

In the case of N_2O^- ion, unlike in the case of HCP, the vibrational frequencies increase when the molecule transforms from the ground to excited state. Hence the force constants of N_2O^- in the excited state are found to be larger than those in the ground state.

In this investigation, we have considered only the \bar{a} excited state since, this state being the first excited state for both the cases, the relative probability of transformation of the molecules to this state is more when compared to the other higher order excited states.

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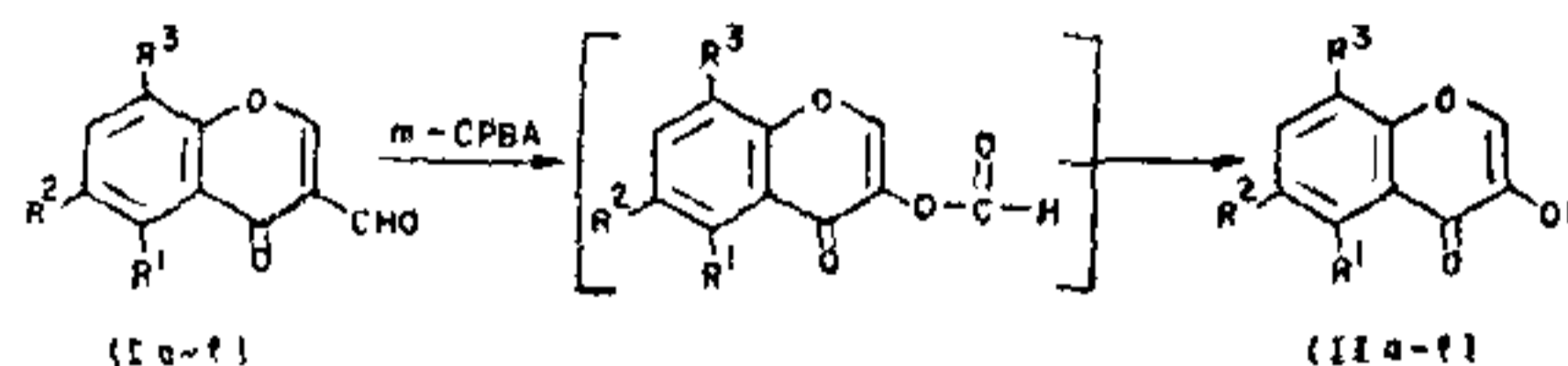
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BAYER-VILLIGER OXIDATION OF CHROMONE 3-CARBOXALDEHYDES— A FACILE METHOD FOR THE SYNTHESIS OF 3-HYDROXYCHROMONES

In this communication we report a facile method for the synthesis of 3-hydroxychromones starting from chromone-3-carboxaldehydes^{1,2}. Bayer-Villiger oxidation of methoxybenzaldehydes to methoxyphenols via their respective formates using *m*-chloroperbenzoic acid (*m*-CPBA) in boiling dichloromethane has been recently reported by Sargent *et al.*³. Similar procedure has now been adopted for oxidising chromone-3-carboxaldehydes (Ia-e)¹, (If)² to the corresponding 3-hydroxychromones (IIa-c)^{4,5} and (IId-f) in good yields, varying from 80-90%. In these reactions, the intermediate formates could not be isolated but the direct formation of 3-hydroxychromones have been observed. The 3-hydroxychromones (IIa-c) thus obtained have been characterised by analytical and spectral characteristics and by direct comparison with authentic samples of IIa⁵, IIb and c⁴ respectively (Table I). Also prepared by this new method are 6-chloro (II d), 6-nitro (II e)-3-hydroxychromone; and 2-hydroxy-1H-naphtho (2, 1-b) pyran-1-one (II f). These compounds, prepared for the first time, were characterised by analytical and spectral data. II f was also characterised by direct comparison with an authentic sample prepared from 1-benzo (f) chromanone⁶ by amyl nitrite method⁴.

The overall yield of 3-hydroxychromones (IIa-c and II f) by the present Bayer-Villiger oxidation, calculated from phenol, works out to be ~ 60%, while the yield of the same 3-hydroxychromones prepared by

amyl nitrite and hydrochloric acid method⁴, also calculated from phenol, works out to be ~ 16%. Therefore, Bayer-Villiger oxidation method, now reported, appears to be a better method in comparison with the other existing methods^{4,5} for the synthesis of 3-hydroxychromones.



- (a) $R^1 = R^2 = R^3 = H$
- (b) $R^1 = R^3 = H; R^2 = CH_3$
- (c) $R^1 = R^2 = H; R^3 = CH_3$
- (d) $R^1 = R^3 = H; R^2 = Cl$
- (e) $R^1 = R^3 = H; R^2 = NO_2$
- (f) $R^1 + R^2 = \text{benzo}; R^3 = H$

Experimental

3-Hydroxychromone (IIa)⁵: The chromone-3-carboxaldehyde (Ia)¹ (0.01 mole) and *m*-chloroperbenzoic acid (0.02 mole) were heated under reflux in dry dichloromethane (20 ml) over a period of 16 hours. During reflux a colourless solid (*m*-chlorobenzoic acid) separated out. The reaction mixture was evaporated and the residue dissolved in ethylacetate and the solution washed with aqueous sodium-bicarbonate solution to remove *m*-chlorobenzoic acid and then washed with water and dried over anhydrous sodium sulphate. Removal of the solvent left a solid residue which crystallised from methanol to yield yellowish brown plates of 3-hydroxychromone (IIa), identical in all respects with the authentic sample⁵ [(mp, mmp and superimposable ir) (Table I)] prepared by the reported procedure⁵.

IIb and IIc were similarly prepared from their respective chromone-3-carboxaldehydes (Ib and Ic)¹ and were found to be identical with the authentic samples (mp, mmp and superimposable ir), prepared by adopting reported procedures^{4,5}.

6-Chloro- (II d)¹, 6-nitrochromone-3-carboxaldehyde (Ie)¹ and 1H-naphtho (2, 1-b) pyran-1-one-carboxaldehyde (If)² on oxidation with *m*-chloroperbenzoic acid yielded 6-chloro-3-hydroxychromone (II d) (found C, 54.98, H, 2.50; calculated for C_9H_5OCl (C, 55.09, H, 2.55); 6-nitro-3-hydroxychromone (II e) (found C, 52.02, H, 2.40, N, 6.69; calculated for $C_9H_5O_5N$ C, 52.17, H, 2.42, N, 6.76) and 2-hydroxy-1H-naphthol (2, 1-b) pyran-1-one (II f) (found C, 73.45; H, 3.75; calculated for $C_{13}H_9O_3$ C, 73.58, H, 3.77) respectively.

II was found to be identical (mp, mmp and superimposable ir) with an authentic sample of 2-hydroxy-1H-naphtho (2, 1-b) pyran-1-one which was prepared by adding a methanolic solution of 1-benzo (f) chroma-

TABLE I
Physical and spectral characteristics of 3-hydroxychromones prepared from chromone-3-carboxaldehydes by Bayer-Villiger oxidation using m-CPBA in CH₂Cl₂

Sl. No.	Compound	M.P. in 0° C*	Lit. M.P. in 0° C	Time of reflux in hours	Percentage of yield*	I.R. $\nu_{\text{KBr max}}$ (cm ⁻¹)	U.V. $\lambda_{\text{MeOH max}}$ Log (ϵ) (nm)
1.	3-Hydroxychromone	180-81	181 ⁶	16	90	-- $\nu_{\text{OH}}/\nu_{\text{C=O}}$ 3280, 1640	233(4.24), 283(3.25), 320(3.63)
2.	6-Methyl-3-hydroxychromone	174-75	175 ⁷	24	85	3270, 1640	237(4.33), 284(3.57), 330(3.86)
3.	8-Methyl-3-hydroxychromone	164-65	166 ⁴	24	87	3280, 1630	237(3.93), 283(3.18), 327(3.42)
4.	6-Chloro-3-hydroxychromone	214-15	..	18	85	3280, 1640	235(4.0), 283(3.32), 327(3.58)
5.	6-Nitro-3-hydroxychromone	200-201	..	24	80	3275, 1640	237(4.14), 285(3.48), 329(3.75)
6.	2-Hydroxy-1H-naphtho-(2,1-b)pyran-1-one	130-132	131-32 [†]	24	80	3270, 1640	240(4.20), 287(3.68), 335(3.90)

* All the compounds were crystallised from methanol.

† Prepared for the first time by amyl nitrite and hydrochloric acid method.

none⁶ (1 g) to amyl nitrite (3 ml) and hydrochloric acid (10 ml) dropwise, simultaneously, at 0° and the mixture refluxed for 2 hours. The resulting solution was poured into ice-water (200 ml). The separated yellow solid was filtered and crystallised from methanol to yield II_f (0.30 g), mp 131-32° C.

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A SYNTHESIS OF 5,5'-DI-O-METHYLCUPRESSU-FLAVONE AND A NEW SYNTHESIS OF DIGITOLUTEIN AND OROXYLIN-A

IN a recent communication¹ we have indicated the utility of methoxymethylation in the synthesis of partial methyl ethers of certain polyphenolic compounds. The general procedure adopted was to methoxymethylate the polyphenol first partially so that all the free unchelated phenolic hydroxyl groups present in it get protected, then methylate the chelated hydroxyl group using dimethyl sulphate and finally demethoxymethylate to get the partial methyl ether. Now we wish to record an extension of the above work and report the synthesis of the naturally occurring compounds, digitolutein (1-methoxy-2-hydroxy-3-

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