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A Green Chemical Approach to Synthesize 1, 2-diaryl-pyridazine-3, 6-diones through *Chapman rearrangement* of 3, 6-diaryloxypyridazines

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ABSTRACT

3, 6-diaryloxypyridazines underwent Chapman rearrangement under conventional heating as well as on microwave irradiation to afford corresponding 1, 2-diaryl-pyridazine-3, 6-diones.

Keywords: 3, 6-diaryloxypyridazines, 1, 2-diarylpyridazine-3, 6-diones, imidates, microwave irradiation, Chapman rearrangement

INTRODUCTION

It is well known that pyridazinones and related compounds that have been utilized as a part of a large number of complex compounds and these compounds exhibit diversified pharmacological activities due to presence of pyridazinone moieties [1-4].

A large number of pyridazinone derivatives have been reported to possess antimicrobial [5, 6], antidiabetic [7], potent analgesic [8], antihypertensive [9], anti-inflammatory, analgesic, COX inhibitor [10, 11] and anticancer [12] effects. Many of them are well known as intermediates for agrochemicals [13, 14] also. Several methods for synthesis are available in literatures which involve addition of hydrazine or its derivative to an appropriately 1, 4-disubstituted carbon chain. *β*-aroylpropionic acid derivatives containing the different aromatic moiety react with different hydrazine derivatives for the synthesis of pyridazine and pyridazinone derivatives [15, 16]. The most common method for the preparation of alkyl or acyl substituted pyridazine consists of the direct one step cyclization from an unsaturated diketone and hydrazine [17]. Reaction of diketone in DMF with cyanoacetohydrazide gives corresponding pyridazine [18, 19]. Another method for formation of the pyridazine ring involves addition of a hydrazine molecule to 1, 4 ketoesters or ketoacids to form pyridazinones [20]. Several methods for synthesis are available in literature which involves addition of hydrazine or its derivative to an appropriately 1, 4-disubstituted carbon chain. *β*-aroylpropionic acid derivatives containing the different aromatic moiety react with different hydrazine derivatives for the synthesis of pyridazine and pyridazinone derivatives [21, 22] . Most preparation of the pyridazinone derivatives depend on the nucleophilic substitution of the starting material of these derivatives prepared from mucochloric acids. 4, 5-dihalo-3-(2H)-pyridazinone derivatives were prepared by different reactions such as direct ring synthesis, alkylation, and halogen- exchange reaction. 4-(O-hydroxyphenyl)-3-(2H)-pyridazinones can be prepared by 1, 3-dipolar cycloaddition of the in situ

prepared diarylnitrilimines and 3-arylidine-2-(3H) benzofuranones [23]. 3-Aroyl propionic acids reacting with hydrazine yielded 6-aryl-4, 5-dihydro-3-(2H)-pyridazinones which on dehydrogenation by bromine gave 6-aryl-3-(2H)-pyridazinones. The latter compounds were converted into 3-(N-*γ*-aminobutyric acid)-6-(substituted phenyl)-pyridazines and 3-(N-butyryllactamyl)-6-(substituted phenyl)-pyridazines by the chlorination and then reaction with *γ*-aminobutyric acid. Several 3-*γ*-aminobutyric acid derivatives of 6-(substituted-phenyl)-pyridazines were synthesized which show anticonvulsant activities [24]. Reaction of a mixture of substituted phenyl/ appropriate hydrocarbon and succinic anhydride/ methyl succinic anhydride/ itaconic anhydride with stirred solution of aluminum chloride in carbon disulphide followed by acidification gave β-4-substituted benzoyl propionic acid/ 4-(4-substitutedphenyl)-4-oxobutyric acid/ β-4-substituted benzoyl-2-methylene propionic acid. Reaction of these with hydrazine hydrate/ hydrazine derivative afforded different pyridazinone derivatives [25-27].

The present paper reports synthesis of 1, 2-diaryl-pyridazine-3, 6-diones by subjecting 3, 6-diaryloxy pyridazines to *Chapman rearrangement.*

MATERIALS AND METHODS

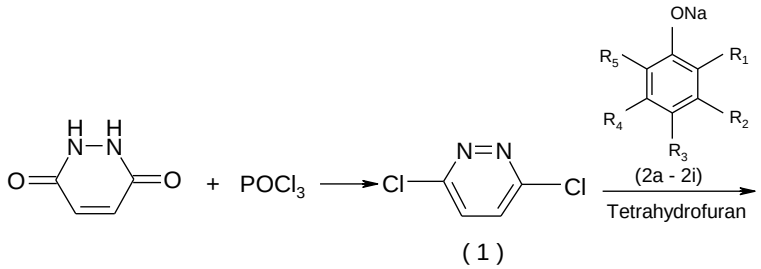
The melting points were determined using capillary tube and are uncorrected. The FTIR spectra were recorded on Spectrum One Perkin Elmer (US). The 1H-NMR spectra were recorded on a Bruker AVANCE (300MHz) spectrometer (with TMS as internal references). 13C-NMR spectra were recorded on Bruker AVANCE (75 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 SiO_2 gel (200mesh). Modified LG microwave laboratory oven was used for microwave irradiation. The solvents were purified by distillation before use.

The thermal conversion of aryl N-arylbenzimidates to N-aroyldiphenylamines is known as the *Chapman rearrangement* [28, 29]. Though imidates of many classes of compounds have been subjected to *Chapman rearrangement*, 3, 6-diaryloxypyridazines 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 3, 6-diaryloxy pyridazines led us to undertake the present work.

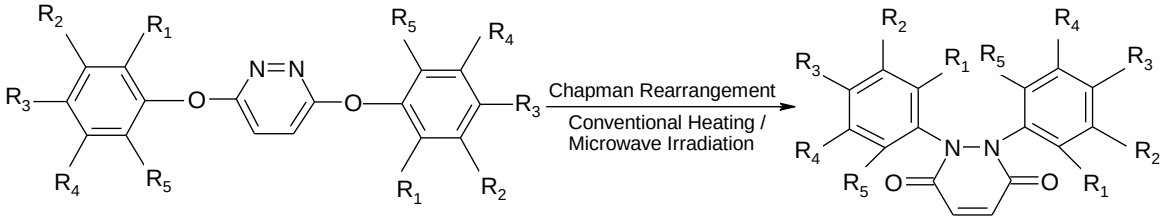
For this purpose, 1, 2-dihydropyridazine-3, 6-dione was visualized as the starting substrate. This on chlorination followed by condensation with various phenols yielded the respective phenoxy derivatives. These were then subjected to *Chapman rearrangement* to afford the corresponding 1, 2-diaryl-pyridazine-3, 6-diones. 3, 6-dichloropyridazine **(1)** has been synthesized as per literature procedure from 1, 2-dihydropyridazine-3, 6-dione [30] **(Scheme)**

General Procedure for preparation of 3, 6-diaryloxy pyridazines (3a-3j): A mixture of sodium hydroxide (0.02M), different phenols **(2a-2j))** (0.02M) in ethanol (85%, 25 ml) was stirred at room temperature for 0.5-1.5 h. After completion of the reaction (TLC),

Scheme: Synthesis of 1, 2-diaryl-pyridazine-3, 6-diones



(1)



(3a - 3i) (4a - 4i)

Compounds	R_1	R_2	R_3	R_4	R_5
2a, 3a, 4a	OC_2H_5	H	H	H	H
2b, 3b, 4b	H	H	OC_2H_5	H	H
2c, 3c, 4c	$COOC_2H_5$	H	H	H	H
2d, 3d, 4d	H	H	$COOCH_3$	H	H
2e, 3e, 4e	H	H	H		
2f, 3f, 4f	OCH_3	H	$COOC_2H_5$	H	OCH_3
2g, 3g, 4g	H	H	H	H	H
2h, 3h, 4h	H	CH_3	Cl	CH_3	H
2i, 3i, 4i	H	CH_3	H	H	H

solvent was recovered under vacuum till dry powder was obtained. This sodium salt was taken in tetrahydrofuran (50 ml) and 3, 6-dichloropyridazine (0.01M) was added in small lots under stirring. The mixture was refluxed under stirring for 5-7 h. After completion of the reaction (TLC), the tetrahydrofuran was recovered under vacuum and 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 NaOH solution (5%) (1 x 25ml). The combined extracts were given water washing (2 x 25ml) and dried over sodium sulphate. Recovery of ether followed by purification afforded solid/ oil.

3, 6-di-(2-ethoxyphenoxy)-pyridazine (3a): Yield: 49%. m.p.: 102^{o}C. Molecular formula: $C_{20}H_{20}N_2O_4$. Elemental analysis: Calculated: C (68.18%), H (5.68%); N (7.95%). Found: C (68.23%), H (5.75%), N (8.01%). IR (KBr, cm^{-1}): 1245 (C-O-C stretch.), 1348 (C-N stretch), 1605 (C=C stretch. Ar), 2840-3100 (-CH_2, -CH_3 stretch.), 3086 (C-H stretch. Ar-H). UV spectrum: λ_{max} 223.6, abs. 1.076. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.4 (t, J=6.9Hz, 6H), 3.8 (q, J=7.6 Hz, 4H), 63-7.5 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.30, 60.56, 121.89, 122.53, 130.19, 131.92, 133.79, 139.67, 156.88, 161.97. MS: *m/z* (%): 352 (42), 341 (28), 333 (28), 324 (44), 313 (21), 291 (42), 283 (15), 274 (100), 261 (18), 249 (32), 232 (19), 221 (34), 198 (19), 188 (42), 171 (41), 159 (32), 142 (21), 131 (26), 121 (27), 94 (19), 71 (32), 46 (27), 32 (24).

3, 6-di-(4-ethoxyphenoxy)-pyridazine (3b): Yield: 52%.Oil. Molecular formula: $C_{20}H_{20}N_2O_4$. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.06%), H (5.74%), N (7.85%), IR (KBr, cm^{-1}): 1225 (C-O-C stretch.), 1354 (C-N stretch), 1600 (C=C stretch. Ar), 2872-3010 (-CH_2, -CH_3 stretch.), 3091 (C-H stretch. Ar-H). UV spectrum: λ_{max} 203.6, abs. 0.689. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5 (t, J=7.3 Hz, 6H), 4.3(q, J=7.8 Hz, 4H); 6.0-7.1(m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.29, 63.71, 114.57, 121.79, 126.61, 158.89, 162.63. MS: *m/z* (%): 352 (29), 339 (36), 322 (47), 310 (36), 296 (21), 284 (100), 273 (19), 261 (24), 252 (27), 234 (26), 221 (29), 210 (52), 195 (29), 178 (37), 153 (23), 139 (21), 118 (42), 94(21), 77 (42), 69 (34), 53 (28), 39 (22).

3, 6-di-(2-carbethoxyphenoxy)-pyridazine (3c): Viscous oil; Yield: 48%; Molecular formula: $C_{22}H_{20}N_2O_6$. Elemental analysis: Calculated: C (64.71%), H (4.90%), N (6.86%). Found: C (64.63%), H (4.95%), N (6.90%); IR (KBr, cm^{-1}): 1236 (C-O-C stretch.), 1350 (C-N stretch.), 1426 (C-O- stretch.), 1609 (C=C stretch. Ar), 1680, 1716 (-C=O stretch. Ester), 2960-2995 (-CH_2, -CH_3 stretch.), 3068 (C-H stretch. Ar-H); UV spectrum: λ_{max} 203.4, abs. 1.811. ^{1}H NMR (300 MHz, $CDCl_3$): δ1.5 (t, J=7.6 Hz, 6H), 3.9 (q, J=7.3Hz, 4H), 6.5-7.4 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.29, 60.56, 121.20, 122.34, 132.34, 134.23, 138.69, 155.82, 162.82, 166.52; MS: *m/z* (%): 408 (28), 383 (51), 367 (28), 345 (31), 331 (24), 311 (32), 292 (39), 281 (100), 254 (35), 240 (61), 228 (37), 212 (44), 193 (23), 181 (42), 162 (36), 146 (33), 131 (39), 113 (38), 82 (41), 47 (51).

3, 6-di-(4-carbmethoxyphenoxy)-pyridazine (3d): Yield: 51%. Viscous oil. Molecular formula: $C_{20}H_{16}N_2O_6$. Elemental analysis: Calculated: C (63.16%), H (4.21%), N (7.37%). Found: C (63.07%), H (4.27%), N (7.41%). IR (KBr, cm^{-1}): 1217 (-C-O stretch. Ester), 1239 (C-O-C stretch.), 1354 (C-N stretch), 1600 (C=C stretch. Ar), 1725 (-C=O stretch. Ester), 2868-3015 (-CH_3 stretch.), 3094 (C-H stretch. Ar-H). UV spectrum: λ_{max} 231.43, abs. 0.834. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.7 (s, 6H), 6.1-7.5 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.24, 120.83, 122.19, 122.83, 131.58, 158.71, 161.98, 167.24. MS: *m/z* (%): 380 (53), 371 (41), 361 (32), 348 (35), 324 (20), 311 (100), 292 (45), 278 (29), 262(19), 243 (37), 229 (23), 202 (32), 182 (40), 172 (48), 148 (51), 131 (21), 119 (32), 102 (42), 92 (23), 71 (25), 58 (24), 43 (21), 38 (29).

3, 6-di-(1-naphthoxy)-pyridazine (3e): Yield: 47%. m.p.:91^{o}C. Molecular formula: $C_{24}H_{16}N_2O_2$. Elemental analysis: Calculated: C (79.12%), H (4.40%), N (7.69%). Found: C (79.18%), H (4.46%), N (7.78%). IR (KBr, cm^{-1}): 1240 (C-O-C stretch), 1341 (C-N stretch), 1600, 1600 (C=C stretch.Ar), 3086 (C-H stretch.Ar-H). UV spectrum: λ_{max} 232.8, abs.1.322. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.2-7.4 (m, 16H). ^{13}C NMR (75 MHz, $CDCl_3$): 108.12, 121.03, 121.78, 122.34, 124.49, 124.89, 125.13, 125.76, 126.56, 127.82, 151.23, 162.61. MS: *m/z* (%): 364 (27), 359 (44), 343 (21), 331 (23), 319 (42), 291 (23), 278 (42), 266 (30), 258 (100), 243 (14), 235 (39), 226 (42), 219 (36), 197 (42), 182 (23), 177 (21),161 (42),148 (26), 134 (43), 126 (28), 96 (25), 67 (31), 49 (19).

3, 6-di-(4-carbethoxy-2, 6-dimethoxyphenoxy)-pyridazine (3f): Viscous oil. Yield: 50%. Molecular formula: $C_{26}H_{28}N_2O_{10.}$ Elemental analysis: Calculated: C (59.09%), H (5.30%), N (5.30%). Found: C (58.99%), H (5.37%), N (5.35%). IR (KBr, cm^{-1}): 1209 (-C-O stretch. Ester), 1241 (C-O-C stretch.), 1336 (C-N stretch), 1620 (C=C stretch. Ar), 1715, 1721 (-C=O stretch. Ester), 2950-3000 (-CH_2,- CH_3 stretch.), 3084 (C-H stretch. Ar-H) UV spectrum: λ_{max} 232.8, abs.1.207. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3(t, J=6.8 Hz, 6H), 4.0(s, 12H), 4.5(q, J=7.4 Hz, 4H), 6.2-7.5 (m, 6H)**.** ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.45, 55.72, 61.03, 122.23, 140.52, 147.45, 156.71, 162.57. MS: *m/z* (%): 528 (48), 505 (33), 489 (27), 468 (32), 451 (29), 432 (100), 419 (35), 393 (41),378 (23), 363 (20), 348 (38), 336 (24), 291 (30), 263 (24), 241 (37), 223 (42), 211 (41), 179 (42), 166 (32), 142 (26), 135 (21), 104 (21), 92 (17), 66 (31), 47 (19), 39 (31).

3, 6-diphenoxypyridazine (3g): Lit [31] m. p.: 78^{o}C

3, 6-di-(4-chloro-3, 5-dimethylphenoxy)-pyridazine (3h): Yield: 51% m.p.: 110^{o}C. Molecular formula: $C_{20}H_{18}N_2O_2Cl_2$. Elemental analysis: Calculated: C (61.70%), H (4.63%), N (7.20%), Cl (18.25%). Found: C (61.80%), H (4.55%), N (7.25%), Cl (18.29%). IR (KBr, cm^{-1}): 775, 1253, 1349, 1610, 2876-2997. IR (KBr, cm^{-1}): 775 (-Cl stretch.), 1253 (C-O-C stretch.), 1349 (C-N stretch), 1610 (C=C stretch. Ar), 2876-2997 (-CH_3 stretch.), 3084(C-H stretch. Ar-H). UV spectrum: λ_{max} 251.5, abs. 1.241. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3 (s, 12H), 6.0-7.4(m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.17, 115.23, 121.78, 125.82, 137.58, 153.23, 156.39. MS: *m/z* (%): 389 (38), 380 (19), 369 (29), 357 (32), 348 (41), 339 (31), 327 (24), 311 (55), 298 (51), 284 (36), 271 (52), 263 (37), 255 (100), 234 (29), 216 (32), 201 (26), 193 (22), 186 (21), 172 (23), 163 (17), 154 (28), 138 (33), 120 (25), 105 (42), 91 (29), 82 (43), 71 (23), 60 (22), 44 (21).

3, 6-di-(3-methylphenoxy)-pyridazine (3i): (Lit [32] m. p.: 98^{o}C)

General procedure for preparation of 1, 2-diaryl-pyridazine-3, 6-dione (4a-4i) by *Chapman rearrangement* of 3, 6-diaryloxypyridazine (3a-3i) under conventional heating : In a flask, equipped with water condenser 3, 6-diaryloxy pyridazine **(3a-3i)** (0.01M) was heated under stirring in nitrogen atmosphere at 180^{o}C-200^{o}C for 55-90 minutes. After completion, (TLC) the reaction mass was cooled to room temperature and petroleum ether (25 ml) was added. It was purified to afford a crystals/ oil.
Thus, 3, 6-diaryloxy pyridazine **(3a-3i)** 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 [33].

General procedure for preparation of 1, 2-diaryl-pyridazine-3, 6-dione (4a-4i) by *Chapman rearrangement* of 3, 6-diaryloxy pyridazine (3a-3i) under microwave irradiation: In a flask, equipped with water condenser 3, 6-diaryloxy pyridazine **(3a-3i)** (0.01M) was irradiated (900 W) in a microwave oven for 13-18 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, 2-di-(2-ethoxyphenyl)-pyridazine-3, 6-dione (4a): Oil. Molecular formula: $C_{20}H_{20}N_2O_4$. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.02%), H (5.77%), N (7.83%). IR (KBr, cm^{-1}): 884 (C=C bending), 1239(C-O-C stretch.), 1351 (C-N stretch), 1608 (C=C stretch. Ar), 1733 (N-C=O stretch), 2890-2987 (-CH_2, -CH_3 stretch.), 3087 (C-H stretch. Ar-H). UV spectrum: λ_{max} 281.4, abs. 1.310.^{1}H NMR (300 MHz, $CDCl_3$): δ ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.0(t, J=6.8 Hz, 6H), 4.2(q, J=7.6Hz, 4H), 6.0-7.3 (m, 10H)**.** ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.62, 58.81, 123.61, 134.02, 131.49, 133.56, 134.70, 135.11, 139.68, 157.61. MS: *m/z* (%): 352 (49), 344 (23), 332 (26), 316 (28), 302 (51), 295 (100), 284 (33), 273 (46), 260 (31), 247 (19), 237 (25),222 (41), 215 (27), 201(28), 194 (40), 183 (32), 169 (21), 161 (24), 142 (20), 129 (14),111 (41), 94 (37), 69 (23), 51 (21), 48 (26).

1, 2-di-(4-ethoxyphenyl)-pyridazine-3, 6-dione (4b): Oil. Molecular formula: $C_{20}H_{20}N_2O_4$. Elemental analysis: Calculated: C (68.18%), H (5.68%), N (7.95%). Found: C (68.21%), H (5.60%), N (8.07%). IR (KBr, cm^{-1}): 883 (C=C bending),1231 (C-O-C stretch.), 1347 (C-N stretch), 1607 (C=C stretch. Ar), 1737 (N-C=O stretch), 2865- 2995 (-CH_2, -CH_3 stretch.), 3096 (C-H stretch. Ar-H). UV spectrum: λ_{max} 218.8, abs. 0.937. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.4(t, J=7.1Hz, 6H); 4.2(q, J=7.8Hz, 4H), 6.2-7.4(m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.61, 62.72, 115.72, 125.71, 134.65, 155.62, 158.79, 161.21. MS: *m/z* (%): 352 (53), 347 (32), 333(26), 327 (47), 311 (34), 298 (29), 287 (100), 271 (30), 262 (21), 249 (19), 242 (24), 231 (36), 219 (28), 208 (27), 189 (34), 171 (37), 163 (27), 147 (22), 132 (48), 121 (34), 97 (19), 77 (41), 62 (16), 56 (19).

1, 2-di-(2-carbethoxyphenyl)-pyridazine-3, 6-dione (4c): Oil, Yield: Molecular formula: $C_{22}H_{20}N_2O_6$. Elemental analysis: Calculated: C (64.71%), H (4.90%), N (6.86%). Found: C (64.81%), H (4.99%), N (6.74%). IR (KBr, cm^{-1}): 880(C=C bending), (1206 (-C-O stretch), 1344(C-N stretch), 1617(C=C stretch. Ar), 1732 (N-C=O stretch), 1713 (-C=O stretch. Ester), 2856-2950(-CH_2, -CH_3 stretch.), 3088 (C-H stretch. Ar-H). UV spectrum: λ_{max} 292.4, abs. 1.249. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5(t, J=6.8 Hz, 6H), 4.4(q, J=7.2Hz, 4H), 6.0-7.4 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.81, 61.02, 122.25, 128.72, 130.12, 133.79, 134.46, 137.96, 156.13, 158.03, 167.11. MS: *m/z* (%): 408 (47), 394 (33), 383 (37), 279 (48), 365 (38), 354 (26), 343 (29), 335 (17), 324 (42), 301 (44), 295 (22), 287 (100), 271 (23), 257 (19), 234 (34), 204 (21), 193 (22), 180 (17), 161 (41), 148 (47), 132 (53), 119 (41), 102 (39), 91 (24), 77 (26), 61 (17), 52 (26).

1, 2-di-(4-carbmethoxyphenyl)-pyridazine-3, 6-dione (4d): Oil. Molecular formula: $C_{20}H_{16}N_2O_6$. Elemental analysis: Calculated: C (63.16%), H (4.21%), N (7.37%). Found: C (63.28%), H (4.28%), N (7.25 %). IR (KBr, cm^{-1}): 871 (C=C bending), 1210 (-C-O stretch. Ester), 1359 (C-N stretch.), 1622 (C=C stretch. Ar), 1720 (N-C=O stretch), 1711 (-C=O stretch. Ester), 2983-3271 (-CH_3 stretch.), 3090 (C-H stretch. Ar-H). UV spectrum: λ_{max} 262.4, abs. 1.853. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.2 (s, 6H), 6-7.7(m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 51.93, 123.11, 133.98, 133.12, 139.71, 157.81, 159.02, 167.71. MS: *m/z* (%): 380 (46), 371 (32), 369 (17), 355 (42), 343 (19), 331 (47), 316 (36), 309 (23), 298 (28), 290 (37), 273 (28), 261 (27), 252 (32), 242 (100),231 (51),219 (28), 207 (17), 196 (24), 179 (32), 163 (48), 151 (17), 139 (26), 122 (24), 109 (26), 91 (19), 81 (35), 68 (17), 47 (41).

1, 2-di-(1-naphthyl)-pyridazine-3, 6-dione (4e): m.p.: 143^{o}C. Molecular formula: $C_{24}H_{16}N_2O_2$. Elemental analysis: Calculated: C (79.12%), H (4.40%), N (7.69%). Found: C (78.99%), H (4.47%), N (7.60%). IR (KBr, cm^{-1}): 881 (C=C bending), 1349(C-N stretch.), 1606 (C=C stretch. Ar), 1735 (N-C=O stretch.), 3088(C-H stretch. Ar-H). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.0-7.5(m, 16H). UV spectrum: λ_{max} 225.8, abs. 0.961. ^{13}C NMR (75 MHz, $CDCl_3$): 107.65, 120.83, 121.58, 122.06, 123.37, 124.66, 125.07, 125.48, 126.23, 128.12, 153.03, 161.86. MS: *m/z* (%): 364 (48), 353 (22), 344 (19), 331 936), 326 (38), 319 (52), 299 (32), 296 (19), 285 (100), 271 (45), 262 (31), 248 (22), 231 (20), 218 (22), 204 (28), 194 (36), 173 (26), 161 (47), 150 (26), 139 (24), 122 (42), 101 (21), 82 (15), 75 (30), 59 (16).

1, 2-di-(4-carbethoxy-2, 6-dimethoxyphenyl)-pyridazine-3, 6-dione (4f): Oil. Molecular formula: $C_{26}H_{28}N_2O_{10}$. Elemental analysis: Calculated: C (59.09%), H (5.30%), N (5.30%). Found: C (58.99%), H (5.37%), N (5.35%). 881 (C=C bending), 1211 (-C-O stretch. Ester), 1240 (C-O-C stretch.), 1346 (C-N stretch), 1615(C=C stretch. Ar), 1685 (N-C=O stretch), 1725 (-C=O stretch. Ester), 2985-3015 (-CH_2, -CH_3 stretch.), 3087 (C-H stretch. Ar-H). UV spectrum: λ_{max} 237.3, abs. 1.859. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5(t, J=7.0 Hz, 6H), 4.0(s, 12H), 4.5(q, J=7.6 Hz, 4H), 6.1-7.5 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.21, 55.71, 61.14, 107.23, 133.78, 138.72, 146.47, 156.97, 157.09, 167.92. MS: *m/z* (%): 528 (49), 517 (21), 498 (18), 482 (14), 474 (31), 463 (23), 455 (32), 442 (18),430 (42), 419 (23), 403 (23), 391 (41), 380 (22), 374 (13), 361 (18), 356 (100), 339 (32), 321 (41), 302 (16), 289 (38), 271 (42), 254 (42), 238 (14), 222 (30), 212 (16), 187 (41), 169 (19), 147 (21), 133 (14), 119 (21), 97 (53), 74 (30), 53 (14), 38 (41).

1, 2-diphenylpyridazine-3, 6-dione (4g): m.p.:121^{o}C. Molecular formula: $C_{16}H_{12}N_2O_2$. Elemental analysis: Calculated: C (72.72%), H (4.55%), N (10.61%). Found: C (72.65%), H (4.64%), N (10.51%). IR (KBr, cm^{-1}): 877 (C=C bending), 1342 (C-N stretch), 1610 (C=C stretch. Ar), 1730 (N-C=O stretch), 3084 (C-H stretch. Ar-H). UV spectrum: λ_{max} 253.2, abs. 1.471. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.3-7.8 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 120.34, 131.68, 142.21, 154.85, 133.63, 158.59. MS: *m/z* (%): 264 (34), 251 (24), 240 (18), 226 (27), 211 (51), 196 (31), 183(100), 172 (35), 161(29), 149(41), 140(15), 129(17), 120 (42),104 (52), 92 (25), 79 (28), 61 (26), 48 (16), 31 (24).

1, 2-di-(4-chloro-3, 5-dimethylphenyl)-pyridazine-3, 6-dione (4h): Oil. Molecular formula: $C_{20}H_{18}N_2O_2Cl_2$. Elemental analysis: Calculated: C (61.70%), H (4.63%), N (7.20%), Cl (18.25%). Found: C (61.64%), H (4.71%), N (7.09%), Cl (18.15%). IR (KBr, cm^{-1}): 886 (C=C bending), 778 (-Cl stretch.), 1342 (C-N stretch), 1615 (C=C stretch. Ar), 1708 (N-C=O stretch), 2945-3005 (-CH_3 stretch.), 3090 (C-H stretch. Ar-H). UV spectrum: λ_{max}234.53, abs.2.412. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3 (s, 12H), 6.3-7.5 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 19.29, 117.23, 124.86, 133.79, 136.81, 154.71, 159.82. MS: *m/z* (%): 389 (41), 371 (35), 359 (31), 343 (24), 330 (28), 313 (36), 301 (29), 293 (46), 282 (46), 273 (27), 260 (26), 247 (35), 230 (18), 224 (22), 208 (32), 193 (27), 179 (100), 164 (29), 148 (26), 121 (19), 104 (41), 83 (25), 73 (12), 52 (16), 43 (27).

1, 2-di-(3-methylphenyl)-pyridazine-3, 6-dione (4i): Oil. Molecular formula: $C_{18}H_{16}N_2O_2$: Elemental analysis: Calculated: C (73.97%), H (5.48%), N (9.59%). Found: C (73.91%), H (5.56%), N (9.67%). IR (KBr, cm^{-1}): 885 (C=C bending), 1349 (C-N stretch), 1610 (C=C stretch. Ar), 1720 (N-C=O stretch), 2873-2993 (-CH_3 stretch.), 3088 (C-H stretch. Ar-H). UV spectrum: λ_{max} 262.9, abs. 1.213. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3 (s, 6H), 6.2-7.5 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.07, 113.18, 117.32, 122.41, 129.67, 134.07, 140.12, 156.13, 158.24. MS: *m/z* (%): 292 (43), 285 (23), 271 (43), 256 (29), 244 (47), 237 (19), 229 (24), 215 (42), 203 (36), 191 (27), 181 (40), 173 (100), 164 (39), 152 (31), 140 (51), 129 (41), 110 (24), 89 (17), 71 (26), 63 (29), 51 (26).

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

	Conventional heating		Microwave irradiation	
	Time (minutes)	**Yield (%)**	**Time (minutes)**	**Yield (%)**
4a	60	41	17	48
4b	55	47	13	52
4c	90	38	16	46
4d	70	40	18	44
4e	80	42	15	48
4f	65	42	16	53
4g	70	40	16	49
4h	70	39	18	44
4i	70	36	13	48

RESULTS AND DISCUSSION

3, 6-diaryloxypyridazines for the first time smoothly underwent *Chapman rearrangement* to afford the corresponding 1, 2-diaryl-pyridazine-3, 6-diones under conventional heating. Same reaction under microwave irradiation underwent facile *Chapman rearrangement* under green chemistry conditions in less time and good yield compared to conventional heating.

APPLICATIONS

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

CONCLUSIONS

3, 6-diaryloxy pyridazines for the first time underwent facile *Chapman rearrangement* to afford the corresponding 1, 2-diaryl-pyridazine-3, 6-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 new pyridazine derivatives reported in this paper has the potential of exhibiting biological activities.

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