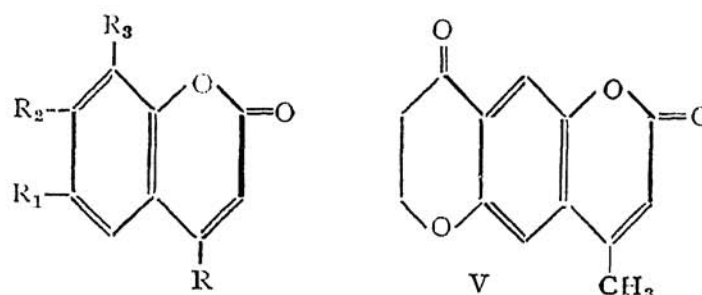


CYANOETHYLATION OF COUMARINS

IN connection with our work on the application of cyanoethylation in the synthesis of polynuclear compounds, we investigated the cyanoethylation of some coumarin derivatives.

When 7-hydroxycoumarin was reacted with acrylonitrile in alkaline solution the compound I was obtained as a crystalline solid (m.p. 167-69°, Found C, 67.3; H, 4.4; N, 6.9; $C_{12}H_9NO_3$ requires C, 67.0; H, 4.2; N, 6.5%). On hydrolysis with acid the corresponding acid II was formed (m.p. 164-66°, Found C, 61.8; H, 4.6; $C_{12}H_{10}O_5$ requires C, 61.5; H, 4.3%).



- I $R = R_1 = R_3 = H$; $R_2 = OCH_2CH_2CN$
 II $R = R_1 = R_3 = H$; $R_2 = OCH_2CH_2COOH$
 III $R = R_2 = H$; $R = CH_3$; $R_1 = OCH_2CH_2CN$
 IV $R_2 = R_3 = H$; $R = CH_3$; $R_2 = OCH_2CH_2COOH$
 VI $R = R_1 = R_2 = H$; $R_3 = OCH_2CH_2CN$
 VII $R = R_1 = R_2 = H$; $R_3 = OCH_2CH_2COOH$

Similarly 6-hydroxy-4-methylcoumarin when cyanoethylated afforded the compound III (m.p. 138-40°; Found C, 68.5; H, 4.4; N, 5.8; $C_{13}H_{11}NO_3$ requires C, 68.1; H, 4.8; N, 6.1%) which on hydrolysis gave the acid IV (m.p. 172-74°; Found C, 63.3; H, 5.2; $C_{13}H_{12}O_5$ requires C, 62.9; H, 4.8%). It is interesting to note that when the acid IV or the compound III is boiled with alkali the original coumarin is obtained back. Cyclisation of the acid IV was attempted under different conditions such as treatment with P_2O_5 , $POCl_3$ and so on. However, on heating with polyphosphoric acid the cyclisation occurred to give the chromanone V (m.p. 210-12°; Found C, 68.0; H, 4.6; $C_{13}H_{10}O_4$ requires C, 67.8; H, 4.4%) which was further characterised by the preparation of a 2,4-dinitrophenylhydrazone (m.p. 298-300°; Found N, 13.3; $C_{19}H_{14}N_4O_7$ requires N, 13.7%). The linear structure for V was favoured by making models and also on the basis of spectral data.

λ_{max}^{MeOH} 370, 290, 220 (log ϵ 3.61, 4.26, 4.33).

In the same manner 8-hydroxycoumarin on cyanoethylation gave the nitrile VI (m.p. 139-40°; Found C, 67.0; H, 4.5; N, 6.4; $C_{12}H_9NO_3$

ires C, 67.0; H, 4.2; N, 6.5%) which on
olysis yielded the acid VII (m.p. 173-75°;
id C, 61.4; H, 4.6; $C_{12}H_{10}O_5$ requires C,
; H, 4.3%).

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