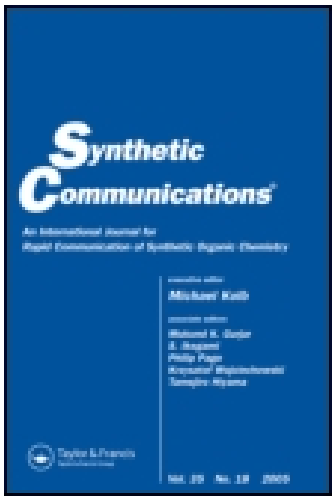

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REGIOSPECIFIC AND REGIOSELECTIVE 1,3-DIPOLAR CYCLOADDITION OF DIPOLAR REAGENTS TO UNSYMMETRICAL BISOLEFINIC KETONES IN THE PRESENCE OF CHLORAMINE-T (CAT)

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REGIOSPECIFIC AND REGIOSELECTIVE 1,3-DIPOLAR CYCLOADDITION OF DIPOLAR REAGENTS TO UNSYMMETRICAL BISOLEFINIC KETONES IN THE PRESENCE OF CHLORAMINE-T (CAT)

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ABSTRACT

The reaction of 1,5-diaryl-3-methyl-1,4-pentadien-3-one with araldehyde phenylhydrazone/araldoxime in the presence of chloramine-T proceeds regiospecifically in MeOH and regioselectively in AcOH leading to mono- and *bis*-pyrazolines/isoxazolines.

The olefinic groups has versatile functions in organic synthesis, offers manifold possibilities of *c*-hetero bond formations and has received considerable attention in recent times. As part of the development of new, simple and efficient procedures for the synthesis of pyrazolines and isoxazolines, we have examined the reaction of nitrile imines and nitrile oxides generated

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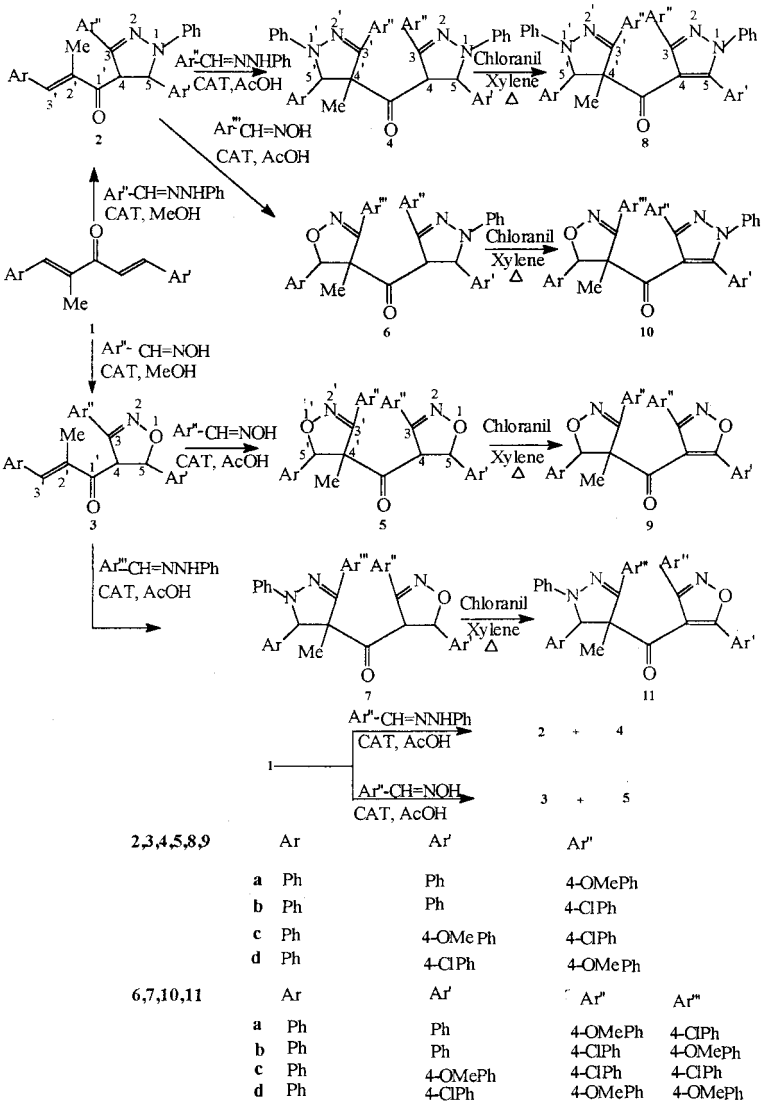
from araldehyde phenylhydrazones and araldoximes with bifunctional olefinic systems.[1,2]

In continuation of our study, the present paper deals with the reaction of these dipolar reagents with unsymmetrical bisolefinic ketones. The former can be generated by the dehydrogenation of araldehyde phenylhydrazones and araldoximes with lead tetraacetate,[3] mercuric acetate,[4] 1-chlorobenzotriazole,[5] chloramine-T (CAT)[6] etc. When the reaction of 1,5-diaryl-3-methyl-1,4-pentadien-3-one[7] (**1**) with two moles of araldehyde phenylhydazone was carried out in the presence of CAT in refluxing MeOH, a solid was separated after 2 h and identified as 1-phenyl-3,5-diaryl-4-(3′-aryl-2′-methyl-2′-propenone)-2-pyrazoline (**2**) by NMR spectra (Scheme). A similar reaction of **1** with two moles of araldoxime in the presence of CAT in refluxing MeOH gave 3,5-diaryl-4-(3′-aryl-2′-methyl-2′-propenone)-2-isoxazoline (**3**) whose structure was confirmed by NMR spectra. The compounds **2a** and **3a** showed δ_H 5.64, 5.61 (d, 4-H), 5.18, 5.23 (d, 5-H), δ_C 155.28, 155.13 (3-C), 87.64, 87.88 (4-C), 64.65, 64.62 (5-C), 197.19, 197.10 (C=O), 161.04, 161.02 (2′-C) and 141.38, 141.69 (3′-C). The DEPT spectra of these compounds exhibited signal at 141.60, 141.61 which indicates the presence of olefinic proton at 3′-C. Thus, the formation of **2** and **3** illustrates that this reaction proceeds in a regiospecific manner. Attempts were made to prepare 1-phenyl-3,5-diaryl-2-pyrazolinyl-1′-phenyl-3′,5′-diaryl-4′-methyl-2′-pyrazolinyl-[4,4′]-ketones (**4**) and 3,5-diaryl-2-isoxazolinyl-3′,5′-diaryl-4′-methyl-2′-isoxazolinyl-[4,4′]-ketones (**5**) by refluxing **2** and **3** with one mole of araldehyde phenylhydrazone and araldoxime in the presence of CAT in MeOH, but could not meet with success, since this forms a heterogeneous medium. However, this was accomplished by refluxing in AcOH. Contrary to the above, when the reaction of **1** was carried out with two moles of araldehyde phenylhydrazone and araldoxime in the presence of CAT in AcOH, it gave **2** & **4** and **3** & **5** in 2.5 : 1 ratio respectively, indicating that the reaction proceeded regioselectively. The two were separated by column chromatography. The authenticity of these compounds was confirmed by their relative NMR spectra. The formation of **4** and **5** in minor amounts may be due to the presence of an alkyl group which deactivates the reactivity of the olefinic bond. The formation of **2** and **3** led us to develop two different heterocycles within the same molecule. Thus **2** on treatment with one mole of araldoxime in the presence of CAT in AcOH gave a product which was found to be 1-phenyl-3,5-diaryl-2-pyrazolinyl-3′,5′-diaryl-4′-methyl-2′-isoxazolinyl-[4,4′]- ketones (**6**). Similar reaction of **3** with araldehyde phenylhydrazone and CAT in AcOH resulted in 3,5-diaryl-2-isoxazolinyl-1′-phenyl-3′,5′-diaryl-4′-methyl-2′-pyrazolinyl-[4,4′]-ketones (**7**). The dehydrogenation of **4**, **5**, **6** and **7** with chloranil in AcOH[8,9] resulted in 1-phenyl-3,5-diaryl-2-pyrazolyl-1′-phenyl-3′,5′-diaryl-4′-methyl-2′-pyrazolin-



2,3,4,5,8,9	Ar	Ar'	Ar"
a	Ph	Ph	4-OMePh
b	Ph	Ph	4-ClPh
c	Ph	4-OMePh	4-ClPh
d	Ph	4-ClPh	4-OMePh

6,7,10,11	Ar	Ar'	Ar"	Ar'''
a	Ph	Ph	4-OMePh	4-ClPh
b	Ph	Ph	4-ClPh	4-OMePh
c	Ph	4-OMePh	4-ClPh	4-ClPh
d	Ph	4-ClPh	4-OMePh	4-OMePh

Scheme.

yl-[4,4′]-ketones (**8**), 3,5-diaryl-2-isoxazolyl-3′,5′-diaryl-4′-methyl-2′-isoxazolinyl-[4,4′]-ketones (**9**), 1-phenyl-3,5-diaryl-2-pyrazolyl-3′,5′-diaryl-4′-methyl-2′-isoxazolinyl-[4,4′]-ketones (**10**) and 3,5-diaryl-2-isoxazolyl-1′-phenyl-3′,5′-diaryl-4′-methyl-2′-pyrazolinyl-[4,4′]-ketones (**11**). The absence of a doublet at

δ_H 5.61–5.64 and 5.18–5.23 in their ^{1}H NMR spectra supports their formation. This reaction sequence shows that the 1,3-dipolar cycloaddition of dipolar reagents to unsymmetrical bisolefinic ketones in the presence of chloramine-T proceeds regiospecifically when the reaction is carried out in methanol and regioselectively in acetic acid.

EXPERIMENTAL

All melting points were determined in open capillaries on Tempo Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by thin layer chromatography over silica gel (Silica gel-G (60–120 mesh, BDH), hexane : ethyl acetate (3 : 1) as eluents). The IR spectra were run as KBr pellets using a Perkin-Elmer 993 infrared spectrometer and ^{1}H NMR spectra were recorded in $CDCl_3$/DMSO-d_6 at 200 MHz on a Brucker Spectrospin with TMS as an internal standard (chemical shifts in δ ppm). Microanalytical data were obtained from Dr. Reddy's Research Foundation, Hyderabad, India. The araldoximes and araldehyde phenylhydrazones were prepared from araldehydes following standard procedures.[10]

1-Phenyl-3,5-diaryl-4-(3′-aryl-2′-methyl-2′-propenone)-2-pyrazoline 2

General procedure: 1,5-Diaryl-3-methyl-1,4-pentadien-3-one **1** (10 mmol) in MeOH was added to a mixture of araldehyde phenylhydrazone (20 mmol) and chloramine-T (20 mmol) in MeOH (20 ml) and refluxed for 5–6 h. Salts formed were filtered off. The solvent was removed under vacuum and the solid obtained was recrystallized from AcOH to get pure **2**.

2a: Yield 72%; m.p. 135–136°C; IR ν_{max} (cm^{-1}) 1444 (C=N), 1638 (C=C), 1669 (C=O); ^{1}H NMR δ 2.12 (s, 3H, CH_3, C-2′), 3.79 (s, 3H, Ar-OCH_3), 5.23 (d, 1H, C_4-H, $J = 6.0$ Hz), 5.61 (d, 1H, C_5-H, $J = 6.0$ Hz), 7.18–8.04 (m, 20H, $C_{3'}$-H & Ar-H); ^{13}C NMR δ 13.56 (CH_3, C-2′), 64.62 (C-4), 87.88 (C-5), 141.69 (C-3′), 155.13 (C-3), 161.02 (C-2′), 197.10 (C=O); DEPT 13.28 (CH_3, C-2′), 64.53 (C-4), 87.79 (C-5), 141.61 (C-3′); Anal. calcd for $C_{32}H_{28}N_2O_2$: C, 81.32; H,5.97; N,5.92. Found: C, 81.45; H, 5.90; N, 6.01.

2b: Yield 75%; m.p. 147–148°C; IR ν_{max} (cm^{-1}) 1448 (C=N), 1644 (C=C), 1668 (C=O); ^{1}H NMR δ 2.12 (s, 3H, CH_3, C-2′), 5.25 (d, 1H, C_4-H, $J = 5.9$ Hz), 5.58 (d, 1H, C_5-H, $J = 5.9$ Hz), 7.22–8.02 (m, 20H, $C_{3'}$-H & Ar-H); Anal. calcd for $C_{31}H_{25}ClN_2O$: C, 78.05; H, 5.28; N, 5.87. Found: C, 77.94; H, 5.25; N, 5.94.

2c: Yield 70%; m.p. 128–129°C; IR ν_{max} (cm^{-1}) 1445 (C=N), 1638 (C=C), 1670 (C=O); ^{1}H NMR δ 2.10 (s, 3H, CH_3, C-2′), 3.81 (s, 3H,

Ar-OCH_3) 5.22 (d, 1H, C_4-H, $J = 6.0$ Hz), 5.63 (d, 1H, C_5-H, $J = 6.0$ Hz), 7.19–8.06 (m, 19H, $C_{3'}$ -H & Ar-H); Anal. calcd for $C_{32}H_{27}ClN_2O_2$: C, 75.80; H, 5.36; N, 5.52. Found: C, 75.71; H, 5.42; N, 5.59.

3,5-Diaryl-4-(3′-aryl-2′-methyl-2′-propenone)-2-isoxazoline 3

General procedure: 1,5-Diaryl-3-methyl-1,4-pentadien-3-one **1** (10 mmol) in MeOH was added to a mixture of araldoxime (20 mmol) and chloramine-T (20 mmol) in MeOH (20 ml) and the mixture was refluxed for 5–6 h. Further workup of the reaction mixture was similar to that of **2**.

3a: Yield 68%; m.p. 142–143°C; IR ν_{max} (cm^{-1}) 1446 (C=N), 1627 (C=C), 1672 (C=O); ^{1}H NMR δ 2.14 (s, 3H, CH_3, C-2′), 3.79 (s, 3H, Ar-OCH_3), 5.20 (d, 1H, C_4-H, $J = 5.9$ Hz), 5.65 (d, 1H, C_5-H, $J = 5.9$ Hz), 7.12–7.94 (m, 15H, $C_{3'}$ -H & Ar-H); ^{13}C NMR δ 12.78 (CH_3 at C-2′), 64.57 (C-4), 85.62 (C-5), 142.63 (C-3′), 153.84 (C-3′), 160.98 (C-2′), 198.02 (C=O); DEPT 12.24 (CH_3 at C-2′), 64.48 (C-4), 85.52 (C-5), 142.62 (C-3′); Anal. calcd for $C_{26}H_{23}NO_3$: C, 78.50; H, 5.83; N, 3.52. Found: C, 78.64; H, 5.80; N, 3.58.

3b: Yield 71%; m.p. 137–138°C; IR ν_{max} (cm^{-1}) 1448 (C=N), 1634 (C=C), 1670 (C=O); ^{1}H NMR δ 2.13 (s, 3H, CH_3, C-2′), 5.24 (d, 1H C_4-H, $J = 6.1$ Hz), 5.63 (d, 1H, C_5-H, $J = 6.1$ Hz), 7.09-8.01 (m, 15H, $C_{3'}$-H & Ar-H); Anal. calcd for $C_{25}H_{20}ClNO_2$: C, 74.75; H, 5.00; N, 3.48; Found: C, 74.84; H, 5.04; N, 3.55.

3c: Yield 66%; m.p. 130–131°C; IR ν_{max} (cm^{-1}) 1444 (C=N), 1637 (C=C), 1669 (C=O); ^{1}H NMR δ 2.10 (s, 3H, CH_3, C-2′), 3.80 (s, 3H, Ar-OCH_3), 5.22 (d, 1H, C_4-H, $J = 6.0$ Hz), 5.66 (d,1H, C_5-H, $J = 6.0$ Hz), 7.12–7.98 (m, 14H, $C_{3'}$-H & Ar-H); Anal. calcd for $C_{26}H_{22}ClNO_3$: C, 72.30; H, 5.13; N, 3.24. Found: C, 72.41; H, 5.17; N, 3.29.

1-Phenyl-3,5-diaryl-2-pyrazolinyl-1′-phenyl-3′,5′-diaryl-4′-methyl-2′-pyrazolinyl-[4,4′]-ketones 4/3,5-Diaryl-2-isoxazolinyl-1′-phenyl-3′,5′-diaryl-4′-methyl-2′-pyrazolinyl-[4,4′]-ketones 7

General procedure: A mixture of **2**/**3** (6 mmol), araldehyde phenylhydrazone (6 mmol) and two-fold excess of chloramine-T in AcOH (20 ml) was added and refluxed for 4–5 h. The contents were cooled and poured onto crushed ice. It was extracted with ether (30 ml), washed with sat. $NaHCO_3$ solution, water and dried over an. Na_2SO_4. Evaporation of the solvent under reduced pressure gave a crude product which was purified by column chromatography.

4a: Yield 66%; m.p. 162–163°C; IR ν_{max} (cm^{-1}) 1444 (C=N), 1706 (C=O); ^{1}H NMR δ 0.81 (s, 3H, CH_3 at C-4′), 3.81 (s, 6H, Ar-OCH_3), 5.25 (d, 1H, C_4-H, $J = 5.7$ Hz), 5.39 (s, 1H, $C_{5'}$-H), 5.58 (d, 1H, C_5-H, $J = 5.7$ Hz), 7.24–8.12 (m, 28H, Ar-H). ^{13}C NMR δ 12.21 (CH_3 at C-4′), 59.87 (C-4′), 64.62 (C-4), 85.92 (C-5′), 87.88 (C-5), 153.24 (C-3′), 155.13 (C-3), 199.24 (C=O); Anal. calcd for $C_{46}H_{40}N_4O_3$: C, 79.28; H, 5.78; N, 8.04. Found: C, 79.42; H, 5.70; N, 7.93.

4b: Yield 62%; m.p. 155–156°C; IR ν_{max} (cm^{-1}) 1447 (C=N), 1710 (C=O); ^{1}H NMR δ 0.84 (s, 3H, CH_3, C-4′), 5.27 (d, 1H, C_4-H, $J = 5.6$ Hz), 5.38 (s, 1H, $C_{5'}$-H) 5.56 (d, 1H, C_5-H, $J = 5.8$ Hz), 7.26–8.03 (m, 28H, Ar-H). Anal. calcd for $C_{44}H_{34}Cl_2N_4O$: C, 74.90; H, 4.85; N, 7.94. Found: C, 76.79; H, 4.89; N, 7.85.

4c: Yield 68%; m.p. 171–172°C; IR ν_{max} (cm^{-1}) 1445 (C=N), 1702 (C=O); ^{1}H NMR δ 0.83 (s, 3H, CH_3, C-4′), 3.81 (s, 3H, Ar-OCH_3), 5.22 (d, 1H, C_4-H, $J = 5.6$ Hz), 5.35 (s, 1H, $C_{5'}$-H), 5.59 (d, 1H, C_5-H, $J = 5.6$ Hz), 7.24–8.12 (m, 27H, Ar-H). Anal. calcd for $C_{45}H_{36}Cl_2N_4O_2$: C, 73.46; H, 4.93; N, 7.61. Found: C, 73.59; H, 5.01; N, 7.74.

7a: Yield 69%; m.p. 182–183°C; IR ν_{max} (cm^{-1}) 1442 (C=N), 1712 (C=O); ^{1}H NMR δ 0.84 (s, 3H, CH_3, C-4′), 3.79 (s, 3H, Ar-OCH_3), 5.21 (d, 1H, C_4-H, $J = 5.9$ Hz), 5.44 (s, 1H, $C_{5'}$-H), 5.63 (d, 1H, C_5-H, $J = 5.9$ Hz), 7.14–8.04 (m, 23H, Ar-H). Anal. calcd for $C_{40}H_{35}N_3O_4$: C, 77.20; H, 5.67; N, 6.75. Found: C, 77.39; H, 5.75; N, 6.80.

7b: Yield 62%; m.p. 173–174°C; IR ν_{max} (cm^{-1}) 1438 (C=N), 1710 (C=O); ^{1}H NMR δ 0.82 (s, 3H, CH_3, C-4′), 3.78 (s, 3H, Ar-OCH_3), 5.19 (d, 1H, C_4-H, $J = 5.8$ Hz), 5.39 (s, 1H, $C_{5'}$-H), 5.64 (d, 1H, C_5-H, $J = 5.8$ Hz), 7.12–8.07 (m, 23H, Ar-H). Anal. calcd for $C_{39}H_{32}ClN_3O_3$: C, 74.57; H, 5.13; N, 6.68. Found: C, 74.44; H, 5.09; N, 6.73.

7c: Yield 66%; m.p. 173–174°C; IR ν_{max}(cm^{-1}) 1444 (C=N), 1713 (C=O); ^{1}H NMR δ 0.83 (s, 3H, CH_3, C-4′), 3.778 (s, 3H, Ar-OCH_3), 5.19 (d, 1H, C_4-H, $J = 5.9$ Hz), 5.43 (s, 1H, $C_{5'}$-H), 5.62 (d, 1H, C_5-H, $J = 5.9$ Hz), 7.09–8.02 (m, 22H, Ar-H). Anal. calcd for $C_{39}H_{31}Cl_2N_3O_3$: C, 70.91; H, 4.72; N, 6.36. Found: C, 70.83; H, 4.81; N, 6.45.

3,5-Diaryl-2-isoxazolinyl-3′,5′-diaryl-4′-methyl-2′-isoxazolinyl-[4,4′]-ketones 5/1-phenyl-3,5-diaryl-2-pyrazolinyl-3′,5′-diaryl-4′-methyl-2′-isoxazolinyl-[4,4′]-ketones 6

General procedure: A mixture of **2/3** (6 mmol), araldoxime (6 mmol) and two-fold excess of chloramine-T in AcOH (20 ml) was refluxed for 2–3 h. Further workup of the reaction mixture was similar to **4/7**.

5a: Yield 69%; m.p. 171–172°C; IR ν_{max} (cm^{-1}) 1452 (C=N), 1712 (C=O); ^{1}H NMR δ 0.84 (s, 3H, CH_3, C-4′), 3.74 (s, 6H, Ar-OCH_3), 5.23 (d, 1H, C_4-H, $J = 6.1$ Hz), 5.40 (s, 1H, $C_{5'}$-H) 5.62 (d, 1H, C_5-H, $J = 6.1$ Hz) 7.19–8.13 (m, 18H, Ar-H). ^{13}C NMR δ 12.46 (CH_3 at C-4′), 59.48 (C-4′), 63.24 (C-4), 84.29 (C-5′), 88.90 (C-5), 154.45 (C-3′), 156.27 (C-3), 197.48 (C=O); Anal. calcd for $C_{34}H_{30}N_2O_5$: C, 74.70; H, 5.53; N, 5.12. Found: C, 74.79; H, 5.45; N, 5.04.

5b: Yield 72%; m.p. 155–156°C; IR ν_{max} (cm^{-1}) 1450 (C=N), 1707 (C=O); ^{1}H NMR δ 0.84 (s, 3H, CH_3, C-4′), 5.20 (d, 1H, C_4-H, $J = 6.0$ Hz), 5.38 (s, 1H, $C_{5'}$-H) 5.65 (d, 1H, C_5-H, $J = 6.0$ Hz) 7.16–8.15 (m, 18H, Ar-H). Anal. calcd for $C_{32}H_{24}Cl_2N_2O_3$: C, 69.19; H, 4.35; N, 5.04. Found: C, 69.20; H, 4.31; N, 5.09.

5c: Yield 70%; m.p. 184–185°C; IR ν_{max} (cm^{-1}) 1442 (C=N), 1712 (C=O); ^{1}H NMR δ 0.85 (s, 3H, CH_3, C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.25 (d, 1H, C_4-H, $J = 6.1$ Hz), 5.37 (s, 1H, $C_{5'}$-H) 5.58 (d, 1H, C_5-H, $J = 6.1$ Hz) 7.17–8.07 (m, 17H, Ar-H). Anal. calcd for $C_{33}H_{26}Cl_2N_2O_4$: C, 67.69; H, 4.47; N, 4.78. Found: C, 67.65; H, 4.49; N, 4.88.

6a: Yield 65%; m.p.157-158°C; IR ν_{max} (cm^{-1}) 1438 (C=N), 1724 (C=O); ^{1}H NMR δ 0.80 (s, 3H, CH_3, C-4′), 3.84 (s, 3H, Ar-OCH_3), 5.27 (d, 1H, C_4-H, $J = 6.1$ Hz), 5.31 (s, 1H, $C_{5'}$-H), 5.52 (d, 1H, C_5-H, $J = 6.1$ Hz), 7.19–8.10, (m, 23H, Ar-H). Anal. calcd for $C_{40}H_{35}N_3O_4$: C,77.29; H,5.67; N,6.75. Found: C, 77.29; H, 5.59; N, 6.84.

6b: Yield 69%; m.p. 142–143°C; IR ν_{max} (cm^{-1}) 1442 (C=N), 1722 (C=O); ^{1}H NMR δ 0.81 (s, 3H, CH_3, C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.25 (d, 1H, C_4-H, $J = 6.0$ Hz), 5.34 (s, 1H, $C_{5'}$-H), 5.50 (d, 1H, C_5-H, $J = 6.0$ Hz), 7.19–8.14, (m, 23H, Ar-H). Anal. calcd for $C_{39}H_{32}ClN_3O_3$: C, 74.57; H, 5.13; N, 6.68. Found: C, 74.42; H, 5.20; N, 6.75.

6c: Yield 61%; m.p. 162–163°C; IR ν_{max} (cm^{-1}) 1432 (C=N), 1721 (C=O); ^{1}H NMR δ 0.83 (s, 3H, CH_3, C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.25 (d, 1H, C_4-H, $J = 6.0$ Hz), 5.33 (s, 1H, $C_{5'}$-H), 5.51 (d, 1H, C_5-H, $J = 6.0$ Hz), 7.17–8.08 (m, 22H, Ar-H). Anal. calcd for $C_{39}H_{31}Cl_2N_3O_3$: C, 70.91; H, 4.72; N, 6.36. Found: C, 71.05; H, 4.79; N, 6.41.

When the reaction was carried out with **1** and araldehyde phenylhydrazone/araldoxime (1.2 mmol) in the presence of chloramine-T in AcOH, the mixture of products **2** & **4**/**3** & **5** were obtained in 2.5 : 1 ratio. These compounds have the same physical and spectral characteristics as above.

Dehydrogenation of 4/5/6/7

General procedure: A mixture of **4/5/6/7** (6 mmol) and chloranil (6.5 mmol) in xylene (15 ml) was refluxed for 24–32 h. The organic layer

was washed with 1N NaOH, water and dried. The solvent was removed under reduced pressure. The solid remaining was purified by recrystallization from AcOH to obtain **8/9/10/11**.

8a: Yield 71%; m.p. 145–146°C; IR ν_{max} (cm^{-1}) 1448 (C=N), 1629 (C=C), 1674 (C=O); ^{1}H NMR δ 0.90 (s, 3H, CH_3 at C-4′), 3.81 (s, 6H, Ar-OCH_3), 5.35 (s,1H $C_{5'}$-H) 7.14–8.12, (m, 28H, Ar-H).

8b: Yield 66%; m.p. 137–138°C; IR ν_{max} (cm^{-1}) 1448 (C=N), 1627 (C=C), 1675 (C=O); ^{1}H NMR δ 0.87 (s, 3H, CH_3, C-4′) 5.32 (s, 1H, $C_{5'}$-H), 7.05–8.10 (m, 28H, Ar-H).

8c: Yield 70%; m.p. 153–154°C; IR ν_{max} (cm^{-1}) 1448 (C=N), 1628 (C=C), 1670 (C=O); ^{1}H NMR δ 0.85 (s, 3H, CH_3, C-4′) 3.80 (s, 3H, Ar-OCH_3), 5.36 (s,1H $C_{5'}$-H,) 7.07–8.12 (m, 27H, Ar-H).

9a: Yield 66%; m.p. 156–157°C; IR ν_{max} (cm^{-1}) 1434 (C=N), 1642 (C=C), 1680 (C=O); ^{1}H NMR δ 0.87 (s, 3H, CH_3 at C-4′), 3.80 (s, 6H, Ar-OCH_3), 5.39 (s, 1H $C_{5'}$-H,) 7.19–8.20, (m, 18H, Ar-H).

9b: Yield 65%; m.p. 134–135°C; IR ν_{max} (cm^{-1}) 1432 (C=N), 1639 (C=C), 1684 (C=O); ^{1}H NMR δ 0.86 (s, 3H, CH_3, C-4′), 5.40 (s, 1H $C_{5'}$-H), 7.16–8.22 (m, 18H, Ar-H).

9c: Yield 69%; m.p. 159–160°C; IR ν_{max} (cm^{-1}) 1437 (C=N), 1642 (C=C), 1681 (C=O); ^{1}H NMR δ 0.89 (s, 3H, CH_3 at C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.41 (s, 1H $C_{5'}$-H,) 7.08–8.15, (m, 17H, Ar-H).

10a: Yield 69%; m.p. 135–136°C; IR ν_{max} (cm^{-1}) 1436 (C=N), 1630 (C=C), 1676 (C=O); ^{1}H NMR δ 0.82 (s, 3H, CH_3, C-4′), 3.88 (s, 3H, Ar-OCH_3), 5.38 (s, 1H, $C_{5'}$-H,) 7.24–8.19 (m, 23H, Ar-H).

10b: Yield 62%; m.p. 112–113°C; IR ν_{max} (cm^{-1}) 1435 (C=N), 1632 (C=C), 1673 (C=O); ^{1}H NMR δ 0.85 (s, 3H, CH_3, C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.35 (s, 1H, $C_{5'}$-H,) 7.17–8.16 (m, 22H, Ar-H).

10c: Yield 65%; m.p. 151–152°C; IR ν_{max} (cm^{-1}) 1438 (C=N), 1630 (C=C), 1669 (C=O); ^{1}H NMR δ 0.84 (s, 3H, CH_3, C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.38 (s, 1H, $C_{5'}$-H), 7.19–8.14 (m, 22H, Ar-H).

11a: Yield 73%; m.p. 165–166°C; IR ν_{max} (cm^{-1}) 1448 (C=N), 1632 (C=C), 1678 (C=O); ^{1}H NMR δ 0.85 (s, 3H, CH_3, C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.32 (s, 1H $C_{5'}$-H), 7.18–8.10 (m, 22H, Ar-H).

11b: Yield 66%; m.p 143–144°C; IR ν_{max} (cm^{-1}) 1444 (C=N), 1635 (C=C), 1674 (C=O); ^{1}H NMR δ 0.84 (s, 3H, CH_3, C-4′), 3.81 (s, 3H, Ar-OCH_3), 5.33 (s, 1H $C_{5'}$-H), 7.05–8.02 (m, 22H, Ar-H).

11c: Yield 70%; m.p. 137–138°C; IR ν_{max} (cm^{-1}) 1443 (C=N), 1632 (C=C), 1675 (C=O); ^{1}H NMR δ 0.85 (s, 3H, CH_3 at C-4′), 3.82 (s, 3H, Ar-OCH_3), 5.35 (s, 1H C_5'-H), 7.07–8.05 (m, 21H, Ar-H).

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REFERENCES

1. Padmavathi, V.; Sumathi, R.P.; Chandrasekhar Babu, N.; Bhaskar Reddy, D. J. Chem. Research (S) **1999**, 610.
2. Padmavathi, V.; Sumathi, R.P.; Venugopal Reddy, K.; Bhaskar Reddy, D. Synth. Commun. **2000**, *30*, 4007.
3. Just, G.; Dahl, K. Tetrahedron **1968**, *24*, 5251.
4. Rai, K.M.L.; Liganna, N.; Hassner, A.; Murthy, C.A. Org. Prep. Proced. Int. **1992**, *24*, 91.
5. Khim, J.N.; Ryu, E.K. Synth. Commun. **1990**, *20*, 1373.
6. Hassner, A.; Rai, K.M.L. Synthesis **1989**, 57.
7. Ramalingam, K.; Berlin, K.D.; Loghry, R.A.; Helm, D.V.; Satyamurthy, N. J. Org . Chem. **1979**, *44*, 477.
8. Padmavathi, V.; Bhaskar Reddy, A.V.; Sumathi, R.P.; Bhaskar Reddy, D. Indian J. Chem. **1998**, *37B*, 1286.
9. Hassaneen, H.M.; Hilal, R.H.; Elwan, N.M.; Harhash, A.; Shawali, A.S. J. Heterocyclic. Chem. **1984**, *21*, 1013.
10. Vogel, A.I. *A Text Book of Practical Organic Chemistry*, Longman's Green & Co. Ltd.: London, 1989.

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