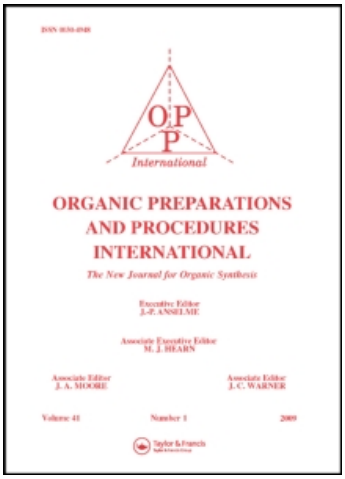

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AN IMPROVED SYNTHESIS OF *s*-TRIAZOLO[1,5-x]AZINES

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AN IMPROVED SYNTHESIS OF s-TRIAZOLO[1,5-x]AZINES

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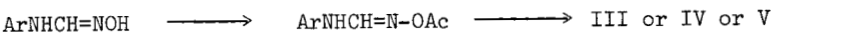
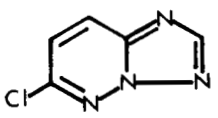
The synthesis of V by an improved method (also suitable for the preparation of III and IV) via previously unknown II is described.

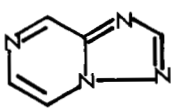


I II

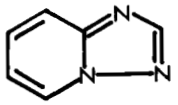
a) Ar = 3-(6-Chloropyrimidyl) b) Ar = 2-Pyrazinyl c) Ar = 2-Pyridyl



III



IV



V

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and mass spectra were recorded on a Hitachi-Perkin-Elmer RMU-6L instrument.

3-Acetoxyiminomethyleneamino-6-chloropyridazine (IIa).- This reaction is best performed in several small runs; for example, 10.2 g of Ia was treated with acetic anhydride (16 ml) with cooling. After 2 hrs at room temperature, the precipitated product was filtered and washed with ethyl acetate to yield 8.5 g mp. ∿ 108° (with conversion into III). The compound can be crystallized from chloroform-pet ether. Another small quantity of the product can be obtained by evaporation of the filtrate at room temperature in vacuo and treatment of the residue with water. From 56 g of Ia, 48 g (69%) of IIa was obtained.

Anal. Calcd. for $C_7H_7ClN_4O_2$: C, 39.17; H, 3.29; N, 26.11.

Found: C, 39.16; H, 3.77; N, 25.61.

In a similar manner the following derivatives were prepared:
2-Acetoxyiminomethyleneaminopyrazine (IIb), 78% yield, mp. ∿ 130° (with conversion into IV) from ethyl acetate. M.S.: m/e 180 (M^+).
Anal. Calcd. for $C_7H_8N_4O_2$: C, 46.66; H, 4.48; N, 31.10.
Found: C, 46.42; H, 4.80; N, 31.08.
2-Acetoxyiminomethyleneaminopyridine (IIc), 64% yield, mp. > 50° (with conversion into V). Because of its instability, the product could not be obtained sufficiently pure for analysis. M.S.: m/e 179 (M^+).

General Procedure. 6-Chloro-s-triazolo[1,5-b]pyridazine (III).- A mixture of the acetoxy compound IIa (14 g) and water (200 ml) was heated under reflux for 2 hrs. The solution was evaporated in vacuo to dryness and the residue was extracted with chloroform.[2] The solvent was evaporated and the residue crystallized from ethanol to yield 3.57 g (36%), mp. 144-146°, lit.[1a] mp. 135-138°; M.S.: m/e/ 154 (M^+).

From a total 48 g of IIa, there were obtained 16.1 g of III and 7.8 g of 3-amino-6-chloropyridazine.[2]

In a similar manner were prepared:

2-Triazolo[1,5-a]pyrazine (IV) in 73% yield, mp. 127°, identical with an authentic specimen.[1a]

s-Triazolo[1,5-a]pyridine (V) in 53% yield, mp. 105-106°, lit.[3] mp. 102-103°; M.S.: m/e 119 (M^+).

Anal. Calcd. for $C_6H_5N_3$: C, 60.49; H, 4.23; N, 35.28.

Found: C, 60.45; H, 4.34; N, 35.00.

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2. The chloroform insoluble compound is 3-amino-6-chloropyridazine (3.1 g).

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A SIMPLE APPARATUS FOR THE SAFE HANDLING OF PALLADIUM BLACK CATALYST

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A simple and inexpensive device made from readily available laboratory materials is described here for the safe handling of palladium black.[1,2] The device allows thorough rinsing of the catalyst (once generated from palladium chloride) with water, any suitable solvent, removal of most of the solvent and safe transfer of the catalyst to the reaction mixture with little or no danger of ignition or of moisture absorption.

This "syringe filter" device (Fig. 1) consists simply of a 10 milliliter Plastipak syringe[3] (Becton-Dickinson and Co., Rutherford, NJ) with the tip cut off at the end of the cylindrical barrel and of a porous polypropylene disc[4] forced-fitted in its place.

The syringe filter method for handling palladium black catalyst has been shown to be much safer than conventional manipulation. Numerous experiments using the syring filter have been performed in our laboratory