5. Insect Antifeedant Active Aryl Enones

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Abstract:

About four series of halogen substituted aryl 2E-enones were synthesized using Ultrasonicated Crossed Aldol condensation of various substituted aryl ketones and aldehydes. The yields of the enones are more than 92%. The synthesized enones were analyzed using their Physico-chemical properties and spectroscopic data. The insect antifeedant activities of synthesized compounds were evaluated using castor *semilooper Achoea Janata L.* The chlorinated enones showed better insect antifeedant activity.

Keywords: Aryl *2E*-enones, Ultrasonication, Aldol condensation, Insect antifeedant activity.

5.1 Introduction:

Aryl enones possess an unsaturation and keto moieties in their structure [1]. Based on the orientation of alkene moiety with respect to keto group, they are classified as *s-cis* and *s-trans* conformers and are confirmed by infrared spectroscopy [2]. The *E* or *Z* configuration of the chalcones were confirmed by the orientation of protons in alkene moiety and are confirmed with their 1H NMR coupling constant 'J' values. If the J value is more than 15 Hz, then the chalcone possess *E* configuration. Suppose the J values is less than 15 Hz, then the chalcone possess Z configuration [3].

In general, *E* configured chalcones are more stable than Z configuration. Chalcones are important intermediates for carbon building blocks [4]. They are the key intermediates for synthesis of flavanones [5], Pyrazolines [6], pyrimidine [7], thiopyrimidine [8] and oxazine [9] derivatives.

Various methods were employed for synthesis of chalcones such as conventional heating, microwave assisted, ground chemistry and Ultrasonications [10-12]. Similarly, numerous catalysts were employed for the aldol condensation leads to synthesis of chalcones [13, 14].

Chalcones possess many biological activities such as antimicrobial [15], antiviral [16], anticancer [17], anti-HIV [18], anticordivascular [19], antioxidant [20], antiplasmodial [21]. Halogenated chalcones showed insect antifeedant activities [22].

Nalwar et. al., have studied and observed the good insect antifeedant activity of some chalcones against the mealy bug of cotton (*Phenacoccus solanopsis*) [23]. Chen and his co-workers [24] reported the antifeedant activity of some enones derived from natural Genus Tephrosia against the legume pod-borer *Maruca testulalis*, with an important pest of cowpea (*Vigna*). An appreciable insecticidal activity of some pyrazolyl enones were evaluated using third instar nymph of *P. solenopsis* was reported by Rani et. al., [25].

The first instar larvae of *Nomophila indistinctalis* was employed for assessing the insect antifeedant activity of enones from natural *Polygonum persicaria* extracts by Romero [26] group of researchers. V′asquez et. al., [27] used the insect *Spodoptera litoralis* and *Myzus persicae* for measuring the insect antifeedant activity of some enone and flavonoids isolated from *Senecio adenotrichius* DC plant. Jackowski et. al., [28] used three coleopteran stored product pests namely *Sitophilus granarius* L., *Tribolium confusum* Duv. and Trogoderma granarium Everts for evaluated the insect antifeedant activity of some flavonoids.

Three insect pests: *lesser mealworm, Alphitobius diaperinus (Panzer); Colorado potato beetle, Leptinotarsa decemlineata (Say); and peach-potato aphid, Myzus persicae (Sulz.)* were incorporated for evaluation of antifeedant activity of some hydroxy lactones and racemic piperitones by Grudniewska and his co-workers [29]. Hidalgo et. al., have studied and reported the insect antifeedant activity of some mono- and bis- chalcones on *Spodoptera frugiperda* (Lepidoptera: Noctuidae) [30]. Morimoto co- workers used the insect Spodoptera litura Larvae for evaluation of insect antifeedants of some aurones [31]. Within the above view the authors also interested to evaluate the insect antifeedant activities of some halogenated enones using Dethler's [32] castor *semilooper Achoea Janata L.*

5.2 Experimental and Results:

5.2.1 General:

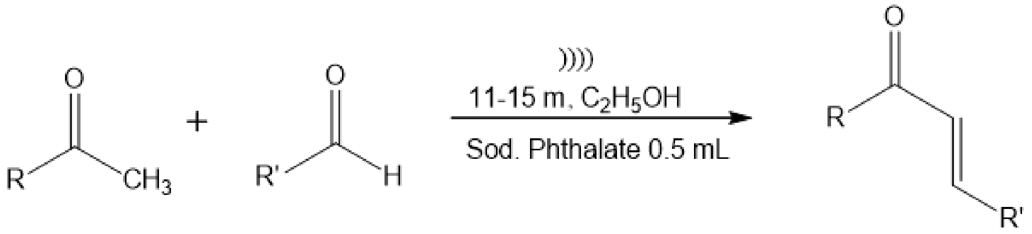
IR spectra of all α, β-unsaturated ketones under investigation were recorded using SHIMADZU 8400 FT-IR spectrophotometer with KBr discs. he ^{1}H and ^{13}C NMR Spectra of all α, β-unsaturated ketones under investigation were recorded using the BRUKER AV 400 NMR spectrometer applying 400MHz for ^{1}H NMR, 125.46 MHz for ^{13}C NMR spectra and TMS as a standard.

5.2.2 Preparation of Enone Compounds (1-40):

a. Synthesis of (E)-1-(Substituted Phenyl)-3-Phenylprop-2-En-1-Ones (1-36):

A mixture of equimolar quantities of substituted acetophenone (1mmol) and substituted benzaldehydes (1mmol), sodium phthalate (1N, 0.5mL) and 10 mL of ethanol were Ultrasonicated at 40 Hz for 10-15 minutes (Citizen Ultra Sonicator, 40 Hz, 120W, 240V, AC) as shown in **Scheme-5.1.**

After the completion of the reaction, as monitored by TLC, the resulted precipitate was filtered and washed with cold water. The products appeared as crude yellow solid. Then these are



Scheme 5.1: Synthesis of (E)-1-(substituted phenyl)-3-phenylprop-2-en-1-ones

Entry	R	R′	Entry	R	R′
1	4-BrPh	H	19	2,4-F$_2$Ph	3-NO$_2$
2	4-BrPh	2-Cl	20	2,4-F$_2$Ph	4-NO$_2$
3	4-BrPh	3-Cl	21	3,4-(OCH$_3$)$_2$Ph	4-Br
4	4-BrPh	4-Cl	22	3,4-(OCH$_3$)$_2$Ph	3-Cl
5	4-BrPh	4-F	23	3,4-(OCH$_3$)$_2$Ph	2-F
6	4-BrPh	2-OH	24	3,4-(OCH$_3$)$_2$Ph	4-F
7	4-BrPh	2-OCH$_3$	25	2,6-(OCH$_3$)$_2$Ph	4-Br
8	4-BrPh	4-OCH$_3$	26	2,6-(OCH$_3$)$_2$Ph	2-Cl
9	4-BrPh	4-CH$_3$	27	2,6-(OCH$_3$)$_2$Ph	4-Cl
10	4-BrPh	3-NO$_2$	28	2,6-(OCH$_3$)$_2$Ph	4-F
11	4-BrPh	4-NO$_2$	29	4-OCH$_3$Ph	4-Br
12	2,4-F$_2$Ph	H	30	4-OCH$_3$Ph	3-Cl
13	2,4-F$_2$Ph	3-Br	31	4-OCH$_3$Ph	4-Cl
14	2,4-F$_2$Ph	4-Br	32	4-OCH$_3$Ph	4-F
15	2,4-F$_2$Ph	4-Cl	33	2-CH$_3$Ph	4-Br
16	2,4-F$_2$Ph	2-OCH$_3$	34	2-CH$_3$Ph	2-Cl
17	2,4-F$_2$Ph	4-OCH$_3$	35	2-CH$_3$Ph	4-Cl
18	2,4-F$_2$Ph	4-CH$_3$	36	2-CH$_3$Ph	4-F

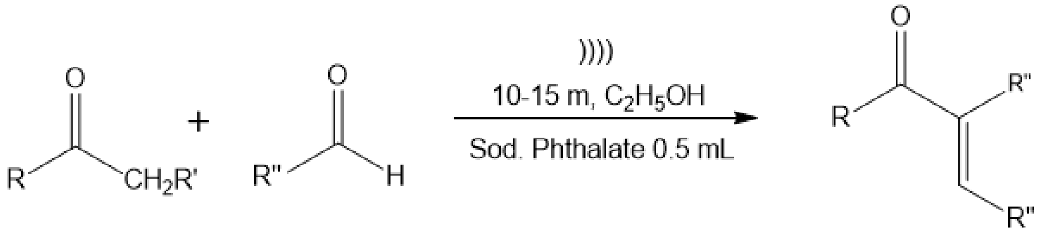
b. Synthesis of (*E*)-1,2,3-triphenylprop-2-en-1-ones (37-40):

A mixture of equimolar quantities of 1,2-diphenylmethanone (1mmol) and substituted benzaldehydes (1mmol), sodium phthalate (1N, 0.5mL) and 10 mL of ethanol were Ultrasonicated at 40 Hz for 10-15 minutes (Citizen Ultra Sonicator, 40 Hz, 120W, 240V, AC) as shown in **Scheme-5.2**.

After the completion of the reaction, as monitored by TLC, the resulted precipitate was filtered and washed with cold water.

The products appeared as crude yellow solid.

Then this was recrystallized using ethanol to afforded pale yellow glittering solids.



Scheme 5.2: Synthesis of (E)-1,2,3-triphenylprop-2-en-1-ones

Entry	R	R′	R″	Entry	R	R′	R″
37	Ph	Ph	2-Br	**39**	Ph	Ph	4-Cl
38	Ph	Ph	2-Cl	**40**	Ph	Ph	4-F

The enones 1-32 and 37-40 were characterized by their physical constants and they are well agreed with literature data [13a, 33-37].

The enones 33-36 were characterized by their yield, physical constants and analytical parameters of these synthesized chalcones were presented in Table 5.a.

The spectroscopic data of these chalcones were given in Table 5.a.

Table 5.a: Analytical parameters of the synthesized enones 33-36.

Entry	R	R′	MF	MW	Yield (%)	Time (m)	m. p. (^{o}C)
33	2-CH_3Ph	4-Br	$C_{16}H_{13}BrO$	301	92	12	58-59
34	2-CH_3Ph	3-Cl	$C_{16}H_{13}ClO$	257	93	11	106-107
35	2-CH_3Ph	4-Cl	$C_{16}H_{13}ClO$	257	94	10	62-63
36	2-CH_3Ph	4-F	$C_{16}H_{13}FO$	240	90	13	60-61

Table 5.b: IR vibrational frequencies (ν, cm 1), NMR chemical shifts (δ, ppm) and Mass spectral fragments (m/z) data of enones 33-36.

<table>
<tr><th rowspan="2">Entry</th><th colspan="8">IR frequencies (ν, cm ^{1})</th></tr>
<tr><th>$CO_{s\text{-}cis}$</th><th colspan="2">$CO_{s\text{-}trans}$</th><th>CH_{ip}</th><th>CH_{op}</th><th colspan="2">$CH{=}CH_{op}$</th><th>$C{=}C_{op}$</th></tr>
<tr><td>**33**</td><td>1670.35</td><td colspan="2">1597.06</td><td>1066.64</td><td>761.88</td><td colspan="2">1008.77</td><td>489.92</td></tr>
<tr><td>**34**</td><td>1618.28</td><td colspan="2">1523.76</td><td>1091.71</td><td>754.17</td><td colspan="2">1091.71</td><td>526.51</td></tr>
<tr><td>**35**</td><td>1668.43</td><td colspan="2">1597.06</td><td>1089.78</td><td>761.88</td><td colspan="2">1008.77</td><td>495.71</td></tr>
<tr><td>**36**</td><td>1664.57</td><td colspan="2">1595.13</td><td>1118.71</td><td>754.17</td><td colspan="2">1001.06</td><td>543.93</td></tr>
<tr><td rowspan="2"></td><th colspan="4">^{1}H NMR chemical shifts (δ, ppm)</th><th colspan="4">^{13}C NMR chemical shifts (δ, ppm)</th></tr>
<tr><th>H_{α}</th><th>H_{β}</th><th colspan="2">Ar-H</th><th>CO</th><th>C_{α}</th><th>C_{β}</th><th>Ar-C</th></tr>
<tr><td>**33**</td><td>7.273</td><td>7.813</td><td colspan="2">7.234-7.764</td><td>179.08</td><td>119.71</td><td>142.08</td><td>124.97-141.45</td></tr>
<tr><td>**34**</td><td>7.281</td><td>7.796</td><td colspan="2">7.290-7.783</td><td>177.98</td><td>123.34</td><td>140.42</td><td>125.23-139.09</td></tr>
<tr><td>**35**</td><td>7.244</td><td>7.761</td><td colspan="2">7.257-7.753</td><td>190.00</td><td>123.48</td><td>142.91</td><td>124.01-141.37</td></tr>
<tr><td>**36**</td><td>7.336</td><td>7.572</td><td colspan="2">7.340-7.487</td><td>189.68</td><td>123.49</td><td>142.83</td><td>124.87-141.73</td></tr>
<tr><td></td><th colspan="8">Mass (m/z)</th></tr>
<tr><td>**33**</td><td colspan="8">301[M^{+}], 303[M^{2+}], 221, 209, 168, 155, 145, 136, 91, 79, 77, 15</td></tr>
<tr><td>**34**</td><td colspan="8">257[M^{+}], 259[M^{2+}], 256, 221, 145, 132, 124, 111, 91, 77, 35, 15</td></tr>
<tr><td>**35**</td><td colspan="8">257[M^{+}], 259[M^{2+}], 256, 221, 165, 145, 137, 132, 124, 119, 111, 91, 77, 35, 15</td></tr>
<tr><td>**36**</td><td colspan="8">240[M^{+}], 242[M^{2+}], 149, 145, 132, 121, 119, 108, 95, 91, 77, 19, 15</td></tr>
</table>

5.2.3 Measurement of Insect Antifeedant Activities

a. Measurement of Insect Antifeedant Activities:

The insect antifeedant activity of all enones measured using Dethler's method [32]. Insect antifeedant measurement test was done with a 4th instar larva *Achoea janata* L against castor *semilooper,* were tended as pronounced on the leaves of castor, *Ricinus communis* in the laboratory at the temperature range of 26 °C ±1 °C and a comparative humidity of 75-85 %.

The leaf – disc bioassay technique was employed with the 4th instar larvae to measure the antifeedant activity. The 4th instar larvae were chosen for conducting the experiment, since the larvae at this level feeded very hungrily. Castor leaf diskettes of a diameter of 1.85 cm were perforated and complete with the dish-petioles.

All synthesized enones were dissolved in acetone with in the diluted concentration of 200 ppm immersed for 5 minutes. The leaf diskettes were air-dried and positioned in one litre beaker having slight water in order to smooth translocation of water.

Therefore, the leaf diskettes persist fresh up to completion of the experiment, 4th instar larvae of the test insect, which was conserved on the leaf diskettes of all enones and allowed to feed on them for 24 h. The zones of the leaf diskettes spent were measured are presented in Table 5.c.

Table 5.c: The insect antifeedant activities of enones.

Entry	4-6 pm	6-8 pm	8-0 pm	10-2 pm	12-6 am	6-8 am	8am 12Nn	12Nn-2pm	2-4 pm	Total leaf disc consumed in 24 h
1	1	1	1	0.5	0.5	1	1	2	2	10
2	1	1	0.5	0.5	1	1	1	1	1	8
3	1	2	1	2	0	0	1	1	1	9
4	0.5	1	1	0.25	0.5	0.5	0.5	0.5	0.5	5
5	1	1	1	1	0.5	0.5	0.5	1	0.5	7
6	1	1	1	1	0	0.5	0.5	1	0.5	6.5
7	1	0.5	1	1	1	1	0.5	0.5	0.5	7
8	1	1	1	0.25	0.25	1	0.5	1	0.5	7
9	1	1	2	0.5	0.5	2	1	1	1	10
10	1	1	0.5	0.5	1	1	0.5	1	0.5	7
11	1	1	1	1	1	1	1	1	1	9
12	1	1	0.5	0.5	1	1	1	1	1	8
13	1	1	0.5	0.5	1	1	1	2	2	10
14	1	1	2	1	1	0	1	1	1	9
15	0.5	1	1.5	0.25	0.5	0.5	0.5	0.5	0.5	5.5
16	1	1	1	1	1	1	1	1	1	9
17	1	1	0.5	0.5	1	1	1	1	1	8
18	1	1	0.5	0.5	1	1	0.5	1	0.5	7
19	1	1	1	1	1	1	1	2	2	11
20	1	1	1	1	1	1	1	2	2	11
21	1	1	1	0.5	0.5	1	1	1	1	8
22	1	1	1	0.5	0.5	1	0.5	1	0.5	7
23	0	1	2	1	1	1	1	1	1	9
24	1	1	1	0	1	1	1	1	1	8
25	1	1	1	1	1	1	1	1	1	9
26	2	1	1	0.5	0	0.5	0.5	1	0.5	7
27	0.5	1	1.5	0	0	0.5	0.5	0.5	0.5	5
28	2	1	1	1	1	1	1	0	0	10
29	2	1	1	0.5	0	0	0	1	0.5	6

Entry	4-6 pm	6-8 pm	8-0 pm	10-2 pm	12-6 am	6-8 am	8am 12Nn	12Nn-2pm	2-4 pm	Total leaf disc consumed in 24 h
30	1	0.5	1.5	0	0	0.5	0.5	0.5	0.5	5
31	1	1	1	1	1	1	1	1	1	9
32	1	1	1	0	1	1	1	1	1	8
33	1	1	1	0	1	1	1	1	1	8
34	2	1	0.5	0.5	0	0.5	0.5	1	0.5	6.5
35	0.5	1	1.5	0.5	0	0.5	0.5	0.5	0.5	5.5
36	1	2	1	1	1	1	1	1	1	10
37	1	1	1	0	1	1	1	1	1	8
38	1	0	1	0	1	1	1	1	1	7
39	0	1	1.5	0.5	0	0.5	0.5	1	1.5	6.5
40	1.5	1	1.5	1.5	0	0.5	0.5	0.5	0.5	8.5

5.3 Discussion:

The results of the obtained insect antifeedant activity of enones are presented in Table 3 and it reveals that all halogenated compounds were found to reflect satisfactory insect antifeedant activities. This test was performed with the insects which ate only two-leaf disc soaked under the solution of this compound. All compounds are active for insect antifeedant activities. The enones **1-11,** the chloro substituted compound **4** good antifeedant activity. The substituents H, $_2$-OH, 4-F, $_2$-OCH_3, 4-OCH_3, and NO_2 were shown least activities. This is due to electronegativity; inductive and hyper conjugative effects of the substituents lack the activity by unfeeding of the insects. In substituted styryl 2,4-difluorophenyl ketones **12-20**, the 4-Cl substituted compound **15** shows good antifeedant activity comparatively other substituents. The electron withdrawing nature of inductive effects enhanced the antifeedant activity by unfeeding the insect. The enones **21-24,** the above said same trend was observed. Here the 4-Cl substituted compound **22** shows good antifeedant activity. Here -I effect of methoxy groups reduced the insect activity. In the chalcone series **25-28 and 29-32**, the chloro substituted compounds **26, 27, 30** and **31** shows good activity. Remaining compounds shows least activity leads by -I effect of methoxy groups. Enones from 2-methyl phenyl ketones **33-36**, the chloro substituted compounds **34** and **35** shows good antifeedant activity. Remaining compounds have less activity. This is due to +I effect of methyl group and electronegativity of fluorine atoms are tend to attract the insect for high feeding.

Chalcones **37-40**, the chloro substituted compounds **38 and 39** shows good antifeedant activities than other. Here the less effect was due to the +I effect of aryl group and electronegativity of fluorine atom enhances the feeding interest of insects. In all the series of enones the chloro substituted compounds shows good activity. Further this test was carried out with the different 50, 100, 150 ppm concentrations and the observation reveal that, the insect antifeedant activity was increased as the concentrations decreased. In this test, the 4-chloro substituted enones shows better insect feedant activity. These are shown in Table 5.d.

Table 5.d: insect antifeedant activity of chloro substituted enones with various dilutions.

Entry	ppm	4-6 pm	6-8 pm	8-10 pm	10-2 pm	12-am	6-8 am	8am 12Nn	12Nn 2pm	2-4 pm	Total leaf disc consumed in 24h
4, 15, 22, 27, 31, 35, 39	**50**	0.25	0	0.25	0.25	0	0	0	0	0	0.75
	100	0.25	0.25	0	0	0	0	0	0	0	0.5
	150	0.25	0	0	0	0	0	0	0	0	0.25

5.4 Conclusions:

About forty halogenated aryl enones were synthesized by ultrasonication method. The antifeedant activities of these enones were tested using Dethler's semilooper method with *Achoea Janata* L insect larvae. All chalcones exhibits antifeedant activities. Among these the chloro substituted enones showed better antifeedant activity with various concentrations. The variation in antifeedant of the enones were due to the electronic effects of substituents such as, electronegativity, Inductive effect, hyper conjugation and electron with-drawing nature.

5.5 Acknowledgement:

Authors thank to DST-NMR Facility, Department of Chemistry, Annamalai University, Annamalianagr-608 002, India for Recording NMR spectra of enones.

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