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Aldehyde Condensation Products of 4-Hydroxycoumarin and Schiff Bases

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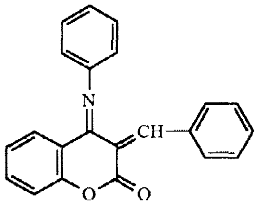
Abstract: 4-Hydroxycoumarin and Schiff bases condense in glacial acetic acid at reflux. Benzylidenephenyliminochroman or 3,3'-(p-substituted-arylmethylidene)-bis-4-hydroxycoumarin are the final products.

Nearly twenty years ago Dike and Merchant investigated the reaction of 4-hydroxycoumarin with Schiff bases in acidic medium.The experiments involved condensation of one mole 4-hydroxycoumarin with two moles benzylideneaniline in glacial acetic acid at 30 °C for 1-3 hrs.The product was benzopyranooxazine with molecular mass 431 ($C_{29}H_{21}NO_3$) and melting point 169-170 °C.[1]

Our attempts to repeat these experiments and results failed. The reaction described above was carefully carried out with 4-hydroxycoumarin and benzylideneaniline, p-methoxybenzylideneaniline and p-chlorobenzylideneaniline at the same molar ratio in glacial acetic acid at 30 °C for 1, 3, 10 hrs and longer but there was not any interaction. Only the starting substances were in the reaction mixture. There was no condensation process too when the reaction was carried out in methanol as a solvent.

The same reaction mixture in glacial acetic acid as a solvent was refluxed for 13 hrs and after cooling a crystalline product was separated. After recrystallization the m. p. of the pure product was 299-302 °C. Elemental analysis revealed a molecular formula $C_{22}H_{15}NO_2$ confirmed by its MS (M^+ 325) taken at 70 eV (Jeol 300 D - Japan). ^{1}H-NMR ([D_6]-DMSO) showed a singlet for a proton at δ 5,3 ppm and a multiplet at δ 6,8 - 7,7 ppm corresponding to 14 aromatic protons. The IR (nujol) spectrum showed a band at 1660-1620 cm^{-1} for the conjugated double bonds and a band at 750 cm^{-1} for the monosubstituted aromatic nucleus.



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On the basis of the structure of the new product we suppose that probably Schiff base is hydrolysed in acetic acid medium. After Schiff base is hydrolysed aromatic aldehyde attacks No 3 carbon atom and aniline attacks No 4 carbon atom in 4-hydroxycoumarin. The final product is 3-benzylidene-4-phenyliminocoumarin after a subsequent (or a simultaneous) detachment of two water molecules.

In order to confirm this type of interaction a condensation process between 4-hydroxycoumarin and aniline at molar ratio 1:17 (w. p.) was carried out. The reaction mixture was refluxed for 45 min. and 4-phenyliminocoumarin was obtained (m. p. 273-4 °C, yield 44 %, TLC pure product).[2] Then 4-phenyliminocoumarin was refluxed with benzaldehyde in glacial acetic acid for 17 hrs. The product was 3-benzylidene-4-phenyliminocoumarin, the same as the one obtained by the condensation process between 4-hydroxycoumarin and benzylideneanilin in glacial acetic acid.

The reaction followed a different pathway with new end produts when starting substances were 4-hydroxycoumarin and 4-methoxybenzylideneaniline or 4-chlorobenzylideneaniline. 3,3′-(Arylmethylidene)-bis-4-hydroxycoumarins were obtained instead of 3-arylmethylidene-4-phenyliminocoumarins. The structures of these compounds were confirmed by elemental analyses, IR, ^{1}H-NMR and MS spectra.

This unexpected way of the condensation process can be explained by the presence of substituents with electronodonors′ properties at para-position of the aromatic nucleus in Schiff bases. That's the reason why the distribution of electrone density prevents further interaction between arylmethylidenechromanocoumarin and phenylammonium acetate. After alkalization anilin is found in the filtrate.

These products are synthesized by the interaction of 4-hydroxycoumarin with aromatic aldehydes (4-methoxybenzaldehyde[3,4,6] and 4-chlorobenzaldehyde[5]) in boiling alcohol or in glacial acetic acid medium at reflux. The structure of the end products is identical to the one of the substances described above, which fact has been proven in an unequivocal way.

REFERENCES

1. Dike, S.Y., Merchant, J. R., Tetrahedron Lett. **1978**, 38, 3607-3608.
2. Tabacovic, K., Tabacovic, I., Ajdini, N., Leci, O. Synthesis **1987**, 308-310.
3. Sullivan, W. R., Huebner, C. F., Stahmann, M. A., Link, K. P. J. Am. Chem. Soc. **1943**, 65, 2288-2291.
4. Klosa, J. Apoth. Ztg. **1952**, 4, 55-56.
5. Fucik, K. Czech. Pat. 86515, **1957**, May 15.
6. Eckstein, M., Kocwa, A., Pazdro, H. Roczniki Chem. **1958**, 32, 801-811.