Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Esters with $NaGaH_4$ in Tetrahydrofuran at 0 ℃[a]

Carboxylic acid ester	Time (h)	Yield of Aldehyde[b] (%)
isopropyl acetate	3	78[c]
phenyl acetate	3	75[c]
ethyl caproate	3	83
isopropyl caproate	3	80
tert-butyl caproate	3	81
ethyl cyclohexanoate	3	87
ethyl benzoate	6	67
isopropyl benzoate	6	75
tert-butyl benzoate	6	75
cyclohexyl benzoate	6	76
ethyl cinnamate	6	68
isopropyl cinnamate	6	63
tert-butyl cinnamate	6	76

[a] Treated with 0.5 equiv of reagent for aliphatic and aromatic esters. [b] Yields weres estimated by GLC. [c] Yield was estimated by 2,4-dinitrophenylhydrazine.

vided the corresponding aldehydes in yields of 67-76%. α,β-unsaturated esters, such as ethyl cinnamate and isopropyl cinnamate, undergo the reduction to afford the corresponding olefinic aldehydes in yields of 68-76%.

One advantage of this reagent for aldehyde synthesis can be carried out at 0 ℃ instead of the very low temperature (−70 ℃) or elevated temperature (65 ℃). Therefore, sodium gallium hydride is also believed to be a good reagent for the synthesis of aldehydes from carboxylic acid esters.

The following procedure for the reduction is representative. An oven-dried, 50-mL flask, fitted with a side arm and a vent adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 0.1253 g (1 mmol) of ethyl benzoate and 5.5 mL of tetrahydrofuran. The flask was immersed into the ice water bath and a precooled solution of sodium gallium hydride (2.5 mL, 0.2 M, 0.5 mmol) in tetrahydrofuran was added slowly with vigorous stirring. After 6 h, the reaction mixture was hydrolyzed with 10 mL of 2 N sulfuric acid and the suitable internal standard was added. And then the mixture was saturated with NaCl. The organic layer was subjected to GLC analysis on a Chromosorb-WHP, 10% Carbowax 20 M, 2 m, 1/8 inch column, indicating benzaldehyde in 67% yield.

Acknowledgment. The authors are thankful to professor N. M. Yoon for his help.

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Reactions of Vinylpyridines and Vinylquinolines with Nitrosonium Tetrafluoroborate: One Step Synthesis of Nitrolic Acids

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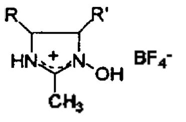
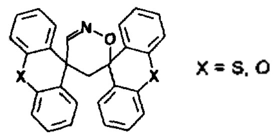
The reactions of nitrosonium tetrafluoroborate ($NOBF_4$) with olefins in acetonitrile gave a different type of products depending on the structure of the olefin. For example, the reactions with primary or secondary olefins, *i.e.*, propene, *cis*- or *trans*-2-butene, and styrene, etc., gave 2-alkyl-*N*-hydroxyimidazolium tetrafluoroborate (1),[1] whereas those with olefines having aryl groups at an olefinic carbon atom, *i.e.*, methylenethioxanthene and methylenexanthene, etc., gave 4*H*-5,6-dihydro-1,2-oxazines (2)[2] as a major product.



1



2

Although $NOBF_4$ has been often utilized as either a single electron transfer oxidant[3] or a weak electrophile,[4] no systematic study on the reactions of $NOBF_4$ with structurally and/or electronically different olefins has been reported.

We have chosen 2-vinylpyridine (**3a**) for the reaction with $NOBF_4$ based on two reasons: First compound **3a** is structurally similar to styrene previously studied[1] in respect of having an aromatic moiety attached to an olefinic carbon atom. Second, pyridine ring might reduce the π-electron density on the vinyl group so that a different reactivity of $NOBF_4$ toward **3a** compared with styrene would be expected.

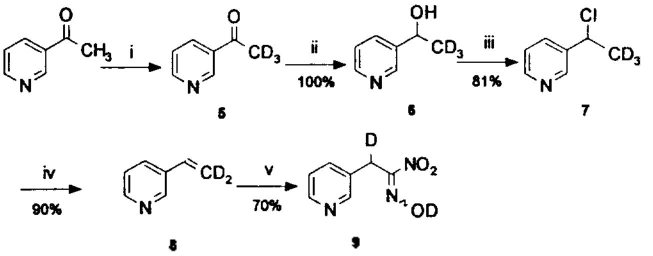
Surprisingly, the reaction of $NOBF_4$ with **3a** in acetonitrile at room temperature gave 2-pyridylacetonitrolic acid (**4a**) as a major product. 3-pyridyl- (**4b**) and 4-pyridylacetonitrolic acid (**4c**) were also obtained from the reactions with 3- (**3b**) and 4-vinylpyridines (**3c**), respectively under the same conditions. The formations of **4a** as well as **4b** and **4c** indicate that the distance between a nitrogen on the pyridine ring and a vinyl group is not important for the formation of the products. The reaction with 2-vinylquinoline (**3f**) under the same conditions gave an analogous product **4f**. However, it was unsuccessful to obtain 4-quinolylacetonitrolic acid as an isolable product from the reaction with 4-vinylquinoline. The yields and melting points of the nitrolic acids **4** prepared are summarized in Table 1.

Nitrolic acids have been synthesized by treatment of alde-

Table 1. Synthesis of acetonitrolic acid derivatives (**4**)[5]

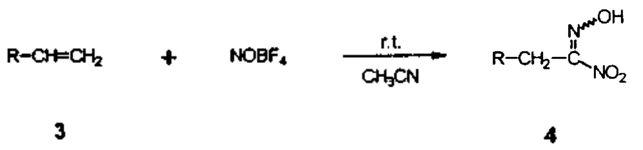
Entry	$NOBF_4$ (equiv)	yield† %	mp (dec.) ℃
4a	2.65	82	142-144 ($CHCl_3$)
4b	2.07	70	143-145 (EtOH)
4c	2.80	80	164-166 (acetone)
4d	2.29	91	102-104 (CCl_4)
4e	4.57	72‡	liquid
4f	2.73	90	123-124 ($CHCl_3$)

†Isolated yield. ‡(2,6-Pyridyl)-*bis*-acetonitrolic acid was isolated in 0.3% yield. All products **4** were fully characterized by their spectroscopic (IR, NMR) and analytical data.



i, NaOD, D_2O, 1 day ii, $NaBH_4$, MeOH, 12 h iii, $SOCl_2$, CH_2Cl_2, 0 °C, 2 h iv, t-BuOK, THF, Δ, 11 h v, $NOBF_4$, CH_3CN, 3 h

Scheme 1.



a, R = 2-pyridyl
b, R = 3-pyridyl
c, R = 4-pyridyl
d, R = 6-methyl-2-pyridyl
e, R = 6-vinyl-2-pyridyl
f, R = 2-quinolyl

hyde oximes,[6] nitronic acids[6b,6c,7] or nitronate salts[6c,8] with dinitrogen tetraoxide. Besides, acetonitrolic acid was synthesized in less than 6% yield by reaction of nitroethane with $NaNO_2$ in 20% aqueous NaOH at 0 ℃.[6e] To the best of our knowledge, no nitrolic acid has been prepared from the reactions of olefinic compounds.

In order to get the information about the origin of a methylene hydrogen of the compounds **4**, 2-(3-pyridyl)ethene-1,1-d_2 (**8**) was synthesized and treated with $NOBF_4$ under the same condition as in the reaction of **3b**. (Scheme 1).[9] ^{1}H NMR signals of nitrolic acid **9** showed *ca*. 1 : 4 ratio of intensities of methylene to aromatic protons. This result indicates that one of methylene hydrogens of **4** is originated from the terminal olefinic hydrogens. In the meantime, an intermediacy of (2′-nitroethenyl)pyridines for the formation of **4** can be ruled out in view of the inertness of 2-methyl-6-(2′-nitroethenyl)pyridine (**10**)[10] to $NOBF_4$ in acetonitrile at room temperature. Further study on the mechanism of the formation of **4** from **3** is in progress.

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5. Representative procedures for **4**: To a solution of $NOBF_4$ (605 mg, 5.18 mmol) in dried CH_3CN (20 mL) was added dropwise a solution of **3a** (205 mg, 1.95 mmol) in dried CH_3CN (30 mL) over a period of 10 min at room temperature. The solution was stirred for 3 h during which time the color of the solution turned from deep yellow to bright yellow. The reaction mixture was quenched with water (40 mL), followed by addition of aqueous $NaHCO_3$ to become pH 8-9. Removal of CH_3CN *in vacuo*, followed by extraction of the aqueous solution with EtOAc. The combined extract was washed with water and dried over $MgSO_4$. Evaporation of EtOAc, followed by chromatography (sillica gel, 70-230 mesh) using a mixture of hexane-EtOAc (1 : 1) gave **4a** (290 mg, 1.60 mmol, 82%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 6.05 (s, 2H, CH_2), 7.56-8.76 (m, 4H, ArH), 12.70 (s, 1H, N-OH); IR (KBr) 3420-2200, 1560, 1550, 1480, 1430, 1380, 1350, 1290, 1050, and 1010 cm^{-1}; *Anal.* Calcd for $C_7H_7N_3O_3$: C, 46.41; H, 3.89; N, 23.19. Found: C, 46.42; H, 4.06; N, 23.26.
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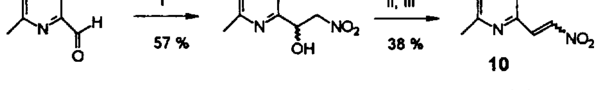
9. Deuterium incorporation: **5** (95%); **6** (91%); **7** (91%); **8** (96%); **9** (96% for methylene hydrogens; 63% for oxime hydrogen).
10. Compound **10** was synthesized according to Scheme 2:



i, CH_3NO_2, NaOH, EtOH, r.t., 3 h ii, $SOCl_2$, CH_2Cl_2, 0 °C, 2 h iii, Et_3N, 2 h

Scheme 2.