

missing, may be due to the weak character of ${}^4T_{1g} \rightarrow {}^4A_{2g}$ transition. The values of $10 D_q$, B and β have been calculated by employing the method described by Lever^{9,10}. These values have been recorded in Table II and are indicative of octahedral Co(II) alanine complex¹¹.

Spectra of Cu(II) Complex

The absorption spectra of Cu(II) complex, in the present case, provides an asymmetric band around 15870 cm^{-1} . It is reasonable, therefore, to assign a distorted octahedral structure (12) to the system.

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SPECTROPHOTOMETRIC ESTIMATION OF VANADIUM(V) AND TITANIUM(III) COMPLEXES WITH 4-METHYL DAPHNETIN

SPECTROPHOTOMETRIC and/or gravimetric estimation of Mo(IV), Nb(V), Ta(V), Th(IV), Fe(III) with 4-methyl daphnetin has been reported^{1,2} however, there is no mention of V(V) and Ti(III) forming coloured complexes with this reagent. Our investigation relates to the use of 4-methyl daphnetin for the spectrophotometric determination of V(V) and Ti(III).

It is found that an alcoholic solution of 4-methyl daphnetin forms a green coloured complex with V(V) (λ_{max} 600 nm) and an orange coloured complex with Ti(III) (λ_{max} 410 nm) in the pH range of 5–7. Beer's law was verified upto 2 ppm in the case of V(V) and 8 ppm in the case of Ti(III). The molar-extinction coefficients are found to be

8.5×10^3 and 8×10^3 for V(V) and Ti(III) respectively.

Estimation of Vanadium(V)

To a solution containing upto $2 \mu\text{g}$ of V(V) (aqueous NH_4VO_3) was added 2 ml of 0.1 M solution of 4-methyl daphnetin³ and the resulting solution made upto 50 ml with distilled water. The colour development is almost instantaneous. The extinction of the complex was measured on spekol at 600 nm against the corresponding reagent blank. The amount of V(V) was then deduced from the calibration curve.

The effect of foreign ions was studied by adding to the V(V) solution (2 ppm) various cations and anions 10 times in excess. It was found that the ions, Co^{2+} , Ni^{2+} , Mg^{2+} , Sr^{2+} , Sn^{2+} , NO_3^- , NO_2^- , SO_4^{2-} , Br^- , I^- , Cl^- , $[\text{Fe}(\text{CN})_6]^{4-}$, CNS^- , did not interfere in the estimation; however, Fe^{2+} , Fe^{3+} , Ti^{3+} , Cu^{2+} , BrO_3^- were found to interfere.

Estimation of Titanium(III)

To a solution containing upto $8 \mu\text{g}$ of Ti(III) (alcoholic TiCl_3) was added 2 ml of 0.1 M solution of 4-methyl daphnetin and the resulting solution made upto 10 ml with ethanol. The experiment was carried out in alcoholic medium to keep the complex in solution. The extinction of the complex was measured at 410 nm with corresponding reagent blank. The amount of Ti(III) was then deduced from the calibration curve.

Ti(III) solution (2 ppm) was mixed with various cations and anions ten times in excess. It was found that Cu^{2+} , Co^{2+} , BrO_3^- , CNS^- did not interfere in the estimation; however, Ni^{2+} , Fe^{2+} , Fe^{3+} , Mg^{2+} , NO_2^- and $[\text{Fe}(\text{CN})_6]^{4-}$ were found to interfere.

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SYNTHESIS OF SOME SUBSTITUTED 4-THIAZOLIDINONE DERIVATIVES

A RECENT publication by Harhash *et al.*¹, on the synthesis of 4-thiazolidinone derivatives prompts us to report some of our earlier work on these compounds which are known to exhibit interesting pharmacological properties².

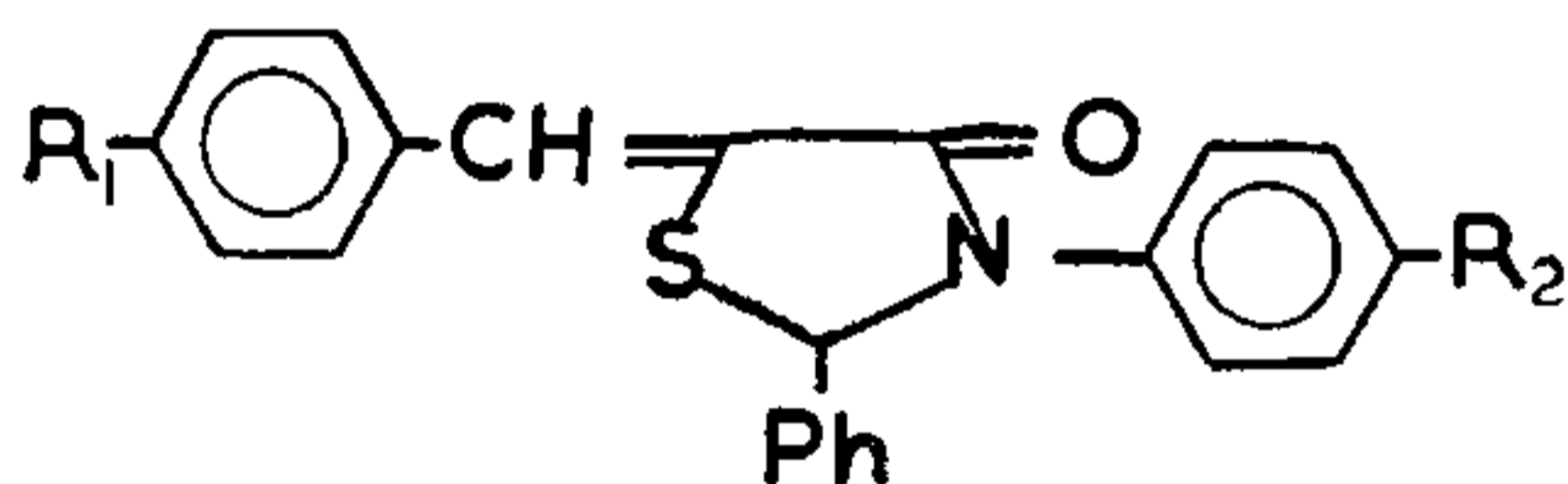
The present work reports the synthesis of some new 2,3-diaryl-5-arylidene-4-thiazolidinones obtained

by the reaction of Schiff bases with β -aryl- α -mercaptoacrylic acids in boiling benzene solution. The thiazolidinones were colourless crystalline compounds (Table I) and were obtained in about 50–60% yields from A (acetic acid), B (benzene) or C (alcohol).

The u.v. spectra of these compounds showed $\lambda_{\text{max}}^{\text{MeOH}}$ around 230–240 and 320–330 nm. The latter absorption is attributed to conjugation of the phenyl ring in the '5' position. The i.r., spectra (Nujol) showed bands at 1700 (C=O), 1500–1600 (aromatic) and 800–850 cm^{-1} (*p*-substituted phenyl ring).

To confirm the 4-thiazolidinone structure of the compounds obtained by the above method, the compound VI was synthesised also by a different route. In this case, the Schiff base obtained by condensation of benzaldehyde with *p*-anisidine was reacted with thioglycolic acid as described by Surrey³ to yield a thiazolidinone derivative which was condensed with *p*-chlorobenzaldehyde in presence of sodium ethoxide to afford VI obtained by the direct reaction of the appropriate Schiff base with β -*p*-chlorophenyl- α -mercaptoacrylic acid prepared as described in literature⁴.

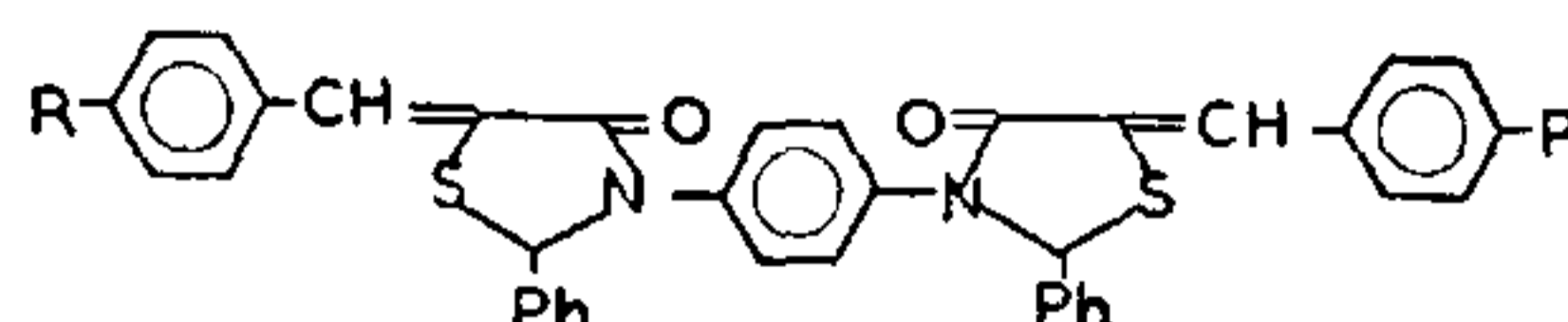
2, 3-Diaryl-5-arylidene-4-thiazolidinones



No.	R ₁	R ₂	m.p. and Solvent
I	Cl	COOH	280 (A)
II	Cl	Cl	185 (C)
III	Cl	CH ₃	194 (B, C)
IV	Cl	Br	205 (B)
V	Cl	I	226 (B)
VI	Cl	OCH ₃	198 (B, C)
VII	H	I	181 (C)
VIII	H	COOH	275 (A)

We also prepared thiazolidinone derivatives in about 40% yields by the condensation of the Schiff base, prepared from 2-moles of benzaldehyde and one mole of *p*-phenylenediamine with β -phenyl- and β -4-chlorophenyl- α -mercaptoacrylic acids in

benzene solution to which the following structure was assigned. Both the compounds were obtained as white granular solids from acetic acid.



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

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SOME TRANSITION METAL COMPLEXES WITH N-4-METHYL-2-HYDROXY ACETOPHEN-ACYLIDENE-*p*-DIMETHYL AMINO ANILINE

CRYSTALFIELD splitting energy parameter Δ , Racah parameter B, Nephelauxetic coefficient β , magnetic moments and molar conductance have been determined for N-4-methyl-2-hydroxyacetophenacylidene-*p*-dimethylaminoaniline complexes with Cu(II), Ni(II) and Co(II). Spectrochemical series based on Δ was found in the order Cu(II) > Ni(II) > Co(II).

Experimental

The Schiff base N-4-methyl-2-hydroxyacetophenacylidene-*p*-dimethyl amino aniline was prepared by refluxing equimolar quantities of *p*-dimethylaminoaniline and 4-methyl-2-hydroxyacetophenone in ethanolic solution, on water-bath for 2.5 hrs. The contents were cooled, poured into water and the solid product obtained was washed with petroleum ether (b.p. 60–80° C). Analytical data: (Found: C, 76.0; N, 10.23; H, 7.28; For C₁₇H₂₀N₂O