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REVISION OF AN ENAMINE SYNTHESIS; THE PREPARATION AND REACTIONS OF 2-MORPHOLINOISOFLAV-3-ENE.

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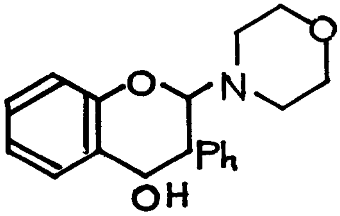
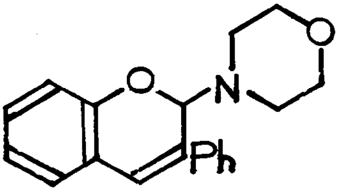
ABSTRACT: The condensation of *N* -styrylmorpholine with salicylaldehyde does *not* give a product that can be oxidised to isoflavone; the product is *N*-morpholino-isoflav-3-ene which can be used to prepare other compounds related to isoflavan and upon oxidation gives 3-phenylcoumarin.

Paquette and Stucki[1] reported an enamine-mediated synthesis of isoflavone to which they ascribe m.p. 150°, quoting Joshi and Venkataraman[2] (m.p. 148°) although later workers[3] give a revised figure (m.p. 131°). We fail to obtain isoflavone by this method. We find the initial product from salicylaldehyde (0.015 mol) and *N*-styrylmorpholine (0.015 mol) under N_2 in boiling benzene (8 ml) for 3 hrs. to be a gum (4.2 g) which may contain the intermediate alcohol(1) as suggested by the earlier authors but which resists oxidation (CrO_3 in pyridine) and when chromotographed on basic alumina from ether-petroleum (1:10) supplies what is presumably the dehydration product, 2-morpholino-isoflav-3-ene (2) (*ca.* 55%). Thus the reaction is parallel to that described for some steroidal enamines.[4] In acetic acid, chromium(VI) oxide does oxidise the isoflavene (2) but the product, m.p. 139° , is 3-phenylcoumarin(3) (m.p. 140°)[5] isomeric with isoflavone and displaying very similar chromatographic behaviour.



(1)



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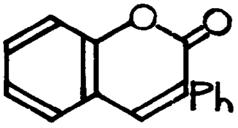
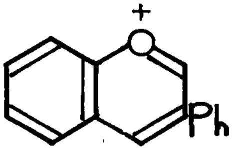


(3)

From hexane, (2) separates as transparent rods, m.p. 105-106°, ν_{max} (KBr) 1620, 1592 and 1562 cm^{-1}. The U.V. spectrum[6] λ_{max} (EtOH) 289 (16200) and 329(11900) nm shows that the compound is an E -stilbene; derivatives of Δ^2-isoflavene are known to have no maxima above 300 nm.[7] The p.m.r. spectrum is in accord: δ (CDCl$_3$) 7.67-6.96 (9H, m, ArH), 7.04 (1H, s, H-4), 5.74 (1H, s, H-2), 3.56 (4H), 3.04 (2H) and 2.61 (2H), [m, morpholine] . The molecular ion at m/e 293 collapses giving a base peak at m/e 207 indicating the formation of the phenyl-3-benzopyrilium ion (4) which is obtained, quantitatively, as the perchlorate[8] by warming (2) with triphenylmethyl perchlorate in acetic acid at 110-130°C for 5-10 min. and forms yellowish brown needles, m.p. 140-141° (CH$_3$COOH) with δ (CDCl$_3$-TFA) 9.83(1H,d,J=2Hz,H-2), 9.7(1H,d,J=2Hz,H-4) and 8.46-7.56 (9H,m,Ar-H). With perchloric acid (2) gives not the salt but an ether (5), m.p. 242-243°, similar to but not identical with the ether described by Molho and his colleagues.[9] Hydrogenolysis of (2) is a satisfactory method for preparing isoflavan[10] (6).



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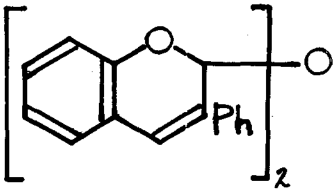

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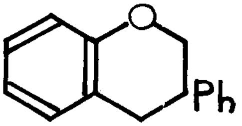

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6. We thank Dr. (Mrs.) Manju Varma for determining the UV spectra.
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