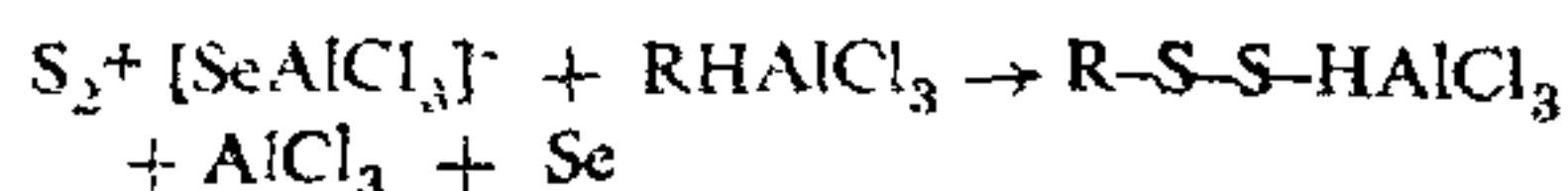


$S_2^+ [SeAlCl_3]^-$. This complex undergoes subsequent reactions as shown below :



The composition of the complex gains support from the mass spectrum of SeS_2 which shows the predominant molecular ion being S_2^+ . Further the postulation of such a complex also explains the nonformation of diaryl selenides owing to the poor nucleophilicity of selenium. The present work affords an elegant method towards the synthesis of simple diaryl sulphides in nearly quantitative yields.

Materials and Methods

All the chemicals used are of Analar grade and the solvents are distilled and dried before use. The infrared spectra are recorded on Perkin Elmer 237-B Infrared Grating Spectrometer. The GLC of diphenyl and tolyl sulphides are taken on 2-5% DC-11 silicone grease column at 150° and 174° respectively. The mass spectrum is recorded on MS 702 spectrometer using electron bombardment for molecular fragmentation. SeS_2 was synthesised⁷ by the reaction of aqueous solutions of selenious acid with Na_2S at 5-7° and used without purification.

Diphenyl sulphide : About 20 g of anhydrous $AlCl_3$ was introduced into a three-necked flask containing 300 ml of benzene fitted with a stirrer, condenser and an addition flask containing 10 g SeS_2 . The addition of SeS_2 was done slowly under an atmosphere of nitrogen and the reaction commenced immediately with the evolution of H_2S . The reaction was completed in about 2 hrs. The reaction mixture was hydrolysed with ice and the solvent removed under reduced pressure. This left behind a pale yellow liquid and it was passed through a column of silica gel to remove any possible disulphides. The product was distilled under vacuum and the pure colourless liquid distilling at 162-163°/18 mm was collected. Yield : 90%. Similar procedure was adopted for the synthesis of ditolyl, and dixylyl sulphides. Di *p*-tolyl sulphide was obtained as colourless liquid boiling at 179-180°/11 mm. Yield : 80%. Di *p*-xylyl sulphide was obtained as colourless crystals, m.p. 75-76°. Yield : 80%.

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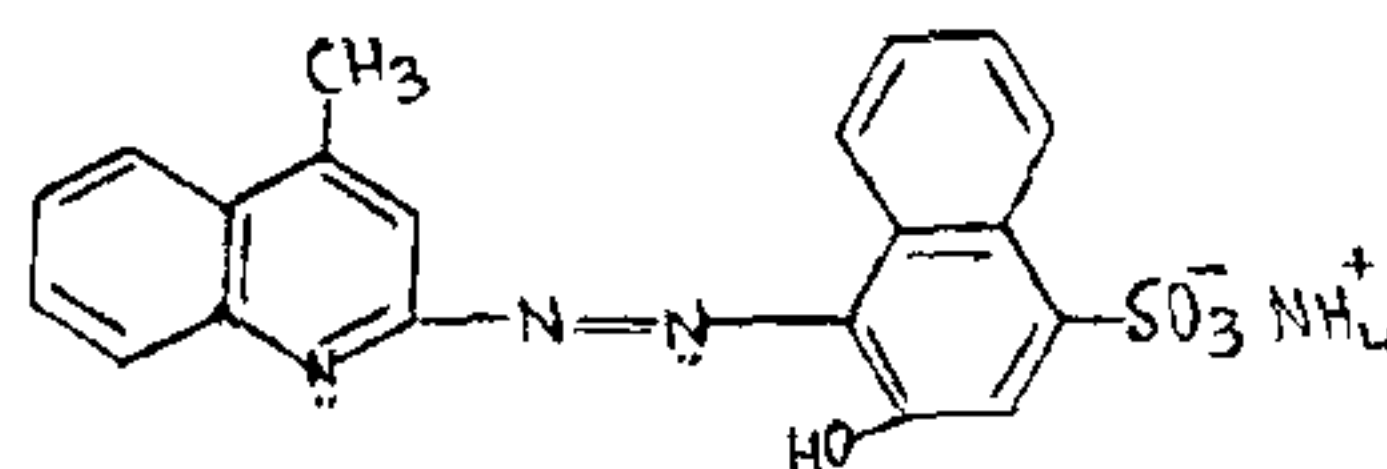
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1. Blatt, A. H., *Organic Synthesis*, Collective Volume II, John Wiley, N.Y., 1950, p. 242.
2. Hampson, G. C., Farmer, R. H. and Sutton, L. E., *Proc. Roy. Soc. London*, 1933, 142 A, 147.
3. Ziegler, J. H., *Ber.*, 1895, 28, 1674.
4. (a) Bourgeois, *Ibid.*, 1895, 28, 2312 ;
(b) Martinowicz, Z., *Chem. Zentr.*, 1910, 2, 1048.
5. Agenas, L. B., In *Organic Selenium Compounds ; Their Chemistry and Biology*, Ed. by Klayman, D. L. and Gunther, W. H. H., John Wiley, N.Y., 1973, p. 173.
6. Kudchadker, M. V. and Irgolic, K. J., In *Selenium*, Ed. by Zingaro, R. A. and Cooper, W. C., Van Nostrand, Reinhold Pub. Co., N.Y., 1974, p. 408.
7. Krafte, M. Ya., Bordina, G. M. and Rubina, Z. O., *USSR*, Feb. 1, 1960, 125, 797.
8. Avram, M. and Mateescu, G. D., *Infrared Spectroscopy, Applications in Organic Chemistry*, Wiley, Interscience, 1970, p. 217.

ANALYTICAL POTENTIALITIES OF A NEW HETEROCYCLIC AZO DYE: 1-(2-LEPIDYLAZO)-2-NAPHTHOL-4-AMMONIUM SULPHONATE (LANAS) AS A METALLOCHROMIC INDICATOR FOR TITRIMETRIC DETERMINATION OF MERCURY (II) WITH EDTA

HETEROCYCLIC azo dyes introduced recently¹ find intensive applications in analytical chemistry for micro determinations of metal ions spectrophotometrically² or complexometrically³⁻⁵. Only very few water soluble heterocyclic azo dyes have been explored so far as analytical reagents for micro determination of metal ions. In this communication, a new water soluble heterocyclic azo dye, 1-(2-lepidylazo)-2-naphthol-4-ammonium sulphonate (LANAS) has been synthesised, characterised and used as metallochromic indicator for complexometric determination of mercury (II).



(I)

TABLE I
Determination of mercury (II) with EDTA : Precision and accuracy

Sl. No.	Amount of Hg(II) in mg	Standard deviation Si	Variation coefficient	Relative width of confidence interval	% Relative error
1.	20	0.038	0.18	22.02 ± 0.015	+0.1
2.	100	0.106	1.06	100.1 ± 0.04	+0.1
3.	200	0.26	1.30	200.4 ± 0.11	+0.2
4.	4	0.006	0.15	4.008 ± 0.002	+0.2

LANAS (I) has been synthesised by condensing 2-hydrazino lepidine and sodium salt of 1, 2-naphthoquinone-4-sulphonic acid in presence of dilute hydrochloric acid and neutralizing the resulting solution with dil. ammonium hydroxide. The purity of LANAS has been checked by thin layer chromatography. The analysis for C, H, N (Found C = 59.43%, N = 13.51%, H = 4.5%; calculated C = 58.53%, N = 13.66%, H = 4.39%) and I.R. spectrum (3650–3540 cm^{-1} bonded OH; 1600 cm^{-1} —N=N—; 1500 cm^{-1} —CH₃ rocking; 1400 cm^{-1} NH₄⁺; 1220, 1280 cm^{-1} —SO₃⁻; 1000, 1050 cm^{-1} C—O) for LANAS justify the structure (I) for LANAS.

Mercury (II) forms water soluble blue coloured complex with LANAS. The blue colour of Hg(II)—LANAS is discharged quickly on adding EDTA solution. This has been taken advantage of in developing a sensitive and rapid method for titrimetric determination of mercury (II).

The pH and temperature ranges found suitable for an accurate determination are 6.0 to 7.5 (hexamine or pyridine—nitric acid buffer) and 0 to 70° C respectively. At higher temperatures the amount of EDTA used is less and below 0° C the end point is sluggish. Two to three drops of 0.01% of LANAS in distilled water are sufficient to cause a sharp colour change at the end point. The minimum and maximum amount of mercury that can be titrated accurately are 1 mg and 200 mg respectively.

Recommended Procedure

To aliquots containing mercury (II) add two drops of 0.01% LANAS solution and a few drops of dilute nitric acid till yellow colour is obtained. Then add sufficient amount of hexamine or pyridine—nitric acid buffer (former is preferred) till blue colour is obtained (pH 6.0 to 7.5). Titrate this with EDTA solution till the blue colour changes sharply to yellow. The titration precision is characterized by the standard deviation of single determination, Si, the variation coefficient %, $Si \cdot 100/x$, the confidence interval and its width for a statistical significance of $\alpha = 0.005$. The titration accuracy is expressed by relative error $(\mu - x) \cdot 100/\mu$, where μ is the accurate value.

Results and Discussion

The following foreign ions did not cause any interference in the titration of 100 ppm of mercury (II), when they were present in amounts in ppm (in parenthesis) :

Results and Discussion

Bromide (1000), Fluoride and Sulphate (5000), Nitrite and Phosphate (2000), Acetate (large excess), Oxalate (5000), Tartrate (4500), Citrate (4000) and Sulphite (4000).

Sulphide, thiosulphate, iodide and cyanide interfere seriously. Hydroxyl amine (3 ml of 0.1 M), thiourea (2 ml of 0.1 M) do not interfere. Ascorbic acid gives permanent bluish turbidity.

Ruthenium, rhodium and osmium (150), palladium (20), platinum (500), tungsten (800), Mo(VI) and rare earths (5), alkaline earths (250) also do not interfere. Other metals interfere and the interference in a few cases has been overcome through masking. The amount of cations which have been masked are as follows :

Iron (III) (300)*, lead (II) (500)**, aluminium (III) (400)*, and bismuth (III) (100)***. Attempts to mask zinc and cadmium were unsuccessful.

Visual indicator reactions are not widely used for micro determination of mercury⁶. The present titrimetric method developed for mercury (II) is rapid and sensitive and many complexing anions do not interfere.

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* Masked with fluoride.

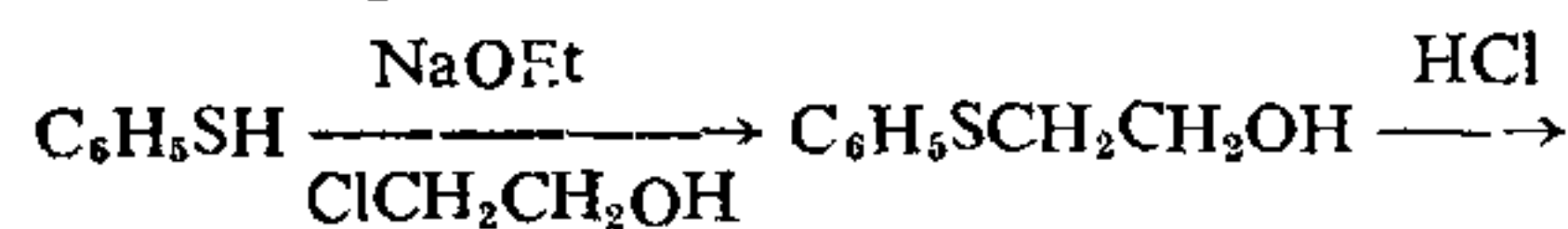
** Masked with sulphate or phosphate.

*** Masked with chloride.

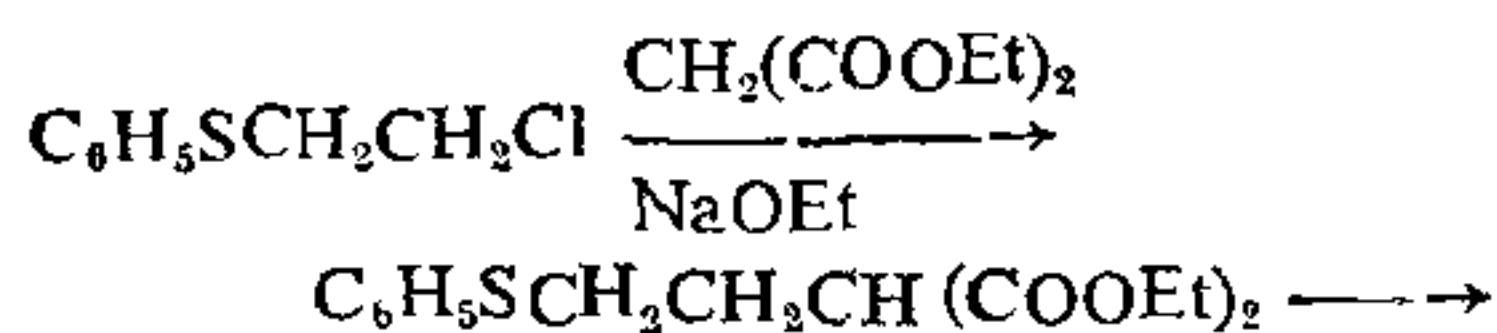
1. Anderson, R. G. and Nickless, G., *Analyst*, 1967, 92, 1093.
2. Flaschka, H. A. and Barnard, A. J., *Chelates in Analytical Chemistry*, Marcel Dekker, Inc., New York, 1972, Vol. 4.
3. —, *EDTA Titrations*, Pergamon Press Ltd, Oxford, 1964.
4. Schwarzenbach, G., *Complexometric Titrations*, Methuen and Co. Ltd., London, Inc., New York, 1960.
5. Welcher, F. J., *The Analytical Uses of Ethylenediamine Tetraacetic Acid*, D. Van Nostrand Co. Inc., Princeton, New Jersey, New York, 1961.
6. Chilov, S., *Talanta*, 1975, 22, 205.

SYNTHESIS OF 5-HOMOTHIOCHROMANONE

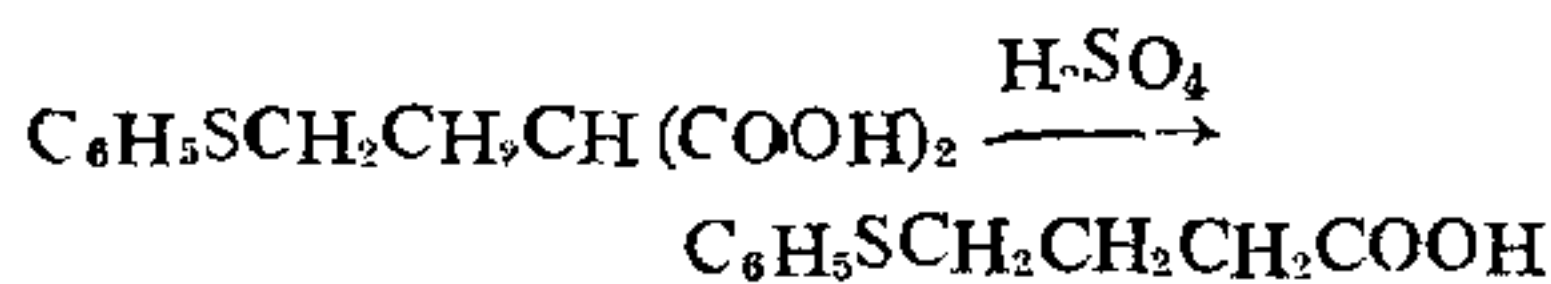
IN connection with our work on the kinetics of acetylation of hydroxy sulphones, we required 5-homothiochromanone. The present work describes a new method for its synthesis and the scheme followed is given below.



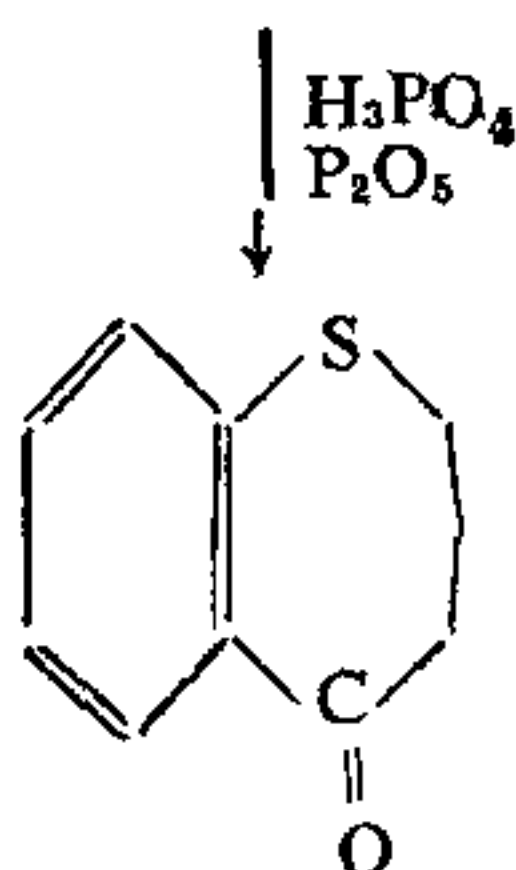
I



II



III



γ-Phenylmercaptobutyric acid.—β-Hydroxyethyl phenyl sulphide (I) was obtained from thiophenol and ethylene chlorohydrin by adopting the procedure of Smith and Davis¹. A mixture of I and concentrated hydrochloric acid was refluxed to give β-chloroethyl phenyl sulphide¹ (II); b.p. 123–124°/15 mm. Diethyl malonate (8 g) was added from a dropping funnel to sodium ethoxide in absolute alcohol (1.5 g

of sodium and 50 ml of absolute alcohol). To this II (8 g) was added slowly and refluxed for an hour, cooled and after the addition of aqueous potassium hydroxide (25%, 100 ml), it was refluxed again for 4 hours and then neutralized with concentrated hydrochloric acid. The dicarboxylic acid separated as a solid; m.p. 156–158°. A mixture of the dicarboxylic acid (2.7 g), concentrated sulphuric acid (20 ml) and water (50 ml) was refluxed for 4 hours and on cooling *γ*-phenylmercaptobutyric acid (III) separated as a solid; m.p. 61–62° (Found: C, 61.1; H, 6.4%. C₁₀H₁₂SO₂ requires: C, 61.2; H, 6.2%). Cagniant and Deluzarche² obtained this acid by the hydrolysis of C₆H₅S(CH₂)₃CN; m.p. 63°.

5-Homothiochromanone.—A solution of III (6 g) in syrupy phosphoric acid (20 ml, *d* 1.750) was made by gentle heating and phosphorus pentoxide (50 g) gradually but quickly added with vigorous shaking. Large quantity of heat was evolved and a brown paste obtained. After 3½ hours, ice was added to the mixture. The product was isolated by extraction with ether; the ethereal solution was washed with aqueous sodium carbonate and then with water, dried and evaporated and 5-homothiochromanone was obtained as an oil; b.p. 180–181°/24 mm (yield 3.5 g). (Found: C, 67.6, H, 5.8%. C₁₀H₁₀SO requires: C, 67.4, H, 5.7%). Its semicarbazone had m.p. 212–214°. Cagniant and Deluzarche² obtained 5-homothiochromanone from the acid chloride of (III) using aluminium chloride and reported b.p. 175–176°/22 mm; semicarbazone, m.p. 213°.

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Tuticorin 3, March 20, 1976.

1. Smith, L. I. and Davis, Jr., H. R., *J. Org. Chem.*, 1950, 15, 824.
2. Cagniant, P. and Deluzarche, A., *Compt. Rend.*, 1946, 223, 677; *Chem. Abstr.*, 1947, 41, 1669.

A NEW METHOD FOR SYNTHESIS OF 3-PHENYLISOQUINOLONES

3-PHENYLISOQUINOLONE (IIIa) assumes importance because of anti-inflammatory, antibacterial, anti-protozoal and antifungal activity reported¹ recently for its various N-substituted derivatives that can be synthesised¹ directly from IIIa. Synthesis of IIIa was first reported by Gabriel² by action of ammonia on 3-phenylisocoumarin but because of low yield of the latter by the methods^{8,9} employed then, it did not receive much acceptance and that led to development of many other methods¹⁻⁷ for synthesis