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BEHAVIOUR OF *O*- HYDROXYCHALCONES TOWARDS THE ACTION OF PHENYLHYDRAZINE, HYDROXYLAMINE, PRIMARY ALIPHATIC AMINES AND PARAFORMALDEHYDE

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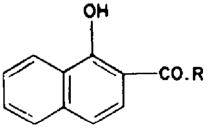
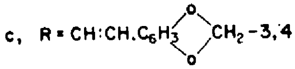
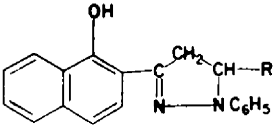
Abstract—The action of phenylhydrazine and hydroxylamine hydrochloride on the *o*-hydroxychalcones (Ia and b) yields the pyrazoline and iso-oxazoline derivatives (IIa and b; IIIa and b) respectively. The action of primary aliphatic amines on IIa and b affords 2-acetyl-1-naphthol N-alkylimines (Va–c). Ia–d react with paraformaldehyde, yielding quantitatively the 3,3′-diacyl-4,4′-dihydroxydinapthylmethane derivatives IVa–d. The IR and NMR spectra of the products are discussed.

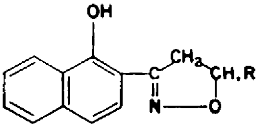
IN GENERAL, phenylhydrazine and hydroxylamine hydrochloride react readily with α, β-unsaturated ketones producing pyrazolines and iso-oxazolines respectively. This reaction has now been extended to 2-cinnamoyl-1-naphthol (Ia) and 2-*p*-methoxycinnamoyl-1-naphthol (Ib). The reaction with phenylhydrazine in boiling pyridine yields phenylhydrazones which rearranged immediately to the isomeric pyrazolines IIa and b. The products give the colour test[1] for pyrazolines (a drop of ferric chloride solution added to a concentrated sulphuric acid solution of the compound gives a blue-violet colour). When a pyridine solution of Ia and/or Ib and hydroxylamine hydrochloride are refluxed the iso-oxazoline derivatives IIIa and b are obtained.



Ia, $\mathrm{R = CH{:}CH.C_6H_5}$
b, $\mathrm{R = CH{:}CH.C_6H_4.OCH_3}$-*p*
c, 
$\mathrm{R = CH{:}CH.C_6H_3{<}^{O}_{O}{>}CH_2}$-3,4
d, $\mathrm{R = CH{:}CH.CH{:}CH.C_6H_5}$
e, $\mathrm{R = CH_3}$



IIa, $\mathrm{R = C_6H_5}$
b, $\mathrm{R = C_6H_4.OCH_3}$-*p*



IIIa, $\mathrm{R = C_6H_5}$
b, $\mathrm{R = C_6H_4.OCH_3}$-*p*

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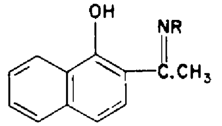
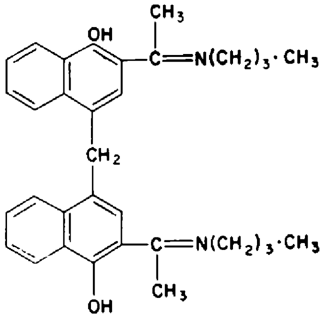
[1] V. Knorr, *Liebigs Ann.* **238**, 200 (1887).

The action of primary aliphatic amines on Ia and b has also been investigated. Thus treatment of an alcoholic solution of Ia and/or Ib with aliphatic amines namely, methylamine, ethylamine and/or butylamine, does not yield the addition products VI (R′ = C_6H_5 or $C_6H_4 \cdot OCH_3$-*p*), but the chalcone undergoes fission at the double bond (CH=CH) by the action of the amine, with the formation of 2-acetyl-1-naphthol (Ie). The resulting Ie condenses rapidly with the amine yielding the 2-acetyl-1-naphthol N-alkylimines (IVa–c). Acid hydrolysis of IVa–c affords Ie. The same products (IVa–c) have been obtained[2] by the condensation of primary aliphatic amines with Ie. In a similar way V has been obtained by the action of butylamine on either VIIa or VIIe. The hydrolysis of Ia and b to Ie by the action of primary aliphatic amines simulates the hydrolysis of flavones with alcoholic potassium hydroxide.[3]

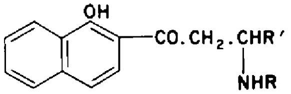


IVa, R = CH_3
b, R = CH_2CH_3
c, R = $CH_2.CH_2.CH_2.CH_3$

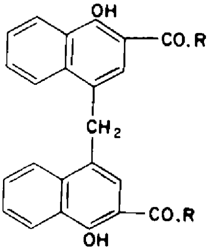


V

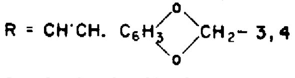
VI



Recently,[4] it has been found that the action of paraformaldehyde on Ie in boiling amyl alcohol and in presence of hydrochloric acid yields the corresponding methylene-bis-derivative (VIIe). This reaction has now been extended to Ia, b, c and d. Two molecules of the chalcone condense with one molecule of paraformaldehyde yielding quantitatively the 3,3′-diacyl-4,4′-dihydroxydinaphthylmethane derivatives (VIIa–d).



VIIa, R = CH:CH. C_6H_5
b, R = CH:CH. $C_6H_4.OCH_3$-*p*



c, R = CH·CH. $C_6H_3\langle{}^{O}_{O}\rangle CH_2$– 3,4
d, R = CH·CH.CH·CH. C_6H_5
e, R = CH_3

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[2] A. E. A. Sammour, *J. Org. Chem.* in press.
[3] S. K. Mukerjee and T. P. Seshadri, *Chem. & Ind.* 271 (1955).
[4] A. Schönberg, A. Fateen and A. Sammour, *J. Org. Chem.* **23**, 2025 (1958).

The formation of the methylene-bis-derivatives of the chalcones and not of the isomeric flavanones is confirmed by the fact that these products give colour reactions with ferric chloride and that VIIb and VIIc were also obtained by the condensation of VIIe with anisaldehyde and piperonal in alcoholic sodium hydroxide solution.

The intense IR absorption of compounds IIa and b are due to the C=N group at 1625 cm, the OH group at 3300 cm^{-1}, the $>$CH group at 2590 cm^{-1} and the $C_6H_5\overset{|}{N}$ group at 1590 cm^{-1}. The condensed NMR absorption spectrum of IIa and b show a hydroxyl group (4·3 ppm) and CH_2 group (1·8 ppm).

The IR spectra of IIIa and b exhibit bands attributable to OH group (3300 cm^{-1}); $>$C=N (1625 cm^{-1}), and $>$CH group (2590 cm^{-1}) and their condensed NMR spectra show an hydroxyl group (4·3 ppm) and CH_2 group (1·8 ppm).

The intense IR absorption of IVb at 1625 cm^{-1} and 3300 cm^{-1} is due to the $>$C=N and the OH groups respectively. The spectrum does not show the CH=CH nor the NH bands. The NMR absorption spectrum of IVb shows the CH_2 of ethyl group (3·5 ppm in the wide spectrum and 1·8 ppm in the condensed spectrum), CH_3 of ethyl group (1·4 ppm in the wide spectrum and 0·7 ppm in the condensed spectrum), CH_3 of the $>$C=N—CH_3 (2·3 ppm in the wide spectrum and 1·2 ppm in the condensed spectrum) and *a*-hydroxyl group (4·3 ppm in the condensed spectrum and 3·4 ppm in the wide spectrum). The NMR spectrum of IVb does not show any other protons. If the number of protons (other than the methyl and ethyl groups) are counted by comparing the integrated area of the aromatic rings (between 6·7 and 7·6 ppm) with the integrated area of the methyl group, we find only six protons which are those on the naphthalene ring. The NMR spectrum does not show CH=CH C_6H_5, a methylene nor NH groups.

The suggested structure for VIIa–d is given support by the presence of a medium intensity band at 970 cm^{-1} (*cis*-CH=CH) and 735 cm^{-1} (*trans*-CH=CH). The hydroxyl group does not appear in the IR spectrum due to chelation but in the NMR spectrum it appears at 3·4 ppm.

EXPERIMENTAL

All m.p.s are uncorrected. The IR absorption spectra were determined with a Perkin-Elmer model 137 B spectrophotometer in KBr discs in concentrations of 0·1–0·5%. All NMR measurements were determined on 5% solutions in chloroform at 40 MC. with a Varian Associates Model V4300 B spectrometer, using tetramethylsilane as the internal reference.

2-*Cinnamoyl*-1-*naphthol* (Ia) *and phenylhydrazine*

A mixture of phenylhydrazine (2 ml) and 2-cinnamoyl-1-naphthol[5] (2 g) in 10 ml pyridine was refluxed 4 hr. The cooled mixture was acidified with dil. acetic acid. The deposit was crystallized from benzine (b.p. 100–120°) as yellow crystals, m.p. 185°, yield 85%. Compound IIa gives a blood red solution with conc. H_2SO_4 which on treatment with $FeCl_3$ aq. gives a blue colour Its alcoholie solution gives a deep green colour with alcoholic $FeCl_3$ and gives a blue colour with phosphomolybdic acid. (Found: C, 82·13; H, 5·68; N, 7·72; $C_{25}H_{20}N_2O$, requires: C, 82·39; H, 5·53; N, 7·69%).

2-(p-*Methoxy cinnamoyl*)-1-*naphthol* (Ib) *and phenylhydrazine*

The same procedure was followed with Ib,[6] and IIb was crystallized from benzine (b.p. 100–120°)

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[5] V. Kostannecki, *Ber. Dtsch. Chem. Ges.* **21**, 705 (1898).

[6] Pfeiffer and Grimmer, *Ber. Dtsch. Chem. Ges.* **50**, 911 (1917).

as yellow crystals, m.p. 179°; yield 80%. (Found: C, 79·32; N, 5·80; N, 6·98; $C_{26}H_{22}N_2O_2$, requires: C, 79·16; H, 5·62; N, 7·10%).

2-*Cinnamoyl*-1-*naphthol and hydroxylamine hydrochloride*

A mixture of 1·2 g hydroxylamine hydrochloride in 5 ml water and 1 g of Ia in 10 ml pyridine was refluxed 4 hr. The cooled mixture was acidified with dil. acetic acid and the deposit crystallized from benzene as colourless crystals, m.p. 208°; yield 87%. Compound IIIa gives a yellow colour with conc. H_2SO_4 and no colour with alcoholic $FeCl_3$ solution. (Found: C, 79·12; H, 5·30; N, 5·17; $C_{19}H_{15}NO_2$, requires: C, 78·97; H, 5·23; N, 4·84%).

2-(p-*Methoxy cinnamoyl*)-1-*naphthol and hydroxylamine hydrochloride*

The same procedure was followed and the IIIb obtained was crystallized from benzene as colourless crystals, m.p. 214° with red melt; yield 84%. (Found: C, 75·43; H, 5·40; N, 4·52; $C_{20}H_{17}NO_3$, requires: C, 75·22; H, 5·37; N, 4·39%).

Action of methylamine on Ib

An alcoholic solution of Ib (0·01 mole) and methylamine (0·03 mole) was refluxed 5 hr. The yellow solid product was crystallized from benzine (b.p. 100–120°); identified as IVa; m.p.[2] and mixed m.p. 140°; yield 79%. (Found: C, 78·46; H, 6·58; N, 7·05; Calc. for $C_{13}H_{13}NO$: C, 78·36; H, 6·59; N, 7·03%).

Action of ethylamine on Ia

An alcoholic solution of Ia (0·01 mole) and ethylamine (0·03 mole) was refluxed 5 hr. The reaction mixture was cooled and the yellow solid product crystallized from benzine (b.p. 80–100°); identified as IVb; m.p.[3] and mixed m.p. 129°, yield 70%. (Found: C, 78·43; H, 7·15; N, 6·61; Calc. for $C_{14}H_{15}NO$: C, 78·84; H, 7·08; N, 6·57%).

Action of ethylamine on Ib

An alcoholic solution of Ib (0·01 mole) and ethylamine (0·03 mole) was refluxed 5 hr. The yellow solid product crystallized from benzine (b.p. 80–100°), identified as IVb; m.p.[3] and mixed m.p. 129°; yield 70%. (Found: C, 78·73; H, 7·39; N, 6·56; Calc. for $C_{14}H_{15}NO$; C, 78·84; H, 7·09; N, 6·57%).

Action of butylamine on Ia

The IVc, m.p.[3] and mixed m.p. 109° was obtained in a 72% yield. (Found: C, 79·48; H, 7·94; N, 5·85; Calc. for $C_{16}H_{19}NO$: C, 79·62; H, 7·94; N, 5·80%).

Action of butylamine on Ib

The IVc, m.p.[3] and mixed m.p. 109° was obtained in a 72% yield. (Found: C, 79·81; H, 8·00; N, 5·78; Calc. for $C_{16}H_{19}NO$: C, 79·62; H, 7·94; N, 5·80%).

Action of hydrochloric acid on IVa

Compound IVa (0·5 g) was heated under reflux with 25 ml dil. HCl aq. (20%) for ½ hr. The pale yellow solid product was identified as 2-acetyl-1-naphthol (0·3 g), m.p. and mixed m.p. 103°. The original aqueous mother liquors were evaporated (red. press.) and the residue washed with ether and dried, identified as methylamine hydrochloride (0·1 g), m.p. and mixed m.p. 230°.

Action of butylamine on VIIe

A mixture of VIIe (2 g); amyl alcohol (20 ml) and butylamine (3 ml) was heated under reflux for 2 hr. The yellow solid (V) was crystallized from benzene; m.p. 220°, yield 65%. (Found: C, 80·02; H, 7·53; N, 5·66; $C_{33}H_{38}N_2O_2$, requires: C, 80·12; H, 7·74; N, 5·66%).

Action of butylamine on VIIa

A mixture of VIIa (2 g), amyl alcohol (20 ml) and butylamine (3 ml) was heated under reflux for

5 hr. The yellow solid product was crystallized from benzene, identified as V, m.p. and mixed m.p. 220°; yield 60%.

3, 3′-*Dicinnamoyl-4,4′-dihydroxydinaphthyl)methane* (VIIa)

A mixture of 2-cinnamoyl-1-naphthol (1 g), paraformaldehyde (0·5 g), amyl alcohol (20 ml) and conc. HCl aq. (1 ml) was refluxed 3 hr. The orange crystalline product (VIIa) was crystallized from benzene, m.p. 270°; yield 0·9 g. A solution of VIIa in dioxane gives a wine red colour with alcoholic $FeCl_3$ solution. (Found: C, 83·48; H, 5·16; $C_{39}H_{28}O_4$, requires: C, 83·55; H, 5·03%).

(3,3′-*Di*(p-*methoxy cinnamoyl*)-4,4′-*dihydroxydinaphthyl*) *methane* (VIIb)

(a) A mixture of Ic[7] (1 g), paraformaldehyde (0·5 g), amyl alcohol (20 ml) and conc. HCl aq. (1 ml) was refluxed 3 hr. The orange product (VIIb) was crystallized from benzene, m.p. 260°, yield 95%. A solution of VIIb in dioxane gives a wine red colour with alcoholic $FeCl_3$ solution. (Found: C, 79·43; H, 5·30; $C_{41}H_{32}O_6$, requires: C, 79·34; H, 5·20%).

(b) To a mixture of VIIe[4] (1 g) and 8 ml 30% ethanolic NaOH solution was added a solution of anisaldehyde (2 ml) in 10 ml ethanol. The red solution was heated on a steam bath for 1 hr then allowed to stand for 24 hr. The mixture was diluted with water and acidified and the orange solid crystallized from benzene, identified as VIIb, m.p. and mixed m.p. 260°, yield 76%. Its dioxane solution gives a wine red colour with alcoholic $FeCl_3$ solution. (Found: C, 79·49; H, 5·26; Calc. for $C_{41}H_{32}O_6$, C, 79·34; H, 5·20%).

3,3′-*Di*(3″,4″-*methylenedioxy cinnamoyl*)-4,4′-*dihydroxydinaphthyl*)-*methane* (VIIc)

(a) A mixture of Ic (1 g), paraformaldehyde (0·5 g), amyl alcohol (20 ml) and conc. HCl aq. (1 ml) was refluxed 3 hr. The orange red crystals of VIIc were crystallized from benzene, m.p. 282°, yield 94%. The dioxane solution of VIIc gives a wine red colour with alcoholic $FeCl_3$ solution. (Found: C, 76·24; H, 4·51; $C_{41}H_{28}O_8$, requires: C, 75·92; H, 4·32%).

(b) To a mixture of VIIe[4] (1 g) and 8 ml 30% ethanolic NaOH solution was added a solution of piperonal (1·5 g) in 10 ml ethanol. The red solution was heated on a steam bath for 1 hr then allowed to stand 24 hr. On dilution with water and acidification the orange red product was crystallized from benzene; identified as VIIc, m.p. and mixed m.p. 282°, yield 75% (Found: C, 76·26; H, 4·59; Calc. for $C_{41}H_{28}O_8$: C, 75·92; H, 4·32%).

3,3′-(*Dicinnamylideneacetyl*)-4,4′-(*dihydroxydinaphthyl*)-*methane* (VIId)

This was obtained from Id[8] and paraformaldehyde. It was crystallized from benzene as orange crystals, m.p. 210°, yield 89%. Its solution in dioxane gives a wine red colour with alcoholic $FeCl_3$ solution. (Found: C, 84·49; H, 5·38; $C_{43}H_{32}O_4$, requires: C, 84·31; H, 5·22%).

Ethylation of VIIe

A mixture of VIIe (2 g), anhydrous acetone (50 ml), anhydrous K_2CO_3 (3 g) and ethyl iodide (10 ml) was heated under reflux till one drop of the solution gives no green colour with alcoholic $FeCl_3$ solution (10 hr). The acetone was evaporated, water was added to dissolve the inorganic, substances and the residue crystallized from benzine (b.p. 100–120°) as colourless crystals, m.p. 164°, yield 85%. (Found: C, 79·07; H, 6·36; $C_{29}H_{28}O_4$, requires: C, 79·09; H, 6·36%).

Acknowledgement—The author is greatly indebted to Dr. Tawfik Elzimaity, University of Delaware, for determination of and his interest and advice in the infrared and NMR spectra.

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[7] Pfeiffer, Kalckrennee, Kunze and Levin, *J. Prakt. Chem.* (2) **119**, 109 (1928).

[8] U. Cheema, K. Gulati and K. Venkataraman, *J. Chem. Soc.* 925 (1932).