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Insect antifeedant potent 9*H*-fluorenacylbromides

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ABSTRACT

Background: Attempts to produce greener bromination of 2-acetyl 9*H*-fluorene with KBr+$KBrO_3$ reagent using fly-ash:H_2O catalyst in aqueous media gave 9H-fluorenacylbromides. Generally, the halo-keto compounds possess insect antifeedant activities. Therefore, the insect antifeedant activities of these acyl bromides have been studied using 4^{th} instar larvae *Achoea janata L* against castor semilooper.

Methods: Solvent free bromination method was used for synthesizing some 9H-fluorenacylbromides. They were characterized by UV, IR, NMR and mass spectroscopic data. Castor-leaf discs were used for evaluation of insect antifeedant activities of the synthesized acyl bromides.

Results: The yields of synthesized acyl bromides were over 60%. The physical constants, analytical and spectral data of these ketones has been determined. Halo substituted acyl bromides gave good insect antifeedant activities.

Conclusion: Easy handling, non-hazardous and environmentally benign bromination methods have been adopted for synthesizing acyl bromides with good yields. Bromo substituted acyl bromides show better insect antifeedant activity.

Keywords: 9*H*-fluorenacyl bromides, fly-ash:H_2O, Infrared spectra, NMR spectra, Insect antifeedant activity

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INTRODUCTION

Green synthetic methods are useful for the synthesis of various biologically active, stereospecific, stereo selective organic substrates, such as alkenes, alkynes, saturated and unsaturated carbonyl compounds,[1] acids, esters,[2] acid chlorides, lactones, calixaranes[3,4] and halo hydrocarbons. Solvent-free synthetic organic reactions have been used for synthesis of carbonyl compounds due to their eco-friendly nature, economy, operational simplicity, easy work-up and better yield.[5–8] Green bromination reaction is useful for the formation of carbon-bromine bonds in various carbonyl compounds.[9,10] Methylene structural moiety is found in many naturally occurring compounds and is important for their medicinal activities, such as antibiotics. This is used as precursor for the synthesis of cyclic and acyclic ketones, esters and lactones which can be used for the synthesis of flavones and coumarone derivatives.[11,12] Many reagents and metal salts are employed for the bromination of alkyl as well as aryl compounds, some examples include copper (II) bromide,[13] N,N-dimethylformamide,[14,15] 1,4-dioxane bromooxonium bromide,[16] dioxane dibromide,[17] N-bromosaccharin,[18] tribromoacetyl-tetrabutylammonium bromide derivatives,[19,20] human eosinophils,[21] peroxo-Mn-tetrabutylammonium bromides,[22] bromide-bromates,[9,10] acylammonium salts and LDA quenches with bromine,[23] benzylic brominating agents,[24] pyridinium bromide perbromide,[25] potassium tri-bromide[26] and pyridinium bromochromate.[27] The author wishes to report an efficient and selective method for bromination of side chain in a 2-acetyl 9*H*-fluorene with potassium bromide-bromate mixture (Winkler's reagent) in the presence of fly ash in an aqueous medium. The corresponding acyl bromides were synthesized in this method using fly-ash in aqueous medium to a yield of more than 60%. These acyl bromides exist as different rotomers. These rotomers are identified by their infrared spectral data of carbonyl absorptions. Also studied were the insect antifeedant activities of all acyl bromides using 4^{th} instar larvae *Achoea janata L* against castor *semilooper*

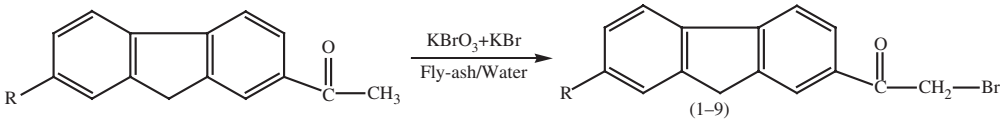
METHODS

General

The fly ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamil Nadu, India. All chemicals used were purchased from Sigma-Aldrich and E-Merck Chemical Company. Melting points of acyl bromides 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 the Avatar-300 Fourier transform spectrophotometer. An Instrum AV300 NMR spectrometer was used and operated at 500 MHz for ^{1}H NMR spectra and 125.46 MHz for ^{13}C NMR spectra in $CDCl_3$ solvent using TMS as the internal standard. Electron impact (EI, 70 eV) and chemical ionization mode FAB^{+} mass spectra were recorded with a Varian 500 spectrometer. Microanalyses of all compounds were performed in Vario EL III analyzer.

General procedure for bromination of 2-acetyl 9*H*-fluorene

In a 100 mL flask, 7-substituted 2-acetyl 9*H*-fluorene (4.16 mmol) in aqueous ethanol (20 ml), 0.5 g of fly ash and 10 mL of water were taken. To this mixture 10 mL Winkler's solution (bromate-bromide solution) was added drop by drop, with stirring for 45 minutes until a decoloration of orange solution took place (Scheme 1). The completion of reaction was monitored by TLC. After completion of the



R= H, NH_2, Br, Cl, Et, OH, OMe, Me, NO_2

Scheme 1. Synthesis of 7-substituted 9*H*-fluorenacyl bromides.

reaction, the brominated products were separated by column chromatography using ethyl acetate-dichloromethane (6:4) to obtain the pale yellow products of ω-bromo-9*H*-fluorones with more than 60% yield. The complete characterization data are given below.

2-Bromo-1-(9H-Fluorene-2-yl) ethanone 1
Yield 65%, m.p. 97–98°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1674.43(CO*cis*), 1644.82(CO*gauche*), 1278.11(C-Br), 3020.34(C-H Ar), 2995.02(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 4.25(s, 2H,-CH_2-), 7.38–8.15(m, 7H, Ar), 3.36(s, 2H, ring,-CH_2-); ^{13}C NMR ($CDCl_3$) δ(ppm): 188.28(CO), 32.83(C-Br), 122.43–146.31 (Ar-C), 35.32(C, ring —CH_2-); Mass (m/z): 287[M^+], 289[M^{+2}], 207, 190,166, 165, 92, 91, 81, 78, 77, 29, 15; Anal. Calcd. for $C_{15}H_{11}BrO$: C, 62.74; H, 3.87%. Found: C, 62.69; H, 3.80%.

2-Bromo-1-(2-amino-9H-Fluorene-7-yl) ethanone 2
Yield 62%, m.p. 107–108°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1668.21(CO *cis*), 1638.41(CO *gauche*), 1223.28(C-Br), 3012.05(C-H Ar), 2998.34(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 4.87(s, 2H,-CH_2-), 7.23–8.08(m, 7H, Ar), 3.23(s, 2H, ring,-CH_2-), 4.23 (s, 2H,-NH_2-); ^{13}C NMR ($CDCl_3$) δ(ppm): 187.23(CO), 31.45(C-Br), 125.23–147.29 (Ar-C), 31.23(C, ring —CH_2-); Mass (m/z): 302[M^+], 304[M^{+2}], 301, 284, 222, 208, 181, 180, 165, 106, 81, 78, 77, 29, 15; Anal. Calcd. for $C_{15}H_{12}BrNO$: C, 59.62; H, 4.10; N, 4.64%. Found: C, 59.58; H, 4.04; N, 4.59%.

2-Bromo-1-(2-bromo-9H-Fluorene-7-yl) ethanone 3
Yield 66%, m.p. 86-87°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1671.23(CO *cis*), 1648.21(CO *gauche*), 1245.18 (C-Br), 3011.05(C-H Ar), 2994.28(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 4.45(s, 2H,-CH_2-), 7.58–8.32(m, 7H, Ar), 3.43(s, 2H, ring,-CH_2-); ^{13}C NMR ($CDCl_3$) δ(ppm): 188.18(CO), 33.58(C-Br), 123.25-147.01 (Ar-C), 32.14(C, ring —CH_2-); Mass (m/z): 366[M^+], 368[M + 2], 370[M^{+4}], 361, 284, 270, 244, 242, 230, 193, 154, 91, 79, 77, 29, 15; Anal. Calcd. for $C_{15}H_{11}Br_2NO$: C, 49.23; H, 2.75%. Found: C, 49.18; H, 2.69%.

2-Bromo-1-(2-chloro-9H-Fluorene-7-yl) ethanone 4
Yield 70%, m.p. 78–79°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1673.41(CO *cis*), 1652.32(CO *gauche*), 1238.15(C-Br), 3004.21(C-H Ar), 2992.01(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 4.01(s, 2H,-CH_2-), 6.76-8.01 (m, 7H, Ar), 3.02(s, 2H, ring,-CH_2-); ^{13}C NMR ($CDCl_3$) δ(ppm): 186.38(CO), 33.78(C-Br), 122.01–145.02 (Ar-C), 32.98(C, ring —CH_2-); Mass (m/z): 321[M^+], 323[M^{+2}], 325[M + 4], 302, 299, 242, 227, 209, 199, 111, 93, 91, 77, 35, 29, 15; Anal. Calcd. for $C_{15}H_{11}BrClO$: C, 56.03; H, 3.13%. Found: C, 55.97; H, 3.09%.

2-Bromo-1-(2-hydroxy-9H-Fluorene-7-yl) ethanone 5
Yield 61%, m.p. 102–103°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1663.51(CO *cis*), 1648.06(CO *gauche*), 1234.38(C-Br), 3012.08(C-H Ar), 2996.37(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 3.97(s, 2H,-CH_2-), 6.98-7.86(m, 7H, Ar), 3.01(s, 2H, ring,-CH_2-); ^{13}C NMR ($CDCl_3$) δ(ppm): 189.78(CO), 33.74(C-Br), 122.35–145.61 (Ar-C), 32.98(C, ring —CH_2-); Mass (m/z): 303[M^+], 305[M^{+2}], 304, 302, 284, 223, 209, 193, 182, 169, 165, 93, 91, 77, 35, 29, 16; Anal. Calcd. for $C_{15}H_{11}BrO_2$: C, 59.43; H, 3.66%. Found: C, 59.45; H, 3.60%.

2-Bromo-1-(2-ethyl-9H-Fluorene-7-yl) ethanone 6
Yield 67%, m.p. 112–113°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1667.62(CO *cis*), 1651.38(CO *gauche*), 1253.24(C-Br), 3012.62(C-H Ar), 2999.28(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 4.32(s, 2H,-CH_2-), 7.02-7.39(m, 7H, Ar), 3.03(s, 2H, ring,-CH_2-), 3.04(q, 2H, -CH_2- side chain), 1.23(t, 3H CH_3- side chain); ^{13}C NMR ($CDCl_3$) δ(ppm): 188.10(CO), 33.63(C-Br), 126.29-141.32 (Ar-C), 33.91 (ring —CH_2-), 33.76(-CH_2- side chain), 14.96(CH_3-); Mass (m/z): 317[M^+], 319[M^{+2}], 316, 314, 301, 299, 272, 193, 165, 105, 93, 91, 77, 35, 29, 16; Anal. Calcd. for $C_{17}H_{15}BrO$: C, 64.78; H, 4.80%. Found: C, 64.72; H, 4.76%.

2-Bromo-1-(2-methoxy-9H-Fluorene-7-yl) ethanone 7
Yield 63%, m.p. 98–99°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1668.25(CO *cis*), 1649.35(CO *gauche*), 1249.35(C-Br), 3002.59(C-H Ar), 2998.34(C-H Ali), 1216.38(C-O-C); ^{1}H NMR ($CDCl_3$)δ(ppm): 3.02 (s, 2H,-CH_2-), 6.08-7.18(m, 7H, Ar), 3.07(s, 2H, ring,-CH_2-), 3.94(s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ(ppm): 186.23(CO), 33.12(C-Br), 125.32–147.86 (Ar-C), 32.87 (ring —CH_2-), 58.36(OCH_3-); Mass (m/z): 317[M^+], 319[M^{+2}], 316, 318, 303, 300, 285, 237, 223, 210, 195, 165, 105, 93, 91, 77, 35, 31, 29, 16; Anal. Calcd. for $C_{16}H_{13}BrO_2$: C, 60.59; H, 4.13%. Found: C, 60.49; H, 4.97%.

2-Bromo-1-(2-methyl-9H-Fluorene-7-yl) ethanone 8
Yield 67%, m.p. 118–119°C, IR (KBr, 4000–400) $\nu(cm^{-1})$: 1670.36(CO *cis*), 1656.65(CO *gauche*), 1254.28(C-Br), 3009.20(C-H Ar), 2998.72(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 3.76(s, 2H,-CH_2-), 6.87–7.76(m, 7H, Ar), 3.37(s, 2H, ring, -CH_2-), 2.48(s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ(ppm): 189.96(CO),

33.34(C-Br), 124.12–139.58(Ar-C), 32.98 (ring —CH_2-), 28.67(CH_3-); Mass (m/z): 301[M^+], 303[M^{+2}], 300, 284, 223, 221, 207, 180, 178, 120, 105, 93, 91, 77, 35, 29, 15; Anal. Calcd. for $C_{16}H_{13}BrO$: C, 63.81; H, 4.35%. Found: C, 63.76; H, 4.29%.

2-Bromo-1-(2-nitro-9H-Fluorene-7-yl) ethanone 9

Yield 69%, m.p. 103–104°C, IR (KBr, 4000–400) ν(cm^{-1}): 1679.23(CO *cis*), 1652.34(CO *gauche*), 1258.53(C-Br), 3011.02(C-H Ar), 2997.29(C-H Ali); ^{1}H NMR ($CDCl_3$)δ(ppm): 3.86(s, 2H,-CH_2-), 8.01–8.46(m, 7H, Ar), 3.56(s, 2H, ring, -CH_2-); ^{13}C NMR ($CDCl_3$) δ(ppm): 191.52(CO), 33.87(C-Br), 123.25–145.26(Ar-C), 32.98 (ring —CH_2-); Mass (m/z): 304[M^+], 306[M^{+2}], 300, 284, 252, 238, 210, 198, 165, 122, 120, 105, 93, 91, 77, 35, 29, 15; Anal. Calcd. for $C_{14}H_{10}BrNO_2$: C, 54.25; H, 3.32; N, 4.23%. Found: C, 5.28; H, 3.28; N, 4.18%.

Measurement of insect antifeedant activity of 9H-fluorenacyl bromides

Castor leaf discs with a diameter of 1.85 cm were punched with the petioles intact.[28–30] All synthesized acyl 9*H*-fluorones 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 beakers containing a little water in order to facilitate translocation of water. Therefore, the leaf discs remain fresh throughout the duration. The 4th instar larvae of the test insect, which had been preserved on the leaf discs of all acyl bromides was allowed to feed on them for 24 hours. The consumed areas of the leaf disc were measured by Dethler's method.[31] The observed antifeedant activity of acyl 9*H*-fluorones was presented in Table 1.

Table 1. Insect antifeedant activity of 2-bromo-1-(2-substituted-9*H*-fluorene-7-yl) ethanones.

Entry	R	4–6pm	6–8pm	8–10pm	10–12pm	12am-6am	6–8am	8am-12Nn	12Nn-2pm	2–4pm	Total leaf disc consumed in 24 hrs
1	H	0.5	1	0.5	0.5	0.5	0	0	0	0	3
2	NH_2	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	0.5
3	Br	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	0.4
4	Cl	0.25	0.25	0.25	0	0	0.25	0	0	0	0.1
5	CH_3-CH_2	0.25	0	0	0.25	0	0	0.20	0.20	0	0.90
6	OH	0.5	1	0.5	1	0	1	0	1	1	6
7	OCH_3	2	0	1	0	1	0	1	0	0	5
8	CH_3	1	0.5	0.5	1	1	0	1	1	1	9
9	NO_2	0.5	0.5	0.5	2	2	1	1	1	1	9

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

RESULTS AND DISCUSSION

Various solvent assisted brominating methods are available in literature for alkyl aryl compounds with direct use of bromine solution. In the present work an attempt was made to brominate aromatics with alternative reagents like Winkler solution (bromate–bromide solution) and aqueous phase catalyst fly ash, which are harmless to the reaction.[32–34] Various 7-substituted 2-acetyl 9*H*-fluorene contain electron withdrawing groups and electron donation groups in seventh position are subjected to bromination on acyl methyl groups with Winkler's solution in the presence of fly-ash: water catalyst under solvent free conditions (Scheme 1). The reaction was completed within one hour and good yields of 7-substituted ω-bromo-9*H*-fluorones were obtained. Under these conditions it was observed that there is no bromination occurring in fluorene ring. These acyl bromides exist as different rotomers. These rotomers, shown in Figure 1, are identified by their infrared spectral data of carbonyl absorptions.

The waste air-pollutant fly ash has many chemical species[32–34] SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO and insoluble residues. During the course of the reactions these species involve the promoting effects of bromination in aryl methyl group in the side chain. In these experiments the products were isolated and the catalyst discarded by filtering and washing. Further usage of the catalyst is found to be ineffective. In this protocol the reaction gave good yields of the brominated products, during ∝-bromination (substitution) without any environmental discharge.

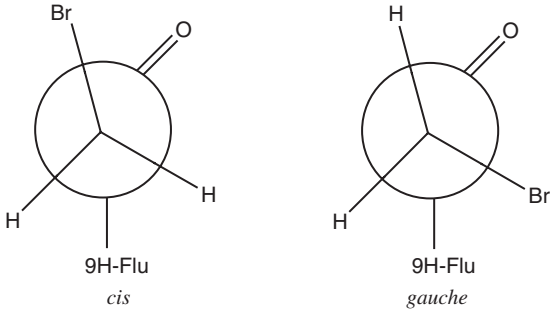


Figure 1. The *cis*- and *gauche* rotomers of 7-substituted 9H-fluorenacyl bromides.

Insect antifeedant activity

Acyl compounds possess various multipronged and biological activities such as antibacterial, antifungal and weedicidal. Generally compounds that possess halo ketones along with polar groups possess insect antifeedant activities. An aim of this study was to examine the insect antifeedant activity of these acyl compounds. This test was performed with a 4th instar larva *Achoea janata* L against castor *semilooper*, that 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[19] 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.

The results of the antifeedant activity of acyl 9*H*-fluorones, presented in Table 1, reveals that all compounds were found to reflect satisfactory antifeedants. This test was performed with the insects that ate two-leaf discs soaked under the solution of this compound.[29,35] Compound 4 showed some antifeedant activity but less than compound 3. Compound 3 was then subjected to measurements of the antifeedant activity at concentrations of 50, 100, 150 ppm. Our observations reveal that as the concentrations decreased, the activity also decreased. Shown in Table 2, the acyl 9*H*-fluorone 3 bromo-1-(2-bromo-9*H*-fluorene-7-yl) ethanone] has an appreciable antifeedant activity at 150 ppm concentration.

Table 2. Insect antifeedant activity of compound 3 [bromo-1-(2-bromo-9*H*-fluorene-7-yl) ethanone] at 3 different concentrations - number of leaf discs consumed by the insect (Values are mean + SE of five).

ppm	4–6pm	6–8pm	8–10pm	10–12pm	12am-6am	6–8am	8am-12Nn	12Nn-2pm	2–4pm	Total leaf
50	0	0.25	0.5	0	0	0	0	0	0	0.75
100	0	0.25	0	0.25	0	0	0	0	0	0.05
150	0	0	0	0	0	0	0	0	0	0

CONCLUSIONS

More than 60% yield of 9H-fluorenayl bromides have been synthesized by solvent-free aqueous phase fly ash:H_2O catalyzed bromination method. The synthesized acyl bromides were characterized by their physical constant and spectroscopic data. The insect antifeedant activities of these acyl bromides have been studied using 4th instar larvae *Achoea janata L*. The halo-substituted acyl bromides showed insect antifeedant activities.

COMPETING INTERESTS

The authors of this work have no competing interests.

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