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A selective synthesis for novel pyranodipyrimidines

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An environmentally benign approach to the selective synthesis of novel compounds 5,8-diaryl-5,7-dihydro-1*H*-pyrano[2,3-*d*:6,5-*d'*]dipyrimidine-2,4,6-triones under microwave irradiation (MWI) using inorganic solid supports is described. The reaction time decreases from hours to minutes along with yield enhancement. In addition, catalytic role of various inorganic supports is studied, and acidic alumina is found to be the best in terms of selectivity.

Keywords: Pyranodipyrimidines, barbituric acid, microwave, solid support, montmorillonite K-10 clay, acidic alumina

Synthetic studies of fused pyrimidines have been documented extensively because of their structural diversity and association with a wide spectrum of biological activities[1-5]. Barbituric acids and its thio analogues have been employed as convenient starting materials for the preparation of wide variety of fused pyrimidines such as pyranopyrimidines[6,7], pyrano-dipyrimidines[8], pyridopyrimidines[9], pyrazolo and isoxazolopyrimidines[10] and pyrimidotriazepines[11].

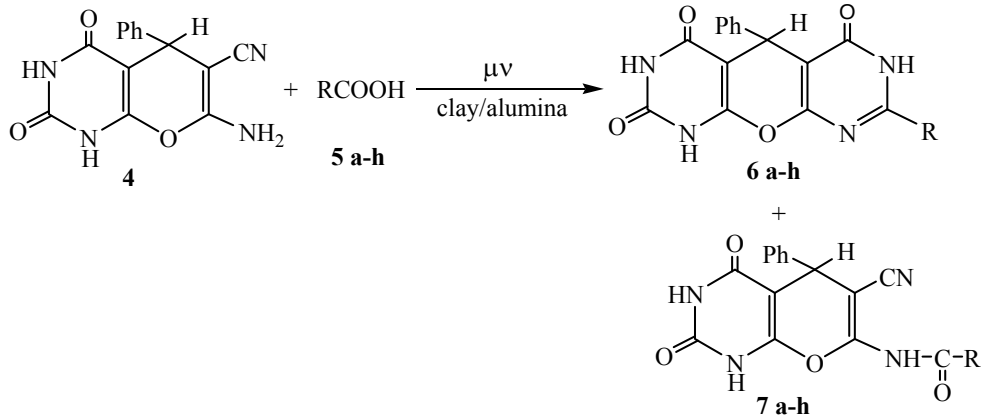
Among these, pyranodipyrimidines are the least investigated compounds and only few syntheses are found to be reported in literature[12]. This tricyclic system plays an important role in various biological activities such as HIV-I integrase inhibitor[13], antibacterial, immunomodulating, antitumor[14] and also used as antiretroviral drug[15]. Besides the usefulness of pyranodipyrimidines, the *N*-alkylated product showed enhanced bioactivity due to the increase in solubility in common organic solvents[16] that is indicative of the high lipophilicity which facilitates membrane transport and strengthens functional activity. Protocol followed by this group also shows an *N*-alkylated pyranopyrimidine **7** as a byproduct, although present in smaller quantities but possessing various biological activities[17-21], therefore, important enough to be characterized after isolation. Pyranodipyrimidines are good precursors for further development into new drugs and to be included in future combination regimens.

MW assisted synthesis of heterocycles has attracted immense attention due to simplicity, enhanced reaction rate[22], formation of pure products and high yields with ease of manipulation[23].

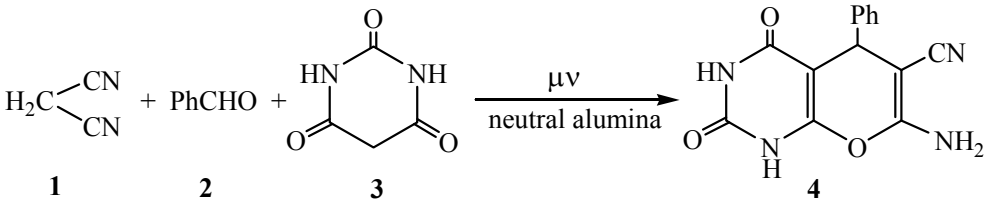
In view of the above mentioned biological activities of pyranodipyrimidines and in continuation of the interest in the development of environmentally benign synthesis, herein is reported a selective, novel and facile synthesis of pyranodipyrimidines on various solid supports. Conventional synthesis is also reported for comparison.

Results and Discussion

Pyranodipyrimidines **6a-h** were prepared by the reaction of 7-amino-6-cyano-5-aryl-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4(1*H*, 3*H*)-diones (intermediate) **4** with different aromatic carboxylic acids, **5a-h** (**Scheme I**). The intermediate in turn was synthesized by MWI using neutral alumina as solid support (**Scheme II**). To synthesize title compound, intermediate **4** and different aromatic carboxylic acids **5a-h** were adsorbed on clay/alumina and subjected to MWI. Initially, the ditopic property[24] of montmorillonite K-10 clay *viz.* various catalytic sites with diversities was explored. Using montmorillonite K-10 clay, two products **6** and **7** were obtained as monitored by TLC. Moreover, to explore the acidic property of the solid support the same protocol was followed using another solid support *i.e.* acidic alumina and surprisingly, only one product was obtained in sufficient quantity *i.e.*, upto 55-65% (**Table I**). This highlighted the selectivity of a particular support for the reaction. Further, for comparative studies, conventional synthesis was also tried using dilute hydrochloric acid as acidic medium, but it again led to two products **6** and **7** with longer reaction times and poor yields (**Table I**). So, neither



Scheme I



Scheme II

selectivity nor good yields could be achieved conventionally. Thus, in comparison to the conventional method, solid supported reactions with MWI gave better results in terms of selectivity, duration of reaction and yield. The reaction catalyzed by acidic alumina as solid support was found to be the most suitable in terms of selectivity.

The structures of the compounds **6** and **7** were established on the basis of elemental analysis and spectral data. The disappearance of absorbtion band at 2210 cm^{-1} in IR spectra due to –C≡N stretching frequency in **6** confirms the ring formation which is formed by the condensation of **4** with different aromatic carboxylic acids **5a-g**. Further, the disappearance of the doublet at 3200-3250 cm^{-1} due to NH_2 in products **6** and **7** confirms the proposed structure. Distinction between **6** and **7** is made on the basis of polarity difference between the two, as monitored by TLC. Absorption band at 2200 cm^{-1} due to C≡N still present in IR spectra of **7** supports the N-alkylated product eliminating the possibility of the cyclized compound. In addition, the molecular formulae of the two products are the same as seen by CHN analysis.

Experimental Section

Melting points were taken on a Thomas Hoover melting point apparatus and are uncorrected. IR (Nujol) were recorded on a Perkin-Elmer FTIR-1710 spectrometer and ^{1}H NMR were recorded on a Bruker Avance Spectrospin 300 (300 MHz) instrument using TMS as internal standard. Elemental analysis was performed on a Heraeus CHN rapid analyser. Mass spectra were recorded on KC455 Waters TOF-MS. The homogeneity of compounds were determined on aluminium foil backed silica gel plates (Merck). A Kenstar microwave oven, Model OM 9925E (2450 MHz, 800 W) was used for MWI.

General procedure for the synthesis of 5, 8-Diaryl-5, 9-dihydro-1*H*-pyrano[2, 5-d:6, 5-d′]-dipyrimidine-2, 4, 6-trione

Method A (microwave synthesis)

Synthesis of 7-Amino-6-cyano-5-aryl-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4(1*H*, 3*H*)-diones 4 (intermediate)

To the ethanolic solution of malononitrile (1 mmol) **1**, benzaldehyde (1 mmol) **2**, and barbituric acid (1 mmol) **3**, 20 g of neutral alumina[25] was added. The reaction mixture was stirred well for best adsorption and dried in air. The beaker containing reaction mixture was placed in an alumina bath[26] and subjected to MWI for the time interval of 30 s. Upon completion of reaction (progress monitored by TLC), the reaction mixture was cooled and product extracted using 2×10 mL DMF.

Table I — Comparison of reaction time and yields for the compounds **6a-h** and **7a-h**

Compd	R	Method A					Method B		
		A_1		A_2			Time	Yield	
		Time (min)	Yield (%)	Time (min)	Yield (%)		(hr)	(%)	
			6		**6**	**7**		**6**	**7**
6a/7a	$-C_6H_5$	5	60	4	63	28	8	40	20
6b/7b	2-$CH_3COOC_6H_5$	4.5	55	4.5	65	25	7.5	42	23
6c/7c	2-ClC_6H_4	5	57	4.5	62	28	8	41	25
6d/7d	3-ClC_6H_4	5	60	5	63	26	7	45	22
6e/7e	4-ClC_6H_4	4.5	62	4	65	22	7.3	40	21
6f/7f	3-$NO_2C_6H_4$	5	64	4.5	70	20	6.5	35	20
6g/7g	$-CH_2C_6H_5$	4.2	58	5	69	25	7.5	46	20
6h/7h	4-$MeOC_6H_4$	4.5	65	4.5	65	26	8.5	48	22

A_1: Acidic alumina
A_2: Montmorillonite K10 clay

Synthesis of 5, 8-Diaryl-5, 9-dihydro-1*H*-pyrano[2, 5-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione

Method A_1

Acidic alumina[27] was added to the intermediate **4** (1 mmol) and aromatic carboxylic acids **5a-h** (1 mmol) dissolved in DMF at RT. The reaction mixture was thoroughly mixed and dried in air. It was then placed in alumina bath and subjected to MWI. After each interval of 30 s, the progress of reaction was monitored using TLC. Upon completion of the reaction, the product **6a-h** was extracted using 3×10 mL chloroform and purified by recrystallization from ethanol.

Method A_2

The procedure is analogous to method A_1, using montmorillonite K-10 clay[28] as solid support in place of acidic alumina. The progress of reaction was monitored using TLC at intervals of 30 s. After completion of reaction, the mixture of two products **6a-h** and **7a-h** were extracted using chloroform. The two products were separated using column chromatography over column of silica gel (60-120 mesh); preadsorption of crude product on silica gel; elution with benzene/ethylacetate = 90:10 v/v.

Method B (Conventional Procedure)

To the ethanolic solution of different aromatic carboxylic acids **5a-h** (1 mmol), intermediate **4** dissolved in minimum amount of DMF was added. It was acidified with dil. HCl (~ 1 mL). The resulting reaction mixture was then stirred under reflux. Progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was cooled and the solvent was evaporated *in vacuo*. The crude product thus isolated was washed with water and dried. The mixture of two products was separated using preparative TLC plates (chloroform as eluent). The products were purified by recrystallization from ethanol.

5,8-Diphenyl-5,7-dihydro-1*H*-pyrano[2,3-*d*:6,5-*d*']dipyrimidine-2,4,6-trione, 6a. m.p. 102-04°C; IR(Nujol): 1720, 1591, 1568, 1451, 1376, 3320, 3250 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.32 (1H, brs, NH), 10.79 (1H, brs, NH), 8.42 (1H, brs, NH), 7.06-7.6 (10H, m, ArH), 4.13 (1H, s, CH). Anal. Calcd. for $C_{21}N_4H_{14}O_4$: C, 65.25; H, 3.62; N, 14.50. Found C, 65.05; H, 3.14; N, 14.78%. EI-MS: *m/z* 386.10.

5-Phenyl-8(*o*-acetoxyphenyl)-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6b. m.p. 120-22°C; IR(Nujol): 3335, 3260, 1719, 1568, 1591, 1450 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.22 (1H, brs, NH), 10.62 (1H, brs, NH), 8.64 (1H, brs, NH), 7.2-7.8 (9H, m, ArH), 4.24 (1H, s, CH), 2.3 (3H, s, CH). Anal. Calcd. for $C_{23}N_4H_{16}O_6$: C, 62.16; H, 3.60; N, 12.61. Found C, 61.12; H, 3.42; N, 12.53%. EI-MS: *m/z* 444.10.

5-Phenyl-8(*o*-chlorophenyl)-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6c. m.p.140-42°C; IR(Nujol): 3482, 1761, 1560, 1720, 3380 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.24 (1H, brs, NH), 10.89 (1H, brs, NH), 8.68 (1H, brs, NH), 7.12-7.92 (9H, m, ArH), 4.41 (1H, s, CH). Anal.Calcd. for $C_{21}H_{13}N_4O_4Cl$: C, 59.92; H, 3.09; N, 13.31. Found C, 60.12; H, 2.92; N, 13.72%. EI-MS: *m/z* 420.06.

5-Phenyl-8(*m*-chlorophenyl)-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6d. m.p. 118-20°C; IR(Nujol): 3343, 1619, 1529, 1393,

1448 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.32 (1H, brs, NH), 10.72 (1H, brs, NH), 8.72 (1H, brs, NH), 7.2-8.1 (9H, m, ArH), 4.42 (1H, s, CH). Anal.Calcd. for $C_{21}H_{13}N_4O_4Cl$: C, 59.92; H, 3.09; N, 13.31. Found C, 59.46; H, 3.12; N, 13.46%. EI-MS: *m/z* 420.06.

5-Phenyl-8(*p*-chlorophenyl)-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6e. m.p. 98-100°C; IR(Nujol): 3320, 3543, 1721, 1667, 1531 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.31 (1H, brs, NH), 10.74 (1H, brs, NH), 8.42 (1H, brs, NH), 7.2-7.9 (9H, m, ArH), 4.48 (1H, s, CH). Anal.Calcd. for $C_{21}H_{13}N_4O_4Cl$: C, 59.92; H, 3.04; N, 13.31. Found C, 59.82; H, 3.22; N, 13.09%. EI-MS: *m/z* 420.06.

5-Phenyl-8(*m*-nitrophenyl)-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6f. m.p.190-92°C; IR(Nujol): 3343, 1619, 1529, 1393, 1448 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.34 (1H, brs, NH), 10.72 (1H, brs, NH), 8.72 (1H, brs, NH), 7.2-7.83 (9H, m, ArH), 4.19 (1H, s, CH). Anal.Calcd. for $C_{21}H_{13}N_5O_6$: C, 58.46; H, 3.01; N, 16.24. Found C, 58.91; H, 3.51; N, 16.02%. EI-MS: *m/z* 430.09.

5-Phenyl-8(*p*-methoxyphenyl)-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6h. m.p. 210-12°C; IR(Nujol): 3393, 3458, 1725, 1820, 1421 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.53 (1H, brs, NH), 10.26 (1H, brs, NH), 8.42 (1H, brs, NH), 7.15-7.62 (9H, m, ArH), 4.23 (1H, s, CH), 3.56 (3H, s, CH). Anal.Calcd. for $C_{22}H_{16}N_4O_5$: C, 63.46; H, 3.84; N, 13.46. Found C, 63.63; H, 3.91; N, 13.42%. EI-MS: *m/z* 416.11.

5-Phenyl-8-benzyl-5, 7-dihydro-1*H*-pyrano[2, 3-*d*:6, 5-*d*']dipyrimidine-2, 4, 6-trione, 6g. m.p.160-62°C; IR(Nujol): 3583, 3198, 3031, 1811, 1720, 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.63 (1H, brs, NH), 10.49 (1H, brs, NH), 8.51 (1H, brs, NH), 7.1-7.66 (10H, m, ArH), 4.34 (1H, s, CH), 2.26 (2H, s, CH). Anal.Calcd. for $C_{22}H_{16}N_4O_4$: C, 66.0; H, 4.0; N, 14.0. Found C, 65.48; H, 4.10; N, 14.23%. EI-MS: *m/z* 400.12.

6-Cyano-5-phenyl-7-(benzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7a. m.p. 80-82°C; IR(Nujol): 3397, 3166, 2120, 1694, 1596, 1572 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.31 (1H, brs, NH), 10.62 (1H, brs, NH), 8.65 (1H, brs, NH), 7.1-7.8 (10H, m, ArH), 4.22 (1H, s, CH). Anal.Calcd. for $C_{21}H_{14}O_4N_4$: C, 65.28; H, 3.62; N, 14.50. Found C, 65.92; H, 3.83; N, 14.23%. EI-MS: *m/z* 386.10.

6-Cyano-5-phenyl-7-(2'-acetoxybenzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7b. m.p. 76-78°C; IR(Nujol): 3443, 3329, 3242, 2160, 1742, 1642 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.22 (1H, brs, NH), 10.52 (1H, brs, NH), 8.46 (1H, brs, NH), 6.9-7.3 (9H, m, ArH), 4.25 (1H, s, CH), 2.91 (3H, s, CH). Anal. Calcd. for $C_{23}H_{16}O_6N_4$: C, 62.16; H, 3.60; N, 12.61. Found C, 62.02; H, 3.48; N, 12.05%. EI-MS: *m/z* 444.19.

6-Cyano-5-phenyl-7-(2'-chlorobenzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7c. m.p. 120-22°C; IR(Nujol): 3353, 3254, 3295, 3411, 2161, 1722 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.26 (1H, brs, NH), 10.62 (1H, brs, NH), 8.41 (1H, brs, NH), 6.9-7.6 (9H, m, ArH), 4.12 (1H, s, CH). Anal. Calcd. for $C_{21}H_{13}O_4N_4Cl$: C, 59.92; H, 3.09; N, 13.31. Found C, 59.48; H, 2.83; N, 13.64%. EI-MS: *m/z* 420.06.

6-Cyano-5-phenyl-7-(3'-chlorobenzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7d. m.p. 90-92°C; IR(Nujol): 3354, 3249, 2361, 1696, 1597, 1575 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.41 (1H, brs, NH), 10.51 (1H, brs, NH), 8.62 (1H, brs, NH), 6.8-7.6 (9H, m, ArH), 4.23 (1H, s, CH). Anal. Calcd. for $C_{21}H_{13}O_4N_4Cl$: C, 59.92; H, 3.09; N, 13.31. Found C, 59.13; H, 3.22; N, 13.72%. EI-MS: *m/z* 420.06.

6-Cyano-5-phenyl-7-(4'-chlorobenzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7e. m.p. 88-90°C; IR(Nujol): 3402, 3349, 3292, 2159, 1769, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.39 (1H, brs, NH), 10.65 (1H, brs, NH), 8.52 (1H, brs, NH), 7.2-7.8 (9H, m, ArH), 4.15 (1H, s, CH). Anal. Calcd. for $C_{21}H_{13}O_4N_4Cl$: C, 59.92; H, 3.19; N, 13.31. Found C, 60.15; H, 3.19; N, 13.62%. EI-MS: *m/z* 420.06.

6-Cyano-5-phenyl-7-(3'-nitrobenzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7f. m.p. 76-78°C; IR(Nujol): 3343, 3210, 3439, 2112, 1619, 1529 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 11.26 (1H, brs, NH), 10.42 (1H, brs, NH), 8.51 (1H, brs, NH), 7.2-8.1 (9H, m, ArH), 4.19 (1H, s, CH). Anal. Calcd. for $C_{21}H_{13}O_6N_5$: C, 58.46; H, 3.01; N, 16.24. Found C, 57.92; H, 2.99; N, 16.45%. EI-MS: *m/z* 430.09.

6-Cyano-5-phenyl-7-(4'-methoxybenzoylamino)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione, 7g. m.p. 88-90°C; IR(Nujol): 3489, 3393, 3210, 1750, 1690, 1520, 2310; ^{1}H NMR ($CDCl_3$): δ 11.12 (1H, brs, NH), 10.31 (1H, brs, NH), 8.49 (1H, brs, NH), 7.25-8.12 (9H, m, ArH), 4.16 (1H, s, CH), 3.56 (3H, s, CH). Anal. Calcd. for $C_{22}H_{16}O_5O_4$: C, 63.46; H, 3.84; N, 73.40. Found C, 63.89; H, 3.42; N, 13.06%. EI-MS: *m/z* 400.12.

6-Cyano-5-phenyl-7-(benzylamido)-1, 3, 5-trihydro-5*H*-pyrano[2, 3-*d*]pyrimidine-2, 4-dione,

7h. m.p. 116-18°C; IR(Nujol): 3583, 3198, 3031, 2117, 181, 1720, 1696 cm^{-1}; ^1H NMR ($CDCl_3$): δ 11.34 (1H, brs, NH), 10.62 (1H, brs, NH), 8.43 (1H, brs, NH), 6.82-7.51 (10H, m, ArH), 4.25 (1H, s, CH), 2.31 (2H, s, CH). Anal. Calcd. for $C_{22}H_{16}O_4N_4$: C, 6.0; H, 4.0; N, 14.0. Found C, 65.50; H, 4.23; N, 17.10%. EI-MS: *m/z* 416.11.

Conclusion

In conclusion, the proposed methodology provides an easy, practical, convenient, environmentally benign and selective one pot synthesis of pyranodipyrimidines. The procedure clearly highlights the selectivity of the acidic alumina solid support when compared with montmorillonite K-10 clay.

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28 Montmorillonite K10: K Catalyst (69866 Fluka), surface area 200 ± 20 m^2/g.