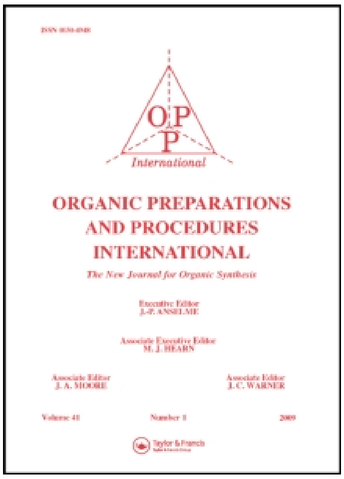

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ARSENIC TRICHLORIDE AS HALOGENATING AGENT. THE TRANSFORMATION OF HYDROXYMETHYL TO METHYL GROUP

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ARSENIC TRICHLORIDE AS HALOGENATING AGENT.
THE TRANSFORMATION OF HYDROXYMETHYL TO METHYL GROUP

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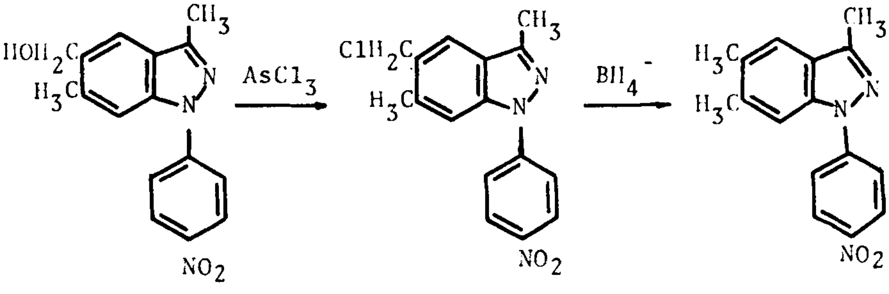

I II III

Hydroxymethyl indazoles obtained during our study of photochemical reactions of heterocyclic compounds[2,3] have been transformed into the corresponding methyl indazole *via* a two-step reaction sequence. In the first reaction, 1-(*p*-nitrophenyl)-3,6-dimethyl-5-hydroxymethyl indazole (I) was converted into the chloromethyl derivative (II) by treatment with AsCl$_3$. Arsenic trichloride was found to be a convenient reagent and solvent for unstable hydroxymethyl indazoles. Very little is recorded in the literature on the use of AsCl$_3$ in organic chemistry. Recently, the chlorination of nucleosides was reported[4] using a mixture of AsCl$_3$-HCON(Me)$_2$ (where the active intermediate is $(CH_3)_2N{=}CHCl^+\ Cl^-$). This mixture was previously employed as formylating agent. We know of no example where AsCl$_3$ is used alone to carry out the chlorination of alcohols.

The second step of our transformation was the selective reduction of the chloro compound II to indazole III without affecting the nitro group present. For this purpose, we used $NaBH_4$ in dioxane-water solution.[5]

Experimental

1-(p-Nitrophenyl)-3,6-dimethyl-5-chloromethyl indazole (II). Compound I (105 mg) was dissolved in arsenic trichloride (2 ml) and the solution was heated at 70° for 2 hrs. After that time, water was added and the organic compound was extracted with chloroform. The residue obtained after removing the solvent was taken up in methylene chloride and filtered through a short silica-gel column (1 x 5 cm) using the same solvent as eluent. The filtrate was evaporated to give 76 mg (68%) of a product which was recrystallized from benzene, yellow needles m.p. 229-231°.

nmr ($AsCl_3$) 3-CH_3 δ 2.70; 6-CH_3 δ 3.05; CH_2 δ 4.85; H_4 δ 8.10; H_7 δ 7.65; $H_{2',-6'}$ δ 8.08; $H_{3',-5'}$ δ 8.58

uv ($CHCl_3$) λ max. (nm) 360 (log ϵ 4.33); 241 (4.52).

Anal. Calcd. for $C_{16}H_{14}ClN_3O_2$: C, 60.96; H, 4.48; Cl, 11.25; N, 13.33. Found: C, 60.79; H, 4.63; Cl, 11.12; N, 13.26.

1-(p-Nitrophenyl)-3,5,6-trimethyl indazole (III). To a solution of compound II (42 mg.) in a mixture of dioxane (50 ml.) and water(5 ml.) $NaBH_4$ (150 mg.) was added and the reaction was kept at 70° for 20 min. After dilution with water the product was extracted with $CHCl_3$ and the extracts were evaporated. The indazole (41 mg.) was purified by chromatography on a silica-gel column (solvent, light petroleum 100-ethyl acetate 2) and recrystallization from ethanol, yielding 20 mg. (54%) of yellow prims, mp. 204-205°.

nmr ($AsCl_3$) 3-CH_3 δ 2.97; 5-CH_3 δ 2.50; 6-CH_3 δ 2.47; H_4 δ 7.71; H_7 δ 7.48; $H_{2',-6'}$ δ 7.91; $H_{3',-5'}$ δ 8.47.

uv ($CHCl_3$) λmax. (nm) 368 (log ϵ 4.29); sh 300 (3.58); sh 265 (3.98).

Anal. Calcd. for $C_{16}H_{15}N_3O_2$: C, 68.30; H, 5.37; N, 14.94. Found: C, 68.15; H, 5.67; N, 14.72.

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