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Decarbonylation of 7–Norbornenones. Structural Factors Influencing Activation Energies of the Transition States in Cheletropic Reactions. An *ab initio* study

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Decarbonylation of 7–Norbornenones. Structural Factors Influencing Activation Energies of the Transition States in Cheletropic Reactions. An *ab initio* study [#]

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Abstract

Motivation. Computational study of decarbonylation of 7–norbornenones was employed in order to rationalize experimental results. It was found that activation barriers of these cheletropic reactions depend on the structures of 7–norbornenones and products obtained after decarbonylation. This study was motivated by the lack of experimental and computational results for decarbonylation of polycyclic systems such as 7–norbornenones.

Method. Density functional theory, *ab initio*, MP2 and semiempirical calculations were employed.

Conclusions. Quantum–chemical calculations have been used to study of decarbonylation of 7–norbornenones. It was found that activation barriers of these cheletropic reactions depend on the molecular structures of 7–norbornenones and the driving force of aromatized products obtained after decarbonylation.

Keywords. 7–Norbornenones; *ab initio* calculations; decarbonylation; cheletropic reaction.

Abbreviations and notations

B3LYP, Becke3 method with Lee, Young and Parr functionals	RHF, restricted Hartree–Fock method
DFT, density functional theory	TS, transition state

1 INTRODUCTION

Our ongoing research program is to build large rigid polycyclic systems or to delivery appropriate functionalities at the proper distance/angle [1]. One of recently studied reactions involved the introduction of functionality onto carbocyclic alkene by reaction with substituted cyclopentadien–3–ones (phencyclones).

Variously substituted cyclopentadienones undergo in the first reaction step [4π+2π] Diels–Alder reaction yielding bridged polycyclic structures. If the reaction is conducted under vigorous

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conditions, loss of carbon monoxide is often observed, resulting in the production of the corresponding dienes [2,3]. Synthetic methodology based on this behavior was exploited in preparation of various polycyclic compounds [4]. Furthermore, there are several literature described attempts to isolate norbornadien–7–one and benzonorbornadien–7–one. These attempts have failed because of very facile decarbonylation reaction [5]. For instance, 9,10–dihydro–9,10–methanoanthracen–11–one (dibenzo norbornadienone) was prepared and spontaneously undergoes decarbonylation with formation of anthracene [6]. Furthermore, it was found that the cheletropic decarbonylation does manifest in the ground state structures of norbornenones as measurable deviations of bond distances. Structural deviations from 'normal' C–C(O) and C=O bond distances are consistent with the early stages of the cheletropic extrusion of carbon monoxide [7] . Successful synthesis of 7–norbornadienone have been only recently described by Berson [8] and Sheridan [9] where it was necessary to work at low temperatures in an argon matrix. Warrener and co–workers, have described the formation of a highly substituted derivative of norbornadien–7–one stable to decarbonylation below –30 °C [10].

While several papers was dealing with semi–empirical calculations of cheletropic reactions [11] in polycyclic systems have been published [12], calculations using more accurate *ab initio* methods have been recently employed. The aim of this computational study is to explain experimentally observed behavior in reactions involving elimination of carbon monoxide from phencyclone adducts prepared in our laboratories.

2 MATERIALS AND METHODS

All calculations were conducted using the SPARTAN program [13] on a Silicon Graphics R4600 workstation. Initial geometries for *ab initio* calculations have been prepared using semi–empirical AM1 [14] method. Geometric optimizations were carried out without using symmetry or other structural restrictions. All calculations were performed at the restricted Hartree–Fock level [15] with 3–21G and 6–31G* basis sets [16], as well as using DFT B3LYP/6–31G* method. For all structures the frequency analysis was performed with the same basis set used for optimization. Each transition structure was located using a standard routine within SPARTAN and verified by the possession of only one imaginary frequency of vibration, corresponding to the motion of breaking C–C bonds for transition structures [17]. The key transition states were also confirmed with forward and backward IRC calculations. The activation energies were estimated from RHF/6–31G* and MP2/6–31G* [18] single point calculations on the RHF/3–21G and RHF/6–31G* optimized geometries. Some geometries were also optimized with MP2/6–31G* method (frozen core approximation) using *Gaussian94* [19] with an IBM SP2 supercomputer. Results are collected in Tables 1-4.

3 RESULTS AND DISCUSSION

The reaction of interest in this study is decarbonylation of 7–norbornenones. Berson and coworkers have experimentally studied decarbonylation of 7–norbornadienone to produce benzene (Figure 1) [8]. On the basis of the kinetic measurements they estimated the activation barrier for this process of 16 kcal mol^{-1} at 300 K. Sheridan *et al.* [9] have obtained similar experimental value of 17±2 kcal mol^{-1} (at 198–218 K). In his theoretical paper Dewar estimated the barrier to be 21.5 (MINDO/3) and 25.7 (MNDO) kcal mol^{-1}. These results show a great difference between experimental and theoretical values, suggesting that more accurate *ab initio* calculations should be applied to gain better predictions. Furthermore, all transition structures reported in Dewar papers obtained by semi–empirical methods (either RHF or UHF) are actually very unsymmetrical, suggesting asynchronous, non–concerted biradical reaction mechanism.

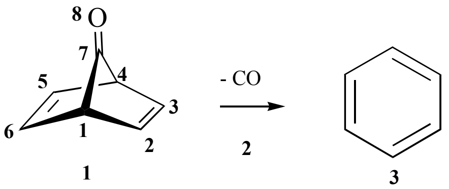


Figure 1. Decarbonylation of 7–norbornadienone.

Our preliminary AM1 calculations for this process gave essentially the same geometry for transition state (TS), highly unsymmetrical (Figure 2a, Table 1).

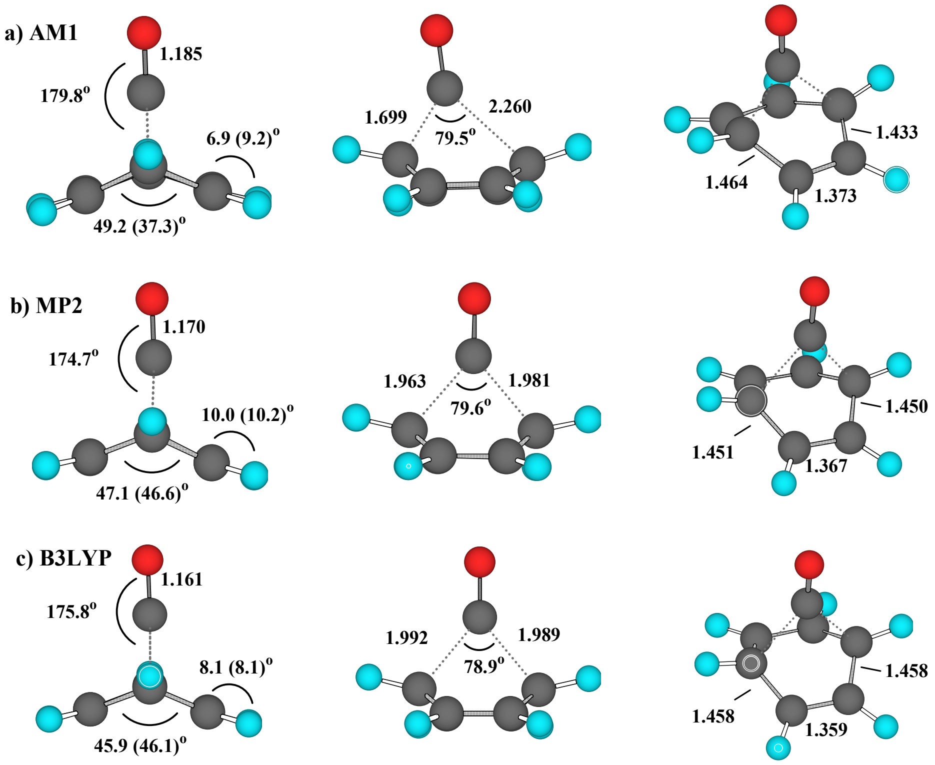
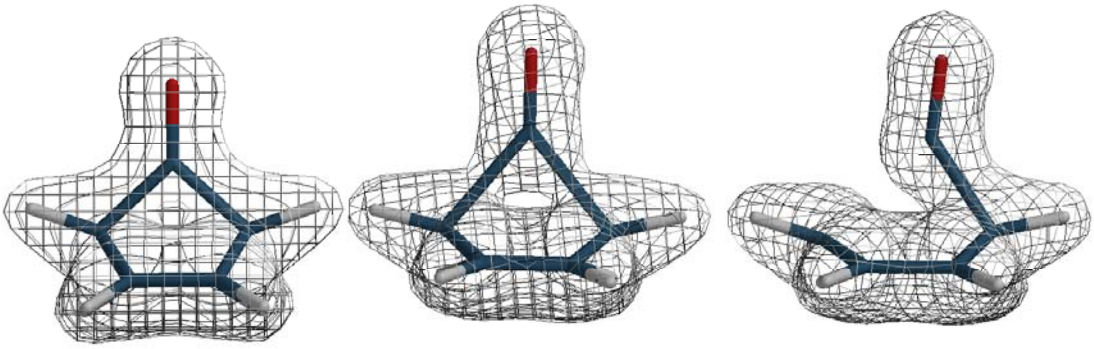


Figure 2. Transition state structures for 7–norbornadienone decarbonylation: a) AM1; b) RMP2(fc)/6–31G*; c) B3LYP/6–31G*.

This result is in line with the known tendency of semi–empirical calculations to predict asynchronous transition structures for pericyclic reactions [20], therefore we did not pursue this calculation method any further. On the other hand, all employed *ab initio* levels gave symmetrical TSs, as shown for RMP2(fc)/6–31G* calculation (Figure 2b), suggesting synchronous, concerted mechanism. Similarly, density functional theory methods (DFT) gave symmetrical structures, employing both local and non–local methods, as illustrated for Becke3LYP/6–31G* method (Figure 2c). The AM1 C_1...C_7 and C_4...C_7 bond distances were calculated to be 2.260 and 1.699 Å, while corresponding MP2 and B3LYP values are 1.981 (1.963) and 1.989 (1.992) Å, respectively. Furthermore, while CO fragment is being extruded, cyclohexadiene ring is starting to planarize, having in all three computed structures ethylene C_5C_6 moiety positioned out of $C_1C_2C_3C_4$ ring plane by 37.3–49.2°. Interestingly, all computed methods predict that the olefinic protons are pyramidalized in *exo* direction, which is opposite to the experimentally known *endo*–pyramidalization of norbornenes [21,22]. As expected from the pyramidalization studies, the largest pyramidalization was predicted by MP2 calculations (10.2°), while B3LYP gives smaller value (8.1°) and finally, AM1 structure has a highly unsymmetrical structure (6.9° and 9.2°).



(*a*) (*b*) (*c*)

Figure 3. Electron density surfaces of transition states for 7–norbornadienone decarbonylation: (*a*) 7–norbornadienone; (*b*) B3LYP/6–31G* method; (*c*) RHF/AM1 method (0.1 electrons/au^3).

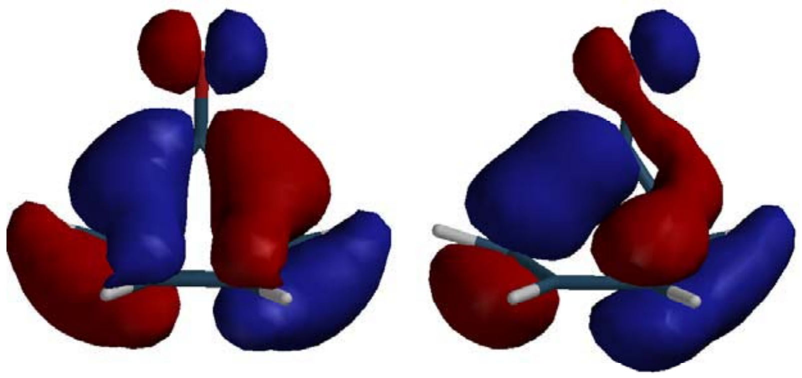
Table 1. Total energies (au) of molecules under studies – reaction 1 [a,b]

Species	E_1	E_2	E_3	E_4	E_5	E_6	E_7
1	43.722	–341.443965	–343.355472	–344.420845	–343.356843	–344.420727	–344.424969
2 CO	–5.679	–112.093299	–112.737267	–113.020129	–112.737877	–113.018041	
3 bz	22.022	–229.419445	–230.700154	–231.457125	–230.703137	–231.456487	
TS1	64.958	–341.410383	–343.317661	–344.400242	–343.318396	–344.399017	–344.403137

	E_8	E_9	E_{10}
1	–345.498857	–343.587611	–346.509788
TS1	–345.475541	–343.553405	–346.481087

[a] E_1=E(AM1); E_2=E(RHF/3–21G); E_3=E(RHF/6–31G*//RHF3–21G); E_4=E(MP2/6–31G*//RHF/3–21G); E_5=E(RHF/6–31G); E_6=E(MP2/6–31G*//RHF/6–31G*); E_7=E(MP2/6–31G*); E_8=E(B3LYP/6–31G); E_9=E(SVWN/6–31G); E_{10}=E(B3P86/6–31G); [b] AM1 heats of formation are given in kcal/mol^{-1}.

Figure 3 depicts electron density surfaces of transition states for 7–norbornadienone decarbonylation showing bonding in transition states, while Figure 4 depicts corresponding highest occupied molecular orbitals (HOMOs) of transition states showing orbital interactions between CO and cyclohexadiene fragments.



(*a*) (*b*)

Figure 4. HOMOs of transition states for 7–norbornadienone decarbonylation: (*a*) B3LYP/6–31G*; (*b*) AM1 method.

Table 2. Activation energies for decarbonylation of norbornadien–7–one (kJmol^{-1}, kcal mol^{-1} in parentheses) [a]

Species	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7
TS1	88.851 (21.236)	88.168 (21.073)	99.342 (23.726)	54.092 (12.928)	101.013 (24.125)	56.999 (13.623)	57.318 (13.699)
ΔH_{rxn}	–114.554	–180.578	–215.154	–148.099	–220.972	–141.253	
	E_8	E_9	E_{10}				
TS1	61.215 (14.631)	89.808 (21.465)	75.354 (18.010)				

[a] ΔE_1=ΔE(AM1); ΔE_2=ΔE(RHF/3–21G); ΔE_3=ΔE(RHF/6–31G*//RHF3–21G); ΔE_4=ΔE(MP2/6–31G*//RHF/3–21G); ΔE_5=ΔE(RHF/6–31G); ΔE_6=ΔE(MP2/6–31G*//RHF/6–31G*); ΔE_7=ΔE(MP2/6–31G*); ΔE_8=ΔE(B3LYP/6–31G); ΔE_9=ΔE(SVWN/6–31G); ΔE_{10}=ΔE(B3P86/6–31G)

MP2/6–31G* structure and activation barrier (13.7 kcal mol^{-1}) we obtained here are identical to values reported by Birney [23]. As expected, the MP2/6–31G* method underestimates activation barrier (experimental value is 15.2 kcal mol^{-1}) [8,9], while RHF methods overestimate (for instance RHF/6–31G* value is 24.1 kcal mol^{-1}). Ideal match to experiment was obtained by much more computer demanding MP4–(SDTQ)/D95** level, which gives the correct value of 15.2 kcal mol^{-1} [24]. On the other hand, as shown recently, DFT methods, especially B3LYP method gives activation energies close to experimental, which are of the better quality than MP2 values, by a fraction of computational cost needed for post–Hartee–Fock calculations. For this particular reaction, B3LYP/6–31G* estimated activation barrier is 14.6 kcal mol^{-1}. This result is in an excellent agreement with experimental results, with an error less than 1 kcal mol^{-1}, proving the reliability of DFT methodology for the computational study of this class of pericyclic reactions.

After the most viable computational approach for study of decarbonylation reactions has been established, we turned our attention from model reaction (Figure 1) to the experimental results. We have found experimentally that norbornene reacts with 3,4–diphenyl–2,5–dimethyl (or 2,5–diethyl and 2,5–diphenyl) cyclopentadienone to yield a mixture of *exo*,*exo* (**4**) and *exo*,*endo* (**5**) adducts, with the preferential formation of *exo*,*endo* adduct **4** (Figure 5). When the cycloaddition reaction was carried out at elevated temperatures a mixture of adduct **4** and diene **6** was produced, suggesting that the initially formed *exo*,*endo* adduct **5** eliminates carbon monoxide while adduct **4** is stable under these reaction conditions.

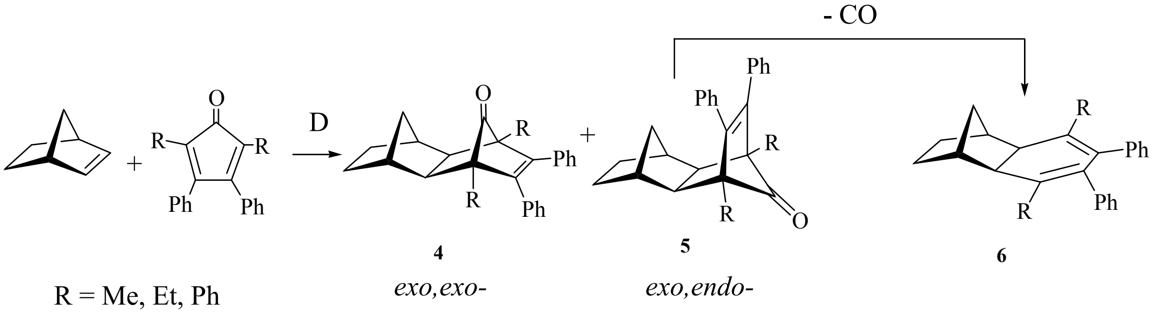


Figure 5. Decarbonylation of 3,4–diphenyl–2,5–dimethyl-cyclopentadienone – norbornene adducts.

In order to explain this experimental result, a series of calculations was performed and results collected in Tables 3 and 4. To minimize computational efforts, phenyl substituents were omitted and cyclopentadienone was used as model system (Figure 6). RHF/6–31G*//3–21G activation energies for the CO elimination from adducts **7** and **8** (via transition states **TS7** and **TS8**) were estimated to be 48.9 and 39.6 kcal mol^{-1}, respectively (Table 4). It was found that there is 9.3 kcal mol^{-1} lower activation barrier for decarbonylation of isomer **8**, which is prediction in good agreement with our experimental observations. The comparison of these values with the previously studied decarbonylation of compound **1** (at the same level of theory is 23.7 kcal mol^{-1}) suggests greater thermal stability of compounds **7** and **8**. It could be explained by the lack of driving force for the formation of an aromatic product.

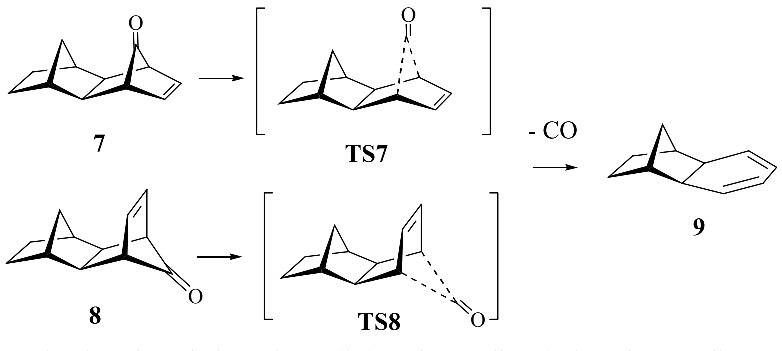


Figure 6. Model reactions for decarbonylation of 3,4–diphenyl–2,5–dimethyl-cyclopentadienone – norbornene adducts.

Table 3. Total energies (au) of molecules under studies [a,b]

Species	E_1	E_2	E_3	E_4	E_5
7	12.107	–534.420576	–537.387149		
8	16.399	–534.410402	–537.379162		
9	23.839	–422.322491	–424.666032		
TS7	55.110	–534.341326	–537.309062		
TS8	53.282	–534.350713	–537.316004		
10	3.299	–342.643455	–344.555675	–345.625779	–344.556991
11	17.485	–230.543231	–231.831608	–232.590755	–231.831898
TS10	45.047	–342.571878	–344.482654	–345.573313	
12	–6.161	–420.292422	–422.633512		
13	1.322	–308.190133	–309.911085		
TS12	32.147	–420.217074	–422.559316		
16	25.031	–686.235002	–690.052772		
17	52.268	–574.094332	–577.294699		
TS16	72.153	–686.144942	–689.965878		
18	57.640	–533.210502	–536.177366		
19	64.074	–421.125419	–423.467487		
18a	37.059	–191.717080	–192.791378		
TS18a	93.787	–533.152335	–536.115487		
TS18b	121.027	–533.096178	–536.067249		
18 CPD	37.059	–191.717080	–192.791378		
20 nb	25.957	–269.369085	–270.861003		
TS7a	76.415	–534.311303	–537.282331	–539.041309	–537.284308
TS8a	77.735	–534.308234	–537.277744	–539.035439	–537.280015
22	2.285	–383.540799	–385.681284		–385.681918
23	45.821	–382.315110	–384.459430		–384.460726
24	–5.181	–1.122960	–1.126803	–1.144135	–1.126828

[a] E_1=E(AM1); E_2=E(RHF/3–21G); E_3=E(RHF/6–31G*//RHF3–21G); E_4=E(MP2/6–31G*//RHF/3–21G); E_5=E(RHF/6–31G); [b] AM1 heats of formation are given in kcal mol^{-1}

Table 4. Activation energies of studied reactions (kJ mol^{-1}, kcal mol^{-1} in parentheses) [a]

Species	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5
TS7	179.924	208.068	205.014 (48.9)		
ΔH_{rxn}	6.053	12.565	–42.401 (–10.1)		
TS8	154.344	139.955	165.819 (39.6)		
ΔH_{rxn}	7.393	–14.146	–63.371 (–15.1)		
TS10	174.674	187.923	191.714 (45.8)	137.746	
ΔH_{rxn}	8.507	–18.194	–34.456 (–8.3)	–39.159	
TS12	108.725	197.824	194.799 (46.6)		
ΔH_{rxn}					
TS16	197.158	237.819	228.137 (54.5)		
ΔH_{rxn}	90.199	124.371	54.625 (13.1)		
TS18a	151.239	152.728	162.461 (38.8)		
ΔH_{rxn}	0.755	–21.571	–71.906		
TS18b	265.211	298.578	289.108 (69.1)		
ΔH_{rxn}	96.822	–129.847	–80.119		
24 ΔH_{rxn}	160.477	269.711	249.788		247.759

[a] ΔE_1=ΔE(AM1); ΔE_2=ΔE(RHF/3–21G); ΔE_3=ΔE(RHF/6–31G*//RHF3–21G); ΔE_4=ΔE(MP2/6–31G*//RHF/3–21G); ΔE_5=ΔE(RHF/6–31G)

Further simplification of the model system represents decarbonylation of 7–norbornenone **10** yielding 1,3–cyclohexadiene **11** (Figure 7).

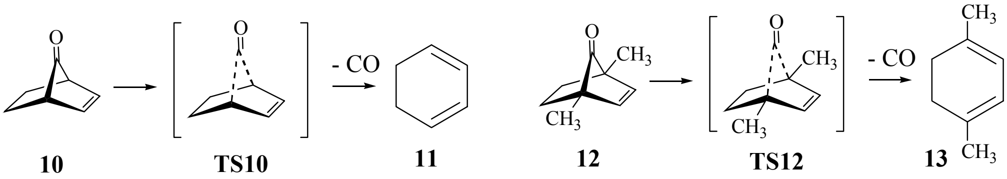


Figure 7. Decarbonylation of 7–norbornenone and 1,4–dimethyl–7–norbornenone.

Decarbonylation of 1,4–dimethyl–7–norbornenone **12** was also modeled in order to determine the influence of substituents on the activation barrier height, (Figure 7). For these two model reactions, RHF/6–31G*//3–21G activation barriers were estimated to be 45.8 and 46.6 kcal mol^{-1} (CO elimination from **10** and **12**, respectively) indicating that bridgehead methyl substituents slightly increase activation barrier. These activation energy values are smaller than obtained for decarbonylation of an adduct **8**, suggesting that ring strain caused by incorporation of 7–norbornenone (and cyclohexadiene) into polycyclic skeleton slightly destabilizes both TS and corresponding product.

On the other hand, our experimental findings showed that cycloaddition of 5,7–dimethyl–6H–cyclopenta[*f*][1,10]phenanthrolin–6–one with norbornene gives only *exo*,*endo* adduct **14** [25]. Despite being a derivative of adduct **5**, product **14** does not undergo decarbonylation when similar thermal conditions have been applied, suggesting its higher thermal stability (Figure 8).

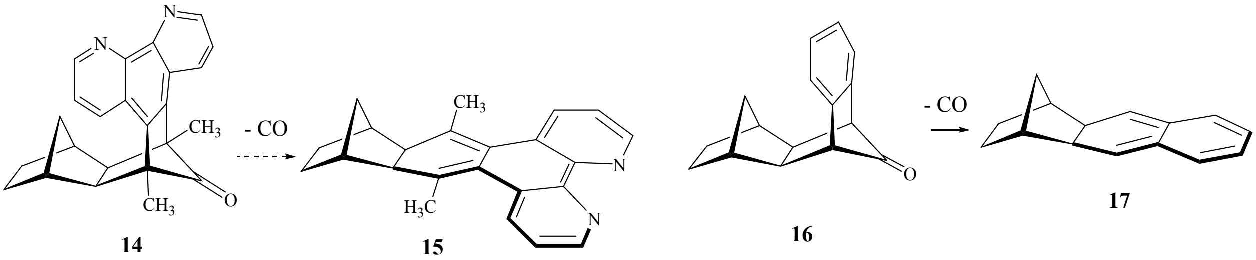


Figure 8. Decarbonylation of adduct **14**.

The size of the polycyclic adduct **14** is significantly greater than reaction depicted in Figure 1, precluding the use of highly accurate *ab initio* calculations. Therefore, methyl substituents were removed from molecule and 1,10–phenanthroline moiety was replaced with benzene to make **16** as a model for computational study (Figure 6). RHF/6–31G*//3–21G activation barrier was estimated to be 54.5 kcal mol^{-1}, which is a larger value than previously obtained for compound **7**. These numbers indicate that thermal decarbonylation of **14** is very unfavorable process. One may assume that one of the reasons for such stability of **14** would be the formation of unstable *o*–quinodimethane derivatives **15** (or **17)** after elimination of CO.

The mechanistic details of decarbonylation of cyclopentadienone adduct of norbornadiene **18** are depicted at Figure 9. In this scheme, retro Diels–Alder reaction involving cyclopentadiene elimination is also possible, yielding benzene as the most stable product. RHF/6–31G*//3–21G activation energies for **TS18a** and **TS18b** are 38.8 and 69.1 kcal mol^{-1}, respectively, suggesting that decarbonylation is more likely process to occur.

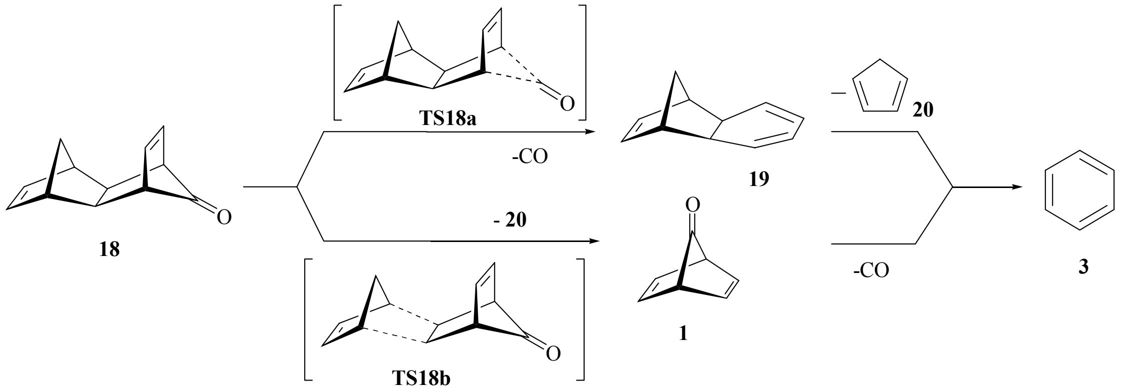


Figure 9. Reaction pathways for decarbonylation of adduct **18**.

The development of an aromatic π–system [26] has often been invoked as contributing to the “driving force” of reactions and thus to low barriers often associated with such decarbonylation reactions. The pericyclic reactions which form an aromatic product have been of particular interest. One of the most important classes of these reactions is fragmentation, in which the σ–framework of the aromatic system already exist and the π–system is completed by the conversion of σ–bond(s) into π–bond(s). The low barrier has been shown to be correlated with the overall exothermicity of the reaction (6–31G*//3–21G value is –10.1 kcal mol^{-1}), which in turn reflects the aromatic stabilization of the products (as in the case of **1**). Quantum–chemical calculations predict that the decarbonylations of **7** and **8** are also exothermic, (6–31G*//3–21G values are –10.1 and –15.1 kcal mol^{-1}, respectively). From the other hand, in molecule **16**, it is necessary to disrupt the aromatic system in order to produce *o*–xylylene moiety. This is energetically less favorable process as indicated by calculations (process in endothermal, where computed 6–31G*//3–21G heat of reaction is 13.1 kcal mol^{-1}). This result was further corroborated by calculation of the model process of formation of 2,3–dihydronaphthalene **22** from decalin **21** (Figure 10). Calculations show that this reaction is highly endothermal (6–31G*//3–21G heat of reaction is 59.6 kcal mol^{-1}) indicating much greater stability of **21**.

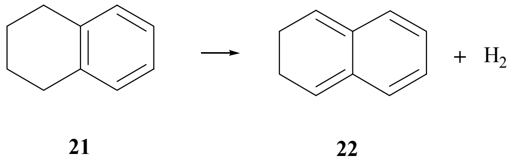


Figure 10. Dehydrogenation of 1,2,3,4–tetrahydronaphthalene.

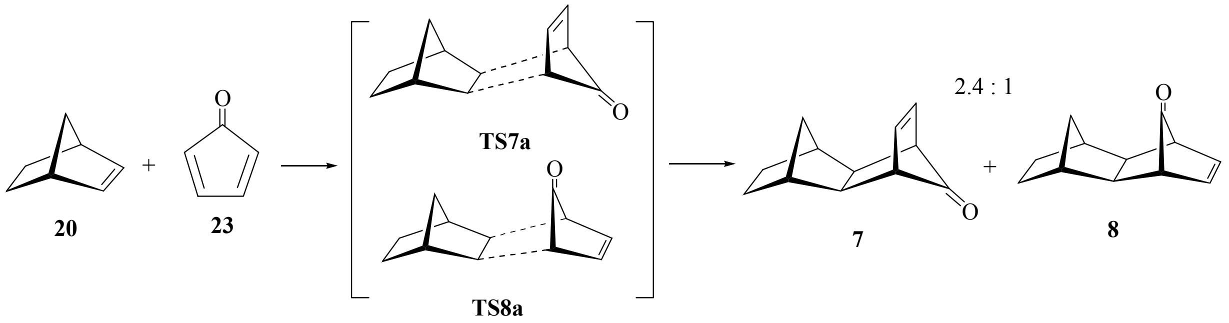


Figure 11. Cycloaddition reaction of norbornene with cyclopentadienone.

Finally, transition state calculations of norbornene – cyclopentadienone cycloaddition were also included in this computational study (Figure 11). The aim of these calculations was to determine activation barriers of formation of two different products and to predict the observed stereospecificity of this cycloaddition reaction. It was found that the relative activation energies estimated at various levels of theory always prefer the formation of *exo*,*endo* adduct **7**, what is in good accordance with experimental observations. The calculated *exo*,*endo*/*exo*,*exo* activation energy differences are 1.93, 2.88, 3.7 and 2.7 kcal mol^{-1}, as obtained at the RHF/3–21G, RHF/6–31G*//RHF/3–21G, MP2/6–31G*//RHF/3–21G and RHF/6–31G* levels, respectively.

4 CONCLUSIONS

Quantum–chemical calculations have been used to study of decarbonylation of 7–norbornenones. It was found that activation barriers of these cheletropic reactions depend on the molecular structures of 7–norbornenones and the driving force of aromatized products obtained after decarbonylation.

Acknowledgment

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Supplementary Material

Cartesian coordinates of calculated transition state structures depicted in Figure 2 are available on request from authors.

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