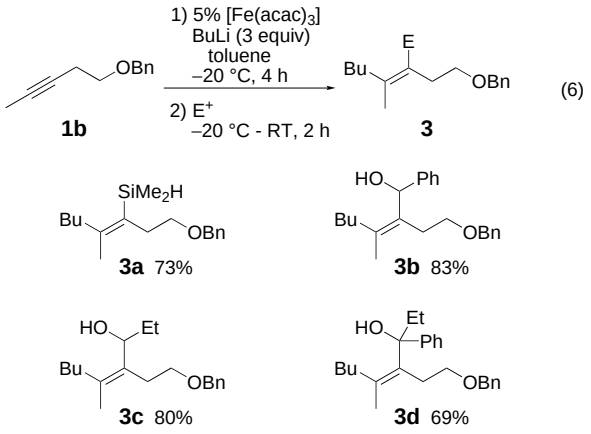

Experimental Section

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 $-40\,^{\circ}C$ and a solution of butyllithium in hexane (1.5 M, 1.5 mmol) was added to the mixture. Reaction temperature was immediately raised to $-20\,^{\circ}C$ and the mixture was stirred at $-20\,^{\circ}C$ for 2 h. The reaction was quenched with 1N 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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[3] a) J. E. Mulvaney, Z. G. Gardlund, S. L. Gardlund, *J. Am. Chem. Soc.* **1963**, *85*, 3897; b) J. E. Mulvaney, D. J. Newton, *J. Org. Chem.* **1969**, *34*, 1936–1939; c) W. Bauer, M. Feigel, G. Müller, P. von R. Schleyer, *J. Am. Chem. Soc.* **1988**, *110*, 6033–6046; d) L.-I. Olsson, A. Claesson, *Tetrahedron Lett.* **1974**, 2161–2162.

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

[5] a) M. Tamura, J. K. Kochi, *J. Am. Chem. Soc.* **1971**, *93*, 1487–1489; b) S. M. Neumann, J. K. Kochi, *J. Org. Chem.* **1975**, *40*, 599–606; c) R. S. Smith, J. K. Kochi, *J. Org. Chem.* **1976**, *41*, 502–509.

[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_2O at RT for 7 h using 20 mol% of $[Fe(acac)_3]$) and the corresponding allylated product was obtained in quantitative yield.

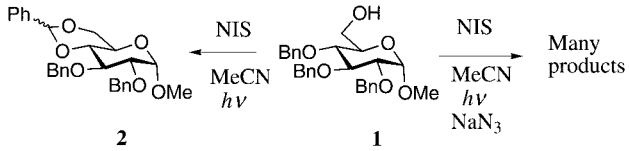
[11] The produced vinyl anion seems to be unstable at room temperature. Yield of **2b** and its deuterium content were decreased to 90% and 82%-D, respectively when the reaction mixture was kept at ambient temperature for 3 h before quenching with DCl/D_2O, the reaction was conducted under the same conditions 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**

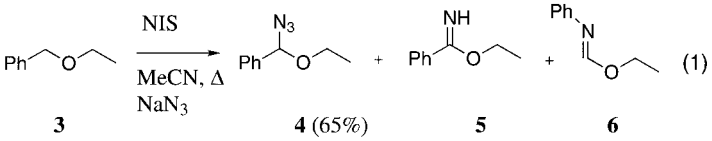
Christel Viuf and Mikael Bols*

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



Scheme 1. The NIS-promoted transformation of benzyloxy alcohols into benzylidene derivatives and the effect of NaN_3 addition. Bn = benzyl.

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]



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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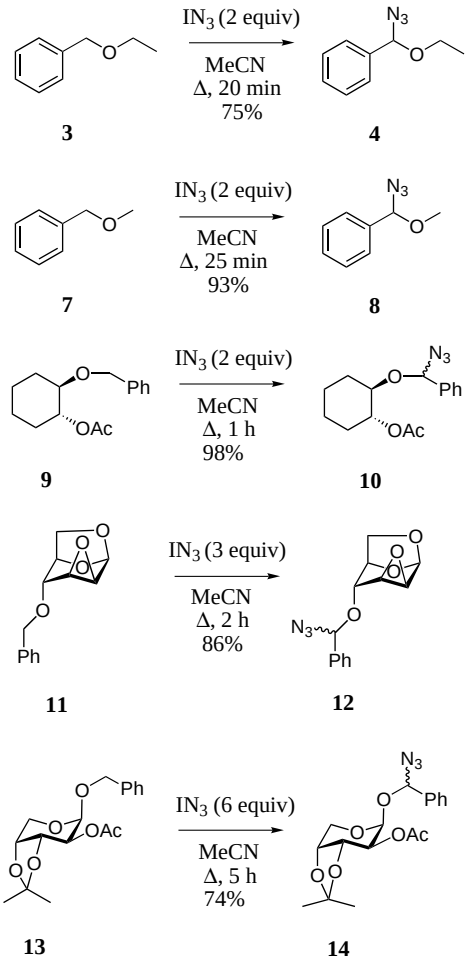
causing the reaction. Indeed if IN_3 was used, **3** could be transformed to **4** in 75% yield (Scheme 2).



Scheme 2. Reaction of various benzyl ethers with IN_3 in MeCN.

Some related chemistry has been reported in a series of papers by Magnus et al. They used PhIO/trimethylsilylazide ($TMSN_3$) at low temperature to azidonate a carbon atom α to amino and enol ether functionalities.[3] It has also been reported that $PhI(OAc)_2/NaN_3$ can be used to generate carbon-centered radicals.[4] Hassner et al. have pioneered and extensively studied the addition of IN_3 and other haloazides to alkenes.[5] They found that though the addition of haloazides to alkenes normally follows an ionic mechanism, in certain cases, in particular when ClN_3 or BrN_3 is the reagent, the products of a radical addition to the alkene are obtained.[5b] However, substitution of activated hydrogens by azido groups with IN_3 has not been carried out nor has the introduction of an azido group in a benzylic position.

As can be seen from Scheme 2 the reaction is highly efficient[6] when carried out in refluxing acetonitrile: The yields of azides (Table 1) were 74–98%. The transformations **9**→**10**, **11**→**12**, and **13**→**14** show that the reaction tolerates other functionalities such as ester, epoxide, or acetal units. The reaction of **13** is more sluggish than the others requiring more reagent and time. The reason is presumably that the acetal functionality makes the benzylic position less reactive because it is more electron withdrawing than a regular ether unit.

Table 1. Analytical data of the azido compounds **4**, **8**, **10**, **12**, and **14**.[a]

4: ^{1}H NMR: $\delta = 7.25-7.41$ (m, 5H), 5.38 (s, 1H), 3.85 (dqv, 1H, $J = 7.0$, 9.5 Hz), 3.58 (dqv, 1H, $J = 7.0$, 9.5 Hz), 1.19–1.24 (t, 3H, $J = 7.0$ Hz)
8: ^{1}H NMR: $\delta = 7.22-7.38$ (m, 5H), 5.24 (s, 1H), 3.43 (s, 3H)
10: ^{1}H NMR (diasteromeric ratio 1:1): $\delta = 7.25-7.50$ (m, 10H), 5.59 (s, 1H), 5.42 (s, 1H), 4.93 (m, 2H), 3.82 (m, 2H), 2.11 (s, 3H), 2.30–1.90 (m, 4H), 1.82 (s, 3H), 1.68–1.84 (m, 4H), 1.25–1.49 (m, 8H); MS (EI): m/z: calcd ($C_{15}H_{19}N_3O_3$+Na) 312.1324, found 312.1322
12: ^{1}H NMR (diasteromeric ratio 1:1): $\delta = 7.39-7.53$ (m, 10H), 5.72 (s, 1H,), 5.70 (s, 1H), 5.68 (s, 1H), 5.67 (s, 1H), 4.51 (t, 1H, $J = 4.4$ Hz), 4.49 (t, 1H, $J = 4.4$ Hz), 4.05 (br s, 2H), 3.72 (d, 2H, $J = 4.4$), 3.70 (d, 2H, $J = 4.4$), 3.48 (dd, 2H, $J = 3.7$), 3.28 (br d, 1H, $J = 3.7$), 3.16 (br d, 1H, $J = 3.7$); MS (EI): m/z: calcd ($C_{13}H_{13}N_3O_4$+Na) 298.0804, found 298.0804
14: ^{1}H NMR (diasteromeric ratio 1:1):[b] $\delta = 7.40-7.50$ (m, 5H, 5H′), 5.64 (s, 1H′), 5.55 (s, 1H), 5.47 (d, 1H, $J = 3.50$ Hz), 5.08 (d, 1H′, $J = 3.50$ Hz), 5.01 (dd, 1H, $J = 3.50$, $J = 8.1$ Hz), 4.91 (dd, 1H′, $J = 3.50$ Hz, $J = 7.7$ Hz), 4.31–4.46 (m, 1H, 2H′), 4.17–4.25 (m, 1H, 1H′), 4.09 (d, 1H′), 3.99 (d, 1H, $J = 13.6$ Hz), 3.83 (dd, 1H, $J = 13.6$, 2.9 Hz), 2.15 (s, 3H), 2.03 (s, 3H′), 1.56 (s, 3H), 1.53 (s, 3H′), 1.37 (s, 3H′), 1.20 (s, 3H); MS (EI): m/z: calcd ($C_{17}H_{21}N_3O_6$+Na) 386.1328, found 386.1329

[a] 200 MHz for all ^{1}H NMR spectra, in $CDCl_3$. [b] Primed protons refer to the second diasteromer.

Strong support was found for the reaction to follow a radical mechanism: Compound **8** was not formed when **7** was allowed to react in the presence of the radical trap *N-tert*-butyl-α-phenylnitrone (Scheme 2).[8] Substrate **7** and most of the radical trap (2 equiv) were recovered unconverted, which shows that capture of a small amount of radicals prevented the reaction. A certain electron-donating capacity is necessary at the benzylic position for the reaction to occur: When an ester is attached to this position as in benzyl benzoate no reaction is observed. Benzyl alcohol, on the other hand, is oxidized to benzaldehyde under the reaction conditions. Based on these results we suggest the following reaction course: Homolysis of IN_3 results in an azide radical that abstracts a hydrogen atom from the substrate to form a benzylic radical. This radical is oxidized by IN_3 or I_2 to a benzylic cation that combines with the azide ion to form the product.[9]

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[2] The by-products **5** and **6** were presumably formed from **4** through light-induced decomposition of the latter to a nitrene followed by H and Ph migration, respectively.
[3] a) P. Magnus, J. Lacour, *J. Am. Chem. Soc.* **1992**, *114*, 767–769; b) P. Magnus, J. Lacour, W. Weber, *J. Am. Chem. Soc.* **1993**, *115*, 9347–9348; c) P. Magnus, J. Lacour, P. A. Evans, P. Rigollier, H. Tobler, *J. Am. Chem. Soc.* **1998**, *120*, 12486–12499; d) P. Magnus, J. Lacour, W. Weber, *Synthesis* **1998**, 547–551.
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[6] General reaction conditions: A solution of IN_3[7] was prepared by mixing ICl (101 mg, 0.6 mmol) in MeCN (2 mL) with NaN_3 (107 mg,

  0044-8249/01/11303-0644 $ 17.50+.50/0

1.4 mmol) in MeCN (3 mL) at $-10\,^{\circ}C$.[5c] After 15 min the cooling bath was removed, and the ether compound (0.3 mmol) was added. The mixture was refluxed for between 0.4 and 5 h. Then CH_2Cl_2 (25 mL) was added, and the mixture was washed with 5% $Na_2S_2O_3$ solution (20 mL). The dried ($MgSO_4$) and evaporated organic phase was purified by flash chromatography.

[7] IN_3 is an explosive substance, particularly as a solid (see ref. [5a]). We encountered no problems, but took care to remove IN_3 after the reaction by washing with $Na_2S_2O_3$ solution.

[8] K. Yelekci, X. Lu, R. B. Silverman, *J. Am. Chem. Soc.* **1989**, *111*, 1138–1140.

[9] We have also investigated some amine substrates in order to compare IN_3 with the Magnus reagent $PhIO/TMSN_3$. Reaction of *N*,*N*-dimethylaniline with IN_3 gave several products, the major one being 4-iodo-*N*,*N*-dimethylaniline, while benzyldimethylamine led to a number of very labile products that on decomposition gave benzaldehyde and benzylmethylamine. This is in agreement with the formation of α-azidoamines like those obtained in the Magnus reaction. Magnus et al. could isolate such α-azidoamines by using nonaqeous work-up, but they are clearly much less stable than the α-azidoethers.