Orientation in the Wallach Rearrangement for the Naphthyl Azoxy Series[1]

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The acid-catalyzed Wallach rearrangement of azoxybenzenes has been extended to the naphthyl azoxy series in order to evaluate the effect of annelation of benzene rings on the course of rearrangement. The six known azoxy derivatives containing the α-naphthyl, β-naphthyl, and phenyl moieties, in various combinations, have been examined with respect to product orientation in moderately strong sulfuric acid solutions. The course of rearrangement (eqs. 2–6) is discussed on the basis of current mechanisms.

Le réarrangement de Wallach, sous catalyse acide, d'azoxybenzènes a été appliqué à la série d'azoxynaphtalène afin d'évaluer l'effet d'annellation d'anneaux benzéniques sur le mécanisme du réarrangement. Les six dérivés azoxy connus, contenant les groupes α-naphtyle, β-naphtyle et phényle dans des combinaisons différentes, ont été étudiés en fonction de l'orientation du produit dans des solutions d'acide sulfurique modérément fortes. On discute du processus de réarrangement (eqs. 2–6) en se basant sur les divers mécanismes connus. [Traduit par le journal]

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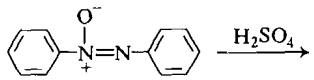
The transformation of azoxybenzene (**1**) to *p*-hydroxyazobenzene (**2**) in strongly acidic media has been the subject of a number of investigations since its discovery by Wallach and Belli in 1880 (1). Studies related to this rearrangement

[1] 

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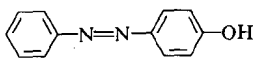

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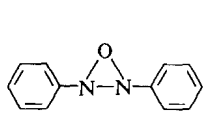
have included evaluation of the effect of substituents in one or both phenyls on the course of rearrangement (2, 3), the employment of isotopic tracers including ^{14}C (4), ^{15}N (5), and ^{18}O (6, 7), and kinetic investigations, performed on azoxybenzene and some substituted derivatives (2, 3, 8). As a result of these studies a number of mechanisms have been proposed (9), involving some rather unusual species as reaction intermediates. The postulated key intermediates are shown in structures **3**–**8**.



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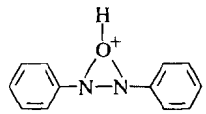

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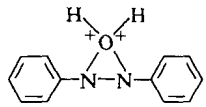

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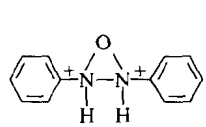

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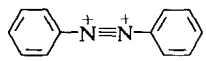

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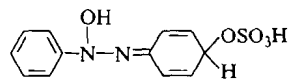

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In order to broaden the scope of the previous studies, which until now have involved only azoxybenzene or its substituted derivatives, and to perhaps shed more light on the controversy surrounding the nature of the reactive intermediate, an investigation of the reactions of the series of azoxy compounds containing the naphthyl moiety has been undertaken. In the case of the benzidine rearrangement, extension of the studies from phenyl- to naphthyl-containing hydrazo compounds revealed new facets relating to product orientation which resulted in a better understanding of the reaction mechanism (10). Other aromatic rearrangements have received similar investigation (11).

[1]Part XII in the series on the Wallach Rearrangement. For Part XI see ref. 31. A portion of this work has appeared in a preliminary communication (ref. 14).

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In this present study our objectives were to determine the effects of annelation of the benzene rings on the course of the Wallach rearrangement and to establish product orientation in these systems. To this end the transformation of the currently known phenyl–naphthyl and naphthyl–naphthyl azoxy derivatives (**9–14**) in moderately concentrated sulfuric acid has been investigated and the products identified.

Results

The naphthyl azoxy series investigated and the corresponding rearrangement products observed are summarized in eqs. 2–6. Thus β-1-phenylazoxynaphthalene (**9**) gives 4-phenylazo-1-naphthol (**15**), α-2-phenylazoxynaphthalene (**10**) and β-2-phenylazoxynaphthalene (**11**) yield 2-phenylazo-1-naphthol (**16**), 1,1′-azoxynaphthalene (**12**) gives rise to 4-naphthylazo-1-naphthol (**17**), β-1,2′-azoxynaphthalene (**13**) yields 4-(2′-naphthylazo)-1-naphthol (**18**), and 2,2′-azoxynaphthalene (**14**) gives 2-(2′-naphthylazo)-1-naphthol (**19**).

In determining the reaction products of this series it was necessary to accommodate certain experimental constraints. Previous studies with azoxybenzene have demonstrated that a number of other products (azobenzene, sulfonic acids, etc.) may be obtained when the reactions are run at high substrate and acid concentrations, high temperatures, and prolonged reaction times (12, 13). Subsequent work which has been carried out under controlled kinetic conditions, using low substrate concentrations ($\leqslant 10^{-3}\ M$), has shown the formation of a single primary product, the hydroxyazobenzene (8). The other products

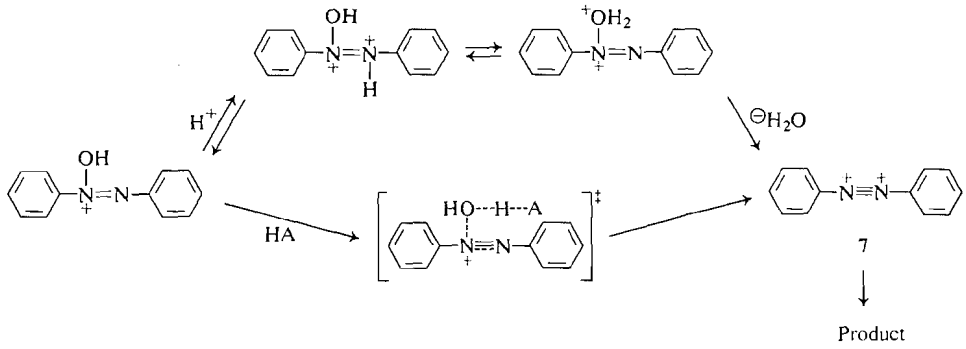
[2] **9** → **15**

[3] **10** + **11** → **16**

[4] **12** → **17**

[5] **13** → **18**

[6] **14** → **19**



SCHEME 1

have apparently no relation to the actual Wallach rearrangement. Due to the very low solubility of the naphthyl azoxy compounds, complete solubilization in the acid concentrations of interest could only be achieved at very low substrate concentrations (*ca.* 10^{-5} *M*). Even so, the addition of organic cosolvents, 0.5% v/v ethanol for the phenyl–naphthyl azoxy compounds and 5.0% v/v dioxane in the case of the even less soluble naphthyl–naphthyl derivatives, was necessary to assist in solubilization. In view of these considerations, normal product isolation and characterization was quite impractical. Nevertheless this was carried out in two representative cases, the reactions of **9** and **12**.

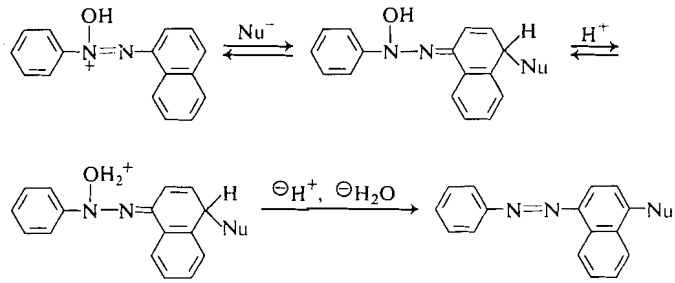
The primary means of product identification was by quantitative comparison of the u.v.-visible spectra of the observed reaction product with the spectra of similar equimolar solutions of a number of authentic compounds considered to be among the most probable products. Repeated scanning of the spectra during reaction ensured that its course was known throughout and that the final spectra examined were representative of the primary rearrangement and not of some subsequent process. These spectral comparisons were carried out directly in the sulfuric acid reaction solutions and indirectly after quenching the reaction in an alcoholic base solution. In the case of each azoxy compound a preliminary survey was carried out to determine the optimum acid concentration for the study in terms of substrate solubility, reaction speed, and formation of side products, if any. With these precautions, and with the measurement of spectral characteristics under the various conditions of acidity–basicity (representative of different forms of ionization of the species concerned), identification of products could be satisfactorily accomplished.

Discussion

The studies described here have demonstrated that the main reaction pathway for the naphthyl azoxy compounds in moderately concentrated sulfuric acid solutions is rearrangement to hydroxyazo derivatives (eqs. 2–6). Moreover, for the phenyl–naphthyl azoxy compounds (**9–11**) it is found that rearrangement occurs preferentially to the naphthyl rather than to the phenyl ring. In the case of the azoxy substrates **10** and **11** this preference gives rise to instances of acid-catalyzed *ortho* rearrangements, of which only few are known (see ref. 14). In the case of the dinaphthyl azoxy compounds containing the 1- and/or 2-naphthyl ring systems, rearrangement occurs preferentially to the 4-position of the 1-naphthyl ring if such is available. If such a position is not available, as in the case of **14**, then *ortho* rearrangement to the 1-position of the 2-naphthyl ring system results, yielding the same product as obtained in the photochemically induced rearrangement (15).

Kinetic studies of the Wallach rearrangement have provided evidence concerning the reaction mechanism in establishing the form of the acid catalysis (2, 3, 8). The simultaneous measurement of the rate of rearrangement and the extent of monoprotonation of the substrate has revealed a continued dependence of rate on acidity beyond the monoprotonation stage (8). The reaction mechanism proposed to account for these data is given in Scheme 1 and involves a dicationic intermediate (**7**). It was argued that formation of the dication from the conjugate acid of azoxybenzene might occur by two possible reaction pathways, as shown in Scheme 1, and that the dication would then undergo nucleophilic attack by H_2O or HSO_4^- to give *p*-hydroxyazobenzene as the reaction product (8).

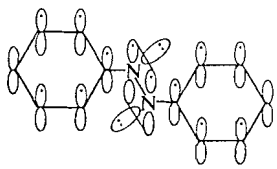
On the basis of similar studies on azoxyben-



SCHEME 2

zene and a number of its substituted derivatives, Duffey and Hendley (3) have proposed a mechanism involving an unsymmetrical quinoid intermediate (**8**) formed by nucleophilic attack on the monoprotonated substrate. This mechanism is outlined in Scheme 2 as it would apply to the case of β-1-phenylazoxynaphthalene (**9**). The two reaction mechanisms, as given in Schemes 1 and 2, can both account satisfactorily for the rearrangement products observed in these systems. On the basis of resonance structures which may be written for the dicationic intermediates, the positions predicted to undergo nucleophilic attack are the same ones which are expected to give rise to the most stable quinoid type intermediates.

Previously we carried out a theoretical examination of the dicationic type of intermediate derived from azoxybenzene using the m.o. method (16) for both linear and bent configurations, which have different π-electron systems as shown in the orbital diagrams **20** and **21**, respectively. The calculations have been extended



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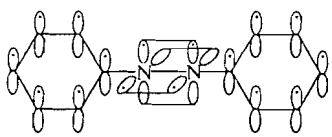

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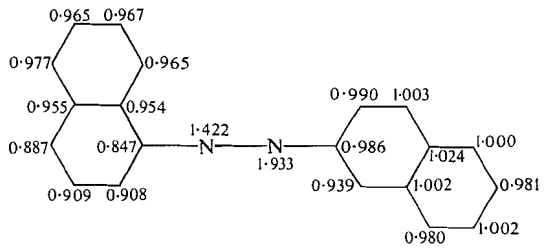
to the dications corresponding to the present series of azoxy compounds. Electron density values have been obtained by means of Hückel calculations (17) using the iterative ω technique (18, 19). In each case the observed product orientation corresponds to the entry of OH (through nucleophilic attack) at the carbon position (*ortho* or *para*) with the lowest π-electron density as determined for the corresponding linear dicationic structures. A typical example of the electron density values obtained is given below for the linear dicationic intermediate **22** pertaining to reaction 5.



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These results are interesting in terms of the correspondence which exists between the experimental results and the theoretical predictions based upon relatively simple calculations. They are also noteworthy in view of the fact that the dicationic intermediate derived from azoxybenzene has recently been observed by Olah *et al.* (20).

We will discuss in a future communication the consequences of the observed dependence of the rates of these rearrangements on solution acidity, as derived from a kinetic study of these reactions.

Experimental

Materials and Methods

Fisher certified grade dioxane was refluxed over sodium for 24 h and fractionally distilled prior to use. The fraction boiling at 101.5° and showing no absorption maxima at 261, 255, and 249 nm due to ethylene acetal was collected and stored in the dark. Sulfuric acid solutions of various concentrations were prepared by diluting Fisher or C.I.L. Reagent grade 96% sulfuric acid and analyzed by standard methods. A 1.0 *N* base quenching solution was prepared by dissolving 40 g of sodium hydroxide in

1.0 l of a solution of absolute ethanol – water (1:3). This solution was used immediately after preparation.

The reactions were carried out in aqueous sulfuric acid solutions containing a small amount of an organic co-solvent (0.5% v/v ethanol or 5% v/v dioxane) at 44.5 °C unless otherwise specified. Spectra of the acidic reaction media and of the base quenched solutions were obtained by the so-called "direct" and "indirect" techniques previously described (8), employing a Unicam model SP 800 B spectrophotometer.

Preparation of Compounds

The azoxy compounds were prepared by oxidation of the corresponding azo precursors as described previously (21). The hydroxyazo compounds of interest are itemized below with a brief statement concerning method of preparation. All compounds were purified by column chromatography, recrystallized to the highest level of purity which could be achieved and characterized. A detailed account may be found in ref. 22 along with the pertinent physical data.

4-Naphthylazophenol (**23**) was obtained by diazotization of 1-naphthylamine and coupling with phenol (23). 1-Phenylazo-2-naphthol (**24**) was prepared by coupling the diazonium salt of aniline with 2-naphthol (24). 4-Phenylazo-1-naphthol (**15**) was synthesized by coupling the diazonium salt of aniline with 1-naphthol (25). 4-(2′-Naphthylazo)phenol (**26**) was prepared by diazotization of 2-naphthylamine and coupling with phenol (26). 2-(2′-Naphthylazo)phenol (**27**) was obtained by condensing *o*-nitroanisole with 2-naphthylamine in the presence of alkali at elevated temperatures, followed by demethylation according to the procedure outlined by Badger and Buttery (15). 2-Phenylazo-1-naphthol (**16**) was prepared by coupling 2-naphthoquinone with phenylhydrazine in an acidic solution (27). 1-Naphthylazo-2-naphthol (**30**) was obtained by diazotization of 1-naphthylamine and coupling with 2-naphthol (28). Similarly 4-naphthylazo-1-naphthol (**17**) was synthesized by coupling with 1-naphthol (29). 2-(1′-Naphthylazo)-1-naphthol (**31**) was obtained by coupling 2-naphthoquinone and naphthylhydrazine in acid solution. 1-(2′-Naphthylazo)-2-naphthol (**32**) was prepared by diazotization of 2-naphthylamine and coupling with the 2-naphthol produced *in situ* by decomposition of the diazonium salt (30). 4-(2′-Naphthylazo)-1-naphthol (**18**) and 2-(2′-naphthylazo)-1-naphthol (**19**) were synthesized by diazotization of 2-naphthylamine hydrochloride and coupling with 1-naphthol.

Product Isolation From Reaction of β-1-Phenylazoxynaphthalene (9)

Due to the limited solubility of **9** in acidic media it was necessary to carry out the reaction in a large volume of acid in order to have a workable amount of substrate.

The reaction solution was prepared by dissolving **9** (0.1011 g) in 83.25% H_2SO_4 (490 ml) contained in a 1-l stoppered flask wrapped in aluminum foil and thermostatted at 25°. After 61 min, equivalent to 1 half-life, the reaction was halted by immersing the flask in an ice–methanol bath. The solution was then diluted to *ca.* 15% H_2SO_4 by the slow addition of the reaction mixture to 3.2 l water also cooled in an ice–alcohol bath. During the dilution the temperature did not rise above −2°. The resulting suspension was extracted with chloroform in a semicontinuous liquid–liquid extraction apparatus. The chloroform solution was dried ($MgSO_4$) and the solvent removed under vacuum. The residue was redissolved in 10 ml acetone and 2.5 ml of the solution was spotted on a large thin-layer plate (Eastman chromagram Sheets Type K301-R) along with the reference compounds **9**, **15**, **23**, **24**, and **25**. Development in petroleum ether (40–60°) – ethylacetate (20:1 v/v) gave two major bands which were cut separately and extracted with acetone until colorless. These solutions were filtered, evaporated to dryness, the residues dissolved in ethanol and their u.v.-visible spectra examined quantitatively. The composition of recovered material was 46.5% of **15** and 50.5% of **9**, based on amount of reactant used.

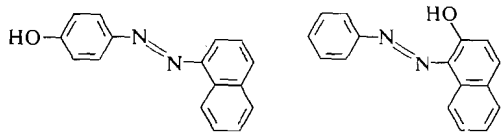
Product Isolation in the Reaction of 1,1′-Azoxynaphthalene (12)

The reaction solution was prepared by dissolving 0.075 g of **12** in dioxane and was added to a flask wrapped in aluminum foil containing 4.78 l of 67.95% sulfuric acid and 200 ml dioxane maintained at 25°. The dioxane content of the reaction solution was raised to 5% (v/v). The final substrate concentration was 5.0×10^{-5} *M*. After a period of time corresponding to 1 half-life (42 min) the reaction was stopped by cooling in an ice–methanol bath. The reaction mixture was then diluted to *ca.* 20% H_2SO_4 by slowly adding it to 11.5 l water contained in a 20 l flask which was cooled to 5°. The resulting suspension was extracted with 2 l of chloroform using a liquid–liquid extractor. After drying and removal of the solvent a portion of the residue was dissolved in acetone and spotted on a thin-layer plate together with **12**, **17**, **29**, and **30** as reference compounds and developed in the solvent system petroleum ether (40–60°) – 5% ethyl acetate (v/v). The remainder of the residue was purified on an alumina column and the u.v.-visible spectrum of each band examined. In addition, the i.r. spectrum (KBr disc) of the major product band was obtained and compared with those of **17** and **29**. The u.v.-visible and i.r. spectra confirmed that **17** is the major product by comparison with the authentic material. The minor product could not be identified though no trace of **29** was detected.

Spectral Identification

Rearrangement of 9

The reaction of **9** was followed to completion, (9 half-lives), in 77.00% H_2SO_4 – 0.5% EtOH and was characterized by the disappearance of a broad, low intensity band at *ca.* 450 nm due to **9** and the formation of an intense asymmetric band at 556 nm, ε 33 600, due to the product **15**. In base the formation of a strong asymmetric band at 494 nm, ε 25 600, was observed concurrently with the disappearance of a low intensity band at 380 nm (quenching after 3 half-lives). These spectral data correspond closely with those of **15** (λ_{max} 557 nm, ε 32 900, in acid and 494 nm, ε 28 100, in base) and indicate that the extent of formation of **15** is almost 100%. In separate experiments it was found that **15** is stable in this acid concentration for a period of time corresponding to at least 10 half-lives of reaction. Other compounds considered to be possible reaction products of **9** included 4-naphthylazophenol **23**, 1-phenylazo-2-naphthol **24**, and 1-phenylazonaphthalene **25**. Their spectra were determined in 77.00% H_2SO_4 – 0.5% ethanol and in base but showed no correspondence with the observed reaction product.



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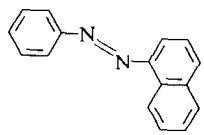

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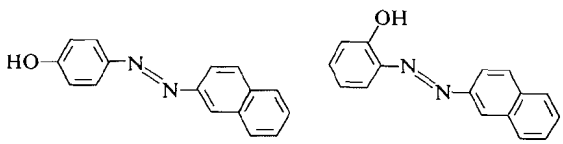
*Rearrangement of **10** and **11***

A comparison of the spectral data obtained in 77.00% H_2SO_4 – 0.5% ethanol and in base after almost complete reaction of the azoxy isomers **10** and **11** showed that **16** is the common product of both. Thus the positions of maximum absorbance of **16** (539 and 432 nm in acid, and 494 and 319 nm in base) coincide nicely with those of the product derived from **10** (539 and 432 nm in acid, and 495 and 320 nm in base) and from **11** (538 and 432 nm in acid, and 495 and 320 nm in base). However these spectral data also indicated that the extent of formation of **16** differs for the two azoxy isomers. For example, **16** is formed almost exclusively in the case of **10** as evidenced by the molar extinction values: ε_{539} 22 900, ε_{432} 19 300 after 4 half-lives reaction at this acid concentration, and ε_{495} 18 400, ε_{320} 15 800 after 3 half-lives as determined in base; this compares with actual values ε_{539} 24 700, ε_{432} 19 600, respectively, for **16** in acid and ε_{495} 20 800, ε_{320} 16 000 in base. In the case of **11** it appears that some other product(s) is being formed concurrently, ε_{538} 20 900 and ε_{432} 17 600 after 6 half-lives in acid and ε_{495} 17 600 and ε_{320} 14 400 after 10 half-lives as determined in base. The reaction of **11** in acid was also characterized by the formation of twin absorption bands of almost equal intensity at 258 and 263 nm. The intensity of these bands was found to increase with increasing acid concentration while at the same time the molar extinction at 538 nm due to **16** decreased. These bands were not due to **16**, which showed only a single band of low intensity at 255 nm in this region, nor were they due to any decomposition product of **16** since it was found to be completely stable at these acid concentrations. Compounds whose spectra were also characterized in acid and base were 4-(2′-naphthylazo)phenol (**26**), 2-(2′-naphthylazo)-phenol (**27**), and 2-phenylazonaphthalene (**28**), and were eliminated as possible reaction products on this basis.



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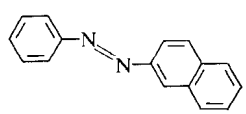

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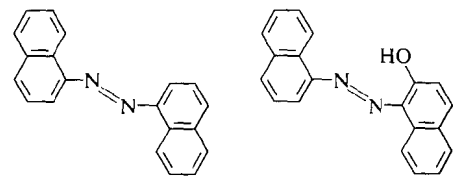
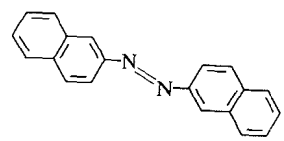
*Rearrangement of **12***

Spectral changes occurring during the reaction of **12** in 70.50% H_2SO_4 – 5.0% dioxane were characterized by the disappearance of a low intensity band at *ca.* 390 nm due to the substrate and the development of a single asymmetric band at 598 nm due to the formation of **17**. After 4.5 half-lives of reaction the molar extinction at 598 nm reached a maximum value of 21 300, or 81% of the theoretical value (26 400) given by **17** alone, and then began to decrease. This decrease was due, at least in part, to the fact that **17** is unstable in concentrated acid solution and undergoes a consecutive reaction resulting in a decrease in the molar extinction at 598 nm; *e.g.*, a 15% decrease in the molar extinction occurred at this acid concentration over a period of time corresponding to 3 half-lives of reaction. In base the spectrum of **12** after 2.7 half-lives reaction time in 67.95% H_2SO_4 – 5.0% dioxane showed a maximum at 505 nm with ε 15 600. This compared favorably with the spectrum of **17** which showed λ_{max} 505 nm, ε 18 500.

Other possible reaction products whose spectra were characterized included 1,1′-azonaphthalene, **29**, and 1-naphthylazo-2-naphthol, **30**. Of these compounds the



29 30



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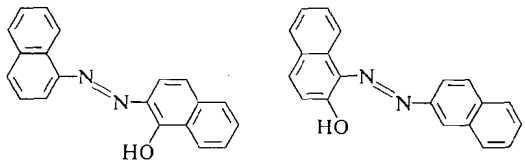
spectrum of **29** displayed some similarity to that of **17** in acidic media, λ_{max} 591 nm, ε 26 700. However, the spectrum of **29** in base, λ_{max} 400 nm, ε 11 800, was very different from **17**. This example demonstrates the utility of spectral characterization in both acidic and basic media.

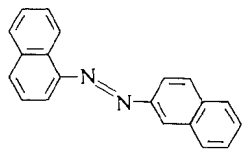
*Rearrangement of **13***

The reaction of **13**, as followed by the direct method in 70.50% H_2SO_4 – 5.0% dioxane, was described by the formation of a strong asymmetric band at 582 nm with a shoulder at 622 nm due to the formation of the hydroxyazo product, **18**. The developing band at 582 nm reached a maximum molar extinction of 32 300 after 5 half-lives reaction time and then began to decrease in intensity, indicating that **18** undergoes a subsequent reaction in concentrated H_2SO_4 solution. An equimolar solution of **18** gave a molar extinction value of 42 500 at 582 nm. In basic solutions the reaction was characterized by the disappearance of a single weak band at 388 nm due to **13** and the formation of a maximum at 509 nm, ε 28 000, due to **18**. An equimolar solution of **18** in base gave λ_{max} 508 nm and ε 35 800. Among the compounds examined as possible reaction products were the following: 2-(1′-



31

32



33

naphthylazo)-1-naphthol (**31**), 1-(2′-naphthylazo)-2-naphthol (**32**), and 1,2′-azonaphthalene (**33**). These compounds were excluded upon analysis of their spectra in acid and basic media.

*Rearrangement of **14***

The reaction of **14**, as followed directly in 77.00% H_2SO_4 – 5.0% dioxane, was characterized by the development of twin maxima of about equal intensity at 588 (ε 25 600) and 562 nm (ε 26 600), and a broad band at 430 nm (ε 12 200) after a period of time corresponding to 5 half-lives. Simultaneously, a slight decrease in the intensity of an absorption at *ca.* 410 nm was observed due to the disappearance of the substrate and this was accompanied by a shift to higher wavelength (430 nm, ε 12 700). These data correspond very closely to those of an equimolar solution of **19** at the same acid concentration, *i.e.*, λ_{max} 590 (ε 33 100), 564 (ε 32 900), and 429 nm (ε 14 900). However on the basis of these data it appears that **19** accounts for only about 75% of the original azoxy material. Contributing factors include the observations that **19** is not stable at this acid concentration (*e.g.*, the molar extinction coefficient of **19** decreases to 93% of its original value after a time equivalent to 3 half-lives) and that a competing reaction is occurring, manifested by the formation of twin maxima at 258 and 264 nm which are not due to decomposition of **19**. The nature of the material(s) responsible for these bands has not been determined. The spectral data obtained in base after 5 half-lives showed λ_{max} 505 nm (ε 20 200), compared with λ_{max} 507 (ε 27 000) and 328 nm (ε 18 900) given by an authentic sample of **19**. The spectral characteristics of 2,2′-azonaphthalene (**34**) were also determined in acid and base as a possible reaction product.

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