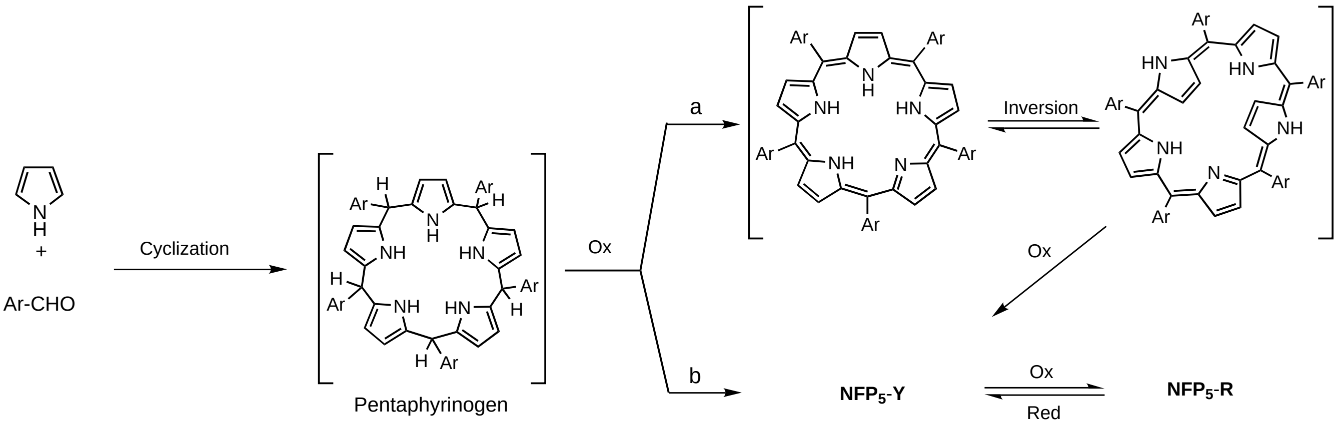

Scheme 2. A possible reaction mechanism for the formation of **NFP$_5$**.

for 2 h under nitrogen. After adding DDQ (2.27 g, 10 mmol), the solution was stirred for 10 h, then passed through a short alumina column to remove the tar. The reaction mixture was then separated by column chromatography on silica gel with CH_2Cl_2:*n*-hexane (1:4). The red solution of **1-R** was eluted after the purple fraction of *meso*-pentafluorophenylhexaphyrin. The solution of **1-R** was evaporated, and the residue recrystallized from *n*-hexane to give pure **1-R** (146 mg, 15%).

1-Y: $NaBH_4$ (22.7 mg, 0.6 mmol, 15 equiv) was added to a solution of **1-R** (50 mg, 0.04 mmol) in CH_3OH (10 mL) and the solution was stirred for 10 min under nitrogen. After removing the solvent, the residues were dissolved in CH_2Cl_2, and filtered through a short alumina column. After evaporation, the residue was recrystallized from *n*-hexane to give **1-Y** (50 mg, 100%).

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[6] H. Furuta, T. Ishizuka, A. Osuka, T. Ogawa, *J. Am. Chem. Soc.* **1999**, *121*, 2945–2946; H. Furuta, T. Ishizuka, A. Osuka, T. Ogawa, *J. Am. Chem. Soc.* **2000**, *122*, 5748–5757.

[7] A variety of higher homologues, such as octaphyrins, nonaphyrins, decaphyrins, undecaphyrins, and dodecaphyrins, are isolated from the reaction mixture: J.-Y. Shin, H. Furuta, A. Osuka, unpublished results.

[8] Spectral data and the X-ray structure of **2-Y** are shown in the Supporting Information.

[9] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147880. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[10] *The Porphyrin Handbook*, *Vol. 10* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **1999**, pp. 1–254.

[11] The absorption spectral changes of the redox reaction between **1-Y** and **1-R** are shown in the Supporting Information.

[12] Supporting this facile interconversion, the two-electron redox processes between **1-Y** and **1-R** were recorded at low potential, −0.447 V and +0.067 V (versus the ferrocene/ferrocenium couple (F_c/F_c^+)) by cyclic voltammetry.

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Iron-Catalyzed Regio- and Stereoselective Carbolithiation of Alkynes[**]

Makoto Hojo, Yoshio Murakami, Hidenori Aihara, Rie Sakuragi, Yu Baba, and Akira Hosomi*

Organolithium compounds are one of the most popular organometallics and have been used for organic synthesis as nucleophiles in carbon–carbon bond formation, and as transmetalation agents onto other metals.[1] Carbometalation of alkynes is recognized to be useful in the preparation of stereochemically defined tri- and tetrasubstituted alkenes, while in reactions of alkynes without a conjugated electron-withdrawing group, the regioselectivity becomes the principal problem.[2] The carbolithiation of alkynes has limited synthetic use because only particular kinds of alkynes can be used, and as for the stereochemistry, the vinyllithium intermediates produced tend to isomerize with ease.[3] We report herein a preliminary result on the regio- and stereoselective carbolithiation of alkynes by a simple procedure that uses cheap iron salts as a catalyst.

We found that 3-pentynyl 3-phenylpropyl ether (**1a**), upon addition of a catalytic amount of $FeCl_3$, reacted with

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[*] Prof. Dr. A. Hosomi, Dr. M. Hojo, Y. Murakami, Dr. H. Aihara,
R. Sakuragi, Y. Baba
Department of Chemistry
Graduate School of Pure and Applied Sciences
University of Tsukuba, Tsukuba, Ibaraki 305-8571 (Japan)
Fax: (+81)298-53-6503

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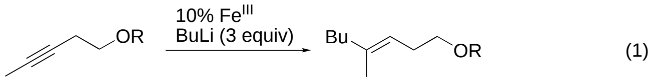
butyllithium to yield (*E*)-4-methyl-3-octenyl 3-phenylpropyl ether (**2a**) as a single isomer [Eq. (1)]. As shown in Table 1, the choice of a solvent is crucial for this reaction. In benzene or toluene, a butylated product **2a** was obtained in high yield (entries 4 and 5). In diethyl ether or THF, the cleavage of the C–O bond to yield the corresponding alkynyl alcohol or the β-elimination of ROH, such as 3-phenylpropanol or benzyl alcohol, takes place in preference to the desired butylation. As for an iron catalyst,[4] when an Fe^{III} salt was employed, **2** was produced in high yield, while with $FeCl_2$, only a poor yield of **2** was obtained. The actual catalyst for the present carbometalation has not been clearly determined. Previously, cross-coupling reactions with catalytic amounts of Fe^{III} species were reported and in those reactions, an Fe^{I} center generated by the reduction of the Fe^{III} species with a Grignard reagent was proposed as a catalyst.[5] In our system, a low-valent iron species may possibly catalyze the reactions. To determine the stoichiometry of butyllithium to Fe, we attempted the reaction with an equimolar amount of $[Fe(acac)_3]$ and the substrate **1b** (acac = 2,4-pentanedione (acetylacetone)). When 8 equivalents of butyllithium were introduced, the yield of **2b** was 63 %, and using 12 equivalents of the lithium reagent 89 % of **2b** was obtained.[6] These experiments suggest that the present iron catalysis may be based on an iron–ate complex. $[Fe(acac)_3]$ is soluble in toluene, thus, we could carry out most of the reactions simply using a stock solution of $[Fe(acac)_3]$ in toluene.



(1)

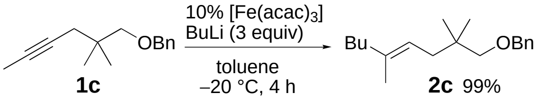
1a: R = $CH_2CH_2CH_2Ph$
1b: R = CH_2Ph
2a: R = $CH_2CH_2CH_2Ph$
2b: R = CH_2Ph

Table 1. Reaction of 3-pentynyl ethers **1** with butyllithium in the presence of Fe^{III}.[a]

Entry	Substrate	Fe salt	Solvent	Conditions	Yield (**2**) [%][b]
1	**1a**	$FeCl_3$	THF	– 40 °C, 4 h	0[c]
2	**1a**	$FeCl_3$	Et_2O	– 40 °C, 3 h	79 (**2a**)
3	**1b**	$FeCl_3$	Et_2O	– 40 °C, 3 h	79 (**2b**)[d]
4[e]	**1a**	$FeCl_3$	benzene	– 20 °C, 2 h	86 (**2a**)
5[e]	**1a**	$FeCl_3$	toluene	– 20 °C, 2 h	97 (**2a**)
6	**1b**	$[Fe(acac)_3]$[f]	toluene	– 20 °C, 2 h	97 (**2b**)
7	**1b**	$[Fe(dbm)_3]$[f]	toluene	– 20 °C, 2 h	85 (**2b**)
8	**1b**	$FeCl_3$	toluene	– 20 °C, 2 h	13 (**2b**)[g]

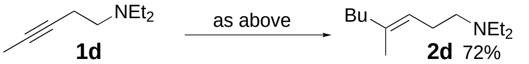
[a] All reactions were carried out using 3.0 equivalents of butyllithium and 10 mol % of Fe^{III}, unless otherwise noted. Reactions were quenched with 1N HCl solution. [b] Isolated Yield. [c] **1a** (18 %) was recovered. 3-Phenylpropanol (80 %) and nona-2,3-diene[7] (20 %) were found in the reaction mixture. [d] Benzyl alcohol (13 %) was produced. [e] Suspension of $FeCl_3$ in the respective solvent was used. [f] The amount of Fe^{III} was reduced to 5 mol %. [g] **1b** (45 %) was recovered and benzyl alcohol (34 %) was produced. DBM = 1,3-diphenyl 1,3-propanedione (dibenzoylmethane).

4-Hexynyl ether **1c**, a one-carbon homologue, also reacted with butyllithium in toluene to afford the corresponding addition product **2c** as the sole product in quantitative yield [Eq. (2)], while in diethyl ether the reaction resulted only in the recovery of **1c**, showing a clear solvent effect. The butylation was not only successful with alkynyl ethers, even the pentynylamine **1d** gave a butylation product (**2d**) in 72 % yield [Eq. (3)]. Interestingly, a simple alkyne, 6-dodecyne did not react at all under the conditions shown in Equations (2)–(4). *o*-Methoxy-1-pentynylbenzene (**1e**) also reacted with butyllithium to give a mixture of two stereoisomeric products **2e** in moderate yield [Eq. (4)]. In these reactions, a Lewis-basic moiety in a substrate alkyne not only activates the triple bond toward butylation, but possibly also controls stereoselectivity. Recently, Nakamura et al. reported iron-catalyzed olefin carbometalation, where organomagnesium and zinc reagents were employed.[8] As for the present reaction, when BuMgBr[9] was used for the reaction of **1b**, the yield of **2b** was low; 56 % (– 20 °C, 4 h), 60 % (RT, 4 h),[10] and further synthetic use seems to be difficult, as indicated by the low D-content of the product **2b** in a deuteration experiment.



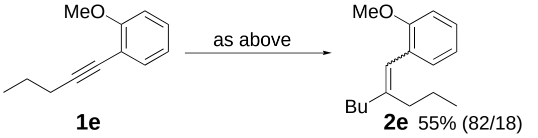
(2)

1c **2c** 99%



(3)

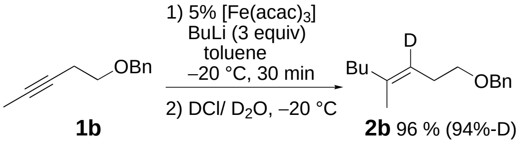
1d **2d** 72%



(4)

1e **2e** 55% (82/18)

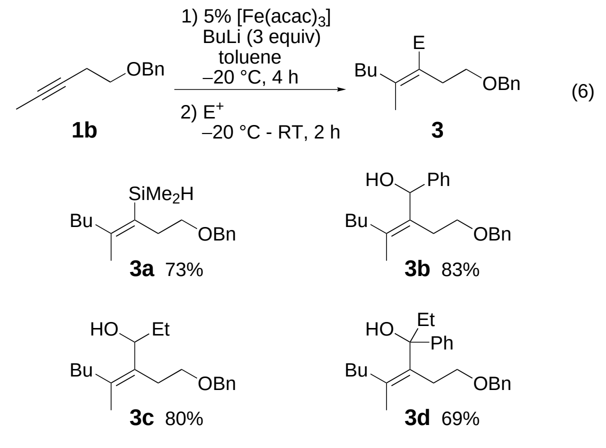
When a reaction of **1b** was quenched with DCl/D_2O, deuterated **2b** (94 %-D) was obtained in 96 % yield [Eq. (5)].[11] The postulated vinyllithium intermediate further reacted with electrophiles (E^+) such as chlorosilane to afford stereochemically defined vinylsilane **3a** in 73 % yield [Eq. (6)]. Both aromatic and aliphatic aldehydes also reacted to give the corresponding allylic alcohols **3b** and **3c**, respectively, in high yields. Even a ketone could be used as an electrophile, and a tetrasubstituted alkene **3d** was isolated in 69 %, as a single isomer.



(5)

1b **2b** 96 % (94%-D)

It was found that cheap iron salts catalyze carbometalation[12] of alkynes bearing an alkoxy or amino group. The simple protocol presented here allows us to access tetrasubstituted alkenes in a stereoselective manner. Further synthetic applications of this process are now under investigation.



(6)

Experimental Section

Full experimental details are in the Supporting Information. A representative procedure is as follows: to a flask purged with argon, a solution of [Fe(acac)$_3$] in toluene (0.025 M, 0.025 mmol, 1 mL), toluene (4 mL), and a substrate **1b** (0.5 mmol) were introduced. The flask was cooled to −40 °C and a solution of butyllithium in hexane (1.5 M, 1.5 mmol) was added to the mixture. Reaction temperature was immediately raised to −20 °C and the mixture was stirred at −20 °C for 2 h. The reaction was quenched with 1 N HCl. After the conventional workup and purification by chromatography on silica gel, a pure product **2b** was obtained in 97 % yield.

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[4] In the absence of a catalyst, a complex mixture without a normal product **2b** was produced.

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[6] Conditions for all reactions reported here are not fully optimized. A sufficient amount of butyllithium per iron catalyst (5 mol %) seems to be required during the reaction for the successful carbolithiation. Therefore, 3 equivalents used in reactions are a large enough amount for the present carbolithiation, and, indeed, a reaction of **1b** with 2 equivalents of butyllithium gave essentially the same result (95 % of **2b**, cf. Table 1, entry 6).

[7] This product was possibly obtained by the addition of butyllithium to pent-1-en-3-yne, produced by the β-elimination of phenylpropanol from **1a**. a) A. A. Petrov, V. A. Kormer, T. V. Yakovleva, *Zh. Obshch. Khim.* **1960**, *30*, 2238; b) A. A. Petrov, Yu. I. Porfir'eva, V. A. Kormer, *Zh. Obshch. Khim.* **1961**, *31*, 1518.

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[9] BuMgBr was prepared in diethyl ether, and most of the solvent was replaced with toluene before use.

[10] Only allylmagnesium bromide successfully added to **1b** (in Et$_2$O at RT for 7 h using 20 mol % of [Fe(acac)$_3$]) and the corresponding allylated product was obtained in quantitative yield.

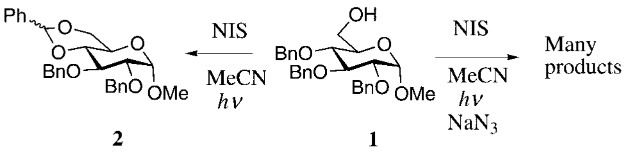
[11] The produced vinyl anion seems to be unstable at room temperature. Yield of **2b** and its deuterium content were decreased to 90 % and 82 %-D, respectively when the reaction mixture was kept at ambient temperature for 3 h before quenching with DCl/D$_2$O, the reaction was conducted under the same conditions as in Equation (5).

[12] Ethyllithium and hexyllithium were also added to **1b** to afford alkenes in high yields (Et: 96 %, Hex: 92 %).

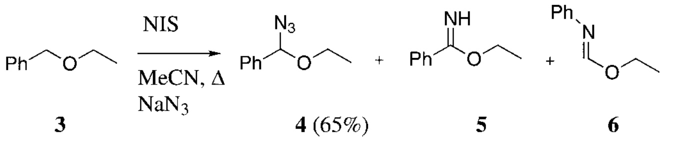
Radical Azidonation of Benzylic Positions with Iodonium Azide**

Christel Viuf and Mikael Bols*

We recently reported a procedure for the conversion of benzyloxy alcohols like **1** into benzylidene derivatives like **2** with *N*-iodosuccinimide (NIS) and light (Scheme 1).[1] During the investigation of this reaction we noticed that **1** was transformed with excess NaN$_3$ very rapidly into a variety of products of which many had, according to mass spectrometry, one to three hydrogen atoms replaced with azido groups. When the analogous reaction was carried out on benzyl ethyl ether **3** [Eq. (1), light substituted with heat to avoid decomposition of azides] the monoazido derivative **4** was isolated in 65 % yield together with small amounts of the by-products **5** and **6**.[2]



Scheme 1. The NIS-promoted transformation of benzyloxy alcohols into benzylidene derivatives and the effect of NaN$_3$ addition. Bn = benzyl.



(1)

Since this azidonation reaction appeared faster than the benzylidene derivative formation promoted by NIS alone and since the red color of the reaction mixture indicated that IN$_3$ was present, it was suggested that iodine azide was the reagent

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[*] Dr. M. Bols, C. Viuf
University of Aarhus
Department of Chemistry
Langelandsgade 140, 8000 Aarhus C (Denmark)
Fax (+45) 86196199
E-mail: mb@kemi.aau.dk

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