



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

A novel and environmentally benign synthesis of 1,3-disubstituted-(1H,3H)-pyrimidine-2,4-diones

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ABSTRACT

2, 4-diaryloxy pyrimidines underwent Chapman rearrangement under conventional heating as well as on microwave irradiation to afford corresponding 1, 3- disubstituted (1H, 3H)-pyrimidine-2, 4-diones.

Keywords: 2, 4-diaryloxy pyrimidines, 1, 3-disubstituted, pyrimidine-2, 4-diones, microwave irradiation, imidates, Chapman rearrangement

INTRODUCTION

A number of N-substituted pyrimidinediones possess biological activity [1]. N-Glycosides of substituted pyrimidine-2, 4-diones are widely used in therapy, mainly as antiviral and antineoplastic agents. The most prominent representatives are 5-fluoro-1H, 3H-pyrimidine-2, 4-dione and 5-Methyl-(1H, 3H)-pyrimidine-2, 4-dione derivatives [2, 3]. Uramustine, 5-[N, N'-bis (2'-chloroethyl) amino] pyrimidine-2, 4-dione is used orally in the treatment of several leukemias [4] and 5-nitro-1H, 3H- pyrimidine-2, 4-dione derivatives exhibit macrophage growth inhibition [5]. 1-Aryl-5-substituted pyrimidine-2,4-dione are also useful intermediate in the synthesis of other 1H, 3H-pyrimidine-2, 4-dione derivatives [6-8]. Some pyrimidinedione derivatives are used for treating or preventing metabolic disorders, dyslipidemia, neurological disorders, hematological diseases, cancer, inflammation, respiratory diseases, gastroenterological diseases, diabetic complications, an obesity- related disorders and non-alcoholic fatty liver diseases [9].

It has been demonstrated that 3-methyl-1-(4-nitrophenyl)-pyrimidine-2, 4-dione derivatives possessing an electron withdrawing group such as nitro, cyano, or carbamoyl group, at the 5- position, when treated with different N-centered nucleophiles readily undergo ring transformation according to the ANRORC type reaction [6-8].

Some pyrimidinedione derivatives are also used as pesticides [10] and antiphotosynthetic herbicides [10, 11]. Hence they have got agricultural importance also.

1-Aryl pyrimidine-2, 4-diones have been synthesized from substituted ureidopropanoic acids or 1-acryloyl-3-arylureas [12]. 6-methyl-1, 3-oxazine-2, 4-(1H, 3H)-dione when treated with an excess of arylamines was transformed into the appropriate 1-aryl-6-methyl pyrimidine-2, 4-diones [13]. Pyrimidine-2,4-dione derivatives, in reactions with diarylidonium salts, gave the appropriate N-mono- and N, N'-diarylation products with high regioselectivity [14,15]. The reaction of pyrimidine-2-(1H)-one with triphenylbismuth or tris-(3-methoxyphenyl) bismuth gave the appropriate N-aryl derivatives in moderate yields [16].

Attempts at direct N-arylation of (1H, 3H)-pyrimidine-2, 4-dione derivatives have also been reported [14, 17, 18]. All these methods are tedious and involve substrates that are not easily accessible.

EXPERIMENTAL SECTION

The melting points were determined using capillary tube and are uncorrected. The FTIR spectra were recorded on Spectrum One Perkin Elmer (US). The ¹H-NMR spectra were recorded on a Bruker AVANCE (300MHz) spectrometer (with TMS as internal references). ¹³C-NMR spectra were recorded on Bruker AVANCE (75 MHz) spectrometer. Mass spectra were recorded on API-3000MD-series (US). UV spectra were recorded on Shimaduz 2401 PC and Shimaduz 2450, Japan, Spectrophotometer. Elemental analyses were carried out in EA 3000, Euro Vector, Italy. The purity of the compounds was checked by TLC on pre-coated SiO₂ gel (200mesh). Modified LG microwave laboratory oven was used for microwave irradiation. The solvents were purified by distillation before use.

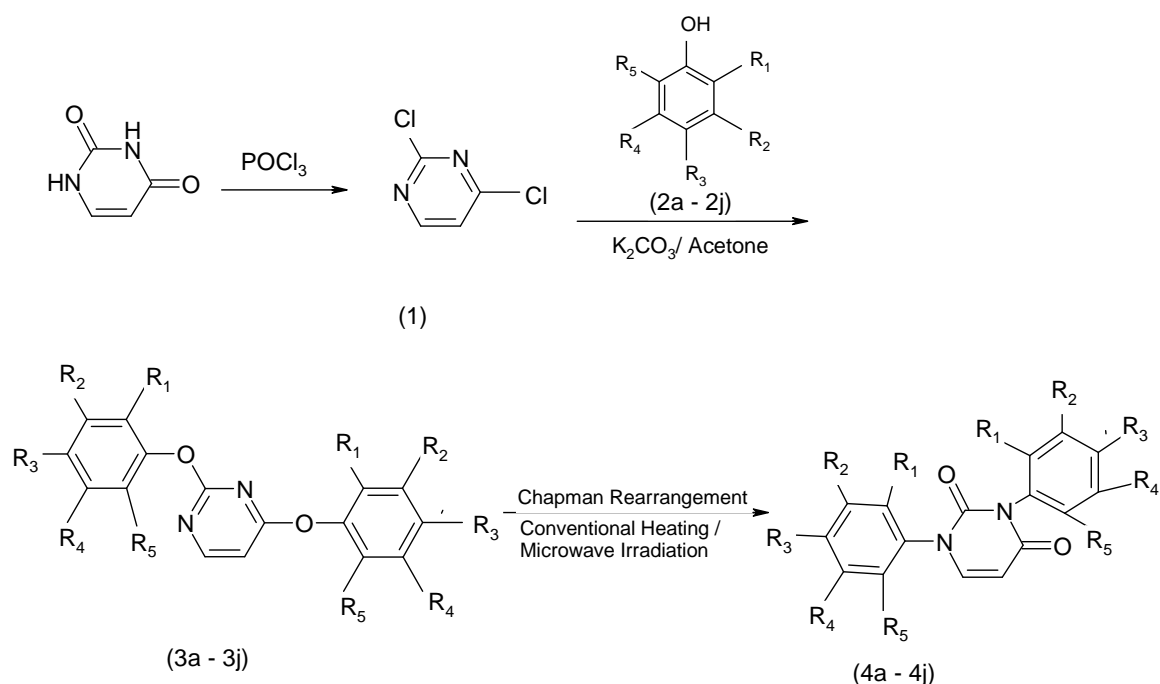
RESULTS AND DISCUSSION


The present paper reports the synthesis of 1, 3-diaryl-(1H, 3H)-pyrimidine-2, 4-diones via *Chapman rearrangement* of 2, 4-diaryloxyimidines.

The thermal conversion of aryl N-arylbenzimidates to N-aryldiphenylamines is known as the *Chapman rearrangement* [19]. Though imidates of many classes of compounds have been subjected to *Chapman rearrangement*, 2, 4-diaryloxyimidines have not been investigated.

In light of the observations from literature survey as well as our interest in evolving new, simpler, ecofriendly, convenient methodologies in organic synthesis and absence of reports on the *Chapman rearrangement* of 2, 4-diaryloxyimidines led us to undertake the present work.

Scheme 1



Compounds	R ₁	R ₂	R ₃	R ₄	R ₅
2a, 3a, 4a	H	H	H	H	H
2b, 3b, 4b	COOC ₂ H ₅	H	H	H	H
2c, 3c, 4c	H	H	COOCH ₃	H	H
2d, 3d, 4d	H	H	H		H
2e, 3e, 4e	OCH ₃	H	COOC ₂ H ₅	H	OCH ₃
2f, 3f, 4f	OC ₂ H ₅	H	H	H	H
2g, 3g, 4g	H	H	OC ₂ H ₅	H	H
2h, 3h, 4h	H	CH ₃	Cl	CH ₃	H
2i, 3i, 4i	CH ₃	H	H	H	H
2j, 3j, 4j	H	CH ₃	H	H	H

For this purpose, (1H, 3H)-pyrimidine-2, 4-dione was visualized as the starting substrate. This on chlorination followed by condensation with various phenols yielded the respective imidates. These were then subjected to *Chapman rearrangement* to afford the corresponding 1, 3- diaryl-(1H, 3H)-pyrimidine-2, 4-diones. (**Scheme 1**)

2, 4-dichloropyrimidine (**1**) has been synthesized as per literature procedure [20].

General Procedure for preparation of 2, 4-diaryloxy pyrimidine (3a-3j)

A mixture of 2, 4-dichloropyrimidine (**1**) (0.02M), different phenols (**2a-2j**) (0.04M) and K_2CO_3 (0.04M) in dry acetone (50 ml) was slowly refluxed for 4-5 hours under dry conditions. The reaction was monitored on. After completion (TLC), of the reaction the acetone was recovered by flash distillation. The reaction mass was cooled to room temperature and quenched in water (50ml) under stirring. The heterogeneous solution was extracted in ether (2 x 25ml) followed by washing with 5% NaOH solution (2 x 25ml). The combined ether extracts were given water washing (2 x 25ml) and dried over sodium sulphate. Recovery of ether followed by purification afforded solid/ oil.

2, 4-diphenoxypyrimidine (3a)

m.p.: 111°C (Lit [21] m. p.: 111°-112°C)

2, 4-di(2-carbethoxyphenoxy)pyrimidine (3b)

Yield: 64%. Viscous oil. IR (KBr, cm^{-1}): 1242 (C-O-C stretch.), 1358 (C-N stretch.), 1426 (C-O stretch.), 1609 (C=C stretch. Ar), 1708, 1710 (-C=O stretch. Ester), 2978-2985 (-CH₂, -CH₃ stretch.), 3074 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.4 (t, J=7.3 Hz, 6H), 4.1(q, J=7.6Hz, 4H), 6.3-7.0 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 14.52, 61.98, 108.41, 115.26, 121.98, 128.92, 132.32, 136.09, 155.02, 155.52, 158.25, 165.21, 166.37. MS: *m/z* (%): 408 (39), 376 (43), 354 (31), 322 (42), 307 (100), 287 (44), 264 (37), 243 (52), 231 (34), 219 (21), 198 (36), 178 (44), 147 (21), 128 (29), 107 (44), 73 (41), 58 (49). UV spectrum: λ_{max} 223.4, abs. 1.981. Molecular formula: C₂₂H₂₀N₂O₆. Elemental analysis: Calculated: C (64.71%), H (4.90%), N (6.86%). Found: C (64.78%), H (4.93%), N (6.93%).

2, 4-di(4-carbomethoxyphenoxy)pyrimidine (3c)

Yield: 62%. Viscous oil. IR (KBr, cm^{-1}): 1215 (-C-O stretch. Ester), 1253 (C-O-C stretch.), 1350 (C-N stretch), 1606 (C=C stretch. Ar), 1720 (-C=O stretch. Ester), 2978-3032 (-CH₃ stretch.), 3092 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 3.9 (s, 6H), 6.4-7.6 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 53.02, 104.87, 112.19, 113.91, 117.02, 130.94, 154.32, 158.01, 158.39, 168.04, 168.75. MS: *m/z* (%): 380 (47), 365 (32), 349 (17), 312 (25), 291 (100), 279 (43), 258 (21), 241(16), 220 (33), 195 (16), 175 (60), 136 (51), 124 (32), 108 (42), 97 (53), 74 (45), 63 (34), 59 (31), 41 (26), 38 (41). UV spectrum: λ_{max} 259.60, abs. 0.912. Molecular formula: C₂₀H₁₆N₂O₆. Elemental analysis: Calculated: C (63.16%), H (4.21%), N (7.37%); Found: C (63.21%), H (4.28%), N (7.42%).

2, 4-di(1-naphthoxy)pyrimidine (3d)

Yield: 62% m.p.:129°C (Lit.[22] m.p.: 129°-130°C)

2, 4-di(4-carbethoxy-2, 6-dimethoxyphenoxy)pyrimidine (3e)

Yield: 59%. Viscous oil. IR (KBr, cm^{-1}): 1190(-C-O stretch. Ester), 1248 (C-O-C stretch.), 1342 (C-N stretch), 1600(C=C stretch. Ar), 1710, 1725 (-C=O stretch. Ester), 2925-3005 (-CH₂, -CH₃ stretch.), 3096 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.5 (t, J=7.1 Hz, 6H), 3.7(s, 12H), 4.4(q, J=7.6 Hz, 4H), 6.1-7.3 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 14.41, 54.62, 62.95, 106.82, 103.08, 140.15, 146.98, 154.03, 156.02, 157.14, 158.60, 166.73. MS: *m/z* (%): 528 (42), 495 (46), 479 (37), 466 (100), 442 (25), 428 (22), 381 (21), 344 (25), 316 (22), 276 (30), 241 (26), 213 (21), 196 (43), 166 (33), 141 (26), 123 (20), 96 (18), 71 (30), 45 (23), 33 (24). UV spectrum: λ_{max} 208.4, abs. 0.821. Molecular formula: C₂₆H₂₈N₂O₁₀. Elemental analysis: Calculated: C (59.09%), H (5.30%), N (5.30%). Found: C (59.14%), H (5.36%), N (5.19%).

2, 4-di(2-ethoxyphenoxy)pyrimidine (3f)

Yield: 63%. m.p.: 102°C. IR (KBr, cm^{-1}): 1251 (C-O-C stretch.), 1355 (C-N stretch), 1605 (C=C stretch. Ar), 2854-3120 (-CH₂, -CH₃ stretch.), 3094 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.2 (t, J=6.7 Hz, 6H), 3.9 (q, J=7.4 Hz, 4H), 6.2-7.2 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 14.27, 63.87, 102.78, 123.04, 128.93, 150.11, 152.28, 157.11, 157.89, 158.12, 160.02. MS: *m/z* (%): 352 (39), 335 (26), 329 (27), 316 (42), 302 (28), 298 (100), 281 (25), 264 (15), 236 (22), 214 (21), 202 (16), 193 (49), 176 (41), 163 (33), 137 (21), 121 (26), 93 (19), 69 (30), 51 (23), 39 (22), 31 (21). UV spectrum: λ_{max} 210.6, abs. 0.796. Molecular formula: C₂₀H₂₀N₂O₄. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.24%), H (5.73%), N (8.03%).

2, 4-di(3-ethoxyphenoxy)pyrimidine (3g)

Yield: 65%. m.p.: 109°C. IR (KBr, cm⁻¹): 1247 (C-O-C stretch.), 1346 (C-N stretch), 1609 (C=C stretch. Ar), 2983-3005 (-CH₂, -CH₃ stretch.), 3094 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.4 (t, J=6.9 Hz, 6H), 4.3 (q, J=7.6 Hz, 4H), 6.3-7.3 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 14.57, 64.13, 102.21, 122.34, 129.58, 154.61, 156.32, 156.97, 158.14, 159.58, 160.19. MS: *m/z* (%): 352 (19), 329 (21), 319 (100), 306 (41), 282 (23), 268 (41), 249 (26), 231 (27), 202 (17), 186 (20), 157 (43), 123 (19), 98 (31), 66 (23), 51 (16), 28 (20). UV spectrum: λ_{max} 209.8, abs. 0.926. Molecular formula: C₂₀H₂₀N₂O₄. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.25%), H (5.74%), N (8.02%).

2, 4-di(4-chloro-3, 5-dimethylphenoxy)pyrimidine (3h)

Yield: 69%. m.p.: 107°C. IR (KBr, cm⁻¹): 780 (-Cl stretch.), 1251 (C-O-C stretch.), 1356 (C-N stretch), 1608 (C=C stretch. Ar), 2906-2987 (-CH₃ stretch.), 3097(C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.4 (s, 12H), 6.2-7.5(m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 20.79, 103.24, 115.89, 125.96, 137.71, 153.78, 154.89, 156.32, 158.62, 160.01. MS: *m/z* (%): 389 (29), 375 (24), 359 (37), 341 (18), 322 (24), 308 (15), 283 (28), 264 (51), 236 (22), 276 (30), 241 (26), 213 (21), 196 (100), 161 (23), 144 (16), 131 (19), 98 (31), 63 (23), 34 (24). UV spectrum: λ_{max} 221.8, abs. 0.743. Molecular formula: C₂₀H₁₈N₂O₂Cl₂. Elemental analysis: Calculated: C (61.70%), H (4.63%), N (7.20%), Cl (18.25%). Found: C (61.76%), H (4.57%), N (7.27%), Cl (18.11%).

2, 4-di(2-methylphenoxy)pyrimidine (3i)

Yield 71% m.p.: 93°C (Lit. [23] m.p.: 93°-94°C)

2, 4-di(3-methylphenoxy)pyrimidine (3j)

Yield: 67%. m.p.: 103°C. IR (KBr, cm⁻¹): 1239 (C-O-C stretch.), 1343 (C-N stretch), 1609 (C=C stretch. Ar), 3009-3097 (-CH₃ stretch.), 3098 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.5 (s, 6H), 6.3-7.6 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 21.25, 103.21, 112.25, 116.26, 129.51, 153.71, 154.51, 155.25, 157.97. MS: *m/z* (%): 292 (21), 281 (40), 269 (17), 246 (100), 232 (21), 218 (15), 181 (27), 162 (22), 143 (18), 126 (36), 116 (29), 103 (52), 92 (23), 76 (27), 47 (16), 34 (28). UV spectrum: λ_{max} 223.7, abs. 0.374. Molecular formula: C₁₈H₁₆N₂O₂. Elemental analysis: Calculated: C (73.97%), H (5.48%), N (9.59 %). Found: C (74.02%), H (5.53%), N (9.48 %).

General procedure for preparation of 1, 3-diaryl-(1H, 3H)-pyrimidine-2, 4-dione (4a-4j) by Chapman rearrangement of 2, 4-diaryloxy pyrimidines (3a-3j) under conventional heating.

In a flask, equipped with water condenser 2, 4-diaryloxy pyrimidine (**3a-3j**) (0.01M) was heated under stirring in nitrogen atmosphere at 180°C-200°C for 90-120 minutes. After completion, (TLC) the reaction mass was cooled to room temperature and petroleum ether (25 ml) was added. It was purified to afford crystals/ oil.

Thus, 2, 4-diaryloxy pyrimidines (3a-3j) smoothly underwent *Chapman rearrangement* but the reaction times were larger and percentage yields were moderate. It was therefore thought worthwhile to carryout the *Chapman rearrangement* of these compounds under microwave irradiation.

Reduced reaction times, less effect on the environment and better reaction yields are some of the common advantages of using microwave irradiation for chemical reactions [24].

General procedure for preparation of 1, 3-diaryl-(1H, 3H)pyrimidine-2, 4-dione (4a-4j) by Chapman rearrangement of 2, 4-diaryloxy pyrimidines (3a-3j) under microwave irradiation.

In a flask, equipped with water condenser 2, 4-diaryloxy pyrimidine (**3a-3j**) (0.01M) was irradiated (900 W) in a microwave oven for 12-18 minutes. After completion (TLC), the reaction mass was cooled to room temperature and petroleum ether (25 ml) was added under stirring. It was purified to afford crystals/ oil.

Percentage yield and reaction time under conventional heating and microwave irradiation are presented in the **Table 1**.

1, 3-diphenyl-(1H, 3H)-pyrimidine-2, 4-dione (4a)

m.p.: 142°C (Lit. [25] m.p.: 142°-143°C)

1, 3-di(2-carbethoxyphenyl)-(1H, 3H)pyrimidine-2, 4-dione (4b)

m.p.: 123°C. IR (KBr, cm⁻¹): 1200 (-C-O stretch), 1341(C-N stretch), 1600, 1640(C=C stretch. Ar), 1680, 1691 (N-C=O stretch), 1700, 1713 (-C=O stretch. Ester), 2854-2955(-CH₂, -CH₃ stretch.), 3090 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.3(t, J=6.9 Hz, 6H), 4.6(q, 7.4Hz, 4H), 6.2-7.4 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 14.31, 60.52, 102.09, 121.89, 122.91, 126.75, 128.32, 131.25, 142.91, 152.49, 165.17, 167.66. MS: *m/z* (%): 408 (17), 382 (63), 358 (26), 341 (19), 322 (13), 294 (22), 247 (100), 221 (13), 207 (17), 194 (44), 174 (21), 153 (12),

130 (17), 111 (51), 92 (22), 73 (24), 59 (15), 45 (36). UV spectrum: λ_{\max} 211.4, abs. 0.949. Molecular formula: $C_{22}H_{20}N_2O_6$. Elemental analysis: Calculated: C (64.71%), H (4.90%), N (6.86%). Found: C (64.76%), H (4.87%), N (6.90%).

1, 3-di(4-carbomethoxyphenyl)-(1H, 3H)pyrimidine-2, 4-dione (4c)

m.p.: 130°C. IR (KBr, cm^{-1}): 1210 (-C-O stretch. Ester), 1358 (C-N stretch.), 1606, 1635 (C=C stretch. Ar), 1688, 1700 (N-C=O stretch), 1715 (-C=O stretch. Ester), 2990-3278 (-CH₃ stretch.), 3092 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 3.5 (s, 6H), 6-7.2(m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 3.02, 102.21, 112.12, 115.03, 131.43, 131.81, 142.90, 152.55, 154.32, 157.83, 165.43, 167.77, 168.45. MS: m/z (%): 380 (35), 369 (21), 347 (14), 333 (17), 309 (33), 277 (38), 257 (21), 237 (100), 208 (17), 198 (14), 174 (22), 158 (17), 133 (16), 124 (14), 101 (16), 95 (17), 84 (25), 71 (13), 47 (16), 32 (22). UV spectrum: λ_{\max} 208.4, abs. 0.953. Molecular formula: $C_{20}H_{16}N_2O_6$. Elemental analysis: C (63.16%), H (4.21%), N (7.37%). Found: C (63.07%), H (4.25%), N (7.41%).

1, 3-di(1-naphthyl)-(1H, 3H)pyrimidine-2, 4-dione (4d)

Viscous oil. IR (KBr, cm^{-1}): 1327(C-N stretch.), 1601, 1629 (C=C stretch. Ar), 1685, 1691(N-C=O stretch.), 2949-3079 (-CH₃ stretch.), 3098(C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 6.2-7.3 (m, 16H). ¹³C NMR (75 MHz, CDCl₃): δ 108.67, 109.03, 120.81, 121.32, 124.12, 125.19, 125.82, 127.53, 134.06, 146.45, 152.39, 153.91, 167.33. MS: m/z (%): 364 (71), 351 (34), 340 (21), 296 (29), 265 (68), 250 (42), 239 (100), 224 (18), 218 (16), 202 (58), 192 (36), 180 (23), 168 (57), 153 (21), 144 (14), 132 (16), 125 (89), 117 (81), 98 (27), 82 (15), 73 (33), 63 (12), 57 (32). UV spectrum: λ_{\max} 205.4, abs. 0.832. Molecular formula: $C_{24}H_{16}N_2O_2$. Elemental analysis: C (79.12%), H (4.40%), N (7.69%). Found: C (79.19%), H (4.49%), N (7.76%).

1, 3-di(4-carbomethoxy-2, 6-dimethoxy phenyl)-(1H, 3H)pyrimidine-2, 4-dione (4e)

Viscous oil. IR (KBr, cm^{-1}): 1205 (-C-O stretch. Ester), 1249 (C-O-C stretch.), 1350 (C-N stretch), 1606, 1642(C=C stretch. Ar), 1681, 1695 (N-C=O stretch), 1710 (-C=O stretch. Ester), 2990-3000 (-CH₂, -CH₃ stretch.), 3087 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.7(t, J=6.7 Hz, 6H), 3.9(s, 12H), 4.4(q, J=7.3 Hz, 4H), 6.0-7.2 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 14.92, 56.23, 62.12, 103.68, 109.13, 112.02, 137.32, 141.22, 143.02, 144.23, 146.09, 153.09, 167.21, 167.89. MS: m/z (%): 528 (31), 512 (14), 503 (32), 491(19), 482 (14), 461 (17), 459 (18), 423 (18), 383 (12), 364 (18), 352 (10), 329 (41), 298 (100), 241 (14), 212 (26), 191 (32), 177 (21), 163 (18), 145 (32), 122 (14), 101 (11), 98 (70), 78 (20), 58 (14), 40 (14), 32 (13). UV spectrum: λ_{\max} 220.8, abs. 2.159. Molecular formula: $C_{26}H_{28}N_2O_{10}$. Elemental analysis: Calculated: C (59.09%), H (5.30%), N (5.30%). Found: C (59.01%), H (5.35%), N (5.38 %).

2, 4-di(2-ethoxyphenyl)-(1H, 3H)pyrimidine-2, 4-dione (4f)

Viscous oil. IR (KBr, cm^{-1}): 1241 (C-O-C stretch.), 1358 (C-N stretch), 1618 (C=C stretch. Ar), 1644, 1688 (N-C=O stretch), 2997-3038 (-CH₂, -CH₃ stretch.), 3097 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.9 (t, J=6.9 Hz, 6H), 4.1(q, J=7.8Hz, 4H), 6.1-6.9 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 13.91, 63.54, 102.13, 109.82, 110.68, 124.09, 127.45, 138.91, 144.03, 148.01, 152.01, 157.76, 165.13. MS: m/z (%): 352 (47), 340 (29), 329(33), 321 (52), 304 (34), 292 (44), 287 (31), 362 (100), 351 (21), 346 (15), 331 (16), 303 (21), 286 (13), 261 (26), 239 (26), 214 (17), 201 (23), 183 (34), 161 (24), 145 (23), 121 (16), 98 (17), 68 (14), 48 (13), 31 (21). UV spectrum: λ_{\max} 210.6, abs. 0.512. Molecular formula: $C_{20}H_{20}N_2O_4$. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.07%), H (5.75%), N (7.90%).

2, 4-di(4-ethoxyphenyl)-(1H, 3H)pyrimidine-2, 4-dione (4g)

Viscous oil. IR (KBr, cm^{-1}): 1238 (C-O-C stretch.), 1340 (C-N stretch), 1611, 1633 (C=C stretch. Ar), 1691, 1692 (N-C=O stretch), 2923- 3010 (-CH₂, -CH₃ stretch.), 3094 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.5(t, J=6.8 Hz, 6H), 4.5(q, J=7.9Hz, 4H), 6-7.3 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 14.03, 64.45, 102.39, 108.19, 112.69, 124.24, 130.33, 138.45, 145.61, 147.34, 152.56, 157.11, 165.01. MS: m/z (%): 352 (32), 341 (38), 335(22), 324 (38), 315 (41), 293 (32), 287 (100), 265 (26), 242 (14), 228 (39), 208 (20), 183 (14), 163 (17), 140 (21), 121 (11), 99 (13), 62 (26), 47 (19). UV spectrum: λ_{\max} 206.7, abs. 0.548. Molecular formula: $C_{20}H_{20}N_2O_4$. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.24%), H (5.73%), N (8.02%).

1, 3-di(4-chloro-3, 5-dimethylphenyl)-(1H,3H)pyrimidine-2, 4-dione (4h)

Viscous oil. IR (KBr, cm^{-1}): 788 (-Cl stretch.), 1349 (C-N stretch), 1612, 1621 (C=C stretch. Ar), 1689, 1708 (N-C=O stretch), 2976-3046 (-CH₃ stretch.), 3088 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.4 (s, 12H), 6.1-7.3 (m, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 20.32, 111.03, 113.16, 115.34, 126.36, 142.25, 151.92, 152.47, 165.46. MS: m/z (%): 389 (13), 378 (15), 362 (29), 349 (36), 333 (41), 320 (50), 303 (22), 294 (29), 282 (42), 275 (31), 260 (21), 249 (31), 228 (19), 214 (42), 201 (32), 197 (47), 191 (100), 176 (16), 164 (25), 143 (16), 131 (11), 109 (40), 89 (27), 78 (12), 69 (14), 52 (16), 43 (27), 32 (12). UV spectrum: λ_{\max} 220.3, abs. 2.138 Molecular

formula: C₂₀H₁₈N₂O₂Cl₂. Elemental analysis: Calculated: C (61.70%), H (4.63%), N (7.20%), Cl (18.25%). Found: C (61.74%), H (4.67%), N (7.24%), Cl (18.29%).

1, 3-di(2-methylphenyl)-(1H, 3H)pyrimidine-2, 4-dione (4i)

Viscous oil. IR (KBr, cm⁻¹): 1356 (C-N stretch), 1619, 1631 (C=C stretch. Ar), 1683, 1697 (N-C=O stretch), 2923-3034 (-CH₃ stretch.), 3090 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.6 (s, 6H), 6.2-7.6 (m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 16.34, 110.82, 115.34, 120.94, 124.15, 127.01, 131.13, 143.02, 152.22, 165.07. MS: *m/z* (%): 292 (24), 280 (22), 269 (14), 252 (26), 238 (17), 228 (28), 205 (42), 192 (100), 178 (17), 161(19), 152(31), 141(15), 133 (17), 121 (51), 93 (15), 77 (18), 57 (26), 45 (36), 32 (24). UV spectrum: λ_{max} 209.2, abs. 1.061. Molecular formula: C₁₈H₁₆N₂O₂. Elemental analysis: Calculated: C (73.97%), H (5.48%), N (9.59%). Found: C (73.92%), H (5.39%), N (9.64%).

1, 3-di(3-methylphenyl)-(1H, 3H)pyrimidine-2, 4-dione (4j)

Viscous oil. IR (KBr, cm⁻¹): 1341 (C-N stretch), 1605, 1620 (C=C stretch. Ar), 1685, 1716 (N-C=O stretch), 2923-3034(-CH₃ stretch.), 3092 (C-H stretch. Ar-H). ¹H NMR (300 MHz, CDCl₃): δ 1.6 (s, 6H), 6.1-7.4(m, 10H). ¹³C NMR (75 MHz, CDCl₃): δ 21.06, 109.92, 115.54, 121.02, 127.79, 131.03, 139.45, 141.89, 152.51, 166.12. MS: *m/z* (%): 292 (31), 273 (29), 260 (27), 248 (16), 229 (13), 218 (42), 209 (45), 198 (20), 187 (100), 171 (12), 163 (23), 151 (21), 143 (19), 128 (13), 107 (39), 84 (19), 67 (16), 51 (22), 39 (36). UV spectrum: λ_{max} 207.9, abs. 1.101. Molecular formula: C₁₈H₁₆N₂O₂: Elemental analysis: Calculated: C (73.97%), H (5.48%), N (9.59%). Found: C (74.04%), H (5.55%), N (9.65%).

Table 1: Time and yield of the synthesized compounds 4a-4j

	Conventional heating		Microwave irradiation	
	Time (minutes)	Yield (%)	Time (minutes)	Yield (%)
4a	90	58	12	82
4b	70	47	13	69
4c	100	51	15	76
4d	90	54	13	71
4e	120	48	18	71
4f	70	64	15	72
4g	90	45	13	67
4h	80	51	15	72
4i	100	43	15	64
4j	90	51	13	70

CONCLUSION

2, 4-diaryloxypyrimidines for the first time underwent facile *Chapman rearrangement* to afford the corresponding 1, 3-disubstituted-(1H, 3H)-pyrimidine-2, 4-diones under conventional heating as well as microwave irradiation.

Microwave assisted method of synthesis provides a simpler and environmental-friendly alternative for the conventional procedures.

The synthesis of novel heterocycles reported in this paper has the potential of exhibiting pharmacological and agrochemical activities.

Acknowledgement

Authors are thankful to Department of Chemistry, University of Mumbai for the facilities and financial support.

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