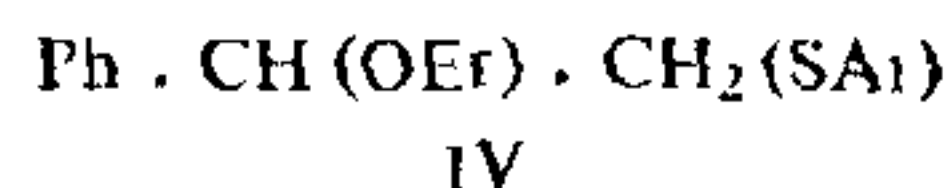
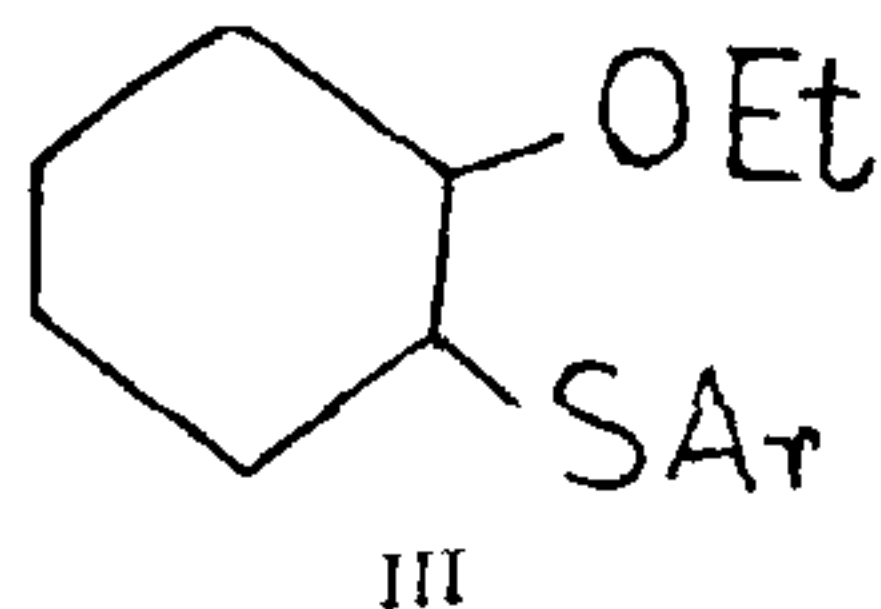
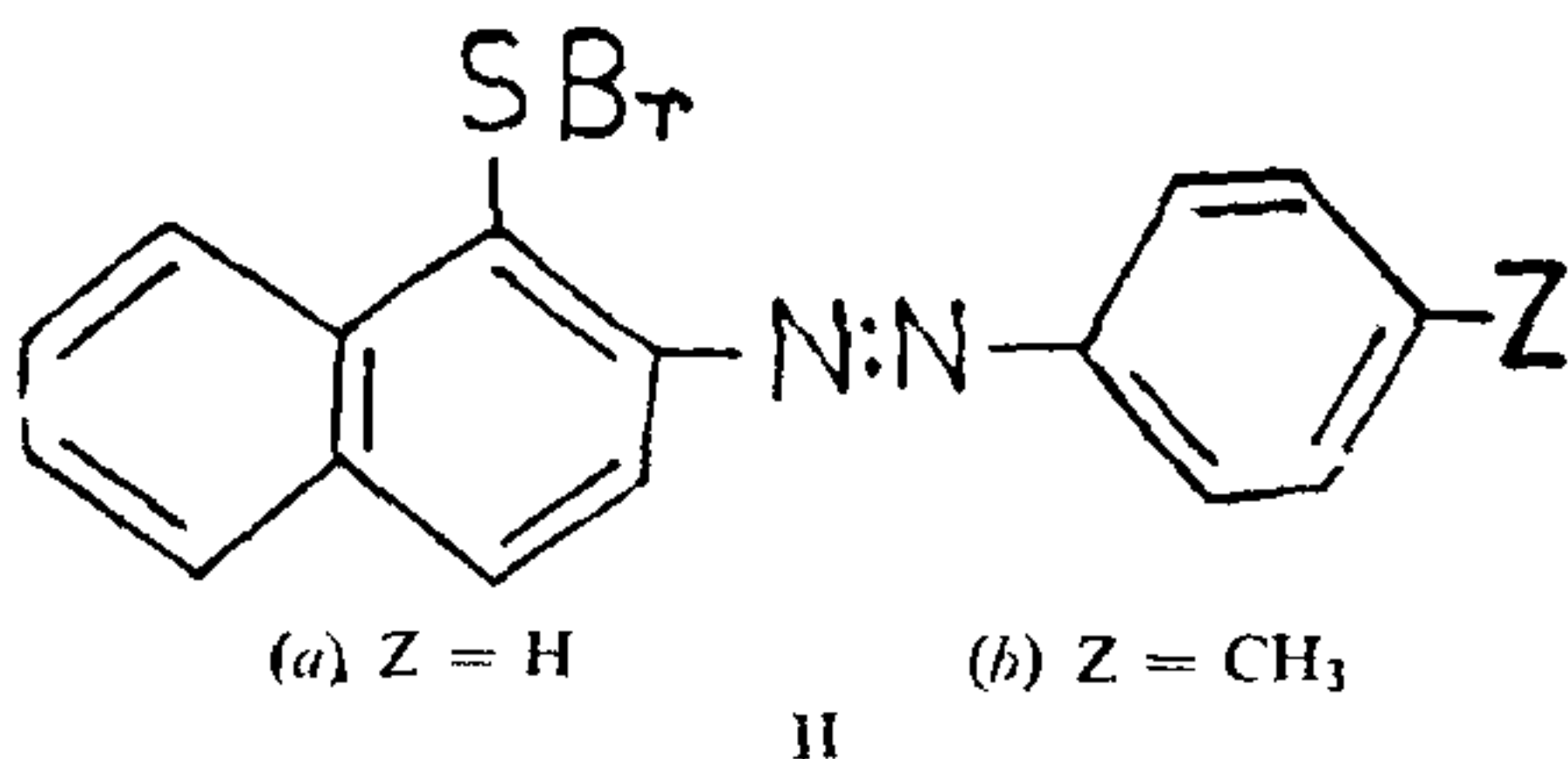
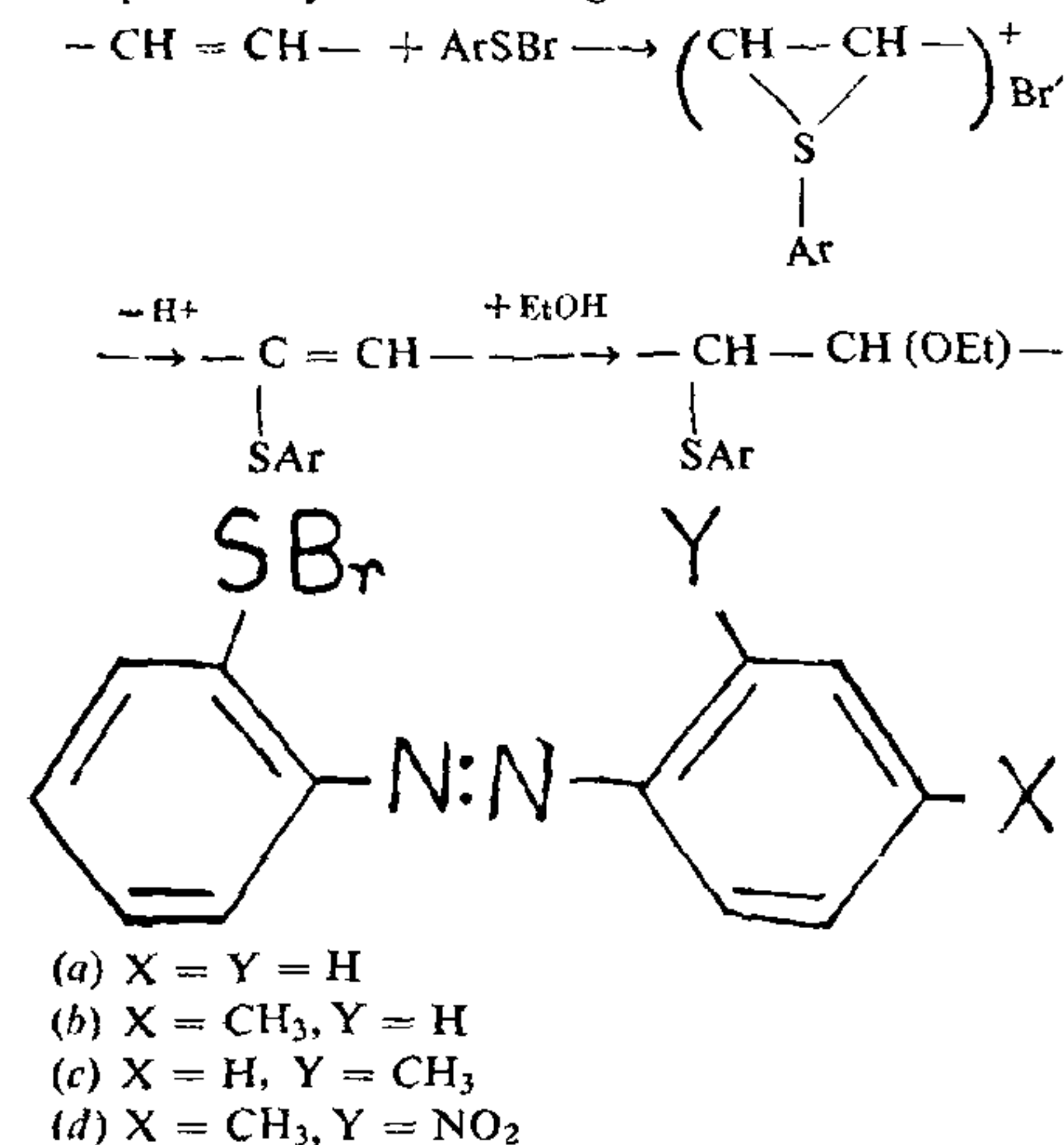


With a view to obtaining evidence for the existence of 2-aryldiazo arylsulphenium ion in solution, we have synthesized a few azobenzene-2-sulphenyl bromides (I, *a, b, c, d*)<sup>4</sup> and 2-aryldiazo-naphthalene-1-sulphenyl bromides (II, *a, b*)<sup>5</sup> and have studied their reactions with cyclohexene and styrene in ethanolic medium. It has been found that only the compound (I *d*) reacts with these olefins to give the corresponding  $\beta$ -ethoxy sulphides (III and IV respectively) instead of the expected  $\beta$ -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  $\text{cm}^{-1}$  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:



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- $\beta$ -ethoxy cyclohexyl sulphide (III) was filtered, washed and dried (350 mg). Crystallized from ethanol, m.p. 133–134 ( $\text{C}_{21}\text{H}_{25}\text{N}_3\text{O}_3\text{S}$  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- $\beta$ -ethoxy- $\beta$ -phenyl ethyl sulphide (IV) (380 mg) was crystallized from ethanol, m.p. 84–85° ( $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_3\text{S}$  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.

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March 22, 1978.

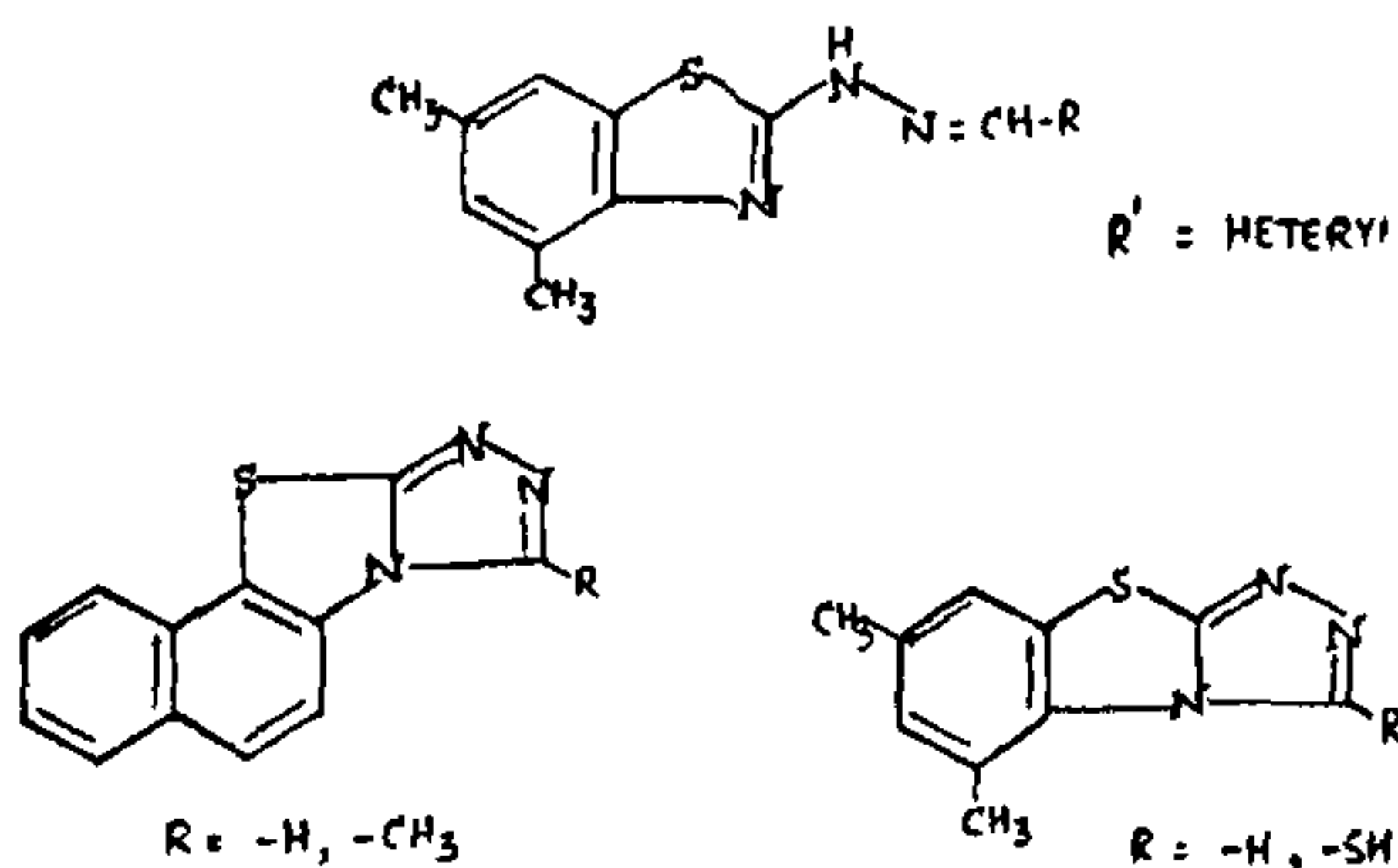
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S. K. BHATTACHARJEE.  
P. SENGUPTA.

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#### STUDIES OF SOME CONDENSED THIAZOLE SYSTEMS ON THE NODULATION

It is reported that some benzothiazolyl hydrazones are found to be plant growth promoters<sup>1</sup>. With a view to studying the effect of naphthothiazoles and xyldindinothiazoles in place of benzothiazole this work was undertaken. The xyldindinothiazoles 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.

TABLE I  
Effect of some condensed thiazole systems on nodulation



Sr. No.	Name of compound	Total No. of nodules three replicas					Average No. of nodules.
		Five observations					
		1	2	3	4	5	
1.	<i>s</i> -Triazolo (5, 4- <i>b</i> ) naphtho (2, 1- <i>d</i> ) thiazole	5	26	13	16	24	28
2.	3-Methyl- <i>s</i> -triazolo (5, 4- <i>b</i> ) naphtho (2, 1- <i>d</i> ) thiazole	8	20	16	29	14	29
3.	3-Mercapto 5, 7-dimethyl- <i>s</i> -triazolo (3, 4- <i>b</i> ) benzothiazole	5	22	35	32	26	40**
4.	5, 7-Dimethyl- <i>s</i> -triazolo (3, 4- <i>b</i> ) benzothiazole	8	19	9	29	13	26
5.	2 (3'-Pyridyl) 4, 6-dimethyl benzothiazolyl hydrazone	9	28	20	35	28	40**
6.	2 (2'-Thienyl) 4, 6-dimethyl benzothiazolyl hydrazone	2	19	24	33	21	33*
7.	2 (2'-Furyl) 4, 6-dimethyl benzothiazolyl hydrazone	2	22	19	25	25	31
8.	Gibberellic acid (standard)	7	19	24	19	12	27
9.	Control	7	18	23	27	15	30
		MESS	77.1.				
		SE	0.94.				
		L.S.D.	0.05.,	2.81*.			
			0.01	3.88**	at 12 df.		

The following compounds (Table I Nos. A-I) have been employed in this laboratory. The methods of preparation are already reported<sup>2</sup>.

(A) *s*-Triazolo (5, 4-*b*) naphtho (2, 1-*d*) thiazole<sup>3</sup>,

(B) 3-Methyl-*s*-triazolo (5, 4-*b*) naphtho (2, 1-*d*) thiazole,

(C) 3-Mercapto-*s*-triazolo (5, 4-*b*) naphtho (2, 1-*d*) thiazole,

(D) 5, 7-Dimethyl-*s*-triazolo (3, 4-*b*) benzothiazole,

(E) 3,5, 7-Trimethyl-*s*-triazolo (3, 4-*b*) benzothiazole,

(F) 3-Mercapto-5, 7-dimethyl-*s*-triazolo (3, 4-*b*) benzothiazole,

(G) 2 (3'-Pyridyl) 4, 6-dimethyl benzothiazolyl hydrazone,

(H) 2 (2'-Thienyl) 4, 6-dimethyl benzothiazolyl hydrazone,



(1) 2 (2'-Furyl) 4, 6-dimethyl benzothiazolyl hydrazine.

The preliminary trials on germination show that (C) and (E) are not so effective. On the strength of these germination experiments, field trials of these compounds were undertaken, along with control and gibberellic acid\* as a standard. All solutions were of 5 ppm dilution. Forty seeds of *Cicer arietinum* were soaked in 100 ml solution of each compound for five hours. The seeds were sown in earthen pots and arranged in randomized block design, in three rows with nine treatments. On 5th day 100% germination was found in control whereas in standard it was only 80%. On 25th day nodulation was initiated. Three plants from each pot were removed at interval of 7 days for nodule count. In all five observations were made till crop attained the preflowering phase, when the experiment was terminated. Treatments with (A), (B) and (D) were having more or less the same number of nodules as in standard whereas the nodulation was better than control and standard with (F), (G), (H) and (I). This clearly showed that naphthalene ring prevented the nodule formation whereas electron donating methyl groups on benzonucleus stimulates the nodulation provided it is a uncyclized compound or having a mercapto substituent at 3 position in cyclic system. Even in germination result the compounds (F) and (G) were found to be superior.

The results on number of nodules in the different treatments (Table I) show that (F), (G), (H) are statistically significant at 5% whereas (F) and (G) results are statistically significant even at 1% at 12 df. (A) and (B) seem to have retardatory effect on nodule formation.

One of the authors [APK (JRF)] gratefully acknowledges C.S.I.R. for financial assistance.

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\* Known plant growth regulator, used in earlier references.

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## TAUTOMERISM OF 2-HYDROXY CHROMONES AND 4-HYDROXYCOUMARINS

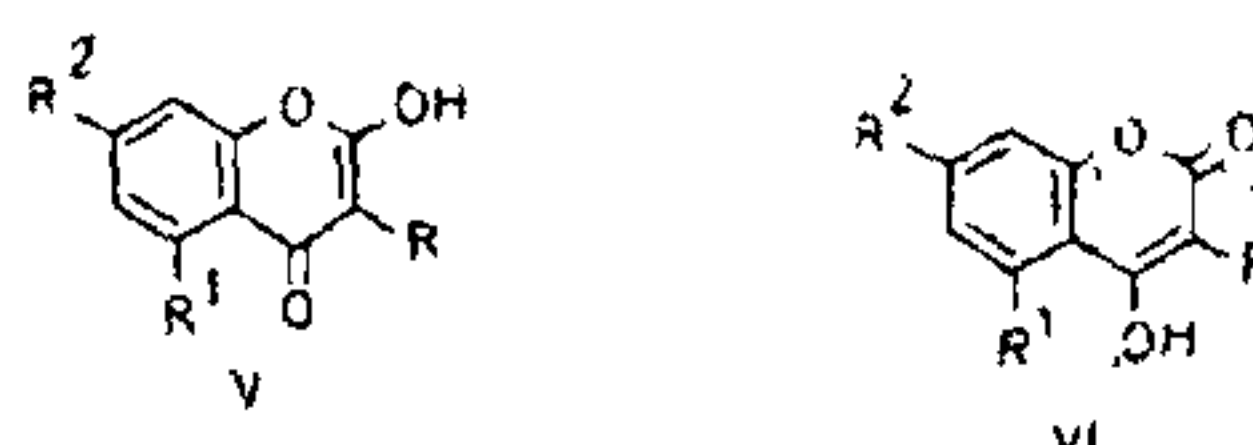
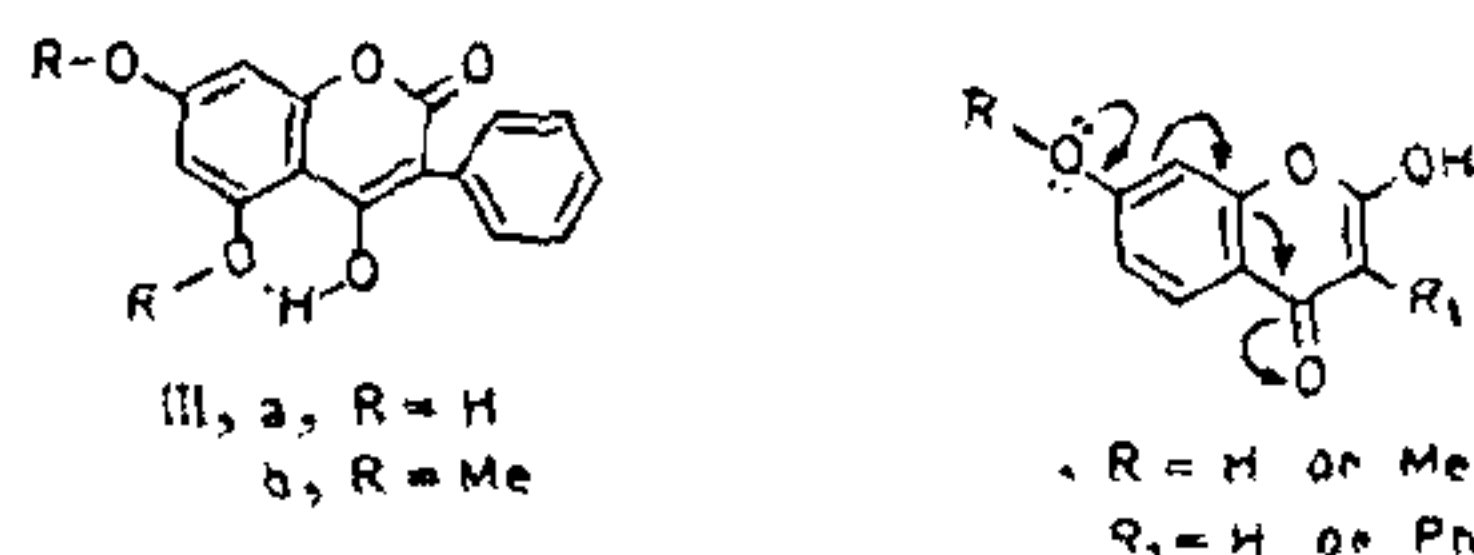
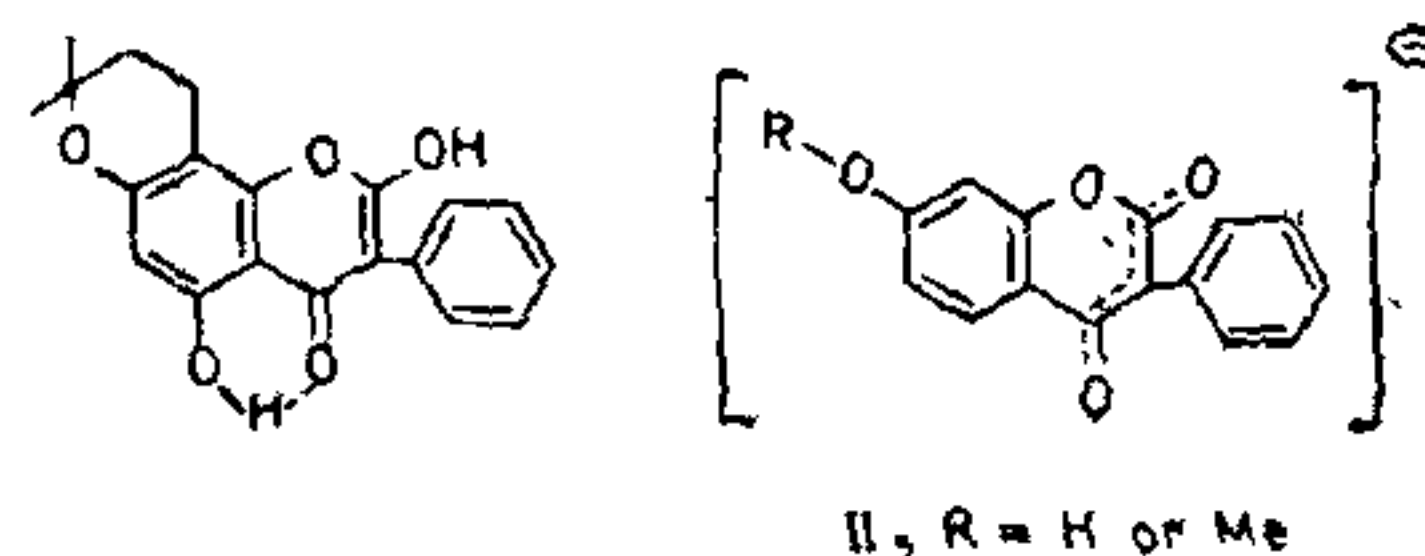
4-HYDROXYCOUMARINS and 2-hydroxychromones/2-hydroxyisoflavones exist as tautomers. As to which of the tautomer is thermodynamically more stable has been shown to depend upon the substitution pattern. In the present communication guidelines

for predicting the stability of tautomers with different substitution pattern and explanation for the same are given.

From study of the IR spectra of 4-methoxycoumarin and 2-methoxychromone it was shown by Knobloch and Prochazka<sup>1</sup> that the coumarins absorb at about  $1712\text{ cm}^{-1}$  and the chromones at about  $1645\text{ cm}^{-1}$ . On this basis they deduced a coumarin structure for 4-hydroxycoumarin ( $\nu_{\text{C=O}} 1708\text{ cm}^{-1}$ , solid) but a chromone structure for dicoumarol ( $\nu_{\text{C=O}} 1650\text{ cm}^{-1}$ , solid). The formation of the former has been attributed to the more facile enolisation of ketonic carbonyl in 4-position than the ester carbonyl in 2-position.

Johnson and Pelter<sup>2,3</sup> on the basis of IR spectra of 3-phenyl-5-hydroxy derivative (I,  $\nu_{\text{C=O}} 1640\text{ cm}^{-1}$ ) showed that the isoflavone structure is preferred over the corresponding coumarin tautomer due to hydrogen bonding between 5-hydroxyl and 4-carbonyl groupings. In the case of 5-methoxy derivatives such a bonding is not possible and therefore the coumarin structure ( $\nu_{\text{C=O}} 1704\text{ cm}^{-1}$ ) is more stable.

According to Subba Rao *et al*<sup>4</sup> 3-phenyl-4-hydroxy- and 3-phenyl-4, 5-dihydroxycoumarins are more stable as compared to their corresponding isoflavones and have attributed the low frequency absorption ( $\nu_{\text{C=O}} 1645\text{ cm}^{-1}$ ) of carbonyl group of the former, to the existence of a dianion state (II). In the latter hydrogen bonding (III a, b) between C<sub>4</sub>-hydroxyl and C<sub>5</sub>-hydroxyl or methoxyl prevents the formation of a dianion and therefore it absorbs at a higher frequency ( $\nu_{\text{C=O}} 1700\text{ cm}^{-1}$ ) as for coumarins.



- |   |   |
|---|---|
| a, R = R <sup>1</sup> = H, R <sup>2</sup> = OH      | a, R = H, R <sup>1</sup> = R <sup>2</sup> = OMe     |
| b, R = Ph, R <sup>1</sup> = H, R <sup>2</sup> = OH  | b, R = Ph, R <sup>1</sup> = R <sup>2</sup> = OMe    |
| c, R = Ph, R <sup>1</sup> = H, R <sup>2</sup> = OMe | c, R = OMe, R <sup>1</sup> = H, R <sup>2</sup> = OH |
| d, R = Ph, R <sup>1</sup> = R <sup>2</sup> = OH     | d, R <sup>1</sup> = H, R = R <sup>2</sup> = OMe     |
| e, R = H, R <sup>1</sup> = R <sup>2</sup> = OH      | e, R = R <sup>1</sup> = R <sup>2</sup> = OMe        |