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Reductive Rearrangement of 5-Nitrobicyclo[2.2.1]hept-2-enes. Formation of 3-Arylpyridines

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Abstract: Treatment of 6-aryl-5-nitrobicyclo[2.2.1]hept-2-enes with tin(II) chloride in refluxing THF or dioxane gave 3-arylpyridines via a deep-seated rearrangement.

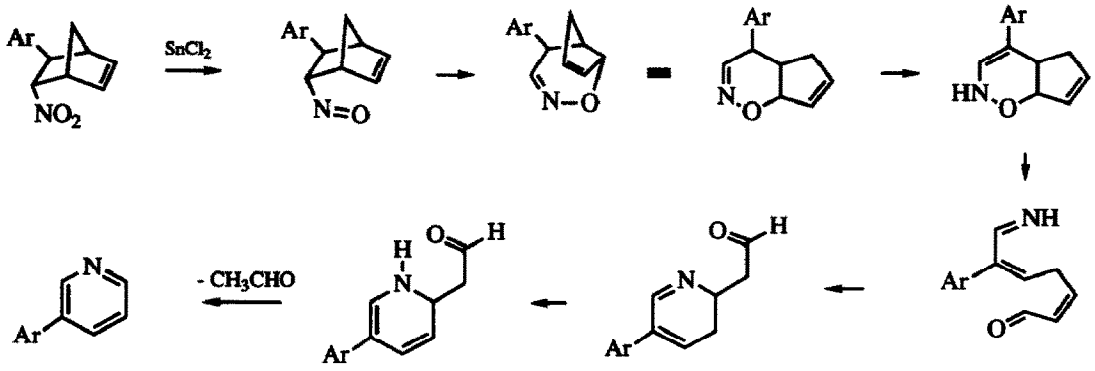
While seeking more convenient methods than reduction with titanium(III) chloride[1] for converting 5-nitro-6-(*p*-tolyl)bicyclo[2.2.1]hept-2-ene into the bicyclo[2.2.1]hept-5-en-2-one, we submitted the nitro compound to tin(II) chloride in refluxing THF. To both our disappointment and surprise, the major product of this reaction was identified as 3-(*p*-tolyl)pyridine. Thus, upon refluxing the nitro compound (8 mmol) with $SnCl_2.2H_2O$ (24 mmol) in THF (35 mL) for 24 h, solvent removal, and extraction of the residue with 2*N* hydrochloric acid, a product was isolated (37.5% yield) in a chromatographically pure state from the aqueous solution on addition of ammonia and re-extraction with dichloromethane. Its very characteristic and unambiguous analytical and spectral features left no doubt about the structure. Using dioxane as solvent the reaction proceeded in slightly better yield. A series of 6-aryl-5-nitrobicyclo[2.2.1]hept-2-enes[2] were then prepared by the Diels-Alder reaction of cyclopentadiene with β-nitrostyrenes and then reduced in the same manner to afford the corresponding pyridines: 3-phenyl (31%), 3-(*p*-anisyl) (30%), 3-(β-naphthyl) (25%), 3-(2-furyl) (17%).

The mechanism for the pyridine formation likely involves the following steps (see Scheme). Reduction of the nitro group to the nitroso level sets up a [3,3]-sigmatropic rearrangement to furnish a substituted 4,4a,5,7a-tetrahydrocyclopent[*e*]-1,2-oxazine. Cleavage of the ring system leads to an isomer containing an imine and an enal. An intramolecular Michael reaction between these subunits gives the dihydropyridine which is susceptible to retro-Mannich excision of acetaldehyde.

Previously the synthesis of our postulative 1,2-oxazine intermediates was achieved by hetero-Diels-Alder reaction of cyclopentadiene (as dienophile) and unsaturated nitroso compounds. These oxazines are indeed transformable into the pyridines on pyrolysis.[3] However, the conditions are much more drastic, i.e. at a temperature 150-200°C higher than that employed in our reactions. It is possible that in the reductive route the tin ions played a role in N-O bond heterolysis (the temperature is probably too low for homolytic cleavage) and thereby helped the deannulation process. On the other hand, the lower temperature may be responsible for the lesser yields. Since in our reaction at least five separate steps must be accomplished in

tandem,[4] and only the *(Z)*-isomer of the acyclic conjugated imine can cyclize, the present results are still quite remarkable.

Scheme



It should be noted that reduction of the 5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene afforded the *endo*-amine with either tin in acetic acid[5] or iron in hydrochloric acid.[6] Apparently under these conditions further reduction of the nitroso compounds was rapid and the sigmatropic rearrangement was superseded.

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