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Solvent and catalyst free efficient chemoselective synthesis of 1,1-diacetate under visible light irradiation

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One of the synthetic intermediates is used in many organic transformations. A method for highly efficient synthesis of 1,1-diacetate **(3a-j)** from mixture of various substituted benzaldehydes and acetic anhydride under solvent- and catalyst free using visible light irradiation (150 W tungsten lamp) has been developed. The main advantages of this protocol includes shorter reaction time, eco-friendly, mild reaction condition, easy work-up procedures, high yields of products, are the attractive features of the present methodology. All synthesized **3a-j** compounds were characterized by IR, ^{1}H NMR and mass spectral analysis.

Keywords: 1,1-Diacetate, Visible light, Solvent- and catalyst free

One of the important strategies in devising organic synthesis is the protection and deprotection of functional groups. Selective protection of carbonyl function as acylals is an important transformation in organic chemistry because of their stability under neutral and basic conditions as well as under critically controlled acidic conditions[1-2].

1,1-Diacetates are main synthetic precursors for the preparation of α,β-unsaturated diacetates which are important starting materials for Diels–Alder reactions[3]. It is a useful intermediate in various transformations such as nucleophilic substitution reactions[4-8]. As protecting role, acylals are also important precursors for the synthesis of dienes, chiral allyclic esters and as cross linking reagents for the cellulose in cotton[9-10]. It is usual in organic chemistry to produce 1,1-diacetates by using aldehydes and acetic anhydride under acidic medium. A variety of catalysts including sulfamic acid[11], triflic acid[12], NBS[13], CAN[14], H_2SO_4-SiO_2[15], $H_6P_2W_{18}O_{62}.24H_2O$[16], $Bi(NO_3)_3.5H_2O$[17], PVA-$FeCl_3$[18], Fe^{+3} on montmorillonite[19], zirconium sulfophenyl phosphonate[20] and zeolites[21].

Although some of these methods have convenient protocols with good to high yields, the majority of these methods suffer from at least one of the following disadvantages: reaction under oxidizing conditions, prolonged reaction time, high temperatures, use of sensitive moisture and expensive catalysts, use of harmful solvents, stringent conditions, difficulty in scaling up, etc. With increasing environmental concern, development of benign organic reactions is a current topic of research in modern organic chemistry. Our aim is to develop novel methodologies in organic synthesis under mild conditions[22]. Herein we developed rapid, efficient, and practical green approach for the solvent- and catalyst free synthesis of 1,1-diacetates using 150 W tungsten lamp under visible light irradiation.

Experimental Details

Materials and Methods

All necessary chemicals were purchased from Aldrich chemicals and used without further purification. Melting points were recorded in open capillaries with super fit melting point apparatus and were uncorrected. ^{1}H NMR spectra were recorded on 400 MHz using tetramethylsilane as an internal standard, chemical shifts are reported in (δ) units and the coupling constant (J) are reported in Hertz. Splitting pattern has been described as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

Synthesis of substituted phenylmethylene1,1-diacetate, (3a-j)

The mixture of various substituted aromatic aldehyde (1 mmol) with freshly distilled acetic anhydride (2 mmol) was irradiated under 150 W tungsten lamp for the appropriate time. The rate of reaction was monitored by thin layer chromatography (TLC). After completion, the reaction mass was poured onto ice cold water and extracted with ethyl acetate (3 x 15mL). Organic layer was separated, dried over anhydrous sodium sulphate (Na_2SO_4) and concentrated under reduced pressure. The synthesized derivatives are purified by column chromatography using silica gel (100-200 mesh) with n-hexane: ethyl acetate as an eluent to afford 1,1-diacetate **(3a-j)** with good yield.

Spectral data of selected compounds

Phenylmethylene diacetate, (3a)

Yield 85%; white solid; m. p. 46-48^{o}C. IR (KBr): 3068, 1756, 1510, 1440, 1015 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.51 (m, 2H), 7.38 (m, 3H), 2.11 (s, 6H); Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; O, 30.74%; Found: C, 63.71; H, 5.70; O, 30.82%.

(4-Methoxyphenyl)methylene diacetate, (3b)

Yield 90%; colourless solid; m. p. 95-97^{o}C. IR (KBr): 3014, 2937, 1749, 1618, 1378, 1244, 1207, 1018, 936 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H), 2.11 (s, 6H); Anal. Calcd. for $C_{12}H_{14}O_5$; C, 60.50; H, 5.92; O, 33.58%; Found: 60.57; H, 5.96; O, 33.65%.

(4-Bromophenyl)methylene diacetate, (3c)

Yield 80%; white solid; m. p. 95-97^{o}C. IR (KBr): 3025, 2942, 1757, 1687, 1593, 1490, 1369, 1234 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.55 (m, 2H), 7.41 (m, 2H), 2.12 (s, 6H); Anal. Calcd. for $C_{11}H_{11}ClO_4$: C, 46.02; H, 3.86; Br, 27.83; O, 22.29%; Found: C, 46.10; H, 3.92; Br, 27.89; O, 22.35%.

(4-Chlorophenyl)methylene diacetate, (3d)

Yield 85%; colourless solid; m. p. 82-84^{o}C. IR (KBr): 3019, 2924, 1769, 1745, 1492, 1373, 1241, 1070, 1006 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 2.12 (s, 6H); Anal. Calcd. for $C_{11}H_{11}ClO_4$: C, 54.45; H, 4.57; Cl, 14.61; O, 26.37%; Found: C, 54.36; H, 4.68; Cl, 14.72; O, 26.42%.

(4-Nitrophenyl)methylene diacetate, (3e)

Yield 90%; light pale yellow solid; m. p. 126-128^{o}C. IR (KBr): 3123, 3017, 2945, 2854, 1756, 1610 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.2 (d, *J* = 8.8 Hz, 2H), 7.74 (s, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 2.12 (s, 6H); Anal. Calcd. for $C_{11}H_{11}NO_6$: C, 52.18; H, 4.38; N, 5.53; O, 37.91%; Found C, 52.23; H, 4.45; N, 5.60; O, 38.03%.

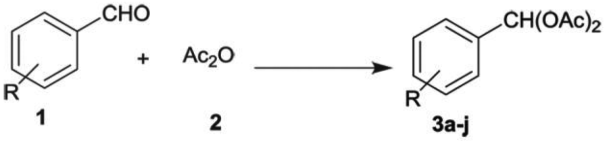
_P_-Tolyl methylene diacetate, (3f)

Yield 87%; white solid; m. p. 83-85^{o}C. IR (KBr): 3112, 3027, 2985, 2875, 1764, 1620 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8 Hz, 2H), 7.771 (d, *J* = 8 Hz, 2H), 7.12 (s, 1H), 2.37 (s, 6H), 2.12 (s, 3H); Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35; O, 28.80%; Found: C, 64.90; H, 6.40; O, 28.89%.

Results and Discussion

For the synthesis of 1,1-diacatates under solvent- and catalyst free from reaction of various substituted benzaldehyde (1 mmol) with acetic anhydride (2 mmol) under visible light irradiation was chosen as a model reaction. Herein we wish to report a simple, efficient, and chemoselective synthetic methods of 1,1-diacetates (**3a-j**) (Scheme 1).

The condensation reaction of various substituted benzaldehyde with acetic anhydride compound under solvent- and catalyst free under visible light irradiation conditions are described. The reaction without using solvent- and catalyst, observed 85% yields within 30 min (Table 1, entry 7). The use of this solvent-free conditions approach is better, because when the reaction is carried out in solvent including ethyl acetate, acetonilrile, tetrahydrofuran, dichloromethane, dimethylsulphoxide, ethyl formate and hydrogen peroxide solvents for same reaction under visible light irradiation it observed that it

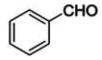
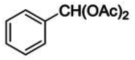
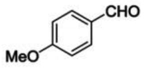
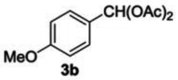
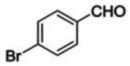
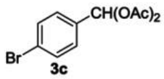
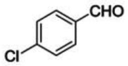
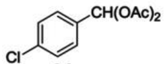
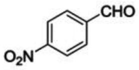
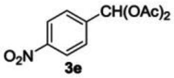
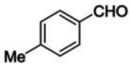
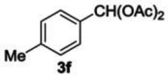
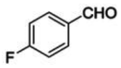
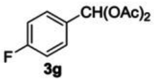
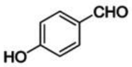
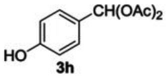
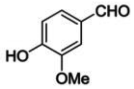
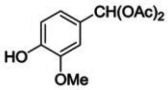
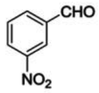
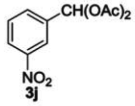


Scheme 1 — Synthesis of 1,1-diacetates (**3a-j**) using visible light irradiation, solvent and catalyst free medium

Table 1 — Optimization of the solvent

S. No.			
1	Solvent	Time (min)	Isolated yield (%)
2	Ethyl acetate	85	40
3	Acetonitrile	90	42
4	Tetrahydrofuran	88	30
5	Dichloromethane	78	47
6	Dimethylsulfide	95	32
7	Ethyl formate	98	25
8	Hydrogen peroxide	96	22
9	Solvent free	30	85

Table 2 - Solvent - and catalyst free synthesis of 1,1-diacetate under visible light irradiation (**3a-j**)

Entry	Benzaldehyde	Product	Time (min)	Yield (%)
1		 **3a**	30	85
2		 **3b**	45	90
3		 **3c**	25	80
4		 **3d**	30	85
5		 **3e**	25	90
6		 **3f**	20	87
7		 **3g**	28	82
8		 **3h**	40	91
9		 **3i**	35	80
10		 **3j**	50	83

required longer reaction time of 78-98 min with 22-47% yields, (Table 1, entries 1- 7).

Thus we have synthesized 1,1- diacetates (**3a-j**) under solvent and catalyst free condition using visible light irradiation. The results are summarized in Table 2 show that various substituted benzaldehyde reacts smoothly with acetic anhydride to afford the corresponding 1,1-diacetates (**3a-j**) that all these products are obtained good to excellent yield with appropriate reaction time (Table 2, entries 1-10).

It was observed that various substituted benzaldehyde containing electron donating substituents (Table 2, entries 1,2,6,8 and 9) required 20-45 min with 85-91% yields while electron withdrawing substituents required 25-35 min with 80-87% yields (Table 2, entries 3,4,5,7 and 10). Both **e**lectron withdrawing and donating substituted 1,1-diacetaes gives near quantitative yields in shorter times.

Conclusion

In summary, we have developed a new, efficient, clean, versatile and environment friendly light induced green procedure devoid of any catalyst or promoter for the synthesis of 1,1-diacetate derivatives. Possibly, this is the first report for the successful synthesis of 1,1-diacetate derivatives without using any solvent and catalyst. Moreover, milder conditions, shorter reaction times, low costs, easy work-up and high yields will make this process attractive over the other available methods and may be considered as an excellent improvement over the existing methods.

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References

1 Green T W & Wuts G M, *Protective Groups in Organic Synthesis*, 3rd Ed, (Wiley, New York), 1999, p. 76.

2 (a) Kalita D J, Borah R & Sarma J C *Tetrahedron Lett,* 39 (1998) 4573; (b) Balini R, Bosica G, Frullanti B, Maggi R, Sartori G & Schroar F, *Tetrahedron Lett,* 39 (1998) 1615.

3 Snider B B & Amin S G, *Synth. Commun,* 8 (1978) 117.

4 Heerden F R V, Huyser J J, Bradley W D & Holzapfel C W, *Tetrahedron Lett,* 38 (1998) 5281.

5 Sandberg M & Sydnes L K, *Tetrahedron Lett,* 39 (1998) 6361.

6 Sandberg M & Sydnes L K, *Org Lett*, 2 (2000) 687.

7 Sydness L K & Sandberg M, *Tetrahedron,* 53 (1997) 12679.

8 Yadav J S, Reddy, B V S & Srihari P, *Synlett*, 5 (2001) 673.

9 Frick J G & Harper R J, *J Appl Polym Sci,* 29 (1984) 1433.

10 Shelke K, Sapkal S, Kategaonkar A, Shingate, B, Shingare M S, *South Afr J Chem,* 62 (2009) 109.

11 Jin T S, Sun G, Li Y W & Li T S, *Green Chem,* 3 (2002) 255.

12 Firouzabadi H, Iranpoor N & Amani K, *Synthesis,* 1 (2002) 59.

13 Karimi B, Seradj H & Ebrahimian G R, *Synlett,* 5 (2000) 623.

14 Roy S C & Banerjee B, *Synlett,* 10 (2002) 1677.

15 Pourmousavi S A & Zinati Z, *Turk J Chem,* 33 (2009) 385.

16 Romanelli G. P, Thomas H J, Baronettic G T & Autino J C, *Tetrahedron Lett,* 44 (2003) 1301.

17 Aggen D H, Arnold J N, Hayes P D, Smoter N J & Mohan R S, *Tetrahedron,* 60 (2004) 3675.

18 Li Y Q, *Synth Commun,* 30 (2000) 3913.

19 Li T S, Zhang Z H & Gao Y J, *Synth Commun,* 28 (1998) 4665.

20 M Curini, F Epifano, M C Marcotullio, O Rosati & M Nocchetti, *Tetrahedron Lett*, *43 (*2002) 2709.

21 Kumar P, Hedge V R & Kumar T P, *Tetrahedron Lett,* 36 (1995) 601.

22 (a) Hote B S, Lokhande P D, *Syn Commun,* 44 (2014) 1492; (b) Hote B S, Sawant A S & Sawant S S, *Polycyclic Aromatic Compounds,* 40 (2020) 1501; (c) Hote B S, Mandawad G G, Patil S G & Hallale S N, *Polycyclic Aromatic Compounds,* 41 (2021) 929; (d) Hote B S, Sawant A S & Sawant S S, *Polycyclic Aromatic Compounds,* 42 (2022) 635; (e) Hote B S, Siddiqui T A J, Pisal P M & Mandawad G G, *Polycyclic Aromatic Compounds*, 42 (2022) 1761; (f) Hote B S, Muley D B & Mandawad G G, *J Appl Organomet Chem*, 1 (2021) 9.