



Fly-ash:water catalyzed greener synthesis and insect antifeedant activities of some chalcones

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ARTICLE INFO

Article history:

Received: 11 February 2012;

Received in revised form:

25 March 2012;

Accepted: 18 April 2012;

Keywords

Fly-ash:water;

Aldol reaction;

E-2-Propen-1-ones;

Insect antifeedant activities.

ABSTRACT

Some aryl chalcones [E-2-Propen-1-ones] have been synthesized using Fly-ash:water catalyzed solvent free Crossed-Aldol reaction between aryl methyl ketones and aryl aldehydes. The yield of chalcones is more than 60%. The purities of these chalcones are checked by their physical constants and spectral data published literature in earlier. The insect antifeedant activities of chalcones have been studied using 4th instar larvae *Achoea Janata L.*

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Introduction

There are numerous solvent free synthetic methods available in chemical literature for synthesis of organic substrates without solvent[1]. Regioselective, regiosepecific, stereo selective[2], stereospecific[3] and enantioselective[4] green synthetic reactions has been employed for synthesis of E, Z isomers of alkenes[5], conjugated and non-conjugated polyenes[6], s-cis and s-trans conformers of unsaturated ketones[7], acids[8], acid chlorides[9], esters[10] and αS, βR epoxy ketones[11]. This synthetic method follows the hypothesis of atom economy and twelve principles of green chemistry. Many named green reactions such as Crossed-Aldol, Claisen-Schmidt, Knoevenagel, Michael, Friedel-Crafts, Halogenation, Expoxidation and Cyclization have been demonstrated with good yields of product. Various green catalysts such as aqueous NaOH at 20°C[12], ground chemistry-grinding the reactants with aqueous bases in pestle and mortar[13], Barium hydroxide[14], Silica-sulphuric acid[15], Clay[16], Alumina[17], Iron oxides[18] Zinc chloride[19], anhydrous Sodium carbonate[20], Sodium hydroxide-cetylammmonium bromide [21]Ultrasonic sound waves [22], ionic liquids [23] Magnesium oxide [24]and Nano particle of Titanium oxide[25], Fly-ash: aqueous potassium bromide[26] and microwave heating[27]has been used for carbon-carbon bond formation synthetic reactions. Solvent free Aldol, Crossed-Aldol, Friedel-Crafts and Knoevenagel reactions are suitable for good yields of α, β-unsaturated ketone synthesis. These green reactions occupy a unique place in synthetic organic research, due to less toxicity, no hazardousness, pollution free environment, easy handling procedure, process and techniques, lesser amount of solvent usage, environmentally benign and good percentage of yields. Chalcones are biomolecules having many multipronged activities and used as agro chemicals. Keto, alkene and the polar groups substituents in aryl or styryl phenyl moieties in the chalcones are responsible

for their biological activities. Hydroxy chalcones possess more antioxidant activities. Halogenated chalcones possess insect antifeedant activities[28]. The various biological activities of E-2-propen-1-ones are antibacterial[29], antifungal [30], antioxidant[31], antiviral[32], antimalarial[33], anticancer[29], antiplosmodial[34], antituberculosis [35], antiproliferative[36], antileishmanial [37], anti-inflammatory[38], antianalgesic and sedative[39], Radical scavenging[40], antitumour[41], antiparasitic[42], cytotoxicity[43], HIV-antiAIDS[44], cardiovascular[45], inhibition of lipid peroxidation[46] and insect antifeedants[28]. Herein the author wishes to report a new method for synthesis of some aryl chalcones using eco-friendly Fly-ash:water catalyzed Crossed-Aldol reaction of aryl methyl ketones and substituted benzaldehydes. The insect antifeedant activities of halogenated chalcones have been studied using 4th instar larvae *Achoea Janatha L.*

Experimental

Materials and methods

All Chemicals and solvents were procured from E-Merck and Aldrich Chemical companies. Fly-ash was collected in II Thermal Unit, Neyveli Lignite Corporation, Tamilnadu, India. The melting points of all synthesized chalcones have been determined in melting point apparatus and are uncorrected. The infrared spectra (KBr, ν, 400-4000cm⁻¹) of all chalcones were recorded in AVATAR-NICOLET 300 Fourier transform spectrophotometer. Nuclear magnetic resonance spectra of all chalcones were recorded in INSTRUM AV300 and BRUKER 300 spectrometers operating 300MHz frequency was utilized for recording ¹H NMR spectra and 75.46 MHz frequency for ¹³C spectra in CDCl₃ solvent using TMS as internal standard. The chemical ionization mode FAB⁺ and Electron impact (EI) (70 eV) mass spectra of all chalcones were recorded in JEOL

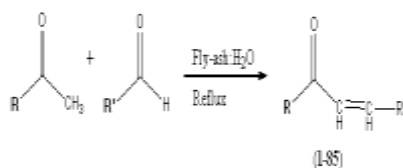
JMSH600H and VARIASATYURN 2000 GC/GC-MS spectrometers.

Fly-ash:water catalyzed Crossed-Aldol reaction for synthesis of chalcones.

Appropriate equal molar quantities of aryl methyl ketones (0.1mol), substituted benzaldehydes (0.1mol), 0.5g of fly-ash and 15ml of water were refluxed for 6h[47]. The completion of reaction was confirmed by Thin Layer Chromatogram. The reaction mixture was mixed with 10mL of dichloromethane and filtered off through Whatmann filter paper No.1. Evaporation of solvent afforded the chalcones and crystallized from ethanol. The catalyst fly-ash was washed with 5mL ethyl acetate, dried in oven at 110°C for 1h and reused for further runs. The purities of known compounds are checked by their physical constants and spectral data. Analytical and Mass spectral data are presented in **Table 1**.

Results and discussion

Many solvent assisted methods available in literature for synthesis of alkyl-alkyl, alkyl-aryl and aryl-aryl kinds of chalcones. In the present work we attempt was made to synthesis of aryl-aryl chalcones by Crossed-Aldol condensation between aryl methyl ketones and substituted benzaldehydes with alternative reagent aqueous phase catalyst fly-ash which is harmless to the reaction[1a] under refluxation condition (**Scheme 1**). The yield and analytical data are presented in **Table 1**. The reaction was completed within 6 hr and good yields of aryl-aryl chalcones are obtained. Fly ash is a waste air-pollutant and it has many chemical species[59] SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO and insoluble residues. During the course of the reactions these species involve the promoting effects of formation of carbon-carbon bonds between methyl carbon of aryl ketone and aldehydic carbon of aryl aldehyde. In these experiments the products were isolated by filtration. Further usage as catalyst is found to be ineffective for this reaction. In this protocol the reaction gave good yield of chalcones without any environmental discharge.



Scheme 1. Synthesis of chalcones

Insect antifeedant activity

The multipronged activities present in different chalcones are intended to examine their insect antifeedant activities against castor semilooper. The larvae of *Achoea Janata L* were reared as described on the leaves of castor *Ricinus communis* in the laboratory at the temperature range of 26°C ±1°C and a relative humidity of 75-85%. The leaf – disc bioassay method[28] was used against the 4th instar larvae to measure the antifeedant activity. The 4th instar larvae were selected for testing because the larvae at this stage feed very voraciously.

Measurement of insect antifeedant activity of 2,4-dichlorophenyl chalcones

Leaf discs of a diameter of 1.85 cm were punched from castor leaves with the petioles intact. 2,4-dichlorophenyl chalcones were dissolved in acetone at a concentration of 200 ppm dipped for 5 minutes. The leaf discs were air-dried and placed in one litre beaker containing little water in order to facilitate translocation of water. Therefore the leaf discs remains

fresh throughout the duration of the rest, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all epoxides and allowed to feed on them for 24 hours. The area of the leaf discs consumed were measured by Dethlers' method[60]. The observed antifeedant activity of oxiranes was presented in **Table 2**.

The results of the antifeedant activity of chalcones presented in **Table 2** reveal that the compounds **23-25** are found to reflect remarkable antifeedant among all other oxiranes. This test is performed with the insects which took only two-leaf disc soaked under the solution of this compound[61]. Compounds **23-25** also showed enough antifeedant activity but their activities are lesser than **23**. Further, compound **23** was subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentrations are decreases, the activity also decreases. From the results in **Table 3**, it is observed that the chalcone **23** showed an appreciable antifeedant activity at 150 ppm concentration.

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Table 1. Analytical data of 2*E*-chalcones synthesized by fly-ash:water catalyzed Crossed-Aldol reaction of the type $\text{Ar-COCH}_3 + \text{Ar}'\text{CHO} \rightarrow \text{Ar-CO-CH=CH-Ar}'$

Entry	Ar	Ar'	Product	M. F.	F.W.	Yield (%)	m.p.(°C)	Mass(m/z)
1	Phenyl	Phenyl	<i>E</i> -1-phenyl-3-phenyl-2-propen-1-one	C ₁₅ H ₁₂ O	280	68	56-57 (55-58) ^[48]	280[M ⁺]
2	Phenyl	4-Aminophenyl	<i>E</i> -1-phenyl-3-(4-aminophenyl)-2-propen-1-one	C ₁₅ H ₁₃ NO	224	60	117 (117-18) ^[49]	224[M ⁺]
3	Phenyl	4-Bromophenyl	<i>E</i> -1-phenyl-3-(4-bromophenyl)-2-propen-1-one	C ₁₅ H ₁₁ BrO	286	67	101-102 (101-03) ^[48]	286[M ⁺], 288[M+2]
4	Phenyl	4-Chlorophenyl	<i>E</i> -1-phenyl-3-(4-chlorophenyl)-2-propen-1-one	C ₁₅ H ₁₁ ClO	252	67	116-117 (112-17) ^[49]	252[M ⁺], 254[M+2]
5	Phenyl	4-Dimethylaminophenyl	<i>E</i> -1-phenyl-3-(4-dimethylaminophenyl)-2-propen-1-one	C ₁₇ H ₁₇ NO	234	62	115-116 (116) ^[50]	234[M ⁺]
6	Phenyl	4-Fluorophenyl	<i>E</i> -1-phenyl-3-(4-fluorophenyl)-2-propen-1-one	C ₁₅ H ₁₁ FO	225	62	85-86 (84-88) ^[51]	225[M ⁺], 227[M+2]
7	Phenyl	4-Hydroxyphenyl	<i>E</i> -1-phenyl-3-(4-hydroxyphenyl)-2-propen-1-one	C ₁₅ H ₁₂ O ₂	224	63	187-188 (183-5) ^[52]	224[M ⁺]
8	Phenyl	4-Iodophenyl	<i>E</i> -1-phenyl-3-(4-iodophenyl)-2-propen-1-one	C ₁₅ H ₁₁ IO	333	61	127-128 (127-28) ^[49]	333[M ⁺], 335[M+2]
9	Phenyl	4-Methoxyphenyl	<i>E</i> -1-phenyl-3-(4-methoxyphenyl)-2-propen-1-one	C ₁₅ H ₁₄ O ₂	276	65	71-72 (69-71) ^[48]	276[M ⁺]
10	Phenyl	4-Methylphenyl	<i>E</i> -1-phenyl-3-(4-methylphenyl)-2-propen-1-one	C ₁₅ H ₁₃ O	219	66	42-47 (42-47) ^[48]	219[M ⁺]
11	Phenyl	4-Nitrophenyl	<i>E</i> -1-phenyl-3-(4-nitrophenyl)-2-propen-1-one	C ₁₅ H ₁₁ NO ₃	254	68	158-159 (158-59) ^[53]	254[M ⁺]
12	4-Aminophenyl	Phenyl	<i>E</i> -1-(4-aminophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₃ NO	234	68	100-101 (100-01) ^[54]	234[M ⁺]
13	4-Bromophenyl	Phenyl	<i>E</i> -1-(4-bromophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₁ BrO	286	62	103-104 (104-05) ^[54]	286[M ⁺], 288[M+2]
14	4-Chlorophenyl	Phenyl	<i>E</i> -1-(4-chlorophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₁ ClO	252	65	101-102 (100-01) ^[54]	252[M ⁺], 254[M+2]
15	4-Dimethylamino Phenyl	Phenyl	<i>E</i> -1-(4-dimethylamino phenyl)-3-phenyl-2-propen-1-one	C ₁₇ H ₁₇ NO	234	62	88-89 (87-88) ^[54]	234[M ⁺]
16	4-Fluorophenyl	Phenyl	<i>E</i> -1-(4-fluoroaminophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₁ FO	225	64	51-52 (49-50) ^[54]	225[M ⁺], 227[M+2]
17	4-Hydroxyphenyl	Phenyl	<i>E</i> -1-(4-hydroxyphenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₂ O ₂	224	62	63-64 (62) ^[54]	224[M ⁺]
18	4-Iodophenyl	Phenyl	<i>E</i> -1-(4-iodophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₁ IO	333	65	45-46 (44-45) ^[54]	333[M ⁺], 335[M+2]
19	4-Methoxyphenyl	Phenyl	<i>E</i> -1-(4-methoxyphenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₄ O ₂	226	65	106-107 (106-07) ^[54]	226[M ⁺]
20	4-Methylphenyl	Phenyl	<i>E</i> -1-(4-methylphenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₃ O	219	68	96-97 (96-97) ^[54]	219[M ⁺]
21	4-Nitrophenyl	Phenyl	<i>E</i> -1-(4-nitrophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₁ NO ₃	253	68	121-122 (121-22) ^[54]	254[M ⁺]
22	2,4-Dichlorophenyl	Phenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-phenyl-2-propen-1-one	C ₁₅ H ₁₀ Cl ₂ O	276	69	81-82 (80-82) ^[7]	276[M ⁺], 278[M+2], 280[M+4]
23	2,4-Dichlorophenyl	4-Bromophenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(4-bromophenyl)-2-propen-1-one	C ₁₅ H ₉ BrCl ₂ O	354	68	129-130 (128-30) ^[7]	354[M ⁺], 355[M+2], 357[M+4], 259[M+6]

24	2,4-Dichlorophenyl	3-Chlorophenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(3-chlorophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₃ O	310	66	101-102 (100-02) ^[7]	310[M+], 312[M+2], 314[M+4], 316[M+6]
25	2,4-Dichlorophenyl	4-Chlorophenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₃ O	310	66	128-129 (126-28) ^[7]	310[M+], 312[M+2], 314[M+4], 316[M+6]
26	2,4-Dichlorophenyl	4-Hydroxyphenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(4-hydroxyphenyl)-2-propen-1-one	C ₁₅ H ₁₀ Cl ₂ O ₂	292	63	126-127 (125-27) ^[7]	292[M+], 294[M+2], 296[M+4]
27	2,4-Dichlorophenyl	4-Methoxyphenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(4-methoxyphenyl)-2-propen-1-one	C ₁₆ H ₁₂ Cl ₂ O ₂	306	68	106-107 (106-07) ^[7]	306[M+], 308[M+2], 310[M+4]
28	2,4-Dichlorophenyl	4-Methylphenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(4-methylphenyl)-2-propen-1-one	C ₁₆ H ₁₂ Cl ₂ O	290	68	138-139 (138-40) ^[7]	290[M+], 292[M+2], 294[M+4]
29	2,4-Dichlorophenyl	2-Nitrophenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(2-nitrophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₂ NO ₃	334	67	169-170 (170-72) ^[7]	334[M+], 336[M+2], 338[M+4]
30	2,4-Dichlorophenyl	4-Nitrophenyl	<i>E</i> -1-(2,4-dichlorophenyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₂ NO ₃	334	67	164-166 (164-66) ^[7]	334[M+], 336[M+2], 338[M+4]
31	3,4-Dichlorophenyl	Phenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-phenyl)-2-propen-1-one	C ₁₅ H ₁₀ Cl ₂ O	276	68	100-101 (100-01) ^[21]	276[M+], 278[M+2], 280[M+4]
32	3,4-Dichlorophenyl	3-Aminophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-aminophenyl)-2-propen-1-one	C ₁₅ H ₉ BrCl ₂ O	354	62	111-112 (111-12) ^[21]	354[M+], 356[M+2], 358[M+4]
33	3,4-Dichlorophenyl	4-Bromophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-bromophenyl)-2-propen-1-one	C ₁₅ H ₉ BrCl ₂ O	354	67	168-169 (168-169) ⁱ	354[M+], 355[M+2], 357[M+4]
34	3,4-Dichlorophenyl	2-Chlorophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(2-chlorophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₃ O	310	65	121-122 (121-22) ^[21]	310[M+], 312[M+2], 314[M+4], 316[M+6]
35	3,4-Dichlorophenyl	3-Chlorophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(3-chlorophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₃ O	310	64	145-146 (145-46) ^[21]	310[M+], 312[M+2], 314[M+4], 316[M+6]
36	3,4-Dichlorophenyl	4-Chlorophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₃ O	310	63	142-143 (142-43) ^[21]	310[M+], 312[M+2], 314[M+4], 316[M+6]
37	3,4-Dichlorophenyl	4-Fluorophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-fluorophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₂ FO	293	65	104-105 (103-04) ^[21]	293[M+], 295[M+2], 297[M+4]
38	3,4-Dichlorophenyl	4-Dimethylaminophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-dimethylaminophenyl)-2-propen-1-one	C ₁₁ H ₁₅ Cl ₂ NO	324	64	126-127 (125-26) ^[21]	324[M+], 326[M+2], 238[M+4]
39	3,4-Dichlorophenyl	2-Hydroxyphenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(2-hydroxyphenyl)-2-propen-1-one	C ₁₅ H ₁₀ Cl ₂ O ₂	292	64	107-108 (107-08) ^[21]	292[M+], 294[M+2], 296[M+4]
40	3,4-Dichlorophenyl	4-Hydroxyphenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-hydroxyphenyl)-2-propen-1-one	C ₁₅ H ₁₀ Cl ₂ O ₂	292	64	116-117 (117-18) ^[21]	292[M+], 294[M+2], 296[M+4]
41	3,4-Dichlorophenyl	3-Methoxyphenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(3-methoxyphenyl)-2-propen-1-one	C ₁₆ H ₁₂ Cl ₂ O ₂	306	66	105-106 (105-06) ^[21]	306[M+], 308[M+2], 310[M+4]
42	3,4-Dichlorophenyl	4-Methoxyphenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-methoxyphenyl)-2-propen-1-one	C ₁₆ H ₁₂ Cl ₂ O ₂	306	67	153-154 (152-53) ^[21]	306[M+], 308[M+2], 310[M+4]

43	3,4-Dichlorophenyl	4-Methylphenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-methylphenyl)-2-propen-1-one	C ₁₆ H ₁₂ Cl ₂ O	290	68	136-137 (137-38) ^[21]	290[M+], 292[M+2], 294[M+4]
44	3,4-Dichlorophenyl	2-Nitrophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(2-nitrophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₂ NO ₃	334	65	184-185 (184-85) ^[21]	334[M+], 336[M+2], 338[M+4]
45	3,4-Dichlorophenyl	3-Nitrophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(3-nitrophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₂ NO ₃	334	67	218-219 (218-19) ^[21]	334[M+], 336[M+2], 338[M+4]
46	3,4-Dichlorophenyl	4-Nitrophenyl	<i>E</i> -1-(3,4-dichlorophenyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₅ H ₉ Cl ₂ NO ₃	334	68	204-205 (205-06) ^[21]	334[M+], 336[M+2], 338[M+4]
47	1-Naphthyl	Phenyl	<i>E</i> -1-(1-naphthyl)-3-phenyl-2-propen-1-one	C ₁₉ H ₁₄ O	257	61	100-101 (100-02) ^[55]	257[M+]
48	1-Naphthyl	4-Chlorophenyl	<i>E</i> -1-(1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₁₉ H ₁₃ ClO	276	63	108-109 (108) ^[55]	276[M+], 278[M+2]
49	1-Naphthyl	4-Nitrophenyl	<i>E</i> -1-(1-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₉ H ₁₄ NO ₃	296	62	114-115 (114) ^[55]	296[M+]
50	4-Bromo-1-naphthyl	Phenyl	<i>E</i> -1-(4-bromo-1-naphthyl)-3-phenyl-2-propen-1-one	C ₁₉ H ₁₃ BrO	336	60	103-104 (103-4) ^[15a]	336[M+], 338[M+2]
51	4-Bromo-1-naphthyl	4-Chlorophenyl	<i>E</i> -1-(4-bromo-1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₁₉ H ₁₂ BrClO	312	65	101-102 (100-1) ^[15a]	312[M+], 314[M+2], 316[M+4]
52	4-Bromo-1-naphthyl	4-Nitrophenyl	<i>E</i> -1-(4-bromo-1-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₉ H ₁₂ BrNO ₃	382	66	117-118 (116-7) ^[15a]	382[M+], 384[M+2]
53	4-Chloro-1-naphthyl	Phenyl	<i>E</i> -1-(4-chloro-1-naphthyl)-3-phenyl-2-propen-1-one	C ₁₉ H ₁₃ ClO	276	65	122-123 (122-23) ^[19]	276[M+], 278[M+2]
54	4-Chloro-1-naphthyl	4-Chlorophenyl	<i>E</i> -1-(4-chloro-1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₁₉ H ₁₂ Cl ₂ O	326	64	115-116 (115-16) ^[19]	326[M+], 328[M+2], 330[M+4]
55	4-Chloro-1-naphthyl	4-Nitrophenyl	<i>E</i> -1-(4-chloro-1-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₉ H ₁₂ ClNO ₃	338	66	102-103 (101-02) ^[19]	338[M+], 340[M+2]
56	4-Methoxy-1-naphthyl	Phenyl	<i>E</i> -1-(4-methoxy-1-naphthyl)-3-phenyl-2-propen-1-one	C ₂₀ H ₁₆ O ₂	288	65	113-114 (113-14) ^[56]	288[M+]
57	4-Methoxy-1-naphthyl	4-Chlorophenyl	<i>E</i> -1-(4-methoxy-1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₂₀ H ₁₅ ClO ₂	332	68	137-138 (137-38) ^[56]	332[M+], 334[M+2]
58	4-Methoxy-1-naphthyl	4-Nitrophenyl	<i>E</i> -1-(4-methoxy-1-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₂₀ H ₁₅ NO ₄	318	68	142-143 (141-42) ^[56]	318[M+]
59	4-Methyl-1-naphthyl	Phenyl	<i>E</i> -1-(4-methyl-1-naphthyl)-3-phenyl-2-propen-1-one	C ₂₀ H ₁₆ O	262	68	98-99 (98-99) ^[13]	262[M+]
60	4-Methyl-1-naphthyl	4-Chlorophenyl	<i>E</i> -1-(4-methyl-1-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₂₀ H ₁₅ ClO	294	66	80-81 (80-81) ^[13]	294[M+], 296[M+2]
61	4-Methyl-1-naphthyl	4-Nitrophenyl	<i>E</i> -1-(4-methyl-1-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₂₀ H ₁₅ NO ₃	306	68	96-94 (96-97) ^[13]	306[M+]
62	2-Naphthyl	Phenyl	<i>E</i> -1-(2-naphthyl)-3-phenyl-2-propen-1-one	C ₁₉ H ₁₄ NO	257	67	104-105 (105-06) ^[54]	257[M+]
63	2-Naphthyl	4-Chlorophenyl	<i>E</i> -1-(2-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₁₉ H ₁₃ ClO	276	66	146-147 (146) ^[57]	276[M+], 278[M+2]
64	2-Naphthyl	4-Nitrophenyl	<i>E</i> -1-(2-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₉ H ₁₃ NO ₃	296	66	147-148 (147) ^[57]	296[M+]

65	6-Methoxy-2-naphthyl	Phenyl	<i>E</i> -1-(6-methoxy-2-naphthyl)-3-phenyl-2-propen-1-one	C ₂₀ H ₁₆ O ₂	288	68	67-68 (67-68) ^[1b]	288[M ⁺]
66	6-Methoxy-2-naphthyl	4-Chlorophenyl	<i>E</i> -1-(6-methoxy-2-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₂₀ H ₁₅ ClO ₂	332	64	122-123 (122-23) ^[1b]	332[M ⁺], 334[M+2]
67	6-Methoxy-2-naphthyl	4-Nitrophenyl	<i>E</i> -1-(6-methoxy-2-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₁₉ H ₁₅ NO ₄	356	65	148-149 (148-149) ^[1b]	356[M ⁺]
68	6-Methyl-2-naphthyl	Phenyl	<i>E</i> -1-(6-methyl-2-naphthyl)-3-phenyl-2-propen-1-one	C ₂₀ H ₁₆ O	262	67	123-124 (123-24) ^[1c]	262[M ⁺]
69	6-Methyl-2-naphthyl	4-Chlorophenyl	<i>E</i> -1-(6-methyl-2-naphthyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₂₀ H ₁₅ ClO	294	66	155-156 (154-55) ^[1c]	294[M ⁺], 296[M+2]
70	6-Methyl-2-naphthyl	4-Nitrophenyl	<i>E</i> -1-(6-methyl-2-naphthyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₂₀ H ₁₅ NO ₃	306	62	177-178 (177-78) ^[1c]	306[M ⁺]
71	9H-Fluorenyl	Phenyl	<i>E</i> -1-(9H-Fluorene-2-yl)-3-phenyl-2-propen-1-one	C ₂₂ H ₁₆ O	296	66	149-150 (149-50) ^[58]	296[M ⁺]
72	9H-Fluorenyl	4-Chlorophenyl	<i>E</i> -1-(9H-Fluorene-2-yl)-3-(4-chlorophenyl)-2-propen-1-one	C ₂₂ H ₁₅ ClO	210	64	83-84 (83-84) ^[58]	210[M ⁺], 212[M+2]
73	9H-Fluorenyl	4-Nitrophenyl	<i>E</i> -1-(9H-Fluorene-2-yl)-3-(4-nitrophenyl)-2-propen-1-one	C ₂₂ H ₁₅ NO ₃	342	68	85-86 (85-86) ^[58]	342[M ⁺],
74	4-Biphenyl	Phenyl	<i>E</i> -1-(4-biphenyl)-3-phenyl-2-propen-1-one	C ₂₁ H ₁₆ O	284	68	155-156 (155-56) ^[58]	284[M ⁺]
75	4-Biphenyl	4-Chlorophenyl	<i>E</i> -1-(4-biphenyl)-3-(4-chlorophenyl)-2-propen-1-one	C ₂₁ H ₁₅ ClO	318	66	184-185 (184-85) ^[58]	318[M ⁺], 320[M+2]
76	4-Biphenyl	4-Nitrophenyl	<i>E</i> -1-(4-biphenyl)-3-(4-nitrophenyl)-2-propen-1-one	C ₂₁ H ₁₅ NO ₃	330	64	189-190 (189-90) ^[58]	330[M ⁺]
77	4-Bromobiphenyl	Phenyl	<i>E</i> -1-(4'-bromo-4-biphenyl)-3-phenyl-2-propen-1-one	C ₂₁ H ₁₄ BrO	362	64	171-172 (171-72) ^[1c]	362[M ⁺], 364[M+2],
78	4-Chlorobiphenyl	Phenyl	<i>E</i> -1-(4'-chloro-4-biphenyl)-3-phenyl-2-propen-1-one	C ₂₁ H ₁₄ ClO	318	66	154-54 (154-156) ^[1c]	318[M ⁺], 320[M+2]
79	4-Nitrobiphenyl	Phenyl	<i>E</i> -1-(4'-nitro-4-biphenyl)-3-phenyl-2-propen-1-one	C ₂₁ H ₁₅ NO ₃	330	65	161-162 (160-61) ^[1c]	330[M ⁺]
80	2-Pyrenyl	Phenyl	<i>E</i> -1-(2-pyrenyl)-3-phenyl-2-propen-1-one	C ₂₅ H ₁₆ O	332	67	161-162 (161-62) ^[1c]	332[M ⁺]
81	9-Anthryl	Phenyl	<i>E</i> -1-(9-anthryl)-3-phenyl-2-propen-1-one	C ₂₃ H ₁₆ O	318	65	123-124 (123-24) ^[1c]	318[M ⁺]
82	2-Thienyl	Phenyl	<i>E</i> -1-(2-thienyl)-3-phenyl-2-propen-1-one	C ₁₃ H ₁₀ SO	214	66	111-112 (111-12) ^[1c]	214[M ⁺]
83	2-Furyl	Phenyl	<i>E</i> -1-(2-furyl)-3-phenyl-2-propen-1-one	C ₁₃ H ₁₀ O ₂	208	69	79-80 (80-81) ^[1c]	208[M ⁺]
84	2-Pyrryl	Phenyl	<i>E</i> -1-(2-pyrryl)-3-phenyl-2-propen-1-one	C ₁₃ H ₁₀ NO	196	68	137-138 (137-38) ^[1c]	196[M ⁺]
85	2-Pyridenyl	Phenyl	<i>E</i> -1-(2-pyridenyl)-3-phenyl-2-propen-1-one	C ₁₄ H ₁₁ O	195	66	104-104 (103-04) ^[1c]	195[M ⁺]

Table 2. The Insect antifeedant activities of 4-bromostyryl-2,3-dichlorophenyl ketones

Entry	Subst.	4-6	6-8	8-10	10-12	12-6	6-8	8am-	12Nn-	2-4	Total leaf disc consumed
		pm	pm	pm	pm	am	am	12Nn	2pm	pm	in 24 hrs
22	H	1	0.5	0.5	0.5	0.5	0	1	1	1	6
23	4-Br	0.5	0.5	0.25	0	0.5	0.5	0.25	0.25	0.25	2.5
24	3-Cl	0.5	0.5	0.25	0	0	0.5	0.25	0.25	0.25	2
25	4-Cl	0.0	0.25	0.25		0	0.25	0	0.25	0	1
26	4-OH	1	1	1	1	0	0	1	1	1	7
27	4- OCH ₃	0.5	1	0	0	0	0	0	0	1	2.5
28	4-CH ₃	0.5	0	0	0.5	0	0.25	0	0.25	0.5	2
29	3-NO ₂	0	0.5	0.5	1	1	0	0	1	1	5
30	4- NO ₂	0.5	0	0	2	2	0.5	0.5	1	1	5

Number of leaf discs consumed by the insect (Values are mean + SE of five).

Table 3 . The Insect antifeedant activities of 4-bromostyryl-2,3-dichlorophenyl ketone (23) in the concentration of 50, 100 and 150 ppm concentration.

ppm	4-6	6-8	8-10	10-12	12am-	6-8	8am-	12Nn-	2-4	Total leaf disc consumed
	pm	pm	pm	pm	6am	am	12Nn	2pm	pm	in 24 hrs
50	0.25	0.25	0	0	0.25	0.25	0	0	0	0.1
100	0	0.25	0.25	0	0	0	0	0	0	0.05
150	0	0.5	0.25	0	0.25	0	0	0	0	0.1

Number of leaf discs consumed by the insect (Values are mean + SE of five).