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NOTE

Intramolecular Thermal Cyclizations of Substituted N-Phenyl Cinnamamides by Polyphosphoric Acid

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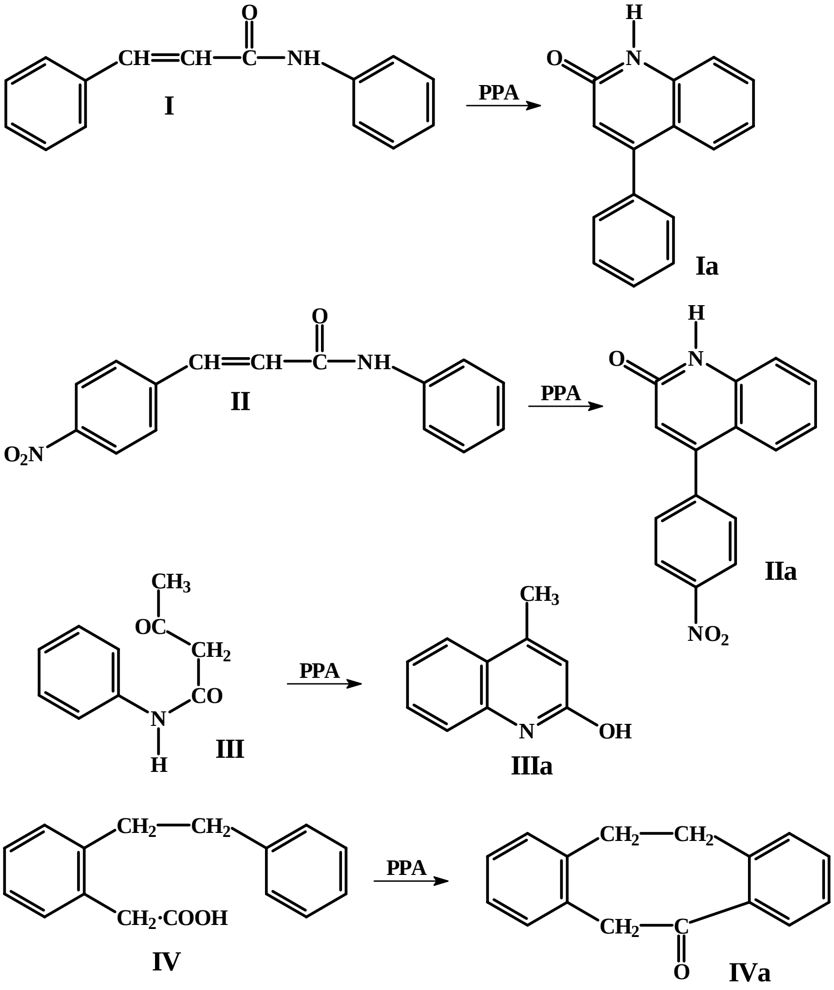
An efficient and simple method has been devised for the synthesis of substituted 3,4-dihydrophenyl carbostyrils using polyphosphoric acid as a reagent in excellent yields (80-95%).

Key Words: Carbostyrils, Cyclization, Polyphosphoric acid, Thermal reactions.

Carbostyrils[1] (nitrogen analogs of coumarins) are the important six membered heterocycles, which are the constituents of a variety of natural and synthetic products. Many different synthetic methods for the synthesis of the carbostyril rings have been developed. Various five, six, seven and eight membered ring compounds have been prepared in presence of PPA in good yields. Among five membered ring compounds many indanones[2], thianaphthenes, benzimidazoles[3], *etc.* have been reported in good yields[4,5]. A large number of carbostyrils in PPA have also been synthesized by Conley and koneke[6]. In the present work, the mixture of polyphosphoric acids (PPA) has been chosen for the preparation of substituted 3,4-dihydrophenyl carbostyrils.

Preparation of PPA : Polyphosphoric acid was prepared by adding phosphorus pentaoxide (50 g) gradually to glacial phosphoric acid (30 mL) with continuous stirring at room temp. After the addition of phosphorus pentaoxide, the mixture was heated at 60-70ºC for 2-4 h until a clear solution was obtained.

General preparation of carbostyrils: For the rearrangement of substituted (N-phenyl cinnamamides) and acetoacetanilide (4-5 g) were added to PPA (30-40 g), taken in a three necked round bottomed flask fitted with a mechanical stirrer and a thermometer. The mixture was then heated for 15-45 min at 70-145ºC. After the completion of the reaction which was indicated by the darkening of reaction mixture, it was cooled, poured into ice cold water and a crystalline solid was obtained, which was then filtered, dried and recrystallized from ethanol (**Scheme-I**).



Scheme-I

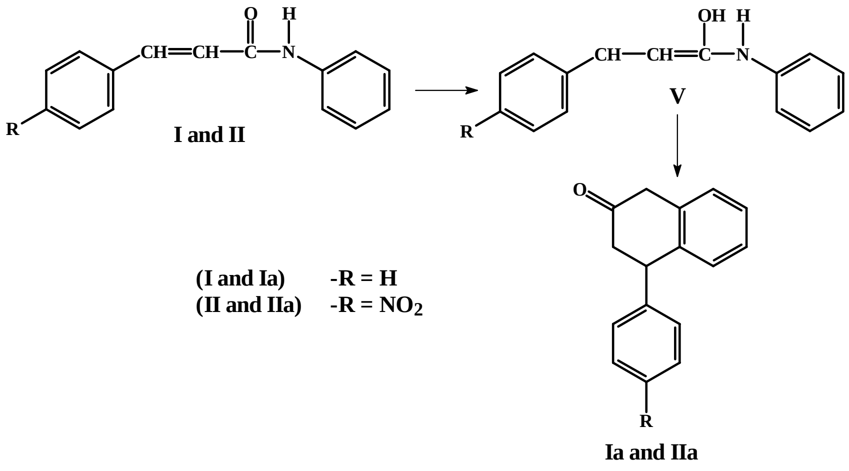
3,4-Dihydro-4-phenyl carbastyril (Ia): Prepared from N-phenyl cinnamamide (4 g) and PPA (40 g), heated at 80ºC for 15 min with continuous stirring, yield; 3.9 g (95 %), recrystallized from aqueous alcohol to get colourless shining needles m.p. 176ºC, IR (KBr, cm^{-1}); 3200-2700 (-NH str.), 1650 (>C=O, *sec*-amino), 1590, 1520 (arom.), NMR (DMSO, d$_6$: δ 9.75 (S, 1H, CONH), δ 6.63-7.65 (m, ArH).

3,4-Dihydro-4-(*p*-nitro)phenyl carbostyril (IIa): Prepared from N-phenyl-(*p*-nitro)cinnamamide (2 g) and PPA (30 g) at 140-150ºC for 20-25 min. Yield, 1.6 g (80%) recrystallized from methanol to get yellowish white shining needles, m.p. 278ºC. IR (KBr, cm^{-1}): 3200-2700 (NH), 1680 (>C=O *sec*-amide), 1510, 1330 (-NO$_2$), 1620 (arom.),840 (*p*-sub.), NMR (DMSO, d$_6$) : δ 9.23 (S, 1H, CONH), δ 7.5-8.2 (m, ArH).

4-Methyl carbostyril (IIIa): Prepared from acetoacetanilide (5 g), and (30 g), at 75ºC till darkening of the colour of the reactions. Yield 4.1 g (95 %). Recrystallized from ethanol to get white shining crystals, m.p. 223ºC, $C_{15}H_{10}N_2O_3$, Calcd. (found) %: N 10.48 (10.02), IR (KBr, cm^{-1}): 3320(-OH), 1640 (arom.), 1430, 1380 (-CH_3).

1,2,5,6-Dibenzo-1,5-cyclooctadiene-3-one (IVa): Prepared from O-(β-phenyl ethyl)phenyl acetic acid (5 g), PPA (250 g), at 100ºC for 2 h. The yellow coloured reaction mixture was then allowed to stand for 1 h at room temperature, poured in to ice cold water to get white solid which was filtered, washed first with 10% Na_2CO_3 solution and finally with water. Recrystallized from methanol to get shining colourless crystals, yield: 4.3 g (93%), m.p. 92ºC, $C_{10}H_9NO$, Calcd. (found) %: N 8.80 (8.92). IR (KBr, cm^{-1}: 1700 (>C=O), 1500, 1420 (arom.); NMR ($CDCl_3$) - δ 2.82 (s, 4H, CH_2-CH_2), 3.48 (s, 2H,CH_2CO), 7.57 (s, 8H,Ar).

The suggested mechanism for these cyclizations is as follows[7]: Substituted N-phenyl cinnamamide (**I & II**) readily undergoes protonation in hot PPA to give an intermediate (**V**) capable of undergoing a friedel crafts cyclization to give the required carbostyril.



(I and Ia) **-R = H**
(II and IIa) **-R = NO_2**

REFERENCES

1. H.R. Snyder and F.X. Werber, *J. Am. Chem. Soc.*, **72**, 2962 (1950).
2. S.I. Dev, *J. Indian Chem. Soc.*, **32**, 403 (1955).
3. N.Yu. Lebendenko, *Chem. Abstr.*, **92**, 94288 (1980).
4. C.L. Arcus and Prydal, *J. Chem. Soc.*, 1091 (1957).
5. O.P. Singhal and P.I. Ittyerah, *Curr. Sci.*, **36**, 373 (1967).
6. R.T. Conley and W.N. Knopka, *J. Org. Chem.*, **29**, 496 (1964).
7. J. Koo, *J. Org. Chem.*, **28**, 1134 (1963).

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