Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(6):71-75

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis of polycyclic heterocycles through domino Knoevenagel intramolecular hetero Diels–Alder reaction under solvent free and microwave irradiation conditions

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ABSTRACT

Benzopyrano-pyrano-pyrazoles were synthesized through domino Knoevenagel intramolecular hetero Diels–Alder reaction under solvent free and microwave irradiation conditions. These compounds have the potential to exhibit biological activity. A high degree of chemoselectivity was achieved by the application of microwave irradiation. This green chemistry protocol showed to be very useful under milder reaction conditions.

Keywords: Diels-Alder reaction, Domino reaction, Green Chemistry, Solvent free, Microwave Irradiation, Benzopyrano-pyrano-pyrazoles.

INTRODUCTION

The domino Knoevenagel intramolecular hetero Diels–Alder (IMHDA) reaction is an important method in organic chemistry particularly in the area of polycyclic compounds containing heteroatoms such as benzo-pyrano-pyrano-pyrazole derivatives and some in natural product chemistry because domino reaction allows multiple transformations in single step [1]. In simple way domino reaction is useful in synthesis of complex compounds with increase in synthetic efficiency by use of simple substrates [2]. Synthesis of many dihydropyrans has been already carried out by using domino Knoevenagel intramolecular hetero Diels–Alder reaction [3, 4]. Benzopyrano-pyrano-pyrazole derivatives have been reported to be biologically active [5]. Benzopyran ring is found in a large number of natural products and also in many synthetic compounds exhibiting wide range of biological activities [6]. Pyrrazole derivatives are also important heterocyclic compounds possessing wide range of biological activities such as antimicrobial [7], antipyretic [8], ant-inflammatory [9], antitumor [10], anticonvulsant [11], antiviral [12], antihistaminic [13], antidepressant [14].

Today organic chemistry mainly comprises the use of Green Chemistry tools by use of environmentally safe reagents particularly solvent free reactions and Microwave technology [15]. Reactions carried out under solvent free conditions results in eco-friendly, clean and highly efficient transformations with simplified workup procedures. Gedye in 1986 introduced for the first time the use of microwave heating in organic synthesis [16]. In the last two decades, Microwave technology has become more and more powerful in organic synthesis due to lesser reaction time [17]. Microwave irradiation also provides high chemoselectivity in organic synthesis, especially in domino Knoevenagel/hetero-Diels−Alder process (the so-called Tietze reaction) [18].

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 ^{1}H-NMR spectra were recorded on a Bruker AVANCE (300 MHz) spectrometer (with TMS as internal reference). Mass spectra were recorded on API-3000MD-series (US). The purity of the compounds was checked by TLC on pre-coated SiO_2 gel (200mesh). The reagents were purified by distillation before use. Microwave reactions were carried out by using StartSYNTH Microwave Synthesis Labstation microwave reactor.

RESULTS AND DISCUSSION

Synthesis of (5a*R*,11b*S*)-3,5a,6,11b-Tetrahydro-1-methyl-3-phenyl-5*H*-[l] benzopyrano [4′,3′:4,5]pyrano[2,3-c]pyrazole (IX) has been already reported by Lutz F. Tietze and coworkers by using decalin as a solvent heating at 180^{0}C with overall 75% yield [19].

Most of these methods have their own advantages but have some drawbacks mainly the use of high boiling solvents and longer reaction time and some expensive catalyst. So as a part of our ongoing research we report here the synthesis of some new benzopyrano-pyrano-pyrazole derivatives with and without the use of microwave irradiation under solvent free and catalyst free conditions as a green chemistry approach **(Scheme-1).**

The starting materials required for synthesis of IX-XX such as 2-(alkenyloxy)-benzaldehydes (I-III) and pyrazolones (IV-VII) have been prepared by reported methods [20, 21]. Benzopyrano-pyrano-pyrazole derivatives (IX-XX) were obtained with 100% chemoselectivity with cis compound as major product and with considerable reduction in time. The results obtained under solvent free and microwave irradiation is summarized in **Table-1**.

Scheme:-1 Synthesis of polycyclic heterocycles (IX-XX) through domino Knoevenagel intramolecular hetero Diels–Alder reaction

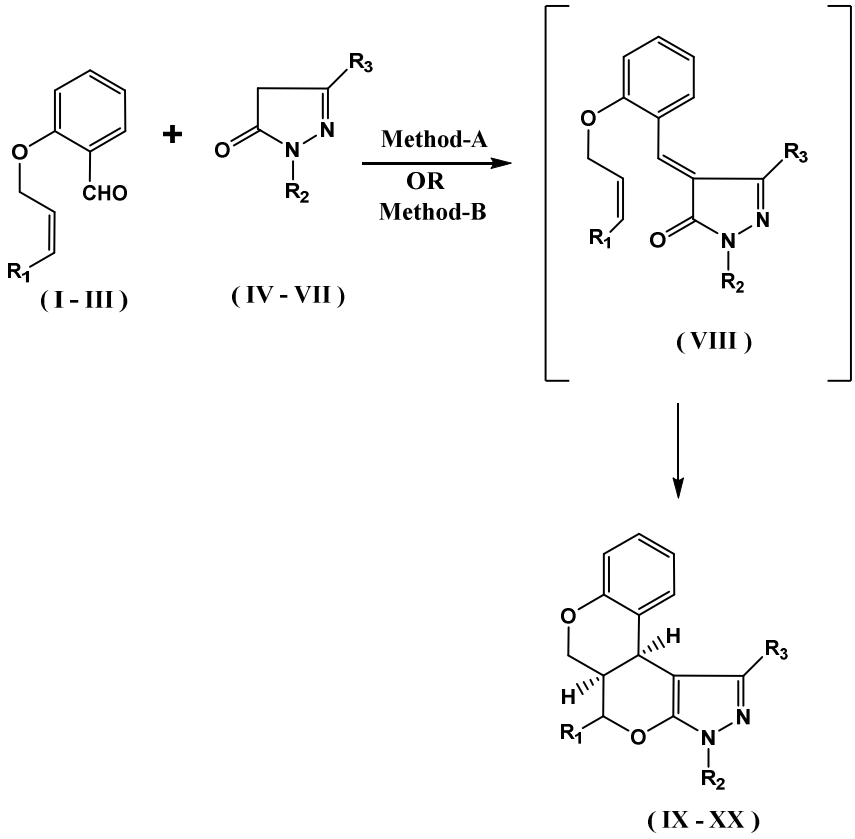

Table:-1 Synthesis of IX-XX from the domino Knoevenagel intramolecular hetero Diels-Alder reaction of I-III and IV-VII under various conditions

Entry	R_1	R_2	R_3	Yield (%)* Method A	Yield (%)* Method B
IX	H	Ph	CH_3	78.9	80.5
X	H	p-$PhCH_3$	CH_3	78.3	80.4
XI	H	m-PhCl	CH_3	78.8	80.4
XII	H	Ph	$COOC_2H_5$	77.9	78.7
XIII	CH_3	Ph	CH_3	81.6	83.7
XIV	CH_3	p-$PhCH_3$	CH_3	75.1	76.3
XV	CH_3	m-PhCl	CH_3	78.7	81.1
XVI	CH_3	Ph	$COOC_2H_5$	81.8	83.1
XVII	Ph	Ph	CH_3	81.5	81.5
XVIII	Ph	p-$PhCH_3$	CH_3	77.7	81.4
XIX	Ph	m-PhCl	CH_3	78.5	80.3
XX	Ph	Ph	$COOC_2H_5$	78.3	79.4

*Where * is the isolated yield after column chromatography.*

Method-A: Solvent free condition, Time-10 Hrs., Temp.-160^{0}C
Method-B: Microwave irradiation, Solvent free, Time-5 Min.

General Procedure:-
Method (A):- A mixture of aldehyde (I-III) (1.0 mmol) and, pyrazolone (IV-VII), (1.0 mmol) was thoroughly ground in a mortar, and was then heated in a heating mantle at 160^{0}C for the period of 10 hrs. After completion of the reaction, the product was extracted in dichloromethane (3X15 ml). Recovery of solvent and purification of crude product by column chromatography afforded the pure product (IX-XX).

Method (B):- A mixture of aldehyde (I-III) (1.0 mmol) and, pyrazolone (IV-VII), (1.0 mmol) was thoroughly ground in a mortar. The reaction mixture was subjected to microwave irradiation for 5 min. After completion of the reaction, the product was extracted in dichloromethane (3X15 ml). Recovery of solvent and purification of crude product by column chromatography afforded the pure product (IX-XX).

1)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1-methyl-3-phenyl-5*H*-[l]benzopyrano[4′,3′:4,5] pyrano [2,3-c] pyrazole (IX) [19].**
White crystal, m.p. 152-154^{0}C. The spectral data (IR, ^{1}H NMR and Mass) are in agreement with the reported data [19].

2)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1-methyl-3-(4′-methylphenyl)-5*H*-[1] benzopyrano[4′, 3′:4, 5] pyrano [2, 3-c] pyrazole(X).**
White crystal, m.p. 181-183^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595, 1510 and 1480 ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 280 (5.34) , 268 (5.35); ^{1}H NMR (300MHz, $CDCl_3$): δ_H 2.45 (s, 3H, 1-CH_3), 2.40-2.56 (m, 4H, p-CH_3, 5a-H), 4.15 (d, J=5.2Hz, 1H, 11b-H), 4.31-4.60 (m, 4H, 5,6-CH_2), 6.80 (dd, J=8.0Hz, J=1.0Hz, 1H, 8-H) , 6.95 (td, J=7.5Hz, J=1.3Hz, 1H, 10-H), 7.08-7.46 (m, 4H, 9-H, 11-H, m-Ph), 7.68 (d, J=8.1Hz, 2H, o-Ph); MS, m/z 332 (80, M^+), 318(8), 303(8), 261(6), 145(100), 91(40).

3)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1-methyl-3-(3′-chlorolphenyl)-5*H*-[1] benzopyrano [4′,3′:4,5] pyrano [2,3-c] pyrazole(XI).**
White crystal, m.p. 141-143^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595, 1585 and 1520 ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 290 (5.33), 281 (5.27) , 249 (5.26); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.42 (s, 3H, 1-CH_3), 2.45-2.56 (m, 1H, 5a-H), 4.14 (d, J=5.2Hz, 1H, 11b-H), 4.32-4.60 (m, 4H, 5,6-CH_2), 6.81(dd, J=8.2Hz, J=1.0Hz, 1H, 8-H), 6.92 (td, J=7.5Hz, J=1.3Hz, 1H, 10-H), 7.10-7.45 (m, 4H, 9-H, 11-H, m-Ph, p-Ph), 7.68 (d, J=8.0Hz, 1H, 6'-Ph), 7.77 (s, 1H, 2'-Ph); MS, m/z 354 (16.9, M^{+2}), 352 (51.9, M^+), 176 (12.3), 145 (100), 115(33.9), 41(52.8).

4)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1-carbethoxy-3phenyl-5*H*-[1]benzopyrano [4′,3′:4,5] pyrano [2, 3-c] pyrazole(XII).**
White crystal, m.p. 181-183^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1720 ($\nu_{C=O}$), 1515 and 1500 ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 301 (5.20), 249 (4.20), 228 (4.12), 224 (4.11), 206 (4.11); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.45 (t, J=7.0Hz, 3H, 1-CH_3), 2.40-2.56 (m, 1H, 5a-H), 4.15-4.65 (m, 7H, 1-CH_2, 11b-H, 5,6-CH_2), 6.81(dd, J=8.2Hz, J=1.0Hz, 1H, 8-H),

6.94 (td, J=7.6Hz, J=1.3Hz, 1H, 10-H), 7.08-7.46(m, 5H, 9-H, 11-H, m-Ph, p-Ph), 7.68-7.77 (m, 2H, o-Ph); MS, m/z 377(100, M^{+1}), 376(17, M^+), 330(15), 303(61.7), 131(15).

5)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1,5-dimethyl-3-phenyl-5*H*-[1]benzopyrano [4′,3′:4,5] pyrano [2, 3-c] pyrazole(XIII).**
White crystal, m.p. 134-136^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595, 1495 and 1480 ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 255 (5.23); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.70(d, J=7.0Hz, 3H, 5-CH_3), 2.44(s, 3H, 1-CH_3), 2.40-2.50(m, 1H, 5a-H), 4.15-4.20(m, 2H, 11b-H, 5-H), 4.32(dd, J=11.0Hz, J=10.0Hz, 1H, 6-H_{ax}), 4.45(dd, J=11.0Hz , J=3.5Hz, 1H, 6-H_{eq}), 6.81(dd, J=8.0Hz, J=1.0Hz , 1H, 8-H) , 6.90(td, J=7.6Hz, J=1.3Hz , 1H, 10-H), 7.08-7.55(m, 5H, 9-H, 11-H, m-Ph, p-Ph), 7.68-7.80 (m, 2H, o-Ph); MS, m/z 332(64.4,M^+), 303(22.0), 277(22.0), 261(20.3), 226(11.9), 185(10.2), 154(44.0), 144(13.6), 131(30.5), 115(38.9), 91(28.8), 77(100).

6)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1,5-dimethyl-3-(4′-methylphenyl)-5*H*-[1] benzopyrano [4′,3′:4,5] pyrano [2, 3-c] pyrazole(XIV).**
White crystal, m.p. 134-136^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1605, 1600 and 1520 ; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 262(5.34) ; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.70(d, J=7.0Hz, 3H, 5-CH_3), 2.40-2.56 (m, 1H, 5a-H), 2.44(s, 3H, 1-CH_3), 2.50(s, 3H, p-CH_3), 4.14 (d, J=5.0Hz, 1H, 11b-H), 4.30-4.66(m, 3H, 5-H, 6-CH_2), 6.81(dd, J=8.0Hz, J=1.0Hz , 1H, 8-H), 6.95(td, J=7.6Hz, J=1.0Hz , 1H, 10-H), 7.08-7.35(m, 4H, 9-H, 11-H, m-Ph), 7.60 (d, J=8.1Hz, 2H, o-Ph); MS, m/z 346(70.4,M^+), 333(6), 332(8), 318(8), 247(6), 91(45), 77(100).

7)**(5a*R*,llb*S*)-3,5a,6,11b-Tetrahydro-1,5-dimethyl-3-(3′-chlorolphenyl)-5*H*-[1]benzopyrano[4′,3′:4,5] pyrano [2,3-c] pyrazole(XV).**
White crystal, m.p. 164-166^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595 and 1510 ; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 261(5.31); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.70(d, J=7.0Hz, 3H, 5-CH_3), 2.41-2.56 (m, 1H, 5a-H), 2.45(s, 3H, 1-CH_3), 4.12(d, J=5.0Hz, 1H, 11b-H), 4.30(dd, J=11.0Hz, J=10.0Hz, 1H, 6-H_{ax}), 4.48-4.52(m, 2H, 5-H, 6-H_{eq}), 6.81(d, J=8.0Hz, 1H,8-H), 6.95(td, J=7.6Hz, J=1.0Hz, 1H, 10-H), 7.08-7.35(m, 4H, 9-H, 11-H, m-Ph, p-Ph), 7.70(d, J=8.0Hz, 1H, 6'-Ph), 7.80(s, 1H, 2'-Ph); MS, m/z 368(16.9, M^{+2}), 366(51.9,M^+), 354(3), 352(9), 176(12.3), 160(100).

8)**(5a*R*,llb*S*)3,5a,6,11b-Tetrahydro-1-carbethoxy-5-methyl-3-phenyl-5*H*-[1] benzopyrano[4′,3′:4,5] pyrano [2,3-c] pyrazole(XVI).**
White crystal, m.p. 165-167^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1720($\nu_{C=O}$), 1495 and 1480; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 261(5.26); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.45(t, J=7.0Hz, 3H, 1-CH_3), 1.7(d, J=7.0Hz, 3H, 5-CH_3), 2.41-2.54(m, 1H, 5a-H), 3.92-4.45(m, 5H, 1-CH_2, 5-H, 6-H_{ax}, 11b-H), 4.51(dd, J=11.0Hz, J=3.5Hz, 1H, 6-H_{eq}), 6.82(d, J=8.0Hz, 1H, 8-H), 6.92(td, J=7.5Hz, J=1.0Hz, 1H, 10-H), 7.08-7.35(m, 5H, 9-H, 11-H, m-Ph, p-Ph), 7.80 (d, J=8.1Hz, 2H, o-Ph); MS, m/z 391(100, M^{+1}), 390(17, M^+), 345(15).

9)**(5a*R*,llb*S*)3,5a,6,11b-Tetrahydro-1-methyl-3,5-diphenyl)-5*H*-[1]benzopyrano [4′,3′:4 5] pyrano [2,3-c] pyrazole(XVII).**
White crystal, m.p.>235^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595 and 1495; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 285(5.50), 234(4.13), 219(4.12), 209(4.12); ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 2.40-2.58(m, 1H, 5a-H), 2.57(s, 3H, 1-CH_3), 4.12(d, J=5.0Hz, 1H, 11b-H), 4.20-4.30(m, 2H, 6-CH2), 4.52 (d, J=3.9Hz, 1H, 5-H), 6.8-7.0(m, 2H, 8-H, 10-H), 7.08-7.46(m, 10H, 9-H, 11-H, m-Ph, p-Ph, 5-Ph), 7.68-7.77(m, 2H, o-Ph); MS, m/z 394(4.6, M^+), 262(55.3), 185(10.7), 117(100), 115(35.5), 91(19.9), 77(21.5).

10)**(5a*R*,llb*S*)3,5a,6,11b-Tetrahydro-1-methyl-3-(4′-methylphenyl)-5-phenyl-5*H*-[1]benzopyrano[4′, 3′: 4, 5] pyrano [2,3-c] pyrazole(XVIII).**
White crystal, m.p.>235^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595, 1490 and 1480; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 251 (5.11); ^{1}H NMR (300MHz, $CDCl_3$): δ_H 2.40-2.58(m, 1H, 5a-H), 2.50(s, 3H, p-CH_3), 2.57(s, 3H, 1-CH_3), 4.12(d, J=5.0Hz, 1H, 11b-H), 4.20-4.30 (m, 2H, 6-CH_2), 4.52(d, J=3.9Hz, 1H, 5-H), 6.78-7.0(m, 2H, 8-H, 10-H), 7.08-7.48(m, 9H, 9-H, 11-H, m-Ph, 5-Ph), 7.68-7.77(m, 2H, o-Ph); MS, m/z 408(4.6, M^+), 277(55.0), 202(10.7), 132(100), 91(21.9), 77(27.5).

11)**(5a*R*,llb*S*)3,5a,6,11b-Tetrahydro-1-methyl-3,-(3′-chlorophenyl)-5-phenyl-5*H*-[1] benzopyrano [4′,3′:4,5] pyrano [2,3-c] pyrazole(XIX).**
White crystal, m.p. 217-219^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1595, 1580 and 1520; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 261(5.42); ^{1}H NMR (300MHz, $CDCl_3$): δ_H 2.39-2.56(m, 1H, 5a-H), 2.57(s, 3H, 1-CH_3), 4.13(d, J=5.0Hz, 1H, 11b-

H), 4.22-4.32(m, 2H, 6-CH2), 5.25(d, J=5.9Hz, 1H, 5-H), 6.78-7.0 (m, 2H, 8-H, 10-H), 7.08-7.46(m, 9H, 9-H, 11-H, m-Ph, 5-Ph), 7.65(d, J=7.9Hz, 1H, 6'-Ph), 7.82(s, 1H, 2'-H); MS, m/z 431(16.9, M^{+2}), 429(51.9, M^{+}), 298(55), 238(15), 222(100).

12)**(5a*R*,llb*S*)3,5a,6,11b-Tetrahydro-1-carbethoxy-3,5-diphenyl-5*H*-[1] benzopyrano [4′, 3′: 4, 5] pyrano [2, 3-c] pyrazole(XX).**
White crystal, m.p. 209-211^{0}C. IR (KBr) (ν_{max} cm^{-1}): 1740 ($\nu_{C=O}$), 1580; ($\nu_{C=C}$); UV ($CHCl_3$) λ_{max} (logε) 259(5.20); ^{1}H NMR (300MHz, $CDCl_3$): δ_H 1.45(t, J=7.0Hz, 3H, 1-CH_3), 2.38-2.55(m, 1H, 5a-H), 4.11(d, J=5.0Hz, 1H, 11b-H), 4.20(dd, J=11.0Hz, J=10.0Hz, 1H, 6-H_{ax}), 4.55(q, 2H, 1-CH_2), 4.80(dd, J=11.0Hz , J=3.5Hz, 1H, 6-H_{eq}), 5.30(d, J=5.9Hz, 1H, 5-H), 6.78-7.0(m, 2H, 8-H, 10-H), 7.08-7.46(m, 10H, 9-H, 11-H, m-Ph, p-Ph, 5-Ph), 7.68-7.77(m, 2H, o-Ph); MS, m/z 453 (100, M^{+1}), 452(17, M^{+}), 378(15), 322(17).

CONCLUSION

In conclusion we have described an efficient synthesis of benzopyrano-pyrano-pyrazole derivatives via a domino Knoevenagel intramolecular hetero Diels–Alder reaction under solvent free and microwave irradiation conditions with good overall yields. Microwave irradiation was found to be useful in achieving a high degree of chemoselectivity.

Acknowledgement
Authors are thankful to Department of Chemistry, University of Mumbai, Mumbai for the facilities.

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