

sulphate. Dry hydrogen chloride was passed into the chloroform solution giving the phenyl amidine chloride. Similarly other amidine chlorides were prepared.

Amidine sulphides—To a solution of this amidine chloride in chloroform was added a solution of N-acetyl-N'-phenyl thiourea (2.0 g) in acetone. For completion of the reaction further hydrogen chloride was passed in the reaction mixture. After some time a crystalline product separated, m.pt. 149 C. The product could not be recrystallized without decomposition and desulphurised alkaline lead acetate solution. The aqueous solution of the compound gave a picrate with picric acid, m.pt. 128 C. Other amidine sulphides were also prepared similarly and their physical properties are given in Table II.

Biological

(i) **Local anaesthetic activity**—Frogs were used for local anaesthetic activity by nerve block method. A transverse incision is made on the abdominal wall and Viscera (through this opening) is removed carefully to expose the lumbar plexus. Frog is hanged by its lower jaw. The solution of the compound (0.1 g/100 ml) is poured into this pocket and the foot withdrawal response with 0.1 N HCl and 0.05 N HCl is tested. The time required, when the foot withdrawal is completely stopped, is noted (Table III).

(ii) **Antifungal testing**—The fungal testing was done on *Alternaria alternata* employing Czapek-Dox liquid growth medium mixed with the amidine sulphides (0.1% solution). The growth was noticed after twelve hours by hanging drop method for spore germination. The percent inhibition of germinating fungi was determined (Table III).

(iii) **Antibacterial testing**—Different bacterial cultures were taken and sub-cultured on nutrient agar plates. Filter paper discs (3–4 mm diameter) soaked in the amidine sulphide solution (200 µg) were fixed at different places. Next day after 24 hrs of incubation sensitivity was observed. All the compounds were found to be inactive.

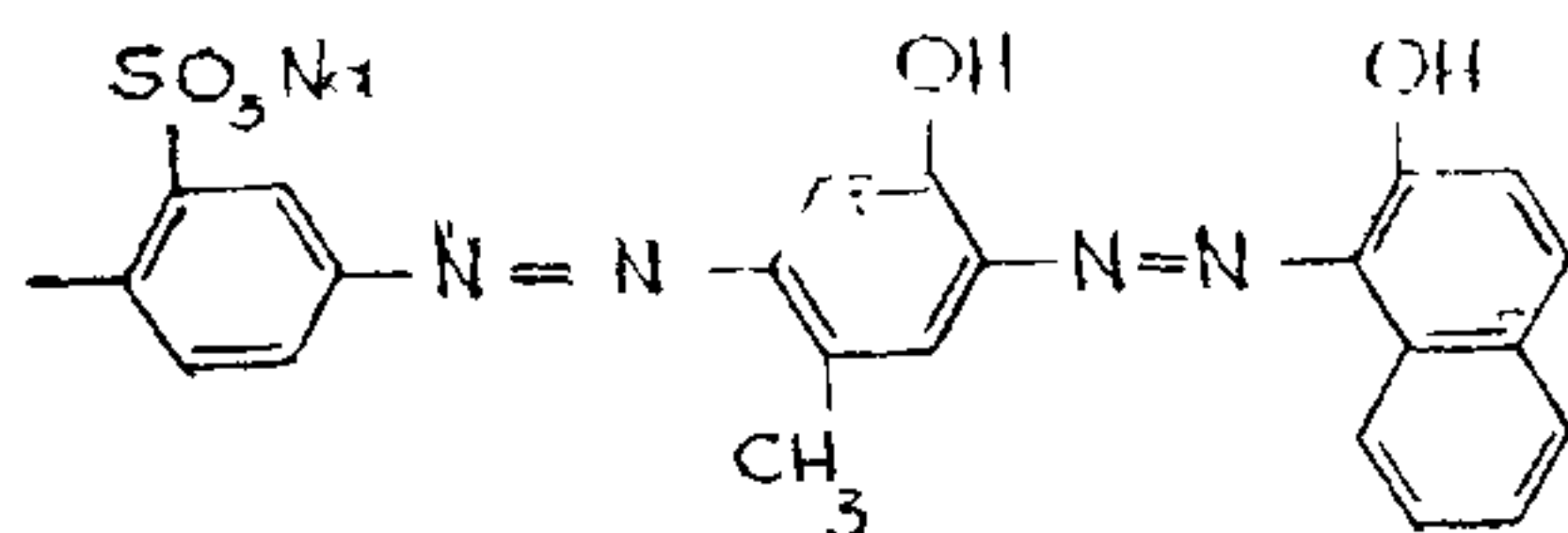
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EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF ATROPINE SULFATE BY SOLOCHROME GREEN V 150

THE analysis of atropine is of particular interest to pharmaceutical and forensic chemists and toxicologists. Many of the commonly employed methods are indirect and time-consuming¹⁻⁴; the precipitation methods are only applicable with large amounts of atropine. The range of absorbance by the picrate method is small. The iodine method gives a very stable colour but does not permit the use of standard curves. A few direct spectrophotometric methods are available that make use of acidic dyes which form extractable ion pair complexes with the basic alkaloids. Generally, triphenylmethane dyes are used for the determination of atropine⁵⁻⁷; very few azo dyes⁸ have been employed for its determination. The author, in his investigations on the use of diazo dyes for the determination of alkaloids, found that these dyes are more sensitive than the commonly employed triphenylmethane dyes and proposed methods for strychnine⁹ and brucine¹⁰. The present communication describes the microdetermination of atropine sulfate by a diazo dye, Solochrome Green V 150 (I) supplied by ICI, Calcutta. The method is rapid, sensitive and applicable to 2 µg/ml of the solution.



(I)

Experimental

Absorbance measurements were carried out using a Bausch and Lomb Spectronic-20 spectrophotometer. Walpole and Clarke and Lübs buffers were used. All other chemicals used were of analytical grade.

Results and Discussion

Aqueous solutions of Solochrome Green V 150 have a maxima at 490 nm. Change in pH of the solution does not affect the λ_{\max} of the dye. The dye is not extracted into chloroform at any pH in the range 1-11. The molar absorptivity of the dye is $7.6 \times 10^3 \text{ lit mol}^{-1} \text{ cm}^{-1}$. The ion pair complex of atropine with the dye is extracted into chloroform, the pH of maximum extraction being 4. The ion pair shows a maxima at 520 nm. Change in pH does not affect this maximum. Of the three halogenated solvents, chloroform, 1, 2 dichloroethane and dichloromethane, chloroform has been found to be the best extractant. About one minute of shaking is sufficient for complete extraction of ion pair. Excess of shaking may sometimes result in emulsion formation. The colour of the extract is stable for hrs after which sedimentation sets in. The Beer's law is obeyed in the range 30-840 μg with the minimum amount of determination being 2 $\mu\text{g/ml}$. The Sandell's sensitivity is $0.2 \mu\text{g/cm}^2/0.005 \text{ abs. unit}$. The molar absorptivity of the ion pair complex is $7665 \text{ lit mol}^{-1} \text{ cm}^{-1}$. The composition of the ion pair complex as found by Job's continuous variation and mole ratio methods is 1:1 (Alkaloid: Dye). Five fold excess of the dye is required for the maximum colour development. Concentrated solution of the dye results in emulsion formation. The precision of the method, based on four determinations each, has been found to be $\pm 2\%$.

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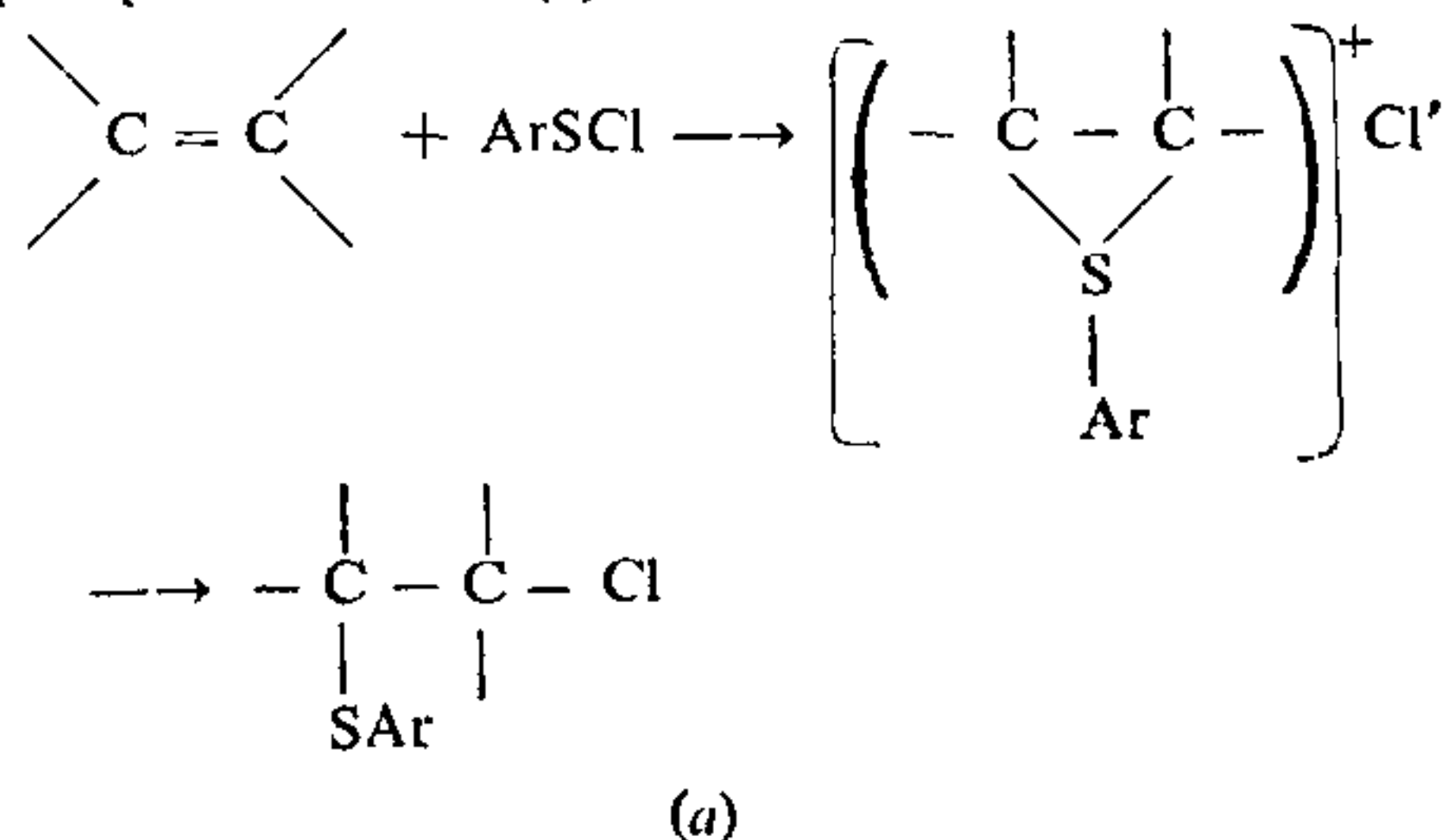
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REACTIONS OF 2-ARYLAZO-ARYLSULPHENYL BROMIDES WITH OLEFINS

THOUGH considerable literature has been accumulated on the reactions of sulphenyl halides with olefins and acetylenes^{1,2}, similar reactions of sulphenyl halides of ortho-mercapto-azo compounds are not reported so far. Kharasch *et al.*³ have found that the additions of aryl sulphenyl chlorides with various olefins, to give β -chlorosulphides, are consistent with a mechanism involving the intermediate formation of an episulphonium ion (a).



It would be expected, if the addition involves an intermediate of the type (a), that the intermediate could be diverted by other nucleophiles. It is also possible for the intermediate to undergo a loss of proton rather than complete the reaction by addition, e.g.,

