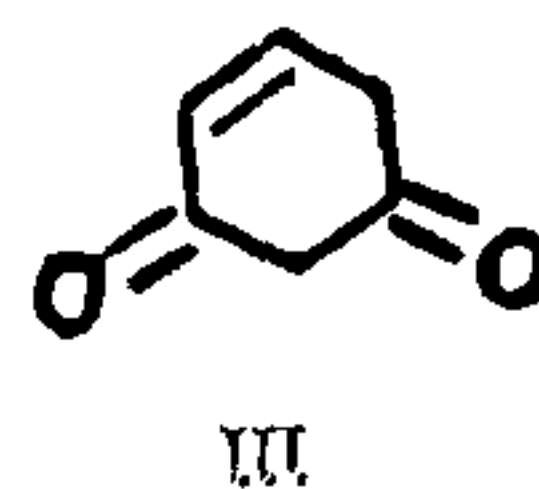
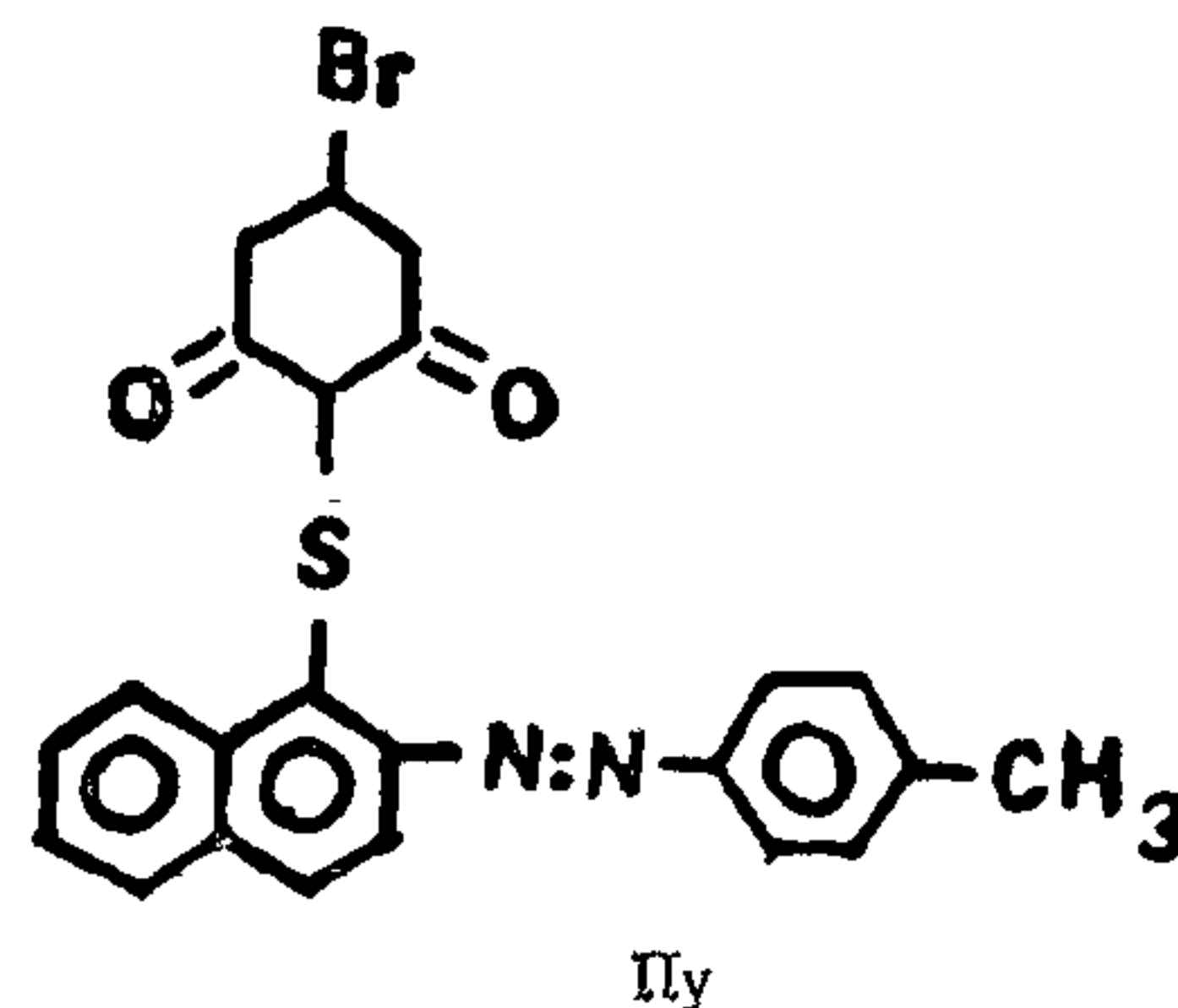
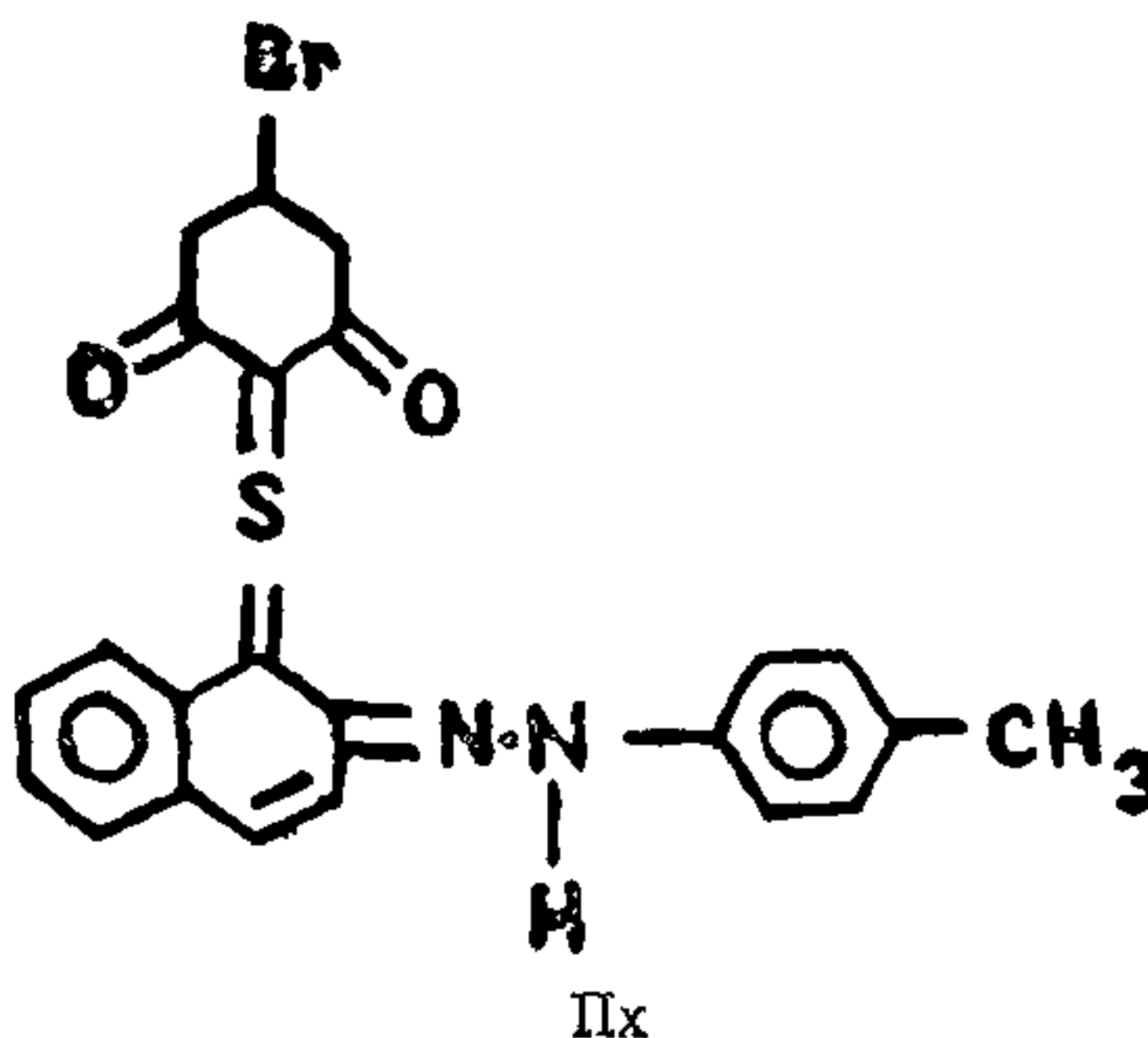
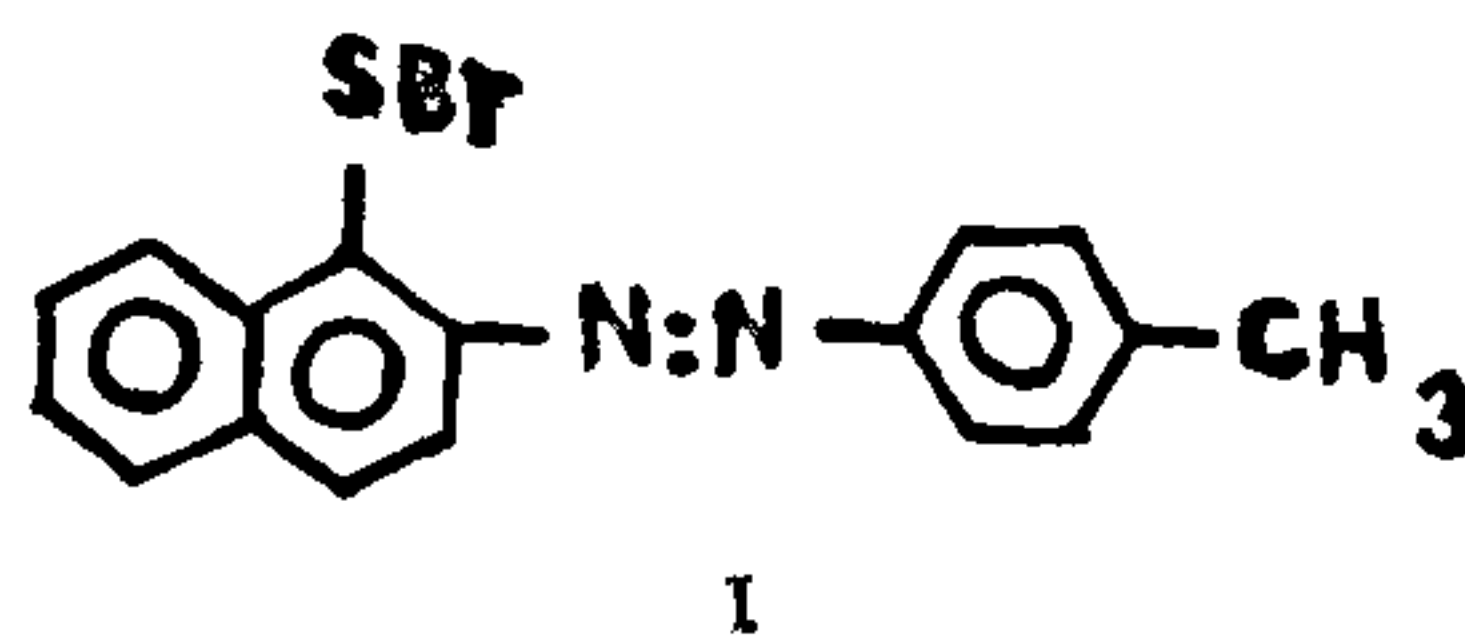


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REACTION OF 2-*p*-TOLYLAZONAPHTHALENE-1-SULPHENYL BROMIDE WITH RESORCINOL TAUTOMER

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 substrates¹. 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 completion¹, 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 (IIx) 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 ethylenic 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.

Experimental

A. UV and visible spectra (in ethanol): The strong $\pi - \pi^*$ band due to 2-*p*-tolylazonaphthalene

chromophore, which normally appears around 330–340 nm in cases of other related compounds¹, 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 $n - \pi^*$ 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),¹ 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 CDCl₃, the following important absorptions are observed.

τ -value	Types of protons
8.1-8.2	Poorly resolved quadruplet which are probably obtained from protons $-\text{CH}_2-\text{CHBr}-\text{CH}_2$ of the structure (IIx)/(IIy).
7.5	Singlet due to protons $\phi-\text{CH}_3$
6.4	Complex multiplet, probably due to $\text{HC}-\text{Br}$ proton
5.4	Singlet due to proton $\text{H}-\text{N}-\text{N}=\text{}$
4.7	Singlet due to proton $\text{HC}-\text{S}-$
4.4	Doublet, probably due to protons $\text{HC}=\text{CH}$ and 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. C₂₃H₁₉N₂O₂SBr requires C, 59.1; H, 4.1; N, 6.0%, found C, 59.4; H, 4.4; N, 5.9%.

Thanks are due to Dr. K. Verma and Dr. S. R. Das for their kind help in taking the spectra.

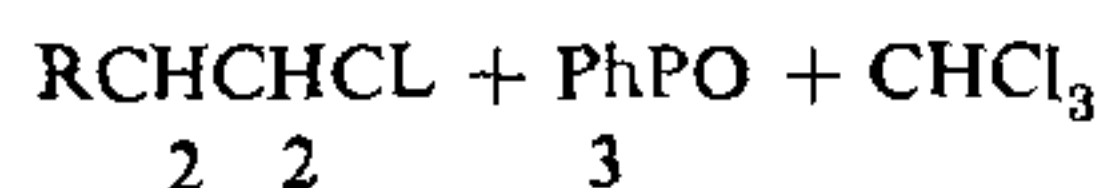
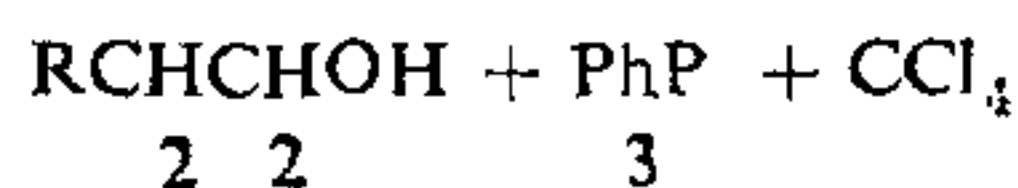
Department of Chemistry, Gauhati University, Assam, February 25, 1980.

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ALKENES FROM ALCOHOLS USING TRIPHENYL PHOSPHINE

ALCOHOLS and acids can be converted into halides by heating with triphenyl phosphine and carbon tetrachloride^{1,2}.



This reaction is normally free from the interference of rearrangement and elimination, although occasionally an alkene is formed together with halide.

In preparing 4,7-dimethoxyindene from the corresponding indanol, it was found that commonly used acid catalysed dehydrations gave low yields and tarry products. In view of the ready polymerisation of indenenes and also the activation of the benzene ring, 4,7-dimethoxyindene appears to be a particularly sensitive molecule. By modification of the above method, elimination became the main reaction and high yields of the indene (bp. 182-183°/9 mm) were obtained. The modified method, which was applied to a number of alcohols, is as follows. The alcohol and triphenylphosphine in equimolecular proportions are heated with carbon tetrachloride (about 200 ml per mole of alcohol) in a water bath at about 80° for 25 minutes and the mixture is set aside at room temperature for an hour. The excess of carbon tetrachloride and the chloroform produced in the reaction are removed by evaporation and the product slowly distilled (over about 50 minutes) leaving a residue of triphenylphosphine oxide. Any hydrogen chloride in the product may be removed by washing a solution in ether with dilute sodium hydroxide solution. The conditions of temperature required for the elimination vary considerably with the alcohol used. From cyclohexanol, cyclohexene distilled at the same temperature as the excess of carbon tetrachloride. This was identified from i.r. and n.m.r. spectra. The yield was 93%, determined by assay of distillate by vapour phase chromatography. 2-Phenylethanol gave 90% of styrene (142-146°) by distillation at atmospheric pressure: under reduced pressure, 2-phenyl-chloride was formed—this indicates temperature as the factor turning this reaction towards elimination. The styrene gave a good yield of dibromide and i.r. spectrum identical with that from an authentic specimen. *n*-Decanol required heating at 235° before distillation and gave 61% of decene (identified by n.m.r. spectrum and refractive index) and decyl chloride (bp. 80-82°/4 mm) about 10% was also obtained. Indan-1-ol and indan-2-ol were also successfully dehydrated by the same procedure to give 90% of indenenes (bp. 180-182°). These products were identified by comparing their i.r. spectra with authentic specimens.