REPRINTS.

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SULPHENYL DERIVATIVES OF ORTHO-MERCAPTO AZO COMPOUNDS: SYNTHESIS OF 4-DIMETHYLAMINO-AZOBENZENE-2'-SULPHENYL BROMIDE—ITS U.V. AND VISIBLE SPECTRA

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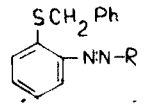
ABSTRACT

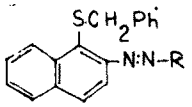
With a view to synthesizing new sulphenyl bromides of ortho-mercapto-azo-compounds, the debenzylation reactions of 2-arylazo-1-phenyl benzyl sulphides (I, *a*, *c*, *d*) and 2-arylazo-1-naphthyl benzyl sulphides (II) are carried out. Only (I *d*) yields the sulphenyl bromide (I *e*), all other compounds are converted into their respective disulphides [(III *a*, *b*) and (IV)]. The U.V. and visible spectra of (I *e*) are discussed.

THOUGH Specklin and Meybeck[1] failed to diazotise *o*-benzyl thioaniline under a variety of conditions, Burawoy *et al.*[2] could diazotise the same with nitrosyl sulphuric acid and conc. sulphuric acid at 0° C and coupled this diazonium compound successfully with 2-naphthol to get (I *a*). They were unable to debenzylate (I *a*), to sulphenyl bromide but obtainedt he disulphide (III *a*) instead.



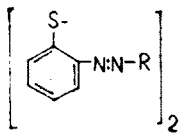
(I)

a. R = 2-hydroxy-1-naphthyl
b. R = *p*-hydroxy phenyl
c. R = 5-methyl-2-hydroxy phenyl
d. R = *p*-dimethyl amino phenyl
e. —SCH$_2$Ph = —SBr; R = *p*-dimethyl amino phenyl



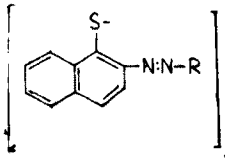
(II)

R = 2-hydroxy-1-naphthyl



(III)

a. R = 2-hydroxy-1-naphthyl
c. R = 5-methyl-2-hydroxy phenyl



(IV)

R = 2 hydroxy-1-naphthyl

So far no sulphenyl halide of ortho-mercapto azo compound is known to contain any electron donating groups like phenolic-hydroxy, amino, substituted amino or phenolic-ether group, in their ring systems. With a view to synthesizing such compounds, we diazotised 2-benzylthio-aniline and 1-benzylthio-2-naphthylamine with nitrous acid in ethanol medium. Though these diazonium compounds proved to be stable for 5–15 secs, they could be effectively coupled with a number of active substrates like 2-naphthol, phenol, *p*-cresol and dimethyl aniline, under alkaline conditions below 0° C, to give the expected compounds (I *a*, *b*, *c*, *d* and II)

Attempted debenzylation of (I *a*, *c*) and (II *a*) by bromination in hot acetic acid or in warm or cold carbon tetrachloride (both in presence and in absence of iodine catalyst) yielded no sulphenyl bromide but only the corresponding disulphides (III *a*, *c*) and (IV).

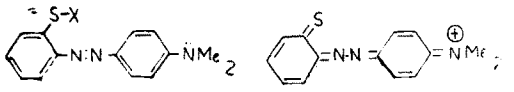
On the other hand 2'-benzylthio-4-dimethylamino-azobenzene (I *d*) could successfully be converted to the sulphenyl bromide (I *e*) by treating it with bromine in carbontetrachloride at 40° C; debenzylation proceeded faster in the presence of iodine. But debenzylation reaction failed with bromine in hot acetic acid. This sulphenyl bromide was found to be stable towards water and alcohol and could be recrystallised unchanged from aqueous alcohol. Like other sulphenyl bromides of the series, it also underwent double decomposition with potassium iodide. Preliminary investigations show that this compound is an effective electrophile.

U.V. and visible spectra of 4-dimethylamino-azobenzene-2'-sulphenyl bromide:

The U.V. and visible spectra of this compound in ethanol show three bands — one high intensity band at 470 nm and two low intensity bands at 560 nm and 375 nm; whereas, in solvents benzene, chloroform and water, only two bands are shown, one high intensity band around 550 nm and a low intensity band around 375 nm. The band at 375 nm is a $\pi \rightarrow \pi^*$ band, the band around 550 nm may be due to a "Hydrazone" structure (VI) of the compound in the solvents. The band at 470 nm in ethanol solution is perhaps due to the "azo-structure" (V) of the compound formed due to partial solvolysis. This is supported by the fact that the 470 nm band disappears when the spectrum

of the ethanolic solution of the sulphenyl bromide was taken in presence of added bromide ions. In ethanol, therefore, the sulphenyl bromide remains as a mixture of the "azo-structure" with a small amount of "hydrazone structure".

In sulphuric acid solution, however, only the band at 350 nm is obtained. Both the "azo-structure" and the "hydrazone structure" are not formed due to protonation of—$\ddot{N}Me_2$ group and the—$\ddot{N}$=$\ddot{N}$—group.



(V) (VI)

EXPERIMENTAL

A. *Diazotisation of o-benzylthioaniline and coupling of the diazonium compound with 2-naphthol*:

o-Benzylthioaniline (2 g) dissolved in ethanol (10 ml) at 0° C was mixed with sodium nitrite (0·5 g) in water (10 ml) at − 5° C. Then hydrochloric acid (5 ml, 4 N) was added and the resulting diazonium chloride solution was immediately poured into a well stirred ice cooled solution of 2-napthol (1·5 g) in sodium hydroxide (20 ml, 20%) at a time. The stirring was continued for 30 minutes, at − 3° C. The resulting red precipitate of 2-(2′-hydroxy-1′-naphthyl-azo-)-phenyl benzyl sulphide (I *a*) was filtered off, washed and dried (1·95 g, 53% yield) gave brown red crystals from ethanol.

m.p. 161° - 162° C.

$C_{23}H_{18}N_2SO$ requires C = 74·59%, H = 4·86%, N = 7·56%.
Found C = 74·42%, H = 4·74%, N = 7·49%.

The compound (I *a*) was identical with the compound obtained by the condensation of *o*-benzylthioaniline with 1-nitroso-2-naphthol.

B. The coupling reactions of diazotised *o*-benzylthioaniline with phenol and *p*-cresol and that of diazotised 1-benzylthio-2-naphthyl amine with 2-naphthol were carried out similarly as under A, to get the compounds 2-(*p*-hydroxy phenyl)-phenyl benzyl sulphide (I *b*), 2-(5-methyl-2-hydroxy phenyl)-phenyl benzyl sulphide (I *c*) and 2-hydroxy-1′-benzylthio-2′, 1-azo naphthalene (II) respectively. All of them were crystallised from hot ethanol.

I. (*b*) Crystallised as orange red crystals. m.p. = 143°–144° C, yield = 45%.

$C_{19}H_{16}N_2SO$ requires C = 71·25%, H = 5·00%, N = 8·75%.
Found C = 70·98%, H = 5·31%, N = 8·24%.

I. (*c*) Crystallised as red plates. m.p. = 102° − 103° C. yield = 51%.

$C_{20}H_{18}N_2SO$ requires C = 71·82%, H = 5·38%, N = 8·38%.
Found C = 71·20%, H = 5·33%, N = 8·51%.

II. Crystallised as red needles with a greenish lustre
m.p. = 204°–205° C,
yield = 57%.

C $H_{20}N_2SO$ requires C = 77·14%, H = 4·76%, N = 6·66%.
Found C = 77·56%, H = 4·37%, N = 6·83%.

C. 4-*Dimethylamino-2′-benzylthio-azobenzene* (I *d*) :

The diazonium solution prepared as under A was immediately added to a solution of dimethyl aniline (3 ml) in ethanol (10 ml) kept at − 5° C and the resulting solution was quickly made alkaline with sodium acetate solution (10 ml, 20% solution). A red precipitate formed at once, filtered and dried (1·4 g, 40% yield). It gave orange red crystals from hot ethanol, m.p. = 137°–139° C.

$C_{21}H_{21}N_3S$ requires C = 72·62%, H = 6·05%, N = 12·1%.
Found C = 72·45%, H = 5·92%, N = 11·85%.

D. *Attempted debenzylation of* (I *a*, *c*) *and* (II) :

(*a*) *In hot acetic acid.*—I *a* (1·85 g) in glacial acetic acid (10 ml) was refluxed. To it was added a solution of bromine (0·8 g) in acetic acid (5 ml) through the condenser. The mixture was refluxed (10 minutes), the solution was cooled. Red crystals of III *a* filtered off, washed and dried (1·23 g), gave red crystals from ethanolic benzene. m.p. = 182°–183° C.

$C_{32}H_{22}N_4S_2O_2$ requires C = 67·02%, H = 3·94%, N = 5·73%.
Found C = 66·98%, H = 4·12%, N = 5·78%.

(*b*) *In carbon tetrachloride.*—To a solution of I *a* (1·85 g) in carbon tetrachloride (10 ml) kept at 40° C was added a solution of bromine (0·8 g) in carbon tetrachloride (5 ml). The solution was kept for one hour and the red ppt. thus obtained was filtered washed and dried (0·98 g); crystallised from ethanol-benzene mixture. m.p. = 182°–183° C.

$C_{32}H_{22}N_4S_2O_2$ requires C = 67·02%, H = 3·94%, N = 5·78%.
Found C = 66·87%, H = 3·91%, N = 5·67%.

E. The debenzylation reactions of I *c* and II were carried out similarly as under D. In both the cases disulphide were isolated.

(I *c*) gave (III *c*) crystallised from ethanolic benzene as red crystals, m.p. = 199°–201° C.

$C_{26}H_{22}N_4S_2O_2$ requires C = 64·19%, H = 4·52%, N = 11·52%.

Found C = 64·93%, H = 4·38%, N = 11·57%.

(II) gave the disulphide (IV *a*), recrystallised from alcohol benzene mixture as deep red crystals with green lustre, m.p. = 243°–244° C.

$C_{40}H_{26}N_4S_2O_2$ requires C = 78·68%, H = 4·26%, N = 9·15%.

Found C = 78·92%, H = 4·13%, N = 8·96%.

F. *4-Dimethylamino-azobenzene-2'-sulphenyl bromide:*

To a well stirred solution of I *d* (1·73 g) in CCl_4 (10 ml) kept at 40° C was added a solution of bromine (0·8 g) in carbon tetrachloride (5 ml). The mixture was kept at 40° C (30 min.). A violet red precipitate with a greenish lustre appeared, which was filtered off, washed and dried (0·72 g, 43% yield). It gave violet red crystals from alcohol-benzene mixture, m.p. 250°–252° C.

$C_{14}H_{14}N_3SBr$ requires C = 50·0%, H = 4·16%, N = 12·5%.

Found C = 49·76%, H = 4·45%, N = 12·11%.

G. Ultraviolet-visible spectra of the compound were taken in D.K-2 Beckmann Instrument.

1. Specklin, R. and Meyback, J., *Bull. Soc. Chim.*, 1951, **18**, 627.
2. Burawoy, A., Turner, C., Hyslop, W. I. and Raymakers, P., *J. Chem. Soc.*, 1954, p. 82.

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SYNTHESIS OF SULPHENAMIDE, SULPHENIMIDE AND SULPHENIMINE WITH SULPHENYL BROMIDE OF ORTHO-MERCAPTO-AZO COMPOUND

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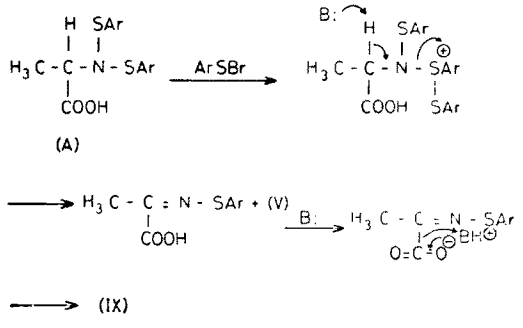
N-SULPHENYLATION of 2-naphthylamine, phthalimide, thiourea, and alanine with 4-dimethylaminoazobenzene-2'-sulphenyl bromide (I)[1] is studied. The rearranged product (II) dominates in the case of 2-naphthylamine, whereas the sulphenimine (IX) is the main product obtained from alanine. Thiourea undergoes S-sulphenylation (VII) and phthalimide gives the expected sulphenimide (VI).

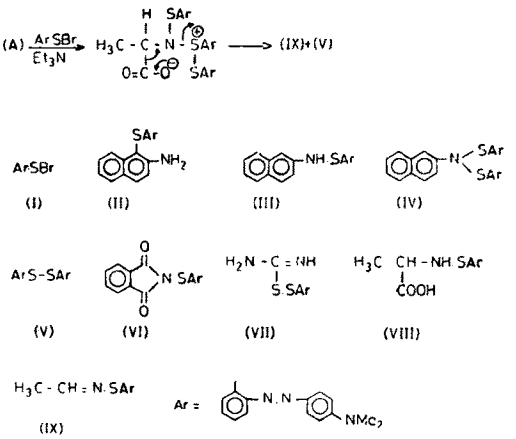
To investigate the utility of *o*-mercaptoazo compound in the preparations of sulphenamides, we have studied the reactions of 4-dimethylaminoazobenzene-2'-sulphenyl bromide[1] with 2-naphthylamine phthalimide, thiourea and alanine in a polar solvent in the presence of an acid scavenger triethylamine at room temperature. With 2-naphthylamine the diarylsulphide (II) is obtained as the major product. Small amounts of the sulphenamide (III), the di-N-sulphenylated product (IV) and the disulphide (V) are also obtained. N-sulphenylation of phthalimide is slow and forms the sulphenimide (VI) in a low yield, the disulphide being the other main product. Thiourea undergoes S-sulphenylation instead of N-sulphenylation giving a mixture of the disulphides (VII) and (V). From the complex reaction products of alanine the sulphenamide (VIII) is obtained only as a minor product. Its IR spectra show that N-sulphenylation of alanine does not destroy its zwitter ionic nature, though the characteristic amino acid band in the range 3000–2000 cm^{-1} disappears. The major product of the reaction is found to be the thiooxime (IX). The disulphide (V) is the third product identified.

The formation of (IX) may be rationalized as per Scheme 1 or 2.

Scheme 1



Scheme k



Experimental

Reaction with 2-naphthylamine

To a solution of the sulphenyl bromide (I, 1·0 g) in ethanol (100 ml) was added a solution of 2-naphthylamine (400 mg) in ethanol (100 ml) and 4–5 drops of triethylamine. The mixture was shaken well and kept at room temperature (2 days). The precipitate of the diarylsulphide (II, 250 mg ~ 24%) was crystallized from dilute ethanol as brown crystals, m.p. 95–97° C, IR ($\nu_{cm^{-1}}^{nujol}$) 1590 (w, N=N stretch), 1650 (m, NH_2 deformation), 3450 and 3500 (s, NH_2 stretch). Chromatography of the mother liquor over alumina gave on elution with benzene-light petrol the red-disulphide (V, m.p. 222–24° C, 60 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1590 (w, N=N stretch), the brown diarylsulphide (II, m.p. 95–97° C, 30 mg), the yellow sulphenamide (III, m.p. 46–48° C, 110 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1585 w, N=N stretch), 1640 (m, NH deformation), 3210 (s, SNH stretch) and the dazzling orange crystals of the diarylpsulphenamide (IV, m.p. 78–80° C, 120 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1590 (w, N=N stretch).

Reaction with phthalimide

To a solution of (I, 1·0 g) in ethanol (100 ml) was added a solution of phthalimide (400 mg in ethanol (200 ml) and 4–5 drops of triethylamine. The mixture was swirled well and kept at room-temperature (5 days).

Chromatography of the concentrated mixture over alumina gave on elution with benzene-light petrol, the disulphide (V, 70 mg) and the sulphenimide (VI, m.p. 153–55° C), 200 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1600 (w, N=N stretch) 1720 (s, C=O stretch).

Reaction with thiourea

A mixture of I (1·0 g) in ethanol (100 ml) thiourea (220 mg) in ethanol (50 ml) and 4–5 drops of triethylamine was swirled well and kept at room temperature (6 hr). The yellow crystals of S-sulphenylated isothiourea was crystallized from ethanol (VII, m.p. 68–70° C, 300 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1590 (w, N=N stretch), 1650 (s, NH_2 deformation and C=N stretch overlapped), 3220 (s, =NH stretch), 3450 and 3500 (s, NH_2 stretch), The mother liquor gave the disulphide (V, 20 mg).

Reaction with alanine

To a solution of I (1·0 g) in methylene chloride (200 ml) was added a solution of alanine (260 mg) in methylene chloride (50 ml) and 4–5 drops of triethylamine. The mixture was shaken well and kept ta room temperature (3 days). On removing the solvent the residue was dissolved in minimum volume of benzene. The chromatography of the resulting solution over silica gave on elution with benzene-light petrol the disulphide (V, 50 mg), the yellow crystals of the sulphenamide (VIII, m.p. 109–10° C, 90 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1590 (w, N=N stretch) 1600 and 1620 (m, partially overlapped bands due to C=O and NH_2),

3050–3100 (s, single broad band due to SNH stretch) and the dazzling blue violet crystals of the thiooxime (IX, m.p. 147–49° C, 200 mg) IR ($\nu_{cm^{-1}}^{nujol}$) 1590 (w, N=N stretch), 1690 (w, C=N stretch).

The analytical results for C, H and N of the compounds (II-IX) agreed with the calculated values.

December 20, 1980.

1. Bhattacharjee, S. K. and Dasgupta, S. K., *Curr. Sci.*, 1977, p. 893.

J. Indian Chem. Soc.,
Vol. LV, July 1978. pp. 702-704

Reactions of 2-Arylazo-Naphthalene-1-Sulphenylbromide with "Carbon Acids" : Synthesis of 2-Substituted Naphthothiazoles and their U. V. and I. R. Spectra

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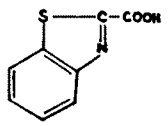
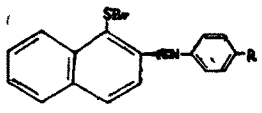
2-*n*-Tolylazonaphthalene-1-sulphenylbromide (IIb) condenses with carbon acids of the type-Z-CH_2-Z-where 'Z' is an acidifying keto-carbonyl group, to yield 2-substituted naphtho-2′ : 1′ : 4:5-thiazolyl compounds (III). 2-phenylazonaphthalene-1-sulphenylbromide(IIa) also reacts similarly. With weaker carbon acids e.g., acetone acetophenone,(IIb) reacts only under more stringent conditions, but (IIa) fails to react. The U. V as well as I. R. spectra of the 2-substituted naphthothiazoles are presented.

IN an earlier publication Burawoy *et al*[1] observed that azo-benzene-2-sulphenyl bromide reacted with malonic acid to yield benzothiazolyl-2-carboxylic acid(I), together with aniline salt. Similar reactions of 2-arylazo-naphthalene-1-sulphenylhalides have not been reported so far. We have now studied the reactions of 2-phenyl-azonaphthalene-1-sulphenyl bromide (IIa) and 2-*p*-tolyl-azonaphthalene-1-sulphenyl bromide (IIb) with compounds of the type-Z-CH_2-Z-, where 'Z' is an acidifying keto-carbonyl group. Thus both of these sulphenyl-bromides reacted with acetylacetone to yield -2′ : 1′ : 4 : 5-thiazolyl-2-methyl ketone (IIIa), with acetoacetic ester, malonic ester and cyanacetic ester to yield ethyl-naphtho-2′ : 1′ : 4 : 5-thiazolyl-2-carboxylate (IIIb), with acetoacetanilide to yield anilide of naphtho-2′ : 1′ : 4 : 5-thiazolyl-2-carboxylic acid (IIIc) and with malonic acid to yield naphtho-2′ : 1′ : 4 : 5-thiazole (IIId). Aniline or *p*-toluidine hydrobromide was also isolated from the mother liquors.

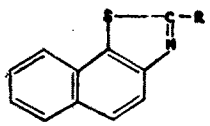


(I)



(II)

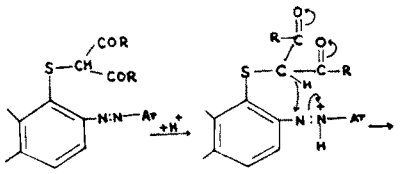
a R=H
b R=CH_3



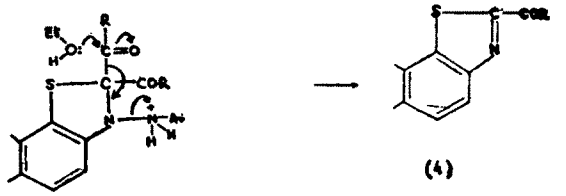
(III)

a, R=CH_3CO.
b, R=$COOC_2H_5$
c, R=$CONHC_6H_5$
d, R=H
e, R=C_6H_5. CO.

2-Phenylazo-naphthalene-1-sulphenylbromide did not react with weaker carbon acid e.g. acetone and acetophenone even on long refluxing for over 100 hours in presence of 2 drops of conc. hydrochloric acid. 2-*p*-tolylazo-naphthalene-1-sulphenylbromide however reacted with acetone and acetophenone on prolonged refluxing with 2 drops of conc. hydrochloric acid to yield naphtho-2′ : 1′ : 4 : 5-thiazolyl-2-methyl ketone (IIIa) and naphtho-2′ : 1′ : 4 : 5-thiazolyl-2-phenyl ketone (IIIe) respectively. The formation of the heterocyclics may be assumed to take place as follows :—At first 2-arylazo-naphthalene-1-sulphenylbromide reacts with "carbon acids" to form the corresponding sulphides (1) with the elimination of hydrobromic acid. The azo-group of these sulphides gets protonated (2) and subsequently intramolecular five-membered hetero-ring closure takes place (3) by the action of protonated azo-group with the potential nucleophilic centre. These cyclized products get aromatized to 1 : 3-thiazole-derivatives (4) by partial ethanolysis accompanied with the elimination of an arylamine molecule.



(1) (2)



(3) (4)

**U-V spectra of 2-substituted naphtho-2' : 1' : 4 : 5-thiazoles*

Like benzothiazoles and benzoxazoles[2], the first band system of naphtho-2' : 1' : 4 : 5-thiazoles retain the vibrational structure of the benzo ring chromophore, only difference is that it suffers a bathochromic shift. It appeared around 325 nm (three peaks at 332 nm, 325 nm and 317 nm). The weak conjugation of the ring system with the heteroatoms would result in such a moderate bathochromic shift. The second band at 302 nm appears as a shoulders and the foot of it is implanted with the third band at shorter wavelength (at 288 nm). The intensities of these two bands at shorter wavelengths are higher than that of the longer wavelength band.

TABLE

COR	First band λ (nm)	First band ε	Second band λ (nm)	Second band ε	Third band λ (nm)	Third band ε
R=H	332	1727				
	325	1364	302	4091	288	5727
	317	1273				
$R=CH_3$	358	7900	315	8750	286	6830
$R=C_2H_5$	359	8500	318	9251	288	8821
R=OEt	347	4640	314	10320	288	9600
R=NHPh	349	12879	318	20606	288	14424
$R=C_6H_5$	372	2998	326	8650	286	9000

When 2-position of napbtho-2' : 1' : 4 : 5-thiazole is substituted with a group-COR (where R-=CH_3, C_2H_5, Ph-, OEt and NHPh), the effect is smoothening of the longer wavelength band (325 nm band) which looses its vibrational fine structure and is attended with a moderate bathochromic shift. As expected the bathochromic shift is the highest for the compound where R=Ph (the band appears at 372 nm) followed by the compound where R=CH_3 and C_2H_5 (at 358 nm and 359 nm respectively) and for the compounds where R-=OEt or NHPh the band appears at 347 nm and 349 nm respectively.

The difference between the nature and position of these bands of naphthiazole and its above mentioned 2-substituted derivatives may be ascribed to the conjugation between C=O of the substituent and the C=N of the hetero ring.

The third band at shorter wavelength (i.e., the band at 288 nm) of naphtho-2' : 1' : 4 : 5-thiazole practically remains unaffected by the 2-substituent.

But 2-substitution of naphtho-2' : 1' : 4 : 5-thiazole ring brings a clear separation of the 302 nm band. This band in the 2-substituted naphthothiazoles, appears at slightly longer wavelength region (around 315 nm).

*** The I.R. Spectra of 2-substituted naphtho-2' : 1' : 4 : 5-thiazoles*

The infra-red spectra of all these 2-substituted naphtho 2' : 1' : 4 : 5-thiazoles were taken in KBr pellets. Besides the carbonyl vibrations in the region 1750-1650 Cm^{-1} (for the groups like -$COOC_2H_5$, CONHPh, -$COCH_3$ and -COC_2H_5), a pair of bands of medium intensity at 1470 cm^{-1} and 1430 cm^{-1} were found to be characteristic of all these compounds, including the unsubstituted naphtho-2' : 1' : 4 : 5-thiazole. Thus this pair of bands may be identified to be characteristic of the structures like naphtho-2' : 1' : 4 : 5-thiazole. It was interesting to note that the carbonyl conjugation of the 2-substituents with hetero ring had practically no effect on these two bands.

Experimental

1. *Reaction with acetylacetone* : 0.5 g of (II,b) was dissolved in ethanol (25 ml) and 1 ml of acetylacetone was added to it. The mixture was allowed to stand at room temperature till the reaction was complete (72 hrs). Yellow plates of (III,a) thus formed was filtered off, washed and dried (0.22 g, 68%). Recrystallization from ethanol gave light yellow plates, m.p. 179°-181°. (Found, C, 68.3 ; H, 4.1 ; N, 5.9. $C_{18}H_9NSO$ requires C, 68.7; H, 4.0 ; N, 6.2%). *p*-Toluidine hydrobromide was recovered from the mother liquor.

(II,a) also reacted with acetylacetone under similar conditions to yield (III,a) in four days.

2. *Reaction with acetoacetic ester* : 0.5 g of (II, b) was dissolved in ethanol (25 ml) and acetoacetic ester (1 ml) was added to it and allowed to stand at room temperature till the reaction was complete (6 days). The residue after removal of the solvent was recrystallized from ethanol whereby greenish-white crystals of (III, b) was obtained (0.26 g, 71%), m.p. 131°-133°. (Found, C, 65.6 ; H, 4.3 ; N, 5.3. $C_{14}H_{11}NSO_2$ requires C, 65.4 ; H, 4.3 ; N, 5.5%).

3. *Reaction with malonic ester* : 0.5 g (II, b) reacted with malonic ester according to the procedure as under (2) to give (III, b) in 9 days. Yield, 0.22 g (60%), m.p. & mixed m.p. 131-133°. (Found, C, 65.6 ; H, 4.5 ; N, 5.5. $C_{14}H_{11}NSO_2$ requires C, 65.4 ; H, 4.3 ; N, 5.5%). The mother liquor yielded *p*-toluidine hydrobromide.

(II, a) also reacted with malonic ester similarly to yield (III, b) in 12 days.

4. *Reaction with cyanacetic ester* : (II, b) reacted with cyanacetic ester according to the procedure as under (2) to yield (III, b) in five days with an yield of 60%, m.p. and mixed m.p. 131-133°. (Found, C,65.5 ;

* U. V.—Visible spectra werl taken in DK-2 Spectrophotometer

** IR-Spectra were taken in Karl Zeiss Jena U. R.-10 infrared Spectrophotometer in KBr pellets.

H, 4.4; N, 5.9. $C_{14}H_{11}NSO_2$ requires, C, 65.4; H, 4.3; N, 5.5%). From the mother liquor *p*-toluidine hydrobromide was obtained.

(II, a) also reacted with cyanacetic ester under similar experimental conditions to yield (III, b) in 6 days. The mother liquor yielded aniline hydrobromide.

5. *Reaction with acetoacetanilide*: 0.5 g of (II, b) was dissolved in ethanol (25 ml) and acetoacetanilide (0.5 g) in ethanol (5 ml) was added to it. The reaction was complete in 24 hrs. The shining yellow precipitate of the anilide of naphtho-2':1' : 4:5-thiazole-2-carboxylic acid (III, c) was filtered off, washed and dried, (0.4 g, 90%). Recrystallized from ethanol, m.p. 208-210°. (Found, C, 71.2; H, 4.1; N, 8.8. $C_{18}H_{12}N_2SO$ requires C, 71.1; H, 4.0; N, 9.2). The mother liquor contained *p*-toluidine hydrobromide. (II, a) also reacted with aceto-acetanilide under similar conditions to give (III, c). From the mother liquor aniline-hydrobromide was obtained.

6. *Reaction with malonic acid*: Malonic acid (0.5 g) in ethanol (5 ml) was added to a solution of II, b (0.5 g) in ethanol (25 ml) and the reaction was complete in 12 days, at room temperature. The solvent was evaporated off and was extracted with cold water (25 ml) and filtered. The residue (0.15 g, 60%) on recrystallization from aqueous ethanol gave colourless crystals of (III, d), m.p. 63-65°. (Found, C, 71.0; H, 4.1; N, 7.9. $C_{11}H_7NS$ requires C, 71.4; H, 3.8; N, 7.6). The water extract on evaporation gave *p*-toluidine hydrobromide. (II, a) reacted with malonic acid in 15 days under similar experimental procedure, to yield (III, d). The mother liquor gave aniline hydrobromide on evaporation.

7. *Reaction with acetone at room temperature*: Acetone (3 ml) was added to a solution of (II, b) (0.5 g) in ethanol (25 ml) and the mixture was allowed to stand at room temperature till the reaction was complete (30 days). The resulting yellow plates of (III, a) was filtered, washed and dried (0.21 g, 67%). Recrystallized from ethanol, m.p. 179-181°. (Found, C, 68.3; H, 4.2; N, 6.2. $C_{18}H_9NSO$ requires C, 68.7; H, 4.0; N, 6.2%).

8. *Reaction with acetone at high temperature*: A mixture of II, b (0.5 g) in ethanol (25 ml), acetone (3 ml) and conc. hydrochloric acid (2 drops) was refluxed (18 hrs), till the reaction was complete. The solution on cooling gave (III, a) which was filtered off, washed and dried, (0.2 g, 63%). Recrystallized from ethanol, m.p and mixed m.p. 179-181°.

9. *Reaction with acetophenone at high temperature*: A mixture of II, b (0.5 g), acetophenone (A. R., 3 ml) and conc. hydrochloric acid (2 drops) in ethanol (30 ml) was refluxed till the reaction was complete (50 hrs). The solution on cooling yielded III, e (0.3 g, 76%). Recrystallized from ethanol, m.p. 150-151°. (Found, C, 74.6; H, 4.2; N, 5.2. $C_{18}H_{11}NOS$ requires C, 74.7; H, 3.8; N, 4.9%).

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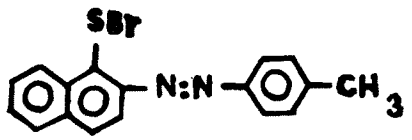
REACTION OF 2-*p*-TOLYLAZONAPHTHALENE-1-SULPHENYL BROMIDE WITH RESORCINOL TAUTOMER

2-*p*-TOLYLAZONAPHTHALENE-1-SULPHENYL BROMIDE(I) is found to be a much poorer electrophile than its azobenzene counterparts, in its thioarylation reactions with active aromatic substrates[1]. In an attempt to thioarylate resorcinol with (I) in methylene chloride we have obtained an unexpected product in an excellent yield. Whereas thioarylations of *m*-phenylenediamine and *m*-aminophenol with (I) in ethanol medium take 15–20 days for completion[1], the reaction with resorcinol in methyl enechloride is found to be astonishingly fast, being completed in 60 seconds at room temperature. The brilliant red precipitate obtained does not respond to the routine tests for phenols. But qualitative tests show the presence of bromine in the compound. The spectroscopic examinations and elemental analysis have supported the structure (IIxy) of the compound. Though aromatic enols, *i.e.*, phenols exist exclusively in the enolic form, the ketonic properties become more pronounced in polyhydric phenols. The introduction of new enolic centres should assist the development of ketonic character, since the energy which accrues in the formation of multiple keto groups would compensate for the loss of resonance stabilization. It is known that the addition of sodium hydrogen sulphite to resorcinol gives an adduct which implies that the addition has occurred at the ethylenic double bond as well as at the carbonyl groups of the resorcinol tautomer (III)[2]. The thioarylation of resorcinol with (I) perhaps, also proceeds in an analogous manner. The electrophilic sulphenyl bromide attacks the active methylene group of the tautomer (III) and the liberated HBr subsequently adds to the etylenic double bond giving the compounds (IIx, IIy). It is possible that the 'azo-structure' (IIy) may tautomerize to the 'hydrazone-structure' (IIx). The carbanion formed due to the migration of the proton may be stabilized by the overlap of the orbital containing the electron pair of the anionic carbon and the 3*d*-orbital of the sulphur atom.



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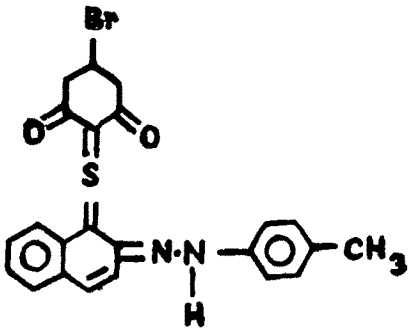

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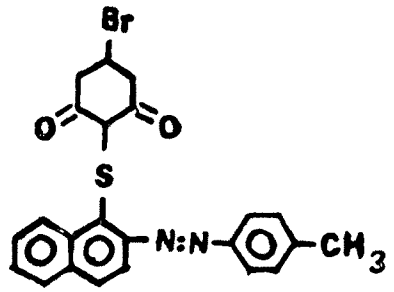
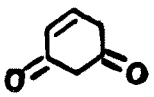


IIy



III

Experimental

A. UV and visible spectra (in ethanol) : The strong $\pi \rightarrow \pi^*$ band due to 2-*p*-tolylazonaphthalene chromophore, which normally appears around 330–340 nm in cases of other related compounds[1], undergoes a bathochromic shift of about 50 nm giving a broad band with the maxima at 383 nm. Tautomerization to the 'hydrazone form' may result in a red shift and the presence of both the tautomers in solution may cause the broadening of the band. In addition to this, a weak $n \rightarrow \pi^*$ band due to the azo group appears at 435 nm.

B. IR spectra ν (nujol) cm^{-1} : The IR spectra of the compound displays a strong peak in the relatively transparent region for organic molecules, which is usually attributed to the asymmetric stretch of cumulated double bonds of the type X = Y = Z. Peaks

are also obtained in the double bond stretching and hydrogen stretching regions as noted below :

2300 (strong, C=S=C asymmetric stretch), 1700 (strong, C=O stretch), 1640 (medium, probably C=N stretch), 1585 (weak, N=N stretch), 1300 (weak, probably C=S=C symmetric stretch) 3480 and 3510 (both medium, hydrazone N-H stretch), 3600 (medium, probably enolic O-H group formed by enolization of one of the two keto groups). Besides these peaks, a few more peaks are also obtained in the 'aromatic regions'.

C. PMR spectra : In the PMR spectra of the compound in $CDCl_3$ the following important absorptions are observed.

τ-value	Types of protons
8·1–8·2	Poorly resolved quadruplet which are probably obtained from protons $-CH_2-CHBr-CH_2$ of the structure (IIx)/(IIy).
7·5	Singlet due to protons $\phi-CH_3$
6·4	Complex multiplet, probably due to HC–Br proton
5·4	Singlet due to proton H–N–N=
4·7	Singlet due to proton HC–S–
4·4 and	Doublet, probably due to protons HC=CH of (IIx)
2·4–2·6	Complex multiplet due to aromatic protons.

The above PMR values support the tautomeric structure (IIxy) of the compound.

D. Reaction of the sulphenyl bromide(I) with resorcinol : The sulphenyl bromide (0·5 g) was dissolved in methylene chloride (50 ml) and resorcinol (0·25 g) was dissolved in methylene chloride (150 ml) on boiling. The two clear solutions are mixed together and shaken well. A brilliant red precipitate is formed almost immediately. It is filtered, washed with warm methylene chloride (50 ml) and dried (0·6 g, 92%). Crystallized from chloroform-methylene chloride mixture (40 : 60) as shining red crystals, m.p. 169–71° C. $C_{23}H_{19}N_2O_2SBr$ requires C, 59·1; H, 4·1; N, 6·0%, found C, 59·4; H, 4·4; N; 5·9%.

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