

the reaction, and the liberated iodine was titrated against standard sodium thiosulphate.

Physical Chemistry Department,
University of Madras,
Madras 600 025,
January 21, 1978.

N. AMIRTHA.
R. GANESAN.

1. White, E. P. and Robertson, P. W., *J. Chem. Soc.*, 1939, p. 1509.
2. Gero, A., Joseph, Kershner, J. and Perry, R. E., *J. Amer. Chem. Soc.*, 1953, p. 5119.
3. Ganesan, R. and Viswanathan, S., *Z. Physik. Chem. Neue Folge (Frankfurt)*, 1969, 66, 243.
4. Viswanathan, S. and Ganesan, R., *Indian J. Chem.*, 1971, 9, 674.
5. Ganesan, R., *Z. Physik. Chem. Neue Folge (Frankfurt)*, 1974, 90, 82.
6. Nanjan, M. J. and Ganesan, R., *Ibid.*, 1974, 71, 183.
7. —, Seshadri, K. V. and Ganesan, R., *Indian J. Chem.*, 1975, 13, 629.

EFFECT OF ANIONS IN THE PAPER CHROMATOGRAPHIC SEPARATION OF Co(II), Ni(II), Cu(II) AND Zn(II), WITH DIFFERENT NEUTRAL MONODENTATE LIGANDS

COMPLEXING agents are often used in paper chromatographic separation of transition metal ions¹⁻⁵. The mobility of these ions on the paper depends very much on the composition of the complexes formed with the ligands. In the presence of non-coordinating anions, divalent 3d transition metal ions normally form six coordinate complex species of the general formula $[ML_6]^{2+}$ where L is a neutral monodentate ligand. It has been proved already that these transition metal ions form complexes of varied composition with the ligands in presence of different halide anions⁶⁻¹⁰. It is proposed to study the effect of varying composition of complexes brought about by different anions on the R_f values of metal ions.

Experimental

For the present investigation, the ligands Diphenylsulphoxide (DPSO), Pyridine-N-Oxide (PNO) and Quinoline-N-Oxide (QNO) and the anions ClO_4^- , Cl^- and Br^- with the divalent transition metal ions Co, Ni, Cu and Zn were chosen.

Chromatography was performed on Whatmann No. 1. paper strips (18 × 2.5 cm) in glass jars (20 × 4.5 cm). Metal perchlorates were prepared by treating 70% perchloric acid with metal carbonates and crystallising them in water. 0.06 Molar solution of metal ions were prepared by dissolving the metal perchlorates in 95% ethanol and were used for spotting. The ligands DPSO, PNO and QNO were prepared by methods

reported previously^{11, 12}. The R_f values of the cations were calculated for the following solvent systems:

1. 6M $HClO_4$ + iso-Propanol + Acetone
(1:1:1, V/V)
2. 6M $HClO_4$ + iso-Propanol + Acetone
(1:1:1, V/V) + 2% ligand
3. 6M HCl + iso-Propanol + Acetone
(1:1:1, V/V)
4. 6M HCl + iso-Propanol + Acetone
(1:1:1, V/V) + 2% ligand
5. 6M HBr + iso-Propanol + Acetone
(1:1:1, V/V)
6. 6M HBr + iso-Propanol + Acetone
(1:1:1, V/V) + 2% ligand.

Cu(II), Co(II) and Ni(II) were identified by spraying with 0.1% alcoholic solution of rubeanic acid and exposing to vapours of ammonia¹³. Cu(II), Co(II) and Ni(II) gave olive green, yellow and bright blue spots respectively. Zn(II) was detected by spraying with a mixture of 0.02% cobalt sulphate solution and ammonium mercury thiocyanate reagent²¹. It gave a blue spot.

Results and Discussion

The R_f values of the transition metal ions Co(II), Ni(II), Cu(II) and Zn(II) in different solvent systems with and without the neutral monodentate ligands DPSO, PNO and QNO are listed in Table I.

TABLE I
 R_f values of metal ions in different solvent systems

Solvent system	Cobalt	Nickel	Copper	Zinc
1	0.76	0.71	0.78	0.77
2 with DPSO	0.25	0.28	0.22	0.30
2 with PNO	0.47	0.41	0.52	0.40
2 with QNO	0.33	0.39	0.31	0.35
3	0.68	0.58	0.72	0.68
4 with DPSO	0.56	0.46	0.59	0.55
4 with PNO	0.61	0.53	0.72	0.59
4 with QNO	0.60	0.49	0.67	0.57
5	0.54	0.49	0.62	0.61
6 with DPSO	0.37	0.34	0.55	0.59
6 with PNO	0.52	0.49	0.69	0.64
6 with QNO	0.42	0.39	0.60	0.61

In solvent system 1 the cations are considered to be in hydrated form, since perchlorate anion is essentially non-coordinating. But in systems 3 and 5 where coordinating anions alone are present they may form the species $[MX_4]^{2-}$ or $[MX]_4^{2-}$ where X is Cl^- or Br^- . It has been reported in literature¹⁴⁻¹⁶, that divalent metal perchlorates form solid complexes of the type $[ML_6](ClO_4)_2$, with neutral monodentate ligands.

It has also been reported²² that the R_f values of the metal ions after being complexed with ligands present in solvent have not been found to be appreciably different from the R_f values obtained by spotting the prepared complexes. Hence a similar behaviour may be expected in solvent system 2. Halide anions have been shown to influence the composition of the divalent metal ion complexes with neutral monodentate ligands¹⁷⁻²⁰. A similar effect of anions on the composition may be expected during the partition of the metal ions leading to differences in the R_f values in solvent systems 4 and 6. Further work in extracting and characterising the actual species formed during the chromatographic separation is in progress.

The present investigation indicates that separation of metal ions could be achieved by the use of solvent systems containing neutral monodentate ligands and halide anions.

The authors thank the authorities of St. Joseph's College, Tiruchirapalli, for the facilities provided.

Department of Chemistry,
 St. Joseph's College,
 Tiruchirapalli 620 002,
 and

Department of Inorganic and
 Physical Chemistry,
 Indian Institute of Science,
 Bangalore 560 012,
 February 18, 1978.

K. DURAI RAJ.
 S. J. ARULRAJ.

C. C. PATEL.

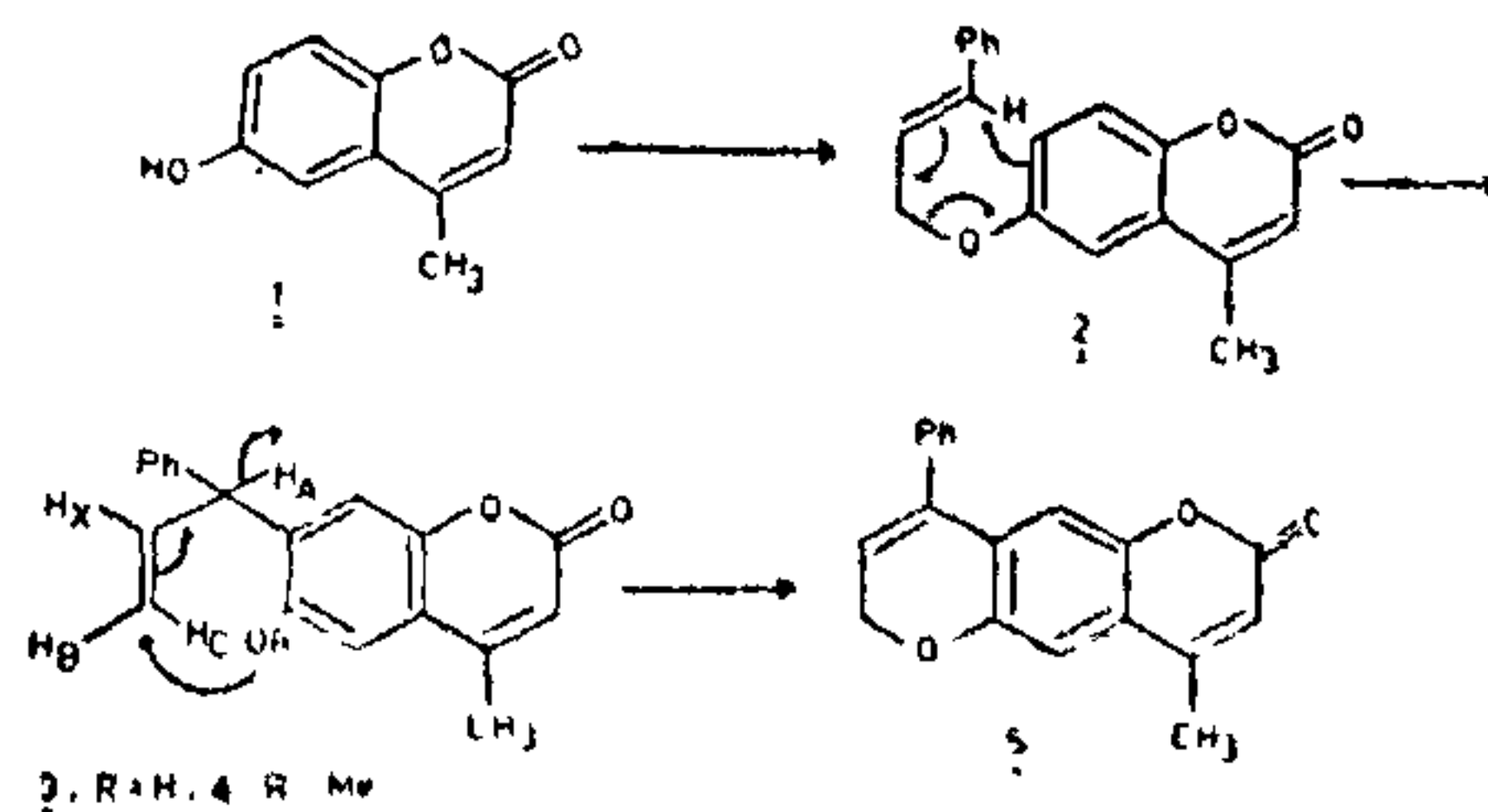
- Murthy, A. S. R., *J. Karnatak Uni.*, 1972, **17**, 19.
- Deshpande, K. R. and Munshi, K. N., *Curr. Sci.*, 1975, **44**, 425.
- Singh, E. J. and Dey, A. K., *J. Ind. Chem. Soc.*, 1960, **37**, 235.
- Markl, P. and Jettmar, A. A., *Microchim. Acta.*, 1974, **3**, 429.
- Durai Raj, K., Arulraj, S. J. and Patel, C. C., *Ind. Journ. Chem.*, 1977, **15A**, 476.
- Quagliano, J. V., Fujita, J., Franz, G., Philips, D. J., Walmsley, J. A. and Tyree, S. Y., *J. Am. Chem. Soc.*, 1961, **83**, 3770.
- Issleib, K. and Kreibich, A., *Z. anorg. allg. Chem.*, 1961, **313**, 338.
- Majumdar, A. K. and Bhattacharyya, R. G., *J. Ind. Chem. Soc.*, 1973, **50**, 646.
- Prabhakaran, C. P. and Patel, C. C., *Ind. Journ. Chem.*, 1972, **10**, 438.
- and —, *Journ. Inorg. Nucl. Chem.*, 1970, **32**, 1223.
- Shriner, R. L., Struck, H. C. and Jorison, W. J., *Journ. Am. Chem. Soc.*, 1930, **52**, 2060.
- Ochiai, E., *J. Org. Chem.*, 1953, **18**, 534.
- Markina, N. A., *Chem Abstr.*, 1973, **79**, 121563 a.
- Nathan, L. C. and Ragsdale, R. O., *Inorg. Chem. Acta*, 1969, **3**, 473.

- Currier, W. F. and Weber, J. H., *Inorg. Chem.*, 1967, **6**, 1539.
- Carlin, R. L., *Journ. Am. Chem. Soc.*, 1963, **83**, 3773.
- Karayannis, N. M., Paleos, C. M., Pytlewski, L. L. and Labes, M. N., *Inorg. Chem.*, 1969, **8**, 2559.
- Robin, Whyman, Copley, D. B. and Hatfield, W. E., *Journ. Am. Chem. Soc.*, 1967, **89**, 3135.
- Watson, W. H., *Inorg. Chem.*, 1969, **8**, 1879.
- Prabhakaran, C. P. and Patel, C. C., *Journ. Inorg. Nucl. Chem.*, 1972, **34**, 3485.
- Ramanujam, V. V., *Semimicro Analysis of Inorganic Mixtures*, p. 31, National Publishing Co., 1970.
- Upadhyay, R. K. and Bansal, R. R., *Jour. Ind. Chem. Soc.*, 1976, **53**, 15.

A NOVEL PRODUCT IN THE CLAISEN REARRANGEMENT OF 6-CINNAMYLOXY-4-METHYL COUMARIN

DURING the Claisen rearrangement, 6-cinnamyloxy-4-methyl coumarin (2) forms the normal rearranged product, viz., 4-methyl-6-hydroxy-7-(1-phenyl-allyl) coumarin (3) and its oxidatively cyclised neoflavene (5). The latter type of product has been noted for the first time in this reaction.

The Claisen rearrangement of cinnamyl ethers of polyphenols could be a method alternative to direct C-cinnamylation method for the preparation of cinnamylated polyphenols or their modified forms^{1,2}. While studying this rearrangement in various cinnamyloxy coumarins, a novel product has been observed in one case, i.e., 6-cinnamyloxy-4-methyl coumarin (2).



6-Hydroxy-4-methyl coumarin³ (1) when refluxed with one mole of cinnamyl bromide in the presence of K_2CO_3 and acetone yielded 6-cinnamyl ether (2), m.p., 145-46; R_f 0.35 (solvent)⁴; UV (nm)⁵, 218, 254 and 320 (4.53, 4.57 and 4.46 respectively); NMR⁶, 2.34 (s, 3H, CH_3 in 4 position), 4.67 (d, J = 6 Hz, 2H, CH_2O), 6.20 (s, 1H, H-3), 6.39-6.82 (m, 2H, $H_2C-CH=CH-Ph$), 7.05 (d, J = 9 Hz, 1H, H-8), 7.30 (d, J = 9 Hz, 1H, H-7), 7.05-7.35 (m, 5H, C_6H_5) and 7.37 ppm (d, J = 3 Hz, 1H, H-5). When