

obtained from the above determinations are summarized in Table I.

TABLE I
Results of gravimetric estimation of copper(II)

Weight of complex mg	Copper, mg		
	Found	Calcd.	Error%
329.4	58.19	58.31	0.20
298.6	52.76	52.89	0.24
268.0	47.35	47.46	0.23
228.8	40.41	40.50	0.23
199.3	35.21	35.29	0.24

Effect of foreign ions.—Interfering ions like Fe^{3+} and V^{5+} were masked with help of sodium potassium tartarate and Ti^{4+} by potassium fluoride. Anions like SO_4^{2-} , PO_4^{3-} , Cl^- , F^- , NO_3^- and cations like Co^{2+} , Ni^{2+} did not interfere in the pH range 7.20–7.60.

Structure.—The molecular weight of the copper(II) complex in benzene was found by ebulliometry to be 358 ± 12.0 . Its magnetic moment was found 1.90 B.M. at 298°K . The elemental analysis and molecular weight data suggest 1:1 metal-ligand stoichiometry besides the presence of three water molecules. The electronic absorption spectra of the copper(II) complex in benzene gives one band with its peak located at $11,800 \text{ cm}^{-1}$ which is shifted slightly to $12,200 \text{ cm}^{-1}$ in pyridine and $12,500 \text{ cm}^{-1}$ in picoline. This peak may be assigned to the transition ${}^2E_g \rightarrow {}^2T_{2g}$, suggesting its octahedral structure. The i.r. spectra of H_2NE shows three intense bands at 3647 , 1650 and 1190 cm^{-1} which may be assigned to the presence of νOH , $\nu\text{C}=\text{N}$ and $\nu\text{SO}_3\text{H}$ respectively. In the copper(II) complex the bands at 3647 cm^{-1} and 1190 cm^{-1} have disappeared indicating the complexation of OH and SO_3H . In this spectra three new bands at 1610 , 650 and 615 cm^{-1} appeared which may be assigned to the presence of $\nu\text{C}=\text{N}$, $\nu\text{Cu}-\text{N}$ and $\text{Cu}-\text{O}$, respectively. A new band at 3370 cm^{-1} is also observed which may be due to the presence of νOH of the water molecules confirming its octahedral structure.

The authors are thankful to UGC, New Delhi, for the award of fellowship to one of them (PKK).

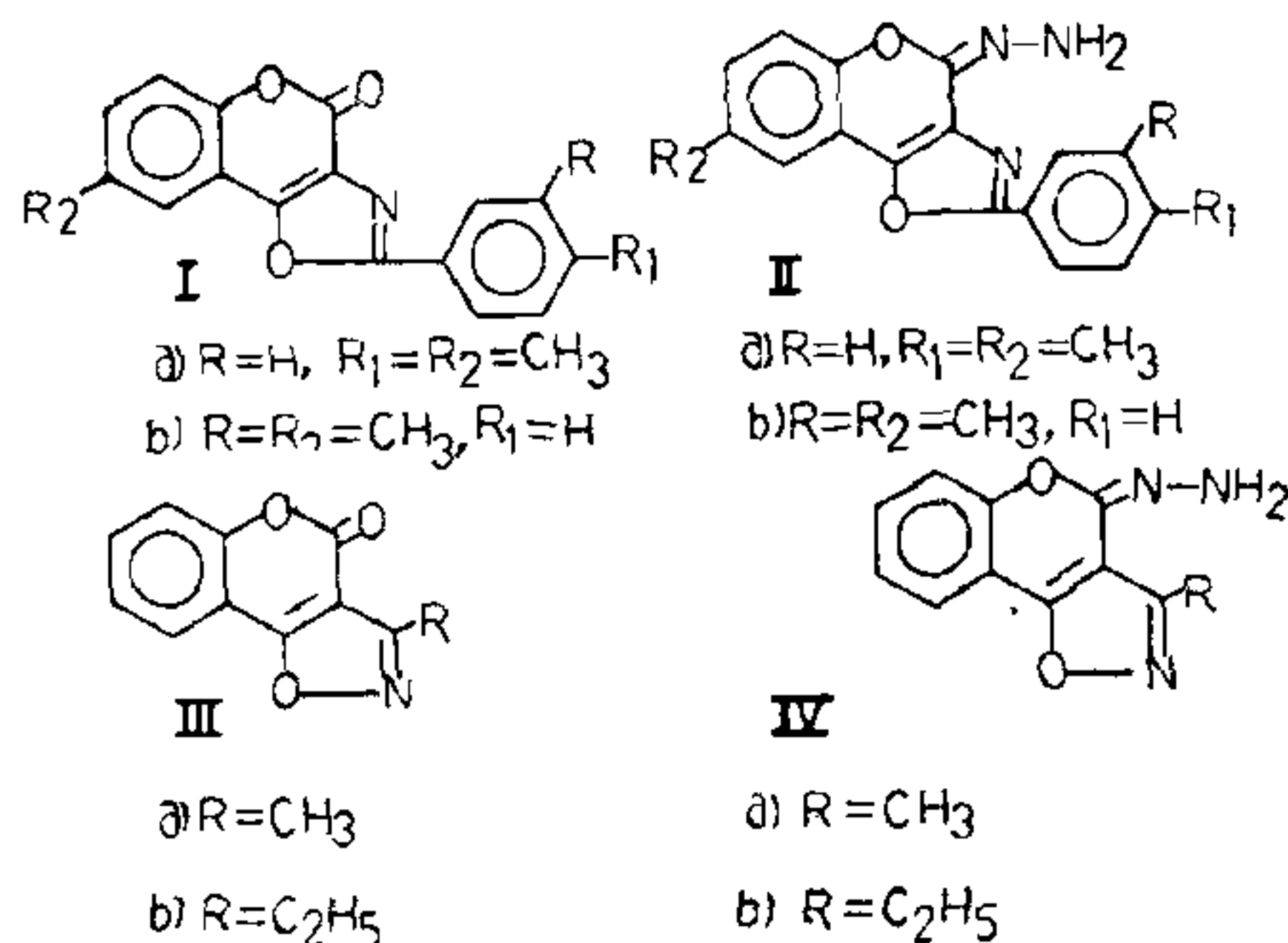
Department of Chemistry,
University of Jodhpur,
Jodhpur,
July 18, 1977.

P. K. KANUNGO.
D. C. SEHGAL.
R. K. MEHTA.

1. Holm, R. H., Everette, Jr., G. W. and Chakravorty, A., *Prog. Inorg. Chem.*, 1966, 7, 83.
2. Syamal, A., *Coord. Chem. Rev.*, 1975, 16, 309.
3. Singhvi, B. R. and Mehta, R. K., *Indian J. Chem.* (In press).
4. Mehta, R. K. and Singhi, V. C., *Z. Naturforsch.*, 1971, 27 b, 304.

AN INTERESTING REACTION OF 4H-1-BENZOPYRANO (3, 4-d)-OXAZOL- AND ISO-OXAZOL-4-ONES

In a previous communication¹, we have reported the synthesis of 4H-1-benzopyrano(3, 4-d) oxazol-4-one derivatives. With a view to studying some of the reactions of these compounds such as the replacement of the heterocyclic oxygen by nitrogen, we investigated the reaction of (Ia) with hydrazine hydrate. It is pertinent to mention that Baddar *et al.*² have reported the replacement of heterocyclic O by N with Hydrazine hydrate in some α -pyrones to form 1-amino-2-pyridones.



The reaction was carried out by refluxing equimolecular quantities of the reactants, *e.g.*, (Ia) and hydrazine hydrate in alcohol solution for 5 hr. Dilution with water afforded a colourless crystalline compound (IIa), m.p. $147-49^\circ$. Its molecular weight (mass spectrum) was found to be 323 and the elemental analysis corresponded with the molecular formula $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_3 \cdot \text{H}_2\text{O}$. It u.v. had $\lambda_{\text{max}}^{\text{MeOH}}$ 215 nm ($\log \epsilon 4.39$), 290 nm ($\log \epsilon 4.37$), 320 nm ($\log \epsilon 4.21$). In the i.r. spectrum the lactone band, which in the original compound appeared at 1765 cm^{-1} , was completely absent. Further, the spectrum showed a NH_2 band at 3400 cm^{-1} , whereas the $\text{C}=\text{N}$ band appeared at 1610 cm^{-1} . The n.m.r. spectrum (CDCl_3 , δ) of the compound

integrated for fifteen protons and showed the following signals : 2.4 (s, 6H, Ar-CH₃), 4.3 (b, s, 2H, -NH₂), 7.0 ~ 8.0 (m, 7H, aromatic).

From the above evidence the compound was assigned the structure (IIa). The latter is consistent with the observation that on boiling it with either acetic anhydride or with dilute hydrochloric acid the original compound (Ia) was obtained in almost quantitative yield.

The formation of IIa may be due to the opening of the coumarin ring in (Ia) by a strong base like hydraline hydrate giving the hydroxy hydrazide as an intermediate which recyclizes to give back the resulting compound.

The reaction also succeeds with other 4H-1-benzopyrano (3, 4-d) oxazole-4-one derivatives. The compound (IIb) had m.p. 158-60°. However, a similar hydrazide formation is not observed with 4H-1-benzothiopyrano (3, 4-d) oxazol-4-ones.

The same reaction occurs also in the case of the known³ 3-methyl- and 3-ethyl-4H-1-benzopyrano (3, 4-d)-isooxazol-4-ones giving the corresponding hydrazones IVa, m.p. 148-50°, IVb, m.p. 114-16°.

In our procedure for the preparation of the two isooxazol-4-ones, which is somewhat different from that reported,³ the oximes of 4-hydroxy-acetyl- and 4-hydroxy-3-propionyl coumarins were acetylated to yield the corresponding unknown acetates of the oximes, m.p. 183-84° and 128-30° respectively. The oxime acetates on boiling with pyridine afforded the required isooxazole-4-ones in 50-60% yields.

With a view to study the general applicability of the reaction we studied the reaction of hydrazine hydrate with 7-hydroxy-3-ethyl-4-methylcoumarin. In this case the reaction failed and the original coumarin was obtained back. The reaction was unsuccessful with 7-hydroxy-6-ethyl-3, 4-cyclopenteno- and 7-hydroxy-6-ethyl-3, 4-cyclohexenocoumarins. The reactions also failed to give a pure product with 4-methoxy-6-methylcoumarin. It, therefore, seems that the presence of an oxazole or an isooxazole ring in 3, 4 positions is very necessary for the reaction to occur.

All compounds gave satisfactory C, H and N analyses.

We are thankful to Ciba-Geigy Research Centre, Bombay, for n.m.r. and mass spectra.

Department of Organic
Chemistry,
Institute of Science,
Bombay 400 032,
October 19, 1977,

J. R. MERCHANT,
S. S. SHIRALI,
KUM. K. M. BAKRE.

1. Merchant, J. R. and Shirali, S. S., *Chem. and Ind.*, 1977, 1, 33.
2. Baddar, F. G., Al-Hajjar, F. H. and El-Rayyes, N. R., *J. Het. Chem.*, 1976, 13, 195.
3. Desai, M. K. and Usgaonkar, R. N., *Indian J. Chem.*, 1977, 4, 379.

AMINOPHOSPHINE COMPLEXES OF COPPER(II), COBALT(II) AND NICKEL(II)

COMPOUNDS, in which trivalent phosphorus being bound to the nitrogen directly and also forming coordinate bonds with metals, have been little investigated so far. These amino-phosphines clearly serve as potential ligands for many metal ions¹⁻⁶. The present paper records the synthesis and characterisation of some aminophosphine complexes of copper(II), cobalt(II) and nickel(II) phthalimides.

The aminophosphine used in the study is diphenylpyridylphosphine (A) and has been obtained by the treatment of diphenylchlorophosphine with pyridine in anhydrous ether, followed by crystallisation. When treated with copper(II), cobalt(II) and nickel(II) phthalimides, it yields blue and pink coloured complexes, the structures of which have been resolved on the basis of elemental analysis, conductivity, magnetic susceptibility and electronic spectra.

(i) *Diphthalimido (diphenylpyridylphosphine)* Copper(II)

Found C = 67.90%; H = 3.25%; N = 6.95%.
Calcd. C = 67.35%; H = 3.90%; N = 7.10%

(ii) *Diphthalimidobis (diphenylpyridylphosphina)* Cobalt(II).

Found C = 73.62%; H = 4.90%; N = 7.20%.
Calcd. C = 73.44%; H = 4.65%; N = 6.98%.

(iii) *Diphthalimidobis (diphenylpyridylphosphina)* nickel(II).

Found C = 74.00%; H = 4.92%; N = 7.54%.
Calcd. C = 73.49%; H = 4.70%; N = 7.02%.

The conductivity of the complexes was measured in nitrobenzene on a Philips PR 9500/90 magic eye type instrument. Magnetic susceptibility was obtained by Gouy's method, at room temperature while the electronic spectra were measured in the form of solid samples on a Cary 14 recording instrument.

The molar conductances of the complexes are in the range 0.5-0.75 mhos in nitrobenzene and indicate the neutral nature of the complexes. It thus appears that the two phthalimide (phth) ions besides neutralising the charge of the metals are also coordinated to it, and the formulas of the complexes can be represented as [Cu(phth)₂A] and [Co or Ni(phth)₂A₂]