

(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 $\mu\text{g/cm}^2/0.005$ 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 $\pm 2\%$.

Central Forensic Science
Laboratory,
5-9-201/2, Chirag Ali Lane,
Hyderabad 500 001, A.P.,

N. V. RAMA RAO.*

and
Department of Chemistry,
Univ. of Roorkee, Roorkee.
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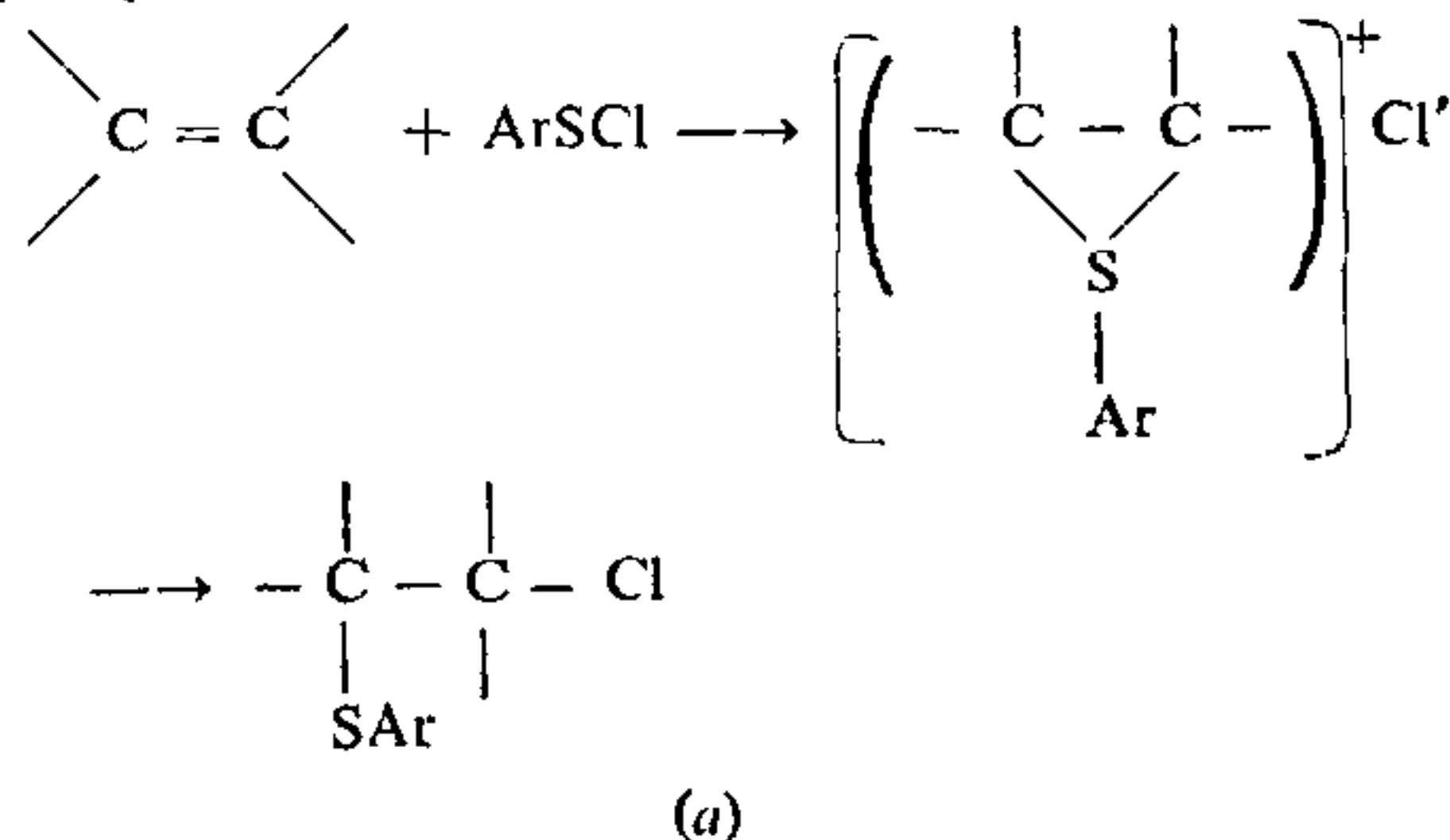
V. B. RIDDY.

* Present address : N. V. Rama Rao, G 4, Azad Bhawan, University of Roorkee, Roorkee 247 672, U.P., India.

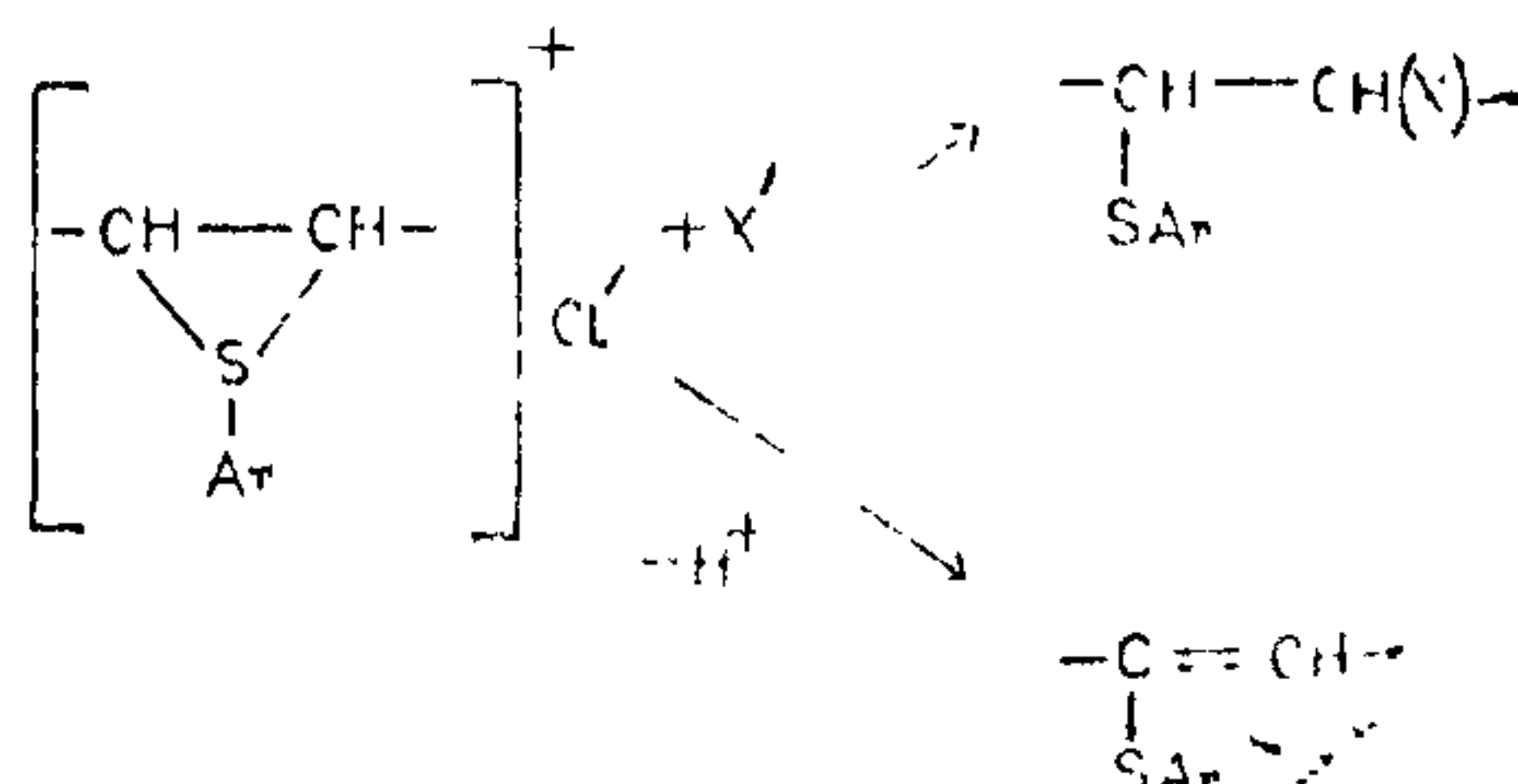
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REACTIONS OF 2-ARYLAZO-ARYLSULPHENYL BROMIDES WITH OLEFINS

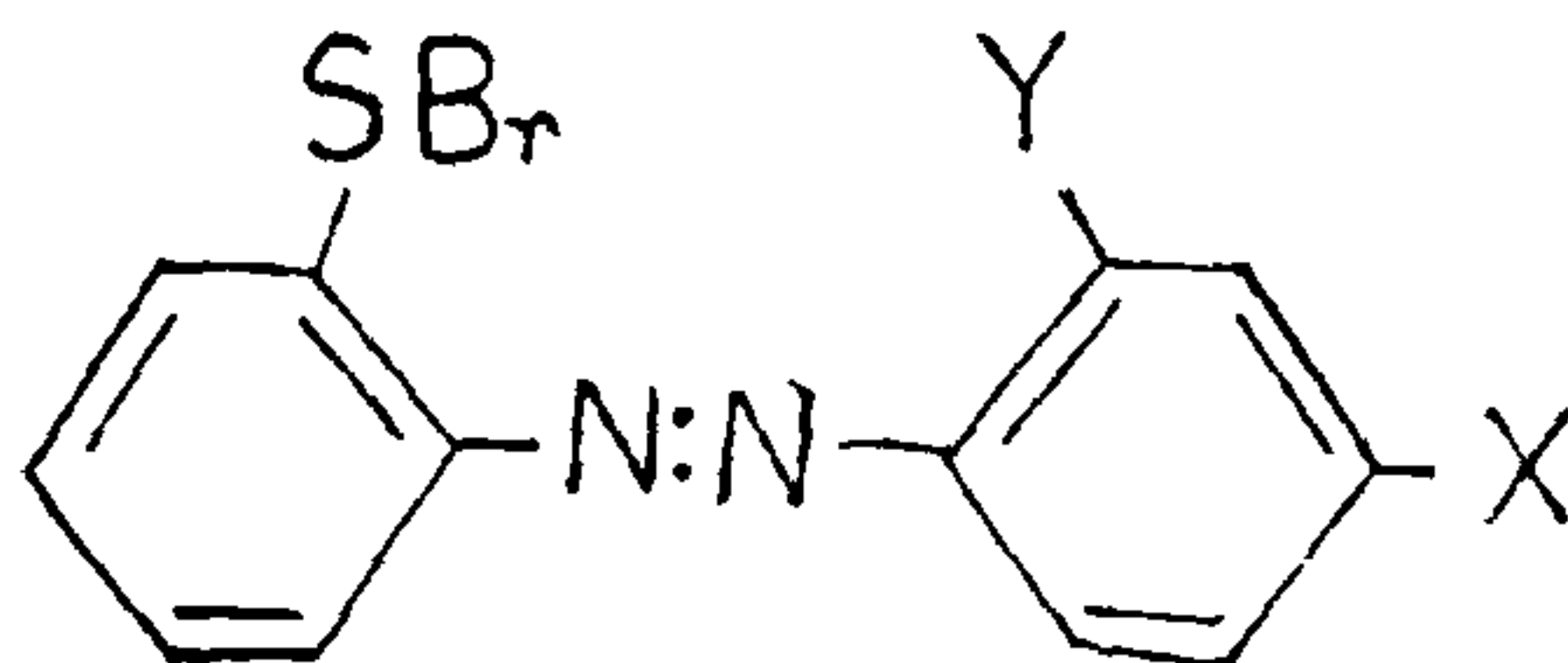
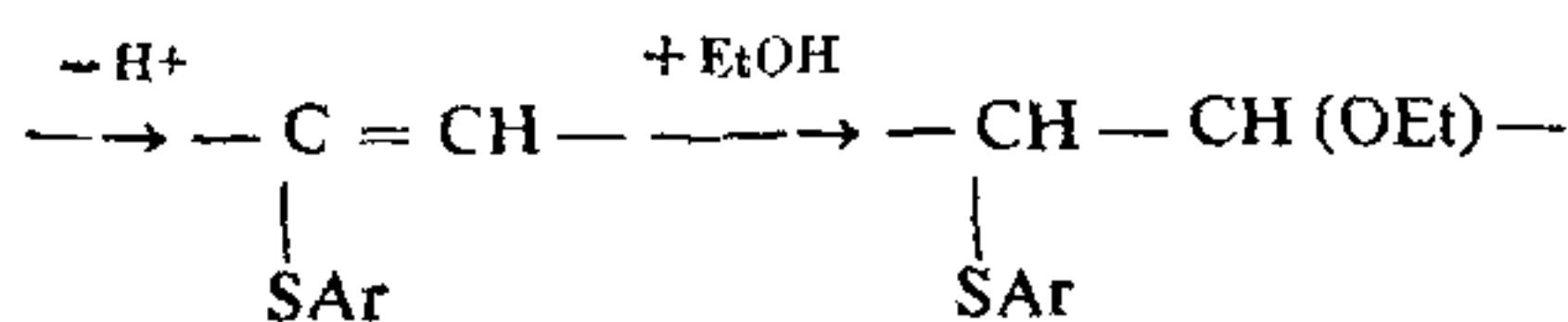
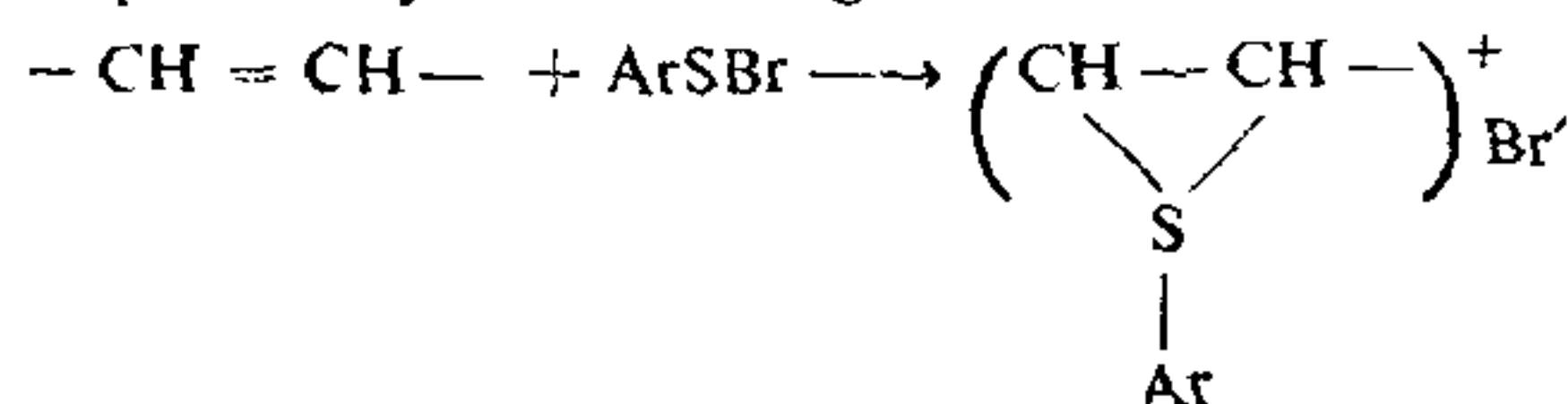
THOUGH considerable literature has been accumulated on the reactions of sulphenyl halides with olefins and acetylenes^{1,2}, similar reactions of sulphenyl halides of ortho-mercapto-azo compounds are not reported so far. Kharasch *et al.*³ have found that the additions of aryl sulphenyl chlorides with 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.,

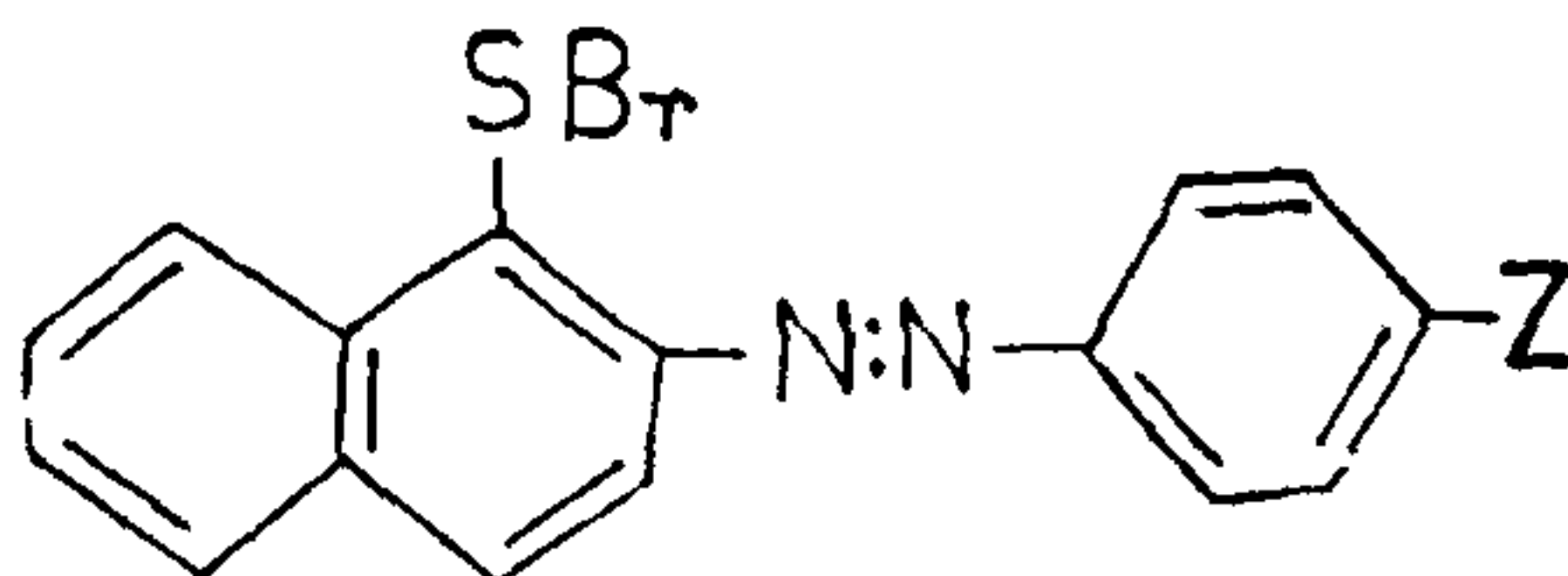


With a view to obtaining evidence for the existence of 2-aryloxy arylsulphenium ion in solution, we have synthesized a few azobenzene-2-sulphenyl bromides (I, a, b, c, d)⁴ and 2-aryloxy-naphthalene-1-sulphenyl bromides (II, a, b)⁵ and have studied their reactions with cyclohexene and styrene in ethanolic medium. It has been found that only the compound (I d) reacts with these olefins to give the corresponding β -ethoxy sulphides (III and IV respectively) instead of the expected β -bromo sulphides. The presence of the ethoxy group in the addition products is established by the IR spectra of the compounds (a medium band at 1110 cm^{-1} is observed for both the compounds) and by elemental analysis of the compounds (III) and (IV). The mechanism of these reactions may be explained by the following scheme:



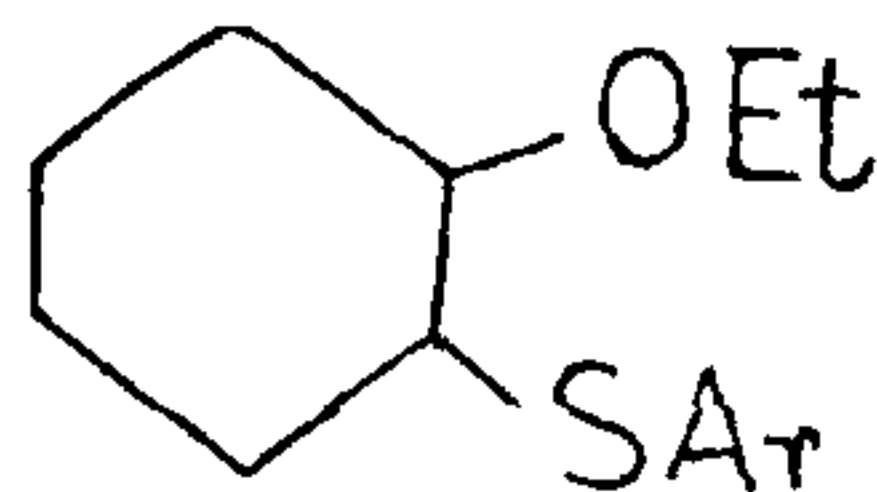
- (a) X = Y = H
 (b) X = CH₃, Y = H
 (c) X = H, Y = CH₃
 (d) X = CH₃, Y = NO₂

I

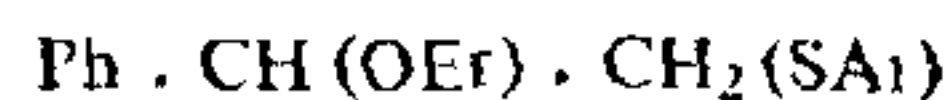


- (a) Z = H
 (b) Z = CH₃

II



III



IV

where Ar = *o*-(2-nitro-4-methyl phenylazo-) phenyl group.

Experimental

1. *Reaction with cyclohexene.*—2-Nitro-4-methylazobenzene-2'-sulphenyl bromide (I d, 500 mg) was dissolved in ethanol (150 ml) and to it cyclohexene (1 ml) was added. The solution was swirled well and kept at room temperature for 8 days. The resulting yellow precipitate of *o*-(2-nitro-4-methyl-phenylazo-) phenyl- β -ethoxy cyclohexyl sulphide (III) was filtered, washed and dried (350 mg). Crystallized from ethanol, m.p. 133–134 (C₂₁H₂₅N₃O₃S requires C, 63.1; H, 6.2; N, 10.5% found C, 62.8; H, 6.2; N, 10.1%).

2. *Reaction with styrene.*—2-nitro-4-methylazobenzene-2'-sulphenyl bromide (I d, 500 mg) was dissolved in ethanol (150 ml) and to it was added styrene (1.5 ml). The mixture was shaken and kept at room temperature for 6 days. Red plates of *o*-(2-nitro-4-methyl-phenylazo-) phenyl- β -ethoxy- β -phenyl ethyl sulphide (IV) (380 mg) was crystallized from ethanol, m.p. 84–85° (C₂₃H₂₃N₃O₃S requires C, 65.5; H, 5.5; N, 9.7%; found C, 66.0; H, 5.7; N, 9.6%).

3. IR spectra of the compounds were taken in nujol mull in a Carl-Zeiss Jena UR 10 spectrophotometer.

Department of Chemistry,
 Gauhati University, Assam,
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A. CHAUDHURI.
 S. K. BHATTACHARJEE.
 P. SENGUPTA.

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5. Under publication.

STUDIES OF SOME CONDENSED THIAZOLE SYSTEMS ON THE NODULATION

It is reported that some benzothiazolyl hydrazones are found to be plant growth promoters¹. With a view to studying the effect of naphthothiazoles and xylindinothiazoles in place of benzothiazole this work was undertaken. The xylindinothiazoles are prepared by the usual method of condensing hydrazino compound with different aldehydes. Heteryl substituents are specifically selected since they have featured prominently in physiological activity. The other series has been selected with tricyclic and tetracyclic compounds with or without substituent at 3 position.