methylsilyl protected cyanohydrin of crotonaldehyde. After a period of 10 min, 0.15 mL (1.43 mmol) of cyclohexanone is added followed by additional stirring for 10 min and then quenching the reaction with 0.20 mL of glacial acetic acid. The mixture is partitioned between ether and water, extracted three times with ether, dried over $MgSO_4$, and concentrated in vacuo. Chromatography on silica gel (20% Et_2O/hex) followed by Kugelrohr distillation [bp 100 °C (0.05 torr)] affords 220 mg (0.9 mmol, 64%) of α-trimethylsilyloxy enone **12b.**

The α-trimethylsilyloxy enone (123 mg, 0.51 mmol) and 116 mg of TsOH (0.61 mmol) are dissolved in 8 mL of toluene and refluxed through 4 Å molecular sieves for 4 h. Standard workup followed by chromatography on silica gel (20% Et_2O/hexane) and Kugelrohr distillation [bp 130 °C (10 torr)] affords 34 mg (48%) of the cyclopentenone.

Further development of this method of three-carbon annelation and its application to the total synthesis of a wide variety of natural products is under current investigation in our laboratories.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this work.

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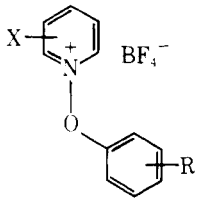
Richard M. Jacobson,* George P. Lahm
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received September 25, 1978

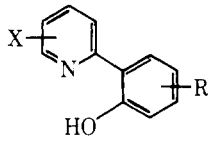
Azide-Catalyzed Rearrangement of *N*-(Aryloxy)pyridinium Salts. Facile Synthesis of 3-(*o*-Hydroxyphenyl)pyridines

Summary: *N*-(Aryloxy)pyridinium tetrafluoroborates react with azide (and other) ions in solution to give good yields of 3-(*o*-hydroxyphenyl)pyridines under mild conditions; the rearrangements may be rationalized by invoking either a 3,5 shift or a homolysis and radical recombination.

Sir: *N*-(Aryloxy)pyridinium tetrafluoroborates (**1**) are proving to be versatile compounds. They have been used to generate aryloxenium ions,[1] and undergo base-catalyzed rearrangement to give 2-(*o*-hydroxyphenyl)pyridines (**2**).[2] *N*-(Mesityloxy)- (**1**: R = 2,4,6-Me_3) and *N*-(duryloxy)pyridinium tetrafluoroborate (**1**: R = 2,3,5,6-Me_4) generated in situ undergo base-catalyzed rearrangement to *N*-(hydroxybenzyl)pyridinium salts, probably via quinone methide intermediates.[3] We now report a remarkably facile and convenient rearrangement of **1** to give good yields of 3-(*o*-hydroxyphenyl)pyridines (**3**), so that, depending on the conditions used, **1** can be converted into the 2- or the 3-*o*-hydroxyarylated pyridine derivative. All other rearrangements to C-3 or C-5 reported by us previously have involved a migrating group bound to both oxygen and C-2.



1



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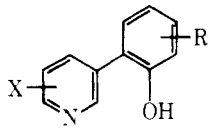

3

Attack by a nucleophile on **1** might be anticipated to proceed by one of at least three pathways.[4] Reaction could take place at C-1 of the activated aryl nucleus leading to displacement of the pyridine 1-oxide; alternatively, attack could take place at C-2 (and possibly, but to a lesser extent, at C-4) of the pyridine ring to give a dihydro-1-(aryloxy)pyridine derivative.[5] In the latter case, at least two options are available: (i) loss of ArOH with formation of the 2-substituted pyridine,[5] or (ii) rearrangement to give a 3-substituted pyridine. Indeed, it was suggested[3] that a 1-(aryloxy)-2-chloro-1,2-dihydropyridine derivative might undergo a 3,5-shift to give a 3-(*o*-hydroxyaryl)pyridine.

Reaction of *N*-(*p*-nitrophenoxy)pyridinium tetrafluoroborate (**1**: R = 4-NO_2; X = H) with sodium azide in dry acetonitrile at room temperature gave a highly insoluble, initially amorphous material (M^+· 216) melting over a wide range. This could be recrystallized from DMF to give pale yellow crystals, mp 294–298 °C dec (70.3%), of 3-(2-hydroxy-4-nitrophenyl)-pyridine (**3**: R = 4-NO_2; X = H).[6] Acetylation of the crude product gave the pure *O*-acetate of **3** (75%), mp 133–134 °C (ethanol–hexane). The structure of the rearrangement product was confirmed by its authentic synthesis by nitration of 3-(2-hydroxyphenyl)pyridine.[7] The high melting point (and its lack of sharpness) as well as the relative insolubility of this product is to be contrasted with the properties of its *O*-acetate and of its hydrogen tetrafluoroborate salt [mp 205 °C (from ether–acetone)], and suggests that **3** (R = 4-NO_2) exists mostly in the zwitterionic form. Blocking either the phenolic oxygen or the pyridine nitrogen atoms then prevents formation of the zwitterion.

Other inorganic ions were also effective in achieving the transformation **1** → **3** (X = H; R = 4-NO_2). Thus cyanide, iodide, carbonate (needed 48 h for maximum yield), thiosulfate, and acetate gave **3** (crude yields reported) in 89, 68, 90, 42, and 47% yields, respectively. On the other hand, no rearrangement products could be obtained with nitrate, chloride, bromide, thiocyanate, sulfite, chlorate, perchlorate, nitrite, dihydrogen phosphate, or sulfide ions. The reaction with azide ion can be carried out at room temperature or in boiling acetonitrile; aqueous acetonitrile may also be used as can DMF. The reaction with azide also takes place in water but the yields are lower.

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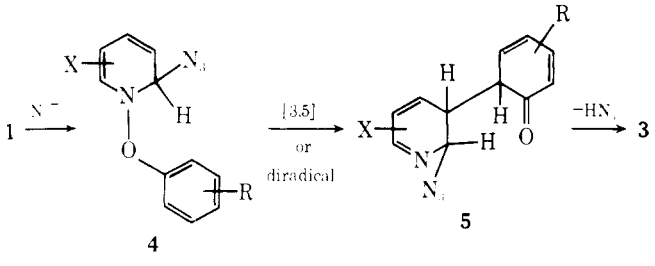
Table I. Rearrangement of 1 to 3 with Azide Ion in Acetonitrile

R	X	mp (3), °C	% yield
4-NO_2	H	294–298 dec	70.3
4-CN	H[a]	283–285 dec	70
4-NO_2	5-Br	192–193	50.4
4-NO_2	5-Me	>360	60
4-NO_2	4-Ph[a]	274–275	31
4-NO_2	4-OMe[a]	194–195	59

[a] Reaction carried out in boiling acetonitrile

The rearrangement appears to be quite general, at least for *N*-(aryloxy)pyridinium salts bearing electron-withdrawing substituents in the benzene ring. For example, **1** (X = 3-Br; R = 4-NO_2) and azide ion gave **3** (X = 5-Br; R = 4-NO_2) (50.4%): mp 192–193 °C; *O*-acetate, mp 128–129 °C; NMR ($CDCl_3$) δ 8.05 (d, 1, $J_{4,6}$ = 3 Hz, H_6), 7.97 (d, 1, J = 2 Hz, H_2), 7.69 (m, 2, H ortho to NO_2), 7.30 (m, 1, H_4), 6.78 (d, 1, J = 9 Hz, H ortho to AcO), 1.92 (s, 3, CH_3). These and other rearrangements are summarized in Table I.

Assuming that the nucleophile adds mainly[8,9] at C-2 to give (**4**),[9] this could undergo a [3,5] sigmatropic shift to yield the 2,3-dihydro derivative **5**, which would eliminate HN_3 and aromatize to **3**. Alternatively, **4** could undergo homolysis to a tight radical pair (to account for the good yields of products) followed by radical recombination to give **5**. In support of the



intervention of *some* radical pathway is the isolation of pyridine (6.7%) (as the picrate) and *p*-nitrophenol (1.9%) from the reaction of **1** (X = H; R = 4-NO_2) with azide in dry CH_3CN. It is conceivable that the radical and concerted pathways are in competition with each other. Studies are under way to distinguish between these and other possible mechanisms.

Acknowledgements. The work at Clemson University was supported by an NIH grant (GM 25242-01), that in Częstochowa by grant no. 0IP75-02094 from the NSF Excess Foreign Currency Program.

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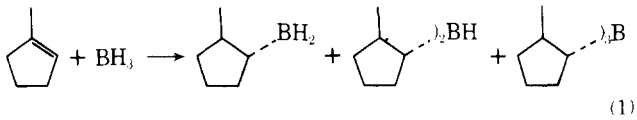
Rudolph A. Abramovitch,* Adrian L. Miller
Department of Chemistry and Geology
Clemson University, Clemson, South Carolina 29631

Teresa A. Radzikowska, Piotr Tomasik*
Pedagogical University, Zawatzkiego St.,
42-201 Częstochowa, Poland
Received October 16, 1978

An Improved Synthesis of Monoalkylborane Derivatives via Bis(Thexylborane)-*N,N,N',N'*-tetramethylethylenediamine

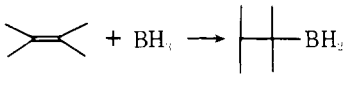
Summary: Bis(thexylborane)-*N,N,N',N'*-tetramethylethylenediamine (2ThBH$_2$·TMED) reacts with olefin with the facile displacement of tetramethylethylene and the formation of the corresponding bis(monoalkylborane)–tetramethylethylenediamine adducts in nearly quantitative yield. Treatment of the adducts with boron trifluoride etherate quantitatively precipitates TMED·2BF_3 and liberates free monoalkylborane providing a convenient general synthesis for such monoalkylboranes.

Sir: Hydroboration of olefins with THF·BH_3[1] or Me_2S·BH_3[1] generally proceeds rapidly past the monoalkylborane stage to the dialkylborane or trialkylborane stage.[2,3] Consequently, it is generally not possible to synthesize monoalkylboranes by the direct reaction of olefins with borane (eq 1). Only in the

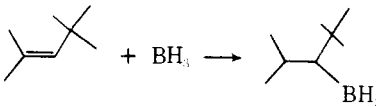


(1)

case of certain highly hindered olefins, such as tetramethylethylene (TME) or 2,4,4-trimethyl-2-pentene (diisobutylene-2 ≡ DIB-2), is it possible to control the hydroboration so as to achieve the synthesis of the monoalkylborane (RBH$_2$).[4,5] In this way, thexylborane (ThBH$_2$)[6] and diisobutylene-2-borane (DIBBH$_2$)[7] are readily prepared (eqs 2, 3).



(2)



(3)

ThBH$_2$·NEt$_3$ reacts with olefins with displacement of TME and formation of the corresponding adduct, RBH$_2$·NEt$_3$.[8] Treatment with THF·BH_3[9] or Et_2O·BF_3[10] produces the corresponding free monoalkylborane. Unfortunately, the byproducts, Et_3N·BH_3 and Et_3N·BF_3, are highly soluble and cannot easily be separated from the desired product. A further difficulty is the liquid nature of the RBH$_2$·NEt$_3$ adducts, rendering difficult their purification.

We recently observed that both monoisopinocampheylborane and BF_3 form crystalline bisadducts with TMED.[11] Accordingly, we undertook to explore the displacement reaction with TMED. Indeed, we observed that in refluxing ethyl ether TME is rapidly displaced from a mixture of 2ThBH$_2$·TMED and selected olefins, providing the crystalline bisadducts 2RBH$_2$·TMED in excellent yields. Moreover, BF_3 rapidly and quantitatively precipitates TMED·2BF_3 from the

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