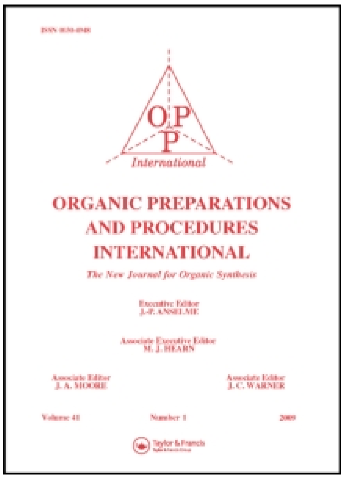

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DEALKYLATION OF N-PYRIDYLETHYL-2-ARYLBENZIMIDAZOLES BY ALUMINUM CHLORIDE

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OPPI BRIEFS

DEALKYLATION OF N-PYRIDYLETHYL-2-ARYLBENZIMIDAZOLES BY ALUMINUM CHLORIDE

Submitted by (2/22/79)
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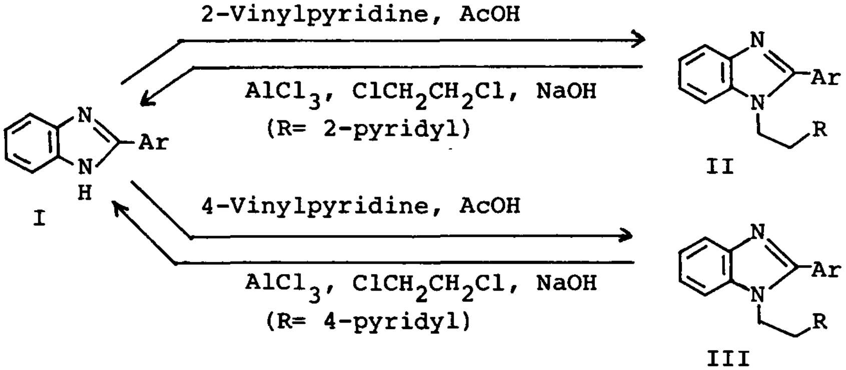
Although vinylpyridines have been used to protect the NH group of imidazole,[1,2] there has been little information available for the elimination reaction of the N-pyridylethyl group from 2-arylbenzimidazoles. The present work describes the smooth removal of the pyridylethyl group by aluminum chloride.



a) Ar= Ph; b) Ar= 2-Pyridyl; c) Ar= 4-Pyridyl

TABLE I. Dealkylation of N-Pyridylethyl-2-arylbenzimidazoles

Compound	Benzimidazole	mp (°C)	Yield (%)
IIa	Ia	293-294[3]	40
IIb	Ib	216-218[4]	30
IIc	Ic	195[5]	30
IIIa	Ia	293-294[3]	85
IIIb	Ib	216-218[4]	90
IIIc	Ic	195[5]	85

EXPERIMENTAL

All melting points were uncorrected. IR spectra were recorded on Nippon Bunko DS-701G Infrared Spectrophotometer. MS spectra were taken with JEOL-JMS-01SG Spectrometer.

Preparation of N-Pyridylethyl-2-arylbenzimidazoles. General Procedure.- To a mixture of 0.005 mole of a 2-arylbenzimidazole and 0.005 mole of a vinylpyridine, 0.01 mole of glacial acetic acid was added and heated at 140° for 6 hrs. After cooling, the reaction mixture was dissolved in 5 ml. of $CHCl_3$ and chromatographed over 25 g. of Al_2O_3(300 mesh), chloroform being used as an eluent. The tarry residue obtained from the first fraction was triturated with a small amount of a mixture of ether and pet. ether and solidified. The resulting solid was collected by suction and recrystallized to give an analytical sample.

Dealkylation of 1-(2-Pyridyl)-2-arylbenzimidazoles by Aluminum Chloride Catalyst. Typical Procedure.- To a solution of 1-[2-(4-pyridyl)ethyl]-2-(2-pyridyl)benzimidazole(IIIb)(0.9 g., 0.003 mole) in 50 ml. of dry tetrachloroethane, powdered anhyd. $AlCl_3$(0.4., 0.003 mole) was added and the mixture heated at 150° for 5 hrs. After the reaction was over, the reaction mixture was poured into 100 ml. of 5N NaOH aq. soln. with stirring and extracted with dichloromethane. The extract was washed with H_2O, dried over anhyd. Na_2CO_3 and evaporated *in vacuo*. The residue was recrystallized from EtOH-H_2O(1:1) to give 2-(2-pyridyl)benzimidazole(Ib) as colorless needles.

TABLE II. Data of Preparation of N-Alkyl-2-arylbenzimidazoles

Compd.	mp.,°C(lit.)	Appearance(Recryst.solvent)	Yield(%)
IIa	82(80-81)[1]	colorless prisms(n-hexane)	71.0
IIIa	129	colorless needles(n-hexane-Me_2CO)	23.4
IIb	80-81(75.5)[2]	colorless needles(H_2O-EtOH)	63.3
IIIb	113(113.5)[2]	colorless needles(n-hexane-Me_2CO)	60.0
IIc	123	colorless needles(n-hexane-Me_2CO)	69.0
IIIc	141	colorless needles(pet.ether-ether)	43.3

Compd.	MS(m/e) M^+	MS(m/e) M^+-92	Formula	Analysis Calcd(Found) C	H	N
IIa	299	207	$C_{20}H_{17}N_3$	80.24 (80.06)	5.73 (5.91)	14.04 (13.93)
IIIa	299	207	$C_{20}H_{17}N_3$	80.24 (80.24)	5.73 (5.68)	14.04 (13.91)
IIb	300	208	$C_{19}H_{16}N_4$	75.97 (76.13)	5.37 (5.26)	18.66 (18.71)
IIIb	300	208	$C_{19}H_{16}N_4$	75.97 (76.18)	5.37 (5.26)	18.66 (18.91)
IIc	350	258	$C_{23}H_{18}N_4$	78.83 (78.73)	5.18 (5.29)	15.99 (15.78)
IIIc	350	258	$C_{23}H_{18}N_4$	78.83 (78.66)	5.18 (5.02)	15.99 (16.22)

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A STEREOSELECTIVE SYNTHESIS OF endo-7-PHENYL-2-OXABICYCLO[4.1.0]HEPTANE

Submitted by (7/8/80)

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The epimeric 7-chloro-7-phenyl-2-oxabicyclo[4.1.0]heptanes (I) have been reduced with zinc in sodium ethoxide to give a mixture of the *endo* and *exo*-7-phenyl-2-oxabicyclo[4.1.0]-heptanes (IIa and IIb respectively),[1] which are difficult to separate due to the small difference in their boiling points. Jensen and Patterson[2] reported the use of triphenyltin hydride prepared *in situ* from lithium aluminum hydride and triphenyltin chloride for the stereoselective reduction of structurally related compounds, the 7-chloro-7-phenylnorcaranes. We ob-