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IRON-MEDIATED SYNTHESIS OF t-BUTYL-N-(ARLYOXY)CARBAMATES

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The anion of t-butyl-N-hydroxycarbamate displaces halogens from (η^6-haloarene)(η^5-cyclopentadienyliron) salts. The resulting complexes are demetallated by photolysis in sunlight to generate t-butyl-N-(aryloxy)carbamates.

Recently, Baldoli and coworkers described the synthesis of t-butyl-N-(aryloxy)carbamates (3) utilizing a nucleophilic attack of deprotonated t-butyl-N-hydroxycarbamate on (η^6-chloroarene)(tricarbonylchromium) species 1 (Scheme I, M=Cr(CO)$_3$).[1] The products (2) were demetallated, and the free (aryloxy)carbamates were hydrolyzed to O-arylhydroxylamines, which are useful precursors to a number of systems, including benzofurans.[2] We set out to determine if the same conversion could be performed with (η^6-chloroarene)(η^5-cyclopentadienyliron) salts 1 (Scheme, M=$^+$Fe(η^5-C$_5$H$_5$)) as

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a, R=H
b, R=o-CH$_3$
c, R=p-CH$_3$
d, R=p-OCH$_3$
e, R=p-Cl
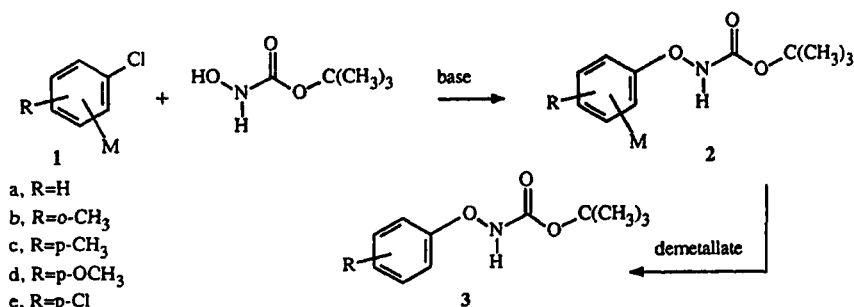
SCHEME

Table 1. Effect of Conditions on the Substitution Reaction of 1a

equivalents of carbamate	base	solvent	temperature	sm:product	2(%)
1.0	KOH	Me$_2$CO	-78°C to rt, 4h	55:45	32
1.0	KOH	Me$_2$CO	-78°C, 4h	70:30	13
1.0	KOH	Me$_2$CO	-42°C to rt, 4h	60:40	38
1.0	NaH	THF	rt, 2h	60:40	27
1.1	NaH	THF	rt, overnight	0:100	41
2.0	NaH	THF	rt, overnight	0:100	85

electrophiles. There were a number of reasons for undertaking this study: The requisite starting materials are much less expensive to make than the organochromium compounds,[3] and iron wastes are less toxic, and easier to dispose of, than chromium wastes.[4] Furthermore, the "$^+$Fe(η^5-C$_5$H$_5$)"[5] moiety is more electronegative than the "Cr(CO)$_3$" fragment, which should make the iron-complexed arene more reactive in nucleophilic substitution reactions.[5]

A variety of reaction conditions were tried on the chlorobenzene salt before a satisfactory system was found. As shown in Table 1, best results were

Table 2. Substitution Reactions of Iron Salt 1[a]

Iron Salt	2(%)
1a	85
1b	82
1c	88
1d	85
1e	[b]

[a]Reaction conditions described in Experimental
Section. [b]Clean product could not be isolated.

obtained with sodium hydride as base, utilizing two equivalents of the
carbamate, stirred overnight at room temperature in THF solvent. It was
necessary to use an excess of the N-hydroxycarbamate in order to obtain a good
yield of product. Use of a stoichiometric amount of the carbamate not only led
to lower yields, but it is interesting to note that the product was the only isolable
organoiron compound, all starting material having being consumed. Apparently,
some type of decomposition is a competing process.

As can be seen from Table 2, a variety of complexed haloarenes undergo
this substitution in good yield. Only in the case of p-dichlorobenzene did it
prove impossible to isolate clean product. In that case, nmr spectra were
inconclusive, but seemed to indicate a mixture of mono- and di-substituted
products.

As expected, use of the fluorobenzene complex led to increased yield.[6]
Treating (η^6-fluorobenzene)(η^5-cyclopentadienyliron) hexafluorophosphate
with 1.1 equivalents of carbamate anion, utilizing NaH in THF at room
temperature overnight, the yield of product increased to 72% from the 41% yield
obtained under identical conditions with the chlorobenzene salt.

Table 3. Photolytic Demetallation of 2[a]

Iron salt	3(%)
2a	58
2b	76
2c	69
2d	62

[a]Reaction conditions described in
Experimental Section.

Several methods exist for the removal of the iron fragment from the arene. Attempts to isolate the free arenes by pyrolytic sublimation[7] led to only black tars. Photolysis[8] yielded much better results. Placing the iron salt in acetonitrile solution in sunlight gave moderate yields of the free aryloxycarbamates 3, as summarized in Table 3. These photolysis reactions were very clean, as the aryloxycarbamates were the only organic-soluble products in the reaction mixture.

The free t-butyl-N-(aryloxy)carbamates may then be converted to O -arylhydroxylamines by hydrolysis. This method is, then, shown to be an effective approach to O -arylhydroxylamines, at a much lower cost and hazard level than the organochromium route.

Experimental Section

General Comments.   All reactions were carried out under an atmosphere of purified nitrogen. Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Acetonitrile, sodium hydride

and t-butyl-N-hydroxycarbamate were purchased from Aldrich and used as received. The (η^6-haloarene)(η^5-cyclopentadienyliron) salts were made by the standard method.[9] ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as an internal reference. IR spectra were recorded on a Perkin-Elmer 1310 Infrared Spectrophotometer. Melting points were obtained on a Laboratory Devices Mel-Temp apparatus.

Substitution Reaction of (η^6-chloroarene)(η^5-cyclopentadienyliron) hexafluorophosphates. General Procedure. A 25 mL round-bottomed flask was charged with 5 mL of THF, 133 mg (1.0 mmol) of t-butyl-N-hydroxycarbamate and a magnetic stirring bar. The system was placed under balloon pressure of nitrogen, then sodium hydride (30 mg of an 80% suspension in mineral oil, 1.0 mmol) was added. After 10 min of stirring, 0.5 mmol of the iron salt was added, the system was wrapped in foil to exclude light, and allowed to stir at room temperature overnight. At the end of the reaction period, a solution of 60 mg of ammonium hexafluorophosphate in 20 mL of water was added, and the solution was extracted with 2x20 mL of methylene chloride. The combined organic layers were dried ($MgSO_4$), filtered and the solvent removed in vacuo. The resultant semi-solid was filtered through a short column (pipet) of neutral alumina, utilizing acetone as the eluant. The solvent was removed in vacuo, and the product purified by precipitation from acetone-ether.

2a. Treatment of 190 mg (0.5 mmol) of (η^6-chlorobenzene)(η^5-cyclopentadienyliron) hexafluorophosphate as above generated 208 mg (85%) of 2a as a yellow solid, mp 140°C (dec). ^{1}H NMR [60 MHz, $(CD_3)_2CO$]: δ 6.2-

6.6 (m, 5H, C_6H_5), 5.15 (s, 5H, C_5H_5), 1.55 (s, 9H, $C(CH_3)_3$); IR (CH_3CN) 3400-3700, 3050-3250, 1750 cm^{-1}.

2b. Treatment of 196 mg (0.5 mmol) of (η^6-o-chlorotoluene)(η^5-cyclopentadienyliron) hexafluorphosphate as above generated 216 mg (88%) of **2b** as a yellow solid, mp 118°C (dec). ^{1}H NMR [60 MHz, $(CD_3)_2CO$]: δ 6.1-6.7 (m, 4H, C_6H_4), 5.1 (s, 5H, C_5H_5), 2.55 (s, 3H, $ArCH_3$), 1.55 (s, 9H, $C(CH_3)_3$); IR (CH_3CN) 3350-3600, 3000-3150, 1730 cm^{-1}.

2c. Treatment of 196 mg (0.5 mmol) of (η^6-p-chlorotoluene)(η^5-cyclopentadienyliron) hexafluorophosphate as above generated 200 mg (82%) of **2c** as a yellow solid, mp 124°C (dec). ^{1}H NMR [60 MHz, $(CD_3)_2CO$]: δ 6.4 (d, J = 9 Hz, 2H, ArH), 6.2 (d, J = 9 Hz, 2H, ArH), 5.1 (s, 5H, C_5H_5), 2.45 (s, 3H, $ArCH_3$), 1.5 (s, 9H, $C(CH_3)_3$); IR (CH_3CN) 3380-3720, 3030-3220, 1740 cm^{-1}.

2d. Treatment of 204 mg (0.5 mmol) of (η^6-p-chloroanisole)(η^5-cyclopentadienyliron) hexafluorophosphate as above generated 215 mg (85%) of **2d** as a yellow solid, mp 122-128°C. ^{1}H NMR [60 MHz, $(CD_3)_2CO$] δ 6.45 (d, J = 9 Hz, 2H, ArH), 6.25 (d, J = 9Hz, 2H, ArH), 5.2 (s, 5H, C_5H_5), 3.95 (s, 3H, OCH_3), 1.5 (s, 9H, $C(CH_3)_3$); IR (CH_3CN) 3340-3660, 3050-3200, 1760 cm^{-1}.

Substitution Reaction of (η^6-fluorobenzene)(η^5-cyclopentadienyliron) hexafluorophosphate. A 25 mL round-bottomed flask was charged with 5 mL of THF, 73 mg (0.55 mmol) of t-butyl-N-hydroxycarbamate and a magnetic stirring bar. The system was placed under balloon pressure of nitrogen, then sodium hydride (30 mg of an 80% suspension

in mineral oil, 1.0 mmol) was added. After 10 min of stirring, 181 mg (0.5 mmol) of the iron salt was added, the system was wrapped in foil to exclude light, and allowed to stir at room temperature overnight. Workup as above yielded 172 mg (72%) of **2a**, identical to the material obtained with the chlorobenzene salt.

Photolytic Demetallation. General Procedure. The complexed t-butyl-N-(aryloxy)carbamates were dissolved in 10 mL of acetonitrile in a 50 mL round-bottomed flask, and the system was placed under balloon pressure of nitrogen. The flask was placed in sunlight for 2-3 hours, then the brown solid was filtered off, and the solvent was removed in vacuo. The resultant product was purified by passage through a short column (pipet) of neutral alumina.

3a. Treatment of 283 mg (0.6 mmol) of **2a** as described above generated 68 mg (58%) of **3a** as an off-white solid, identical with the material reported in the literature.[1]

3b. Treatment of 129 mg (0.26 mmol) of **2b** as described above generated 40 mg (69%) of **3b** as an oil, identical with the material reported in the literature.[1]

3c. Treatment of 93 mg (0.19 mmol) of **2c** as described above generated 32 mg (76%) of **3c** as a thin film. ^{1}H NMR [60 MHz, CDCl$_3$]: δ 6.9-7.2 (m, 4H, C$_6$H$_4$), 2.25 (s, 3H, ArCH$_3$), 1.5 (s, 9H, C(CH$_3$)$_3$).

3d. Treatment of 45 mg (0.09 mmol) of **2d** as described above generated 13 mg (62%) of **3d** as a thin film. ^{1}H NMR [60 MHz, CDCl$_3$]: δ 6.7-7.2(m, 4H, C$_6$H$_4$), 3.7 (s, 3H, OCH$_3$), 1.4 (s, 9H, C(CH$_3$)$_3$).

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