

Perusal of Table II (Fig. 2) shows that \bar{n} values never exceed 1.6 indicating thereby the formation of only 1:1 and 1:2 complexes of Tl(I) with DNSA. In view of very low concentration of Tl(I) (1×10^{-4} M) used in the titration, formation of poly-nuclear complexes may be ignored. Titrations performed with different ratios of metal to ligand showed that the formation constants are independent of metal ion concentration.

The ratio $\log K_1/\log K_2$ is positive and that the separation factor between the first and the second formation constants is well within the expected range. A large difference between $\log K_1$ and $\log K_2$ and a high value of $\log K_1/\log K_2$ is due to the possible steric hindrance on the linking of the second ligand molecule expected for Tl(I) ion.

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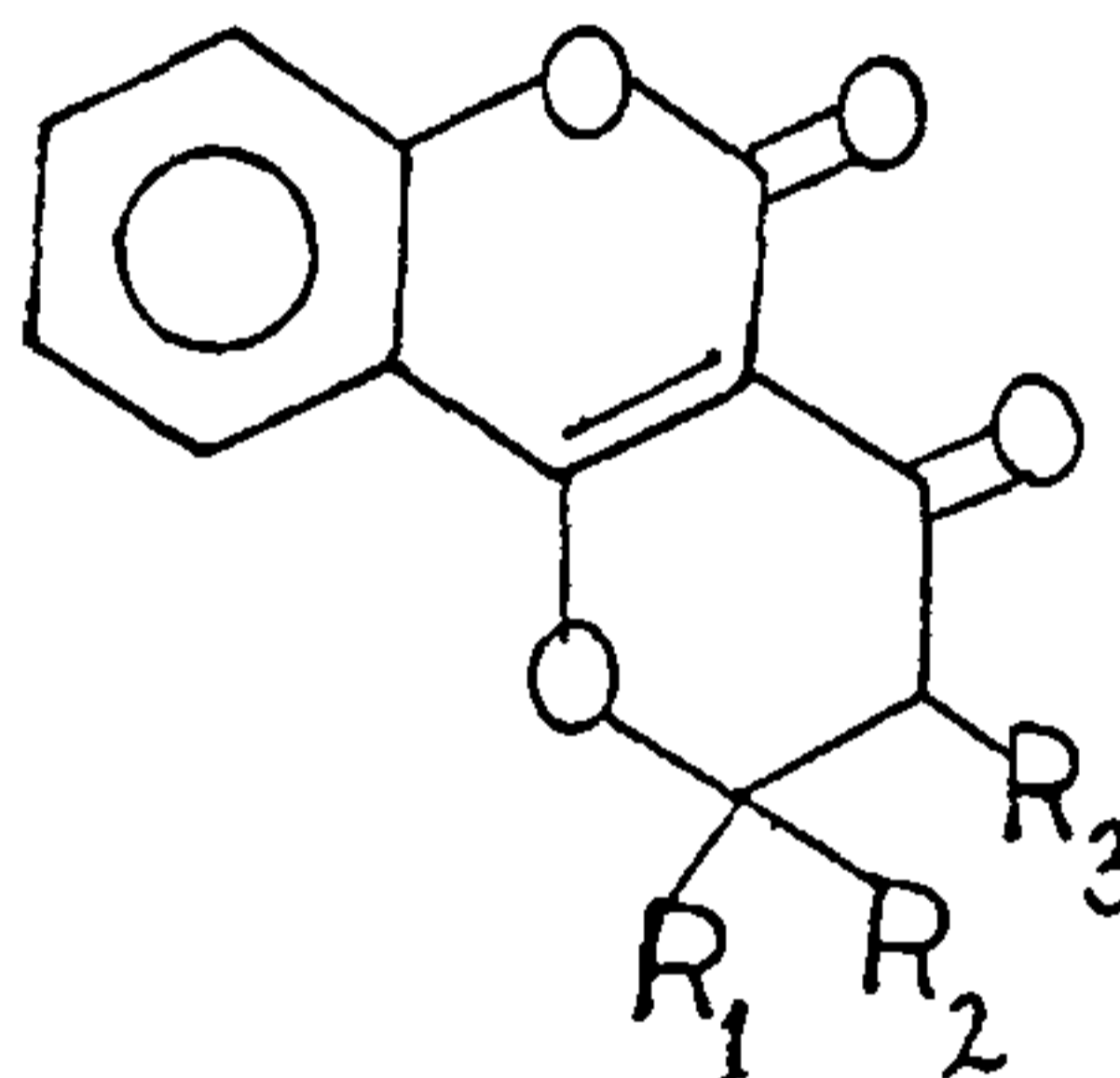
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SYNTHESIS OF CHROMANONES FROM 4-HYDROXYCOUMARIN

IN a previous communication¹ 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): δ 2.9 (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);

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δ 3 (2H; broad S; CH); 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 -dimethylacryloyl 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.

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BIS (2-METHYL- $\Delta^{2(3)}$ -OXADIAZINE-4, 6-DIONE)-5-SULFONYL

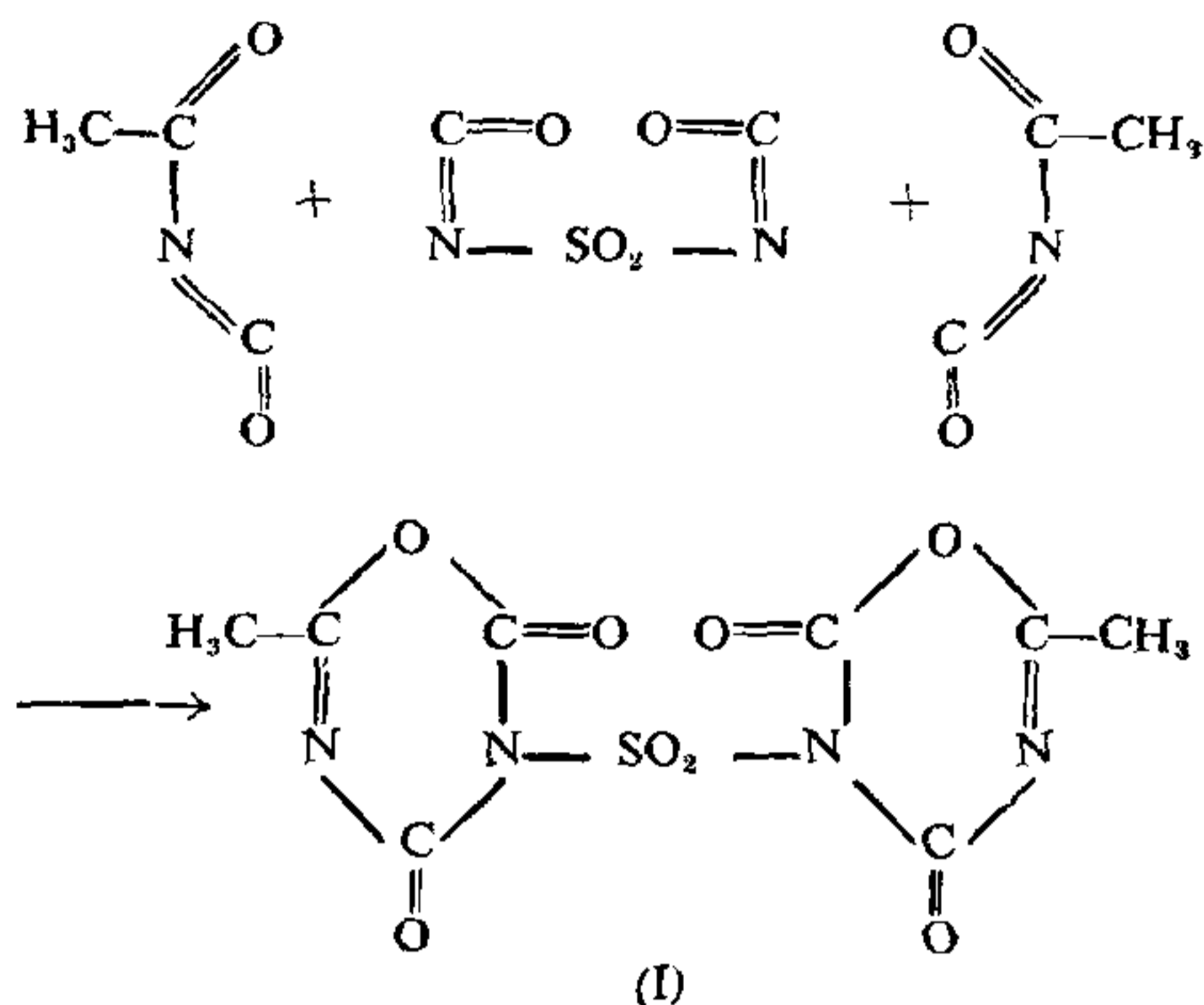
THE reaction of acetylisocyanate with sulfonyldiisocyanate leads to bis (2-methyl- $\Delta^{2(3)}$ -oxadiazine-4, 6-dione)-5-sulfonyl.

Ulrich described the reaction of acetylthiocyanate with methylisocyanate¹. The preparation of bis (2-methyl- $\Delta^{2(3)}$ -oxadiazine-4, 6-dione)-5-sulfonyl, by the reaction of acetylisocyanate and sulfonyldiisocyanate, is analogous to the previously reported preparation for 2,5-dimethyl- $\Delta^{2(3)}$ -oxadiazine-4, 6-dione², 2-methyl-5-phenyl- $\Delta^{2(3)}$ -oxadiazine-4, 6-dione² and 3-chloro-sulfonyl-6-methyl-2H-1, 3, 5-oxadiazine-2, 4 (3H)-dione⁵. The reaction was complete in $\frac{1}{2}$ hour, at 60~70°C, yielding a brown compound (I) (decomp. at 82°C).

The ¹H-NMR spectrum of bis (2-methyl- $\Delta^{2(3)}$ -oxadiazine-4, 6-dione)-5-sulfonyl, which was recorded in deuterium dimethylsulfoxide, shows a signal at $\tau = 7.9$ ppm for the methyl protons.

The I.R. spectrum (in KBr) shows the usual absorptions for the C=O, S=O and C-O-C groups at 1710, 1175 and 1050 cm⁻¹, respectively. The mass spectrum was difficult to interpret due to thermal decomposition in the inlet system.

Reaction Scheme:



EXPERIMENTAL DATA

1. Preparation of acetylisocyanate (see ref. 5).
2. Preparation of $C_8H_8N_4O_8S$ (I).—Acetylisocyanate (2.9 g.; 0.033 mole) was heated with sulfonyldiisocyanate (2.5 g.; 0.017 mole) at 60-70°C for $\frac{1}{2}$ hour. Bis (2-methyl- $\Delta^{2(3)}$ -oxadiazine-4, 6-dione)-5-sulfonyl, crystallized on cooling (yield 1.2 g; 45%). (Found: C—30.07%, H—2.13%, N—17.85% and S—10.72%). (Calculated: C—30.20%, H—1.88%, N—17.53%, O—40.25% and S—10.06%).

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