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1,2-ARYL MIGRATION ONTO ACYLNITRENIUM IONS

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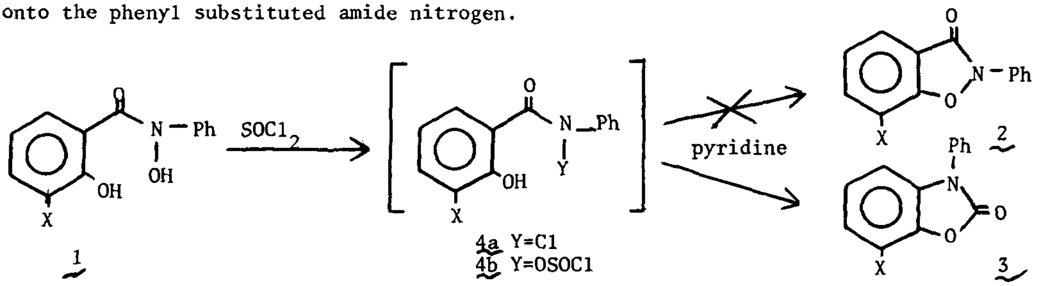
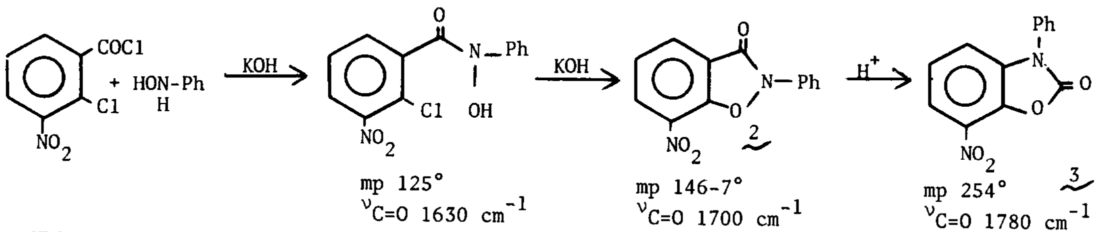
1,2-Shifts from acyl groups onto electron deficient nitrogens are very well known in systems derived from primary amides (Curtius, Hofmann and Lossen rearrangements).[1] In view of recent studies of group migrations onto divalent nitrenium ions[2], it seems that Hofmann and Lossen-like rearrangements might be feasible also in systems derived from secondary amides. This would mean that the actual scope of these classical reactions could be much wider than is generally believed.

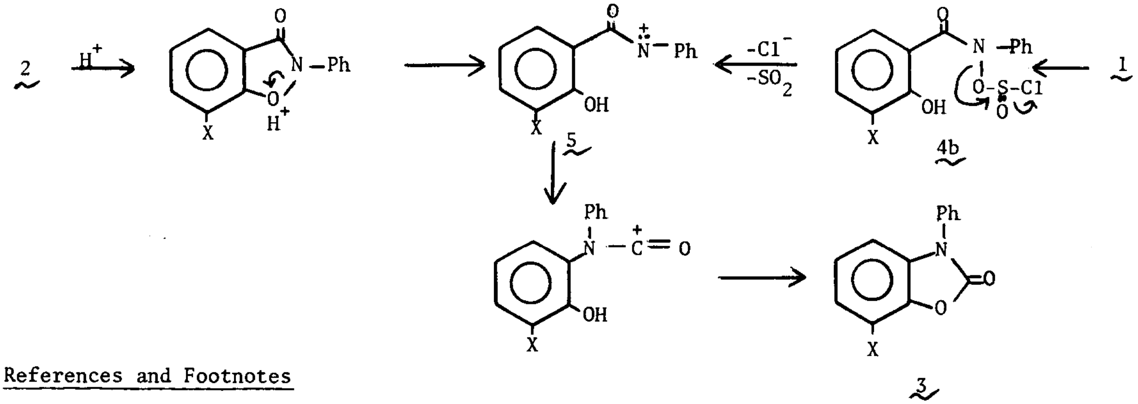
We have first observed this type of transformation during reinvestigation of a published[3] synthesis of a series of 2-phenyl-1,2-benzisoxazol-3-ones (**2**). These compounds were reported to be formed in the reaction of N-phenylsalicylhydroxamic acids (**1**) with thionyl chloride and pyridine via the N-chloroamides **4a**. (It seems more likely that the actual intermediate was the N-chlorosulfinate **4b**). However, neither the spectral properties (the carbonyl absorptions were at 1770-1780 cm^{-1}) or the chemical activity were in accord with structures **2**. Direct comparison of alleged compound **2** (X=H, mp 99°), prepared according to ref. 3, with 3-phenylbenzoxazol-2-one (**3**), prepared from 2-anilinophenol and phosgene[4] (mp 102°), showed them to be identical. The structural assignment of the products as **2** is therefore in error. The true structures are **3** which could have been obtained only by Hofmann-like migration of an aryl group onto the phenyl substituted amide nitrogen.



Furthermore, we have synthesized a genuine compound of type **2** (X=NO$_2$) by the route outlined below.[5] On treatment with acid (HOAc/HCl) it rearranged smoothly to **3** (X=NO$_2$)[6].



This rearrangement represents the N-phenyl version of the Lossen rearrangement.[7] The acylnitrenium ion **5** is probably a common intermediate to both reactions, but is formed by departure of different leaving groups (from 1 through solvolysis of the chlorosulfinate **4b**, and from **2** by heterolysis of the protonated oxygen-nitrogen bond). Aryl migration and cyclization of the resulting carbonium ions lead to the oxazolones **3**. A similar concerted mechanism, in which the leaving groups departs while the migrating group makes the new bond to nitrogen, is also possible.



References and Footnotes

1) P.A.S. Smith in "Molecular Rearrangements" Vol. 1, P. DeMayo Ed., Wiley, N.Y. 1963, p.528.
2) P.G. Gassman, Account. Chem. Res., 3 26 (1970).
3) U.R. Kalkote and D.D. Goswani, Aust. J. Chem., 30 1847 (1977).
4) Ch. Lespagnol, Bull. Soc. Chim. Fr., 393 (1954).
5) Satisfactory elemental analyses (C,H,N) and spectra (I.R., N.M.R. and M.S.) were obtained for all compounds.
6) As a similar photochemical rearrangement of N-alkyl derivatives has been reported, care was taken to exclude light. cf. L.J. Darlage, T.H. Kinstle and C.L. McIntosh, J. Org. Chem., 36 1088 (1971).
7) The reported (E. DiMaio and P.A. Tardella, Proceed. Chem. Soc., 224 (1963)) ring contraction of N-hydroxyvalerolactam to pyrrolidine can also be interpreted as a Lossen rearrangement of N-substituted hydroxamic acid.