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Nitrogen Dioxide Catalyzed Oxidative Thiocyanation of Arenes with Ambient Air as the Terminal Oxidant

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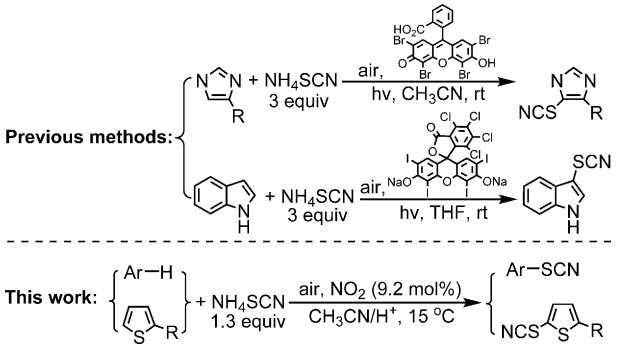
NO_2 is an effective catalyst for the oxidative thiocyanation of arenes. This unique catalyst is inexpensive and separated easily from the final products because of its low boiling point. The mild reaction conditions allow a series of arenes and thiophenes to be thiocyanated smoothly in moderate to high yields. A preliminary mechanistic investigation suggests that the present reaction may proceed through a radical pathway.

Introduction

The thiocyanation of arenes plays an important role in organic synthesis[1] because the resulting products not only occur as a key functionality in certain anticancer natural products[1b] but also serve as versatile starting materials for the preparation of various sulfur-containing compounds, especially heterocycles.[1a] As a result, considerable efforts have been devoted to the development of various methods[1] of thiocyanation using $(SCN)_2$,[2] *N*-thiocyanatosuccinimide,[3] and thiocyanate salts.[4] Among these thiocyanating agents, the inexpensive and readily available thiocyanate salts are the most attractive. However, SCN^- is unreactive towards aromatic rings.[1b] An effective solution to this is the use of the oxidative strategy[1b] in which either SCN^- or aromatic rings are oxidized in situ to the reactive species in the presence of various oxidants, for example, H_2O_2,[5] $K_2S_2O_8$,[6] cyanuric chloride,[4a] oxone,[7] $NaClO_4$,[8] 2,3-dichloro-5,6-dicyanobenzoquinone,[9] NH_4VO_3,[10] and silica-bonded vanadic acid.[11]

Compared with the oxidants mentioned above, O_2, especially air, is a better oxidant because it is inexpensive, readily available, and environmentally friendly, which has prompted many chemists to apply O_2 in the oxidation of organic substrates under the catalysis of various transition metals.[12] Other effective catalysts for aerobic reactions are oxynitride species from several compounds such as $NaNO_2$, NO_2, and HNO_3.[13] Clearly, these compounds are inexpensive and readily available, thus the use of oxynitride species as the catalyst is desirable from an economic perspective.

Surprisingly, oxidative thiocyanation catalyzed by oxynitride species is unknown, and only two examples of the oxidative thiocyanation of arenes have been reported, in which the substrates are limited to N-heteroarenes, which include indoles[14] and imidazoheterocycles (Scheme 1).[15] Moreover, these methods suffer from a disadvantage that a large excess (3 equiv.) of the thiocyanating agent is required. To our knowledge, there is no example of the use of O_2 as the oxidant in the oxidative thiocyanation of benzenes, naphthalenes, and thiophenes. Thus we developed an effective thiocyanation procedure for these substrates using air as the terminal oxidant, and the results are reported herein.



Scheme 1. Examples of the oxidative thiocyanation of arenes with O_2 as the terminal oxidant.

Results and Discussion

Encouraged by our previous success in the application of NO_2 to catalyze aerobic oxidative halogenation,[16] we selected this readily available compound as the catalyst to initiate our inves-

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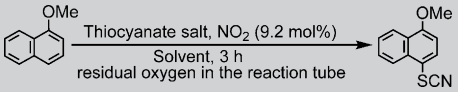
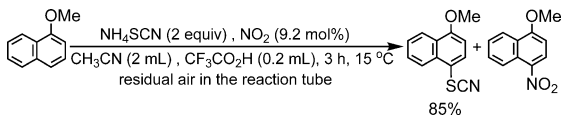
Table 1. Oxidative thiocyanation of 1-methoxynaphthalene catalyzed by NO_2.[a]



Entry	Thiocyanate salt	Solvent	Acid	T [°C]	Conv.[b] [%]	Yield[b] [%]
1	NH_4SCN	CH_3CN	–	15	1	trace
2	NH_4SCN	CH_3CN	CF_3CO_2H	0	≈100	88
3	NH_4SCN	CH_3CN	CF_3CO_2H	10	≈100	86
4	NH_4SCN	CH_3CN	CF_3CO_2H	15	≈100	85
5	NH_4SCN	CH_3CN	CF_3CO_2H	30	93	92
6	NH_4SCN	CH_3CN	CF_3CO_2H	40	54	51
7[c]	NH_4SCN	CH_3CN	CF_3CO_2H	30	96	90
8[c]	NH_4SCN	CH_3CN	CF_3CO_2H	15	≈100	94
9	NH_4SCN	toluene	CF_3CO_2H	15	≈100	17
10	NH_4SCN	DMF	CF_3CO_2H	15	1	trace
11	NH_4SCN	THF	CF_3CO_2H	15	27	23
12	NH_4SCN	CH_3CN	H_2SO_4	15	≈100	26
13	NH_4SCN	CH_3CN	CH_3CO_2H	15	5	5
14	NaSCN	CH_3CN	CF_3CO_2H	15	≈100	85
15	CuSCN	CH_3CN	CF_3CO_2H	15	≈100	17
16[d]	NH_4SCN	CH_3CN	CF_3CO_2H	15	0	0

[a] Reaction conditions: 1-alkoxynaphthalene (0.5 mmol), thiocyanate salt (1 mmol), acid (0.2 mL), solvent (2 mL), NO_2 (0.046 mmol), the air in the tube was not removed, 3 h. [b] Determined by using GC with an internal standard. [c] 1.3 equiv. of NH_4SCN. [d] No NO_2 was added.

tigation. The catalytic ability of NO_2 was very poor if 1-alkoxynaphthalene was stirred with ammonium thiocyanate in acetonitrile in the presence of catalytic NO_2 at 15 °C (Table 1, entry 1). The presence of a Brønsted acid can often facilitate the aerobic oxidative reactions catalyzed by oxynitride species,[17] which prompted us to add a Brønsted acid into the reaction system. To our delight, the addition of trifluoroacetic acid allowed 1-alkoxynaphthalene to be thiocyanated effectively to give the target product in 85% yield (Table 1, entry 4). The only byproduct was 1-methoxy-4-nitronaphthalene, which resulted from the nitration of the naphthalene ring,[18] and no dithiocyanation byproducts were observed (Scheme 2).

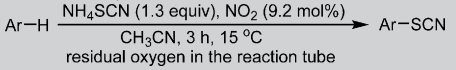


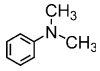
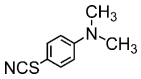
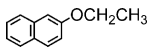
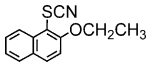
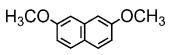
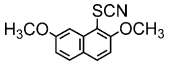
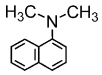
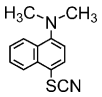
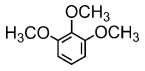
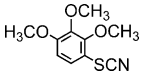
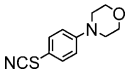
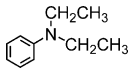
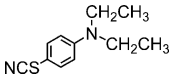
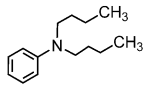
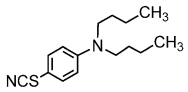
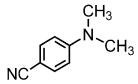
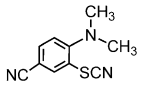
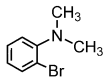
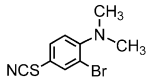
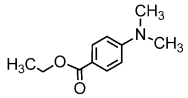
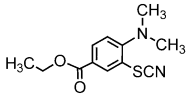
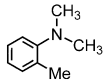
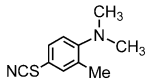
Scheme 2. NO_2-catalyzed oxidative thiocyanation of 1-methoxynaphthalene.

Further studies were undertaken to obtain higher yields and more generally practical reaction conditions. The reaction was highly dependent on the reaction temperature. The reaction with 2 equivalents of ammonium thiocyanate at 30 °C allowed the desired product to be obtained in 92% yield with a high selectivity (Table 1, entry 5), whereas 15 °C was the optimal temperature in terms of yield with 1.3 equivalents of ammonium thiocyanate. It is difficult to understand why the conversion of the substrate became lower with the increase of the reaction temperature from 30 to 40 °C (Table 1, entries 5 and 6), but it can be rationalized if we assume that NO_2 was removed from the reaction medium at a higher temperature. The change of solvent had an important effect on the reaction outcome. For example, the reaction in acetonitrile gave the target product in 85% yield (Table 1, entry 4), whereas THF and DMF were less effective (Table 1, entries 10 and 11). Notably, the complete conversion of the substrate was observed if toluene was used, but the thiocyanation product was obtained in a very low yield (Table 1, entry 9). Among the screened acids, trifluoroacetic acid was the most effective. If we used acetic acid instead of trifluoroacetic acid, a poor conversion of the substrate was observed (Table 1, entry 13). Although the reaction with H_2SO_4 gave a complete conversion, the yield of the target product was low (Table 1, entry 12). The loading of the thiocyanation agent was optimized to 1.3 equivalents (Table 1, entries 7 and 8). By contrast, the selectivity was lower in the presence of 1.5 or 2 equivalents of ammonium thiocyanate, which resulted in a decreased yield of the target product. The thiocyanation reaction proceeded efficiently with 5 mol% of NO_2, but the experimental results were not reproducible. We tried to reduce the catalyst loading to 1 mol% but found that this was not possible without a sacrifice of the product yield even if the reaction time was prolonged to 20 h.

Subsequently, preliminary studies were conducted with a variety of representative aromatic and heterocyclic compounds to explore the scope and generality of this reaction under the optimal conditions (Table 2). A series of arenes, thiophenes, and indoles was thiocyanated smoothly in moderate to high yields. Moreover, the thiocyanation reaction was compatible with various groups, for example, alkoxy, aryloxy, alkyl, substituted amino, ester, cyano, bromo, and benzyloxy groups. Among the tested substituted arenes, N-substituted amino benzenes were effective substrates for the thiocyanation reaction (Table 2, entries 1 and 7–17). For example, the reaction with *N,N*-dimethylaniline gave the target product in 95% GC yield with an excellent selectivity (Table 2, entry 1), and a small amount of nitration and dithiocyanation byproducts was observed. Although the amino group is an *ortho-para*-directing group, no *ortho*-thiocyanation relative to the *N,N*-dimethylamino group was observed, which could be attributed to the larger steric hindrance of the position *ortho* to the amino group. However, if the *para* C–H bond of the amino group was absent, the thiocyanation had to occur at the *ortho* position to this directing group (Table 2, entry 17). Other suitable substrates were alkoxynaphthalenes. Both 1-alkoxynaphthalene and 2-alkoxynaphthalene were converted smoothly to the target product (Table 2, entries 2 and 3). Different from aniline derivatives, the alkoxynaphthalene substrates did not undergo dithiocyanation. This phenomenon has been reported previously.[19] If 2,7-dimethoxynaphthalene was used as the substrate, 2,7-dimethoxy-1-thiocyanatonaphthalene was obtained as the major product in 93% GC yield. Among the test alkoxybenzenes, 1,2,3-trimethoxybenzene was thiocyanated smoothly

Table 2. Oxidative thiocyanation of various aromatic compounds.[a]



Entry	Substrate	Product	Yield [%] GC[b]	Isolated
1			95	87
2			94	94
3			91	89
4			93	65
5			81	75
6			83	–
7			71	70
8			95	77
9			77	68
10			83	68
11[c]			90	71
12			≈100	81
13			52	-
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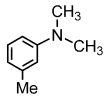
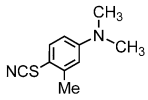
15			18	–
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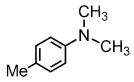
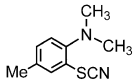
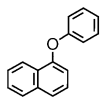
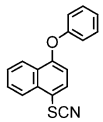
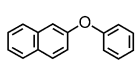
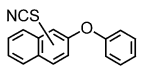
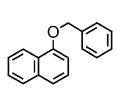
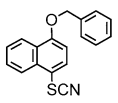
17			≈100	76
18			59	44
19			6	–
20			82	–
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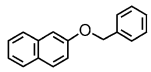
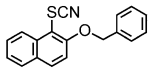
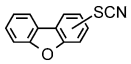
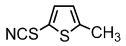
22			70	–
23[c]			89	76
24[d]			87	–

to give the thiocyanation product in a high yield (Table 2, entry 6), but it is difficult to understand why methoxybenzene was unreactive.

Next, *N*,*N*-dimethylanilines with various substituents were used as the substrates to investigate the electronic and steric effects of the substituents on the reaction (Table 2, entries 8–17). Generally, *N*,*N*-dimethylanilines with electron-donating or -withdrawing groups could be used successfully in this system. However, the addition of a greater excess of thiocyanating agent was required to complete the conversion in the case of some substrates with electron-withdrawing groups, for example, the bromo group (Table 2, entries 8–17). If the amino substituent coexists with an alkyl group on the benzene ring, the site-selectivity depended on the directing effects of the amino group. For example, although both amino and methyl groups are *ortho*-*para*-directing groups, 4-methyl-*N*,*N*-dimethylaniline was thiocyanated selectively at the *ortho* position to the amino group (Table 2, entry 17). Among the tested heterocyclic substrates, thiophenes were thiocyanated smoothly in high yields (Table 2, entries 27 and 28). Sometimes the conditions allowed the thiocyanation of indoles and pyrroles to give moderate to high yields of the target products, but the experimental results were not reproducible. Other heterocyclic substrates, which include benzofuran, dibenzofuran, and *N*-methylimidazole, were less reactive, and only trace amounts of the thiocyanation products were observed (Table 2, entries 25, 26, and 29).

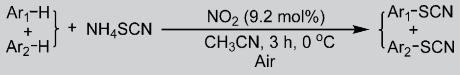
Interestingly, only the naphthalene moiety was thiocyanated selectively if benzyloxynaphthalenes were used as substrates (Table 2, entries 20–24). The thiocyanation of 1-phenoxynaphthalene gave a similar selectivity (Table 2, entry 18). These experimental results suggest that our method was applicable to the selective functionalization of one aromatic ring if the substrate contains two or more aromatic rings, which prompted us to perform several competition reactions between two aromatic substrates. If *N*,*N*-dimethylaniline encountered anisole, phenol, benzaldehyde, benzoic acid, toluene, or benzonitrile, only the benzene ring of *N*,*N*-dimethylaniline underwent thiocyanation with high yields (Table 3, entries 1–6). These results reveal that our method is not only effective for the selective thiocyanation of the amino-substituted benzene ring from numerous electron-rich or electron-deficient phenyl rings but also allows the thiocyanation to be compatible with many functional groups, such as alkoxy, phenolic hydroxyl, aldehyde, carboxyl, and cyano groups. Clearly, the presence of electron-deficient substituents was a disadvantage. For example, *N*,*N*-dimethylaniline reacted preferentially over its bromo-substituted derivative. In addition, the benzene ring of *N*,*N*-dimethylaniline

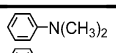
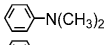
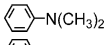
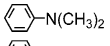
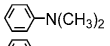
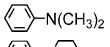
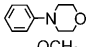
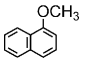
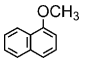
Table 2. (Continued)

Entry	Substrate	Product	Yield [%] GC[b]	Isolated
25			trace	–
26			trace	–
27			78	67
28			89	80
29			trace	–

[a] Reaction conditions: substrate (0.5 mmol), NH_4SCN (0.65 mmol), CF_3CO_2H (0.2 mL), CH_3CN (2 mL), NO_2 (0.046 mmol), the air in the tube was not removed, 15 °C, 3 h. [b] Determined by using GC with an internal standard. [c] 1 mmol of NH_4SCN was used. [d] 1 mmol of NH_4SCN was used, and the reaction time was 10 h.

Table 3. Several competition reactions between different aromatic substrates.[a]



Entry	Ar_1–H	Ar_2–H	Yield [%][b] Ar_1–SCN	Ar_2–SCN
1			92	trace
2			87	trace
3			83	1
4			70	0
5			77	0
6			77	0
7			71	trace
8			97	trace
9			10	80

[a] Reaction conditions: Substrate 1 (0.5 mmol), Substrate 2 (0.5 mmol), NH_4SCN (0.65 mmol), CF_3CO_2H (0.2 mL), CH_3CN (2 mL), NO_2 (0.046 mmol), 3 h, 0 °C, the air in the tube was not removed.

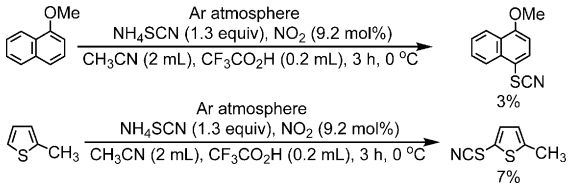
was more reactive than the naphthalene ring of 1-methoxynaphthalene (Table 3, entry 9).

As a nucleophile, the SCN^- anion is unreactive towards aromatic rings.[1b] Thus an oxidizing reagent was present in our thiocyanation system to oxidize the SCN^- or aromatic rings to the reactive species in situ,[1b] which compelled us to consider what played the role of the oxidizing reagent. We inferred that the residual O_2 in the reaction tube played the role of the oxidant. Indeed, only small amount of thiocyanation product was obtained if the O_2 was removed from the reaction system (Scheme 3).

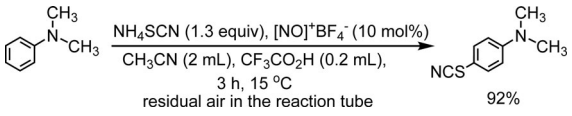
Subsequently, we tried to ascertain the real catalytic species. It is known that NO_2 is an effective catalyst for the activation of O_2.[16] Indeed, oxidative thiocyanation did not occur in the absence of a catalytic amount of NO_2. This suggests that the real catalytic species comes from NO_2. This compound or its dimer can be decomposed to give NO^+ in dilute solutions of strong acid,[17c,20] thus NO^+ seems to be one of the real catalytic species.[21] Indeed, the use of NO^+ allowed *N*,*N*-dimethylaniline to undergo thiocyanation smoothly with a high product yield of 92% (Scheme 4).

Two possible mechanisms have been proposed for oxidative thiocyanation previously.[1b] One starts with the reaction between the oxidative species and the aromatic rings to give the aromatic radical cations or a π complex.[6b,9,22,23] The other starts with the oxidation of SCN^- to $(SCN)_2$, SCN radical, or a reactive species with a pronounced SCN^+ character.[5,7a,8,14,15,24] To gain an insight into the reaction mechanism, we performed several control experiments in which the well-known radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)[14,15] was added to the reaction system. The presence of TEMPO led to a dramatic decrease in the yields of the thiocyanation products, which reveals that the reaction proceeds through either the aromatic radical or the SCN radical pathway (Scheme 5).

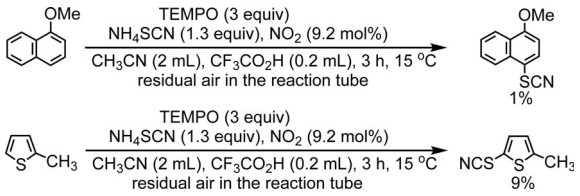
At present, although the mechanism through the SCN radical cannot been excluded, we believe that one of the most probable mechanism pathways involves the oxidation of the aromatic ring by NO^+ because NO^+ species possess the ability to oxidize various aromatic rings to cation radicals.[25] Thus a plausible NO^+-catalyzed mechanism through an aromatic radical is proposed with *N*,*N*-dimethylaniline as the model substrate (Scheme 6). The catalytic cycle starts with the reaction between the aromatic ring and NO^+ to give the aromatic radical cation and NO.[25] The latter is oxidized by O_2 to regenerate the catalytically active NO^+.[17c] The resulting aromatic radical cation reacts with SCN^- to form a neutral radical intermediate, followed by electron transfer and deprotonation to give the targeted aryl thiocyanate product.[6b,9,22,23]



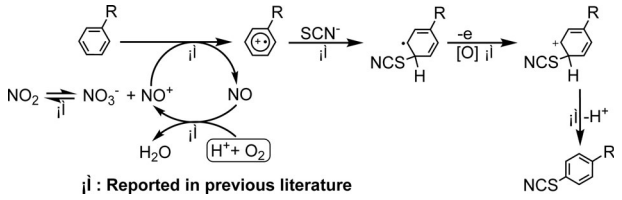
Scheme 3. Oxidative thiocyanation under Ar.



Scheme 4. Oxidative thiocyanation of *N*,*N*-dimethylaniline catalyzed by NO^+.



Scheme 5. Oxidative thiocyanation in the presence of TEMPO.



Scheme 6. One of the most probable mechanism pathways for oxidative thiocyanation.

Conclusions

NO_2 catalyzes the oxidative thiocyanation of arenes effectively with O_2 as the terminal oxidant. This unique catalyst is inexpensive and separated easily from the final products because of its low boiling point. A series of arenes and thiophenes was thiocyanated smoothly in moderate to high yields. Moreover, the present thiocyanation reaction was compatible with various groups, for example, alkoxy, aryloxy, alkyl, substituted amino, ester, cyano, bromo, and benzyloxy groups. Interestingly, the new method was applicable for the selective thiocyanation of one aromatic ring if the substrate contained two or more aromatic rings. A preliminary mechanistic investigation suggests that one of the most probable mechanism pathways involves the aromatic radical cation and the catalytic species NO^+.

Experimental Section

Commercially available compounds were purchased and used without purification unless otherwise stated, and the quality and suppliers of the chemicals are listed in Table S1. All benzyl phenyl ethers were synthesized by the reaction between the corresponding substituted benzyl chlorides and substituted phenols.[26] GC–MS was performed by using an Agilent 6890/5973N instrument. ^1H and ^{13}C NMR spectra were recorded by using a Bruker 500 MHz instrument, and the chemical shifts were reported in ppm relative to the internal standard tetramethylsilane. GC was performed by using a Varian CP-3800 instrument with a flame ionization detector (FID) and a CP-WAX 57CB FS capillary chromatographic column (25 m×0.32 mm).

General procedure for the oxidative thiocyanation of various substrates

Typically, a mixture of the substrate (0.5 mmol), NH_4SCN (0.65 mmol), CF_3CO_2H (0.2 mL), CH_3CN (2 mL), and NO_2 (0.046 mmol) was stirred magnetically in a ≈45 mL tube for 3 h at 15 °C (note: the air in the tube was not removed). Once the reaction time was reached, we used GC analysis of the mixture to provide GC yields of the products. However, if the substrate had an amino group, it was necessary to alkalize the mixture to pH 8–9 with NaOH aqueous solution before GC analysis. Then the crude product from a parallel experiment was purified by silica gel chromatography to give the desired product. All the products were identified by using ^1H and ^{13}C NMR spectroscopy. Analytical data for several representative products are as follows:

4-Thiocyanato-N,N-*dimethylaniline*

Pale yellow solid; m.p. 71–72 °C (lit.[10] 72–74 °C); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.44 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, Ph), 6.70 (d, $^3J_{H-H}$ = 9.0 Hz, 2H; Ph), 3.02 ppm (s, 6H, CH_3); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 151.7, 134.5, 113.2, 112.6, 106.5, 40.2 ppm.

1-Methoxy-4-thiocyanatonaphthalene

Pale yellow solid; m.p. 104–106 °C (lit.[10] 105–107 °C); ^1H NMR (500 MHz, $CDCl_3$): δ = 8.35 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 8.29 (d, $^3J_{H-H}$ = 8.5 Hz, 1H), 7.86 (dd, $^3J_{H-H}$ = 8.2 Hz, 1H), 7.73 (t, $^3J_{H-H}$ = 7.4 Hz, 1H), 7.62 (t, $^3J_{H-H}$ = 7.8 Hz, 1H), 6.82 (dd, $^3J_{H-H}$ = 8.2 Hz, 1H), 4.04 ppm (d, $^5J_{H-H}$ = 1.5 Hz, 3H); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 158.7, 135.3, 133.7, 128.7, 126.8, 126.4, 124.6, 123.1, 111.5, 110.4, 104.1, 55.0 ppm.

4-Thiocyanato-N-*phenylmorpholine*

Pale yellow solid; m.p. 75–77 °C (lit.[5e] 74–76 °C); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.46 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, Ph), 6.90 (d, $^3J_{H-H}$ = 9.0 Hz, 2H, Ph), 3.85 (t, $^3J_{H-H}$ = 5.0 Hz, 4H, CH_2), 3.21 ppm (t, $^3J_{H-H}$ = 5.0 Hz, 4H, CH_2); ^{13}C NMR (500 MHz, $CDCl_3$): δ = 152.6, 133.7, 116.2, 111.9, 111.2, 66.6, 48.1 ppm.

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Keywords: arenes · oxidation · oxygen · radicals · reaction mechanisms

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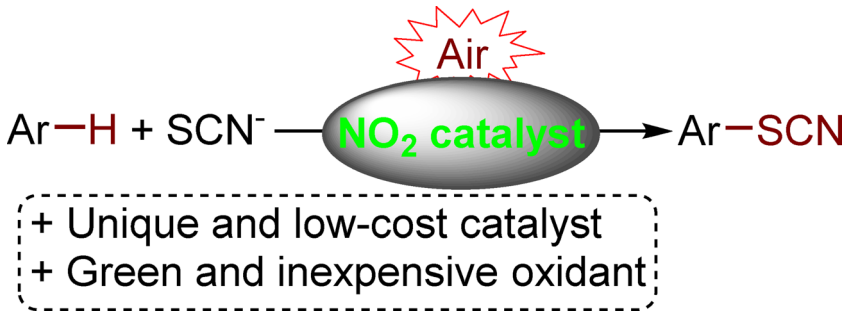

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Nitrogen Dioxide Catalyzed Oxidative Thiocyanation of Arenes with Ambient Air as the Terminal Oxidant

Radical solution: NO_2 is an effective catalyst for the oxidative thiocyanation of arenes. This unique catalyst is inexpensive and separated easily from the final products because of its low boiling point. The mild reaction conditions allow a series of arenes and thiophenes to be thiocyanated smoothly in moderate to high yields. Preliminary mechanistic investigations suggest that this reaction proceeds through a radical pathway.