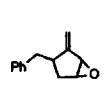
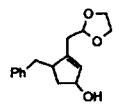
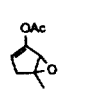
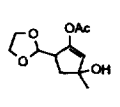
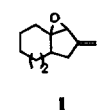
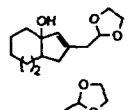
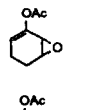
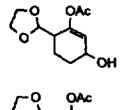
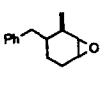
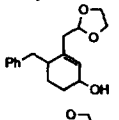
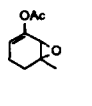
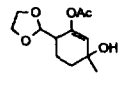
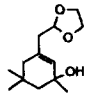
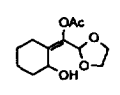
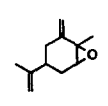
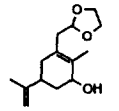
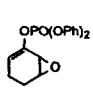
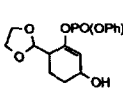
Table 3. Alkylation of *endo* Vinyl Epoxides with 1,3-Dioxolane

vinyl epoxides	products	yields,[a] %	vinyl epoxides	products	yields,[a] %
		75 (71)			74 (68)
		54			71 (64)
		85 (76)			75
		73 (66)			41
		63 (60)			46 (43)

[a]The numbers in the parentheses indicate the isolated yield using 5 equiv of 1,3-dioxolane in refluxing benzene.

cal reactions of endo vinyl epoxides with alkyl iodides and 1,3-dioxolane proceed by mild photochemical generation of tributuyltin radical and are very useful for introducing alkyl groups and a formyl group to a variety of structurally different vinyl epoxides.

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Conversion of Carboxylic Esters to Aldehydes by Sodium Gallium Hydride

Jung Hoon Choi* and Young Joo Oh

Department of Chemistry, Hanyang University, Seoul 133-791, Korea

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The synthesis of aldehydes from carboxylic esters is one of the important reaction in organic synthesis. Many reducing agents have been tested, however, only a few reagents have achieved for the transformation of carboxylic esters to the corresponding aldehydes. The representative metal hydrides for such purpose are diisobutylaluminum hydride (DIBAH),[1] sodium diisobutylaluminohydride,[2] lithium tri-*tert*-butoxy-aluminum hydride (LTBA),[3] and bis(dialkylamino)aluminum hydrides.[4] Of these reagents, LTBA reduces aliphatic phenyl esters to corresponding aldehydes in yields of approximately 70%, but it can not reduce aromatic esters. Although diaminoaluminum hydride is effective for both aliphatic and aromatic esters and gives 50-80% yields of aldehydes, the reaction requires the longer reaction time (6-12 h), usually at elevated temperature (65 ℃). And DIBAH reduces aliphatic and aromatic esters to corresponding aldehydes in yields of aldehydes (48-88%) at very low temperature (−70 ℃). Recently, sodium diethylpiperidinohydroaluminate[5] and lithium tris(diethylamino)aluminum hydride[6] are reported to be good reagents for the partial reduction of carboxylic esters to the corresponding aldehydes.

In 1977, Dilts and Nutt[7] first reported the synthesis of sodium gallium hydride. The sodium gallium hydride is prepared from lithium gallium hydride.

$$LiGaH_4 + NaH \xrightarrow{THF} NaGaH_4 + LiH\downarrow$$

In the course of exploring the reducing properties of sodium gallium hydride, we observed that ethyl caproate and ethyl benzoate consumed one hydride rapidly for reduction, but the further reaction proceeded slowly. This results suggested the possibility of aldehyde synthesis from carboxylic ester using this reagent.

As shown in Table 1, the reagent reduced aliphatic carboxylic esters to the corresponding aldehydes in yields of 75-87%. The reduction of aromatic esters by this reagent pro-

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

Raekyu Chang and Kyongtae Kim*

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

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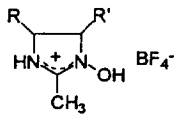
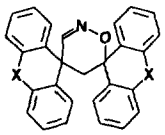
The reactions of nitrosonium tetrafluoroborate ($NOBF_4$) with olefins in acetonitrile gave a different type of products depending on the structure of the olefin. For example, the reactions with primary or secondary olefins, *i.e.*, propene, *cis*- or *trans*-2-butene, and styrene, etc., gave 2-alkyl-*N*-hydroxyimidazolium 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



X = S, O

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-