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ADDITION REACTIONS OF *N*-(CHROMONE-3-YLIDENE)ANILINES

Alan O. Fitton*, Jonathan R. Frost, and Hans Suschitzky*,
The Ramage Laboratories, Department of Chemistry and Applied Chemistry,
University of Salford, Salford M5 4WT, Lancs.

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Whereas chromones normally undergo ring opening when treated with primary aromatic amines,[1,2] 3-formylchromone (Ia) reacted with aniline (1:1 molar ratio) in dry benzene to give a mixture of *N*-(chromone-3-ylidene)aniline (IIa) and the 1,4 adduct (III). Excess of the amine (2:1), produced only the 1,4 adduct (m.p. 142-4^{o}), the structure of which was confirmed by the following data: ν_{max} 3340, 1645 cm^{-1}, λ_{max} ($CHCl_3$) 247, 383 nm; M^+ (30 eV) 342; τ ($CDCl_3$) 4.92 (d, *J*=7.5Hz, Hd); 3.66 (d, *J*=7.5Hz, Hc); 3.2-2.2 (m, aromatic H's); 2.36 (d, *J*=12Hz, Hb); 1.96 (dd, He); -2.3 (d, *J*=12Hz, Ha).

The stability of this keto-amine system has been discussed by Dudek,[3] and may explain the readiness of adduct formation. Corresponding products (IV a-f) were obtained from other *N*-(chromone-3-ylidene)anilines (II b-d) and various alcohols and thiophenol (Table 1).

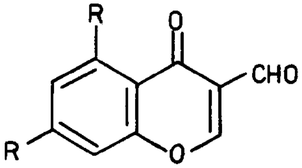
TABLE 1

(IV)*	R	R^1	R^2	M.p.^{o}C	ν_{max}(cm^{-1})	λ_{max}(nm)
a	H	Cl	OMe	112	1650	257; 388
b	H	OMe	OMe	120	1650	262; 396
c	Me	Cl	OEt	154-5	1655	257; 382
d	H	Cl	OPr^i	133-5	1655	258; 388
e	H	Cl	OBz	133	1650	257; 388
f	H	Cl	SPh	148-52	1650	248; 273; 406

* All new compounds had correct analytical data

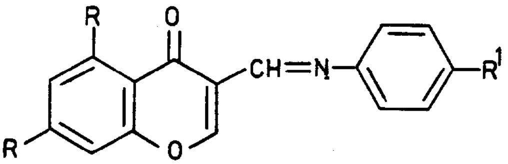
The u.v. spectra of the 1,4 adducts in chloroform[4] were similar, showing a characteristic absorption at 380-410 nm. Their p.m.r. spectra (IV a-f) showed a low field signal due to

Ha (d, J=12-13Hz) at ca. -2τ, coupled to Hb (d, J=12-13Hz) which resonates at ca. 2.5τ. The large coupling constant indicates that Ha and Hb are held antiperiplanar to each other,[5] and this together with the low τ value, suggests strong hydrogen-bonding.[6] The mass spectra of the adducts (at 70 eV) gave usually a fragment corresponding to the parent anil (II) indicating the ease of retroaddition. This reversibility is a convenient method for preparing the pure anils (II), since interaction of the aldehyde and amine invariably gave a mixture of anil and adduct. Merely heating the adducts (IV a,b) near their melting points i.v., readily gave pure anils.



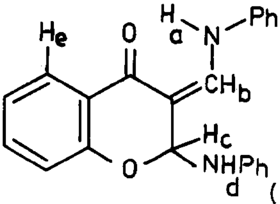
(I) a; R=H

b; R=Me

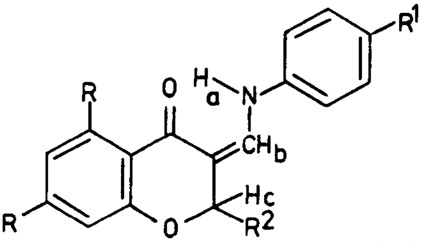


(II) a; R=R'=H b; R=H, R'=OMe

c; R=H, R'=Cl d; R=Me, R'=Cl



(III)



(IV)

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