

The existence of a dianion state as envisaged by Subba Rao is unlikely because in that case the IR spectra should show two carbonyl bands due to the different electronic environment about the two carbonyl groups. However, the IR spectra of different compounds (Table I) in KBr shows only one carbonyl absorption either at about 1650 cm⁻¹ or 1710 cm⁻¹ corresponding to the chromone/isoflavone and coumarin structures respectively.

TABLE I

Compound No.	Substitution pattern	>C=O absorption (cm ⁻¹)	Stable tautomer
1	2, 7-dihydroxy ⁵ (V a)	1667	Chromone
2	3-Phenyl-2, 7-dihydroxy (V b)	1639	Isoflavone
3	3-Phenyl-2-hydroxy-7-methoxy (V c)	1653	Isoflavone
4	3-Phenyl-2, 5, 7-trihydroxy (V d)	1630	Isoflavone
5	2, 5, 7-Trihydroxy (V e)	1650	Chromone
6	4-Hydroxy-5, 7-dimethoxy (VI d)	1720	Coumarin
7	3-Phenyl-4-hydroxy-5, 7-dimethoxy (VI e)	1704	Coumarin
8	3-Methoxy-4, 7-dihydroxy (VI c)	1695	Coumarin
9	4-Hydroxy-3, 7-dimethoxy (VI d)	1690	Coumarin
10	4-Hydroxy-3, 5, 7-trimethoxy (VI e)	1700	Coumarin

Guidelines for predicting the stability of tautomers having hydroxyl or methoxyl in 3, 5 and 7 positions are as follows:

A hydroxy or methoxy group at 7-position, being in conjugation with the C₄-carbonyl through the benzene ring stabilises the 2-hydroxyisoflavone/2-hydroxychromone tautomers as shown in structure (IV) due to the enolization of 2-carbonyl. However, presence of a methoxy group at 3-position feeds the electrons in the direction opposite to that caused by 7-hydroxyl, thus preventing the resonance stabilization of 4-carbonyl. Therefore 3-methoxy derivatives show IR absorption characteristic of coumarins. Thus 2, 7-dihydroxychromone (V a, 1667 cm⁻¹), 2, 7-dihydroxyisoflavone (V b, 1639 cm⁻¹) and 2-hydroxy-7-methoxyisoflavone (V c, 1653 cm⁻¹) are more stable as compared to the corresponding coumarins, whereas 3-methoxy-4, 7-dihydroxycoumarin (VI c), 4-hydroxy-3, 7-dimethoxycoumarin (VI d) and

4-hydroxy-3, 5, 7-trimethoxycoumarin (VI e) have characteristic carbonyl frequency at ν_{\max} 1695, 1690, 1700 cm⁻¹ respectively.

Hydroxyl at 5-position stabilises the isoflavones/chromones because of hydrogen bonding preferably with the carbonyl rather than the hydroxyl at 4-position. Whereas 5-methoxyl favours the coumarin structure because the 4-hydroxyl in that case is hydrogen bonded (III b). Hence 4-hydroxy-5, 7-dimethoxycoumarin (VI a, 1720 cm⁻¹), 3-phenyl-4-hydroxy-5, 7-dimethoxycoumarin (VI b, 1704 cm⁻¹) are more stable than the corresponding isoflavones while 2, 5, 7-trihydroxychromone (V e, 1650 cm⁻¹) and 2, 5, 7-trihydroxyisoflavone (V d, 1630 cm⁻¹) are energetically more favoured than the corresponding coumarins.

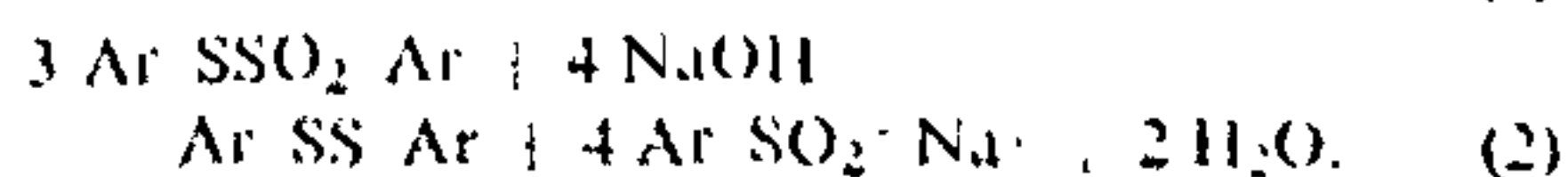
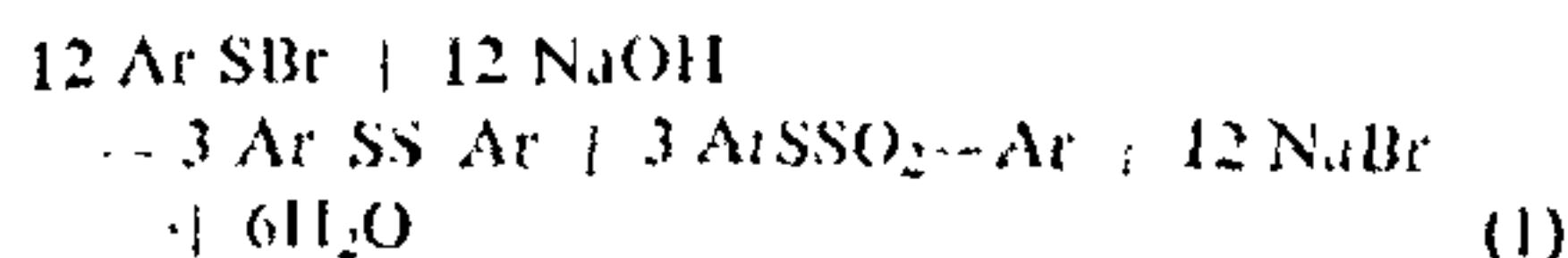
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ACTION OF ALKALI ON 2-*p*-TOLYLAZO-NAPHTHALENE-1-SULPHENYL BROMIDE

THE formation of monosulphide from sulphenyl bromides of orthomeracpto azo compounds in strongly alkaline medium, has not been reported so far¹⁻³. This note gives preliminary report of the formation of the corresponding monosulphide (VI) from the newly synthesized sulphenyl compound, 2-*p*-tolylazo-naphthalene-1-sulphenyl-bromide (II) under strongly alkaline conditions. Generally, the sulphenyl bromides of ortho-mercapto azo compounds react with an appreciable excess of alkali to give the precipitate of the corresponding disulphides and water soluble alkali sulphinates according to the equations (1, 2).

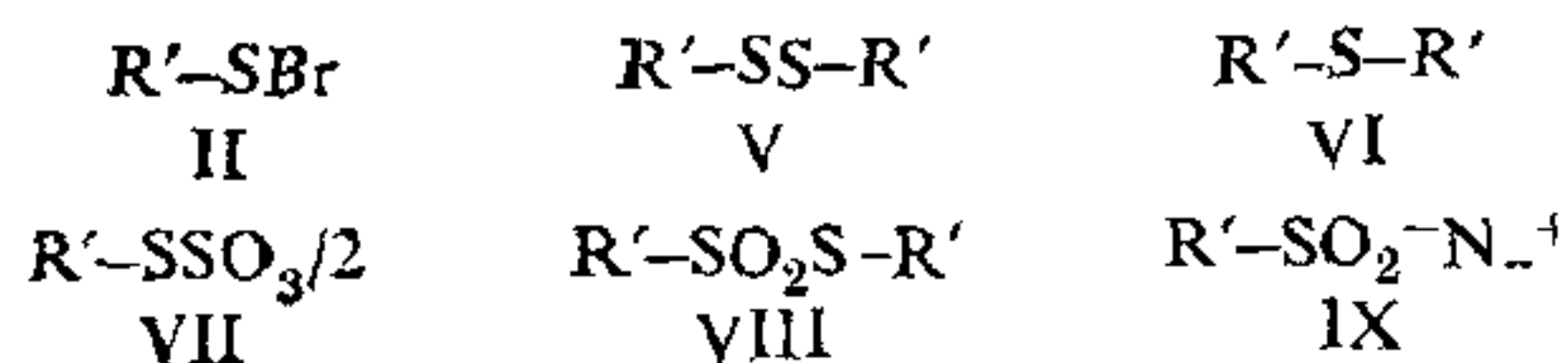
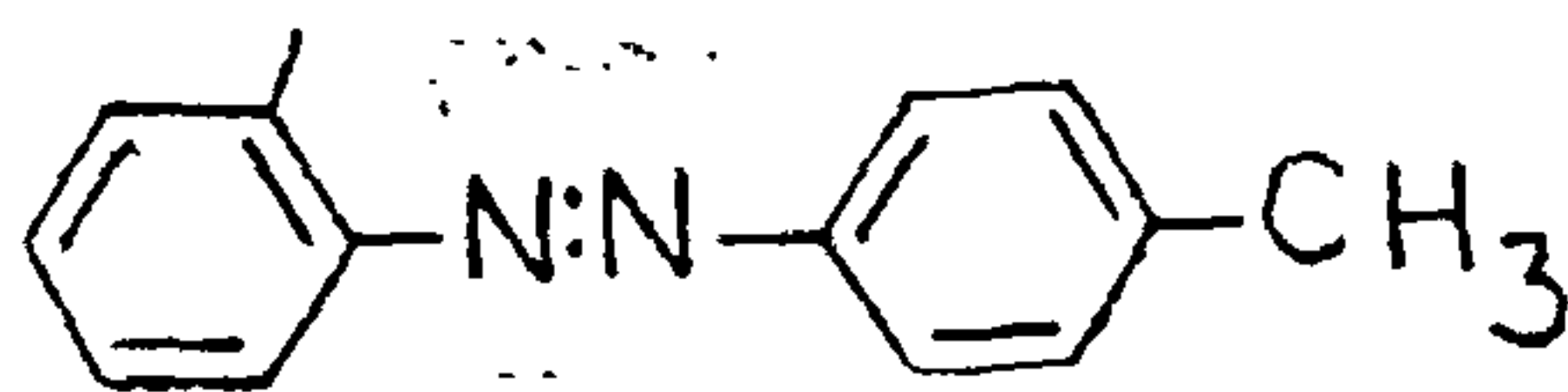


The thiol sulphonates initially formed react instantaneously with excess alkali to give more of disulphides and alkali sulphinates. We have synthesized new

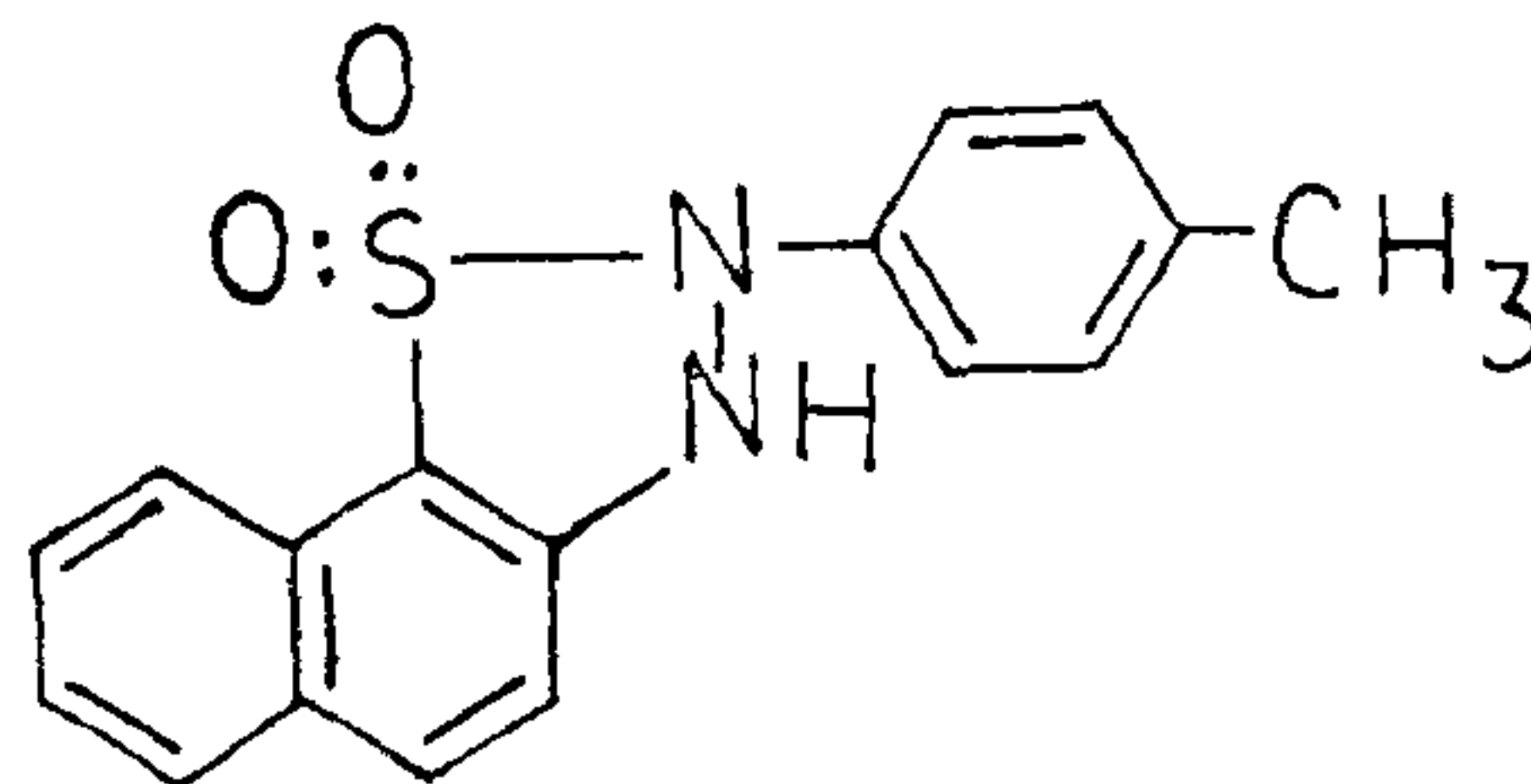
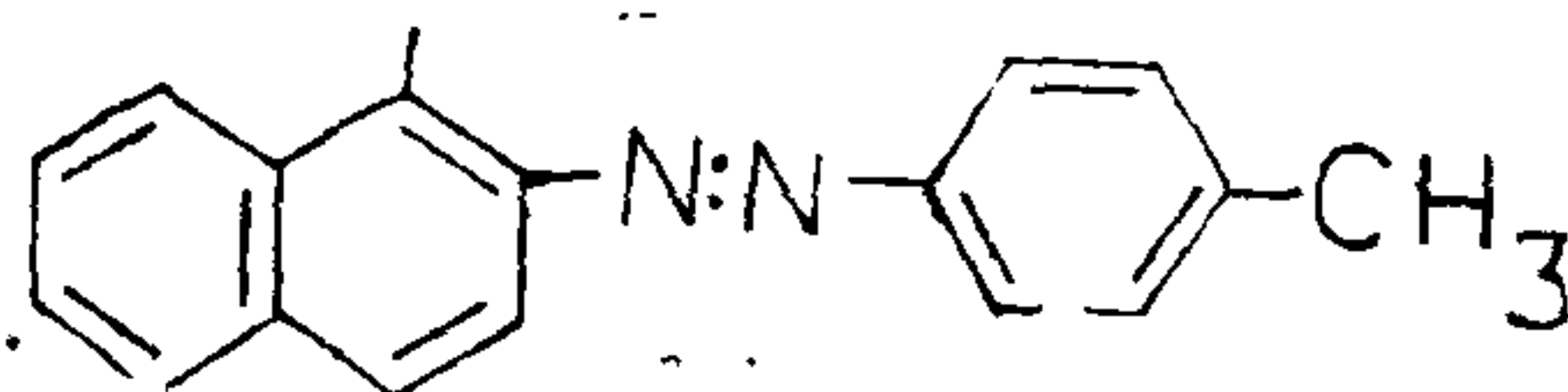
sulphenyl halides of ortho-mercapto azo-compounds, 2-*p*-tolylazo-naphthalene-1-sulphenyl bromide (II)⁵ and 2-*p*-tolylazo-benzene-1-sulphenyl bromide (I)⁴ and studied the action of alkali on them. In strongly alkaline conditions compound (I) behaves similarly to the other reported sulphenyl bromides giving the corresponding disulphide (III) and the sulphinate (IV). However, under similar conditions the compound (II) yields a mixed precipitate consisting of the corresponding disulphide (V), monosulphide (VI), and a small amount of the sulphenyl sulphite (VII). This indicates that unlike other thiosulpho-



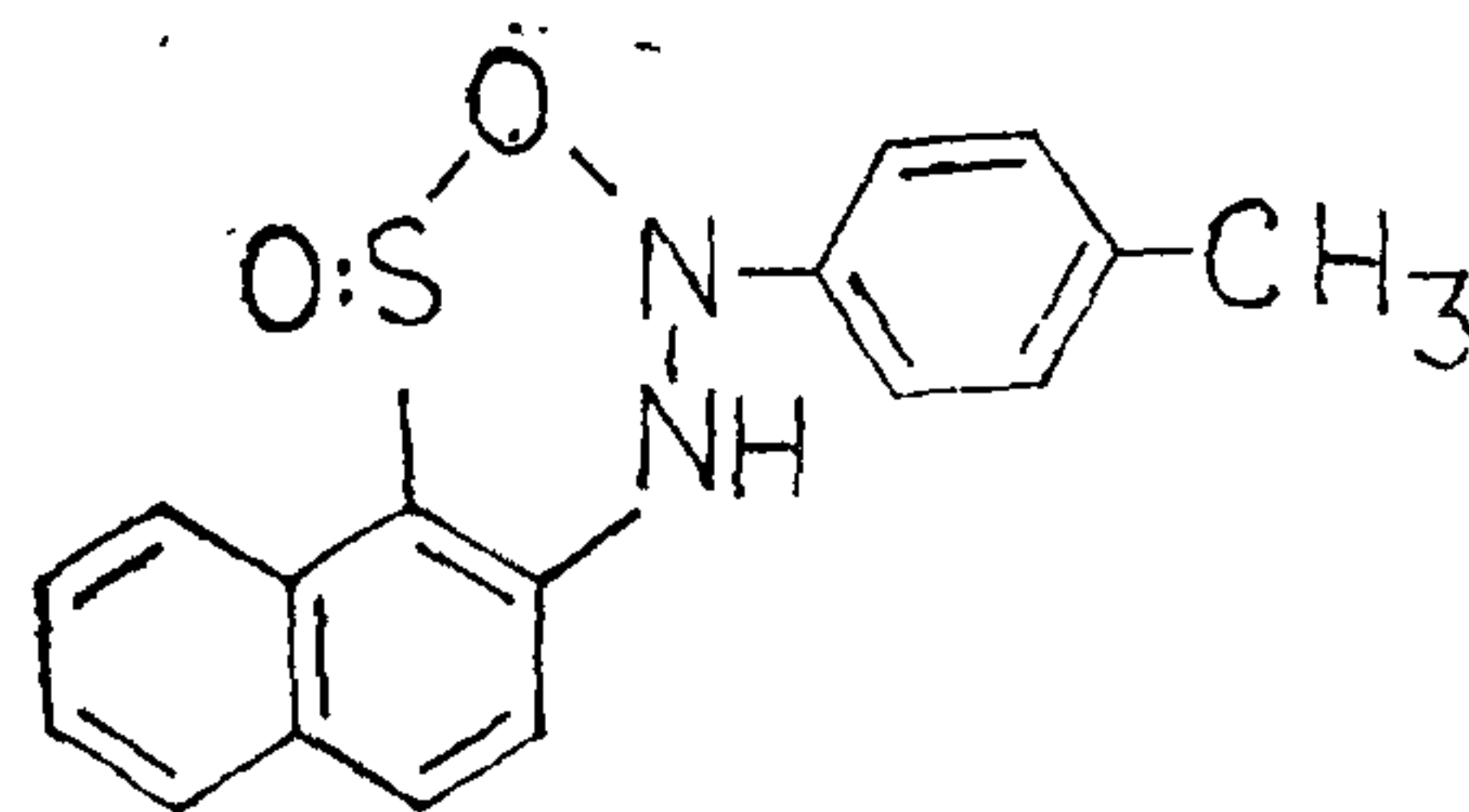
where R =



where R' =



X



XI

nates, even under strongly alkaline conditions, the alkaline cleavage of di-(2-*p*-tolylazo-naphthyl-1) thio-sulphonate (VIII) to the corresponding di-(2-*p*-tolylazo-naphthyl-1) disulphide (V) and 2-*p*-tolylazo-naphthalene-1-sulphinic acid (IX) does not take complete preference over its decomposition to the corresponding di-(2-*p*-tolylazo-naphthyl-1) sulphide (VI) and sulphur dioxide. The liberated sulphur dioxide reacts with any unreacted sulphenyl bromide to give 2-*p*-tolylazo-naphthalene-1-sulphenyl sulphite (VII). The latter is found to be identical with the authentic product obtained by the double decomposition of the sulphenyl bromide with aqueous sodium sulphite. The separation of the mixed precipitate is best carried out by first dissolving the disulphide and monosulphide in benzene and then filtering off the insoluble sulphenyl sulphite. The residue obtained by removing the solvent from the filtrate is refluxed in an aqueous ethanolic suspension with sodium sulphide for a few minutes. The disulphide is converted into water-soluble sodium mercaptide (II, SBr = S⁻Na⁺). The insoluble monosulphide is removed by filtration. The red violet filtrate on acidification and aerial oxidation regenerates the disulphide. The red precipitate of 2-*p*-tolylazo-naphthalene-1-sulphinic acid (IX, SO₂⁻Na⁺ = SO₂H) obtained by acidification of the original alkaline filtrate of alkali sulphinate, crystallizes from benzene and light petrol as colourless plates. In these solvents the acid does not display the $n \rightarrow \pi^*$ band characteristic of the 'azo' group in its uv and visible spectra. These facts suggest that like other sulphinic acids of ortho-mercapto-azo-compounds⁶ this acid also exists as a cyclic tautomer (X or XI) in nonpolar solvents. In polar solvents like ethanol and chloroform, however, the $n \rightarrow \pi^*$ band is displayed at 430 nm which suggests that in polar solvents the cyclic structure tautomerizes to the true azo structure. Unlike sulphinic acids of azobenzene series⁶, this sulphinic acid is found to be sensitive to polar solvents and mineral acids in which it slowly splits off sulphur dioxide to give 2-*p*-tolylazo naphthalene (II, SBr = H). The weakly acidic nature of 2-*p*-tolylazo-naphthalene-1-sulphinic acid (II, SBr = SOH) is shown by its reaction with weak alkalies. It reacts slowly with excess of alkali bicarbonates to yield a mixed precipitate of the disulphide, monosulphide and sulphenyl sulphite. No sulphinate is formed in this case. It suggests that the thiosulphonate initially formed remains insensitive towards such weak alkalies and its dissociation into monosulphide and sulphur dioxide gains complete predominance under such conditions. An attempted synthesis of di-(2-*p*-tolylazo-naphthyl-1-) thiosulphonate from equimolar quantities of the sulphenyl bromide and the sodium sulphinate results in the formation of the monosulphide and a small amount of the sulphenyl sulphite only. Di-(2-*p*-tolylazo-naphthyl-1-) disulphide

can be synthesized by refluxing sulphenyl bromide with zinc dust in dry benzene for six hours.

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A NOTE ON THE INTRAFORMATIONAL RECUMBENT FOLDS IN THE JODHPUR SANDSTONE OF LADNUN, DISTRICT NAGAU, RAJASTHAN

THIS note records a folded cross bedding (Fig. 1), for the first time, in finely laminated alternatively brick-red and light coloured medium grained quartzose sandstone of Sonia Formation, Jodhpur Group, Marwar Super Group (Shrivastava⁷, Paliwal⁴, and Pareek and Sinha⁵), which is available for examination in a quarry section near Ladnun (27° 38' : 74° 23'), district Nagaur, Rajasthan. The structural sedimentary feature is confined to a less than 1 m. thick zone occurring between finely laminated layers, that have a total thickness of 5 to 10 m. increasing SSW wards in the basin. The foreset laminations appear overturned in the upper part, and the shape attained is of a recumbent fold in between upper and lower finely laminated horizontally disposed beds. Fine unfolded horizontal laminations cross-cutting the folded foreset laminations appear in the central part of the zone.

This structure is inferred to have been formed under rapid sedimentation and very strong currents, since these are believed to exert a drag effect on the top of the earlier deposited foreset laminations, when they flow across them, in next stage (cf. Kumar and Tandon², and Mc Kee *et al.*³). The underlying foreset laminations are thus overturned and attain the shape of intraformational recumbent fold. That such structures originate due to unidirectional pressure and overburden of the succeeding strata (cf. Vaidyanandhan⁶), or due to a shear couple provided by two currents flowing in opposite directions facing towards each other (Subramanyan⁸), is refuted by the absence of composition variation in the two zones, and constancy of the palaeocurrent direction (Awasthi *et al.*¹).

Existence of such beds is confirmative of their being deposited under fluviatile conditions (cf. Reineck *et al.*⁶).



FIG. 1. Intraformational recumbent folds—an unusual type of cross-bedding in the Jodhpur sandstone of Ladnun.

Thanks are due to Mrs. S. Paliwal and Shri B. Paliwal for their help in preparing the present note.

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UTILIZATION OF LIPIDS BY *SPODOPTERA LITURA* (FABRICIUS) ON NINE FOOD PLANTS

In recent years emphasis is being given to the quantitative aspect of insect nutrition. Standard gravimetric technique have been used in the majority of studies on the dry matter utilization of food by phytophagous insects (Waldbauer⁵, Bhattacharya and Pant¹),