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NOTE

Synthesis of Some Biphenyl Compounds by Rearrangement of Salicyl Hydrazones in Polyphosphoric Acid

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Synthesis of some 3-(3'-carbamoyl-4'-hydroxy phenyl) aldehydes and ketones has been done by the rearrangement of salicyl hydrazones of aromatic aldehydes and ketones using polyphosphoric acid as a reagent. This procedure resulted in higher yields of compounds (75-85%)

Key Words: Polyphosphoric acid, Rearrangement.

The polyphosphoric acid (PPA) has been found to be of great use[1]. Earlier, it was recognized as an exceptional reagent for cyclizations[2,3], but its utility has also been found useful in various acid catalyzed reactions like condensations, estrifications, acylations, nitrations and sulphonations, *etc.* Intramolecular acylations of some aryl and aroyl aliphalic acids[4] and intermolecular cyclocondensations[5] have also been recently reported. PPA has been chosen because of its several advantages over conc. H_2SO_4 and HF, as it requires less precautions in handling.

In the present work, certain rearrangement reactions involving salicyl hydrazones of benzaldehyde, salicyl aldehyde, cinnamaldehyde and benzophenone have been carried out in presence of PPA.

Preparation of PPA[6]: Phosphorus pentoxide (50 g) was gradually added to glacial acetic acid (30 mL) with continuous stirring at room temperature. The mixture was heated at 60-70ºC for 2-4 h, till a clear solution was obtained. The PPA was prepared fresh each time for rearrangement of hydrazones.

Rearrangement

Step 1: Synthesis of salicyl hydrazones of carbonyl compounds (II-V): Salicyl hydrazone (0.3 g) was dissolved in ethanol (25-50 mL) by slight warming and then benzaldehyde, salicylaldehyde, cinnamaldehyde and benzophenone (3-4 g) were added to get the respective hydrazones. The reaction mixtures were refluxed for 5 to 20 min, then poured in to ice cold water to get the crystalline solid. The solid was filtered, washed, dried and recrystallized from methanol.

Step 2: Synthesis of 3-(3'-carbamoyl-4'-hydroxyphenyl) aldehydes and ketones: Salicylhydrazones prepared in the first step were added in portions (10-15 min) to preheated PPA (60-80ºC) with stirring. Then the warm solution was poured into ice cold water. The crystalline solid was filtered, washed, dried and recrystallized.

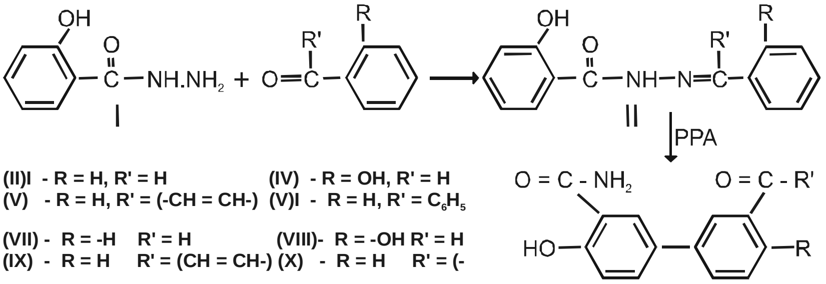
3-(3'carbamoyl-4-hydroxy phenyl) benzaldehyde (VII): Prepared from salicylhydrazones of benzaldehyde (4 g) and PPA (60 g) at 80ºC, recrystallized from isopropanol, yield 75 %, shining yellowish white crystals, m.p. 239ºC. Elemental analysis Found (%) : C = 70.03, H = 4.83, N = 5.92. IR (KBr, cm^{-1}) : 3300-2900, ν(-OH and -NH *Str.*), 1710 ν(>C=O, CHO), 1610 ν(>C=O, primary amide), 1560-1450 (aromatic) NMR (DMSO,d_6) δ 9.5 (s, 2H exchangeable with D_2O, $CONH_2$), 9.1 (s, 1H, CHO), 7.2-7.8 (m, ArH).

3-(3'-Carbamoyl-4'-hydroxy phenyl)salicyl aldehyde (VIII): Prepared from salicylhydrazone of salicylaldehyde (3 g) and PPA (50 g) at 100ºC, recrystallized from isopropanol, yield 83 %, yellowish white prisms, m.p. 209ºC. Elemental analysis Found (%) : C = 65.72, H = 4.82, N = 5.59. IR (KBr, cm^{-1}) : 3320 ν(-OH), 3040 ν(-NH), 1725 ν(>C=O, CHO), 1650 ν(>C=O, $CONH_2$), 1600-1520 (aromatic) NMR (DMSO, d_6) δ 9.62 (s, 2H, exchangeable with D_2O, $CONH_2$) 9.3 (s, 1H, CHO), 6.9-7.6 (m, ArH).

3-(3'-Carbamoyl-4'-hydroxy phenyl)cinnamaldehyde (IX): Prepared from salicylhydrazone of cinnamaldehyde (4 g) and PPA (60 g) at 80ºC, rescrytallized from isopropanol, yield 75 %, shining light yellow crystals, m.p. 244ºC. Elemental analysis Found (%) : C = 72.32, H = 4.96, N = 5.42. IR (KBr, cm^{-1}) : 3310 - 3000 ν(br, -OH, -CH=CH-), 1720 ν(>C=O, CHO), 1630 ν(>C=O, $CONH_2$), 1530-1450 ν(aromatic) NMR (DMSO,d_6) : δ 9.42 (s, 2H, exchangeable with D_2O, $CONH_2$), 9.2 (s, 1H, CHO), 7.8 (-CH=CH-CHO), 7.3 (m, ArH), 6.9 (CH=CH-CHO).

3-(3'-Carbamoyl-4' hydroxyphenyl)benzophenone (X): Prepared from salicylhydrazone of benzophenone (4 g) and PPA (40 g) at 100ºC. Recrystallized from isopropanol, yield 85 %, shining colourless long needles, m.p. 37ºC. Elemental analysis Found (%) : C = 75.93, H = 4.81, N = 4.01. IR (KBr, cm^{-1}) : 3320 ν(-OH), 3060 ν(-NH) 1730 ν(>C=O), 1650 ν(>C=O, $CONH_2$), 1600,1580 ν(aromatic). NMR (DMSO, d_6) δ 9.95 (s, 2H exchangeable with D_2O, $CONH_2$), 7.1-7.6 (m, ArH).

The rearrangement of salicyl hydrazones of carbonyl compounds can be explained on the basis of mechanism reported for Benzidine rearrangement[7]. It proceeds *via* a diprotonated substrate represented by a mesomeric structure with the positive charge localized on the hydroxyl groups. This protonated substrate then undergoes heterotytic fission at the nitrogen-nitrogen bond due to the strong repulsion exerted by the positive charges on the adjacent nitrogen atoms. Simultaneously, the new bond is formed on the basis of most favourable distribution of charges in the transition state (*para* with respect to hydroxy group, These positions are indicated as [5 and 5´], hence according to Woodward Hoffmann rules[8] this type of rearrangement can be coded as [5 and 5´] sigmatropic rearrangement. The same sigmatropic rearrangement has also been observed in the salicyl hydrazones of aldehydes and ketones which we have taken for the synthesis of biphenyl compounds (**V, VII, VIII** and **IX**).



IR spectra (cm^{-1}) showed the characteristic absorption bands at around 3320 (phenolic group), 1720 (aldehyde group) and 1650 (amide group). The formation of aldehyde group in the biphenyl systems has been further confirmed by the IR spectra of their 2,4-dinitro phenyl hydrazones.

In NMR spectra, the exchangeable protons such as amide and phenolic - OH appeared in the range δ 8-10 and aldehyde protons appeared in the range δ 9-9.5.

Conclusion

In conclusion, the use of polyphosphoric acid offers an alternate reagent for rearrangement reactions. The procedure is simple and resulted in higher yields of compounds without any side products.

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