

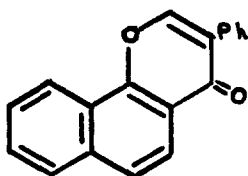
3-PHENYLNAPHTHO [1,2-b]-PYRAN-2-ONE. A REVISION¹.

Arun K. Das Gupta[‡], Rabindra M. Chatterje and Sailendra N. Choudhuri
Department of Chemistry, Research Division, East India Pharmaceutical
Works Ltd., Calcutta-700060, India.

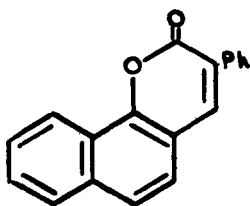
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Condensation of α -naphthol with α -formyl-phenylacetonitrile in the presence of glacial acetic acid and dry hydrogen chloride leading to the formation of an iminochloride, which on hydrolysis cyclises to 3-phenyl-naphtho [1,2-b]-pyran-4-one (1) m.p. 169-170^o, has been reported² by Ghosh. Baker revised³ the structure of the pyrone (1) as the isomeric 3-phenyl-naphtho [1,2-b]-pyran-2-one (2) which has generally being accepted⁴. Venkataraman further corroborated Baker's view by the synthesis of pyrone 1 m.p. 187^o following an unambiguous route⁵. We have recently synthesised⁶ pyrone 2 with m.p. 214-215^o. These discrepancies in the literature led us to repeat the condensation reaction, as the compound described by Ghosh² with m.p. 169-170^o is neither (1) nor (2).

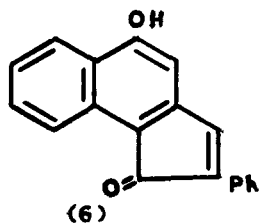
Without any modification to the method described², a material m.p. 130-135^o was obtained which on treatment with dilute sulphuric acid gave a brown solid which could not be purified by crystallisation. By careful column chromatography over deactivated alumina three isolable materials were obtained. The first compound was non-nitrogenous m.p. 248-249^o (MeOH). IR 3340 (OH) and 1745 cm⁻¹; UV 239, 296 (br), 327 nm (log ϵ 4.7, 4.1 and 3.7). Elemental analyses fits all the probable structures 6, 7 and 8. From the IR and mass spectra results (M, 416) it is reasonable to consider the lactonic structure 8 in preference to the other ketonic structures 6 or 7. Methylation of 8 gave the corresponding methoxy lactone (9) m.p. 257-258^o, (M, 430); IR 1760 cm⁻¹ (lactone). The NMR spectra is also in agreement with structure 8.



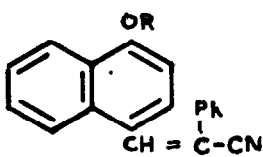
(1)



(2)

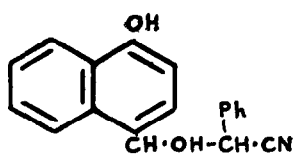


(6)

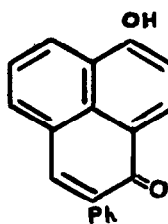


(3) R = H

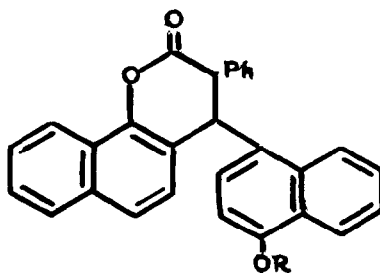
(4) R = Me



(5)



(7)



(8) R = H

(9) R = Me

The second compound is found to be yellow nitrogenous with m.p. 204-205° (MeOH). IR 3350 (OH), 2225 cm⁻¹ (CN); UV 245 (br), 375 nm (log ε 4.3 and 4.2). Methylation with dimethyl sulphate afforded the corresponding methoxy compound (4) m.p. 129-130° found to be identical with an authentic sample of β-(4-methoxy-1-naphthyl)-α-phenyl acrylonitrile⁶ (identical mixed m.p., ir and t.l.c.); IR 2227 cm⁻¹ (CN), UV 244, 360 (br) nm (log ε 4.3 and 4.2). Hence the nitrile is β-(4-hydroxy-1-naphthyl)-α-phenylacrylonitrile (3).

The third compound is also found to be nitrogenous m.p. 224-225° (benzene) IR 3360 (OH), 2240 cm⁻¹ (nitrile); UV 242, 310, 328 nm (log ε 4.4, 4.0 and 3.9). Elemental analyses indicated an empirical formula C₁₉H₁₅NO₂. Treatment of this nitrile with toluene-p-sulphonic acid in boiling benzene gave the nitrile (3) m.p. 204-205° obtained earlier (identical mixed m.p. and ir). Hence structure 5 has been assigned to this hydroxy nitrile which is formed by the 'abnormal' Hoesch condensation⁷ between α-naphthol and α-formyl phenyl acetonitrile, and then undergoes to 3 by dehydration. Thus the compound having m.p. 169-170° claimed by Ghosh as chromone (1) and by Baker as coumarin (2) is a mixture.

Satisfactory elemental and spectral analyses have been secured for all compounds. Further studies of the above condensation by the use of other Lewis acids, e.g. ZnCl₂ and AlCl₃, are in progress and more details will be reported later.

Acknowledgements

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