Asian Journal of Chemistry Vol. 4, No. 4 (1992) 924-926

NOTES

Thin Layer Chromatographic Studies of Some Substituted 4H-[1,4]-Benzothiazines

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Thin layer chromatographic methods for separation and identification are reported for some substituted 4H-[1,4]-benzothiazines developed in submicrogram amounts using silica gel plates in various nonaqueous solvent systems.

Structural specificity responsible for tranquilizing activity in phenothiazines is also present in 4H-[1,4]-benzothiazines[1,2]. Thin layer chromatographic studies of phenothiazines have been reported but no one has studied the TLC of 4H-[1,4]-benzothiazines. In continuation of our work on thin layer chromatography[3,4] we are reporting first time the TLC studies of some newly synthesised 4H-[1,4]-benzothiazines. The compounds were synthesised by oxidative cyclisation of *o*-aminothiophenols with β-diketones and β-ketoesters in the presence of dimethyl sulphoxide[5], and successfully applied TLC to the separation and identification of submicrogram quantities on a thin layer of silica gel G using non-aqueous developing solvent systems.

EXPERIMENTAL

Standard thin layer chromatographic equipment was used. Silica gel G according to Stahl for thin layer chromatography manufactured by E. Merck Darmstadt Germany. Acetone and corbon tetarachloride were of analytical grade.

o-Aminobenzenethiol (0.01 molde), *p*-ketoester or β-diketone (0.01 mole) and dimethylsulphoxide (5 ml) were heated together at 145–150°C for $\frac{3}{4}$ hr. The mixture was concentrated under reduced pressure to give a solid mass (4H-[1,4]-benzothiazoles) which was washed with a small amount of methanol and recrystallised from methanol.

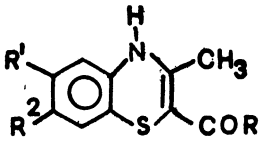
20×20 cm glass plates were coated to a thickness of 1 mm with a slurry of 30 gm of silica gel G in 60 ml distilled water. The plates were than dried in air, activated in an oven at 110°C for 1 hr. and kept in a desicator over anhydrous calcium chloride.

Spots of the compounds containing. 0025 ml of a 1 per cent w/v solution of each compound in acetone were placed. Each drop of the sample was dried before introducing a second to keep the diameter of the spot

within reasonable limits. After drying the spots in an oven at 110°C for 30 minutes, the plates were cooled to room temperature and placed in developing tanks to which 200 ml of developing solvent was added at least 1 hr. prior to use. The solvent was allowed to run upto 10–12 cm at a temperature of 35±.5°C to attain maximum reproducibility. After marking the position of the solvent front, the plates were dried in air. The spots were visible in daylight. R_f values for various newly synthesised 4H-[1,4]-benzothiazines were obtained using this procedure for four solvent systems (Table 1). The results were reproducible within ±0.02 R_f unit.

TABLE 1

R_f VALUES OF SUBSTITUTED 4H-[1,4]-BENZOTHIAZENES



Compound			M.pt. °C	System A	System B	System C	System D
R	R_1	R_2		$R_f \times 100$	$R_f \times 100$	$R_f \times 100$	$R_f \times 100$
CH_3	H	OCH_3	125–127	81.2	71.1	63.3	62.5
OC_2H_5	H	OCH_3	116	91.2	85.5	77.7	71.2
CH_3	CH_3	H	172(D)	93.9	86.6	80.0	76.2
OC_2H_5	CH_3	H	155	95.1	87.7	82.2	77.8
CH_3	H	OC_2H_5	138	87.2	86.5	77.7	72.0
OC_2H_5	H	OC_2H_5	101	91.9	87.6	80.0	75.0
CH_3	H	Cl	180	84.7	72.2	64.4	65.0
OC_2H_5	H	Cl	180–182(D)	93.9	87.5	79.7	72.5
CH_3	H	CH_3	185	92.9	84.4	82.2	76.2
OC_2H_5	H	CH_3	178	94.1	90.0	83.3	78.5

Solvent systems : (Me_2CO : CCl_4)

A = (30 : 70 v/v)

B = (20 : 80 v/v)

C = (15 : 85 v/v)

D = (10 : 90 v/v)

Since one of the major part of the work was an attempt to obtain standard conditions for their separation and identification, the solvents that gave the best shaped spots were considered to be the best. For this

reason Acetone : Carbon tetrachloride systems were chosen. In pure acetone the spots run along with the solvent front hence cannot be used. All the compounds were chromatographically pure, only single spots fairly uniform in shape were obtained in the present investigation. For the series of compounds investigated, we have found that the R_f values increase as the dielectric constant of solvent system increases and is in the following order. Acetone : carbon tetrachloride (10 : 90) < Acetone : carbon tetrachloride (15 : 85) < Acetone : carbon tetrachloride (20 : 80) < Acetone : carbon tetrachloride (30 : 70).

R_f value increases if the 7-chloro group is changed to 7-methyl group. It is also observed that the R_f values for 7-methoxy derivatives are less than those of 7-chloro and 7-methyl derivatives. It was particularly noticeable that 2-ethyl carboxylate derivatives showed higher R_f values than the corresponding 2-acetyl derivatives in this series of compounds.

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[*Received* : 3 December 1990; *Accepted* : 1 July 1991] AJC 372