Aerobic Oxidation of Benzylic Carbons Using a Guanidine Base

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ABSTRACT: Metal-free reaction conditions featuring oxygen and 1,5,7-triazabicyclo-[4.4.0]dec-5-ene (TBD) were employed for the selective oxidation of benzyl amines and active methylene compounds to afford various amides and ketones. Owing to the strong basicity of guanidine bases, TBD is presumed to play an important role in the cleavage of the C−H bond at the benzylic position of peroxide intermediates, which were formed by the reaction with oxygen.

INTRODUCTION

Oxidation is a versatile method of converting raw materials into chemically and pharmaceutically valuable oxyfunctionalized building blocks. Among the wide variety of oxidation processes, metal-free aerobic oxidation is attractive owing to the sustainability and environmental benefits of aerobic oxidation processes without transition-metal catalysts. However, the activation of triplet oxygen without transition-metal catalysts is challenging. To promote aerobic oxidation without transition-metal catalysts, N-oxy radicals such as 2,2,6,6-tertramethylpiperidine-N-oxyl (TEMPO) and phthalimide-N-oxy, or N-oxy radical precursors such as N-hydroxyphthalimide have been employed.1−3 These N-oxy radicals/precursors activate C−H bonds adjacent to amines, alcohols, thiols, and aromatic groups to form a range of imines,4−10 nitriles,11,12 amides,13−15 and ketones under aerobic conditions.16−20 Other than those used for N-oxy-radical-mediated oxidation reactions, efficient and metal-free aerobic oxidation conditions are rarely reported.

Our research group has been interested in aerobic oxidation using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), a guanidine-type base. Owing to the resonance stabilization of its conjugate acids, TBD shows strong basicity and nucleophilicity,21,22 resulting in its use in various organic reactions.23−25 Previously, we reported that the TBD-mediated oxidation of benzyl mercaptans provides thiobenzaldehydes, which were employed in oxidative coupling with amines, alcohols, sulfones, and phosphorus ylides in the presence of copper catalysts (Scheme 1).26−28 Upon comparing the acidity of benzylic C(sp3)−H bonds of thiols with those of amines and active methylene compounds, it was assumed that the C(sp3)−H bonds of amines and active methylene compounds could be cleaved by the oxygen radicals, and resulting oxygen-incorporated intermediate can undergo deprotonation by TBD to complete C=O bond formation.29−31 In this study, it was found that, even in the absence of transition-metal catalysts and chemical oxidants, TBD accelerated the aerobic oxidation of amines and active methylene compounds to afford the corresponding amides and ketones selectively. The scope of this oxidation was examined, and mechanism studies were conducted to understand the reaction pathway.

RESULTS AND DISCUSSION

Studies on the TBD-mediated aerobic oxidation began with benzyl amine 1a (Table 1). A reaction mixture of 1a with 1 equiv of TBD in toluene was heated at 100 °C under 1 bar of oxygen to afford benzamide 1b in 27% yield (entry 1). Reactions in different solvents were examined, and the reaction in dimethyl acetamide (DMAc) produced the highest yield of 1b (entries 1−3). The effect of the bases was examined; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) participated in the oxidation of 1a to give 1b in 38% yield (entry 4), and methyl-substituted TBD (Me-TBD) gave a similar result to that of the reaction using TBD (entry 5). Inorganic base KO−Bu did not promote the desired oxidation reaction (entry 6). Upon decreasing the amount of TBD, the yield of 1b decreased slightly (entry 7). In the absence of TBD, the...
desired amide formation was not observed, but traces of benzaldehyde formed with unreacted starting materials left (entry 8). Pressurized conditions were also employed (entries 9 and 10); the reaction in toluene gave a higher yield of 1b (80%), but the reaction in DMAc did not (62%).

The optimal reaction conditions in Table 1 were employed for the oxidation of amine derivatives (Figure 1). Fluoro- and chloro-substituted benzyl amines were successfully converted into amides 2b and 3b in 66 and 65% yields, respectively. Methyl-substituted benzamide 4b was produced in 56% yield and piperonyl amine was converted into the corresponding amide 5b in 51% yield. The electronic properties of the benzene substituents seem to affect the yield; halogen-substituted amides were produced in higher yields than amides with the electron-donating groups. Accordingly, benzyl amines with one and two trifluoromethyl groups were converted into the corresponding amides in similar yields to those of 2b and 3b.

On the basis of the successful oxidation of amines to amides, the oxidation of active methylene compounds was examined. Fluorene was subjected to the oxidation conditions and afforded fluorenone 8b in 81% yield. Without TBD, trace amounts of the oxidation product were observed with unreacted starting materials left. Bromo-substituted compounds 9b and 10b were obtained from the corresponding reactants in 83 and 69% yields, respectively. 11H-Benzofluoren-11-one, containing more aromatic rings, underwent oxidation to afford desired product 11b in 85% yield. An amine-substituted fluorene was converted into 12b in 89% yield. 9H-Xanthen-9-one, possessing an oxygen atom between benzene rings, gave the highest yield (91%). 9,10-Dihydroanthracene underwent oxidation to generate diketone product 14b in 62% yield.

The proposed reaction mechanisms of the TBD-mediated oxidations are displayed in Scheme 2. In the case of amines, three reaction routes are possible. Benzyl amine 1a can react with O2 to generate a peroxyde intermediate, and then the α proton of the peroxyde intermediate can be abstracted by TBD to produce benzamide 1b (route A). Alternatively, the peroxyde intermediate can eliminate H2O2 to produce an imine that can undergo hydrolysis and oxidation by O2 or H2O2 to generate 1b (route B). The imine can also undergo further oxidation to afford a benzonitrile, which can be hydrolyzed to provide 1b (route C). To probe the working mechanism, 18O-labeled H2O was added into a mixture containing benzyl amine, resulting in the formation of mixtures of 18O-1b and 16O-1b (Scheme 3, eq 1). According to the results of the 18O-labeling experiment, routes A and B both contribute to product formation. A reaction involving benzonitrile under the optimal oxidation conditions produced

Table 1. Optimization of Aerobic Oxidation of 1a

| entry | base (equiv) | solvent | time (h) | yield  |
|-------|-------------|---------|----------|--------|
| 1     | TBD (1)     | toluene | 20       | 27%    |
| 2     | TBD (1)     | dioxane | 20       | 13%    |
| 3     | TBD (1)     | DMAc    | 20       | 58% (68%) |
| 4     | DBU (1)     | DMAc    | 20       | 38%    |
| 5     | Me-TBD (1)  | DMAc    | 20       | 56%    |
| 6     | KOr-Bu (1)  | DMAc    | 20       | 0%     |
| 7     | TBD (0.5)   | DMAc    | 20       | 51%    |
| 8     | TBD (1)     | toluene | 44       | 80%    |
| 9     | TBD (1)     | DMAc    | 44       | 62%    |

Figure 1. Aerobic oxidation of amines and active methylene compounds.

Scheme 2. Plausible Reaction Mechanisms
1b in 26% yield (Scheme 3, eq 2), but benzonitrile was not observed in the reaction mixture through GC and NMR analysis of the reaction solutions. Interestingly, the addition of TEMPO did not impede the reaction (Scheme 3, eq 3). Presumably, the reactions of amines and TEMPO induce single-electron transfer from the amines to TEMPO, and the resulting oxidized amines are converted into peroxide complexes in the presence of superoxide anion radicals. The presence of superoxide anion radicals was confirmed using the nitroblue tetrazolium test.15,35 In the case of active methylene compounds, the reaction proceeds via the formation of a peroxide intermediate followed by the elimination of water, analogous to route A of the amine oxidation.

**CONCLUSIONS**

We report the first example of TBD-mediated aerobic oxidation of amines and active methylene compounds. The acidities of benzylic protons of amines and active methylene compounds allowed feasible oxidation by gaseous oxygen followed by deprotonation by TBD. In addition to TBD, other guanidine and amidine bases (strong organic bases) could participate in this transformation, albeit with variations in the yields. According to the results of this study, aerobic oxidation of benzylamines and active methylene compounds can be promoted by nonradical organic bases in the absence of transition-metal catalysts.

**EXPERIMENTAL SECTION**

**Representative Procedure for the Oxidation of Amines.** A carefully dried round-bottom flask with a magnetic stirring bar was charged with DMAC (1.0 mL), TBD (139.2 mg, 1.0 mmol), and amine (1.0 mmol) under an air atmosphere at room temperature. An oxygen-containing balloon was used to charge the resulting mixture with oxygen, and was stirred at 100 °C under oxygen. Then, the resulting solution was cooled to room temperature, and the solvent was evaporated. The residue was purified using column chromatography on alumina to provide the desired product.

**Analytical Data for Amides and Ketones.** Benzamide (1b). The representative experimental procedure was applied to benzyl amine (107.1 mg, 1.0 mmol) to form 1b as white solid with 80% (96.9 mg) yields. 1H NMR (600 MHz, CD3OD): δ 7.86−7.88 (m, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 171.1, 133.6, 131.6, 128.2, 127.3 ppm. HRMS (EI) m/z: [M]+ calcd for C7H7NO, 121.0528; found, 121.0528. FTIR (neat): 3360, 3176, 1654, 1577, 1424 cm−1.

**4-Fluorobenzamide (2b).** The representative experimental procedure was applied to 4-fluorobenzyl amine (125.1 mg, 1.0 mmol) to form 2b as white solid in 66% (91.8 mg) yields. 1H NMR (600 MHz, CD3OD): δ 7.92 (q, J = 4.6 Hz, 2H), 7.17 (t, J = 8.6 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 169.8, 165.9, 164.2, 130.0 (d, J = 8.8 Hz), 115.0 (d, J = 21 Hz) ppm. HRMS (EI) m/z: [M]+ calcd for C7H6FNO, 139.0433; found, 139.0431. FTIR (neat): 3357, 3176, 1654, 1519, 1401 cm−1. mp 122–133 °C.

**4-Chlorobenzamide (3b).** The representative experimental procedure was applied to 4-chlorobenzyl amine (141.6 mg, 1.0 mmol) to afford 3b as white solid in 75% (101.1 mg) yields. 1H NMR (600 MHz, CD3OD): δ 7.85 (d, J = 9.0 Hz, 2H), 7.45 (d, J = 9.0 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 169.8, 165.9, 164.2, 130.0 (d, J = 8.8 Hz), 115.0 (d, J = 21 Hz) ppm. HRMS (EI) m/z: [M]+ calcd for C7H5F2NO, 132.0426; found, 132.0425. FTIR (neat): 3357, 3176, 1654, 1519, 1401 cm−1. mp 132–133 °C.

**4-Methylbenzamide (4b).** The representative experimental procedure was applied to 4-methylbenzyl amine (121.2 mg, 1.0 mmol) to form 4b as white solid in 66% (96.9 mg) yields. 1H NMR (600 MHz, CD3OD): δ 7.76 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 2.36 (s, 3H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 169.8, 137.7, 132.3, 129.0, 128.4 ppm. HRMS (EI) m/z: [M]+ calcd for C7H9NO, 135.0684; found, 135.0682. FTIR (neat): 3357, 3176, 1617, 1589, 1401 cm−1. mp 174–176 °C.

**4-Chlorofluoro benzamide (5b).** The representative experimental procedure was applied to piperonyl amine (151.2 mg, 1.0 mmol) to form 5b as white solid in 56% (84.2 mg) yields. 1H NMR (600 MHz, CD3OD): δ 7.46 (d, J = 8.3, 2.1 Hz, 1H), 7.34 (d, J = 1.4 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.03 (s, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 170.2, 150.9, 148.0, 127.5, 122.5, 107.4, 101.9 ppm. HRMS (EI) m/z: [M]+ calcd for C8H7F2NO, 155.0426; found, 155.0425. FTIR (neat): 3357, 3176, 1629, 1574, 1411 cm−1. mp 154–155 °C.

**3,4-Methylenedioxy benzamide (5b).** The representative experimental procedure was applied to piperonyl amine (151.2 mg, 1.0 mmol) to form 5b as white solid in 60% (113.5 mg) yields. 1H NMR (600 MHz, CD3OD): δ 8.00 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 169.5, 137.5, 132.9 (q, J = 32 Hz), 128.0, 128.1 (d, J = 2.9 Hz), 124.0 (d, J = 270 Hz) ppm. HRMS (EI) m/z: [M]+ calcd for C8H9NO2F, 184.0401; found, 184.0403. FTIR (neat): 3357, 3168, 1629, 1577, 1424 cm−1. mp 183–184 °C.
3,5-Bis(trifluoromethyl)benzamide (7b). The representative experimental procedure was applied to 3,5-bis(trifluoromethyl)benzyl amine (243.1 mg, 1.0 mmol) to form 7b as white solid in 85% (167.1 mg) yield. 1H NMR (600 MHz, CD3OD): δ 8.48 (s, 2H), 8.16 (s, 1H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 162.4, 136.3, 131.8 (q, J = 14, 128.0 (d, J = 2.9), 124.7 (t, J = 3.6), 123.2 (d, J = 270) ppm. HRMS (EI) m/z: [M]+ calcd for C13H8F2NO, 257.0275; found, 257.0275 ppm. FTIR (neat): 3354, 3217, 1625, 1577, 1422 cm⁻¹. mp 181–183 °C.

Fluorenone (8b). The representative experimental procedure was applied to fluorenone (166.2 mg, 1.0 mmol) to form 8b as yellow solid in 81% (145.9 mg) yield. 1H NMR (600 MHz, CDCl3): δ 7.56 (d, J = 6.9 Hz, 2H), 7.37 (d, J = 4.1 Hz, 4H), 7.20 (q, J = 3.9 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CDCl3): δ 193.9, 144.4, 134.7, 134.1, 129.1, 124.2, 120.4 ppm. HRMS (EI) m/z: [M]+ calcd for C14H10O, 208.0575; found, 208.0574 ppm. FTIR (neat): 1711, 1610, 1597, 1449 cm⁻¹. mp 84–85 °C.

2-Bromo fluorenone (9b). The representative experimental procedure was applied to 2-bromo fluorenone (245.1 mg, 1.0 mmol) to afford 9b as yellow solid in 83% (215.1 mg) yield. 1H NMR (600 MHz, CD3OD): δ 7.74 (d, J = 2.1 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.59 (dd, J = 7.9, 1.7 Hz, 1H), 7.49 (d, J = 4.1 Hz, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.30–7.32 (m, 1H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 193.9, 143.8, 143.1, 137.2, 135.9, 135.1, 133.8, 129.5, 127.6, 124.7, 123.0, 121.8, 120.5 ppm. HRMS (EI) m/z: [M]+ calcd for C14H9BrO, 257.0275; found, 257.0275 ppm. FTIR (neat): 1713, 1607, 1594, 1440, 733 cm⁻¹. mp 145–146 °C.

2,6-Dibromo fluorenone (10b). The representative experimental procedure was applied to 2,6-dibromo fluorenone (324 mg, 1.0 mmol) to form 10b as yellow solid in 69% (233.2 mg) yield. 1H NMR (600 MHz, CD3OD): δ 7.75 (d, J = 1.7 Hz, 2H), 7.62 (dd, J = 7.9, 1.7 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 191.0, 142.3, 137.6, 135.4, 127.9, 123.4, 121.9 ppm. HRMS (EI) m/z: [M]+ calcd for C14H8Br2O, 353.8785; found, 353.8788 ppm. FTIR (neat): 1720, 1709, 1591, 1444, 1416, 821, 779 cm⁻¹. mp 198–200 °C.

2,3-Benzofluorenone (11b). The representative experimental procedure was applied to 2,3-benzofluorenone (216.2 mg, 1.0 mmol) to afford 11b as yellow solid in 85% (195.7 mg) yield. 1H NMR (600 MHz, CD3OD): δ 8.16 (s, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.85 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.55 (q, J = 7.1 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 193.2, 144.9, 138.5, 137.0, 136.3, 135.1, 133.7, 132.9, 129.3, 129.1, 128.9, 127.0, 125.8, 124.5, 121.1, 119.2 ppm. HRMS (EI) m/z: [M]+ calcd for C15H10O2, 230.0732; found, 230.0733 ppm. FTIR (neat): 1705, 1601, 1511, 1447, 1339 cm⁻¹. mp 154–156 °C.

2-Aminofluorenone (12b). The representative experimental procedure was applied to 2-aminofluorenone (181.2 mg, 1.0 mmol) to form 12b as yellow solid in 85% (195.7 mg) yield. 1H NMR (600 MHz, CD3OD): δ 7.54 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 6.9 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 8.3 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 2.1 Hz, 1H), 6.70 (d, J = 10.3 Hz, 1H), 3.91 (s, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 194.5, 147.7, 145.6, 136.0, 134.9, 134.7, 134.1, 127.4, 124.3, 121.4, 119.7, 119.1, 111.1 ppm. HRMS (EI) m/z: [M]+ calcd for C15H12NO, 195.0684; found, 195.0684. FTIR (neat): 3366, 1715, 1600, 1468, 1455 cm⁻¹. mp 148–150 °C.

Xanthone (13b). The representative experimental procedure was applied to xanthene (182.2 mg, 1.0 mmol) to obtain 13b as yellow solid in 91% (178.5 mg) yield. 1H NMR (600 MHz, CD3OD): δ 6.82 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.9 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 177.1, 156.1, 134.8, 126.7, 123.9, 121.8, 118.0 ppm. HRMS (EI) m/z: [M]+ calcd for C15H12O2, 196.0524; found, 196.0523. FTIR (neat): 1652, 1604, 1478, 1455, 1344, 1329 cm⁻¹. mp 175–178 °C.

Anthraquinone (14b). The representative experimental procedure was applied to dihydroanthracene (180.2 mg, 1.0 mmol) to form 14b as yellow solid in 62% (129.1 mg) yield. 1H NMR (600 MHz, CD3OD): δ 8.32 (q, J = 3.0 Hz, 4H), 7.81 (q, J = 3.0 Hz, 4H) ppm. 13C{1H} NMR (150 MHz, CD3OD): δ 183.3, 134.2, 133.6, 127.3, 77.3, 77.1, 76.9 ppm. HRMS (EI) m/z: [M]+ calcd for C14H12O2, 197.0877; found, 197.0876. FTIR (neat): 1672, 1620, 1578, 1447 cm⁻¹. mp 275–279 °C.
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