

**Aqueous phase fly-ash catalyzed [4+2] Diels-Alder reaction
of aryl enones and cyclopentadiene: Synthesis and insect
antifeedant activities of aryl bicyclo [2.2.1]
heptene-2-yl-methanones**

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A series containing ten aryl 3-(substituted phenyl) bicyclo [2.2.1] heptene-2-yl-methanone derivatives including 3-(substituted phenyl) bicyclo [2.2.1]hepten-2-yl-(pyren-1-yl)-methanones have been synthesized by aqueous phase fly-ash catalyzed [4+2] Diels-Alder cyclo addition reaction of cyclopentadiene and aryl chalcones. The yields of the methanones are more than 60%. The synthesized methanones are characterized by their physical constants and spectral data. The insect antifeedant activities of synthesized methanones have been studied using Dethler's leaf-discs bioassay method.

Keywords: Aqueous phase [4+2]Diels-Alder reaction; 1-pyrenyl chalcones; cyclopentadiene; Bicyclo [2.2.1] heptene-2-yl-Methanones; Insect antifeedant activities.

1. INTRODUCTION

The Diels-Alder reaction is the best stereo selective reaction for the synthesis of six-membered bicyclic compounds by [4+2] cycloaddition of a diene and dienophiles[1]. If this reaction is reversible in thermal condition then it is called as retro-Diels-Alder reaction. From the past

three decades, the characteristic reactivity, selectivity, *endo*-, *exo*-mechanistic aspects and the effect of solvent of this Diels-Alder reaction has been reported[2, 3, 4, 5, 6, 7]. Currently, aqueous phase Diels-Alder reaction is important for the synthesis of organic substrates especially bicyclo compounds with stereo selectivity, specificity, due to easy handling technique and procedure, non-hazardousness, non-polluted to the environment and good yields [1, 8, 9]. Reidant and Breslow [10] have investigated the aqueous phase reaction of cyclopentadiene and vinyl methyl ketones in water and the reaction rate is greater than 700 times faster than in organic solvents. Numerous catalysts including Lewis acids [5], Bronsted acids[5, 11], Asymmetric catalyst with helical polymers [12], Cu²⁺ ion-mediated nanotubes[13], DNA and Micellar based catalysts [7, 14, 15, 16, 17] have been employed for this [4+2] cycloaddition Diels-Alder reaction of cyclopentadiene(diene) and *E*- chalcones (dienophiles). The vinyl ketones, aza- vinyl ketones, bicyclo methanones possess antimicrobial activities and antibodies [18]. The hydroxylated and methoxylated organic compounds possess antioxidant activities [19, 20, 21]. The halo substituted enones possess insect antifeedant activities [20, 21, 22, 23, 24, 25]. Within the above view, there is no report available for the synthesis of 1-pyrenyl based heptane [2.2.1] methanones by aqueous phase fly-ash catalyzed Diels-Alder reaction of cyclopentadiene and 1-pyrenyl chalcones. Hence, the author have taken efforts for synthesize some 1-pyrenyl based heptane [2.2.1] methanones and evaluated their insect antifeedant activities using Dethler's[26] disc-diffusion bio-assay method.

2. MATERIALS AND METHODS

2.1. General

All chemicals were procured from Sigma-Aldrich and E-Merck brands. Fly ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli-607 803, Tamil Nadu, India. Melting points of all bicyclo[2.2.1]heptane-2-yl methanones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm⁻¹) were recorded on Thermo scientific Nicolet iS5, US made Fourier Transform spectrophotometer. The NMR spectra of selective compounds were recorded in Bruker AV 400 spectrometer operating at 400 MHz for ¹H NMR spectra and 100 MHz for ¹³C NMR spectra in CDCl₃ solvent using TMS as

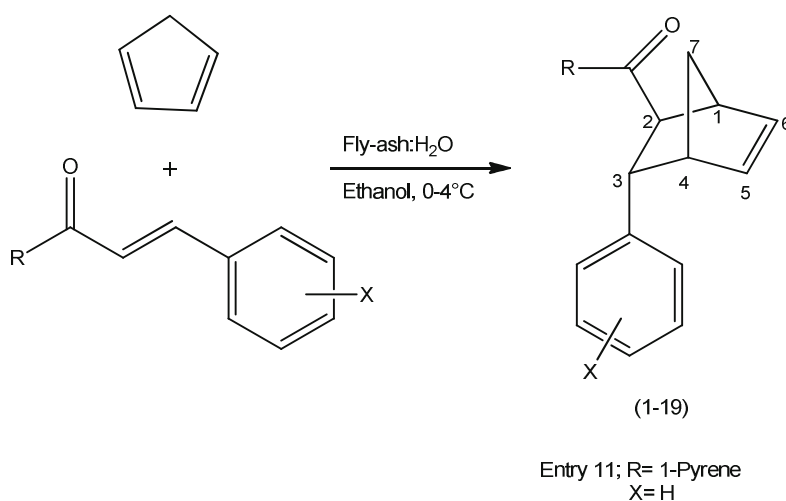
internal standard. Electron impact and chemical ionization mode FAB⁺ mass spectra were recorded with a SHIMADZU spectrometer.

2.1.1. Synthesis of 1-pyrenyl chalcones

The substituted styryl 1-pyrenyl ketones were synthesized by literature method[25].

2.1.2. General procedure for synthesis of aryl 3-(substituted phenyl) bicyclo [2.2.1] heptene-2-yl-methanone derivatives

Appropriate equi-molar quantities of aryl chalcones (2 mmol) in 15 cm³ of ethanol, cyclopentadiene (2 mmol), 20 and 3g of fly-ash in 20 cm³ of water were stirred for 6 h in 0-4°C (Scheme 1) and kept the reaction mixture for an overnight. The completion of the reaction was monitored by thin layer chromatogram. Dichloromethane (10 cm³) was added and the extract was separated by filtration. The filtrate was washed with water, brine (10 cm³), dried over on anhydrous Na₂SO₄ and concentrated gave the solid product. The crude product was further purified by recrystallization with ethanol. The physical constants, analytical and mass fragments of the methanones were presented in Table 1. After isolation of the product, the insoluble fly-ash catalyst was thoroughly washed with 8 mL of ethyl acetate and water heated at 110°C for 3h. Then this is used for further reaction runs.



Scheme 1. Synthesis aryl 3-(substituted phenyl) bicyclo [2.2.1] heptene-2-yl-methanone derivatives by aqueous phase fly-ash catalyzed Diels-Alder reaction of aryl chalcones and cyclopentadiene.

Table 1. The analytical physical constants and mass fragments of aryl 3-(substituted phenyl) bicyclo [2.2.1] heptene-2-yl-methanone derivatives.

Entry	R	X	Product	M.W.	m.p. [°C]	Yield [%]	Mass (m/z)
1	C ₆ H ₅	H	C ₂₀ H ₁₈ O	274	–	64	^a 274[M ⁺]
2	C ₅ H ₄ N(2-pyridine)	H	C ₁₇ H ₁₉ NO	275	–	60	^b 275[M ⁺]
3	C ₃ H ₄ N(2-pyridine)	4-Cl	C ₁₉ H ₁₆ ClNO	309	–	60	^b 309[M ⁺], 311[M ²⁺]
4	C ₃ H ₄ N(2-pyridine)	4-OCH ₃	C ₂₀ H ₁₉ NO ₂	305	–	65	^b 305[M ⁺]
5	C ₃ H ₄ N(2-pyridine)	4-CH ₃	C ₂₀ H ₂₀ NO	289	–	64	^b 289[M ⁺]
6	C ₃ H ₄ N(2-pyridine)	4-NO ₂	C ₁₉ H ₁₆ N ₂ O ₃	320	–	60	^b 320[M ⁺]
7	C ₃ H ₄ N ₂ (2-imidazole)	H	C ₁₇ H ₁₆ N ₂ O	264	–	63	^c 264[M ⁺]
8	C ₃ H ₄ N ₂ (2-imidazole)	2-Br	C ₁₇ H ₁₅ BrN ₂ O	343	–	60	^c 343[M ⁺], 345[M ²⁺]
9	C ₃ H ₄ N ₂ (2-imidazole)	4-Cl	C ₁₇ H ₁₅ ClN ₂ O	299	–	61	^c 299[M ⁺], 301[M ²⁺]
10	C ₃ H ₄ N ₂ (2-imidazole)	4-OCH ₃	C ₁₈ H ₁₈ N ₂ O ₂	294	–	64	^c 294[M ⁺]
11	C ₁₆ H ₉ (1-pyrene)	H	C ₃₀ H ₂₂ O	399	124-125	65	399[M ⁺], 321, 229, 201, 197, 169, 121, 92, 91, 77
12	C ₁₆ H ₉ (1-pyrene)	3-Br	C ₃₀ H ₂₁ BrO	477	116-117	60	477[M ⁺], 479[M ²⁺], 397, 321, 299, 275, 247, 229, 201, 168, 154, 92, 91, 79, 77

cont. Table 1.

Entry	R	X	Product	M.W.	m.p. [°C]	Yield [%]	Mass (m/z)
13	C ₁₆ H ₉ (1-pyrene)	2-Cl	C ₃₀ H ₂₁ ClO	433	126-127	60	433[M ⁺], 435[M ²⁺], 379, 321, 231, 229, 203, 201, 168, 111, 92, 91, 77, 35,
14	C ₁₆ H ₉ (1-pyrene)	3-Cl	C ₃₀ H ₂₁ ClO	433	98-99	62	433[M ⁺], 435[M ²⁺], 379, 321, 231, 229, 203, 201, 168, 111, 92, 91, 77, 35,
15	C ₁₆ H ₉ (1-pyrene)	4-Cl	C ₃₀ H ₂₁ ClO	433	106-107	63	433[M ⁺], 435[M ²⁺], 379, 321, 231, 229, 203, 201, 168, 111, 92, 91, 77, 35,
16	C ₁₆ H ₉ (1-pyrene)	4-F	C ₃₀ H ₂₁ FO	416	113-114	62	416[M ⁺], 418[M ²⁺], 397, 321, 229, 215, 201, 95, 92, 91, 77, 19,
17	C ₁₆ H ₉ (1-pyrene)	4-CH ₃	C ₃₁ H ₂₄ O	413	135-136	64	413[M ⁺], 397, 321, 229, 211, 201, 183, 120, 92, 91, 77, 15,
18	C ₁₆ H ₉ (1-pyrene)	3-NO ₂	C ₃₀ H ₂₁ NO ₃	443	123-124	65	443[M ⁺], 397, 321, 242, 229, 214, 201, 120, 122, 92, 91, 77, 46
19	C ₁₆ H ₉ (1-pyrene)	4-NO ₂	C ₃₀ H ₂₁ NO ₃	443	131-132	60	443[M ⁺], 397, 321, 242, 229, 214, 201, 120, 122, 92, 91, 77, 46

a = Ref. [17]; b = Ref. [6]; c = Ref. [8].

3. RESULTS AND DISCUSSION

The author have attempts for the synthesis of aryl 3-(substituted phenyl) bicyclo [2.2.1] heptene-2-yl-methanone derivatives by aqueous phase fly-ash catalyzed Diels-Alder reaction with cyclopentadiene as diene and *E*-chalcones as dienophiles. The waste air-pollutant fly-ash possess many chemical compounds such as [21, 22, 23, 24, 25, 27] SiO₂, Fe₂O₃, Al₂O₃, CaO, MgO, organic mud and insoluble residues. The waste fly-ash is used as catalyst for organic synthesis. The fly-ash particles are in the silt-sized range of 2-50 microns [28]. Glass, mullite-quartz, and magnetic spinel are the three major mineralogical matrices identified in fly-ash. The elements Si, Al, Fe, Ca, C, Mg, K, Na, S, Ti, P, and Mn are the constituents of fly-ash. The solubility of fly ash has been extensively investigated and it is largely dependent on factors specific to the extraction procedure. Literature study reveals that the long-term leaching studies predict that fly-ash will lose substantial amounts of soluble salts over time, but simulation models predict that the loss of trace elements from fly-ash deposits through leaching will be very slow. Small amounts of radioisotopes are found to be the constituents of fly ash which do not appear to be hazardous. Hence, the author have synthesized aryl 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone by aqueous phase Diels-Alder reaction of *E*-enones and cyclopentadiene under cooling condition. During the reaction the chemical species present in the fly-ash was catalysed the [4+2] cycloaddition reaction. In this reaction the obtained yield is more than 60%. The analytical physical constants and mass fragments are presented in Table 1. The reusability of catalyst in this cycloaddition reaction was studied with 2 mmol of 1-pyrenyl chalcone and 2 mmol of cyclopentadiene (entry 11) and is presented in Table 2. The first run gave 65% of the product. After isolation of the product, the insoluble fly-ash catalyst was washed with 8 cm³ of ethyl acetate and water then heated at 110°C for 3h and kept in a vacuum desiccator. This catalyst was used further second run of the Diels-Alder reaction with the same reactant (entry 11). In this second run the obtained yield was 60%. Then the catalyst was recovered as above and proceeds the same reaction in third time. The obtained yield of third run is 53%. Similarly the fourth and fifth runs gave 40% yield. After fifth run this reaction gave very low yield of less than 10%. The chalcones containing electron donating substituents (OCH₃) gave higher yield than electron withdrawing (halogens and nitro) substituents. The effect of

catalyst on this reaction was studied by varying the catalyst quantity from 0.5 to 3g. As the catalyst quantity increased from 0.5 to 3 g the percentage of product increased from 60-65%. Further increase the catalyst amount beyond 3 g, there is no increase in the percentage of product. The effect of catalyst loading was shown in Fig. 1. The optimum quantity of catalyst loading was found to be 3 g. The effect of solvents on this reaction (entry 11) was studied with the same quantity of reactants with methanol, dichloromethane, dioxane and tetrahydrofuran and is presented in Table 3. The higher yield was obtained in ethanol with fly-ash in water medium.

Table 2. The reusability of the catalyst on the yield of 3-phenyl bicyclo [2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone (entry11).

Run	1	2	3	4	5
Yield	65	60	53	40	40

Table 3. The effect of solvents on the aqueous phase Diels-Alder reaction product 3-phenyl bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone (entry11).

Solvent	Ethanol	Methanol	Dichloromethane	Dioxane	Tetrahydrofuran
Yield	65	63	62	60	62

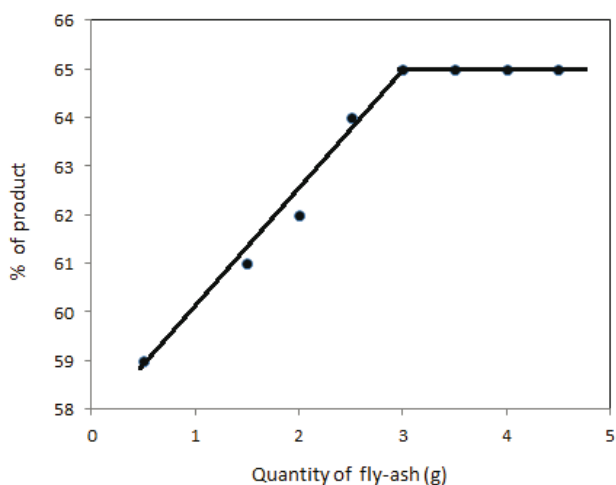


Fig. 1. The effect of catalyst loading.

The infrared and NMR data of selective compounds are summarized below.

11. 3-phenyl bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone: IR(KBr, 4000-400 cm^{-1}) ν = 3011.32, 2989.04, 1672.57, 1567.37, 1432.56, 1076.87, 867.92; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.935(*dd*, 1H, H₁), 3.285(*t*, 1H, H₂), 3.468(*t*, 1H, H₃), 2.795(*dd*, 1H, H₄), 5.961(*d*, 1H, H₅), 5.560(*d*, 1H, H₆), 2.029(*dd*, 1H, H₇), 1.622(*dd*, 1H, H_{7'}), 7.260-8.626(*m*, 14H, Ar-H); ^{13}C NMR(400MHz, CDCl_3 , TMS) δ = 192.72(CO), 47.24(C₁), 37.12(C₂), 31.95(C₃), 32.77(C₄), 136.72(C_{5,6}), 30.06(C₇), 123.28-140.18(Ar-C).

12. (3-(3-Bromophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3015.21, 2985.21, 2815.54, 1675.26, 1601.32, 1576.25, 1525.04, 1125.34, 1073.25, 828.21; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.295(*dd*, 1H, H₁), 3.426(*t*, 1H, H₂), 3.223(*t*, 1H, H₃), 2.179(*dd*, 1H, H₄), 4.125(*d*, 1H, H₅), 5.319(*d*, 1H, H₆), 2.050(*dd*, 1H, H₇), 1.421(*dd*, 1H, H_{7'}), 7.265-9.089(*m*, 13H, Ar-H); ^{13}C (100 MHz, CDCl_3 , TMS) δ = 202.22(CO), 41.35(C₁), 54.18(C₂), 46.17(C₃), 51.85(C₄), 134.05(C_{5,6}), 46.92(C₇), 124.01-131.98(Ar-C).

13. (3-(2-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3016.27, 2935.76, 2812.38, 1673.18, 1601.26, 1598.32, 1536.47, 1525.45, 1128.25, 1036.01, 828.02; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 3.227(*dd*, 1H, H₁), 4.316(*t*, 1H, H₂), 3.496(*t*, 1H, H₃), 2.929(*dd*, 1H, H₄), 5.015(*d*, 1H, H₅), 4.944(*d*, 1H, H₆), 2.174(*dd*, 1H, H₇), 1.603(*dd*, 1H, H_{7'}), 6.028-8.282(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 195.56(CO), 42.03(C₁), 51.12(C₂), 49.06(C₃), 51.95(C₄), 135.54(C_{5,6}), 48.32(C₇), 124.05-141.68(Ar-C).

14. (3-(3-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3019.32, 2902.12, 1668.25, 1603.35, 1558.91, 1436.11, 1135.02, 1062.38, 981.08, 868.27; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.829(*dd*, 1H, H₁), 3.763(*t*, 1H, H₂), 3.582(*t*, 1H, H₃), 2.850(*dd*, 1H, H₄), 5.393(*d*, 1H, H₅), 5.965(*d*, 1H, H₆), 2.160(*dd*, 1H, H₇), 1.612(*dd*, 1H, H_{7'}), 7.263-8.582(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 189.89(CO), 28.34(C₁), 28.64(C₂), 32.80(C₃), 30.91(C₄), 135.34(C_{5,6}), 41.28(C₇), 125.38-147.17(Ar-C).

15. (3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl) methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3007.26, 2992.07, 1662.28, 1615.59, 1538.36, 1468.27, 1249.25, 1162.14, 1065.28, 832.15; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.839(*dd*, 1H, H_1), 3.615(*t*, 1H, H_2), 3.588(*t*, 1H, H_3), 2.710(*dd*, 1H, H_4), 5.437(*d*, 1H, H_5), 5.861(*d*, 1H, H_6), 2.035(*dd*, 1H, H_7), 1.963(*dd*, 1H, H_7'), 6.014-8.558(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 194.56(CO), 28.67(C_1), 30.90(C_2), 32.82(C_3), 45.16(C_4), 135.89($\text{C}_{5,6}$), 28.34(C_7), 124.35-142.35(Ar-C).

16. (3-(4-Fluorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3523.65, 2912.25, 2886.25, 1669.35, 1457.29, 1085.29, 856.27; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.256(*dd*, 1H, H_1), 3.573(*t*, 1H, H_2), 3.873(*t*, 1H, H_3), 2.356(*dd*, 1H, H_4), 5.678(*d*, 1H, H_5), 5.798(*d*, 1H, H_6), 2.346(*dd*, 1H, H_7), 1.789(*dd*, 1H, H_7'), 7.346-8.689(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 198.23(CO), 41.56(C_1), 53.97(C_2), 46.36(C_3), 51.24(C_4), 135.98($\text{C}_{5,6}$), 45.84(C_7), 123.12-139.98(Ar-C).

17. (3-(4-Methylphenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3025.21, 2913.02, 2815.26, 1675.26, 1595.43, 1539.25, 1459.37, 1329.57, 1224.36, 1085.24, 853.27; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.391(*dd*, 1H, H_1), 4.967(*t*, 1H, H_2), 3.217(*t*, 1H, H_3), 2.798(*dd*, 1H, H_4), 5.970(*d*, 1H, H_5), 5.506(*d*, 1H, H_6), 2.174(*dd*, 1H, H_7), 1.973(*dd*, 1H, H_7'), 3.527(*s*, 3H, CH_3), 6.030-8.223(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 196.31(CO), 29.73(C_1), 41.74(C_2), 31.96(C_3), 30.96(C_4), 134.09($\text{C}_{5,6}$), 29.40(C_7), 64.78(CH_3), 124.11-146.35(Ar-C).

18. (3-(3-Nitrophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl) methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3456.37, 3063.24, 1687.36, 1605.10, 1518.32, 1536.49, 1436.58, 1334.13, 1136.16, 936.83, 809.47; ^1H NMR(400MHz, CDCl_3 , TMS) δ = 2.967(*dd*, 1H, H_1), 4.687(*t*, 1H, H_2), 3.214(*t*, 1H, H_3), 2.787(*dd*, 1H, H_4), 5.491(*d*, 1H, H_5), 5.976(*d*, 1H, H_6), 2.215(*dd*, 1H, H_7), 1.732(*dd*, 1H, H_7'), 6.108-8.471(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 205.12(CO), 33.72(C_1), 45.48(C_2), 41.54(C_3), 51.36(C_4), 136.57($\text{C}_{5,6}$), 49.57(C_7), 122.69-142.40(Ar-C).

19. (3-(4-Nitrophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(naphthalen-2-yl) methanone. IR(ν , KBr, 4000-400 cm^{-1}) 3457.9026, 3001.76, 1689.36, 1601.10, 1587.02, 1516.49, 1482.58, 1343.13, 1173.96, 998.23, 829.77;

^1H NMR(400MHz, CDCl_3 , TMS) δ = 3.213(*dd*, 1H, H_1), 4.798(*t*, 1H, H_2), 3.629(*t*, 1H, H_3), 2.901(*dd*, 1H, H_4), 5.592(*d*, 1H, H_5), 5.975(*d*, 1H, H_6), 2.110(*dd*, 1H, H_7), 1.623(*dd*, 1H, H_7), 6.086-8.292(*m*, 13H, Ar-H); ^{13}C NMR(100MHz, CDCl_3 , TMS) δ = 204.19(CO), 42.72(C_1), 51.48(C_2), 43.54(C_3), 51.36(C_4), 1375.72($\text{C}_{5,6}$), 42.57(C_7), 125.55-153.85(Ar-C).

3.1. Insect antifeedant activity

Generally organic compounds which are having carbonyl, unsaturation and halogens they possess insect antifeedant activity. Therefore, the author wishes to examine the insect antifeedant activity of these 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone derivatives and found to be active as insect antifeedants. This test was performed with a 4th instar larva *Achoea janata* L against castor *semilooper*, were reared as described on the leaves of castor, *Ricinus communis* in the laboratory at the temperature range of $26^\circ\text{C} \pm 1^\circ\text{C}$ and a relative humidity of 75-85%. The leaf – disc bioassay method²³ 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.

3.2. Measurement of insect antifeedant activity of 3-(substituted phenyl) bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones

Castor leaf discs of a diameter of 1.85 cm were punched and intact with the petioles. All synthesized 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone 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 remain fresh throughout the duration of the test, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone and allowed to feed on them for 24 h. The areas of the leaf disc consumed were measured by Dethler's method [26]. The observed antifeedant activity of 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone was presented in Table 4.

Table 4. The insect antifeedant activities of the 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanones (entries 11-19)

Entry	R	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12-6 am	6-8 am	8 am-12 Nn	12 Nn-2 pm	2-4 pm	Total leaf discs consumed by 24h
11	H	1	1	1	0.5	0.5	1	1	1	1	8
12	3-Br	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	5
13	2-Cl	0.25	0.25	0.25	0.25	0.5	0.5	0.5	1	0.5	4
14	3-Cl	0.5	0.5	0.5	0	0	0	0.5	1	1	4
15	4-Cl	0.5	0.5	0.5	0.5	0	0	0.5	0.5	0.5	3
16	4-F	0.5	1	0.5	0.25	0.25	1	0.5	1	0.5	5.5
17	4-CH ₃	1	0.5	1	1	1	0.5	1	0.5	0.5	7
18	3-NO ₂	1	1	0.5	1	0.5	0.5	0.5	0.5	0.5	6
19	4-NO ₂	1	0.5	1	0.5	0.5	1	1	1	1	8

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

The results of the antifeedant activity of 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone are presented in Table 4 reveals that compounds 12-16 were found to reflect satisfactory antifeedant. This test is performed with the insects which ate only two-leaf disc soaked under the solution of this compound. Compound 14 showed enough antifeedant activity but lesser than 15. Further compound 15 was subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentrations decreased, the activity also decreased. It is observed from the results in Table 5 and that the 15 (3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone showed an appreciable antifeedant activity at 150 ppm concentration.

Table 5. Antifeedant activity of compound 15 (3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone showed an appreciable antifeedant activity at 3 different concentrations.

ppm	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12-6 am	6-8 am	8 am- 12 Nn	12 Nn- 2 pm	2-4 pm	Total leaf discs consumed by 24h
50	0.25	0.25	0.25	0	0	0	0	0	0	0.75
100	0.25	0.5	0.25	0	0	0	0	0	0	1
150	0.25	0	0.25	0	0	0	0	0	0	0.5

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

4. CONCLUSIONS

A series of aryl bicyclo [2.2.1] hept-5-en-2-yl-methanone derivatives including 3-(substituted phenyl)bicyclo[2.2.1]hept-5-en-2-yl-(pyrene-1-yl) methanone have been synthesized by aqueous phase fly-ash catalyzed Diels-Alder [4+2] cycloaddition of cyclopentadiene and aryl *E*- chalcones. The yields of the methanones are more than 60%. The insect antifeedant activities of methanones have been evaluated using Dethler's leaf-disc bioassay method. The methanone **15** (3-(4-chlorophenyl)bicyclo[2.2.1]hept-5-en-2-yl)(pyrene-1-yl)methanone showed an appreciable antifeedant activity.

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