

Reaction of Aromatic Aldehydes and Nitroso-compounds with 4-Chromanones

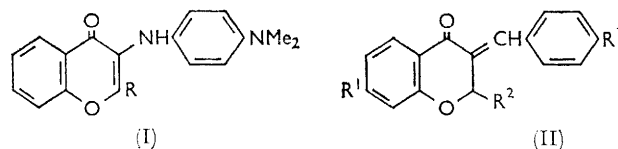
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Reaction of 4-chromanone with *p*-nitrosodimethylaniline affords a substituted 3-aminochromone. The preparation of 3-benzylidene-4-chromanones has been examined further.

WE have recently examined the reaction of *p*-nitrosodimethylaniline with 4-chromanone and flavanone in the presence of alkali and found that the infrared spectra of the products obtained were not consistent with the structures originally assigned.^{1,2}

Arndt and Källner¹ treated 4-chromanone with *p*-nitrosodimethylaniline. Subsequent treatment of the reaction mixture with hydrazobenzene gave a product which they formulated as 3-(*p*-dimethylaminoanilino)-4-chromanone. Pfeiffer and Hesse² reported the formation of *N*-(*p*-dimethylphenyl)-3-iminoflavanone when flavanone reacted with *p*-nitrosodimethylaniline. Examination of these two products has shown NH bands in their infrared spectra (3270, 3256 cm.⁻¹, respectively) and that their carbonyl frequencies (1625, 1633 cm.⁻¹, respectively) were close to that found in 4-chromone (1637 cm.⁻¹) and that reported for 3-aminoflavone (1637 cm.⁻¹).³ The carbonyl band in 4-chromanone occurs at 1685 cm.⁻¹. We therefore believe that these products are 3-(*p*-dimethylaminoanilino)-4-chromone (I; R = H) and its 2-phenyl analogue (I; R = Ph), respectively. The nuclear magnetic resonance spectra are consistent with these structures.

The role of the hydrazobenzene in the reaction with 4-chromanone is not clear. We were unable to obtain the product when it was omitted and yet it was not necessary in the reaction with flavanone.



The structure of the products suggested that a tautomeric shift of a hydrogen atom occurred after the initial condensation. It is known that aldehydes condense with 4-chromanones to give benzylidene derivatives⁴ of general formula (II) and it seemed worthwhile checking whether such a shift occurred in this case. However, the carbonyl frequency (1663 cm.⁻¹) for the condensation product of 4-chromanone and benzaldehyde, together with the ultraviolet spectrum [λ_{max} (in ethanol) 223, 300, 347 m μ (ϵ 17,400, 18,400, 7600)] suggested that formulation (II) was correct. Some new benzylidene derivatives of 4-chromanones prepared during this work are listed in the Experimental section.

¹ F. Arndt and G. Källner, *Ber.*, 1924, **57**, 202.

² P. Pfeiffer and T. Hesse, *J. prakt. Chem.*, 1941, **158**, 315.

³ C. O'Brien, E. M. Philbin, S. Ushioda, and T. S. Wheeler, *Tetrahedron*, 1963, **19**, 373.

⁴ S. G. Powell, *J. Amer. Chem. Soc.*, 1923, **45**, 2708; P. Pfeiffer, E. Breith, and H. Hoyer, *J. prakt. Chem.*, 1931, **129**, 31.

The product obtained by reaction of *p*-nitrosodimethylaniline with 3-phenyl-1-indanone⁵ should similarly be formulated with an NH group and an endocyclic double bond.

EXPERIMENTAL

3-(*p*-Dimethylaminoanilino)-4-chromone (I; R = H).—4-Chromone was treated with *p*-nitroso-*N*-dimethylaniline as described by Arndt and Källner,¹ to give the *anilino-chromone* as golden-yellow leaflets, m. p. 151—153° (lit.,¹ m. p. 154°) (Found: C, 72.4; H, 5.8; N, 10.2. C₁₇H₁₆N₂O₂ requires C, 72.8; H, 5.8; N, 10.0%); ν_{\max} 1625, 3270 cm.⁻¹ (Nujol); 1625, 3295 cm.⁻¹ (CCl₄); n.m.r. peaks (Varian A-60 Spectrometer; CDCl₃ solution) at 2.9(6), 6.04(1), and a multiplet from 6.65—8.48(9). Heating the base at 100° with 2*N*-hydrochloric acid afforded the *hydrochloride* as buff prisms, m. p. 199—201° (decomp.) from ethanol-ether (Found: C, 62.8; H, 5.6; N, 8.8. C₁₇H₁₇ClN₂O₂·½H₂O requires C, 62.7; H, 5.5; N, 8.6%).

3-(*p*-Dimethylaminoanilino)flavone (I; R = Ph).—Flavanone was treated with *p*-nitroso-*N*-dimethylaniline as described by Pfeiffer and Hesse;² the *anilino-flavone* was obtained as red needles, m. p. 148—149° (lit.,² m. p. 149.5°) (Found: C, 77.1; H, 5.5; N, 7.8. C₂₃H₂₀N₂O₂ requires C, 77.5; H, 5.7; N, 7.9%); ν_{\max} 1633, 3256 cm.⁻¹ (Nujol); 1630, 3270 cm.⁻¹ (CCl₄); n.m.r. peaks (Varian A-60 Spectrometer; CDCl₃ solution) at 2.72(6), 6.2(1), 6.53(4), and a multiplet 7.2—8.358(9).

3-Benzylidene-4-chromanone Derivatives (II).—Concentrated hydrochloric acid (4.5 ml.) was added to a hot solution of the chromanone (0.03 mole) and substituted benz-

aldehyde (0.03 mole) in absolute ethanol (50 ml.). The solution was heated under reflux for 4 hr. After cooling, the precipitate was filtered off and recrystallised from ethanol. New benzylidene derivatives prepared by this method were: 3-(*p*-hydroxybenzylidene)-4-chromanone in 53% yield as yellow needles, m. p. 222—224° (Found: C, 76.6; H, 4.9. C₁₆H₁₂O₃ requires C, 76.2; H, 4.8%); 3-(*p*-hydroxybenzylidene)flavanone in 39% yield as cream prisms, m. p. 192—193° (Found: C, 80.9; H, 5.1. C₂₂H₁₆O₃ requires C, 80.5; H, 4.9%); 3-(*p*-hydroxybenzylidene)-7-methoxy-4-chromanone in 56% yield as brick-red needles, m. p. 213—214° (Found: C, 72.2; H, 4.9. C₁₇H₁₄O₄ requires C, 72.3; H, 5.0%); and 7-methoxy-3-(*p*-methoxybenzylidene)-4-chromanone in 37% yield as off-white plates, m. p. 124—125° (Found: C, 72.1; H, 5.3. C₁₈H₁₆O₄·½H₂O requires C, 71.8; H, 5.5%).

2-[*p*-(Dimethylamino)anilino]-3-phenylindone.—Reaction of 3-phenyl-1-indanone with *p*-nitrosodimethylaniline as described by Pfeiffer and de Waal⁵ afforded the *anilino-indanone* as black lustrous plates, m. p. 144—146° (lit.,⁵ m. p. 148—150°) (Found: C, 80.9; H, 5.9; N, 7.8. C₂₃H₂₀N₂O requires C, 81.2; H, 5.9; N, 8.2%); ν_{\max} 1713, 3320 cm.⁻¹ (Nujol).

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⁵ P. Pfeiffer and H. L. de Waal, *Annalen*, 1935, **520**, 185.