7. ABSTRACT OF THE INVENTION:

This invention describes the synthesis of new 1, 2-diaryl-pyridazine-3, 6-diones by subjecting corresponding 3, 6-diaryloxypyridazines to *Chapman rearrangement.*

5. CLAIMS:
We Claim:

1. Synthesis of 1, 2-diphenyl-pyridazine-3, 6-dione **(4a)** as described in **Example-1** by *Chapman rearrangement* of 3, 6-diphenoxypyridazine **(3a)** at 175°C for 70 minutes.
2. Synthesis of 1, 2-di-(2-carbethoxyphenyl)-pyridazine-3, 6-dione **(4b)** as described in **Example-2** by *Chapman rearrangement* of 3, 6-di-(2-carbethoxyphenoxy)-pyridazine **(3b)** at 160°C for 90 minutes.
3. Synthesis of 1, 2-di-(4-carbmethoxyphenyl)-pyridazine-3, 6-dione **(4c)** as described in **Example-3** by *Chapman rearrangement* of 3, 6-di-(4-carbmethoxyphenoxy)-pyridazine **(3c)** at 175°C for 70 minutes.
4. Synthesis of 1, 2-di-(1-naphthyl)-pyridazine-3, 6-dione **(4d)** as described in **Example-4** by *Chapman rearrangement* of 3, 6-di-(1-naphthoxy)-pyridazine **(3d)** at 165°C for 80 minutes.
5. Synthesis of 1, 2-di-(4-carbethoxy-2, 6-dimethoxyphenyl)-pyridazine-3, 6-dione **(4e)** as described in **Example-5** by *Chapman rearrangement* of 3, 6-di-(4-carbmethoxyphenoxy)-pyridazine **(3e)** at 170°C for 65 minutes.
6. Synthesis of 1, 2-di-(2-ethoxyphenyl)-pyridazine-3, 6-dione **(4f)** as described in **Example-6** by *Chapman rearrangement* of 3, 6-di-(2-ethoxyphenoxy)-pyridazine **(3f)** at 160°C for 60 minutes.
7. Synthesis of 1, 2-di-(4-ethoxyphenyl)-pyridazine-3, 6-dione **(4g)** as described in **Example-7** by *Chapman rearrangement* of 3, 6-di-(4-ethoxyphenoxy)-pyridazine **(3g)** at 180°C for 55 minutes.
8. Synthesis of 1, 2-di-(4-chloro-3, 5-dimethylphenyl)-pyridazine-3, 6-dione **(4h)** as described in **Example-8** by *Chapman rearrangement* of 3, 6-di-(4-chloro-3, 5-dimethylphenoxy)-pyridazine **(3h)** at 160°C for 70 minutes.
9. Synthesis of 1, 2-di-(3-methylphenyl)-pyridazine-3, 6-dione **(4i)** as described in **Example-9** by *Chapman rearrangement* of 3, 6-di-(3-methylphenoxy)-pyridazine **(3i)** at 160°C for 70 minutes.
10. Imidates **(3a-3i)** underwent facile *Chapman rearrangement* to afford 1, 2 - disubstituted pyridazine-3, 6-diones **(4a-4i)** which provides a simpler and environmental friendly procedure.

6. DATE: 24th December 2013

SIGNATURE:-

Dr. M. M. V. Ramana

Dr. Sanjay C. Pawar

4. DESCRIPTION:

Title: -

A process for the preparation of 1, 2-diaryl-pyridazine-3, 6-diones.

Field of invention: -

This invention describes the synthesis of new 1, 2-diaryl-pyridazine-3, 6-diones by subjecting corresponding 3, 6-diaryloxypyridazines to *Chapman rearrangement.*

Background of invention and Prior art: -

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 (S. A. Abubshait, *Molecules*, **2007**, 12(1), 25-42; P. Coudert, E. Duroux,, P. Bastide, J. Couquelet, P. Tronche, **1991**, *J Pharm Belg.*, 46(6), 375-80)

A large number of pyridazinone derivatives have been reported to possess antimicrobial (R. R. Kassab, *Egypt. J. Chem.*, **2002**, 45, 1055-1073, A. Katrusiak, S. Baloniak, **1994**, *Tetrahedron*, 50, 12933-12940), potent analgesic (M. Gokce, D. Dogruer, F. Sahin, *Farmaco*, **2001**, 56: 233-237), anti-inflammatory, analgesic, and COX inhibitor (M. Takaya, M. Sato, K. Terashima, H. A. Tanizawa, **1979**, *J. Med. Chem,* 22(1), 53-58; B. Ayla, O. Fugen, U. Oya, G. Zafer, T. Berna, *J. Pharm. Sci.*, **2003**, 28, 19-25), anticancer effects (R. E. Bambury, D. T. Feeley, G. C. Lawton, J. M. Weaver, J. Wemple, *J. Med. Chem.*, **1984**, 27, (12), 1613-21). Other biological and pharmacological properties are well known in the prior arts including US 6469003 B1, GB 2228004, US 5424428, EP 0516297 A1.

Large numbers of pyridazinone derivatives are well known as intermediates for agrochemicals also. (S. C. Cherng, W. H. Huang, C. Y. Shiau, A. R. Lee, T. C. Chou, *Eur J Pharmacol.*, **2006**, 532, (1-2), 32-37) Their application is well known in prior arts including US 8541414 B2, WO 2009035150 A2, EP 1371638 A1, WO 2012091156 A.

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. 1-Phenyl-1, 2-dihydropyridazine-3, 6-dione have been synthesized by refluxing a mixture of maleic anhydride and phenylhydrazine in glacial acetic acid. (S. C. Cherng, W. H. Huang, C. Y. Shiau, A. R. Lee, T. C. Chou, *Eur J Pharmacol.*, **2006**, 532 (1-2), 32-37)

Reaction of diketone in DMF with cyanoacetohydrazide gives corresponding pyridazine.(F. B. Miguel, C. M. Monica, P. M. Elena, L. Berta, P. T. Beatriz de, R. Ana, A. Nuria, L. Francisco, M. M. Dolores, L. Olivier, M. Laurent, *J. Med. Chem.*, **2005**, 48, 6843-6854)

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. (E. Sotelo, A. Coelho, E. Ravina, *Chem. Pharm. Bull,* **2003**, 51, 427-430; N. T. Dawood, S. M. Abdel-Gawad, F. M. Soliman, *Boll. Chim Farm.*, **2001**, 140(3), 149-54)

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. (I. Mojahidul, A. S. Anees, R. Ramadoss, *Acta Poloniae Pharmaceutica*, **2008**, 65, (3), 353-362)

In another method for formation of the pyridazine ring involves addition of a hydrazine molecule to an anhydride or to 1, 4 ketoesters or ketoacids to form pyridazinones. (Q. Li, G. Lin, L. Liu, Z. Yang, L. H. Zhang, *Molecules*, **2009**, 14, (2), 777-84; E. Ravina, C. Teran, L. Santana, N. Garcia, I. Estevez, *Heterocycles*, **1990**, (31), 1967-1974)

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. (I. Mojahidul, A. S. Anees, R. Ramadoss, *Acta Poloniae Pharmaceutica*, **2008**, 65, 3, 353-362; B. Ranju, K. Dinesh, C. Rosalia, , D. L. C. Carmen, P. J. Dharam, *Acta Pharm.*, **2008**, 58, 393–405; A. A., Siddiqui, A. Kushnoor, S. M. Wani, *Indian J. Chem. B*, 43B, **2004**, 1574-1579)

Attempts of direct N-arylation of 3, 6-pyridazinedione derivatives are tedious and involve substrates that are not easily accessible.

Method of preparation of most of the above reported 1, 3-diarylpyridazine-2, 4-diones suffers from one of the disadvantages such as harsh reaction conditions, tedious preparation procedure, use of solvents etc. Thus there is scope for their synthesis by simple and eco-friendly method. The present invention describes their synthesis in two steps through *Chapman rearrangement* in absence of solvents in second step.

Description of the invention:-

The present invention reports synthesis of 1, 3-diaryl-pyridazine-2, 4-diones by subjecting 2, 4-diaryloxy pyridazines to *Chapman rearrangement.*

The main objective of the present invention is to synthesize compounds having (1) few steps of reactions, (2) minimum use of solvents, (3) clean work up, (4) better reaction yield.

The present invention is successful in attaining all the above objectives.

The thermal conversion of aryl N-arylbenzimidates to N-aroyldiphenylamines is known as the *Chapman rearrangement.* (Chapman, *J. Chem. Soc.* **1925**, 569; Chapman, *J. Chem. Soc.* **1927**, 1743; Chapman, *J. Chem. Soc.* **1925**, *127*, 1992).

For this purpose, 1, 2-dihydropyridazine-3, 6-dione was utilized 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-pyridazine-2, 4-diones **(Scheme).**

Examples:-

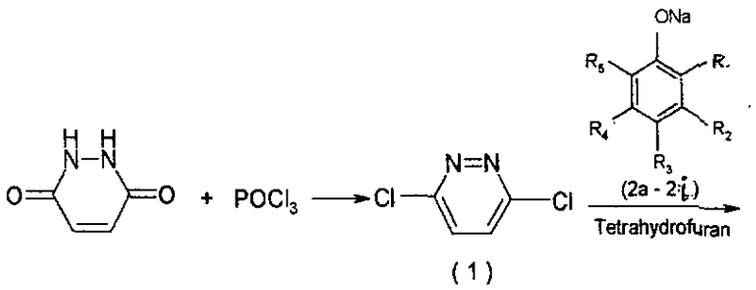
3, 6-dichloropyridazine **(1)** has been synthesized as per literature procedure from **1, 2-dihydropyridazine-3, 6-dione.** (R. H. Mizzoni, *J. Am. Chem. Soc.*, **1951**, (73), 1873)

Example: 1- Preparation of 1, 2-diphenylpyridazine-3, 6-dione (4a).

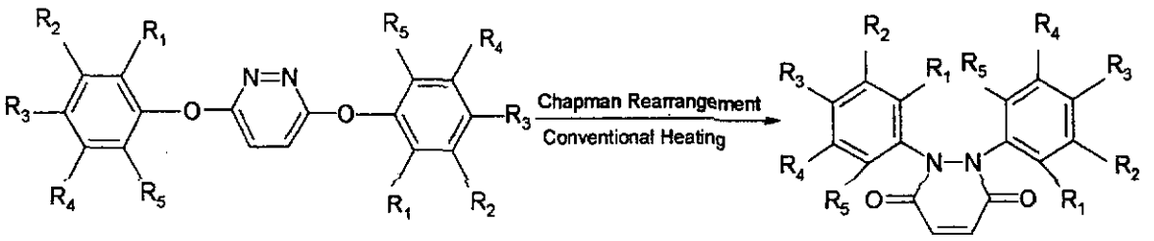
Step A- Preparation of 3, 6-diphenoxypyridazine (3a).

A mixture of sodium hydroxide (0.02M), phenol **(2a)** (0.02M) in ethanol (85%, 20 ml) was stirred at room temperature for 0.5 hours. After completion of the reaction (TLC), 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 7 hours. After completion

Scheme



(1)



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

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

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 dichloromethane (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 solvent afforded viscous oil which on purification afforded a solid (Yield: 56%) of 3, 6-diphenoxypyridazine **(3a)** (m.p.: 78°C) (I. L. Jae, H. Park, Y. S. Yun, and K. S. Kyoung, *J. Kor. Chem. Soc.*, **2001**, 45, 4, 386-390)

Step B- Preparation of compound 4a.

In a flask, equipped with water condenser 3, 6-diphenoxypyridazine **(3a)** (0.01M) was heated under stirring in nitrogen atmosphere at 175°C for 70 minutes. After completion (TLC), the reaction mass was cooled to room temperature and ligroin (25 ml) was added. It was stirred to afford a solid, which was filtered and recrystallised from ligroin to give white crystals of compound **4a** (Yield: 49%). m.p.:121°C

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.3-7.8 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.5, 125-171.

IR (KBr, cm^{-1}): 1342, 1610, 1640, 1720

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%).

HRMS: *m/z* cal. mass for $C_{16}H_{12}N_2O_2$ $[M+H]^+$=264.2801 , obs. mass $[M+H]^+$=264.2856

Example: 2- Preparation of 1, 2-di-(2-carbethoxyphenyl)-pyridazine-3, 6-dione (4b).

Step A- Preparation of 3, 6-di-(2-carbethoxyphenoxy)-pyridazine (3b).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine **(1)** and 2-carbethoxyphenol **(2b)** instead of phenol **(2a)** whereby **3b** was obtained as viscous oil (Yield: 48%) after purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5 (t, J=7.6 Hz, 6H), 3.9 (q, J=7.3Hz, 4H), 6.5-7.0 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 58.5, 125-168.5, 170.

IR (KBr, cm^{-1}): 1236, 1350, 1620, 1695, 2960-2995.

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%).

HRMS: *m/z* cal. mass for $C_{22}H_{20}N_2O_6$ [M+H] =408.4061, obs. mass $[M+H]^+$=408.4049.

Step B- Preparation of compound 4b.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(2-carbethoxyphenoxy)-pyridazine **(3b)** instead of 3, 6-diphenoxypyridazine **(3a)** at 160°C for 90 minutes, whereby **4b** was obtained as oil (Yield: 46%) after purification.

^{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, 59, 127-170, 162, 171.5.

IR (KBr, cm^{-1}): 1216, 1340, 1610, 1640, 1700, 1705, 2864-2985.

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%).

HRMS: *m/z* cal. mass for $C_{22}H_{20}N_2O_6$ $[M+H]^+$=408.4061, obs. mass $[M+H]^+$=408.4078.

Example: 3- Preparation of 1, 2-di-(4-carbmethoxyphenyl)-pyridazine-3, 6-dione (4c).

Step A- Preparation of 3, 6-di-(4-carbmethoxyphenoxy)-pyridazine (3c).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine (1) and 4-carbmethoxyphenol **(2c)** instead of phenol **(2a)**, whereby **3c** was obtained as viscous oil (Yield: 51%) after purification.

^{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 53, 127-171, 169.

IR (KBr, cm^{-1}): 1239, 1354, 1600, 1725, 2868-3015.

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%).

HRMS: *m/z* cal. mass for $C_{20}H_{16}N_2O_6$ $[M+H]^+$=380.3528, obs. mass $[M+H]^+$=380.3556.

Step B- Preparation of compound 4c.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(4-carbmethoxyphenoxy)-pyridazine **(3c)** instead of 3, 6-diphenoxypyridazine **(3a)** at 175°C for 70 minutes, whereby **4c** was obtained as oil (Yield: 40%) after purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.5(s, 6H), 6-7.2(m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 52.5-53.5, 127.5-158, 98, 141, 152.5, 164, 165-167.5.

IR (KBr, cm^{-1}): 1210, 1358, 1606, 1635, 1688, 1700, 1715, 2990-3278.

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 %).

HRMS: *m/z* cal. mass for $C_{20}H_{16}N_2O_6$ $[M+H]^+$=380.3528, obs. mass $[M+H]^+$=380.3507.

Example: 4- Preparation of 1, 2-di-(1-naphthyl)-pyridazine-3, 6-dione (4d).

Step A- Preparation of 3, 6-di-(1-naphthoxy)-pyridazine (3d).

It was prepared as described in **Step A** of Example-1 by using 3, 6-dichloropyridazine **(1)** and 1-naphthol **(2d)** instead of phenol **(2a)**, whereby **3d** was obtained as cream colored solid (Yield: 47%) after purification. m.p.: 91°C

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.2-7.4.

^{13}C NMR (75 MHz, $CDCl_3$): 126-174.

IR (KBr, cm^{-1}): 1240, 1341, 1600.

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%).

HRMS: *m/z* cal. mass for $C_{24}H_{16}N_2O_2$ $[M+H]^+$=364.3982, obs. mass $[M+H]^+$=364.3942.

Step B- Preparation of compound 4d.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(1-naphthoxy)-pyridazine **(3d)** instead of 3, 6-diphenoxypyridazine **(3a)** at 165°C for 80 minutes, whereby **4d** was obtained as a solid (Yield: 46%) after purification. m.p.: 143°C

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.0-7.5.

^{13}C NMR (75 MHz, $CDCl_3$): 123-172.

IR (KBr, cm^{-1}): 1349, 1600, 1642, 1680.

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%).

HRMS: *m/z* cal. mass for $C_{24}H_{16}N_2O_2$ $[M+H]^+$=364.3982, obs. mass $[M+H]^+$=364.3944.

Example 5- Preparation of 1, 2-di-(4-carbethoxy-2, 6-dimethoxy phenyl)-pyridazine-3, 6-dione (4e).

Step A- Preparation of 3, 6-di-(4-carbethoxy-2, 6-dimethoxyphenoxy)-pyridazine (3e).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine **(1)** and ethyl-4-hydroxy-3,5-dimethoxy benzoate **(2e)** instead of phenol **(2a)**, whereby **3e** was obtained as viscous oil (Yield: 50%) after purification.

^{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 19, 55, 59, 169, 124.5-172.

IR (KBr, cm^{-1}): 1239, 1336 , 1620, 1715, 2950-3000 .

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%).

HRMS: *m/z* cal. mass for $C_{26}H_{28}N_2O_{10}$ $[M+H]^{+=}$528.5105, obs. mass $[M+H]^{+=}$528.5078.

Step B- Preparation of compound 4e.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(4-carbethoxy-2, 6-dimethoxy phenoxy)-pyridazine (**3e**) instead of 3, 6-diphenoxypyridazine **(3a)** at 170°C for 65 minutes, whereby **4e** was obtained as an oil (Yield: 42%) after purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.5(t, J=7.0 Hz, 6H), 4.0(s, 12H, 4.0, 4.5(q, J=7.6 Hz), 6.1-7.5 (m, 6H)

^{13}C NMR (75 MHz, $CDCl_3$): δ 23, 53, 62, 127-166.5, 164, 168

IR (KBr, cm^{-1}): 1211, 1240, 1346, 1615, 1640, 1685, 1725, 2985-3015

Molecular formula: $C_{26}H_{28}N_2O_{10}$. Elemental analysis: Calculated: C (59.09%), H (5.30%), N (5.30%). Found: C (59.15%), H (5.21%), N (5.34%).

HRMS: *m/z* cal. mass for $C_{26}H_{28}N_2O_{10}$ $[M+H]^+$=528.5105, obs. mass $[M+H]^+$=528.5129.

Example: 6- Preparation of 1, 2-di-(2-ethoxyphenyl)-pyridazine-3, 6-dione (4f).

Step A- Preparation of 3, 6-di-(2-ethoxyphenoxy)-pyridazine (3f).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine **(1)** and 2-ethoxyphenol **(2f)** instead of phenol **(2a)**, whereby **3f** was obtained as viscous oil (Yield: 49%) after purification. m.p.: 102°C.

^{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, 59, 126.5-170.

IR (KBr, cm^{-1}): 1245, 1348, 1605, 2840-3100

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%).

HRMS: *m/z* cal. mass for $C_{20}H_{20}N_2O_4$ $[M+H]^+$=352.3857, obs. mass $[M+H]^+$=352.3879.

Step B- Preparation of compound 4f.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(2-ethoxyphenoxy)-pyridazine **(3f)** instead of 3, 6-diphenoxypyridazine **(3a)** at 160°C for 60 minutes, whereby **4f** was obtained as an oil (Yield: 48%) after purification.

^{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, 55.5, 127-169, 170.

IR (KBr, cm^{-1}): 1239, 1351, 1608, 1644, 1680, 2890-2987.

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%).

HRMS: *m/z* cal. mass for $C_{20}H_{20}N_2O_4$ $[M+H]^+$=352.3857, obs. mass $[M+H]^+$=352.3878.

Example: 7- Preparation of 1, 2-di-(4-ethoxyphenyl)-pyridazine-3, 6-dione (4g).

Step A- Preparation of 3, 6-di-(4-ethoxyphenoxy)-pyridazine (3g).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine **(1)** and 4-ethoxyphenol **(2g)** instead of phenol **(2a)**, whereby **3g** was obtained as an oil (Yield: 52%) after purification.

^{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 15, 56.5, 126-169.

IR (KBr, cm^{-1}): 1225, 1354, 1600, 2872-3010

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%).

HRMS: *m/z* cal. mass for $C_{20}H_{20}N_2O_4$ $[M+H]^+$=352.3857, obs. mass $[M+H]^+$=352.3811.

Step B- Preparation of compound 4g.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(4-ethoxyphenoxy)-pyridazine **(3g)** instead of 3, 6-diphenoxypyridazine **(3a)** at 180°C for 55 minutes, whereby **4g** was obtained as an oil (Yield: 47%) after purification.

^{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 12, 52.5, 127-169, 170

IR (KBr, cm^{-1}): 1231, 1333, 1608, 1625, 1690, 2765-2995

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%).

HRMS: *m/z* cal. mass for $C_{20}H_{20}N_2O_4$ $[M+H]^+$=352.3857, obs. mass $[M+H]^+$=352.3790.

Example 8- Preparation of 1, 2-di-(4-chloro-3, 5-dimethylphenyl)-pyridazine-3, 6-dione (4h).

Step A- Preparation of 3, 6-di-(4-chloro-3, 5-dimethylphenoxy)-pyridazine (3h).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine **(1)** and 4-chloro-3,5-dimethylphenol **(2h)** instead of phenol **(2a)**, whereby **3h** was obtained as solid (Yield: 51%) after purification. m.p.: 110°C.

^{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, 126-171.

IR (KBr, cm^{-1}): 775, 1253, 1349, 1610, 2876-2997.

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%).

HRMS: *m/z* cal. mass for $C_{20}H_{18}N_2O_2Cl_2$ $[M+H]^+$=389.2773, obs. mass $[M+H]^+$=389.2752.

Step B- Preparation of compound 4h.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(4-chloro-3, 5-dimethylphenoxy)-pyridazine **(3h)** instead of 3, 6-diphenoxypyridazine **(3a)** at 160°C for 70 minutes, whereby **4h** was obtained as an oil (Yield: 44%) after purification.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.3 (s, 12H), 6.3-7.5 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): 17, 127-169, 169.

IR (KBr, cm^{-1}): 778, 1342, 1615, 1610, 1692, 2945-3005.

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 (7.09%), Cl (18.15%).

HRMS: *m/z* cal. mass for $C_{20}H_{18}N_2O_2Cl_2$ $[M+H]^+$=389.2773, obs. mass $[M+H]^+$=389.2736.

Example: 9- Preparation of 1, 2-di-(3-methylphenyl)-pyridazine-3, 6-dione (4i).

Step A- Preparation of 3, 6-di-(3-methylphenoxy)-pyridazine (3i).

It was prepared as described in **Step A** of **Example-1** by using 3, 6-dichloropyridazine **(1)** and 3-methylphenol **(2i)** instead of phenol **(2a)**, whereby **3i** was obtained as a solid (Yield: 66%) after purification. m.p.: 98°C (I. L.Jae, H. Park, Y. S. Yun, K. S. Kyoung, *J. Kor.Chem. Soc.*, **2001**, 45, 4, 386-390)

Step B- Preparation of compound 4i.

It was prepared as described in **Step B** of **Example-1** by using 3, 6-di-(3-methylphenoxy)-pyridazine **(3i)** instead of 3, 6-diphenoxypyridazine **(3a)** at 160°C for 70 minutes, whereby **4i** was obtained as an oil (Yield: 48%) after purification.

^{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 16 , 125-169.5, 171.

IR (KBr, cm^{-1}): 1349, 1600, 1615, 1690, 2873-2993.

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%).

HRMS: *m/z* cal. mass for $C_{18}H_{16}N_2O_2$ $[M+H]^+$=292.3335, obs. mass $[M+H]^+$=292.3370.

5. CLAIMS:
We Claim:

1. Synthesis of 1, 2-diphenyl-pyridazine-3, 6-dione **(4a)** as described in **Example-1** by *Chapman rearrangement* of 3, 6-diphenoxypyridazine **(3a)** at 175°C for 70 minutes.
2. Synthesis of 1, 2-di-(2-carbethoxyphenyl)-pyridazine-3, 6-dione **(4b)** as described in **Example-2** by *Chapman rearrangement* of 3, 6-di-(2-carbethoxyphenoxy)-pyridazine **(3b)** at 160°C for 90 minutes.
3. Synthesis of 1, 2-di-(4-carbmethoxyphenyl)-pyridazine-3, 6-dione **(4c)** as described in **Example-3** by *Chapman rearrangement* of 3, 6-di-(4-carbmethoxyphenoxy)-pyridazine **(3c)** at 175°C for 70 minutes.
4. Synthesis of 1, 2-di-(1-naphthyl)-pyridazine-3, 6-dione **(4d)** as described in **Example-4** by *Chapman rearrangement* of 3, 6-di-(1-naphthoxy)-pyridazine **(3d)** at 165°C for 80 minutes.
5. Synthesis of 1, 2-di-(4-carbethoxy-2, 6-dimethoxyphenyl)-pyridazine-3, 6-dione **(4e)** as described in **Example-5** by *Chapman rearrangement* of 3, 6-di-(4-carbmethoxyphenoxy)-pyridazine **(3e)** at 170°C for 65 minutes.
6. Synthesis of 1, 2-di-(2-ethoxyphenyl)-pyridazine-3, 6-dione **(4f)** as described in **Example-6** by *Chapman rearrangement* of 3, 6-di-(2-ethoxyphenoxy)-pyridazine **(3f)** at 160°C for 60 minutes.
7. Synthesis of 1, 2-di-(4-ethoxyphenyl)-pyridazine-3, 6-dione **(4g)** as described in **Example-7** by *Chapman rearrangement* of 3, 6-di-(4-ethoxyphenoxy)-pyridazine **(3g)** at 180°C for 55 minutes.
8. Synthesis of 1, 2-di-(4-chloro-3, 5-dimethylphenyl)-pyridazine-3, 6-dione **(4h)** as described in **Example-8** by *Chapman rearrangement* of 3, 6-di-(4-chloro-3, 5-dimethylphenoxy)-pyridazine **(3h)** at 160°C for 70 minutes.
9. Synthesis of 1, 2-di-(3-methylphenyl)-pyridazine-3, 6-dione **(4i)** as described in **Example-9** by *Chapman rearrangement* of 3, 6-di-(3-methylphenoxy)-pyridazine **(3i)** at 160°C for 70 minutes.
10. Imidates **(3a-3i)** underwent facile *Chapman rearrangement* to afford 1, 2 - disubstituted pyridazine-3, 6-diones **(4a-4i)** which provides a simpler and environmental friendly procedure.

6. DATE: 24th December 2013

SIGNATURE:-

Dr. M. M. V. Ramana

Dr. Sanjay C. Pawar