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Base-Induced Radical Carboamination of Nonactivated Alkenes with Aryldiazonium Salts

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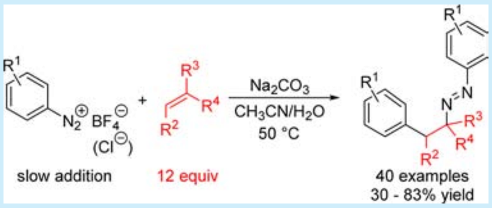
S *Supporting Information*

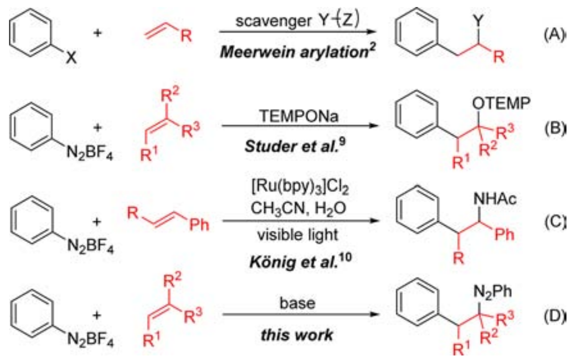
ABSTRACT: A new transition-metal-free version of the Meerwein arylation has been developed. The key feature of this carboamination-type reaction is the slow base-controlled generation of aryl radicals from aryldiazonium tetrafluoroborates, so that a sufficient quantity of diazonium ions remains to enable efficient trapping of the alkyl radical adduct resulting from aryl radical addition to the alkene. Under strongly basic conditions, diazoanhydrides are likely to take over the role of the nitrogen-centered radical scavengers.



The Meerwein arylation[1] has recently become a highly versatile tool for the radical functionalization of alkenes (Scheme 1, A). Besides the traditional diazonium salts ($X = N_2^+$), bromo- and iodobenzenes (X = Br, I) as well as arylhydrazines ($X = NHNH_2$) have been successfully applied as aryl radical sources, and the group of alkenes, which was at first practically limited to activated alkenes (e.g., R = COOR′, CN, Ph) could be extended to nonactivated alkenes. Moreover, a significant number of new radical scavengers have been found, which now allow the introduction of a broad variety of atoms or functional groups Y.[2,3]

Along with these expansions of the scope, the attractiveness of the Meerwein arylation was further increased through the development of transition-metal-free,[4] catalytic,[5] as well as photocatalytic versions.[6,7] Beautiful examples are the TEMPO−Na-mediated carboxygenation[8] developed by Studer[9] (Scheme 1, B) and the photocatalyzed carboamination reported by König[10] (Scheme 1, C). In this context, it is, however, surprising that the base-induced generation of aryl radicals from diazonium salts,[11,12] which is well established for Gomberg−Bachmann reactions,[13−15] has so far only rarely been exploited in alkene functionalizations.[16,17] Especially from an economical point of view, such base-mediated variants could be fully competitive with catalytic and photocatalytic versions.

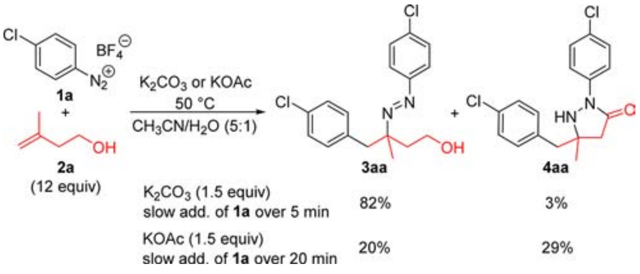
Scheme 1. Meerwein Arylation: Recent Developments



Since carboaminations of alkenes is a highly topical field of research, with many metal-catalyzed versions having been reported recently,[18] we chose a Meerwein-type carboamination reaction as a starting point (Scheme 1, D). In this reaction, aryldiazonium salts play a double role and act as aryl radical sources as well as nitrogen-centered radical scavengers.[19,20] A major drawback of these versatile transformations so far, however, was that a large excess of either iron(II) sulfate or titanium(III) chloride[21] was required to obtain the desired azo compounds in good yields.[22]

In a series of optimization experiments aiming at a base-induced radical carboamination reaction, solutions of 4-chlorophenyldiazonium tetrafluoroborate (**1a**) were added to mixtures of 3-methyl-3-buten-1-ol (**2a**) and a base in aqueous acetonitrile under various conditions (Scheme 2; see the Supporting Information for details).[23] The best yield for the desired azo compound **3aa** was obtained with sodium carbonate at a temperature of 50 °C. Pyrazolidinone **4aa**, which was the most important byproduct of the reaction, was formed in largest quantity when the weaker base potassium acetate was used. By

Scheme 2. Results from Optimization of Reaction Conditions



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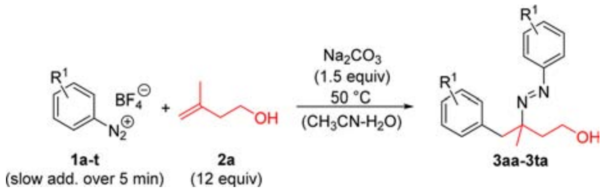
employing the conditions optimized for **3aa**, a scaling-up experiment was also successful in which **3aa** was obtained from **1a** and **2a** on a 10 mmol scale in 72% yield (1.04 g). In parallel, we evaluated the base-induced carboamination starting from the corresponding 4-chlorophenyldiazonium chloride (see the Supporting Information). The best yield for **3aa** (63%), along with 7% of **4aa**, was obtained with 4.5 equiv of Na_2CO_3 in a 1:1 mixture of acetonitrile and water at 50 °C and at an identical addition time of 5 min. On this basis, the tetrafluoroborate-based version was chosen for an extensive evaluation of scope and limitations (Tables 1 and 2), and fewer reactions were carried out under those conditions optimized for the diazonium chlorides (see the Supporting Information).

Table 1. Evaluation of Substrate Scope and Limitations (I)



entry	diazonium salt **1**: R^1 =	yield[a] of **3**[b] (%)
1	**1a**: 4-Cl	**3aa** (83)[c]
2	**1b**: 3-Cl	**3ba** (60)[c]
3	**1c**: 2-Cl	**3ca** (73)
4	**1d**: 3,4-Cl_2	**3da** (78)[c]
5	**1e**: 3,5-Cl_2	**3ea** (48)[c]
6	**1f**: 4-F	**3fa** (51)[c]
7	**1g**: 2-F	**3ga** (62)
8	**1h**: 4-Br	**3ha** (63)
9	**1i**: 3-Br	**3ia** (63)
10	**1j**: 2-Br	**3ja** (59)
11	**1k**: 4-I	**3ka** (43)
12	**1l**: 4-OMe	**3la** (30)[d]
13	**1m**: 3,4-$(OMe)_2$	**3ma** (51)
14	**1n**: 4-CF_3	**3na** (51)[d]
15	**1o**: 4-CN	**3oa** (48)[d]
16	**1p**: 3-CN	**3pa** (47)[d]
17	**1q**: 4-CO_2Me	**3qa** (50)
18	**1r**: 4-COMe	**3ra** (40)
19	**1s**: 4-NO_2	**3sa** (41)[c]
20	**1t**: 4-H	**3ta** (34)

[a] Diazonium tetrafluoroborate **1** (1.0 mmol) in CH_3CN/H_2O (5:1, 4 mL) added over 5 min to a mixture of alkene **2** (12 mmol) and Na_2CO_3 (1.5 mmol) in CH_3CN/H_2O (5:1, 5 mL) at 50 °C. [b] Yields after purification by column chromatography. [c] Byproduct pyrazolidinone **4** observed in low yield <8%. [d] Byproduct pyrazolidinone: **4la** (23%), **4na** (15%), **4oa** (23%), **4pa** (16%).

Table 2. Evaluation of Substrate Scope and Limitations (II)

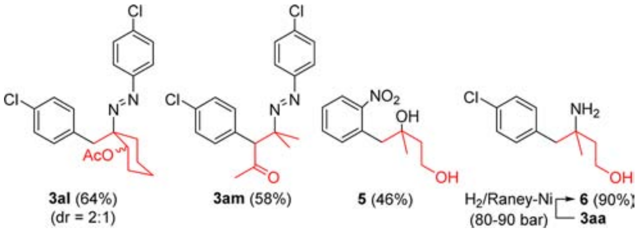
entry	diazonium salt **1**: R^1 =	alkene **2**: R^2 =	yield[a] of **3**[b] (%)
1	**1a**: 4-Cl	**2b**: CH_2OH	**3ab** (72)
2	**1c**: 2-Cl	**2b**: CH_2OH	**3cb** (54)
3	**1d**: 3,4-Cl_2	**2b**: CH_2OH	**3db** (70)
4	**1k**: 4-I	**2b**: CH_2OH	**3kb** (61)
5	**1a**: 4-Cl	**2c**: $(CH_2)_3C(Me)_2OH$	**3ac** (66)
6	**1a**: 4-Cl	**2d**: $(CH_2)_2OAc$	**3ad** (46)
7	**1a**: 4-Cl	**2e**: $(CH_2)OAc$	**3ae** (43)
8	**1a**: 4-Cl	**2f**: $(CH_2)_2COMe$	**3af** (71)
9	**1a**: 4-Cl	**2g**: $CH_2OC_6H_4NO_2$	**3ag** (56)
10	**1a**: 4-Cl	**2h**: $(CH_2)OTHP$[c]	**3ah** (61)
11	**1a**: 4-Cl	**2i**: $(CH_2)_2CO_2Me$	**3ai** (65)
12	**1a**: 4-Cl	**2j**: $(CH_2)_2OCOPh$	**3aj** (44)
13	**1a**: 4-Cl	**2k**: $(CH_2)_2N_3$	**3ak** (56)

[a] Diazonium tetrafluoroborate **1** (1.0 mmol) in CH_3CN/H_2O (5:1, 4 mL) added over 5 min to a mixture of alkene **2** (12 mmol) and Na_2CO_3 (1.5 mmol) in CH_3CN/H_2O (5:1, 5 mL) at 50 °C. [b] Yields after purification by column chromatography. [c] THP = tetrahydropyran-2-yl.

The evaluation of the substrate scope was started with different substitution patterns on the aryldiazonium salt (Table 1). On average, good yields were obtained for halogenated compounds **1a**−**k** (entries 1−11). Donor- and acceptor-substituted diazonium salts **1l**−**s** were tolerated as well (entries 12−19). Within these groups, the largest amounts of the pyrazolidinones **4** were observed, with a maximum yield of 23% for **4oa** (entry 15). The comparably low yield of 34% obtained for the unsubstituted diazonium salt **1t** (entry 20) was not completely surprising as a lack of substituents on the aromatic core had shown negative effects in earlier studies.[15a] Variation of the alkene in the second part of the study (Table 2) at first demonstrated that the undesired pyrazolidinone formation is a particular feature of alcohol **2a** (c.f. entries 1−5), which can be explained by the mechanism presented below (Scheme 3). Second, this series of experiments showed that functional groups other than alcohols, such as esters (entries 6, 7, 11, and 12), ketones (entry 8), phenyl ethers (entry 9), cyclic acetals (entry 10), and azides (entry 13), do not interfere with the chosen reaction conditions.

Additional attempts with 3-butenol demonstrated that the optimized reaction conditions are not equally well suited for monosubstituted alkenes, as the tetrafluoroborate salt **1a** and its corresponding chloride salt gave the related azo compound only in yields of 30% and 25%, respectively (see the Supporting Information). As a lower stability of an azo compound derived from a monosubstituted alkene under the reaction conditions and an isomerization to the corresponding hydrazone could be ruled out,[24] we assume at this point that the slower trapping of less nucleophilic secondary carbon-centered radicals by the diazonium ions is responsible for this trend.[25]

Under conditions identical to those applied in Tables 1 and 2, methylenecyclohex-2-yl acetate and 4-methylpent-3-en-2-one provided the azo compounds **3al** (2:1 mixture of stereoisomers) and **3am**, respectively (Figure 1). A first example for a base-mediated Meerwein-type carbohydroxylation was found in the



3al (64%) (dr = 2:1)

3am (58%)

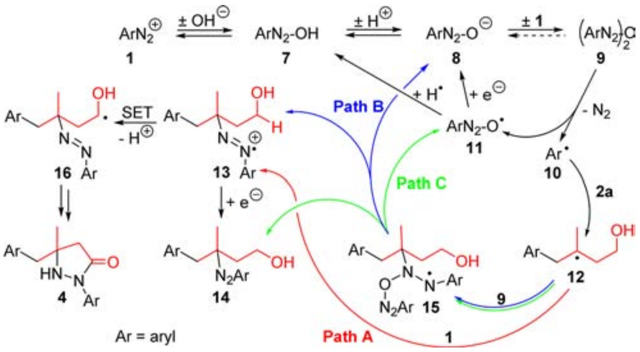
5 (46%)

Figure 1. Additional products.

reaction of 2-nitrophenyldiazonium tetrafluoroborate with alkene **2a**. This reaction gave the tertiary alcohol **5**, probably through a fast intramolecular alkyl radical attack onto the nitro group and subsequent oxidative ring-opening,[26] and no yield of the corresponding azo compound.[27] After unsuccessful attempts with sodium dithionite,[28] the reduction of **3aa** to amine **6** and 4-chloroaniline was achieved through hydrogenation over Raney nickel[29] in 90% yield. Regarding carboamination, this reduction thus allows recovery of the second aniline equivalent, which may then be reused for the reaction via diazotization.

Taking a closer look at the mechanism of the base-induced carboamination, the aryl radical generation is likely to proceed via the intermediates known from Gomberg–Bachmann reactions (Scheme 3).[13b] The diazonium ion **1** is stepwise converted to diazohydroxide **7**, to diazotate **8**, and then to diazoanhydride **9** before homolytic cleavage into an aryl radical **10**, nitrogen, and diazenyloxyl radical **11** occurs.[13,30] Aryl radical addition to **2a** leads to alkyl radical **12**, which may be trapped by a diazonium ion to give at first radical cation **13** and then azo compound **14** via a final reductive step (path A).[20a] As the reaction can also be conducted under strongly basic conditions (see Table S1, Supporting Information), under which no free diazonium ions should be available for the trapping of **12**, it appears plausible that **9** itself may act as radical scavenger to give a well-stabilized nitrogen-centered radical **15**.[31] Fragmentation of **15** could then occur via either path B or C. The formation of pyrazolidinone **4** from **13** can be rationalized by an intramolecular electron transfer out of a suitably positioned and activated C–H bond to give the stabilized radical **16**.[31−33] The intramolecular nature of this step is supported by the fact that the CH_2-shortened alkene **2b** (c.f. Table 2) did not undergo a similar reaction. Later, **4** is formed from **16** via oxidation and cyclization.[34] An alternative mechanism leading to **4** via a Cannizarro-like hydride transfer can currently however not be ruled out.[35] Investigation of the byproducts suggested that the electrons required for the steps **11** → **8** and **13** → **14** come from an oxidation of the alkene (e.g., **2a**) in allylic position.

Scheme 3. Plausible Reaction Mechanisms



To maximize the yield of pyrazolidinone **4**,[36] we combined the most suitable base potassium acetate (Scheme 2) with the best diazonium salt **1o** (Table 1, entry 15). This experiment indeed gave the pyrazolidinone **4oa** in 47% yield along with only 18% of **3oa** (see the Supporting Information). When the same reactants **1o** and **2a** were instead submitted to an iron(II)-mediated reaction,[21b,c] only the carboamination product **3oa** was obtained in 47% yield, thereby showing the critical importance of radical cation **13** for the formation of pyrazolidinones.

In summary, a new transition-metal-free Meerwein-type carboamination reaction has been developed, which relies on the generation of aryl radicals under basic conditions that were so far typical for Gomberg–Bachmann reactions. The product yields compare well and do sometimes even exceed those, which could so far only be reached by employing iron(II) sulfate as reductant in large excess.[21d] The variation of reaction conditions further gave hints that not only diazonium ions but also diazoanhydrides may act as nitrogen-centered radical scavengers. Most importantly, this study shows that base-mediated variants represent, besides recent catalytic and photocatalytic improvements of the Meerwein arylation, a third option to further increase the attractiveness of this powerful radical transformation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03143.

General experimental methods, characterization data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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