SYNTHESIS AND REARRANGEMENT OF 1,2-DIPHENYL-2-(ARYLIMINO)ETHANOL DERIVATIVES

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Condensation of benzoin with *para*-substituted anilines, (X = H, Me, Cl) gave 1,2-diphenyl-2-(arylimino)ethanol derivatives (I), which were thermally stable up to 130 °C, but rearranged to 1,2-diphenyl-2-(arylimino)ethanol derivatives (II), under catalyzed effect of phenylhydrazine, *para*-substituted aniline and triethylamine. The products were characterized by IR- and NMR- spectral analysis.

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Introduction

Many aldehyde and ketones contains α-hydrogen react with primary amines to form Schiff bases (imine) which are in equilibrium with its en-amine tautumer.[1-3]

Reducing sugars like aldoses and ketoses are α-hydroxy aldehydes and ketones containing an α-hydrogen and react with free amino-group of amino acids, peptides and protein in what is known as "Maillarad reaction".[4,5] It is complicated reaction, well described by Hodge,[6,7] with initial formation of an unstable Schiff base (imine) of an open chain aldose or ketose, cyclized to an aldosyl amine or ketosyl amine followed by enolization and molecular rearrangement to give 1-amino-1-deoxy-2-ketose (Amadori product)[7,8] ,and 2-amino-2-deoxyaldose (Heyne product),[8,9] respectively.

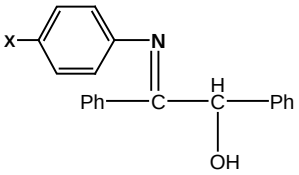
α-Hydroxy ketones with tertiary OH-group undergo basic catalyzed rearrangement, however, in ketones with secondary OH-group enolization is more favored than rearrangement.[10,11] α-Hydroxy Schiff bases in which OH-group is tertiary, undergo thermal rearrangement to yield α-amino ketones.[10,12] Present work involves synthesis of 1,2-diphenyl-2-(arylimino)ethanol derivatives (I) as α-hydroxy Schiff bases with secondary OH-group, and investigation of their rearrangement both thermal and catalyzed by bases like phenylhydrazine, *para*-substituted aniline and triethylamine.

Experimental

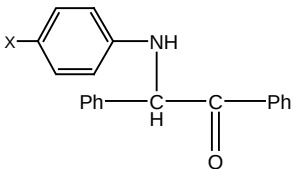
All chemicals used were of reagent grade (supplied by Sigma- Aldrich) and used as supplied. Melting points were recorded on an Electrothermal stuart apparatus and are uncorrected. IR- spectra were recorded on Euro OV Ectro FT-IR 8400s infrared spectrophotometer and ^{1}H NMR spectra were recorded on a DPX400 instrument, with $CHCl_3$ as solvent.

Synthesis of 1,2-diphenyl-2-(arylimino)ethanol derivatives (I), (X = H, Me, Cl).[13]

A mixture of equimolar amount of benzion and *para*-substituted anilines, (X = H, Me, Cl) in a small amount of ethanol was heated at 120 °C for 1 h and then the reaction mixture was cooled. The residue obtained was recrystallized from ethanol to give 1,2-diphenyl-2-(arylimino)ethanol derivatives (I), Table 1.



(I), (X= H, Me, Cl)



(**II**), (X= H, Me, Cl)

Rearrangement of 1,2-diphenyl-2-(arylimino)ethanol derivatives (I), (X = H, Me, Cl).

(i) Thermal effect

Benzoin Schiff bases (IA, IB, IC) (10 mmol) were heated in an oil bath at 130°C for 1h, cooled and recrystallized from ethyl alcohol to give rearrangement products of (IA, IB, IC) respectively. Identity of the products were confirmed by mixed melting points of reaction products (IA, IB, IC) with authentic (IA, IB, IC) compounds, also by comparing the IR-spectra of reaction products with those of authentic compounds.

(ii) Base catalyzed Rearrangement

A mixture of (10 mmol) of benzoin Schiff base (IA, IB, IC) and (10 mmol) solution of (phenylhydrazine hydrochloride-sodium acetate in 2ml water), in 10 ml ethyl alcohol were heated for 30 min. in a water bath, cooled, precipitate formed was filtered and washed with ethyl alcohol-water to give 1,2-diphenyl-2-(arylimino)ethanol derivatives (**II**). The data are given in Table 2.

Table 1. Physical and spectroscopic parameters of compound (I) derivatives.

Compound I	m.p.(°C)	Yield %	IR- υ (cm^{-1})		^{1}H NMR (δ, ppm)			
			OH	CN	OH	CH	Ph	Me
A(X=H)	124-6	76	3400-3375	1667	-	-	-	-
B(X=Me)	118-20	79	3380-3360	1665	4.6	6.0	7.2-7.9	2.2
C(X=Cl)	123-4	87	3400-3370	1670	4.5	5.9	7.2-8.0	-

Table 2. Physical and spectroscopic parameters of compound (II) derivatives.

Compound II	m.p.°C	IR- υ (cm^{-1})		^{1}H NMR (δ, ppm)				^{13}C NMR (δ, ppm)			
		NH	C=O	NH	CH	Ph	Me	Me	CH	Ph	C=O
A(X=H)	138-40	3500	1670	-	-	-	-	-	-	-	-
B(X=Me)	143-5	3507	1670	5.2	5.9	6.5-7.9	2.1	20	63	113-134	197
C(X=Cl)	157-9	3504	1672	5.3	6.0	6.6-8.0	-	-	-	-	-

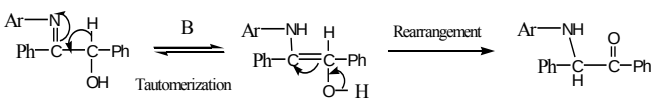
Similar results were obtained as in (i) by refluxing equimolar amounts of benzoin Schiff base (IA, IB, IC) with *para*-substituted aniline and triethylamine in ethyl alcohol for 30 min.

Results and Discussion

Benzoin Schiff bases (IA, IB, IC), α-hydroxy imines with secondary OH-groyp, were synthesized by a direct condensation of benzoin with *para*-substituted anilines, (X = H, Me, Cl) at 120◦C and characterized by their melting points. IR- spectral data showed strong-broad OH-stretching bonds in the range of 3400-3360 cm^{-1} beside sharp-medium stretching bonds of imino (C=N) group at 1667, 1665, 1670 cm^{-1} for (IA, IB, IC) respectively. ^{1}H NMR- spectra showed OH and CH signals for (IB and IC) at (δ, ppm), [4.6 (1H, d), 6.0 (1H, d)] and [4.5 (1H, d), 5.9(1H, d)] respectively.

Benzoin Schiff bases (IA, IB, IC) were found to be thermally stable up to 130°C (above their melting points), but rearranged up on heating with equimolar amount of base like phenylhydrazine to 1,2-diphenyl-2-(arylimino)ethanol derivatives (IIA, IIB, IIC) respectively, which are characterized by their melting points and IR spectra. IR-spectra showed a sharp-medium N-H stretching bands at 3500, 3507, 3504cm-1 and sharp-strong C=O stretching bands at 1670, 1670, 1672cm-1 for (IIA, IIB, IIC) respectively. ^{1}H NMR spectra for compound (IIB and IIC) showed NH and CH signals at (δ, ppm), [5.2 (1H, s), 5.9 (1H,s)] and [5.3 (1H, s), 6.0 (1H, s)] respectively. ^{13}C NMR spectrum for compound (IIB) showed Me, CH, Ph, C=O carbon signal at 20, 63, 113-134, 197 ppm respectively. Similar results were obtained on heating benzoin Schiff base (IA, IB, IC) with equimolar amount of *para*-substituted anilines, (X = H, Me, CL) or triethylamine.

Based on the above results we can conclude that benzoin Schiff base (IA, IB, IC) are thermally stable up to their melting points, but enamination takes place ontreartment with bases like phenylhydrazine, *para*-substituted aniline or triethylamine respectively to enol-amine tautumer which are rearranged to more stable 2-amino ketones (IIA, IIB, IIC) as in the following manner.



(I) (II)

where

Ar = *para*- substituted phenyl with X=H, Me, Cl

B=phenylhydrazine, *para*-substituted aniline, or triethyl amine.

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