CONFIRMATION OF STABILITY OF DIMETHYLAMINO GROUP TO WALLACH REARRANGEMENT[1]

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Abstract. 4-(Dimethylamino)phenylazoxynapthalene resists the formation of photochemical or acid catalysed Wallach rearrangement product, the hydroxyazo derivative due to an unfavourable substituent effect by the strongly electron-releasing $N(CH_3)_2$ group against substitution into the naphthalene ring. It is, presumably, also the result of excitation of dimethylamino group rather than that of the the azoxy group.

Although studies on Wallach rearrangement,[2] the isomerisation of azoxybenzene to hydroxyazobenzene, have been extended to naphthyl azoxy series[3-5] besides substituted azoxybenzenes,[6-9] as well as to the formation of tetrasubstituted azobenzenes during Wallach rearrangement,[10] no attempt has yet been made to confirm or otherwise, the stability of dimethylamino-substituted azoxy compounds to Wallach rearrangement. The only report in the literature is by Tanikaga[11] who proposed that 4,4'-bis-(dimethylamino)azoxybenzene is photochemically unreactive. Hilton, Scriven and Suschitzky[12] have recently synthesised 4-(dimethylamino)phenylazoxynaphthalene (I), (m.p. 135–137°C), by thermolysis of α-naphthyl azide and p-$ONC_6H_4NMe_2$ in bromobenzene at 155°C for 8 hr in nitrogen atmosphere. This prompted us to investigate in detail Tanikaga's suggestion by applying it to azoxy compound (I) and we report our findings here.

Experimental and Results

(a) *Photochemical Wallach Rearrangement of I.* Azoxy compound I was subjected to photochemical Wallach rearrangement with a medium pressure mercury arc (500 W, Hanovia UV lamp) powered by a voltage stabiliser. Photolysis conditions are summarized in Table 1.

Interestingly enough, the colour changes observed during experiments 1–7 were from orange-dark to red-dark brown.

After 30 min photolysis, ethanol solution (expt. 1) showed 2 spots on a TLC plate on developing with (9 : 1 v/v) toluene–ethyl acetate. The major band was the original compound I, while the minor spot was a compound in traces whose IR spectrum showed it having no absorption maxima characteristic of OH groups. It is probable that the frequently observed reduction of azoxy compounds to corresponding azo compounds might have some part to play at this stage. Further investigations to this effect are underway. Photolysis of ethanol solution (Expt. 1) was continued and photolysis solution was analysed after 4, 10, 15, 20 and 47 hr. However,

TLC did not show again 'the minor spot in any of these cases.

IPA solution (expt. 4) showed two spots on a TLC plate after being kept in sunlight for two weeks on development with (9 : 1 v/v) toluene–ethyl acetate. The major spot was the original azoxy compound I, while the minor compound (spot 2) on IR analysis did not show absorption maxima characteristic of OH groups.

(b) *Acid-Catalysed Wallach Rearrangement of I.* Compound I (0.2 g) was treated with 70% H2SO4 for 1 hr at 22°C, immediately a dark red solution produced. The spectroscopic studies were not conclusive about this colour change. After 1 hr the reaction mixture was poured into a mixture of ice and water. The product isolation was found to be extremely difficult. Extraction using acetone, chloroform, carbon tetrachloride, ethanol and benzene was not posssible. It was found that reaction products were only very slightly soluble in ether and product isolation and identification attempts were thus abandoned.

(c) Compound I (0.1 g) was treated with 70% H_2SO_4 containing 20% ethanol.[13] Again, the product isolation using acetone, carbon tetrachloride, ethanol, ether and benzene was not possible but was achieved by using very large quantities of chloroform (2000 ml), which was than removed by vacuum distillation using a rot-vapor. The residue was dissolved in (9 : 1 v/v) toluene–ethyl acetate mixture

TABLE 1. CONDITIONS FOR PHOTOCHEMICAL WALLACH REARRANGEMENT OF AZOXY COMPOUND (CONCENTRATION, 10^{-3} M).

Expt. No.	Solvent	Photolysis	
		Apparatus	Time
1	Ethanol	Pyrex	47 hr
2	Isopropanol (IPA)	Quartz	47 hr
3	Benzene	Pyrex	47 hr
4	Isopropanol (IPA)	Quartz	2 week (Sulight) 12 month
5	Ethanol	Pyrex	
6	Isopropanol (IPA)	,,	,,
7	Benzene	,,	,,

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and spotted on a large TLC plate alongwith the reference compound I. One major and one minor spot was obtained. The major band was found to be the original material (reference compound I) and the minor band identified by mass spectrometry appeared to be a polymer of high molecular weight.

(d) Prolonged treatment of compound I under conditions described in (c) resulted in considerable sulphonation/polymerization and the only resulting degradation product identified by mass spectrometry appeared to be a polymer of high molecular weight. No trace of compound I was observed.

(e) Reduction of azoxy compounds to corresponding azo compounds is a known phenomenon.[10] However, compound I appears to be undergoing sulphonation/polymerization rather then only reduction to azo compound, the occurrencs of which is itself doubtful. A flash photolysis study might be helpful in studying the presulphonation/polymerization (i.e., primary) process of photolysis, if short-lived reduction product is formed, followed by any further reduction to sulphonic acids and then to resulting tars and polymers.

Compound I, recovered after each experiment (1–7) and from (b) was subjected to analysis and on comparison with an authentic samle, was found to be in good agreement. A typical analysis is given here for azoxy compounds recovered in experiment 1: NMR: τ (CDCl$_3$) 90 MHz; τ1.1–3.4 (11 H, m, arom. H); τ6.98(6 H, s, —N(CH$_3$)$_2$). IR: λ_{max} (nujol): 1607, 1522, 1295, 1125, 1090, 960, 885, 840, 816, 785, 645 cm^{-1}. UV: λ_{max} (EtOH): 360–450 nm (411 nm). Melting Point: 135°C–136.5°C. Analysis Found: C, 74.198; H, 5.928; N, 14.676%. C$_{18}$H$_{17}$N$_3$O requires: C, 74.220; H, 5.840; N, 14.430%.

IR spectra were recorded on Perkin–Elmer 257 grating infrared spectrophotometer; UV spectra were recorded on Unicam. SP 800A ultraviolet spectrophotometer; NMR spectra were recorded on Perkin–Elmer R30 spectrometer; and, mass spectra were recorded on AEl-MSl2 mass spectrometer.

Discussion

Tanikaga[11] suggested that 4,4′-bis(dimethylamino) azoxybenzene (II) is photochemically unreactive. It was thought to be presumably the result of excitation of dimethylamino group rather than that of the azoxy group. Although all experiments showed a change in colour, this is not indicative of rearrangement and most likely is due to protonation which is a reversible process. Dolenko et. al.[14] have shown that protonation does not occur in the range 60–80% H$_2$SO$_4$ for unsubstituted naphthyl–phenylazoxy series as illustrated by the spectral changes. In β-1-phenylazoxy-naphthalene (III), an electron pair from oxygen can be delocalized into the naphthyl system. The resulting conjugation between the azoxy oxygen and 1-naphthyl group gives rise to increased basicity of (III). The pK_b of dimethylamine is 3.22 making it more basic then ammonia (pK_b 4.75). This increased basicity is

attributed to the electron release of the methyl group which increases the electron density on nitrogen and hence increases its affinity for a proton. The effect of a second methyl group is much less then that of the first. This is consistent with the effect of one and two chlorine atoms on the ionization of acetic acid. The presence of —N(CH$_3$)$_2$ group makes compound I even more basic then III. It was expected that prolonged treatment with 70% H$_2$SO$_4$ should actually lead to rearrangement, but this resulted into formation of tars and polymers. However, treatment with 70% H$_2$SO$_4$ containing 20% ethanol appeared to be leading to rearrangement, but the new compound (second spot on TLC plate) proved to be a polymer of high molecular weight. It is very doubtful that further changes in reaction conditions will lead to some rearrangement.
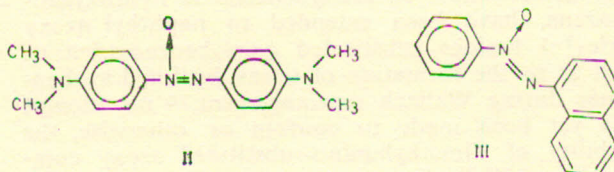
Due to very low solubility of naphthylazoxy compounds, addition of organic solvents is necessary to assist in solubilization. This was also experienced by Dolenko and Buncel[4] during their studies on rearrangement of naphthylazoxy series. Consequently, normal procedure for product isolation like the use of column chromatography was quite impractical and large quantities of chloroform were required to isolate the reaction products.

For the photochemical rearrangement of I, the second compound formed in experiments 1 and 2 as shown by TLC could also be the result of cis–trans isomerization.[15] This is further confirmed by the fact that when freshly photolysed solution was boiled before running the TLC separation, the
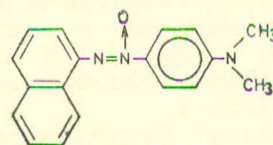
second spot disappeared in some cases. We believe that the stability of compound I to photochemical Wallach rearrangement could be due to two possibilities.[15] (a) an unfavourable substituent effect by strongly electron-releasing —N(C$_3$H)$_2$ group against substitution into the naphthalene ring; and, (b) a change in the nature of excited states, again due to the —N(CH$_3$)$_2$ substituent. Compound III shows a strong absorption in the region 323–390 nm ($\pi^* \leftarrow \pi$ transition), while I shows a strong absorption in the region 360–450 nm, and II had λ_{max}^{EtOH} at 427 nm.

Apparently, the conversion of compound I on irradiation in IPA from orange to colourless is interesting but is hard to understnad. The colour is not restored on standing and the possibility of photochromism can easily be discounted.

The mechanistic aspects of Wallach rearrangement are very well documented.[16-22]

Conclusions

It is now concluded that azoxy compounds with dimethylamino substituents in general, and 4(dimethylamino) phenylazoxynaphthalene in particular resist the formation of corresponding hydroxyazo derivative. The reasons of the later to do so are confirmed by the following observations: (a) azoxy oxygen do not migrate to distant aromatic ring;[16] (b) azoxy oxygen do not involve substitution at *ortho* or *para*-position even though these positions are vacant; and (c) position of the dimethylamino group is very important, which, considering the electronic factors involved prevents *ortho* or *para* substitution during Wallach rearrangement.

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