

Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Esters with NaGaH₄ in Tetrahydrofuran at 0 °C^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 |
| <i>tert</i> -butyl caproate | 3 | 81 |
| ethyl cyclohexanoate | 3 | 87 |
| ethyl benzoate | 6 | 67 |
| isopropyl benzoate | 6 | 75 |
| <i>tert</i> -butyl benzoate | 6 | 75 |
| cyclohexyl benzoate | 6 | 76 |
| ethyl cinnamate | 6 | 68 |
| isopropyl cinnamate | 6 | 63 |
| <i>tert</i> -butyl cinnamate | 6 | 76 |

^aTreated with 0.5 equiv of reagent for aliphatic and aromatic esters. ^bYields were estimated by GLC. ^cYield 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 °C instead of the very low temperature (-70 °C) or elevated temperature (65 °C). 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.

References

- Zakharkin, L. I.; Khorlina, I. M. *Tetrahedron Lett.* **1962**, 619.
- Zakharkin, L. I.; Khorlina, I. K. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 465.
- Weissman, P. M.; Brown, H. C. *J. Org. Chem.* **1966**, 31, 282.
- Muraki, M.; Mukaiyama, T. *Chemistry Lett.* **1975**, 215.
- Yoon, N. M.; Jeong, K. H.; An, D. K. *Bull. Korean Chem. Soc.* **1991**, 12, 7.
- Cha, J. S. *Bull. Korean Chem. Soc.* **1992**, 13, 670.
- Dalts, J. A.; Nutt, W. R. *Inorganic Syntheses* **1977**, 17, 48.

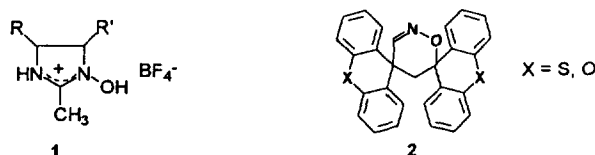
Reactions of Vinylpyridines and Vinylquinolines with Nitrosonium Tetrafluoroborate: One Step Synthesis of Nitrolic Acids

Raekyu Chang and Kyongtae Kim*

Department of Chemistry, Seoul National University,
Seoul 151-742, Korea

Received March 13, 1995

The reactions of nitrosonium tetrafluoroborate (NOBF₄) 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 olefins 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.



Although NOBF₄ has been often utilized as either a single electron transfer oxidant³ or a weak electrophile,⁴ no systematic study on the reactions of NOBF₄ with structurally and/or electronically different olefins has been reported.

We have chosen 2-vinylpyridine (**3a**) for the reaction with NOBF₄ based on two reasons: First compound **3a** is structurally similar to styrene previously studied¹ 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 NOBF₄ toward **3a** compared with styrene would be expected.

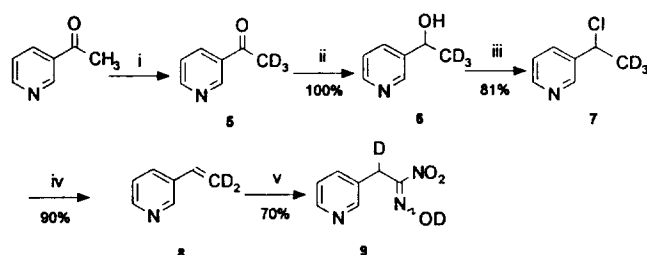
Surprisingly, the reaction of NOBF₄ with **3a** in acetonitrile at room temperature gave 2-pyridylacetone nitrolic acid (**4a**) as a major product. 3-pyridyl- (**4b**) and 4-pyridylacetone nitrolic acid (**4c**) were also obtained from the reactions with 3- (**3b**) and 4-vinylpyridines (**3c**), respectively 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-quinolylacetone nitrolic 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-

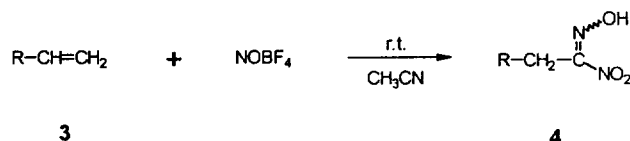
Table 1. Synthesis of acetonitrolic acid derivatives (**4**)⁵

| Entry | NOBF ₄ (equiv) | yield [†] % | mp (dec.) °C |
|-----------|------------------------------|-------------------------|------------------------------|
| 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, D₂O, 1 day ii, NaBH₄, MeOH, 12 h iii, SOCl₂, CH₂Cl₂, 0 °C, 2 h iv, t-BuOK, THF, Δ, 11 h v, NOBF₄, CH₃CN, 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

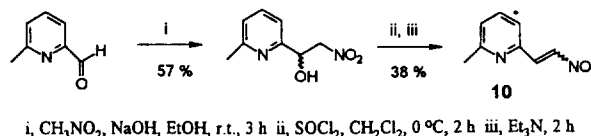
hyde oximes,⁶ nitronic acids^{6b,6c,7} or nitronate salts^{6c,8} with dinitrogen tetroxide. Besides, acetonitrolic acid was synthesized in less than 6% yield by reaction of nitroethane with NaNO₂ in 20% aqueous NaOH at 0 °C.^{6e} To the best of our knowledge, no nitrolic acid has been prepared from the 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-d₂ (**8**) was synthesized and treated with NOBF₄ under the same condition as in the reaction of **3b**. (Scheme 1).⁹ ¹H 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 NOBF₄ in acetonitrile at room temperature. Further study on the mechanism of the formation of **4** from **3** is in progress.

Acknowledgment. This work has been supported by Korea Research Foundation (Non Directed Research Fund), 1993.

References and Notes

- Scheinbaum, M. L.; Dines, M. B. *Tetrahedron Lett.* **1971**, 2205.
- Lee, G. H.; Lee, J. M.; Jeong, W. B.; Kim, K. *Tetrahedron Lett.* **1988**, 29, 4437.
- (a) Bandilish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, 42, 561. (b) Conelly, N. G.; Demidowicz, G.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1975**, 2335. (c) Muser, W. L.; Walford, T. L. *J. Am. Chem. Soc.* **1976**, 98, 3035. (d) Kim, E. K.; Kochi, J. K. *J. Org. Chem.* **1989**, 54, 1692.
- (a) Nielsen, A. T. In *The Chemistry of Nitro and Nitroso Groups*; Part 1, Feuer, H., Ed., John Wiley & Sons, New York, 1969, Chap 7, p 394-398. (b) Klamann, D.; Fligge, M.; Wegerstahl, P.; Kratzer, J. *Chem. Ber.* **1966**, 99, 556. (c) Challis, B. C.; Lawson, A. J. *J. Chem. Soc., Perkin Trans. II*, **1973**, 918.
- Representative procedures for **4**: To a solution of NOBF₄ (605 mg, 5.18 mmol) in dried CH₃CN (20 mL) was added dropwise a solution of **3a** (205 mg, 1.95 mmol) in dried CH₃CN (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 NaHCO₃ to become pH 8-9. Removal of CH₃CN *in vacuo*, followed by extraction of the aqueous solution with EtOAc. The combined extract was washed with water and dried over MgSO₄. Evaporation of EtOAc, followed by chromatography (silica gel, 70-230 mesh) using a mixture of hexane-EtOAc (1 : 1) gave **4a** (290 mg, 1.60 mmol, 82%); ¹H NMR (CDCl₃, 80 MHz) δ 6.05 (s, 2H, CH₂), 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 C₇H₇N₃O₃: C, 46.41; H, 3.89; N, 23.19. Found: C, 46.42; H, 4.06; N, 23.26.
- (a) Bamberger, E.; Seligman, R. *Ber. Dtsch. Chem. Ges.* **1902**, 35, 3884. (b) Khmel'nitskiik, L. I.; Novikov, S. S.; Lebedev, O. V. *Izv. Akad. Nauk., SSSR, Ser. Khim.* **1961**, 477 (*Chem. Abstr.* **1961**, 55, 23389). (c) Khmel'nitskiik, L. I.; Novikov, S. S.; Lebedev, O. V. *Zh. Obshch. Khim.* **1958**, 28, 2303, (*Chem. Abstr.* **1959**, 53, 3111). (d) Khmel'nitskiik, L. I.; Novikov, S. S.; Lebedev, O. V. *Izv. Akad. Nauk., SSSR, Ser. Khim.* **1960**, 1783 (*Chem. Abstr.* **1961**, 55, 1983). (e) Ehan, C.; Clery, M.; Hegarty, A. F.; Welch, A. J. *J. Chem. Soc., Perkin Trans. II*, **1991**, 249.
- Tirov, A. I.; Siminov, V. V. *Dokl. Akad. Nauk. SSSR*, **1952**, 83, 243 (*Chem. Abstr.* **1953**, 47, 4298).
- Novikov, S. S.; Kebedev, O. V.; Khmel'nitskiik, L. I.; Egorov, Yu. P. *Zh. Obshch. Khim.* **1958**, 28, 2305 (*Chem. Abstr.* **1959**, 53, 4112).
- Deuterium incorporation: **5** (95%); **6** (91%); **7** (91%); **8** (96%); **9** (96% for methylene hydrogens; 63% for oxime hydrogen).
- Compound **10** was synthesized according to Scheme 2:

**Scheme 2.**