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THE WALLACH REARRANGEMENT OF α- AND β-2-PHENYLAZOXYNAPHTHALENES. *ORTHO* ORIENTATION IN THE ACID CATALYZED TRANSFORMATION.[1]

E. Buncel and A. Dolenko

Department of Chemistry, Queen's University, Kingston, Ontario, Canada

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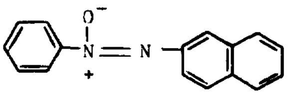
The Wallach rearrangement of azoxybenzene in acid medium yields *p*-hydroxyazobenzene[2] while on irradiation with sunlight (or u.v.) *o*-hydroxyazobenzene is obtained.[3] In the case of substituted azoxybenzenes the "normal" course in the acid rearrangement[4] is also *para* orientation and in the photochemical rearrangement[5] *ortho* orientation. However the literature contains several reports[6-8] of acidic *ortho* rearrangements for substrates in which a *para* position is vacant but the reports[6-8] are conflicting in nature. We now present results for two cases of the acid catalyzed Wallach rearrangement in which *ortho* orientation has been established. The compounds examined are the two isomeric α- and β-2-phenylazoxynaphthalenes, 1 and 2.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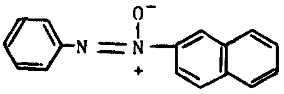
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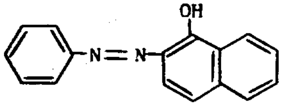
The rearrangement of 1 in 77.0% sulfuric acid-0.5% ethanol at 44.4° was followed spectrophotometrically by methods described previously.[9,10] Reaction was accompanied by the gradual decrease of the 400 nm absorption due to partly protonated substrate[1b] and the growth of two asymmetric bands centred at 434 nm and 540 nm. The pseudo-first order rate constant calculated by the Guggenheim method for formation of the product absorption at 540 nm was $12.1 \times 10^{-5}\ s^{-1}$. Comparison was made between the spectra of the reaction product in acidic and basic medium with spectra of the authentic compounds[11] 3-6, which were considered as the possible reaction products. These are the products for ortho orientation (3 and 5), para orientation (4), and reduction (6). The formation of azobenzenes as the major products in the Wallach transformation of some reactants has been observed previously.[12,13] The extinctions of 3-6 at the absorption maxima are given in Table I. It is seen that there is good correspondence between the spectral characteristics of 3 and those of the reaction product. The correspondence extends over the entire region examined (350-650 nm). In contrast the spectra of 4 to 6 show different character over the spectral region. The results hence establish the nature of the reaction as an ortho rearrangement process, 1→3.



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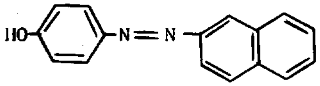

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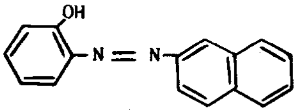

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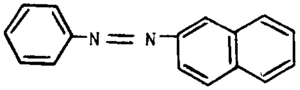

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The rearrangement of 2 in 77.0% H_2SO_4 - 0.5% ethanol at 44.4° was studied in analogous manner and similar observations were made. The spectral characteristics of the product over the visible region are practically identical to those in the reaction of 1 but the extinctions are about 10% smaller (see Table I). It appears that a minor concurrent process takes place with 2 to give an as yet unidentified side product. The minor reaction path apparently does not lead to 4 or 5 since these absorb strongly at 480 nm at which wavelength 3 has an absorption minimum. The product species from reaction of 2 exhibits an absorption minimum at 480 nm with an extinction about 10% below that of 3. The pseudo-first order rate constant for formation of 3 calculated at 540 nm is $4.35 \times 10^{-5}\ s^{-1}$.

The preferential entry of hydroxyl into the naphthyl ring in the rearrangement of 1 and 2 is noteworthy. The mechanism of the acid catalyzed Wallach rearrangement proceeding with ortho orientation is under further investigation.

Table I

Spectral properties (λ_{max}, ε_{max}) of product species in the rearrangement of azoxy substrates 1 and 2 and of the possible products of reaction 3 - 6.

	Acidic medium	Basic medium
	λ_{max} (ε_{max})	λ_{max} (ε_{max})
Product species from 1	539 nm (22,900)[a]	495 nm (18,400)[b]
	432 nm (19,300)	320 nm (15,800)
Product species from 2	538 nm (20,900)[c]	494 nm (17,600)[d]
	432 nm (17,600)	320 nm (14,400)
3	539 nm (24,000)[e]	494 nm (20,800)[f]
	432 nm (19,000)	319 nm (16,000)
4	562 nm (26,000)[e]	434 nm (16,500)[f]
	450 nm (22,300)	310 nm (11,800)
5	496 nm (19,900)[e]	472 nm (12,000)[f]
	410 nm (16,400)	328 nm (14,400)
6	492 nm (18,000)[e]	446 nm (2,000)[f]
	443 nm (25,400)	324 nm (17,300)

[a] Product species from reaction of 1 (1.25 x 10^{-5}M) in 77.0% H_2SO_4 - 0.5% ethanol at 44.4°; spectrum taken after 6 h (4 half-lives) in 40 mm cell.

[b] Product species in 1 M NaOH - aq. EtOH following reaction of 1 (5.93 x 10^{-5}M) in 77.0% H_2SO_4 - 0.5% ethanol at 44.4° for 6 h and basification (1.39 ml: 50 ml). Spectrum taken in 100 mm cell.

[c] Reaction conditions as under (a); spectrum at 24 h (5.5 half-lives).

[d] Product species in 1 M NaOH - aq EtOH following reaction of 2 (1.36 x 10^{-4} M) in 79.0% H_2SO_4 -1% ethanol at 44.4° for 26 h (10 half-lives) and basification.

[e] From spectra of 1.25 x 10^{-5}M solutions in 77.0% H_2SO_4-0.5% ethanol at 44.4°.

[f] From spectra of 1.25 x 10^{-5}M solutions in 1M NaOH - aq. EtOH at 44.4°.

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