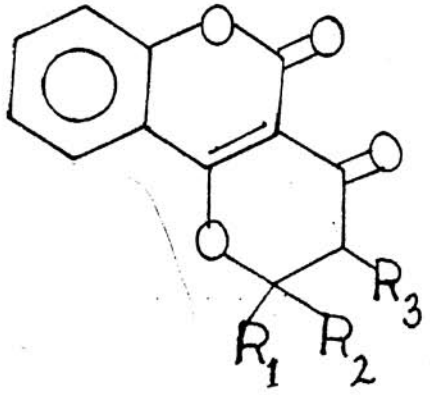
SYNTHESIS OF CHROMANONES FROM 4-HYDROXYCOUMARIN

In a previous communication[1] on the cyanoethylation of hydroxycoumarins, leading to the synthesis of different coumarino-chromanones, we have reported that the cyanoethylation of 4-hydroxycoumarin with acrylonitrile does not take place under different experimental conditions.

We now wish to report a one step synthesis of coumarino-chromanones from 4-hydroxycoumarin by heating the latter with acrylic, α-methylacrylic, crotonic, β, β-dimethylacrylic and cinnamic acids in the presence of PPA at about 120° for five hours. In all cases the coumarino-chromanones were isolated as pale yellow or brown crystalline solids from alcohol in yields ranging from 30 to 35%. The structures of the coumarino-chromanones were evident by the formation of crystalline 2, 4-DNPs as well as from their i.r. and n.m.r. spectral data.



I; $R_1 = R_2 = R_3 = H$
196–97°, 2, 4 D.N.P. M.P. 258–60°
II; $R_1 = R_2 = H$; $R_3 = Me$;
213–14°, 2, 4 D.N.P. M.P. 254–55°
III; $R_1 = Me$; $R_2 = R_3 = H$;
209–10°, 2, 4 D.N.P. M.P. 264–65°
IV; $R_1 = R_2 = Me$ $R_3 = H$;
184–85°, 2, 4 D.N.P. M.P. 249–51°
V; $R_1 = Ph$; $R_2 = R_3 = H$;
258–60°,

Compound V was crystallised from formic acid.

The i.r. (nujol) spectrum of the coumarino-chromanones showed two bands around 1725 and 1680 cm^{-1} corresponding to the C = O band of the coumarin and the chromanone respectively. The n.m.r. ($CDCl_3$ + DMSO) of I, II and III showed the following signals (I): δ2·9 (2H; *t*; CH_2 next to C = O; J = 3Hz); δ 4·95 (2H; *t*; CH_2 next to O; J = 3Hz); δ 7∼8 (4H; *m*; aromatic); II δ 1·2 (3H; *d*; CH_3; J = 3·5 Hz); δ 2·8 (1H; *m*; >CH); δ 4·6–4·8 (2H; *t*; CH_2, J : 3Hz); δ 7∼8 (4H; *m*; aromatic); III in CF_3COOH δ 1·8∼1·9 (3H; *d*; CH_3; J = 6Hz);

δ 3 (2H; broad S; CH_2); δ 5·1 ~ 5·4 (1H; broad S; >CH); δ 7·4–8·4 (4H; *m*; aromatic).

An important evidence for the chromanone structure of the above compounds was also obtained by the fact that the compound IV prepared by the above method was found to be identical (m.m.p.; i.r.) with the chromanone synthesized by Shizuri *et al.*,[2] by the condensation of 4-hydroxycoumarin with β-β-dimethyl-acryloyl chloride in the presence of pyridine.

We have also observed that the above synthesis of coumarinochromanones is a general one and takes place with 6-, 7- and 8-methyl 4-hydroxy coumarins with the above α, β-unsaturated acids in the presence of PPA.

All the compounds gave satisfactory C, H, N analysis.

We are thankful to Ciba-Giegy Research Centre and Hoechst Research Centre for obliging us with i.r. and n.m.r.

Department of Organic Chemistry,
Institute of Science,
Bombay-32, *October* 10, 1975.

SUNEEL DIKE.
J. R. MERCHANT.

Reaction Scheme:

1. Merchant, J. R. and Patell, J. R., *J. Chem. Soc.* 1969, p. 1545.
2. Shizuri, Y., Kato, K., Hirata, Y. and Yamamura, S., *J. Chem. Soc.*, 1969, p. 2774.