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Eaton's reagent catalysed alacritous synthesis of 3-benzazepinones

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ABSTRACT

An expeditious method for the synthesis of 3-benzazepinones has been developed by using a mixture of phosphorus pentoxide-methane sulfonic acid (Eaton's reagent) at room temperature under solvent and metal catalyst free condition. Wide functional group tolerance, mild reaction conditions, simple procedure, ease of work-up and high yields is the citable features of this protocol.

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1. Introduction

Heterocyclic compounds have gained more importance because of their versatile role in the biological field. Among various heterocycles, seven membered nitrogen containing heterocyclic compounds, in particularly, 3-benzazepinones have received considerable attention in the view of its diverse biological importance for example as γ-secretase inhibitors [1], bradycardia agents [2] and it also serves as remedies to several diseases like Parkinson's, cancer, pain and cardiovascular [3-8]. Because of its broad biological importance, many synthetic efforts have been made to construct this motif. Among these widely employed methods are intramolecular hydroamidation of 2-(1-alkylnyl) phenylacetamide [9], intramolecular Friedel-Crafts cyclization of *N*-chloro acetyl-*N*-methyl phenethyl amine [10], inter or intra-molecular condensation of Ɛ-oxo acids with ammonium acetate and 2-(2-oxoalkyl)phenylacetic acid with phenylglycinol [11], microwave assisted condensation of primary amines with keto acids [12]. Many acid and metal catalysed methods are also well documented in the literature which include Conc. HCl/CH_3COOH [13], $Au(PPh_3)Cl/AgSbF_6$ and $AuBr_3/CH_3COOH$ [9], $Pd(OAc)_2(PPh_3)_2$/DMF [9], NH_4OAc/CH_3COOH [11]. In addition to this, 3-benzazepinones were obtained as by product during the synthesis of fully conjugated seven/eight membered heterocyclic systems [14].

However, most of the above described protocols suffers from serious drawbacks such as tedious workup, prolonged reaction time, expensive reagents or catalysts, high reaction temperature and even then yields are not competent. In this connection, we have developed a protocol which circumvents these demerits. In this communication, we report the synthesis of 3-benzazepinones by using Eaton's reagent.

Eaton's reagent (1:10, phosphorus pentoxide in methane sulfonic acid) is a commercially available inexpensive, low viscous, easy to handle reagent and found to be a good alternative to polyphosphoric acid because of its eco-friendly nature [15], shorter reaction time, no additional solvent required, easier workup and products with high purity in a good to excellent yields [16]. In the recent literature, Eaton's reagent emerged as one of the better reagent in organic synthesis for example in the synthesis of 3,4-dihydropyridin-2-(1*H*)-ones [17], quinolones [18], cardo poly[benzimidazoles] [19], 4-hydroxycoumarin [20], cyclopentanones [21], oxazole's [22], aryl mesylates [23], chromones and flavones [24], mono and *bis*-chalcones [25] and *bis*(indolyl)methanes [26]. It is also used as catalyst for Fisher-indole synthesis and Beckmann rearrangement process [19] (Figure 1).

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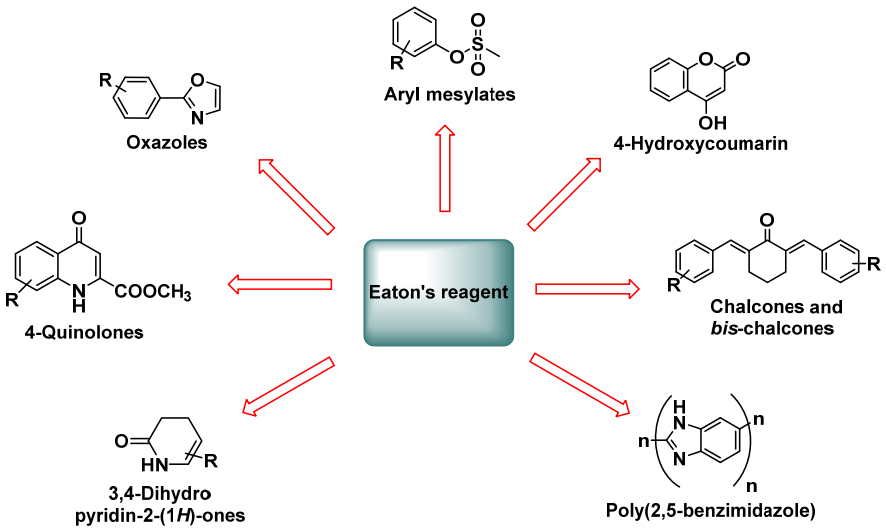


Figure 1. Eaton's reagent: A common reagent in many organic syntheses.

2. Experimental

2.1. Material and methods

Eaton's reagent was purchased from Sigma Aldrich Co., USA. All the other chemicals and reagents were purchased from Merck chemicals used without further purifications. Progress of the reaction were monitored by TLC using ethyl acetate:hexane (1:1, *v*:*v*) as eluent with iodine as developing agents. Melting points of the synthesised compounds were recorded on open capillaries and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker and Varian spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were recorded on Agilent 6330 instrument. Elemental analysis was performed using elemental analysis Perkin-Elmer 2400.

2.2. Synthesis

2.2.1. General procedure for the synthesis of substituted phenyl acetamide analogues (2a-k)

Substituted phenyl acetic acids (0.6 mmol), triethylamine (1.6 mL, 1.2 mmol) and (2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) (2.2 g, 0.6 mmol) were stirred in 5 mL of dry DMF for about 10 min at room temperature. To that reaction mixture amino acetaldehyde dimethyl acetal (0.78 mL, 0.7 mmol) was added slowly and stirring was continued for about 4-5 hrs at room temperature. After the completion of reaction as indicated by TLC, reaction mixture was quenched with water (40 mL) and extracted with ethyl acetate. Combined ethyl acetate layer was washed with saturated sodium bicarbonate solution (20 mL × 2), followed by brine solution and water (20 mL × 3), dried over anhydrous sodium sulphate. Solvent was removed under reduced pressure and obtained crude product was recrystallized using petroleum ether (Scheme 1).

2.2.2. General procedure for the synthesis of 3-benzazepinones (3a-k)

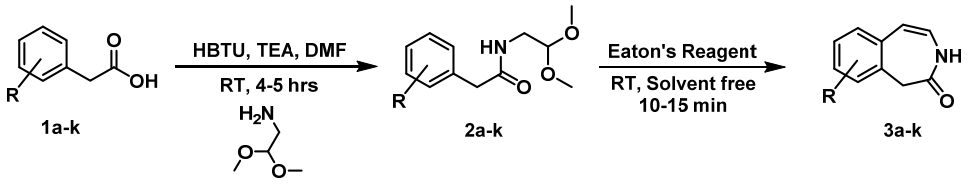
Eaton's reagent (1.5 mmol) was slowly added to substituted phenyl acetamide analogues (1 g, 0.39 mmol) and stirred at room temperature for about 10-15 min. completion of reaction was monitored by TLC. After the completion of reaction, reaction mixture was slowly added to cold saturated solution of sodium bicarbonate and precipitated gummy residue was recrystallized from *n*-hexane (Scheme 1).

8-Methoxy-1,3-dihydro benzo[d]azepin-2-one (**3a**): Color: Pale yellow solid. Yield: 90%. M.p.: 158-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.48 (s, 2H, Azepine-CH_2), 3.81 (s, 3H, OCH_3), 6.18-6.17 (d, 1H, *J* = 4.0 Hz, Azepine-CH), 6.34-6.31 (d, 1H, *J* = 9.2 Hz, Azepine-CH), 6.80 (s, 1H, Ar-H), 6.87-6.86 (d, 1H, *J* = 2.4 Hz, Ar-H), 7.17-7.15 (d, 1H, *J* = 8.4 Hz, Ar-H), 8.44 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 170.40 (1C, CONH), 160.44 (1C, Ar-C), 132.52 (1C, Ar-C), 128.8 (1C, Ar-C), 127.22 (1C, Ar-C), 122.70 (1C, CH-NH), 116.63 (1C, Ar-C), 113.88 (1C, Ar-C), 113.35 (1C, CH-CHNH), 55.50 (1C, OCH_3), 43.66 (1C, CH_2-CONH). MS (EI, *m/z*): 190.2111 (M+1). Anal. calcd. for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40; O, 16.91. Found: C, 69.86; H, 5.84; N, 7.44; O, 16.89%.

7-Methyl-1, 3-dihydro-benzo[d]azepin-2-one (**3b**): Color: Dark brown semi solid. Yield: 89%. M.p.: 116-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 2.38 (s, 3H, CH_3), 3.48 (s, 2H, Azepine-CH_2), 6.18-6.17 (d, 1H, *J* = 4.4 Hz, Azepine-CH), 6.34-6.31 (d, 1H, *J* = 9.1 Hz, Azepine-CH), 6.95 (s, 1H, Ar-H), 6.85-6.84 (d, 1H, *J* = 7.2 Hz, Ar-H), 6.86-6.87 (d, 1H, *J* = 3.6 Hz, Ar-H), 8.41 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 169.40 (1C, CONH), 160.44 (1C, Ar-C), 132.49 (1C, Ar-C), 128.51 (1C, Ar-C), 127.02 (1C, Ar-C), 122.50 (1C, Ar-C), 115.63 (1C, Ar-C), 113.66 (1C, CHNH), 113.25 (1C, CH-CHNH), 56.23 (1C, CH_2-CONH), 36.64 (1C, CH_3). MS (EI, *m/z*): 174.2174 (M+1). Anal. calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09; O, 9.24. Found: C, 76.26; H, 6.44; N, 8.06; O, 9.22%.

8-Hydroxy-1, 3-dihydro-benzo[d]azepin-2-one (**3c**): Color: Light brown solid. Yield: 85%. M.p.: 135-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.44 (s, 2H, Azepine-CH_2), 6.13-6.12 (d, 1H, *J* = 4.8 Hz, Azepine-CH), 6.23-6.20 (d, 1H, *J* = 9.2 Hz, Azepine-CH), 6.65 (s, 1H, Ar-H), 7.10-7.08 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.71-7.69 (d, 1H, *J* = 8 Hz, Ar-H), 9.43 (s, 1H, NH), 9.57 (s, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 168.41 (1C, CONH), 157.74 (1C, Ar-C), 132.35 (1C, Ar-C), 128.44 (1C, Ar-C), 125.76 (1C, Ar-C), 123.20 (1C, CHNH), 114.74 (1C, Ar-C), 114.42 (1C, Ar-C), 114.19 (1C, CH-CHNH), 43.37 (1C, CH_2-CONH). MS (EI, *m/z*): 176.1877 (M+1). Anal. calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00; O, 18.27. Found: C, 68.57; H, 5.21; N, 8.01; O, 18.24%.

7-Nitro-1, 3-dihydro-benzo[d]azepin-2-one (**3d**): Color: Light brown semisolid. Yield: 93%. M.p.: 174-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.38 (s, 2H, Azepine-CH_2), 6.28-6.27



Compound	R
3a	3-OCH_3
3b	4-CH_3
3c	3-OH
3d	4-NO_2
3e	4-F
3f	2-Cl
3g	4-Br
3h	3,4-dichloro
3i	H
3j	3-NO_2
3k	3,4-dimethoxy

Scheme 1

(d, 1H, *J* = 4.4 Hz, Azapine-CH), 6.44-6.41 (d, 1H, *J* = 9.1 Hz, Azepine-CH), 6.68 (s, 1H, Ar-H), 7.20-7.18 (d, 1H, *J* = 8.4 Hz, ArH), 7.81-7.79 (d, 1H, *J* = 8 Hz, Ar-H), 9.41 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 168.51 (1C, CONH), 157.77 (1C, Ar-C), 132.33 (1C, Ar-C), 127.44 (1C, Ar-C), 125.77 (1C, Ar-C), 123.18 (1C, Ar-C), 114.77 (1C, Ar-C), 114.55 (1C, CHNH), 114.21 (1C, CH-CHNH), 41.37 (1C, CH_2-CONH). MS (EI, *m/z*): 205.1857 (M+1). Anal. calcd. for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.95; N, 13.72; O, 23.51. Found: C, 58.81; H, 3.97; N, 13.76; O, 23.50%.

7-Fluoro-1, 3-dihydro-benzo[d]azepin-2-one (**3e**): Color: Light yellow semisolid. Yield: 92%. M.p.: 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.34 (s, 2H, Azepine-CH_2), 6.18-6.19 (d, 1H, *J* = 4.8 Hz, Azepine-CH), 6.33-6.30 (d, 1H, *J* = 9.0 Hz, Azepine-CH), 6.90 (s, 1H, Ar-H), 6.88-6.87 (d, 1H, *J* = 7.2 Hz, Ar-H), 6.96-6.98 (d, 1H, *J* = 8.8 Hz, Ar-H), 9.44 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 170.32 (1C, CONH), 161.54 (1C, Ar-C), 132.45 (1C, Ar-C), 128.14 (1C, Ar-C), 127.30 (1C, Ar-C), 122.77 (1C, CHNH), 116.62 (1C, Ar-C), 113.99 (1C, Ar-C), 113.46 (1C, CH-CHNH), 43.62 (1C, CH_2-CONH). MS (EI, *m/z*): 178.1867 (M+1). Anal. calcd. for $C_{10}H_8FNO$: C, 67.79; H, 4.55; N, 7.91; O, 9.03. Found: C, 67.77; H, 4.53; N, 7.95; O, 9.01%.

9-Chloro-1, 3-dihydro-benzo[d]azepin-2-one (**3f**): Color: Brown semisolid. Yield: 90%. M.p.: 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.25 (s, 2H, Azepine-CH_2), 6.15-6.13 (d, 1H, *J* = 8.4 Hz, Azepine-CH), 7.23-7.22 (d, 1H, *J* = 4.4 Hz, Azepine-CH), 6.98-6.98 (t, 1H, *J* = 2.8 Hz, Ar-H), 7.13-7.14 (d, 1H, *J* = 4.8 Hz, Ar-H), 7.23-7.25 (d, 1H, *J* = 7.6 Hz, Ar-H), 9.41 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 169.32 (1C, CONH), 160.53 (1C, Ar-C), 132.75 (1C, Ar-C), 128.11 (1C, Ar-C), 127.55 (1C, Ar-C), 123.77 (1C, Ar-C), 116.41 (1C, Ar-C), 113.91 (1C, CHNH), 113.22 (1C, CH-CHNH), 42.62 (1C, CH_2-CONH). MS (EI, *m/z*): 193.6322 (M+). Anal. calcd. for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23; O, 8.26. Found: C, 62.01; H, 4.17; N, 7.26; O, 8.22%.

7-Bromo-1, 3-dihydro-benzo[d]azepin-2-one (**3g**): Color: Pale yellow semi solid. Yield: 92%. M.p.: 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.24 (s, 2H, Azepine-CH_2), 6.30-6.31 (d, 1H, *J* = 4.4 Hz, Azepine-CH), 7.29-7.20 (d, 1H, *J* = 4.4 Hz, Ar-H), 7.33-7.35 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.71 (s, 1H, Ar-H), 7.92-7.94 (d, 1H, *J* = 8.0 Hz, Azepine-CH), 9.44 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 169.28 (1C, Ar-C), 160.44 (1C, Ar-C), 132.56 (1C, Ar-C), 128.84 (1C, Ar-C), 127.33 (1C, Ar-C), 122.78 (1C, Ar-C), 116.65 (1C, Ar-C), 113.98 (1C, CHNH), 113.41 (1C, CH-CHNH), 43.66 (1C, CH_2-CONH). MS (EI, *m/z*): 239.0896 (M+1). Anal. calcd. for $C_{10}H_8BrNO$: C, 50.45; H, 3.39; N, 5.88; O, 6.72. Found: C, 50.47; H, 3.37; N, 5.87; O, 6.70%.

7, 8-Dichloro-1, 3-dihydro-benzo[d]azepin-2-one (**3h**): Color: Light brown solid. Yield: 93%. M.p.: 175-177 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.24 (s, 2H, Azepine-CH_2), 6.15-6.13 (d, 1H, *J* = 4.8 Hz, Azepine-CH), 6.22-6.20 (d, 1H, *J* = 8.8 Hz, Azepine-CH), 6.85 (s, 1H, Ar-H), 6.82 (s, 1H, Ar-H), 9.48 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 169.27 (1C, CONH), 157.57 (1C, Ar-C), 132.15 (1C, Ar-C), 128.14 (1C, Ar-C), 126.11 (1C, Ar-C), 123.22 (1C, Ar-C), 114.89 (1C, Ar-C), 114.42 (1C, CHNH), 114.21 (1C, CH-CHNH), 43.07 (1C, CH_2-CONH). MS (EI, *m/z*): 228.0711 (M+). Anal. calcd. for $C_{10}H_7Cl_2NO$: C, 52.66; H, 3.09; N, 6.14; O, 7.01. Found: C, 52.64; H, 3.06; N, 6.15; O, 7.05%.

1, 3-Dihydro-1, 3-dihydro-benzo[d]azepin-2-one (**3i**): Color: Light brown semisolid. Yield: 91%. M.p.: 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.46 (s, 2H, Azepine-CH_2), 6.28-6.29 (d, 1H, *J* = 4.8 Hz, Azepine-CH), 7.21-7.22 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.23 (dd, 2H, *J* = 2.6 Hz, Ar-H), 7.38-7.39 (d, 1H, *J* = 3.6 Hz, Ar-H), 7.56-7.58 (d, 1H, *J* = 8.4 Hz, Azepine-CH), 9.43 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 169.12 (1C, CONH), 159.53 (1C, Ar-C), 132.35 (1C, Ar-C), 128.71 (1C, Ar-C), 127.22 (1C, Ar-C), 123.14 (1C, Ar-C), 116.31 (1C, Ar-C), 113.25 (1C, CHNH), 113.12 (1C, CH-CHNH), 41.62 (1C, CH_2-CHCONH). MS (EI, *m/z*): 160.1826 (M+1). Anal. calcd. for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80; O, 10.05. Found: C, 75.41; H, 5.72; N, 8.83; O, 10.02%.

8-Nitro-1, 3-dihydro-benzo[d]azepin-2-one (**3j**): Color: Light brown semi solid. Yield: 90%. M.p.: 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.33 (s, 2H, Azepine-CH_2), 6.15-6.13 (d, 1H, *J* = 8.4 Hz, Azepine-CH), 6.23-6.22 (d, 1H, *J* = 4.4 Hz, Azepine CH), 6.65 (s, 1H, Ar-H), 7.64-7.65 (d, 1H, *J* = 3.6 Hz, Ar-H), 7.85-7.86 (d, 1H, *J* = 8.8 Hz, Ar-H), 9.41 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 168.31 (1C, CONH), 157.34 (1C,Ar-C), 132.44 (1C, Ar-C), 128.10 (1C, Ar-C), 125.67 (1C, Ar-C), 123.18 (1C, Ar-C), 114.35 (1C, Ar-C), 114.24 (1C, CHNH), 114.15 (1C, CH-CHNH), 43.17(1C, CH_2-CONH). MS (EI, *m/z*): 205.1827 (M+1). Anal. calcd. for $C_{10}H_8N_2O_3$: C, 58.82; H, 3.95; N, 13.72; O, 23.51. Found: C, 58.81; H, 3.98; N, 13.70; O, 23.54 %.

7, 8-Dimethoxy-1, 3-dihydro-benzo[d]azepin-2-one (**3k**): Color: Light brown solid. Yield: 85%. M.p.: 146-147 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 3.25 (s, 2H, Azepine-CH_2), 3.69 (s, 6H, OCH_3), 6.15-6.13 (d, 1H, *J* = 4.8 Hz, Azepine-CH), 6.22-6.20 (d, 1H, *J* = 8.8 Hz, Azepine-CH), 6.82 (s, 1H, Ar-H), 6.85 (s, 1H, Ar-H), 9.45 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 169.11 (1C, CONH), 149.59 (1C, Ar-C), 148.08 (1C, Ar-C), 127.65 (1C, Ar-C), 124.68 (1C, Ar-C), 123.84 (1C, CHNH), 114.78 (1C, Ar-C), 112.50 (1C, Ar-C), 110.78 (1C, CH-CHNH), 56.08 (2C, OCH_3), 43.06 (1C, CH_2-CONH).

Table 1. Comparison of reaction conditions and yield of product with reported methods with the present method.

Entry	Methods	Conditions	Time	Yield (%)	Reference
1	$Pd(PPh_3)_2(OAc)_2$	DMF, 60 °C	16 hr	80	15
2	Conc. HCl/AcOOH	DCM, room temp.	60 hr	59	13
3	$Au(PPh_3)Cl/AgSbF_6$	Toulene, 120 °C	12 hr	89	14
4	$AuBr_3$/AcOOH	THF, 120 °C	5 hr	86	14
5	Microwave irradiation	Toulene, 120 °C	2-3 hr	60	12
6	Eaton's reagent	Solvent free, room temp.	10-15 min	85-93	-

Table 2. Effect of Eaton's reagent concentration on the synthesis 8-methoxy-1,3-dihydro-benzo[*d*]azepin-2-one (**3a**) *.

Entry	Eaton's reagent (mmol)	Reaction time (min)	Yield (%)
1	0.5	10	80
2	1.0	6-8	90
3	1.5	10-15	93
4	2.0	10-14	92
5	2.5	10-14	92

* 0.39 mmol of compound **2a**. Reaction condition: Room temperature, solvent free.

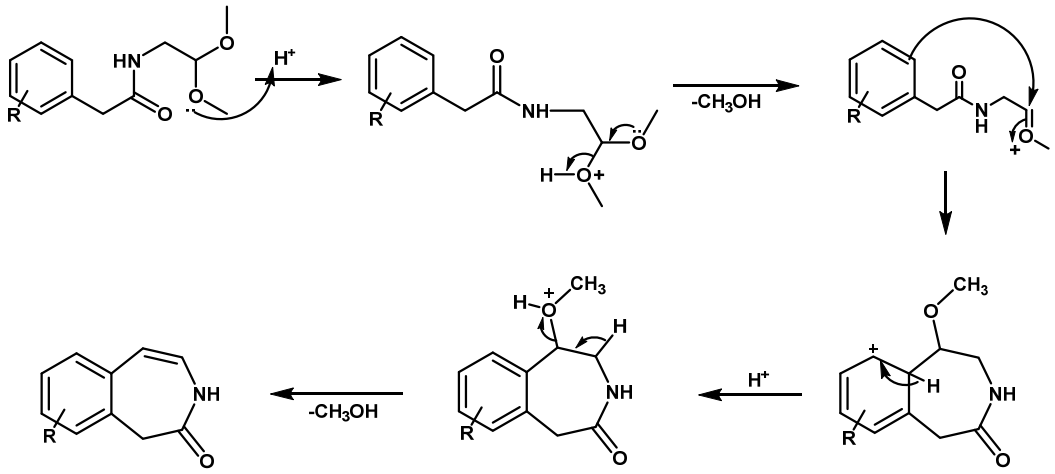


Figure 2. Proposed mechanism for the synthesis of 3-benzazepinones.

MS (EI, *m/z*): 220.2486 (M+1). Anal. calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39; O, 21.89. Found: C, 65.72; H, 5.95; N, 6.33; O, 21.92%.

3. Results and discussion

For every organic chemist it is an unrivalled dream to perform reactions under solvent free and mild conditions for providing green approach towards organic synthesis. As per our knowledge here in, for the first time we are reporting Eaton's reagent catalysed synthesis of 3-benzazepinones. We found that present method is more efficient compared to other reported methods (Table 1).

Reaction protocol for the synthesis 3-benzazepinones using Eaton's reagent is as shown in Scheme 1. In the beginning, substituted phenyl acetamide analogues were synthesized from different substituted phenyl acetic acids and which upon cyclisation using Eaton's reagent at room temperature to get 3-benzazepinones **3a**-**k** (Table 2).

Proposed mechanism for the synthesis of 3-benzazepinones is as shown in Figure 2. Initially, *N*-dimethoxymethyl-2-(3-methoxy-phenyl)-acetamide (**2a**) was selected as model substrate to get optimal reaction condition and obtained results are tabulated in Table 2 and 3. At first, we optimized the amount of Eaton's reagent required for the cyclisation under solvent free conditions and at room temperature. With 0.5 mmol and 1.0 mmol of Eaton's reagent, product obtained in moderate yield 80 and 90%, respectively (Table 2, Entry 1 and 2). The better result is obtained when 1.5 mmol Eaton's reagent is used (Table 2, Entry 3, 93%) providing the desired product in excellent yield with less reaction time, further increasing the amount of Eaton's reagent did not effect on the yield or the reaction time. Therefore it was found that 1.5 mmol of reagent was sufficient enough for the completion of reaction with excellent yield.

Further to check the effect of solvent, we performed cyclisation reaction with different solvents at room temperature. When the reaction was conducted using 1.5 mmol of Eaton's reagent in dichloromethane as solvent required 50 min for completion and the product **3a** obtained in 70% yield (Table 3, Entry 1). Further 42 min and 60 min required for the completion of reaction when dichloroethane and tetrahydrofuran solvent were used with 63 and 78% yield, respectively (Table 3, Entry 2 and 3). While on the other hand, when the reaction was carried out using toluene solvent it takes 70 min for the completion with 58% yield (Table 3, Entry 4). Finally, when the reaction was performed without any solvent it was completed within 10-15 min and product obtained in 93% yield (Table 3, Entry 5). However to check the effect of temperature on the reaction condition, reaction was heated with or without solvent many spots were observed on TLC along with product spot and hence yield of compound **3a** was very poor.

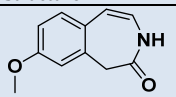
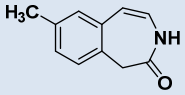
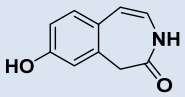
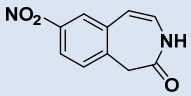
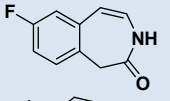
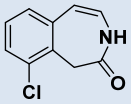
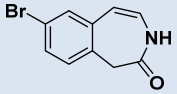
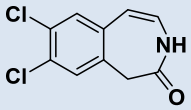
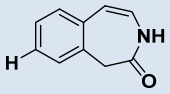
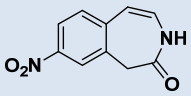
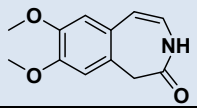
However to explore the scope and limitations of developed methodology, we extended the procedure to various substituted phenylacetamide analogues possessing either electron donating or electron withdrawing groups at different positions and obtained results are tabulated as in Table 4. It is observed that the phenylacetamides possessing electron withdrawing groups on the aromatic ring (Table 4, Entry **3d**, **3e**, **3f**, **3g**, **3h**, **3i** and **3j**) react faster than the electron donating groups (Table 4, Entry **3a**, **3b**, **3c** and **3k**) and we found that the reaction proceeds very efficiently with all the cases and products obtained in high yield.

Table 3. Effect of solvent on the synthesis of 8-methoxy-1,3-dihydro-benzo[*d*]azepin-2-one (**3a**) *.

Entry	Solvent	Time (min)	Yield (%)
1	Dichloromethane	50	70
2	Dichloroethane	60	63
3	Tetrahydrofuran	42	78
4	Toluene	70	58
5	Solvent free	10-15	93

* 1.5 mmol of Eaton's reagent used along with solvent; Reaction condition: Room temperature, 0.39 mmol of compound **2a**.

Table 4. Structures of synthesized 3-benzazepinones **3a-k**.

Compound	Structure	Time (min)	Yield (%) *
3a		13-14	90
3b		14	89
3c		14	85
3d		9-10	93
3e		9	92
3f		13	90
3g		12	92
3h		12	93
3i		13	91
3j		9	90
3k		15	85

* Isolated yield; Reaction condition: Room temperature, solvent free, 1.5 mmol of Eaton's reagent.

4. Conclusion

In conclusion, for the first time we have demonstrated an excellent, mild and efficient protocol for the synthesis of 3-benzazepinones using Eaton's reagent. The noteworthy features of this protocol are shorter reaction time, broad functional group tolerance, and mild reaction condition, avoiding hazardous organic solvent and metal catalyst, green aspects, ease of product purification along with excellent yields.

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