

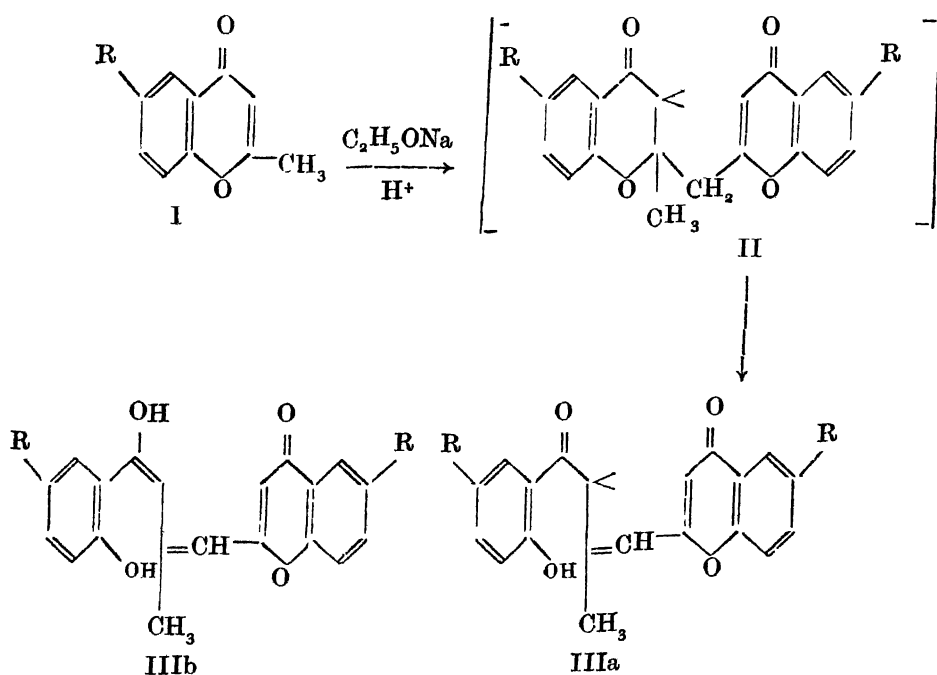
On Dimeric 6-Chloro-2-Methylchromone

M. M. Sidky and M. R. Mahran

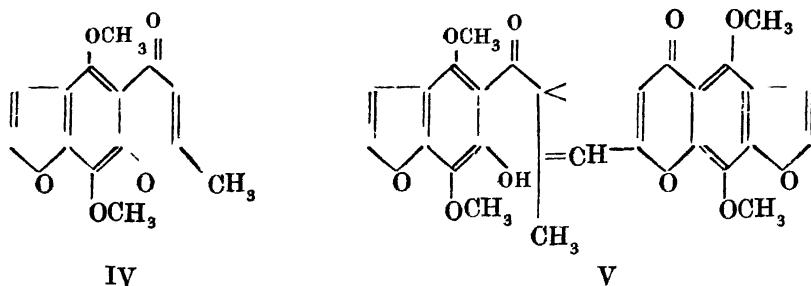
6-Chloro-2-methylchromone, in presence of sodium ethoxide in dry ether, gave a red-coloured solid dimer which was found to exist as a keto-enol mixture (IIIa \rightleftharpoons IIIb, R=Cl). In ethanol, it changes quantitatively into the keto form IIIb (R=Cl).

U. V., I. R. and N. M. R. spectra of the dimers are recorded.

It has been shown¹ that 2-methylchromones (I, R=H or CH₃) upon reaction with sodium ethoxide in dry ether, yielded colourless dimeric products to which structure IIIa (R=H or CH₃) was assigned. The latter could be formed by 1.4 addition of the carbanion to the α,β -unsaturated system of another molecule, followed by ring opening of the intermediate adduct II (R=H or CH₃). The colourless adducts IIIa (R=H or CH₃) dissolve in aqueous alkali hydroxide to give red coloured solutions. This may be attributed to the formation of the corresponding alkali soluble red enol form IIIb' (R=H or CH₃).



Later, Sidky and Mahran² reported that khellin(IV), on similar treatment, gave a yellow khellin-dimer(V) and they ascribed the red-violet colour reaction³ of khellin with alkali to the formation of V.



We have now extended our investigations to include other 2-methylchromone derivatives and found that 6-chloro-2-methylchromone (I, R=Cl) reacts with sodium ethoxide in dry ether to give a red coloured solid product, proved to be the dimer of I(R=Cl). This adduct is proved to be a mixture of tautomers IIIa and IIIb(R=Cl) for reasons given below.

(1) The proton N. M. R spectrum⁴ of the red adduct shows signals at $T7.75$ (singlet) and at $T0.66$ (singlet), indicating the presence of olefinic methyl and enolic hydroxyl groups, respectively. Since the sample was not very soluble it was tried to enhance the signal to noise ratio of the spectral lines by running the sample on HA-100 spectrometer attached to a C1024 unit. The spectrum obtained after 100 scans shows the emergence of a peak (doublet, $J=2$ c.p.s) at $T5.83$ which is assigned to protons belonging to a methylene group which has a doubly-bonded carbon atom and a keto group as its neighbours. The two earlier peaks due to $=C-CH_3$ and $=C-OH$ groups are still present in the spectrum thus indicating that the red adduct is a mixture of tautomers IIIa and IIIb (R=Cl). Another spectrum of the red dimer was obtained after allowing it to slowly dissolve over an 18 hr period * Again, the spectrum shows a keto-enol mixture where the keto form is predominant.

(2) The I R spectrum⁵ of the red adduct in KBr shows a broad absorption band in the 3μ region, due to an OH- group. The intense band around 6.1μ is commonly recorded in conjugated unsaturated ketones and is associated with the stretching vibration of the C=C bond⁶ and this may be assigned for the 1,4-pyrone ring⁷

(3) The U V. absorption spectrum⁸ of the red adduct (III, R=Cl) was carried out in ethanol and $N/20$ ethanolic sodium hydroxide solution. In plain ethanol, the adduct

*This sample was found to be more soluble than the earlier freshly prepared one.

2. Sidky and Mahran; *J. Org. Chem.*, 1962, **27**, 4112.

3. Abd-El-Rahman, Master's thesis, Fouad I University, Cairo (1943); Fahmy, Badian and Messerd, *J. Pharm. Pharmacol.*, 1949, **1**, 529; Schonberg and Sina: *J. Amer. Chem. Soc.*, 1950, **72**, 1611.

4. The samples were run as freshly prepared deuteriochloroform solution containing tetramethylsilane as an internal standard as spectra were obtained on a Varian HA-100 spectrometer.

5. The Infrared absorption spectra were determined with a Perkin-Elmer infracord Spectrophotometer Model 137.

6. Jones, Humphries and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 956.

7. Looker and Hanneman, *J. Org. Chem.*, 1962, **27**, 381.

8. The Ultraviolet measurements were carried out by using a Carl-Zeiss PMQ II spectrophotometer.

absorbs in the region of an extended conjugated carbonyl system ($\lambda_{\text{max}}^{\text{ethanol}}$, 480 μ , $\epsilon=1,100$). Whereas, in alkali solution, it absorbs strongly at 490 μ . This band is characteristic for the enolate structure (cf. IIIb, R=C1), and is not observed in the spectrum of the pure keto form IIIa(R=C1) run in plain ethanol. Again, the spectrum of IIIa, (R=C1) in *N*/20 ethanolic sodium hydroxide solution exhibits the absorption band at 490 μ , $\epsilon=9,800$. Since the colour of the red dimer fades appreciably in ethanol with time (see below), it is difficult to determine the exact percentage of the enol form IIIb in solution.

When the red dimeric product III(R=C1) was dissolved in ethanol and left at room temperature for 24 hours, a complete discharge of the red colour took place and a colourless compound proved to be IIIa(R=C1) was isolated. The crystalline colourless adduct IIIa(R=C1) gives the correct analytical values and its molecular weight corresponds to the dimeric formula. The N.M.R. spectrum of compound IIIa(R=C1) contains signals of an OH-, CH₂-, and CH₃-groups. The resonance of the hydroxyl proton indicates an intramolecular hydrogen bonded OH-group. Boiling in methanol-hydrochloric acid mixture resulted in the formation of two molecules of 6-chloro-2-methylchromone. Treatment of a colourless benzene solution of the adduct IIIa(R=C1) with activated alumina results in acquiring of the surface of the inorganic material with a red-violet colour. The colour of the adsorbates on alumina is similar to the colour shown when alumina is placed into colourless benzene solution of 1,3-diketohydrindene; a violet adsorbate is formed, believed to be due to the enol form⁹. The red adduct III(R=C1) undergoes pyrolytic degradation when heated above its melting point giving the starting 6-chloro-2-methylchromone. This may be regarded as pyro-retro-Michael-reaction¹. Compound III(R=C1) exhibits thermochromic properties in piperidine solution, a phenomenon was also observed with other 2-methylchromone-dimers.¹

EXPERIMENTAL

Melting points are uncorrected. Elemental analyses were performed by the Micro-analytical Laboratory, National Research Centre, Dokki-Cairo.

Action of Sodium Ethoxide on 6-Chloro-2-methylchromone (I, R=C1). Two gms. of 6-chloro-2-methylchromone¹⁰ was added to ethanol-free dry sodium ethoxide suspended in about 50 ml. of dry ether (E. Merck, peroxide free). The sodium ethoxide was prepared by dissolving 1 gm. of sodium metal in absolute alcohol, and the excess alcohol was removed under reduced pressure at 160-170° (bath temperature). The mixture was shaken in a tightly closed vessel for about 2 hrs., then kept at room temperature for 48 hrs. The deep violet-coloured deposit was quickly filtered, washed with dry ether, then decomposed with ice-cold 10% aqueous acetic acid solution. The red substance, which formed, was filtered, dried and crystallised from dry benzene to give III(R=C1) as deep red crystals, yield ca.0.4 gm., m.p. 146-147°; $\lambda_{\text{max}}^{\text{ethanol}}$, 223 μ ($\epsilon=42,800$), 255 μ (shoulder, $\epsilon=21,000$), 310 μ ($\epsilon=14,600$) and 480 μ ($\epsilon=1,100$).

9. Schönberg, Mustafa and Asker, *J. Amer. Chem. Soc.*, 1951, **73**, 2876; *ibid*, 1952, **74**, 5640; *ibid*, 1963, **75**, 4645.

10. Wittig, *Ber.*, 1924, **57**, 88.

Anal. Calc. for $C_{10}H_7ClO_2$: C, 61.71; H, 3.62; Cl, 18.21; mol.wt., 389.2. Found: C, 61.90; H, 3.46; Cl, 18.36; mol. wt., 397.8 (in camphor).

α -[6-Chloro-chromonyl-(2)]- β -methyl- β -(2-hydroxy-5-chloro-phenacyl)-ethylene (IIIa, R=Cl). The red adduct (III, R=Cl) (0.5 gm.), partly dissolved in ethyl alcohol (50 ml., 95%), was left at room temperature for 24 hrs. The colour of the solution became almost colourless. Ethanol was removed under *vacuo*, and the solid residue so obtained was crystallised from ethanol to give IIIa(R=Cl) (yield 0.45 gm) as colourless crystals, m.p. 168-170°; $\lambda_{\max}^{\text{ethanol}}$, 223 m μ ($\epsilon=53,000$) and 310 m μ ($\epsilon=9,000$); $\lambda_{\max}^{N/20}$ ethanolic NaOH 303 m μ ($\epsilon=11,000$) and 490 m μ ($\epsilon=9,800$).

Anal. Calc. for $C_{10}H_7ClO_2$: C, 61.71; H, 3.62; Cl, 18.21; mol.wt., 389.2. Found: C, 61.53; H, 3.48; Cl, 18.06; mol. wt., 381.4 (in camphor).

Degradation Experiments with the Dimers. (a) *Pyrolysis of III(R=Cl)*. 0.1 gm. of the red dimeric product III(R=Cl) was heated in a cold-finger sublimator at 160-170° (bath temperature) under reduced pressure (2 mm/Hg) for about 15 minutes. The substance that sublimed was collected and crystallised from petroleum ether (b.p. 60-80°) and proved to be 6-chloro-2-methylchromone (m.p. and mixed m.p.). Yield ca. 80%.

Similarly, pyrolysis of the adduct IIIa afforded the starting 6-chloro-2-methylchromone in an almost quantitative yield.

(b) *Acid Hydrolysis of III(R=Cl)*. A mixture of the adduct (0.2 gm) in methanol (10 ml) and hydrochloric acid (sp. gr. 1.18, 10 ml.) was refluxed for 6 hrs. After removing the volatile materials under reduced pressure, the residue was crystallised from petroleum ether (b.p. 60-80°) to give 6-chloro-2-methylchromone (yield ca. 80%) (m.p. and mixed m.p.).

Thermochromic Behaviour of III(R=Cl) in piperidine. The red dimeric product III(R=Cl) produced, when dissolved in piperidine (E. Merck), a red-violet colour at room temperature. The colour discharges almost completely on heating. On cooling, the red colour was regenerated. The phenomenon was reversible for several times, but on standing for a long time at room temperature, the colour of the solution fades considerably. This thermochromic behaviour in piperidine was also observed with the colourless adduct IIIa(R=Cl).

Adsorption Colour Experiments with IIIa(R=Cl). When the colourless adduct IIIa(R=Cl) was dissolved in benzene (thiophene-free and dried over sodium) and a small amount of alumina (Aluminiumoxyd. Woelm, Alkali-frei, anahernd neutral, Akt., Stufe I, M. Woe'm-Eschwege) added, a red-violet colour appeared within a few minutes on the surface of the alumina and the benzene solution remained practically colourless over the violet material.

When the above experiment was repeated with alumina (Al_2O_3 , Aktiv, basisch, E. Merck, Darmstadt), the colour of the adsorbates on the inorganic material was deep red.