Organic LETTERS

Letter

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Exploiting Alkylquinone Tautomerization: Amine Benzylation

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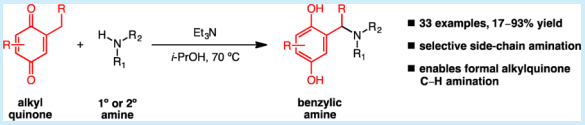
Supporting Information

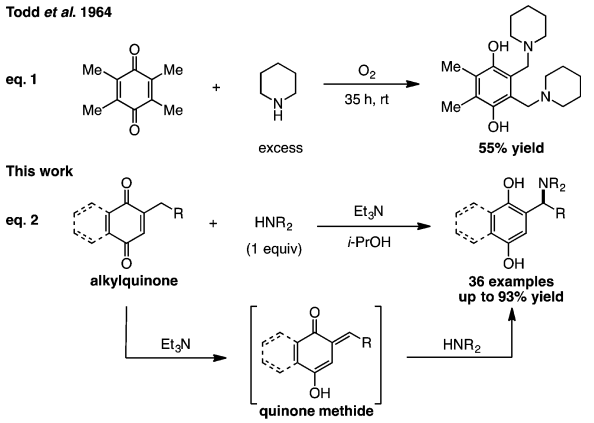
ABSTRACT: A general protocol for the synthesis of benzylic amines via side-chain amination of alkylquinones is reported. The reactions are initiated by the tautomerization of an alkylquinone to the corresponding quinone methide, which is subsequently trapped in situ by an amine nucleophile. This process is promoted by tertiary amines in protic solvents under mild conditions and is compatible with many functional groups. 1,2- and 1,4-benzoquinones, as well as naphthoquinones, participate in this reaction using a wide range of primary and secondary amines/anilines. The synthetic utility of this transformation is also explored.



Benzylic amines are key constituents of pharmaceuticals, agrochemicals, and materials and are commonly found as intermediates in modern organic chemistry.[1] Accordingly, a wide variety of methods for their synthesis have been developed. Traditional methods for amine synthesis, such as nucleophilic addition to imines[2] and nucleophilic substitution of benzylic electrophiles,[3,4] typically require prefunctionalization of the benzylic coupling partner and/or nucleophile. Transition-metal-catalyzed reactions,[4−8] such as the amination of styrene derivatives,[5] the direct benzylic C−H amination of alkylarenes,[6] the α-arylation of aliphatic amines,[7] and imine addition reactions,[8] offer several advantages over traditional methods, including mild reaction conditions and increased functional group tolerance; however, their application is limited by the need to employ expensive and sometimes toxic metal catalysts. Other methods based on the benzylic amination of alkyl-[9] or vinyl-substituted[10] arenes often require superstoichiometric quantities of oxidants or reagents. Therefore, the development of new technologies for the synthesis of benzylic amines that do not depend on the prefunctionalization of reaction partners, or the need for transition-metal catalysts or superstoichiometric reagents, is highly desirable. The utilization of unfunctionalized substrates to access reactive intermediates capable of intercepting primary and secondary amines would allow rapid and direct access to benzylic amines. Herein we report a straightforward and efficient method for benzylic amine synthesis based on the direct coupling of alkylquinones with primary and secondary amines. This new protocol for benzylic amine synthesis proceeds by way of alkylquinone tautomerization[11] to generate a highly electrophilic quinone methide intermediate that is, in turn, trapped by an amine coupling partner.[12,13]

The "side-chain" amination of alkylquinones was first reported by Todd et al. in 1964 and involved a sequence of amination/oxidation events, leading to doubly aminated hydroquinones in modest yields (Scheme 1, eq 1).[14] Based on the related addition of sodium malonate to duroquinone reported decades earlier by Smith et al.,[15] Todd proposed that tautomerization of the alkylquinone generated a key quinone methide intermediate that

Scheme 1. Quinone Side-Chain Diamination by Todd[14] and This Work



immediately reacted with the amine nucleophile. Since then, isolated reports on the amination of alkylquinones have appeared in the literature.[16] However, none of them have provided a general method for efficient benzylic amine synthesis. Given the limited understanding of this potentially powerful transformation, we set out to develop a general protocol for quinone side-chain monoamination and perform a detailed examination of its utility (Scheme 1, eq 2).

Our optimization studies focused on the reaction between 2,6-dimethylquinone and dibenzylamine (Table 1). Examination of various solvents at 70 °C under a nitrogen atmosphere for 24 h revealed that the reaction failed to proceed in nonpolar solvents (entry 1). Only small amounts of the desired benzylamine derivative **3**, together with hydroquinone **4**, were ever obtained in DME (entry 2).[17] Because hydroquinone **4** is presumably generated via single-electron transfer (SET) and hydrogen atom abstraction from dibenzylamine,[18] we reasoned that the use of

Received: June 6, 2016

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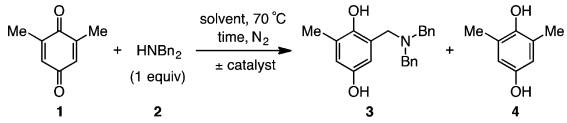
DOI: 10.1021/acs.orglett.6b01629
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Summary of Optimization Studies[a]



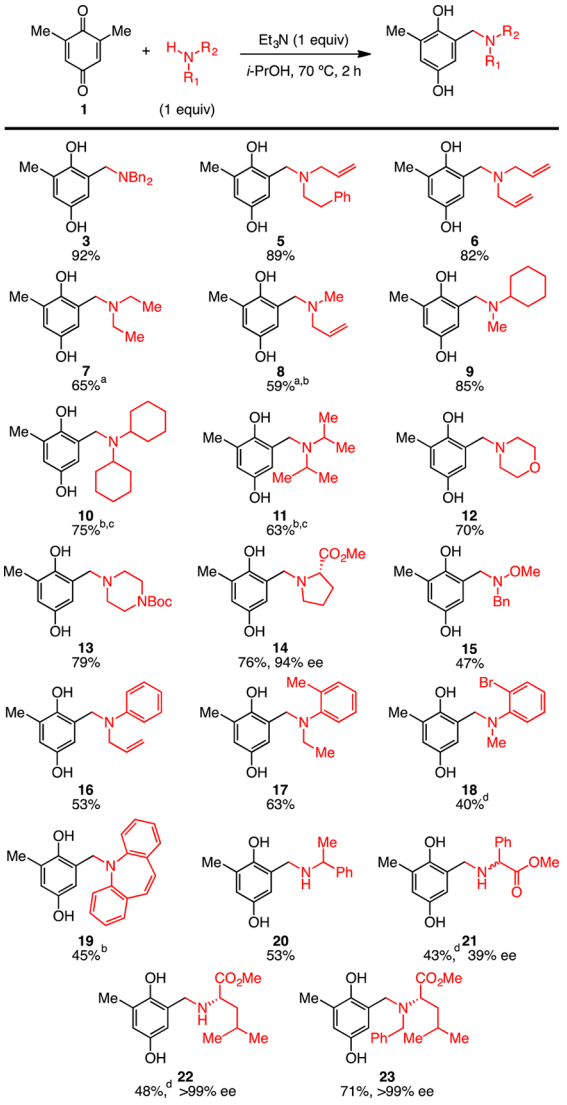
entry	solvent	catalyst	time (h)	yield of **3**[a] (%)	yield of **4**[a] (%)
1	PhMe	none	24	0	0
2	DME	none	24	6	7
3	*i*-PrOH	none	24	66	23
4	EtOH	none	24	65	27
5	MeCN	none	24	43	9
6	DMF	none	24	52	18
7	DMSO	none	24	48	29
8	Et_3N	none	24	85	9
9	***i*-PrOH**	**Et_3N**[b]	**2**	**94**	**6**
10	*i*-PrOH	*i*-Pr_2NEt[b]	2	85	7
11	*i*-PrOH	Bu_3N[b]	2	92	8
12	*i*-PrOH	DMAP[b]	2	47	nd
13	*i*-PrOH	pyridine[b]	2	25	5
14	*i*-PrOH	none	2	25	5
15	*i*-PrOH	Et_3N[c]	2	80	7

[a]Yields determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]1 equiv used. [c]0.2 equiv used. nd = not determined.

protic solvents might attenuate this undesired reaction by accelerating quinone tautomerization. Indeed, the use of protic solvents improved both the reaction efficiencies and product ratios (entries 3 and 4). Highly polar, aprotic solvents provided product **3** in diminished yields and led to increased quinone reduction (entries 5–7). Surprisingly, carrying out the reaction in neat triethylamine provided benzylic amine **3** in 85% yield with only a small amount of byproduct **4** (9%, entry 8). Guided by these results, we examined the use of 1 equiv of triethylamine in 2-propanol and observed significant rate acceleration, affording benzylic amine **3** in 94% yield in just 2 h with only a trace quantity of hydroquinone **4** (entry 9). Other tertiary amines provided similar yields (entries 10 and 11). DMAP provided only a modest yield of product **3** (entry 12, 47%), while pyridine was an ineffective catalyst (entry 13, 25%) and was comparable to the reaction without any additive (entry 14, 25%). Although the majority of our optimization studies employed a stoichiometric amount of an amine catalyst, the catalytic activity was evidenced by the use of a substoichiometric quantity of triethylamine (entry 15, 80%). The combination of an external base and protic solvent presumably aids in quinone tautomerization, thereby accelerating the desired reaction.

With optimized conditions in hand, we next examined a diverse range of primary and secondary amine reaction partners using 2,6-dimethyl-1,4-benzoquinone (**1**) as a representative quinone (Scheme 2). Model substrate **3** was isolated in 92% yield. *N*-Allyl-*N*-homobenzylamine **5** was obtained in good yield (89%). Less hindered secondary amines also participated in this reaction, providing products **6**–**8** in moderate to good yields (59–85%). When volatile amines such as diethylamine and *N*-methylallylamine were used, the reactions were carried out at room temperature, providing **7** and **8** in good yields (65% and 59% respectively). *N*-Methylcyclohexylamine afforded product **9** in 85% yield, but the more sterically encumbered dicyclohexylamine and diisopropylamine led to lower yields of products **10** and **11** (44% and 41%, respectively, not shown) accompanied by a significant amount of hydroquinone **4**. Fortunately, we found

Scheme 2. Scope Evaluation with Respect to the Amine



[a]Reaction ran at room temperature for 24 h. [b]Reaction ran in PhMe/*i*-PrOH (4:1) with 5 equiv of Et_3N. [c]Reaction ran for 3 h. [d]Amine hydrochloride used; reaction ran with 2 equiv of Et_3N.

that the addition of a nonpolar cosolvent (toluene) led to a significant improvement in reaction efficiency, delivering **10** and **11** in good yields (75% and 63%, respectively).

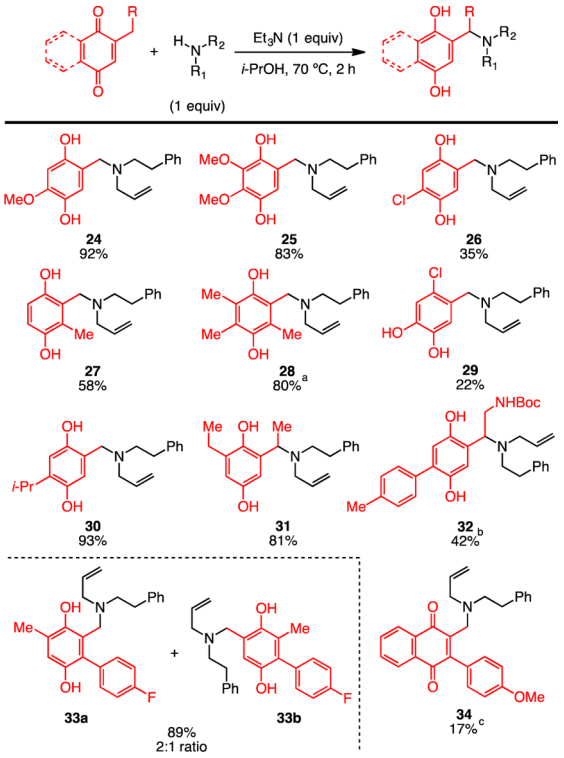
Cyclic amines such as morpholine, *N*-Boc-piperazine, and L-proline methyl ester provided the corresponding benzylic amines in good yields (**12**–**14**, 70–79%). *N*-Benzyl-*O*-methylhydroxylamine provided the product in low yield (**15**, 47%), while the demethylated analogue failed to provide any of the desired product (not shown). *N*-Alkylanilines provided the corresponding benzylic amines in moderate yields (**16**–**18**, 40–63%). Notably, competitive amination of the quinone ring was detected as a byproduct accompanying **16**.[18] *Ortho*-substitution of the arene ring did not substantially change the yield of the reactions (**17**, 63% and **18**, 40%). Employing a dibenzoazepine nucleophile led to the desired benzylic amine **19** in modest yield (45%), perhaps due to the electronic deactivation of this amine by the two aromatic substituents. Primary amines such as (±)-α-methylbenzylamine and α-amino esters reacted in moderate yields (**20**–**22**, 43–53%) due to competitive

DOI: 10.1021/acs.orglett.6b01629
Org. Lett. XXXX, XXX, XXX–XXX

amination of the quinone ring.[18] *N*-Benzyl protection of L-leucine methyl ester provided the desired product in good yield (**23**, 71%). It is important to point out that the benzylation of enantiopure amino acids that might be subject to epimerization provided products **14**, **22**, and **23** with little to no change in enantiomeric purity. However, amino acids bearing a more acidic α-proton, such as phenyl glycine, provided the corresponding benzylic amine product with reduced enantiopurity (**21**, 39% ee).

We also explored the scope of the benzylation reaction with respect to the alkylquinone using *N*-allyl-*N*-homobenzylamine as the nucleophile (Scheme 3). Methoxy-substituted quinones

Scheme 3. Scope Evaluation with Respect to the Quinone



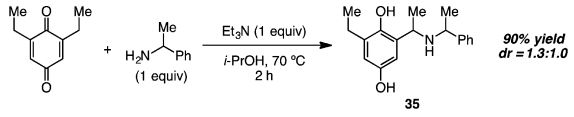
[a]Reaction ran at 80 °C for 6 h. [b]Reaction ran for 3 h. [c]Reaction ran for 4 h.

afforded the amination products **24** and **25** in good yields (92% and 83%, respectively) without substitution of the methoxy substituents. On the other hand, employing a chloroquinone provided amine **26** in modest yield (35%) presumably due to competitive chloride substitution.[18]

Surprisingly, 2,3-dimethyl-1,4-benzoquinone, which is unhindered at the 5- and 6-positions and therefore potentially susceptible to nucleophilic attack,[18] provided benzylic amine **27** in 58% yield. Duroquinone required extended reaction time and higher temperature, affording monoaminated benzylic amine **28** in good yield (80%), as opposed to the diaminated product analogous to those described by Todd.[14] *o*-Quinone 3-chloro-4-methyl-1,2-benzoquinone afforded the corresponding benzylic amine **29** in low yield (22%) accompanied by a significant quantity of the substitution product. Thymoquinone, bearing methyl and isopropyl substituents, underwent regioselective amination at the methyl position to give **30** in 93% yield. This side-chain amination is not limited to methylquinones, as 2,6-diethyl-1,4-quinone afforded the corresponding α-methylbenzylamine **31** in 81% yield. Employing an *N*-Boc-(2-aminoethyl)-quinone delivered diamine **32** in 42% yield. To further explore regiocontrol in these reactions, a nonsymmetrical dimethylquinone was tested, leading to regioisomeric benzylic amines **33a** and **33b** in excellent overall yield (89%), albeit with modest regioselectivity (2:1). Surprisingly, this reaction proceeds through nucleophilic attack at the more hindered position to provide amine **33a** as the major product. Lastly, a methyl naphthoquinone underwent amination in low yield due to competitive reduction of the reacting naphthoquinone and oxidation of the product, affording naphthoquinone **34** in low yield (17%).

Given that the reaction allows the preparation of enantiopure benzylic amines (e.g., **14**, **22**, and **23**, Scheme 2), we wondered if using a chiral amine would induce the diastereoselective amination of a suitable quinone. Thus, we evaluated the reaction of 2,6-diethyl-1,4-benzoquinone with (±)-α-methylbenzylamine (Scheme 4). The reaction proceeded efficiently, but the

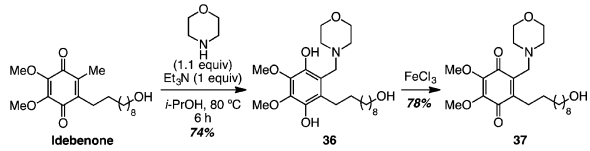
Scheme 4. Evaluation of Diastereoselectivity



diastereoselectivity was poor (dr = 1.3:1.0). Lowering the reaction temperature did not significantly improve the diastereoselectivity (dr = 1.8:1.0 at 0 °C, not shown).

To highlight the utility of this method, we subjected pharmaceutical agent idebenone to our amination reaction with morpholine (Scheme 5). Notably, regioselective amination

Scheme 5. Formal C−H Amination of Idebenone



took place at the less hindered position (methyl substituent) to afford benzylic amine **36** in 74% yield (>20:1 rr). Benzylic amine **36** could be oxidized under mild conditions to provide aminated idebenone derivative **37**. This two-step procedure provides a useful protocol for carrying out the formal C−H amination of alkylquinones.

In conclusion, we have developed a general method for the efficient synthesis of benzylic amines via alkylquinone amination. This transformation enables the synthesis of complex benzylic amines in a single step under mild conditions. We expect this protocol to be adopted as a useful tool to rapidly access benzylic amines and prepare aminated derivatives of quinone-containing natural products and pharmaceuticals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01629.

Additional optimization studies, control experiments, general experimental procedures, and ^{1}H, ^{13}C, and ^{19}F NMR spectra (PDF)

DOI: 10.1021/acs.orglett.6b01629
Org. Lett. XXXX, XXX, XXX−XXX

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the NSF (EPS-0993806) and The University of Kansas is gratefully acknowledged. Support for NMR instrumentation was provided by NIH Shared Instrumentation Grants Nos. S10OD016369 and S10RR024664 and NSF Major Research Instrumentation Grant No. 0320648.

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DOI: 10.1021/acs.orglett.6b01629
Org. Lett. XXXX, XXX, XXX−XXX