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Pyrrolidine catalyzed reactions of cyclopentadiene with α,β-unsaturated carbonyl compounds: 1,2- versus 1,4-additions

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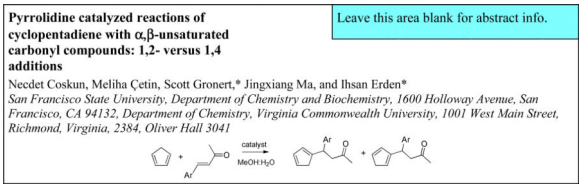
Abstract

A systematic study of the reactions of cyclopentadiene with α,β-unsaturated carbonyl compounds in the presence of catalytic pyrrolidine-H_2O revealed that the reactions can either proceed with a Michael attack at the β-carbon of enone, or 1,2-addition to the carbonyl, leadingeither to 4-cyclopentadienyl-2-butanones or 6-vinylfulvenes. The former can be isolated and/or converted to the corresponding 1,2-dihydropentalenes with base (or in one-pot at longer reaction times). Substitution pattern on the enones on the competing pathways have been studied and consistent mechanisms are proposed.

Graphical Abstract



Keywords

Fulvene; Michael addition; Chalcone; 1,2-Dihydropentalene; Iminium ions

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Supplementary Material

^1H and ^{13}C NMR spectra of compounds **10**, **14a,b**, **16a,b**, **18a,b**, **20a,b**, **22a,b**, **24a,b**, **38**, **41a,b**, **43**, **45**, and **47**. Also details of the computational work at M06/6-311+G** level using the Gaussian 03 program containing enthalpies and free energies are listed in this section. Supplementary data related to this article can be found online at doi:

1. Introduction

Thiele's original method for fulvene synthesis is based on sodium alkoxide promoted condensation of cyclopentadiene (**1**, CpH) with carbonyl compounds and suffers from relatively low yields, in particular with aldehydes (due to competing aldol condensations) as well as α,β-unsaturated aldehydes and ketones.[1] In response to the shortcomings of the Thiele procedure, Little and Stone developed a convenient method for the synthesis of fulvenes derived from simple aldehydes and unhindered aliphatic ketones using pyrrolidine as base in at least stoichiometric amounts in methanol solvent.[2] We extended Little's method onto α,β-unsaturated aldehydes and ketones, though we observed several limitations in terms of 6-vinylfulvene formation vs. Michael attack.[3] The ineffectiveness of the Thiele or Little procedures for the synthesis of various 6-vinylfulvenes,[4] in particular those derived from α,β-unsaturated aldehydes and ketones such as methyl vinyl ketone, acrolein or methacrolein that preferentially undergo Diels-Alder reaction with CpH compelled us to develop alternative syntheses of these types of 6-vinylfulvenes.[5,6] In an early report, Nenitzescu et al. reported exclusive 1,4-addition of cyclopentadiene onto benzalacetone with NaOMe in methanol affording a mixture of the Michael product and isomeric dihydropentalenes.[7] Similarly, Griesbeck obtained 1,2-dihydropentalenes (1,2-DHP) with benzalacetone or chalcone with pyrrolidine, and initial Michael adducts were inferred as intermediates, though never observed or isolated (Scheme 1).[8]

Whereas we observed exclusive 1,2-addition to cinnamaldehyde with either stoichiometric (Little conditions, MeOH) or catalytic pyrrolidine (10 mol% in MeOH/H_2O, 4:1, Coskun, Erden)[9] leading to a 6-vinylfulvene, Hayashi et al. reported exclusive Michael attack with chiral diphenylprolinol TBS ether (10 mol%) and with or without *p*-nitrophenol (20%) as an additive (Scheme 2).[10] They attributed the achieved asymmetric induction and exclusive 1,4-attack to an unprecedented “ene” reaction of cyclopentadiene and postulated a cyclic transition state for a concerted proton transfer from cyclopentadiene to the α-carbon of the iminium ion and concomitant attack of the developing cyclopentadienyl anion at the β-carbon of cinnamaldehyde.

These reports compelled us to undertake a thorough study of the divergent nature of condensations of cyclopentadiene with α,β-unsaturated carbonyl compounds in hopes of isolating possible intermediates and establishing a consistent mechanism for the Michael reactions and elucidating the factors controlling 1,2- versus 1,4-additions. Herein we report our results on the isolation of intermediates in the aforementioned reactions by a new variant of fulvene synthesis utilizing a catalytic pyrrolidine-H_2O system.

2. Results and Discussion

There are several possible modes of reaction between cyclopentadiene and α,β-unsaturated carbonyl compounds, depending on the nature and amount of the base, substitution pattern on the enone or enal, and solvent. With certain enones, such as mesityl oxide, the major pathway with pyrrolidine involves conjugate addition to the enone, followed by a retroaldol reaction leading to acetone and its iminium ion that condenses with cyclopentadiene to give 6,6-dimethylfulvene.[3,11] With some other enones that are particularly reactive dienophiles,

such as acrolein and methyl vinyl ketone, the major pathways involves a Diels-Alder reaction, rather than fulvene formation or 1,4-addition, regardless of base since the cycloaddition is faster that condensation. Some representative examples underlining the diverse modes of reaction of CpH with enones/enals in the presence of pyrrolidine are depicted in Table 1.

The results presented in Table 1 are indicative of the reasons why the synthesis of a large number of 6-vinylfulvenes presents significant problems. Except for a small number or cases where the α,β-unsaturated carbonyl compound is an aldehyde not reactive enough for Diels-Alder, or carrying a substituent at the β-carbon to that impedes rapid Michael attack by pyrrolidine, a consistent method for 6-vinylfulvene synthesis is lacking to date, and indirect syntheses of several key vinylfulvenes needed to be developed. Also, in view of the surprising report by Hayashi postulating a novel ene reaction of cyclopentadiene with cinnamaldehyde resulting in a Michael addition, we studied the reactions of **1** with benzalacetones under our conditions (method C in ref. 9), using 10% pyrrolidine in MeOH/H_20 (4:1). The results from these reactions are shown in Table 2. In each case mixtures of CpH isomers of the Michael adducts were isolated in yields of 70-78%, alongside minor amounts of the corresponding 1,2-dihydropentalenes. In the case of the isopropyl styryl ketone [(*E*)-4-methyl-4-anisyl-1-penten-3-one] (**25**), no reaction was observed and only starting material was recovered.

In order to gain some insight into the mechanistic details of these reactions we performed a rate study on the series **13**, **15**, **19**, **21**, **23**, (entries 1-6). The initial rates for the latter cases were determined at room temperature and plotted versus the Hammett σ constants (Figure 2). Thus the addition of cyclopentadiene to 4-arylsubstituted enones was characterized by a Hammett type equation $\log(\text{rate})_X = \rho\sigma_X - \log(\text{rate})_{X=H}$. The magnitude of the reaction susceptibility constant ρ is *ca.* 1. It is evident that electron-donating substituents decelerate while electron-withdrawing ones accelerate the Michael addition of cyclopentadiene onto β-aryl enones (substrates in entries 1-6). It was not entirely surprising that **25** proved to be unreactive under the conditions applied; neither the use of 2 equivalents of pyrrolidine nor 24 h stirring affected Michael addition or fulvene formation. The only change after 24 h, as determined by ^{1}H NMR analysis of the crude reaction mixture was the β-pyrrolidino derivative as a result of conjugate addition of the catalyst itself (ca 50% conversion).

The lack of reactivity of **25** is also informative in regard to the mechanism: the bulky isopropyl group impedes or completely blocks iminium ion formation, thus, neither the carbonyl group, nor the β-carbon are electrophilic enough for attack by the nucleophile. The substituent effects on the rate of the Michael additions onto benzalacetones indicate that the rate-limiting step is the formation of the iminium ion whose formation would indeed be decelerated by more electron-donating groups, rendering the carbonyl carbon less electrophilic, thus less prone to attack by pyrrolidine.[12] Based on our results, we postulate the mechanism shown in Scheme 3 that is consistent with our results.

The question remains why in Hayashi's case cinnamaldeyde undergoes a Michael reaction (1,4-addition) with **1**, while we observe exclusive 6-vinylfulvene formation via a 1,2-addition (see Table 3) with either stoichiometric pyrrolidine in MeOH or catalytic amounts

(10%) in MeOH/H_2O (4:1), the only difference being the bulky diphenylsiloxymethyl group at the 2-carbon. We decided to repeat the reaction of cinnamaldehyde with **1** under Hayashi's conditions (10% catalyst, 20 mol% *p*-nitrophenol in MeOH at r.t.), except we used pyrrolidine instead of the chiral diphenylprolinol TBS ether. Even under those conditions we obtained the vinylfulvene **5** in 69% yield after chromatography, with no evidence of a Michael product. It is apparent that the catalyst has a profound effect on the fate of the reaction. Mayr and coworkers' excellent kinetic study[13] on the Michael additions of neutral nucleophiles such as ketene acetals onto α,βunsaturated iminium ions established an electrophilicity ranking among a variety of iminium ions, in which the 2-diphenyltrimethylsiloxymethyl group on the pyrrolidine ring renders the iminium ion **31** 20 times as reactive as the parent system **32**.

In the absence of a strong nucleophile (MeOH solution, 10% catalytic base, 20% *p*-nitrophenol additive), it is not surprising that the attack by cyclopentadiene at the strongly electrophilic β-carbon of the iminium ion **33** is favored; in addition, a 1,2-attack at the iminium carbon, considering the bulk of the substituent on the 2-position in the heterocycle would be unfavorable sterically. Besides, the angle of attack would force the broadest dimension of the cyclopentadiene to interact with the bulky side-group in the heterocycle. Taking into account the strong electrophilicity of the iminium ion **31**, as compared to **32**, it is very likely that the β-carbon carrying the aromatic ring bears a significant δ+ charge, and the nucleophilic attack by cyclopentadiene, followed by proton transfer appears to be a reasonable alternative to the reaction. It is not without precedent that cyclopentadiene may attack a sufficiently electrophilic species as a nucleophile, as Hoffmann's report on the reactions of cyclopentadiene with allyl cation intermediates has clearly demonstrated.[14] Also theoretical work by Zora supports a stepwise cycloaddition of allylidene iminium cation with cyclopentadiene in which cyclopentadiene acts as a nucleophile and attacks the β-carbon of the iminium ion in the rate-limiting step.[15] Moreover, in the course of their brilliant work on the synthesis of functionalized fulvenes and diyl trapping reactions, Little and coworkers noted that in one case the addition of acetic acid to the reaction mixture greatly accelerated fulvene formation by encouraging iminium ion formation, clearly the rate-limiting step in *sec*-amine catalyzed fulvene synthesis.[16] Though Hayashi and coworkers did not carry out a kinetic study on substituent effects, based on their qualitative observations it appears that electron-releasing groups in the *para* position of the β-phenyl group enhance reactivity, whereas electron-withdrawing substituents retard the reaction and require the use of larger amounts (20 mol%) of the catalyst, indicative of the fact that the rate-limiting step here is the attack by **1** rather than the iminium ion formation. An argument against the "ene" mechanism in our case using pyrrolidine as catalyst is the fact that the less electron-rich C2 of cyclopentadiene is acting as the nucleophile (Figure 2). Based on the above arguments, and also consistent with the qualitative substituent effects for the Michael reactions of CpH with cinnamaldeydes, we propose an alternative stepwise nucleophilic attack by cyclopentadiene on the delocalized cation **34** followed by proton transfer from the cyclopentenyl cation to the α-carbon in **35** (Scheme 4).

Our computational work[17] was carried out at M06/6-311+G** level using the Gaussian 03 program on the iminium ion derived from acrolein, and without the bulky group at C2 on

pyrrolidine (Figure 3). Our results clearly disfavor the “ene” mechanism for pyrrolidine catalyzed reactions by a wide margin (15.4 kcal/mol), and favor a mechanism shown in Scheme 4.

Evidently under our catalytic conditions in MeOH/H_2O, β-aryl substituted enals do not undergo Michael addition, rather, the corresponding 6-vinylfulvenes are formed (entries 1-3). However, crotonaldehyde, an excellent Michael acceptor,[19] undergoes both 1,2- and 1,4-additions to give a 1/1.14 mixture of the 6-vinylfulvene **40** and isomeric fulvenes **41a,b,** respectively, the latter obviously derived from the Michael product via condensation of the intermediate aldehyde with cyclopentadiene. Crotonaldehyde (or the iminium ion derived from it) appears to be a better Michael acceptor than cinnamaldehyde. This finding is consistent with the relative reactivities of the aforementioned enals in 1,4-additions.[20] In the absence of H_2O, in neat methanol, the pyrrolidine-catalyzed condensation of crotonaldehyde with cyclopentadiene gives almost exclusively the 6-vinylfulvene, the isomeric fulvenes **41a,b** derived from Michael product comprising only 11% of the product mixture. Evidently the presence of 25% H_2O affects the 1,4-addition favorably (and 1,2-addition to some extent favorably). Though there is no clear-cut rationalization for this phenomenon, a possible reason might be the fact that the δ+ charge developing on the β-carbon for the Michael attack is better stabilized by the more polar solvent, thus encouraging the shift of electron density toward the iminium ion to a higher degree.

Finally, the Michael adducts from three benzalacetones, **14a,b**, **16a,b** and **18a,b** were converted to known 1,2-dihydropentalenes (obtained from a formal dipolar 6+2 cycloaddition of fulvenes onto N-isopropenylpyrrolidine)[21] by intramolecular condensation of the cyclopentadiene with the carbonyl group was readily accomplished with 10% pyrrolidine in MeOH.

3. Conclusions

The products formed from nucleophilic attack of cyclopentadiene onto α,β-unsaturated carbonyl compounds is highly particular to substrate structure; moreover, pattern reactivity, i.e., 1,2- versus 1,4-addition/1,2-dihydropentalene formation may depend on the base and solvent. Earlier work by Nenitzescu, as well as Griesbeck using NaOMe of stoichiometric pyrrolidine in MeOH, respectively, resulted in 1,2-dihydropentalene formation, when benzalacetones or chalcone were used as substrates. 1,4-addition products were postulated as intermediates in these reactions Under our catalytic conditions using 10 mol% pyrrolidine as base in MeOH/H_2O (4:1), we obtained the aforementioned 1,4-adducts exclusively, presumably via hydrolysis of the iminium intermediates prior to cyclization to the corresponding 1,2-dihydropentalenes.

Another important finding emerging from our kinetic study on the substituent effects on the base-promoted Michael reactions of benzalacetones with cyclopentadiene was the fact that the rate-limiting step in these reactions is the iminium ion formation. Our experimental and mechanistic studies, supported by computational work render are in accord with the stepwise mechanism involving nucleophilic attack of cyclopentadiene at the highly electrophilic β-

carbon of the iminium ion derived from the enone with a concerted, yet highly asynchronous proton transfer to the α-carbon.

Finally, we have shown that β-substituted α,β-unsaturated aldehydes, as well as selected enones preferentially undergo 1,2-addition leading to 6-vinylfulvenes, even under our catalytic conditions. By omitting H_2O in the solvent, thus encouraging iminium ion formation, selected Michael adducts to benzalacetones were successfully converted to 1,2-DHPs, completing the circle as postulated in Nenitzescu's and Grisebeck's reports.

4. Experimental Section

4.1. General

Melting points were determined in open glass capillary tubes and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on 300 MHz and 500 MHz NMR spectrometers, using $CDCl_3$ as solvent and TMS as internal standard, unless specified otherwise. Most column chromatographic separations were carried out on a flash chromatography system using 40-60 μm silica gel columns using ethyl acetate/n-hexane solvent mixtures. For preparative TLC, Merck silica gel (grade 60 PF_{254}) was used. All reactions were conducted under an atmosphere of dry nitrogen or argon. Non-deuterated solvents were dried and distilled prior to use. Pyrrolidine is an exceptionally foul-smelling and toxic compound and should be handled with care in a well-ventilated hood. Fulvenes are oxygen- and heat-sensitive compounds; all reactions should be carried out under a nitrogen or argon atmosphere. The initial rates of the reactions used in Hammett[22] correlations were measured at 23°C (±) 1°C. The progress of the reactions was monitored by ^1H NMR by integrating the appropriate signals due to the products and the starting enones. Fulvenes **5** and **38** synthesized here by our catalytic method gave identical spectra to those previously reported by us using stoichiometric pyrrolidine.[3] Benzalacetone **13** was obtained commercially. Though the other benzalacetones in Table 2 (entries 2-7) are all known compounds, we found that they are most conveniently prepared by the catalytic method we use for our fulvene synthesis[9] ($MeOH/H_2O$ 4:1, 10% pyrrolidine, see below).

4.2. Synthesis of 4-aryl-but-3-en-2-ones

General Procedure. To a solution of aromatic aldehyde (10 mmol) and ketone (5 mL) in methanol-water mixture (10 mL, 80/20) pyrrolidine (10 mol%, 0.072 g) was added and the mixture stirred at room temperature overnight. The mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine solution successively and dried over $MgSO_4$. Flash column chromatography using silica packed columns and ethyl acetate hexane as eluent provided pure products. In the case of entry 7, 40 mol% catalyst was used and the reaction time is 3 days.

4.2.1. (E)-4-(p-tolyl)but-3-en-2-one[23] (15)—Colorless oil, yield 73%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 16.3 Hz, 1H), 7.43 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.67 (d, J = 16.3 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.43, 143.49, 141.00, 131.65, 129.69, 128.24, 126.24, 27.41, 21.47.

4.2.2. (E)-4-(4-methoxyphenyl)but-3-en-2-one (17)—Yellowish crystals, mp 72-73°C, (lit. mp 74-76°C)[24], yield 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (ddd, *J* = 16.2, 8.4, 6.0 Hz, 3H), 6.97 – 6.84 (m, 2H), 6.60 (d, *J* = 16.2 Hz, 1H), 3.83 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.36, 161.59, 143.22, 129.94, 127.04, 125.01, 114.42, 55.38, 27.39.

4.2.3 (E)-4-(3-methoxyphenyl)but-3-en-2-one (19)[25]—Colorless oil, yield 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 16.3 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.17 – 7.09 (m, 2H), 7.08 – 7.01 (m, 1H), 6.94 (ddd, *J* = 8.2, 2.6, 0.7 Hz, 1H), 6.69 (d, *J* = 16.3 Hz, 1H), 3.83 (d, *J* = 0.6 Hz, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.34, 159.93, 143.32, 135.78, 129.93, 127.40, 120.97, 116.38, 113.01, 55.29, 27.48.

4.2.4. (E)-4-(3,4-dimethoxyphenyl)but-3-en-2-one (21)—Yellowish crystals, mp 84-86°C. (lit. mp 86-87°C)[26], yield 90%.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 16.2 Hz, 1H), 7.12 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.07 (d, *J* = 1.9 Hz, 1H), 6.91 – 6.84 (m, 1H), 6.60 (d, *J* = 16.2 Hz, 1H), 3.91 (d, *J* = 5.4 Hz, 6H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.29, 151.34, 149.27, 143.47, 127.31, 125.24, 122.97, 111.07, 109.61, 55.97, 55.88, 27.33.

4.2.5. (E)-4-(4-chlorophenyl)but-3-en-2-one (23)—Colorless crystals, mp 58-59°C (lit. mp 53-55 °C)[24a], yield 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 12.5, 6.2 Hz, 3H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 16.3 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.00, 141.81, 136.40, 132.91, 129.36, 129.24, 127.46, 77.32, 77.00, 76.68, 27.66.

4.2.6. (E)-1-(4-methoxyphenyl)-4-methylpent-1-en-3-one (25)—Colorless oil,[27] yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.46 (m, 2H), 6.95 – 6.84 (m, 2H), 6.69 (dd, *J* = 15.9, 0.7 Hz, 1H), 3.83 (d, *J* = 0.6 Hz, 3H), 2.97 – 2.83 (m, 1H), 1.17 (dd, *J* = 6.9, 0.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.82, 161.44, 142.13, 129.93, 127.35, 122.26, 114.33, 77.33, 77.01, 76.70, 55.36, 39.13, 18.59.

4.2.7. (E)-2-(4-methoxybenzylidene)cyclobutanone (42)[27]—Yellowish crystals, mp 80-81°C (lit. mp 79.0-79.6 °C)[27a], yield 30%, ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47 (2H, d, *J*=9 Hz), 7.00 (1H, t, *J*=3 Hz), 6.93 (2H, d, *J*=9 Hz), 3.85 (3H, s), 3.15 – 3.06 (2H, m), 2.99 – 2.88 (2H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 199.5, 161.0, 143.5, 131.7, 127.8, 126.2, 114.4, 55.3, 45.4, 23.1.

4.2.8. (E)-2-(4-methoxybenzylidene)cyclopentanone (44)—Yellowish crystals, mp 60-62 °C (lit. mp 63-65 °C)[28], yield 70%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.50 (1H, d, J=9 Hz), 7.35 (1H, t, J=3 Hz), 6.94 (1H, d, J=9 Hz), 3.84 (2H, s), 2.95 (1H, td, J=7, 3 Hz), 2.39 (1H, t, J=8 Hz), 2.02 (1H, p, J=8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 208.0, 160.4, 133.6, 132.2, 132.1, 128.1, 114.1, 55.2, 37.6, 29.2, 20.0.

4.3. 1-(3-(Cyclopenta-2,4-dien-1-ylidene)-2-methylpropyl)-pyrrolidine (10)

A mixture of methacrolein (0.52 mL, 5.0 mmol), freshly distilled cyclopentadiene (0.49 mL, 6.0 mmol) and pyrrolidine (0.41 mL, 5.0 mmol) in 5 mL of methanol was stirred at room temperature for 1h. After addition of 10 mL of water the mixture was extracted with diethyl ether (2 × 10 mL), the combined organic layers washed with each 10 mL of water and brine, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residue was purified with preparative TLC (the TLC plate was treated with 10% triethylamine in hexane prior to chromatography), eluting with hexane/ethyl acetate (5:1) to give **10** as yellow oil (390 mg, 41%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.49-6.56 (m, 2H), 6.44 (dt, J= 5.0 ,1.6 Hz, 1H); 6.30 (d, J= 9.8 Hz, 1H); 6.21 (dt, J= 5.0, 1.6 Hz), 3.07 (m, 1H), 2.53 (m, 2H), 2.49 (m, 4H), 1.73 (m, 4H), 1.14 (d, J= 6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): d 147.6, 145.2, 133.3, 130.8, 126.1, 119.5, 63.3, 54.6, 35.9, 23.7, 20.0 ppm. HRMS (M+H) calcd. for $C_{13}H_{20}N$: 190.1551. Found 190.1589.

4.4. 1,4-Additions of cyclopentadiene onto benzalacetones

General Procedure. To a solution of α,β-unsaturated carbonyl compound (10 mmol) and cyclopentadiene (10 mmol, 0.661 g, 0.820 mL) in methanol-water mixture (10 mL, 80/20) pyrrolidine (10 mol%, 0.072 g) was added and the mixture stirred at room temperature overnight. The mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine solution successively and dried over $MgSO_4$.

4.4.1. 4-(Cyclopenta-1,4-dienyl)- and 4-(cyclopenta-1,3-dienyl)-4-phenylbutan-2-ones (14a, 14b)—^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.10 and 2.11 (2s, 3 H) 2.75-2.90 (m, 1 H) 2.96-3.02 (m, 2 H) 3.08-3.16 (m, 2 H) 4.30-4.37 (m, 1 H) 6.07 - 6.10 (m, 0.5 H) 6.25-6.29 (m, 1 H) 6.34-6.36 (m, 0.5 H) 6.40-6.44 (m, 1 H) 7.19-7.26 (m, 3 H) 7.28-7.33 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 31.25; 41.89; 42.30; 43.15; 43.33; 49.95; 50.36; 126.71; 127.20; 127.23; 127.37; 128.37; 128.59; 129.24; 129.27; 132.50; 132.60; 134.48; 134.90; 144.65;149.54; 151.80; 207.82; 207.93 ppm. HRMS calcd. for $C_{15}H_{16}O$: 212.1201. Found (M-1) 211.1098.

4.4.2. 4-(Cyclopenta-1,4-dienyl)- and 4-(cyclopenta-1,3-dienyl)-4-p-tolylbutan-2-ones (16a, 16b)—^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.09 (s, 3 H) 2.32 (s, 3 H) 2.81 (dq, *J*=4.21, 1.40 Hz, 0.5 H) 2.90 - 3.00 (m, 1 H) 3.03 - 3.14 (m, 0.5 H) 4.25-4.33 (m, 1 H) 6.05-6.08 (m, 0.25 H) 6.23-6.36 (m, 1.75 H) 6.40 (ddt, *J*=6.40, 3.38, 1.69, 1.69 Hz, 1 H) 6.97-7.24 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 207.3, 151.2, 148.9, 139.9, 135.9, 134.0, 133.7, 131.8, 131.6, 129.4, 129.1, 127.6, 127.4, 127.3, 127.0, 126.4, 125.7, 49.6, 49.2, 42.5, 41.9, 41.1, 41.1, 30.4, 20.9 ppm. HRMS calcd for $C_{16}H_{18}O$: 226.1358. Found (M-1) 225.1346.

4.4.3. 4-(Cyclopenta-1,4-dienyl)- and 4-(cyclopenta-1,3-dienyl)- 4-(4-methoxyphenyl)butan-2-ones (18a, 18b)—^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.98 - 1.99 (m, 3H) 2.72 (q, *J*=1.26 Hz, 1 H) 2.74 (q, *J*=1.26 Hz, 1 H) 2.84 - 2.92 (m, 10 H) 2.97 - 3.03 (m, 1H) 3.71 (s, 3 H) 4.16 - 4.22 (m, 1 H) 5.97 - 5.98 (m, 2 H) 6.14 - 6.15 (m, 2 H) 6.19 (dd, *J*=5.36, 1.26 Hz, 2 H) 6.24 - 6.26 (m, 2 H) 6.33 (ddt, *J*=7.13, 3.51, 1.77, 1.77 Hz, 4 H) 6.74 - 6.78 (m, 2 H) 7.03 - 7.08 (m, 2 H) ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 14.91;

21.73; 31.27; 41.51; 41.85; 42.37; 43.28; 50.08; 50.51; 55.89; 55.90; 61.08; 77.53; 77.78; 78.04; 114.60; 114.61; 126.37; 127.09; 129.29; 129.51; 132.39; 132.58; 134.49; 134.84; 135.79; 136.74; 149.88; 152.23; 158.85; 171.83; 208.16 ppm. HRMS calcd. for $C_{16}H_{18}O_2$: 242.1307. Found (M-1) 241.1226.

4.4.4. 4-(Cyclopenta-1,3-dienyl)- and 4-(cyclopenta-1,4-dienyl)-4-(3-methoxyphenyl)butan-2-ones (20a, 20b)—^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.06 and 2.09 (2 s, 3 H) 2.80 (dq, *J*=3.89, 1.39 Hz, 0.5 H) 2.91 - 3.00 (m, 1 H) 3.04 - 3.13 (m, 0.5 H) 3.77 - 3.81 (m, 3 H) 4.24 - 4.32 (m, 1 H) 6.05 - 6.07 (m, 0.5 H) 6.22 - 6.27 (m, 1 H) 6.31 - 6.35 (m, 0.5 H) 6.37 - 6.41 (m, 1 H) 6.72 - 6.83 (m, 3 H) 7.17 - 7.26 (m, 1 H) ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 207.1, 159.6, 144.6, 134.1, 133.6, 131.8, 131.7, 129.4, 126.6, 125.9, 120.1, 119.9, 113.8, 113.6, 111.4, 110.9, 55.0, 54.9, 49.4, 49.0, 42.5, 42.3, 41.4, 41.1, 30.4 ppm. HRMS calcd. for $C_{16}H_{18}O_2$: 242.1307. Found (M-1) 241.1229.

4.4.5. 4-(Cyclopenta-1,3-dienyl)- and 4-(cyclopenta-1,4-dienyl)-4-(3,4-dimethoxyphenyl)butan-2-ones (22a, 22b)—^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.08 and 2.10 (m, 3 H) 2.74 - 2.87 (m, 1 H) 2.87-3.00 (m, 2 H) 3.02-3.10 (m, 1 H) 3.70 - 3.89 (m, 6 H) 4.20-4.28 (m, 1 H) 6.02-6.06 (m, 0.5 H) 6.18-6.29 (m, 1 H) 6.30-6.36 (m, 0.5 H) 6.37-6.42 (m, 1 H) 6.64-6.82 (m, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ (ppm) 31.30; 41.87; 41.92; 42.79; 43.32; 50.08; 50.51; 56.54; 56.57; 111.77; 111.89; 111.91; 112.07; 120.18; 120.39; 126.47; 127.19; 132.44; 132.55; 134.47; 134.87; 136.36; 137.28; 148.29; 148.32; 149.59; 149.62; 149.74; 152.04; 208.04; 208.15 ppm. HRMS (CI): found. for $C_{17}H_{20}O_3$: 272.1412. Found (M-1) 271.1332.

4.4.6. 4-(4-chlorophenyl)-4-(cyclopenta-1,3-dien-1-yl)- and 4-(4-chlorophenyl)-4-(cyclopenta-1,4-dien-1-yl)butan-2-ones (24a, 24b)—^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.25 (2H, d, *J*=9 Hz), 7.15 (2H, d, *J*=8 Hz), 6.40 (1H, d, *J*=5 Hz), 6.31–6.24 (1H, m), 6.22 (0.5H, s), 6.05 (0.5H, d, *J*=1 Hz), 4.36–4.19 (1H, m), 3.16–2.68 (4H, m), 2.09 (3H, s) ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 208.2, 134.4, 133.4, 131.7, 129.2, 129.0, 128.5, 126.1, 49.3, 48.9, 42.5, 41.1, 40.7, 30.5 ppm. HRMS calcd. for $C_{15}H_{15}ClO$: 246.0811. Found (M-1) 245.0730.

4.5. 6-Vinylfulvene synthesis

For entries 1-4, 6, Table 3, the same procedure was used as under *4.4*. For entry 5, the reaction was carried out in dry MeOH in the presence of 20 mol% of pyrrolidine. Compounds **5**, **38** and **40** were identical in all respects to those reported previously. In entry 3, **40** and **41a+b** were separated from one another by flash chromatography on silica gel eluting with hexanes.

4.5.1. Condensation of Cyclopentadiene with crotonaldehyde under catalytic conditions—Pyrrolidine (82 μL, 1.0 mmol, 10 mol%) was added to a mixture of aldehyde (0.82 mL, 10.0 mmol) and freshly prepared cyclopentadiene (0.98 mL, 12.0 mmol) in MeOH/H_2O (4:1, 10 mL) at room temperature. After stirring over night at r.t., the mixture was treated with acetic acid (0.5 mL) and H_2O (20 mL), then extracted with diethyl ether (2 × 20 mL). The combined organic layers were washed with H_2O (20 mL) and brine (20 mL),

then dried over anhydrous $MgSO_4$. After removal of solvent at reduced pressure, the residue was purified by column chromatography (silica gel, hexane) to give 236 mg of **40**[29] (20%) and 405 mg (22%) of a mixture of **41a** and **41b,** with a relative ratio of 2:1, respectively, based on ^{1}H NMR integrals of separated signals.

4.5.2. 2-(4-(Cyclopenta-2,4-dien-1-ylidene)butan-2-yl)cyclopenta-1,3-diene (41a) and 1-(4-(cyclopenta-2,4-dien-1-ylidene)butan-2-yl)cyclopenta-1,3-diene (41b)—^{1}H NMR (500 MHz, $CDCl_3$): δ 6.43-6.57 (m, 5H), 6.40 (t, J= 7.3 Hz, 1H), 6.30 (m, 1H, minor isomer), 6.23 (m, 1H, minor isomer), 6.19 (m, 1H, major isomer), 6.05 (m, 1H, major isomer), 2.98 (m, 2H, major isomer), 2.94 (m, 2H, minor isomer), 2.81 (m, 1H), 2.79 (m, 1H), 2.69 (m, 1H) (the latter two signals due to diastereotopic protons), 1.21 (d, J= 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, both isomers): δ 153.7, 151.4, 174.0, 141.5, 141.4, 134.3, 133.43, 133.37, 132.4, 131.0, 130.9, 130.9, 126.3, 125.8, 125.5, 119.5, 119.4, 41.6, 41.3, 38.7, 37.8, 35.6, 34.7, 21.1, 20.1 ppm. HRMS (M+H) calcd. for $C_{14}H_{17}$: 185.1330. Found 185.1321.

4.5.3 1-((2-(Cyclopenta-2,4-dien-1-ylidene)cyclobutylidene)methyl)-4-methoxybenzene (43)—Mp 116-118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.37 (2H, d, *J*=9 Hz), 6.97 (2H, s), 6.92 (1H, d, *J*=9 Hz), 6.67 – 6.60 (1H, m), 6.50 (1H, d, *J*=5 Hz), 6.45 (1H, d, *J*=5 Hz), 6.31 – 6.26 (1H, m), 3.84 (3H, s), 3.17 – 3.01 (4H, m) ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.5, 154.3, 139.7, 136.9, 131.5, 130.1, 129.9, 129.7, 127.7, 121.3, 119.2, 114.2, 55.2, 29.2, 28.6. HRMS (M+H) $C_{17}H_{17}O$ calcd. for $C_{17}H_{17}O$: 237.1235. Found 237.1231.

4.5.4. 2'-(4-Methoxybenzylidene)-[1,1'-bi(cyclopentylidene)]-2,4-diene (45)—^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40 (2H, d, *J*=9 Hz), 7.21 (1H, s), 6.93 (2H, d, *J*=9 Hz), 6.77 – 6.69 (1H, m), 6.52 (2H, t, J=6 Hz), 6.48 – 6.42 (1H, m), 3.85 (3H, s), 2.97 (2H, t, J=8 Hz), 2.82 (2H, td, J=7, 2 Hz), 2.01 – 1.81 (2H, m) ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.2, 157.3, 140.9, 137.7, 133.4, 131.0, 130.4, 130.3, 122.5, 120.6, 113.8, 55.2, 32.8, 32.6, 23.6. HRMS (M+H) calcd. for $C_{18}H_{19}O$.: 251.1391. Found 251.1445.

4.5.5 3-(Cyclopenta-2,4-dien-1-ylidene)-1-methylcyclohex-1-ene (47)—^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.72 (1H, d, *J* 1 Hz), 6.69–6.65 (1H, m), 6.60 – 6.56 (1H, m), 6.50 (2H, dd, *J* 4, 2 Hz), 2.86–2.78 (3H, m), 2.25 (3H, t, *J* 6 Hz), 1.97 (3H, s), 1.87 (3H, dt, *J* 13, 6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.3, 147.4, 138.9, 130.1, 129.5, 123.6, 119.9, 118.8, 31.2, 28.2, 24.9, 22.4. HRMS (M+H) calcd. for $C_{12}H_{15}$: 159.1129. Found 159.1126.

Synthesis 3-methyl-1-phenyl-1,2-dihydropentalene of 48a-c: General Procedure. To a solution of 4-(cyclopenta-1,3-dienyl)- and 4-(cyclopenta-1,4-dienyl)-4-arylbutan-2-ones (**16a,b**, **18a,b** or **20a,b**) (5 mmol) in methanol-water mixture (5 mL, 4/1) pyrrolidine (10 mol%, 0.036 g) was added and the mixture stirred at room temperature overnight. The mixture was diluted with water and extracted with ether. The combined extracts were washed with water and brine solution successively and dried over $MgSO_4$. The pure compounds were achieved by filtration trough a short silica packed column and elution with

hexane. The products **48a**, **48b** and **48c** were obtained in 54, 63 and 71% yields, respectively. Their spectra were identical to those of authentic material prepared by our fulvene-enamine 1,2-DHP synthesis.[20]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References and notes

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12. Though our results do not preclude nucleophilic attack of CpH without iminium ion formation, it has been well established that in sec-amine catalyzed reactions of CpH, the rate-limiting step does not involve direct 1,2- or 1,4-attack by Cp^-. See refs. 2 and 9.
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18. In addition to the gas phase modeling of the reactions, calculations were also completed using solvent models. Single-point calculations were completed on the M06/6-311+G** geometries using both the PCM and SMD models in Gaussian09 with methanol as the solvent. The PCM model gave activation enthalpies of 25 and 11 kcal/mol for the competing pathways and the SMD model gave activation enthalpies of 26 and 11 kcal/mol. Although solvation has a slightly greater impact in the ene reaction, there is still a strong preference for the nucleophilic attack at the β-carbon.
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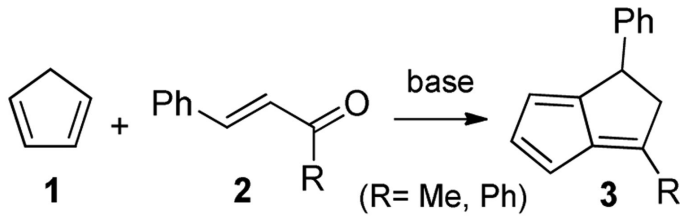
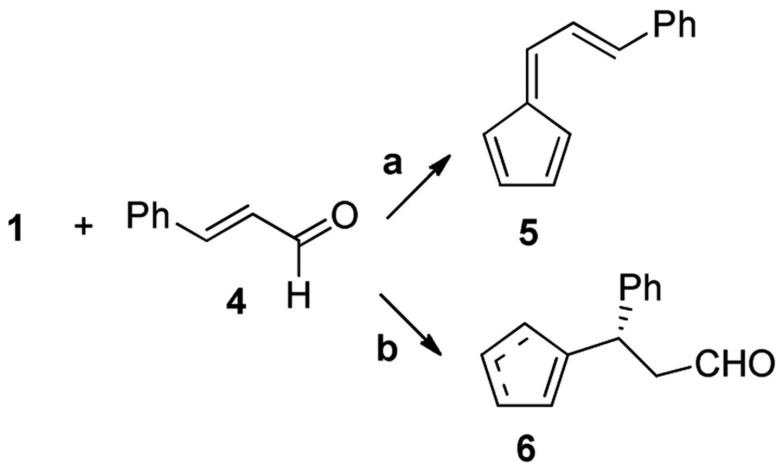


Base: **a**: MeONa (Nenitzescu); **b**: pyrrolidine (Griesbeck)

Scheme 1.

1,2-dihydropentalene formation from β-arylketones



Scheme 2.

1,2-versus 1,4-addition onto cinnamaldehyde **a**: 1 equiv. pyrrolidine; **b**: 10% diphenylprolinol TBS ether, MeOH

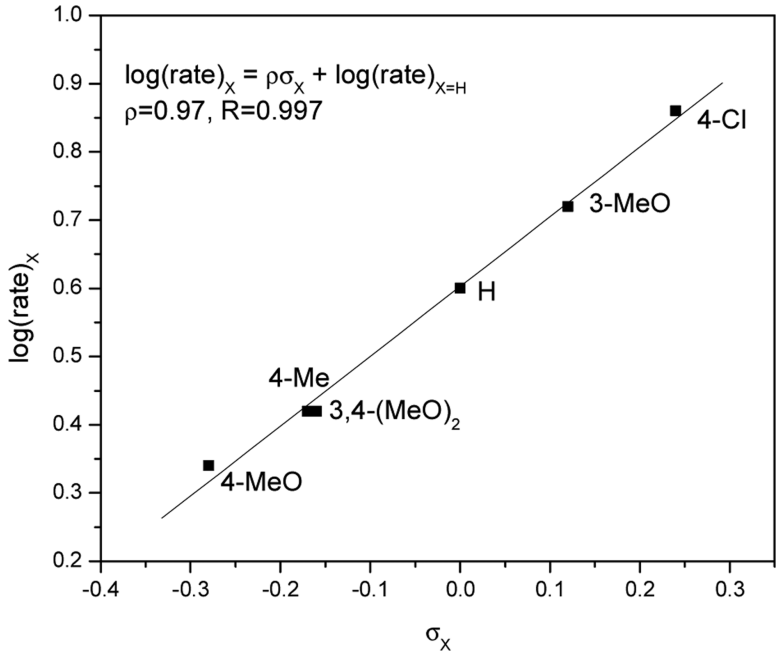
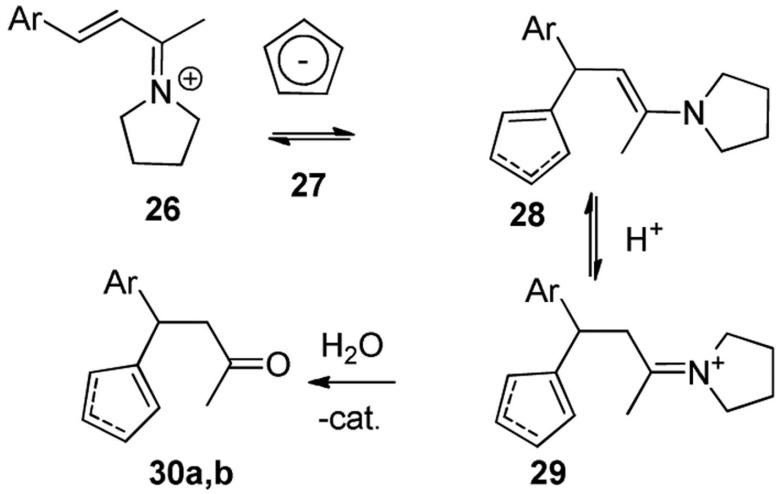


Figure 1.

Substituent effect on the Michael addition of cycopentadiene to (*E*)-4-aryl-3-but-en-2-ones. [a]The initial rates (mole L^{-1} h^{-1}) at room temperature determined at the 0.5^{th} h for the reactions in entries **1-6** are 0.6(0.02), 0.42(0.04), 0.34(0.06), 0.72(0.02), 0.42(0.00) and 0.86(0.01) respectively. The values are average of 2 measurements



Scheme 3.

Mechanism for pyrrolidine catalyzed Michael addition of CpH onto β-aryl enones

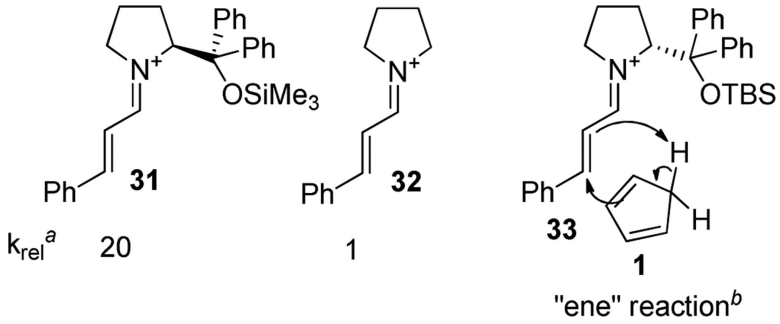
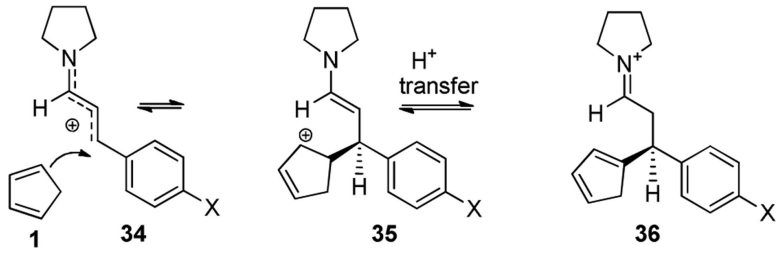


Figure 2.

Relative reactivities of iminium ions **31** and **32** toward Michael attack by a ketene acetal and “ene” mechanism

[a]: relative second-order rate constants for the reaction of the iminium ions with a ketene acetal, ref 12. ; [b]: ref 10.



Scheme 4.

Alternative mechanism for the Michael addition of CpH onto iminium ions derived from cinnamaldehydes

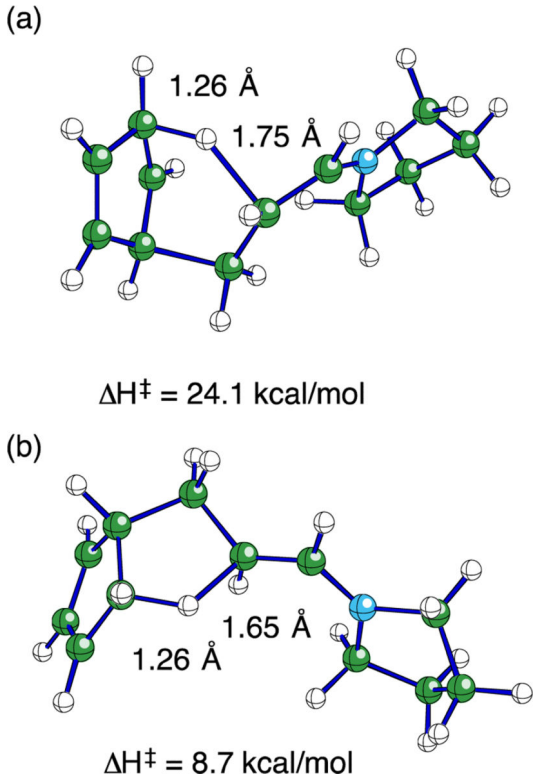
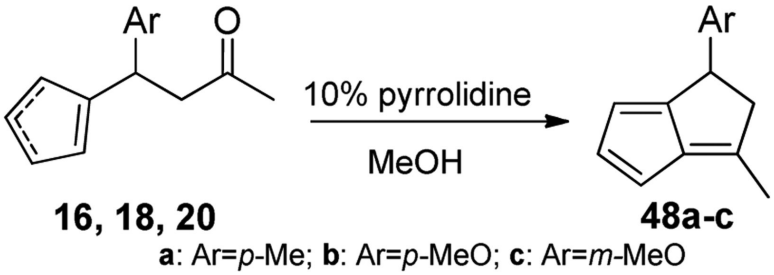


Fig. 3.

Transition state structures[18] for the (a) ene reaction and (b) nucleophilic attack by CpH at the β-carbon



Scheme 4.

1,2-Dihydropentalene formation from Michael adducts **16**, **18** and **20**

Table 1

Pyrrolidine promoted reactions of CpH with enals/enones

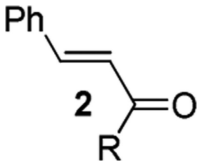
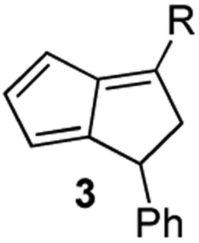
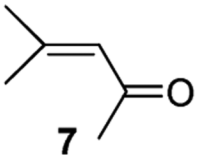
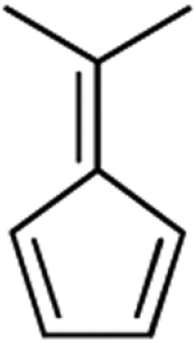
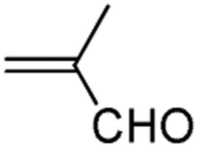
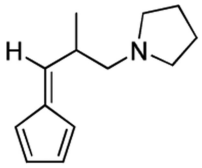
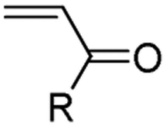
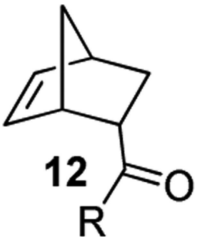
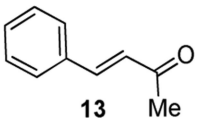
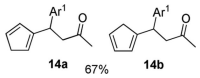
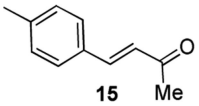
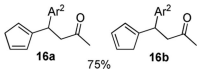
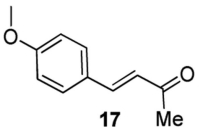
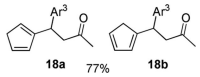
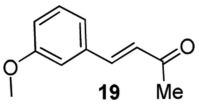
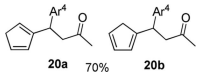
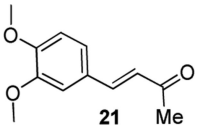
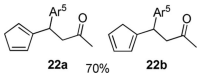
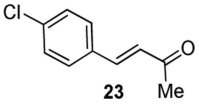
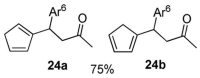
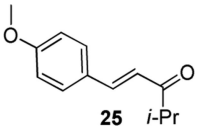
Entry	Enal/enone	Product	Reference
1	 **2**	 **3**	8
2	 **7**	 **8**	3, 11
3	 **9**	 **10**	this work
4	 **11** R=H or Me		11

Table 2

1,4-Additions of cyclopentadiene onto benzalacetones[a]

Entry	Enone	Product(s)/ Yield[b]
1	 13 Me	 14a 67% 14b
2	 15 Me	 16a 75% 16b
3	 17 Me	 18a 77% 18b
4	 19 Me	 20a 70% 20b
5	 21 Me	 22a 70% 22b
6	 23 Me	 24a 75% 24b
7[c]	 25 *i*-Pr	1,4-pyrrolidine addition

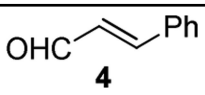
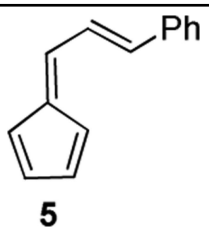
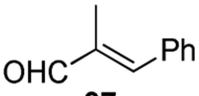
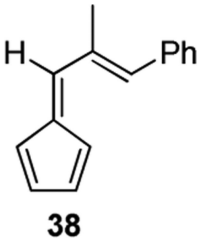
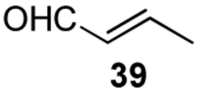
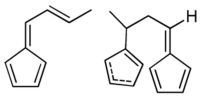
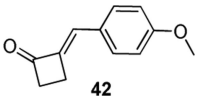
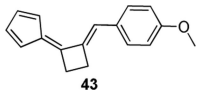
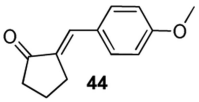
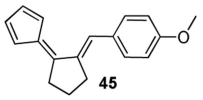
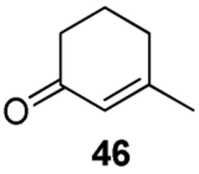
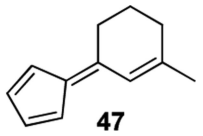
[a] All reactions were performed in MeOH/H_2O (4/1) and 10 mol% pyrrolidine.

[b] From the reactions of enones in entries 1-6 the corresponding known 1,2-dihydropentalenes were also isolated in yields of 18, 15, 10, 20, 15, 10% respectively.

[c] No reaction was observed even when 2 equivs. of catalyst were used.

Table 3

6-Vinylfulvene formation by pyrrolidine catalyzed condensation of selected enones/enals with 1[a]

Entry	Enal/enone	Product	Yield
1	 **4**	 **5**	95%
2	 **37**	 **38**	72%
3	 **39**	 **40** : **41a,b** 1 : 1.14	42%
4	 **42**	 **43**	90%
5	 **44**	 **45**	50%[b]
6	 **46**	 **47**	40%

[a] All reactions were performed in MeOH/H_2O (4/1) and 10 mol% pyrrolidine unless noted otherwise

[b] The reaction is performed in dry MeOH with 20% catalyst.