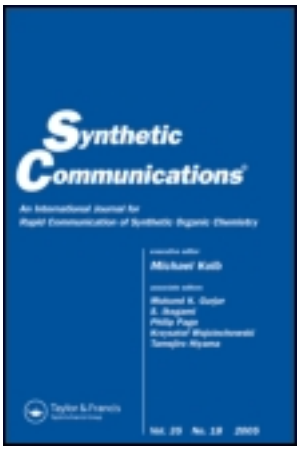

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Synthesis and Spectral Studies of Some Novel 2,5,9,10-Tetrahydro [7,8-g]benzo-8-arylpyrazolo[4,5-e][1,5-b]benzoxazonine via Phase Transfer Catalysis

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SYNTHESIS AND SPECTRAL STUDIES OF SOME NOVEL 2,5,9,10-TETRAHYDRO [7,8-g] BENZO-8-ARYLPYRAZOLO [4,5-e] [1,5-b] BENZOXAZONINE VIA PHASE TRANSFER CATALYSIS

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Abstract

Treatment of 1H-4,5-dihydro-3-aryl-5-(2 -hydroxyaryl)pyrazole with o-dibromoxylene under liquid-liquid phase transfer catalytic conditions using tetra-n-butylammonium hydrogen sulphate or [18]-crown-6 as PT catalyst, benzene/chloroform as organic phase and 50% aqueous potassium hydroxide as second phase, afforded novel 2,5,9,10-tetrahydro [7,8-g] benzo-8-arylpyrazolo[4,5-e] [1,5-b] benzoxazonines.

In recent years Phase Transfer Catalysis (PTC) has aroused great interest of organic as well as organometallic chemists due to its diverse applications. It provides extremely convenient conditions for various type of organic reactions, viz.: C-, N-, O-, and S-alkylations, arylations, heterocyclizations and heterocyclic ring transformations which are well documented in the literature[1-3]. However, perusal of literature revealed that the synthesis of nine membered heterocycles through PTC have not been reported.

Keeping these observations in view, we have therefore, undertaken a comprehensive programme for developing PTC methods for organic synthesis and as a part of this, we have

reported the N-alkylation/ N-arylmethylations of indoles, indole-2,3-diones and 1H-4,5-dihydro-3,5-diarylpyrazoles[4,5]. In continuation with our earlier work, now we wish to report one pot synthesis of novel 2,5,9,10-tetrahydro[7,8-g] benzo-8-arylpyrazolo[4,5-e] [1,5-b] benzoxazonines [5] via PTC. All compounds have been characterized on the basis of spectral studies (IR, PMR and MS) and analytical data, which are in harmony with the proposed structure (Table-3 and -4).

The non-appearance of NH and OH absorption peaks in the region of 3300-3500 cm^{-1} and resonance signals in the region of δ8-10 ppm, provides strong evidence for the formation of compound [5]. Two additional resonance signals at δ4.2 (m, 2H,benzylic coupling, N-CH_2-Ph) and 5 ppm (m, 2H, benzylic coupling, -CH_2-Ph) are also in harmony with the proposed structure [5] as 2,5,9,10-tetrahydro [7,8-g] benzo-8-arylpyrazolo[4,5-e] [1,5-b] benzoxazonine (Table-4).

Experimental

Synthesis of 1-(4-chlorophenyl)-3-(2-hydroxyphenyl)-prop-2-enone (3)

A mixture of salicylaldehyde [1] (10 mmol, 1.22 g) in ethanol (100 ml) and 4-chloroacetophenone [2] (10 mmol, 1.54 g) was heated on a water bath for 15 minutes, then 50% aq. NaOH solution (10 ml) was added slowly with stirring. The resulting thick mass was stirred for 3 hours and then left overnight at room temperature. The resultant mass was decomposed by pouring on ice cold dil. HCl (100 ml). The compound was filtered, dried and recrystallised from ethanol to afford desired chalcone[5] [3].

Yield-2.5 g (98 %), m.p. 140°C.

Other compounds prepared by this method are listed in the Table-1.

Table-1

Physical characterstics and analytical data of 1,3-diaryl-prop-2-enones (3)

S. No.	X	M.P.°C (recrystallization)	Molecular formula	Yield (%)	C(%)	H(%)
					Calculated (Found)	Calculated (Found)
1.	H	124°, ethanol	$C_{15}H_{12}O_2$	57	80.36 (80.30)	5.36 (5.31)
2.	Br	135°, ethanol	$C_{15}H_{11}BrO_2$	91	59.40 (59.35)	3.63 (3.58)
3.	Cl	140°, ethanol	$C_{15}H_{11}ClO_2$	98	69.63 (69.55)	4.25 (4.16)
4.	F	150°, ethanol	$C_{15}H_{11}FO_2$	98	74.38 (74.31)	4.54 (4.45)

Synthesis of 1H-4,5-dihydro-3-(4-chlorophenyl)-5-(2-hydroxyphenyl) pyrazoles (4)

A mixture of 1-(4-chlorophenyl)-3-(2-hydroxyphenyl)-prop-2-enone [3] (4 mmol, 1.03 g) and hydrazine hydrate (5 ml, 80%) in ethanol (50 ml) was refluxed on a water bath for 5 hours. The ethanol was removed and the residue was poured on crushed ice, filtered, dried and recrystallised from ethanol to yield desired compound[5] [4].

Yield - 1.1 g (98%), m.p. 170°C.

Other compounds prepared by this method are listed in the Table-2.

Synthesis of 2,5,9,10-tetrahydro [7,8-g] benzo-8-(4-chlorophenyl)pyrazolo [4,5-e] [1,5-b] benzoxazonine (5)

First Procedure:

A mixture of 1H-4,5-dihydro-3-(4-chlorophenyl)-5-(2-hydroxyphenyl)pyrazole (6 mmol,

Table-2

Physical characterstics and analytical data of 1H-4,5-dihydro-3,5-diarylpyrazoles (4)

S. No.	X	M.P.°C (recrystallization)	Molecular formula	Yield (%)	C(%)	H(%)	N(%)
					Calculated (Found)	Calculated (Found)	Calculated (Found)
1.	H	172°, ethanol	$C_{15}H_{14}N_2O$	82	75.63 (75.51)	5.88 (5.80)	11.76 (11.71)
2.	Br	150°, ethanol	$C_{15}H_{13}BrN_2O$	88	56.78 (56.70)	4.10 (4.01)	8.83 (8.75)
3.	Cl	170°, ethanol	$C_{15}H_{13}ClN_2O$	98	66.05 (66.10)	4.77 (4.70)	10.27 (10.21)
4.	F	74°, ethanol	$C_{15}H_{13}FN_2O$	98	70.31 (70.26)	5.08 (5.00)	10.94 (10.88)

Table-3

Physical characterstics and analytical data of 2,5,9,10-tetrahydro[7,8-g] benzo-8-arylpyrazolo[4,5-e] [1,5-b] benzoxazonine (5) using $TBAHSO_4$ or [18]-crown-6 as PT catalysts

S. No.	X	M.P.°C (recrystallisation)	Molecular formula	Yield (%)	C(%)	H(%)	N(%)
					Calculated (Found)	Calculated (Found)	Calculated (Found)
1	H	70°, P.E.-chloroform	$C_{23}H_{20}N_2O$	75[a] 67[b]	81.17 (81.20)	5.88 (5.90)	8.23 (8.30)
2	Br	140°, P.E.-chloroform	$C_{23}H_{19}BrN_2O$	84[a] 82[b]	65.87 (65.90)	4.53 (4.60)	65.87 (65.95)
3	Cl	100°, P.E.-chloroform	$C_{23}H_{19}ClN_2O$	91[a] 46[b]	73.69 (73.50)	5.07 (5.00)	7.47 (7.50)
4	F	101°, P.E.-chloroform	$C_{23}H_{19}FN_2O$	65[a] 60[b]	77.09 (77.10)	5.3 (5.20)	7.82 (7.85)

a : Yield (Procedure 1)
b : Yield (Procedure 2)

Table-4

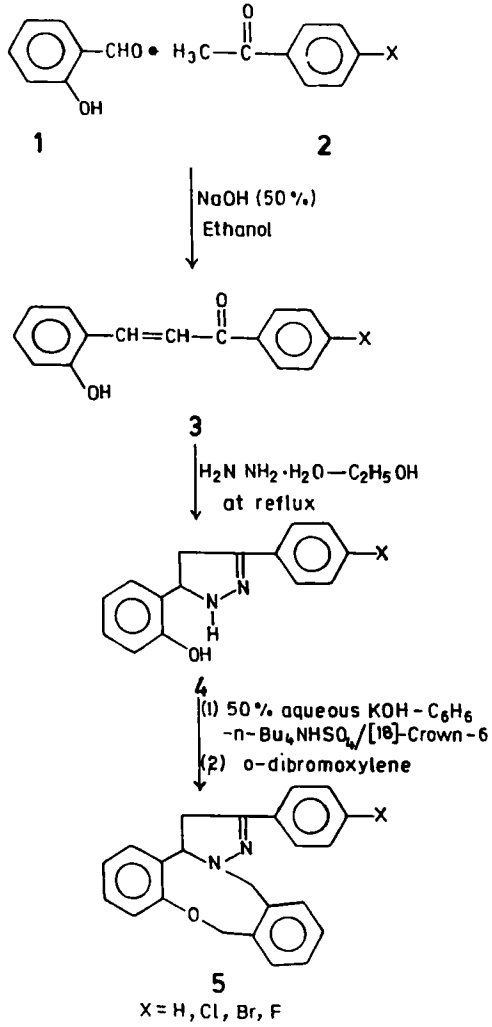
Spectroscopic data of 2,5,9,10-tetrahydro[7,8-g]benzo-8-arylpyrazolo [4,5-e] [1,5-b]benzoxazonine (5)

S. No.*	PMR (δppm) ($CDCl_3$/TMS)	IR (cm^{-1}) (KBr)	MS : (m/z)
1.	3 (m, 2H, -CH_2-), 4.25 (m, 2H, N-CH_2-Ph), 4.4 (m, 1H, -CH), 4.85 (m, 2H, O-CH_2-Ph), 6.2-7.4 (m, 13H, Ar-H)	3040-3080m (C-C stret. Ar), 2860-2990m (C-C stret. aliph.), 1600vs (>C=N), 1500m, 1450m, 1300w, 1240vs (C-O-C), 1100w, 1050w, 1000m, 840m, 780m.	-
2.	3 (m, 2H, -CH_2-), 4.3 (m, 2H, N-CH_2-Ph), 4.6 (m, 1H, -CH), 4.8 (m, 2H, O-CH_2-Ph), 6.0-7.2 (m, 12H, Ar-H)	3040-3080m (C-C stret. Ar), 2840-2990m (C-C stret. aliph.), 1600vs (>C=N), 1500s, 1450s, 1400w, 1350w, 1250 (C-O-C), 1100m, 1000w, 800m, 740m.	-
3.	3 (m, 2H, -CH_2-), 4.4 (m, 2H, N-CH_2-Ph), 4.6 (m, 1H, -CH), 4.8 (m, 2H, O-CH_2-Ph), 6.0-7.4 (m, 12H, Ar-H)	3030-3080m (C-C stret. Ar), 2850-2990m (C-C stret. aliph.), 1600vs (>C=N), 1500vs, 1450s, 1400w, 1350w, 1240 (C-O-C), 1100m, 1000m, 760m.	374 (M^+ 5%) 376 (M^+ 1.5%) 91 (100% $C_7H_7^+$)
4.	3 (m, 2H, -CH_2-), 4.2 (m, 2H, N-CH_2-Ph), 4.5 (m, 1H, -CH), 5.0 (m, 2H, O-CH_2-Ph), 6.3-7.6 (m, 12H, Ar-H)	3040-3090m (C-C stret. Ar), 2860-2990m (C-C stret. aliph.), 1600vs (>C=N), 1500m, 1450s (C-F), 1400m, 1350m, 1260vs (C-O-C), 1100m, 1000m, 760s.	358 (M^+, 6%) 44 (100%, F-C=CH^+)

*These Nos. correspond to S. Nos. of Table-3.

1.63 g) and tetra-n-butylammonium hydrogen sulphate (6 mmol, 2 g) in benzene (150 ml) was stirred. To this, potassium hydroxide solution (50%, 20 ml) was added dropwise with constant stirring at 30-35° C. After 30 minutes o-dibromoxylene (6 mmol, 1.58 g) in benzene (10 ml) was added dropwise and the reaction mixture was stirred for additional 10 hours. The benzene layer was washed with water (5×100 ml) and dried over anhydrous sodium sulphate and filtered. The filtrate was concentrated under vacuum and the product was recrystallised from petroleum ether and chloroform.

Yield - 2g (91%), m.p. 100°C.



Scheme-1

Other compounds prepared by this method are listed in the Table-3.

Second Procedure :

A mixture of 1H-4,5-dihydro-3-(4-chlorophenyl)-5-(2-hydroxyphenyl)pyrazole (4 mmol, 1g) and [18]-crown-6 (4mmol, 1g) in benzene (150 ml) was stirred. Then potassium hydroxide solution (50%, 20 ml) was added dropwise with constant stirring. After 30 minutes, o-dibromoxylene (4mmol, 1g) in benzene (10 ml) was added dropwise and stirring continued for additional 7-8 hours. The product was isolated and recrystallised in the usual manner.

Yield - 0.6g (46%). m.p. 100° C

Other compounds prepared by this method are listed in the Table-4.

A comparative study of these two procedures have revealed that for the preparation of the above mentioned compounds, the use of tetra-n-butylammonium hydrogen sulphate as a catalyst afforded better yields than [18]-crown-6 on equimolar ratio. However, for the generation of anions, the use of [18]-crown-6 is better as it required lesser time than the former.

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References

1. Starks C.M. and Liotta C.L. "Phase Transfer Catalysis Principles and Techniques", Academic Press, NewYork, **1978.**

2. Dehmlow E.V. and Dehmlow S.S. "Phase Transfer Catalysis", Verlag Chemie, Weinheim, **1980.**

3. Gallo R.J., Makosza M., Dou H.J.-M. and Hassanaly P. "Advances in Heterocyclic Chemistry", Academic Press, New York, Vol.*36*, **1984**, pp. 175.

4. Joshi K.C., Pathak V.N. and Gupta R. "*Indian J. Heterocyclic Chem.*" **1992**, *2*, 15.

5. Pathak V.N., Pathak R. and Oza C.K., "*Indian J. Heterocyclic Chem.*" **1995**, *5*, 103.

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