechanism presented in this article will be discussed.

Keywords: Dialkylcadmium reagent; Benzoquionone; Enone; SET mechanism; LUMO

1. Introduction

The organocadmium compounds are known as very mild and regioselective reagents in organic synthesis [1]. The behavior of these reactions especially with α,β-enone systems exhibit ambiguities and results may not be interpreted easily. For example, although these reagents do not react with ketones, reaction with α,β-unsaturated ketones leads mainly to 1,4-type addition products [2]. On the other hand, reaction with *p*-benzoquinone affords quinol or substituted hydroquinone which is consistent with 1,2 and 1,4-addition types respectively [3]. Since mechanistic details of α,β-enones with organocadmium reagents are not clear and sometimes misleading [4], we decided to investigate the subject carefully. We are pleased to report the borderline between the SET and polar mechanisms about these reactions.

2. Results and discussion

In our recent publication, we suggested that reaction of primary dialkylcadmium reagent with *p*-benzoquinone at low temperature generates quinol while 2-alkylhydroquinone is formed under solvent reflux conditions (Scheme 1). Product obtained at low temperatures are consistent with 1,2-type addition while that resulted in harmony with 1,4-type addition is generated at high temperature [3]. On the basis of some experimental evidences such as the development of deep blue color during addition of the reagent to *p*-benzoquinone, scavenging studies and formation of hydroquinone as a byproduct in all experiments, we were convinced that the reaction proceed through a SET mechanism [3]. To explain the formation of 1,2 and 1,4-addition products, we proposed that the cross-conjugated tight intermediate (CCTI) in solvent cage is formed as the first reactive species along the reaction coordinates. At low temperature, the CCTI is responsible exclusively for the formation of quinol (Scheme 2). If the reaction mixture is warmed to room temperature prior to work-up or is carried

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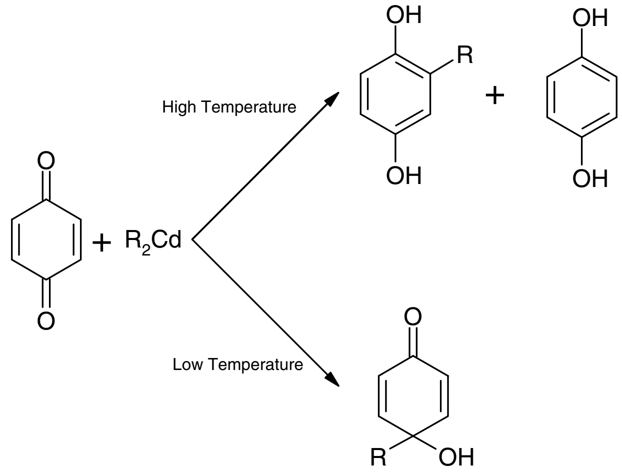


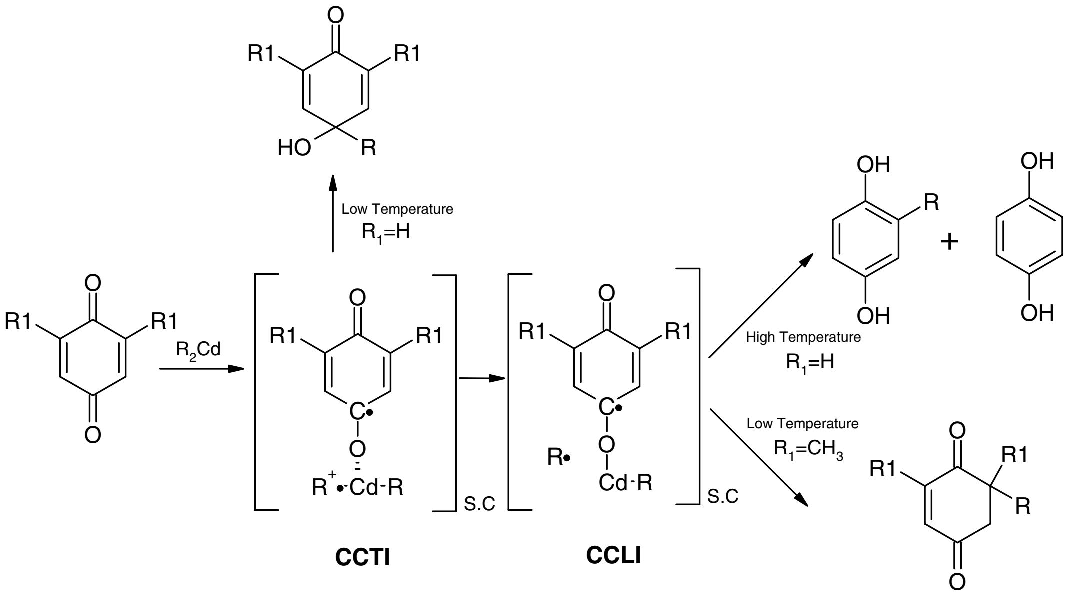
Scheme 1.

out at reflux condition from the beginning, 2-alkylhydroquinone is generated as the main product. The cross-conjugated loose intermediate (CCLI) in solvent cage is formed via CCTI and its subsequent collapse can explain the generation of 1,4-addition product (Scheme 2). That intra or inter dialkylquinol in the presence of cadmium cyclopentane was not identified in the reaction mixture was attributed to the diminished electron acceptability of primary monoalkylquinol product (vide infra) (Scheme 3).

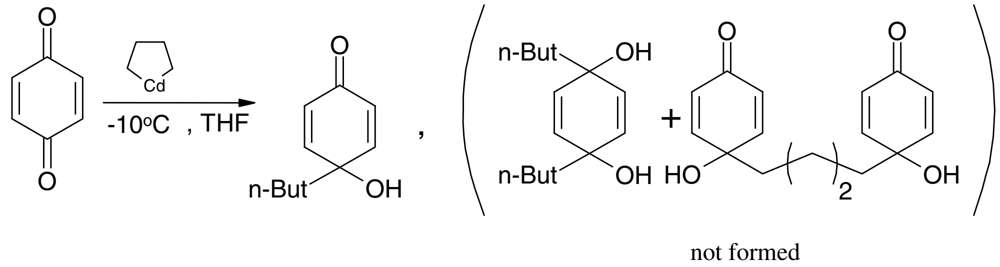
To see whether there is a correlation between the LUMO energy of enone system and reaction type, E_{LUMO} of a number of enone systems were determined by using PM5 method [5]. The results are shown in Table 1. As seen, the lowest LUMO energies of −2.28 to −2.02 eV (entries 1–7 in Table 1) belong to the quinone and its derivatives. When the conjugation in *p*-benzoquinone is interrupted either through a carbonyl group protection (entry 9 in Table 1), or a double bond protection (entry 10 in Table 1), the LUMO energies increase to −1.34 and −1.24 eV respectively. Entries 11–17 in Table 1 belong to the systems containing the LUMO energies in the range of −0.74 to +3.20 eV.

In the next step, we tried to collect the experimental evidences either through literature or from our own studies in order to make a correlation between the LUMO energies of the enone systems and the type of dialkylcadmium additions taking place on these molecules. Our literature survey showed that with the exception of benzoquinone monoethyleneglycol ketal and 1:1 cyclopentadiene–benzoquinone cycloadduct (entries 9 and 10 in Table 1), the experimental results of dialkylcadmium reagents addition to other enones are available [2–4]. Therefore, the 1:1 cyclopentadiene–benzoquinone cycloadduct **5** was prepared according to the procedure reported previously [6]. Table 2 shows the results of the dialkylcadmium reagents addition to 1:1 cyclopentadiene–*p*-benzoquinone cycloadduct (Scheme 4). The structures of compounds **6a–c** were identified on the basis of their spectroscopic information (see Section 4). We have included the results of the addition of the same dialkylcadmium reagents to *p*-benzoquinone in Table 2 in order to make the comparison more convenient. It can be seen that although *p*-benzoquinone mainly undergoes 1,2-addition and forms quinol **2**, the corresponding cycloadduct **5** is attacked through 1,4-addition and affords products **6a–c**.

To the best of our knowledge, with the exception of compound **7d** (R = H), the synthesis of other analogous **7a–c** have not been reported previously. Apparently, these molecules can be conceived to have been driven through Michael addition of dialkylcadmium reagents to *p*-benzoquinone, a process which does not occur in reality. We thought that thermolysis of compounds **6a–c** might afford

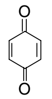
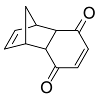
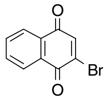
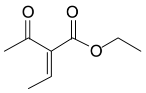
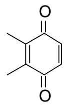
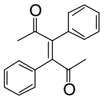
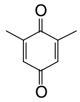
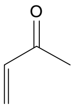
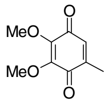
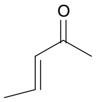
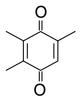
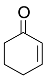
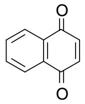
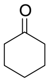
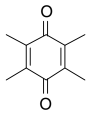
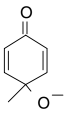
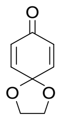


Scheme 2.



Scheme 3.

Table 1
Effect of E_{LU} calculated by using PM5 method on addition type of dialkylcadmium reagents to enones

Entry	Chemical structure	E_{LUMO} (eV)	Type of addition yield [Ref.]	Entry	Chemical structure	E_{LUMO} (eV)	Type of addition yield(%) [Ref.]
1		−2.28	1,2 80 [2b–4]	10		−1.24	1,4 82 [3b]
2		−2.19	1,2 86 [2b,4]	11		−0.74	1,4 85 [2a]
3		−2.12	1,2 86 [4]	12		−0.47	1,4 52 [2a]
4		−2.12	1,4 82 [4]	13		−0.47	1,4 3 [2a]
5		−2.04	1,4 86 [4]	14		−0.41	1,4 6 [2a]
6		−2.04	1,4 80 [4]	15		−0.38	1,4 5 [2a]
7		−2.02	1,2 60 [2]	16		+0.17	N.R [3b]
8		−1.72	N.R [3b]	17		+3.20	N.R [3b]
9[a]		−1.34	N.R [3b]				

[a] Although no reaction is observed with dialkylcadmium reagent, the 1,4-type product is obtained with phSH [11].

the desired products **7a**–**c**. The possibility of this reaction was based on the fact that the synthesis of the parent molecule, i.e., compound **7d** (R = H) has been reported previously via the thermolysis of **6d** [7]. However, thermolysis of compounds **6a**–**c** resulted in the formation of 2-alkylhydroquinones **3a**–**c** (Table 3). Although we could not isolate the desired products, the implication of 5-alkylcyclohexenedione **7a**–**c** as intermediates in these reactions is conceivable.

The correlation between the enone structure, the relevant LUMO energy and the type of addition reactions

Table 2
Yields of **6a**–**c** and reaction type obtained by addition of organocadmium reagents to 1:1 cyclopentadiene–*p*-benzoquinone(**5a**–**c**) and *p*-benzoquinone (**1**) at low temperature

R	Yield (%) and type of addition to **1**	Yield (%) and type of addition to **5**
C_2H_5	78 (1,2)	82 (1,4)
C_3H_7	69 (1,2)	79 (1,4)
C_4H_9	82 (1,2)	63 (1,4)

Table 3
Yields of thermolysis products of **6**

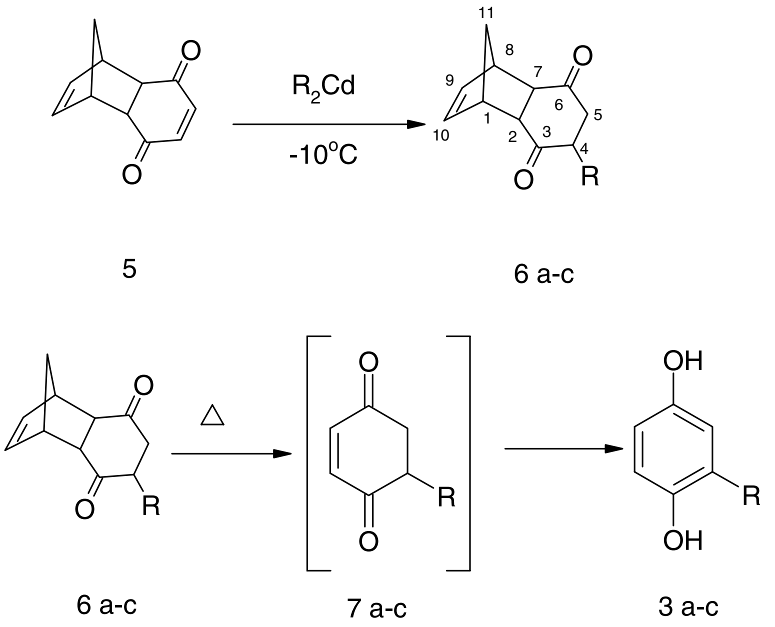
R	Yield (%) of **3**[a]
C_2H_5	48
C_3H_7	35
C_4H_9	37

[a] Isolated yields of 2-alkyl-hydroquinones after distillation.

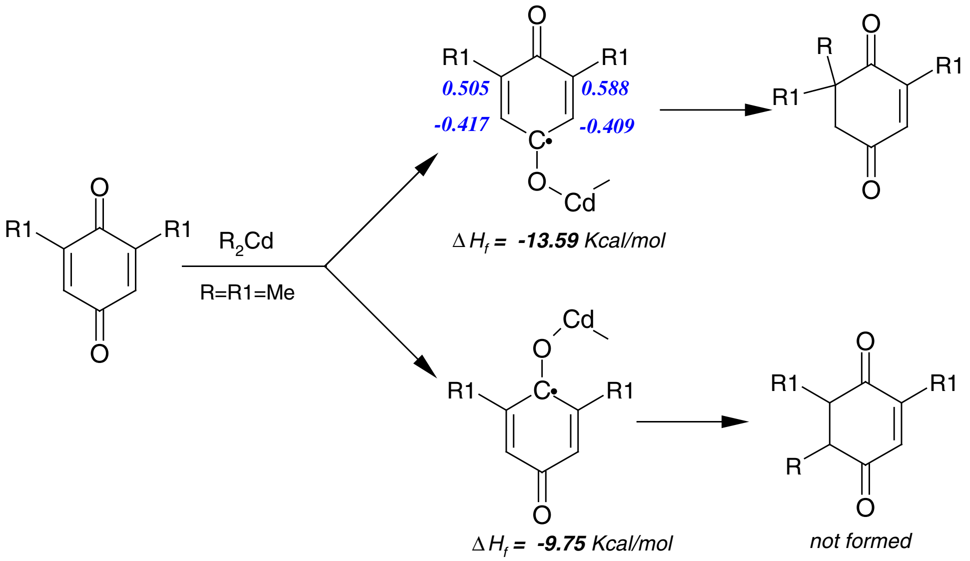
are shown in Table 1. To rationalize the results, the following explanations should be taken into consideration:

(1) As is known, the reaction of *p*-benzoquinone with dialkylcadmium reagent proceeds via SET mechanism with the formation of 1,2-type product [3]. This behavior is expected on the basis of the LUMO energy presented in Table 1. Frontier molecular orbital (FMO) theory can successfully rationalize an enormous range of chemical phenomena [8]. The significance of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) become apparent since the interaction between nondegenerate orbitals is inversely proportional to the energy gap between the orbitals. If this gap is small enough, the interaction is strong and SET mechanism is dominant [9]. In other words, the formation of bond between hard centers, i.e., alkyl and carbon next to the oxygen via CCTI is anticipated due to greater Coulombic interaction. At higher temperature, the CCLI produced from CCTI is attacked by reagent affording 2-alkylhydroquinone with the bond formation between the soft centers, i.e., β-carbon and free alkyl radical.

(2) On the basis of results shown in Table 1, it is expected to observe the similar behavior between *p*-benzoquinone and its derivatives with LUMO energies close to −2.28 eV. Although naphtaquinone (entry 7 in Table 1) mainly undergoes 1,2-type addition, 2,6-dimethylbenzoquinone (entry 4 in Table 1) and 5-methyl, 2,3-dimethoxybenzoquinone (entry 5 in Table 1) afford the 1,4-type addition products. Moreover, 2,6-dimethylbenzoquinone leads to 2,6,6-trisubstituted alkyl cyclohexenedione and not the other 2,5,6-trisubstituted isomer (Scheme 5). To clarify the apparent discrepancy of 1,2 and 1,4-type behaviors, we have calculated the formation enthalpies of cadmium coordinated semibenzoquinone (CSBQ) in CCLI for *p*-benzoquinone and some derivatives by using PM5/UHF method. The results are shown in Table 4. Recall that the formation of 1,2 and 1,4-addition products arise from CCTI and CCLI respectively. The rate constant for the conversion of the former to the latter definitely depends on the stability of cadmium coordinated semibenzoquinone in CCLI. Therefore, CCTI arisen from benzoquinone has no driving force to be converted to the corresponding CCLI with the stabilization energy of 4.3 kcal/mol. The CCTI inevitably collapses to quinol product which is consistent with a 1,2-type addition. On the other hand, reaction of 2,6-dimethylbenzoquinone with dialkylcadmium reagent can lead to two different CCLI intermediates (Scheme 5). As shown in Scheme 5, the intermediate with radical center at C_4 with the formation enthalpy of

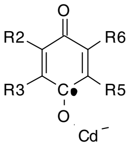
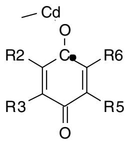


Scheme 4.



Scheme 5.

Table 4
The formation enthalpies of two types of cadmium coordinated semibenzoquinone of the unsymmetrical quinines (CCLI)

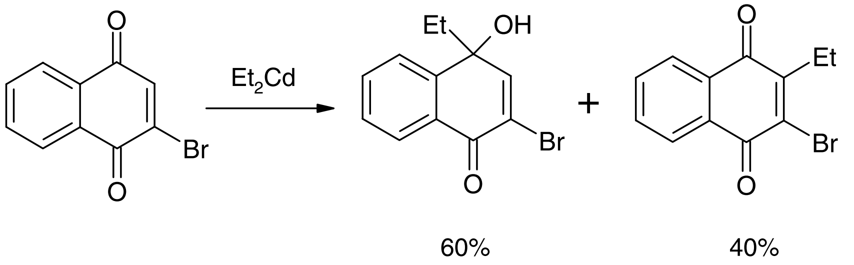
	 (CCLI)1 H_f (kcal/mol)[a]	 (CCLI)2 H_f (kcal/mol)[a]
R2 = R6 = H R3 = R5 = H	+4.13	+4.13
R2 = R6 = Me R3 = R5 = H	−13.59	−9.75
R2 = R3 = R6 = Me R5 = H	−20.42	−17.65
R2 = R3 = OMe R5 = Me, R6 = H	−73.29	−65.34

[a] Calculated by using PM3/UHF method.

−13.95 kcal/mol is favored with respect to the other intermediate with radical center located at C_1 whose formation energy is −9.75 kcal/mol. Compared to cadmium coordinated semibenzoquinone, the similar CCLI arisen from 2,6-dimethylbenzoquinone with lower formation enthalpy has the driving force to be generated under the reaction conditions (Scheme 5). Subsequent collapse of radical pair would finally yield the 2,6,6-trimethylcyclohex-2-ene-1,4-dione consistent with 1,4-type addition product. Moreover, calculation of spin density using PM3/UHF for cadmium coordinated benzoquinone derived from 2,6-dimetylbenzoquinone depicted in Scheme 5 confirms the formation of 2,6,6-trialkylsubstituted product. On the basis of similar explanation, the CCTI arisen from 5-methyl-2,3-dimethoxybenzoquinone with the formation enthalpy of −73.29 kcal/mol is stable and subsequent collapse of radical pair affording the 1,4-type addition is anticipated.

As is expected, 2-bromo-1,4-naphtaquinone with LUMO energy of −2.19 eV (entry 2, Table 1) has been reported to result in a mixture of quinol and 2-bromo-3-ethyl-1,4-naphtaquinone [4] (Scheme 6). As the authors point out, the latter is produced via a silicagel-catalyzed dieneone–phenol type rearrangement [4]. Therefore, the formation of 1,2-type addition in this case is correlated with the LUMO energy of enone.

(3) The 1,4-type addition behavior of enones with higher LUMO energies is predicted from perturbation theory. To check the behavior of the dialkylcadmium with *p*-benzoquinone monoketal (entry 9 in Table 1), in which the con-



Scheme 6.

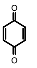
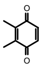
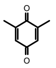
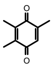
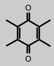
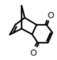
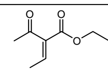
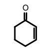
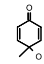
substrate										
E_{LUMO}(eV)[1]	-2.21	-2.12	-2.12	-2.04	-1.72	-1.24	-0.24	-0.38	+0.17	+3.20
Addition type	1,2		1,4		-	1,4			-	-
Mechanism type	SET				NR	Ionic			NR	

Fig. 1. Reactivity scale of primary dialkylcadmium reagents addition to enone system. The correlation between reactivity (type of addition and mechanism) with the substrate LUMO energy. $^1E_{\mathrm{LUMO}}$: calculated by PM5 method.

jugation of quinone system is interrupted and the LUMO energy increases, it was prepared according to the previously reported procedure [10]. Unfortunately, the ketal deprotection occurs under the reaction conditions with dialkylcadmium reagent. However, it is known that the *p*-benzoquinone monoketal undergoes the 1,4-addition reaction with phSH [11]. Since this nucleophilic with the HOMO energy of −8.78 eV is similar with that of diethycadmium reagent with the HOMO energy of −8.43 eV, similar type 1,4 addition is expected from dialkylcadmium reagents. Recall that the stabilization energy is a function of the resonance integral β, and not just the energy gap ΔE, so that the form of the orbital and its symmetry will also play a role in determining the stabilization energy. For this reason it is not always the HOMO–LUMO interaction that dominates structure and reactivity. Overlap effects which are incorporated into resonance integral (β) may override energy gap considerations [8]. The formation of bond between the soft centers, i.e., free alkyl radical and β-carbon is expected in this case.

(4) As seen in Table 1, no reactivities toward dialkylcadmium reagents are observed either from the systems with higher LUMO energies or the 2,3,5,6-tetramethylbenzoquinone having −1.72 eV LUMO energy. Such observations may have arisen from either HOMO–LUMO energy gap enhancement or inefficient overlap effects.

Finally, in order to complete our knowledge about the reactivity pattern, a clear cut scale which correlates the substrates reactivity (type of addition and reaction mechanism) to the LUMO energy of enone system is established. As shown, four groups of reactivity are predicted in Fig. 1. The left side belongs to the region of enones with LUMO energies from −2.28 to −2.04 eV. Depending on the reaction conditions and substrates, either 1,2 or 1,4-type addition products are anticipated through SET mechanism under the effect of dialkylcadmium reagents. Between left and middle region (ionic), there is a gray area with the LUMO energy of −1.72 eV belonging to tetramethylbenzoquinone. No reaction with dialkylcadmium is observed either through SET mechanism or ionic mechanism (may be due to steric effects present in polar reactions). The third region is related to the substrates with the LUMO energies between −1.24 and −0.38 eV. Polar addition mechanism with the exclusive formation of 1,4-type product is the dominant behavior in this part. There is also another gray area between ionic and no reaction region beginning with the LUMO energy of +0.17 eV belonging to cyclohexenone with no reactivity with dialkylcadmium reagents. Due to the larger energy gap between HOMO and LUMO, and in the absence of efficient orbital interaction, neither SET nor polar mechanism behavior is anticipated in this region.

3. Conclusion

In this article, we have shown that the two parameters of HOMO–LUMO energy gap of dialkylcadmium and enone system or the overlap effects manifested in the stabilization energy of the frontier orbital interactions are of fundamental keys in determining the type of addition and mechanism. Whenever the initial energy gap between donor (dialkylcadmium reagent) and acceptor (enone system) is small, the single electron transfer mechanism is dominant and reactions afford exclusively the 1,2 or 1,4-addition type products depending on the reaction temperature or substrate structure. Site and chemoselectivity in unsymmetrical benzoquinone derivatives are determined by the stability of the cadmium coordinated semienone complex (CCLI) intermediates and the carbon spin densities of these reactive species respectively. On the other hand, the reaction mechanism changes to polar addition in the absence of good donor–acceptor pair provided that efficient overlap exists between frontier orbitals. Therefore, one anticipates to obtain the 1,4-type products under these conditions.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on a 80 MHz Bruker spectrometer. Chemical shifts were expressed as ppm with respect to TMS. Mass spectra were obtained with a GCMS-QP 1000EX, Shimadzu. Organocadmium reactions were conducted in oven-dried glassware under nitrogen stream. Diethyl ether and tetrahydrofuran (THF) were distilled over Na-benzophenone before use.

4.2. General procedure for the addition of dialkylcadmium reagent to benzoquinone

The organocadmium reagent solution (0.02 mol) in 100 ml of diethyl ether [12] was cooled to −10 °C and a solution of benzoquinone (0.01 mol) in THF (150 ml) was added to cadmium reagent through a dropping funnel. The reaction mixture was stirred for 1 h. After hydrolysis with saturated aqueous ammonium chloride, the mixture was extracted with 2 × 50 ml of chloroform. The organic layer was washed with water (2 × 50 ml), and dried over anhydrous Na_2SO_4. The crude product was purified by PLTC (silica gel) eluting with chloroform–hexane (9:1) for benzoquinone and chloroform–hexane (1:1) for 2,6-dimethylbenzoqinone.

4.3. General procedure for the preparation of **6**

A solution of the organocadmium reagent (0.02 mol) in 100 ml of diethyl ether was cooled to −10 °C. To this was added a solution of **5** (0.015 mol) in diethyl ether (50 ml) through a dropping funnel. The reaction mixture was stirred for 3 h. After hydrolysis with saturated aqueous ammonium chloride (50 ml), the mixture was extracted with methylene chloride (2 × 50 ml). The organic layer was washed with water (50 ml), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by PTLC (silica gel) eluting with chloroform–hexane (4:1). The product was obtained as a pale yellow oil. The spectral data of resultants are as follow:

Compound **6a**: ^{1}H NMR ($CDCl_3$, δ): 6.3 (t, 2H,1.6 Hz, 9-H, 10-H), 3.0–3.4 (m, 2H, 1-H, 8-H), 2.1–2.7 (m, 4H, 2-H, 4-H, 5-H, 7-H), 1.1–1.4 (m, 4H, CH_2 (aliphatic), 11-H (*syn* & *anti*)), 0.87 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, δ): 193.1, 191.2 (C=O, C-3, C-6), 135.9, 135.7 (C-9, C-10), 51.5, 50.7, 50.1, 49.1 (C-2, C-4, C-5, C-7), 48.7 (C-11), 47.5 (C-1), 43.5 (C-8), 23.6 (CH_2, aliphatic), 11.2 (CH_3, aliphatic). IR (liquid film, cm^{-1}): 3100, 2960, 1710 (C=O, non-conjugate), 1420, 880. MS (EI, *m*/*z* (%))[1]: 138[2] (59%, 5-ethyl-2,3-cyclohex-2-ene-1,4-dione system obtained from decomposition of **6a** in the heated inlet system),[2] 123 (100%,138-CH_3), 81 (22%), 66 (17%, cyclopentadiene system).

Compound **6b**: ^{1}H NMR ($CDCl_3$, δ): 6.3 (t, 2H, 1.6 Hz, 9-H, 10-H), 3.0–3.4 (m, 2H, 1-H, 8-H), 2.1–2.6 (m, 4H, 2-H, 4-H, 5-H, 7-H), 1.1–1.4 (m, 6H, $2CH_2$ (aliphatic), 11-H (*syn* & *anti*), 0.91 (t, 3H, CH_3) ^{13}C NMR ($CDCl_3$, δ): 210.6, 207.8 (C=O, C-3, C-6), 137.5, 137.1 (C-9, C-10), 53.2, 52.8, 52.3, 50.9 (C-2, C-4, C-5, C-7), 49.2 (C-11), 48.1 (C-1), 42.8 (C-8), 29.7 (CH_2, aliphatic), 22.1 (CH_2, aliphatic), 14.2 (CH_3, aliphatic). IR (liquid film, cm^{-1}: 3100, 2950, 1710 (C=O, non-conjugate), 1420,1180. MS (EI, *m*/*z* (%))[1]: 152[2] (65%, 5-propyl-2,3-cyclohex-2-ene-1,4-dione system obtained from decomposition of **6b** in the heated inlet system),123 (100%,152-C_2H_5), 81(16%), 66 (21%, cyclopentadiene system).

Compound **6c**: ^{1}H NMR ($CDCl_3$, δ): 6.2 (t, 2H, 1.5 Hz, 9-H, 10-H), 3.0–3.3 (m, 2H, 1-H, 8-H), 2.1–2.7 (m, 4H, 2-H, 4-H, 5-H, 7-H), 1.13–1.4 (m, 6H, $3CH_2$ (aliphatic),11-H (*syn* & *anti*), 0.97 (t, 3H, CH_3). ^{13}C NMR $CDCl_3$, δ): 211.7, 209.8 (C=O, C-3, C-6), 136.7,136.5 (C-9, C-10), 52.3, 50.9, 49.8, 49.0 (C-2, C-4, C-5, C-7), 48.0 (C-11), 47.6 (C-1), 43.3 (C-8), 29.5 (CH_2, aliphatic), 28.8 (CH_2, aliphatic), 22.6 (CH_2, aliphatic), 14.1 (CH_3, aliphatic). IR (liquid film, cm^{-1}): 3110, 2960, 1715 (C=O, non-conjugate), 1440, 1160, 885. MS (EI, *m*/*z* (%))[1]: 166[2] (57%, 5-butyl-2,3-cyclohex-2-ene-1,4-dione system obtained from decomposition of **6c** in the heated inlet system), 123 (100%, 166-C_3H_9), 81 (20%), 66 (25%, cyclopentadiene system).

4.4. General procedure for the thermolysis of **6**

A round bottom flask (25 ml) containing 10 g of **6** attached to the distillation head, an air condenser (15 cm) and a 25 ml receiver was connected to a vacuum pump. The distillation flask was placed in an oil bath and was heated to 180 °C while magnetic stirring rapidly. Compound **3** was collected at 20 mm Hg as a pale yellow oil.

5. Method of calculation

The structure of compounds was built by chemdraw, version 8, and was saved as MOPAC input files by chem3D for PM3 calculation. All PM5 calculations were done by WINMOPAC v.3.5.

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[1] Parent peaks of the **6a**–**c** do not appear even in high resolution mass spectra, because these compounds are decomposed to 5-alkyl-cyclohex-2-ene-1,4-diones at high temperature.

[2] 5-Alkyl-cyclohex-2-ene-1,4-dione is reduced to the corresponding hydroquinone and subsequent fragmentation occurs [13].

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