peri-*O*→*N*-Acyl (Triazinyl) Rearrangements in Naphthalenes with *N*-Acyl Displacement

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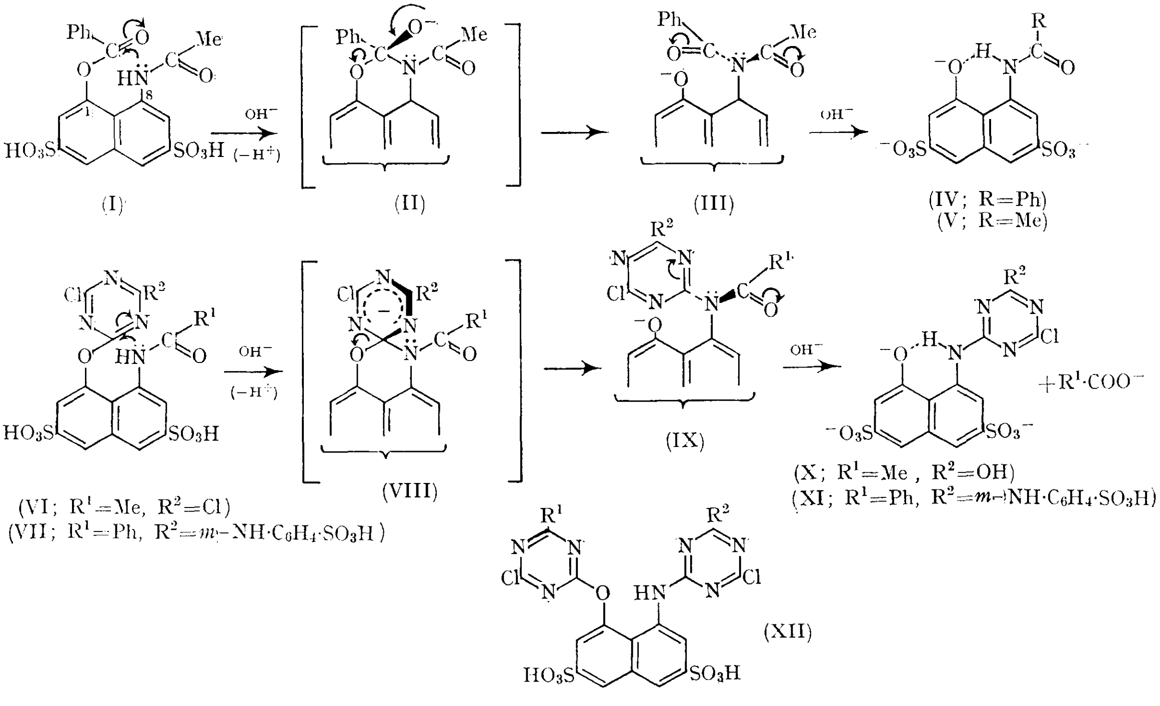
ACYL groups are known to migrate from oxygen to nitrogen in the presence of bases, usually in saturated hydrocarbons; this migration generally involves an amino- or an alkylamino-nitrogen attached to the adjacent carbon atom,[1] although more recently an acetyl transfer to a tertiary nitrogen carrying a cyano-group has been reported.[2] The close proximity of substituents located in the *peri*-positions in naphthalene is responsible for some unique reactions[3] including transfer of groups, such as phenyl, across the *peri*-position, and *peri*-ring closure.[4] We have observed an acyl transfer from a C-1 oxygen atom to the *peri*-acylamino-group. Thus 8-acetamido-3,6-disulphonaphthyl-benzoate (I), obtained by treating 8-acetamido 3,6-disulpho-1-naphthol with benzoyl chloride at pH 7—7·5 in water at room temperature, proved to be rather unstable even in neutral solutions; treatment with aqueous sodium hydroxide at pH 9—11 at 20° gave a product found to be a *ca.*

1 : 1 mixture of 8-benzamido- and 8-acetamido-3,6-disulpho-1-naphthols (IV) and (V), identified by coupling with diazotised *p*-chloro- (or *p*-nitro-) aniline and separation of the two bluish-red azo-compounds by chromatography on cellulose.

Both 8-acetamido- and 8-benzamido-3,6-disulpho-1-naphthols (stable intermediates toward mild alkali at room temperature) reacted readily with either cyanuric chloride or 2,4-dichloro-6-(3-sulphoanilino)-1,3,5-triazine in water at pH 7 at 0—5° and 15—25° respectively to give the corresponding highly soluble and unstable or only moderately stable *O*-triazinyl-*N*-acyl derivatives, *e.g.* (VI) and (VII). In this case, however, treatment with mild aqueous alkali at room temperature gave the 8-triazinylamino-3,6-disulpho-1-naphthol derivatives [(X) from (VI) and (XI) from (VII)] as the main products, identified after coupling with diazotised *p*-chloroaniline. The results can be interpreted mechanistically as follows:



(I) (II) (III) (IV; R=Ph) (V; R=Me)

(VI; R¹=Me, R²=Cl) (VII; R¹=Ph, R²=*m*-NH·C_6H_4·SO_3H) (VIII) (IX) (X; R¹=Me, R²=OH) (XI; R¹=Ph, R²=*m*-NH·C_6H_4·SO_3H)

(XII)

In the presence of a base a labile cyclic intermediate such as (II) or (VIII) is formed. We suggest that cleavage of the O–C_{acyl} bond in the *peri*-ring of compounds (II) and (VIII) occurs before the hydrolysis of one *N*-acyl group to give first *NN*-bis-acyl intermediates, such as (III) and (IX) (triazinyl group equivalent to acyl). This is based on the observation that whereas 8-acetamido- and 8-benzoamido-3,6-disulpho-1-naphthols couple readily with diazotised *p*-chloro-(or nitro-) aniline in water below pH 7 (*e.g.* pH 5—6, to give the well-known bluish-red, sparingly soluble 2-arylazo-compounds), the corresponding *O*-acyl derivatives (I, VI, and VII) did not couple below pH 7. However, in aqueous solutions at pH 7·5—8·5 the *O*-acyl derivatives were found to couple slowly to give first highly-soluble orange–scarlet azo-compounds containing two acyl groups in the molecule and a detectable (in most cases) hydrogen-bonded hydroxy-group (at δ 15—16 in n.m.r. spectrum, solvent dimethyl sulphoxide). Further treatment with mild alkali gave the known bluish-red mono-*N*-acyl azo-compounds [benzoic acid isolated from (VII) after coupling with diazotised *p*-nitroaniline] indicating (*a*) the usual coupling position at C-2 *ortho* to the hydroxy-group, and (*b*) *O* → *N*-acyl transfer during coupling in alkaline solution and the presence of both acyl groups on the nitrogen atom in transient intermediates such as (III) and (IX).

In a base-catalysed reaction similar to that of *O*-benzoyl-*N*-acetyl compound (I), *ON*-bis-triazinyl derivatives containing different substituents on the triazine rings [*e.g.* (XII; R^1 = 3,5-disulphoanilino, R^2 = anilino)], prepared by reaction of 8-(monochlorotriazinyl)amino-3,6-disulpho-1-naphthol[5] with 6-substituted 2,4-dichloro-1,3,5-triazines in water at room temperature and at pH 7 (the pK_{OH} value of the *peri*-*N*-acyl naphthols discussed here is approximately 7), gave a mixture of two mono-(8-triazinylamino)-1-naphthol derivatives each containing one of the R^1 or R^2 substituents. Irrespective of these substituents in (XII), however, reactions with diazonium compounds in dilute aqueous sodium carbonate (pH 8—8·5) indicated $O \rightarrow N$ rearrangement to *NN*-bistriazinyl intermediates preceding a final hydrolysis of one of the triazinyl groups.

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[1] S. Gabriel, *Annalen.*, 1915, **409**, 326; T. Immediata and A. R. Day, *J. Org. Chem.*, 1940, **5**, 516; L. H. Welsh, *J. Amer. Chem. Soc.*, 1947, **69**, 128; 1949, **71**, 3500; A. P. Phillips and R. Baltzly, *ibid.*, 1947, **69**, 200; G. Fodor and J. Kiss, *ibid.*, 1950, **72**, 3495; E. E. van Tamelen, *ibid.*, 1951, **73**, 5773; A. Nickon and L. Fieser, *ibid.*, 1952, **74**, 5566; *cf.* K. Butler, *J. Org. Chem.*, 1968, **33**, 2136.

[2] A. C. Currie, G. T. Newbold, and F. S. Spring, *J. Chem. Soc.*, 1961, 4693.

[3] V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567.

[4] P. T. Lansbury and R. L. Letsinger, *J. Amer. Chem. Soc.*, 1959, **81**, 940; 1956, **78**, 2648; P. T. Lansbury and J. F. Bieron, *J. Org. Chem.*, 1963, **28**, 3564.

[5] B.P. 834,304/1960 and 1,120,204/1968.