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Azobisisobutyronitrile Initiated Aerobic Oxidative Transformation of Amines: Coupling of Primary Amines and Cyanation of Tertiary Amines

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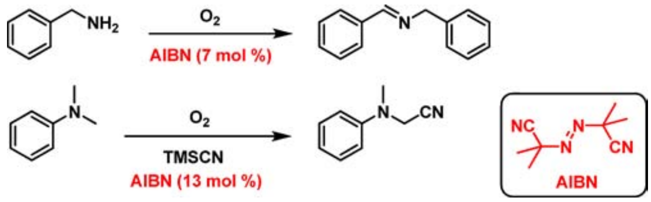
ABSTRACT



In the presence of a catalytic amount of radical initiator AIBN, primary amines are oxidatively coupled to imines and tertiary amines are cyanated to α-aminonitriles. These "metal-free" aerobic oxidative coupling reactions may find applications in a wide range of "green" oxidation chemistry.

Imines and α-aminonitriles are versatile synthetic intermediates in a variety of organic transformations where imines are widely used in addition, reduction, aziridination, *β*-lactamization, and cyclization reactions,[1] and α-aminonitriles are useful precursors to synthesize α-amino acids, α-amino aldehydes, α-amino alcohols, and 1,2-diamines.[2] Oxidative coupling of primary amines provides an alternative strategy to the synthesis of imines,[3−11] and oxidative cyanation of tertiary amines represents one of the most convenient and straightforward methods to prepare α-aminonitriles.[12−19] These two closely related oxidative transformations were proposed to occur through a nucleophilic addition reaction to the key intermediate imines and iminium ions containing C═N units. Compared

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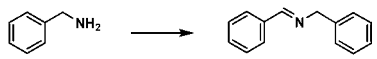
to toxic and/or precious metal systems, metal-free systems using dioxygen as the sole oxidant for oxidative coupling reactions remain scarce.[20]

Azobisisobutyronitrile (AIBN) is extensively used in initiating radical polymerization under anaerobic reaction conditions because carbon centered radicals are prone to capture dioxygen to form peroxy radicals which interrupt the polymer chain propagation.[21] Recently, AIBN was reported to initiate aerobic oxidation reactions by taking advantage of peroxy radicals.[22] In this paper we report on the AIBN initiated metal-free aerobic oxidative coupling of primary amines to imines and oxidative cyanation of tertiary amines to α-aminonitriles through highly reactive imines/iminium ion intermediates.

The results of control experiments for the oxidative coupling of benzylamine are illustrated in Table 1. Without AIBN, only a trace amount of benzylidene-benzylamine (2% yield) is formed (Table 1, entry 1). In the presence of 10 mol % of AIBN under a nitrogen atmosphere, the imine product is observed with a 3% yield (Table 1, entry 2). However, the yield increases to 11% when the reaction is performed in air (Table 1, entry 3). And the conversion reaches as high as 95% with good yield (74%) under 1 atm of dioxygen (Table 1, entry 4). Using 2 equiv of hydrogen peroxide or *tert*-butyl peroxide (TBHP) as the oxidant, the yield is 21% and 15% (Table 1, entries 5−6). The thermal decomposition of AIBN follows first-order kinetics, and the half-time in benzene is about 1.4 h at 80 °C, 5 h at 70 °C, and 21 h at 60 °C.[23] The reaction conditions are examined, and the optimum conditions are 70 °C in toluene where the yield is up to 83% (Table 1, entries 7−9; Table 1S).

Table 1. AIBN Initiated Oxidation of Benzylamine[a]



entry	initiator (mol)	gas	additive (equiv)	temp (°C)	conv[b] (%)	yield[b] (%)
1	–	O_2	–	80	2	2
2	AIBN (10%)	N_2	–	80	3	3
3	AIBN (10%)	Air	–	80	11	11
4	AIBN (10%)	O_2	–	80	95	74
5	AIBN (10%)	N_2	H_2O_2 (2)	80	36	21
6	AIBN (10%)	N_2	TBHP (2)	80	15	15
7	AIBN (10%)	O_2	–	60	44	41
8	AIBN (10%)	O_2	–	70	95	77
9[c]	AIBN (10%)	O_2	–	70	94	83

[a] Reaction conditions: benzylamine (0.60 mmol), benzene (1 mL), in a 45 mL Schlenk tube, the gaseous pressure P_{initial} = 1 bar, 12 h. [b] GC results. [c] In toluene, 8 h.

The oxidation of various primary amines under optimum conditions is listed in Table 2. Benzylamine is oxidized to benzylidene-benzylamine in a yield of 89% using 7 mol % of AIBN (Table 2, entry 1). A variety of substituted benzyl amine derivatives are also observed to form imines in good to excellent yields (Table 2, entries 2−7). Electronic effects associated with electron-donating and -withdrawing substituents on the phenyl ring have little effect on the efficiency of the oxidation reaction (Table 2, entries 2−6). A noteworthy feature of this method is the formation of imine **P7** (Table 2, entry 7), which is a significant improvement for the preparation of sterically hindered imines.[11e,24] Heterocyclic methylamines containing sulfur, oxygen, and nitrogen atoms which usually coordinate and deactive the metal catalysts could also be converted to imines in moderate to high yields indicating a good tolerance of heteratoms (Table 2, entries 8−10). Oxidative coupling of furfurylamine to imine **P9** requires 15 mol % of AIBN to

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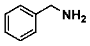
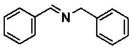
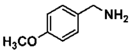
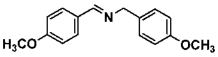
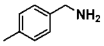
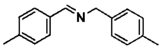
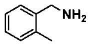
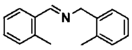
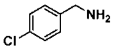
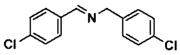
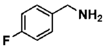
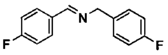
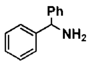
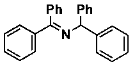
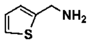
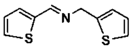
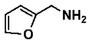
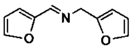
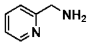
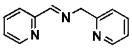
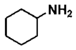
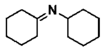
give a 46% yield (Table 2, entry 9) which is higher than Zhao's reported results (33%−38% yield).[5] Surprisingly, 2-picolylamine is efficiently oxidized to imine **P10** in the presence of only 3 mol % of AIBN with good yield and high selectivity (Table 2, entry 10). The oxidation of aliphatic amines under the same reaction conditions produces low yields of imines (Table 2, entry 11).

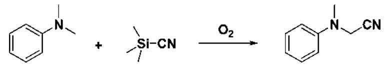
The high efficiency of the AIBN initiated aerobic oxidative coupling of primary amines prompted us to try oxidative cyanation of tertiary amines which may occur in a similar pathway where highly reactive iminium ion intermediates are generated and trapped by the nucleophile cyanide ion to form α-aminonitriles.

Table 2. Scope of the Primary Amines[a]

entry	substartes	products		conversion[b]	yield[b]
1[c, d]			(P1)	94%	89%
2			(P2)	97%	76%
3			(P3)	99%	87%
4			(P4)	98%	88%
5			(P5)	99%	85%
6			(P6)	97%	84%
7[c, d]			(P7)	81%	74%
8			(P8)	93%	83%
9[e]			(P9)	90%	46%
10[f]			(P10)	92%	86%
11			(P11)	32%	7%

[a] Reaction conditions: amine (0.60 mmol), AIBN (0.060 mmol, 10 mol %), toluene (1 mL), in a 45 mL Schlenk tube, oxygen pressure P_{initial} = 1 bar, 70 °C, 8 h. [b] GC results. [c] 12 h. [d] 7 mol % of AIBN. [e] 15 mol % of AIBN. [f] 3 mol % of AIBN.

Table 3. AIBN Initiated Oxidative Cyanation of *N*,*N*-Dimethylaniline[a]



entry	AIBN (mol %)	HO Ac (equiv)	*t* (h)	conv (%)[b]	yield (%)[b]
1	15	–	12	45	36
2	50	–	12	93	63
3	50	1.0	12	99	80
4	20	1.6	12	93	89
5[c]	13	1.6	24	94	89

[a] Reaction conditions: amine (0.20 mmol), TMSCN (0.24 mmol), methanol (1 mL), in a 45 mL Schlenk tube, oxygen pressure P_{initial} = 1 bar, 70 °C. [b] GC results. [c] TMSCN (0.40 mmol), methanol (2 mL).

In the presence of a catalytic amount of AIBN, metal-free oxidative cyanation of tertiary amines was accomplished. A 36% yield is produced with 15 mol % of AIBN (Table 3, entry 1), and 50 mol % of AIBN leads to a 63% yield (Table 3, entry 2). However, the yield dramatically increases to 80% with the addition of 1 equiv of acetic acid (Table 3, entry 3) and is up to 89% using only 20 mol % of AIBN when 1.6 equiv of acid is added (Table 3, entry 4). Prolonging the reaction time resulted in an excellent yield using 13 mol % of AIBN (Table 3, entry 5).

Substituted *N*,*N*-dimethylanilines, with electron-donating or -withdrawing groups, give the corresponding cyanated products with excellent yields (Table 4) except for *N*,*N*-dimethyl-*o*-toluidine with a yield of 50% (Table 4, entry 2). However, *N*,*N*-dimethyl-*m*-toluidine and *N*,*N*-dimethyl-*p*-toluidine are both converted to cyanated products effectively with 82% and 89% yields, respectively (Table 4, entries 3−4). This system can also be applied to bromo- and fluoro-substituted compounds (Table 4, entries 5−6) and cyclic amines (Table 4, entries 7−8). In order to explore the potential practical application of this method, the scale-up experiments were performed in a 500 mL Schlenk flask under 1 bar of oxygen containing 5.0 mmol of *p*-bromo-*N*,*N*-dimethylaniline; a 90% conversion and 78% isolated yield were obtained (Table 4, entry 5).

The mechanism of alkane autoxidation generally occurs via pathways described in Scheme 1.[22h,i,25] In the initiation step, the 2-cyano-2-propylperoxyl radical (CPOO·) is proposed to be the active species which grabs a hydrogen atom from alkane to form 2-cyano-2-propyl hydrogen peroxide (CPOOH) and radical R· initiating chain reactions.

It has been reported that, after releasing one molecule of oxygen, two alkylperoxyl radicals produce two alkyloxyl radicals.[26a] Janzen and cowokers also detected 2-cyano-2-propyl peroxide (CPOOCP) by ESR-MS after heating the AIBN solution under air conditions.[26b] We observed that CPOOCP was the main product in the absence of amines while acetone was the dominant product in the presence of amines from ^{1}H and ^{13}C NMR analysis (Figures 11S, 12S). Combining this information, we propose that the effective initiating species is the 2-cyano-2-propyloxyl radical (CPO·) which is in equilbrium with CPOOCP. After grabbing a hydrogen atom from amines, CPO· is converted to the acetone cyanohydrin (CPOH) intermediate with the formation of an α-aminoalkyl radical **A**. Subsequently, CPOH is rapidly deprotonated to form acetone by releasing a CN$^-$ anion (Scheme 2).

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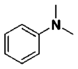
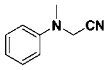
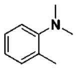
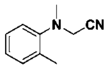
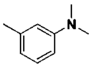
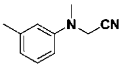
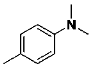
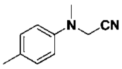
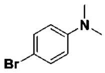
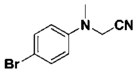
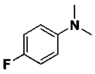
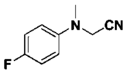
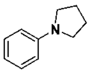
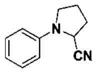
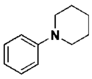
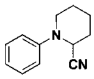
(25) (a) Boozer, C. E.; Hammond, G. S.; Hamilton, C. E.; Sen, J. N. *J. Am. Chem. Soc.* **1955**, *77*, 3233. (b) Mayo, F. R. *Acc. Chem. Res.* **1968**, *1*, 193. (c) Betts, J. *Rev. Chem. Soc.* **1971**, *25*, 265–288. (d) Porter, N. A. *Acc. Chem. Res.* **1986**, *19*, 262.

(26) (a) Bartlett, P. D.; Traylor, T. G. *Org. Biol. Chem.* **1963**, *85*, 2407. (b) Janzen, E. G.; Krygsman, P. H.; Lindsay, D. A.; Haire, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 8279.

Table 4. Scope of Tertiary Amines[a]

entry	amine	product	conversion (%)[b]	yield (%)[b]
1			94	89 (76[e])
2			75	50 (48[e])
3			91	82 (64[e])
4			96	89 (73[e])
5			96 (90[c,d])	85 (78[c,e])
6			95	85 (71[e])
7			98	80 (77[e])
8			85	67 (67[e])

[a] Reaction conditions: amine (0.20 mmol), TMSCN (0.40 mmol), HOAc (0.32 mmol, AIBN (0.025 mmol), methanol (2 mL), in a 45 mL Schlenk tube, oxygen pressure $P_{\text{initial}} = 1$ bar, 70 °C, 24 h. [b] GC results. [c] Amine (5.0 mmol), TMSCN (10 mmol), HOAc (8.0 mmol), AIBN (0.63 mmol), methanol (50 mL), in a 500 mL Schlenk flask. [d] 10% of amine was recycled. [e] Isolated yield.

The radical **A** is readily trapped by oxygen to generate a peroxide radical **B** which abstracts a hydrogen atom from free amines to form one molecule of **C** (Scheme 3). **C** releases a hydrogen peroxide to give an imine intermediate **D** or an iminium cation **E** which rapidly reacts with a nucleophile (amine or cyanide ion) to form the product imine or α-aminonitrile. The lower reactivity of aliphatic amine compared with the aromatic methylamine may originate from the lower stability and poorer selectivity of the radical intermediate formed in these processes.[5a] The enhanced rate of cyanation reactions by acid most probably results from (1) acid promoting formation of free cyanide anions from the reaction of the acetic anion with TMSCN and (2) suppression of the side reaction by inhibiting the hydrolysis of the iminium cation to a secondary amine.

In summary, we developed the AIBN initiated aerobic oxidative coupling of primary amines to imines and cyanation of tertiary amines to α-aminonitriles. A catalytic amount of AIBN is consumed, and dioxygen is the sole oxidant in this metal-free system. This clean and mild synthetic method may provide an ideal strategy for the rational design of systems for the functionalization of sp^3 C−H bonds adjacent to nitrogen.

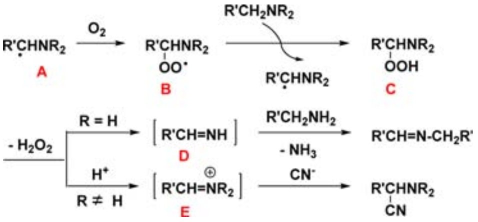
Scheme 1. General Pathways for AIBN Initiated Autoxidation

$$\text{(1)}\quad \text{AIBN} \longrightarrow 2\ \text{CP}^{\bullet} + \text{N}_2$$
$$\text{(2)}\quad \text{CP}^{\bullet} + \text{O}_2 \longrightarrow \text{CPOO}^{\bullet}$$
$$\text{(3)}\quad \text{CPOO}^{\bullet} + \text{R-H} \longrightarrow \text{CPOOH} + \text{R}^{\bullet}$$
$$\text{(4)}\quad \text{R}^{\bullet} + \text{O}_2 \longrightarrow \text{ROO}^{\bullet}$$
$$\text{(5)}\quad \text{ROO}^{\bullet} + \text{R-H} \longrightarrow \text{ROOH} + \text{R}^{\bullet}$$
$$\text{(6)}\quad \text{ROO}^{\bullet} + \text{R}^{\bullet} \longrightarrow \text{non-radicals}$$

Scheme 2. Proposed Pathways of the AIBN Transformation in Our System

$$\text{(7)}\quad 2\ \text{CPOO}^{\bullet} \longrightarrow 2\ \text{CPO}^{\bullet} + \text{O}_2$$
$$\text{(8)}\quad 2\ \text{CPO}^{\bullet} \rightleftharpoons \text{CPOOCP}$$
$$\text{(9)}\quad \text{CPO}^{\bullet} + \text{R'CH}_2\text{NR}_2 \longrightarrow \text{CPOH} + \text{R'}\underset{\bullet}{\text{C}}\text{HNH}_2\ (\textbf{A})$$
$$\text{(10)}\quad \text{CPOH} + {:}\text{B} \longrightarrow (\text{CH}_3)_2\text{C=O} + \text{B}\cdot\text{HCN}$$

Scheme 3. Proposed Mechanism of the Chain-Propagating and Product-Forming Steps



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Supporting Information Available. Experimental procedures and full spectroscopic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.