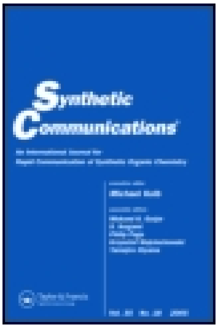

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Boron Triiodide-N-N-diethylaniline Complex: A New Reagent for Cleaving Esters

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BORON TRIIODIDE-*N*-*N*-DIETHYLANILINE COMPLEX: A NEW REAGENT FOR CLEAVING ESTERS.

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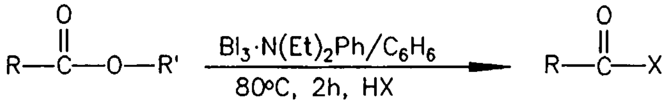
Abstract: Boron triiodide *N*,*N*-diethylaniline complex was used for the hydrolysis, transesterification, and aminolysis of esters.

Ester hydrolysis is one of the fundamental reactions in organic synthesis. The reaction can be achieved by various methods[1] but there is a continued interest in the development of new reagents. Boron trichloride,[2] boron tribromide[3] and aluminum triiodide[4] successfully cleave esters. We wish to report the use of a boron triiodide amine complex for the hydrolysis, transesterification and aminolysis of esters.

N,*N*-Diethylaniline forms a 1:1 complex with BH_3 and this complex has been used for the hydroboration of olefins.[5] BI_3-amine complexes can be prepared by adding a stoichiometric quantity of iodine to the corresponding amine-borane complex in hydrocarbon solvent. We have been examining the use of BI_3 reagents for organic functional group transformations; BI_3-amine complexes have been used to prepare alkyl and alkenyl iodides,[6] cleave ethers and geminal diacetates,[7] reductively dimerize sulfonyl derivatives to disulfides,[8] deoxygenate sulfoxides,[8] and cleave lactones to ω-iodocarboxylic acids and esters.[9]

We have observed that esters are readily hydrolyzed to carboxylic acids using an equivalent of BI_3-amine complex (at 80 °C) and then quenching the reaction with cold H_2O. Transesterification is accomplished by quenching the reaction mixture with the corresponding alcohol and aminolysis with an appropriate amine. When the reaction is carried out at room temperature considerable quantities of starting material remained even after 20 h (TLC). A small quantitity (1-2%) of reductive halogenated products are also formed; these products are presumably derived via reduction of the ester by traces of unreacted boron hydride remaining in the BI_3 complex.[10]

Electron withdrawing groups on the phenyl group inhibit the reaction; as an example, hydrolysis of methyl 4-nitrobenzoate results in only 5-10% of the desired acid. Increasing the reaction time does not improve the yield. When the reaction is performed with phenyl acetate and phenyl benzoate, phenol is isolated in 88 and 86% yield respectively. This is particularly interesting as Lewis acid catalyzed phenyl ester hydrolyses generally yield the Fries migration products.[4] Even refluxing the reaction mixture of phenyl esters for 10 h yielded only traces of (>1%) the Fries rearrangement products. Our results are summarized in the reaction scheme presented on the next page.



R	R^1	X	Yield (%)
a) C_6H_5	CH_3	OH	92%
b) C_6H_5	C_2H_5	OH	91%
c) C_6H_5	C_4H_9	OH	88%
d) C_6H_5	$CH_2C_6H_5$	OH	88%
e) o-C_6H_4OH	CH_3	OH	90%
f) o-C_6H_4Br	C_2H_5	OH	85%
g) C_3H_7	C_2H_5	OH	83%
h) $(CH_2)_8CH{=}CH_2$	CH_3	OH	89%
i) C_6H_5	CH_3	OC_2H_5	78%
j) C_6H_5	C_4H_9	OCH_3	65%
k) C_6H_5	CH_3	NHC_6H_5	58%
l) C_6H_5	C_4H_9	$NHCH_2C_6H_5$	52%

SCHEME

Experimental: All the esters, BH_3-*N*,*N*-diethylaniline complex and iodine are commercially available (Aldrich) and were used as received. Benzene was distilled over sodium-benzophenone and stored over sodium. The products were characterized by comparing their physical properties (mp and mmp) and spectral characteristics [^1H NMR (JEOL FX-90Q) and IR (BioRad FTS-7)] with that of authentic samples.

General Procedure: A flame dried, nitrogen flushed, 100 ml round bottomed flask equipped with a septum inlet, magnetic stirring bar and reflux condensor was cooled to 10 °C. BH_3-*N*,*N*-diethylaniline complex (1.63 g, 10 mmol) was placed in the flask with a syringe followed by benzene (30 mL). Iodine (3.81 g, 30 mmol) was added to the flask (evolution of H_2 gas was observed) and the reaction mixture stirred at ambient temperature for ~3 h (iodine color disappears). Methyl benzoate (1.36 g, 10 mmol) was then added and the temperature raised to 80 °C and the mixture stirred for 2 h.

(a) **Hydrolysis:** The reaction mixture was cooled to RT and poured on to 25 mL of ice cold water and the product extracted into ether (3 × 50 mL). The combined organic extracts were washed with saturated aqueous $Na_2S_2O_3$ (10 mL) and the acidic products extracted into 3*N* NaOH (2 × 20 mL). The carboxylic acids were regenerated using conc. HCL, extracted into ether (3 × 50 mL), washed with water (10 mL), brine (10 mL) and dried over $MgSO_4$. Removal of the solvent yielded benzoic acid, 1.12 g (92%).

(b) **Transesterification:** The reaction mixture was cooled to RT and ethyl alcohol (5 mL, 200-proof) was added and the mixture stirred at RT for 2 h. The mixture was poured on to H_2O (20 mL), extracted into ether (3 × 50 mL) and the combined organic extracts were washed with aqueous $Na_2S_2O_3$ (10 mL), water (10 mL), brine (15 mL) and dried ($MgSO_4$). The solvent was removed on a rotary evaporator and the residue chromatographed on a silica gel column (hexane eluent) to afford ethyl benzoate, 1.17 g (78%).

(c) **Aminolysis:** Aniline (5 mL) was added to the mixture at RT and stirred for 5 h. The mixture was poured on to H_2O (20 mL), the product extracted into ether (3 × 50 mL) and the organic extracts washed with aqueous $Na_2S_2O_3$ (10 mL), water (10 mL) and dried ($MgSO_4$). The solvent was removed on a rotary evaporator and the residue was chromatographed on a silica gel column (15% ethyl acetate in hexanes) to yield benzanilide, 1.14 g (58%).

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