

A NEW METHOD FOR THE AMINATION OF ANIONIC NITROGENS

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The first synthesis of O-(2,4-dinitrophenyl)-hydroxylamine (I) was recently reported from this laboratory (1). Compound I represents a rare case (2) of a stable molecule in which a good leaving group is attached to a nitrogen atom. The dinitrophenoxy group in I should be easily displaced by nucleophilic reagents, thus I can serve as a reagent for the amination of nucleophiles.

The first type of nucleophilic reagents tried were anionic nitrogens:



The displacement reactions were found to proceed very fast, yielding the hydrazines II in very good yields. The three examples shown serve to illustrate the aminations of imides, sulfonamides and pyrroles.

- 1) Phthalimide was converted to N-amino-phthalimide (88% yield) m.p. 200 (lit. (3) m.p. 200-205).
- 2) N-Tosylbenzylamine gave 1-benzyl-1-tosylhydrazine (93% yield) m.p. 131-132° (Benzal derivative m.p. 115-116°).
- 3) 2,4-Dimethyl-3,5-dicarbethoxypyrrole yielded (95%) 1-amino-2,4-dimethyl-3,5-dicarbethoxy pyrrole m.p. 90-91° (Benzal derivative m.p. 75-77°).

The sodium salts of the anions were prepared with sodium methoxide in methanol. The solvent was evaporated and the residue dissolved in dry dimethylformamide. One equivalent of solid I was then added and the dark red

solution left at room temperature for 15 minutes, and poured into excess of water. The precipitated products were filtered, washed with water till the filtrate came out colourless and crystallized from dilute ethanol. Satisfactory elemental analyses were obtained for all new compounds. Spectral measurements were in accord with the assigned structures.

A study of the reactions of other types of nucleophiles with I and their synthetic applications are in progress.

REFERENCES

1. T. Sheradsky, J. Heterocyclic Chem., 4, 413 (1967).
Previous attempts to prepare I were described by A.O. Ilvespaa and A. Marxer, Helv. Chim. Acta, 46, 2009 (1963).
2. Other cases are the unstable O-acylhydroxylamines of which O-mesitylhydroxylamine was used as an amination reagent. cf. L.A. Carpino, J. Org. Chem., 30, 321 (1965).
3. H.D.K. Drew and H.H. Hatt, J. Chem. Soc., 16 (1937).