

Hypervalent Compounds

International Edition: DOI: 10.1002/anie.201807303
German Edition: DOI: 10.1002/ange.201807303

Metal-Free Direct C–H Cyanation of Alkenes

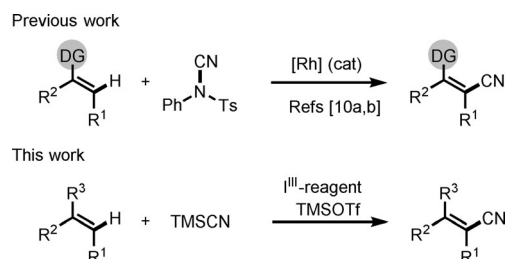
Xi Wang and Armido Studer*

Abstract: A metal-free and direct alkene C–H cyanation is described. Directing groups are not required and the mechanism involves electrophilic activation of the alkene by a cyanoiodine(III) species generated in situ from a [bis(trifluoroacetoxy)iodo]arene and trimethylsilyl cyanide as the cyanide source. This C–H functionalization can be conducted on gram scale, and for noncyclic 1,1- and 1,2-disubstituted alkenes high stereoselectivity is achieved, thus rendering the method highly valuable.

The nitrile functionality is an important structural moiety that can be found in various natural products, drugs, agrochemicals, and in polymers.^[1] Moreover, the cyano group can be used as a synthetic equivalent for primary amines, tetrazoles, aldehydes/ketones and their related functionalities.^[2]

Aryl nitriles are generally prepared by cyanation of halides, pseudohalides, diazonium salts, and organometallic reagents.^[3] Step- and atom-economy in the synthesis of cyanated arenes and alkenes can be improved following a direct C–H cyanation strategy. Significant advances in directing group (DG) assisted arene C–H cyanation have been achieved using transition-metal catalysis (e.g., Pd, Cu, and Rh).^[4] Along these lines, direct C–H cyanation of indoles has also been reported.^[5] Recently, Wang and co-workers disclosed an iron-catalyzed electrophilic cyanation of arenes and heteroarenes using aryl(cyano)iodonium triflates,^[6a] and the group of Nicewicz reported aromatic C–H cyanation with trimethylsilyl cyanide using photoredox catalysis.^[6b]

Established approaches for the synthesis of acrylonitriles comprise carbocyanation,^[7] heterocyanation,^[8] and hydrocyanation^[9] of alkynes with X–CN-type reagents (X = C, Si, B, Sn, Ge, S, O, Br, H). However, as compared to arene C–H cyanation, direct alkene C–H cyanation has not been well investigated. Anbarasan^[10a] and Fu^[10b] reported rhodium-catalyzed direct C(sp²)–H cyanation of alkenes, bearing directing groups, with NCTS (*N*-cyano-*N*-phenyl-*p*-methylbenzenesulfonamide) as the cyanating reagent (Scheme 1).



Scheme 1. Direct C–H cyanation of alkenes. DG = directing group, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

However, nondirected alkene C–H cyanation has not yet been described. We report herein transition metal free alkene cyanation using an aryl(biscyano)iodine(III) reagent as an alkene activator and cyanide source.

α -Phenylstyrene (**1a**) was chosen as a model substrate and various electrophilic cyanation reagents were screened in combination with or without an additive in 1,2-dichloroethane (DCE) at 70 °C for 15 hours (Table 1, Figure 1).^[3g,4b,c,i,5d,11] C–H cyanation of **1a** with the reagents **2a–d**, **2i** and **2j** failed (entries 1–6). Traces of the nitrile **4a** were detected when the benziodoxole **2e** was employed in combination with catalytic amounts of either CuCl or Fe(OAc)₂ (entries 7 and 8). No improvement was noted by using **2f** (entries 9 and 10). TMSCN paired with oxone, (NH₄)₂S₂O₈, or *t*BuOOH did not provide **1a** (entries 11–13). The product **4a** was obtained in 7% yield using **2e** in combination with TMSCN (entry 14). Replacing **2e** by **2f** led to a significant improvement of the yield (entry 15). The electronic nature of the substituents at the aryl moiety in the I^{III} reagent is important: the activity of **2h** was superior to that of **2f** and **2g** (entries 15–17). Pleasingly, direct C–H cyanation using the more stable and easily accessible [bis(trifluoroacetoxy)iodo]arene **3d**, which reacts in situ by sequential ligand exchange with TMSOTf and TMSCN to **2h**,^[12] gave a comparable result (entry 18). The best yield (90%) was achieved upon lowering the temperature to 40 °C (entries 19 and 20). With 2 equivalents of TMSCN, a lower yield resulted, but using 3 and 4 equivalents provided good results (entries 22–24). The benziodoxole **3e** as an oxidant provided a worse result (entry 21). Other cyanide sources such as NaCN, KCN, and Bu₄NCN did not lead to **4a** (entries 25–27).

Under optimized reaction conditions, various alkenes were tested (Table 2). α -Methylstyrenes possessing either electron-withdrawing or electron-donating groups at the *para*-position of the arene ring afforded the acrylonitriles **4b–l** in moderate to high yields with good to excellent *E* selectivity. Generally, systems bearing electron-withdrawing groups provided lower *E* selectivities in this series. An α -methylstyrene bearing a *meta*-substituent (**4m**) worked well and the β -naphthyl congener reacted with similar

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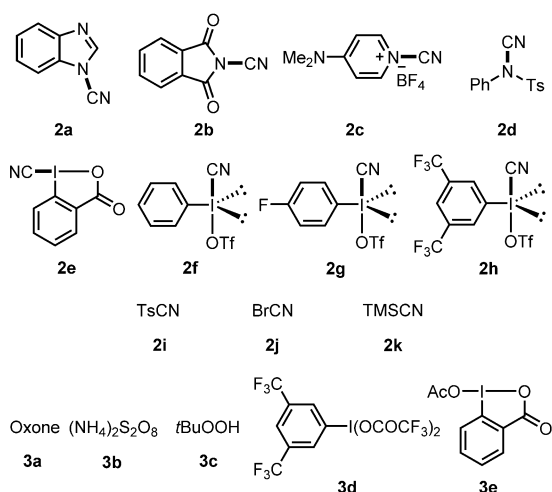
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<https://doi.org/10.1002/anie.201807303>.

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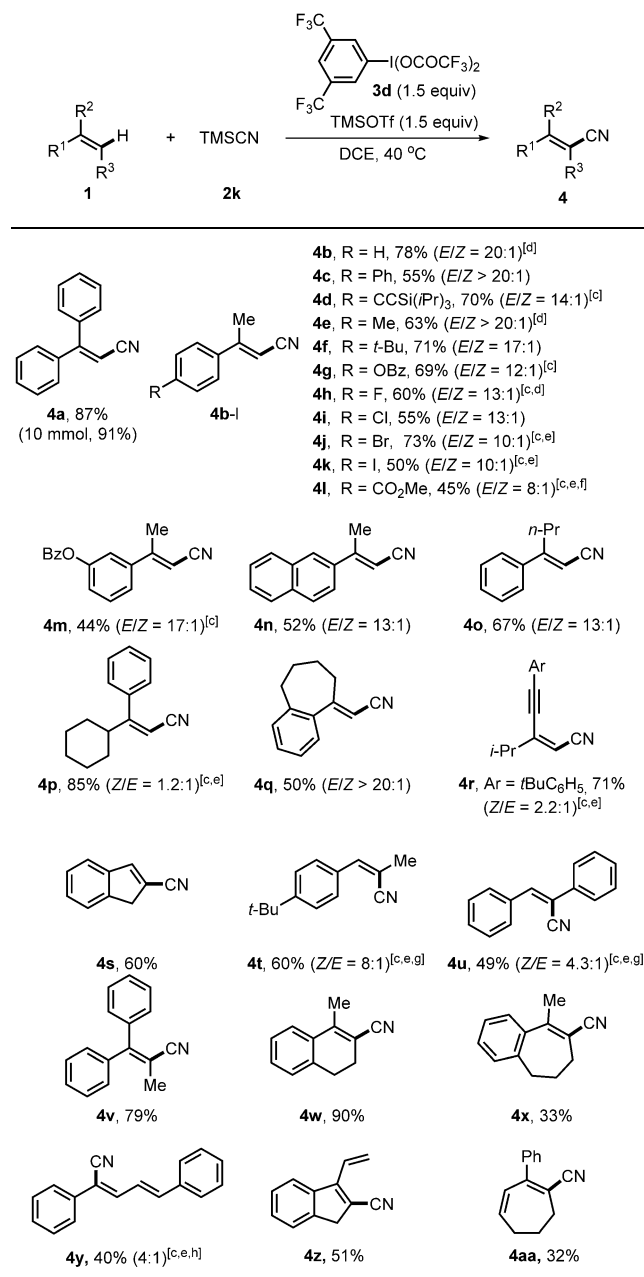
Table 1: Optimization studies.^[a]

Entry	"CN" 2 (equiv)	Oxidant (equiv)	Additive (equiv)	Yield [%] ^[b]
1	2a (2.0)	none	none	—
2	2b (2.0)	none	AuCl ₃ (0.05)	—
3	2c (2.0)	none	CuCl (0.1)	—
4	2d (2.0)	none	BF ₃ ·Et ₂ O (2.0)	—
5	2i (2.0)	none	none	—
6	2j (2.0)	none	none	—
7	2e (2.0)	none	CuCl (0.1)	traces
8	2e (2.0)	none	Fe(OAc) ₂ (0.1)	traces
9	2f (2.0)	none	none	traces
10	2f (2.0)	none	Fe(OAc) ₂ (0.1)	traces
11	2k (2.0)	3a (2.0)	none	—
12	2k (2.0)	3b (2.0)	none	—
13	2k (2.0)	3c (2.0)	none	—
14	2k (4.0)	2e (1.5)	none	7
15	2k (4.0)	2f (1.5)	none	32
16	2k (4.0)	2g (1.5)	none	44
17	2k (4.0)	2h (1.5)	none	87
18	2k (5.5)	3d (1.5)	TMSOTf (1.5)	88
19 ^[e]	2k (5.5)	3d (1.5)	TMSOTf (1.5)	90 ^[d]
20 ^[e]	2k (5.5)	3d (1.5)	TMSOTf (1.5)	14
21	2k (5.5)	3e (1.5)	TMSOTf (1.5)	34
22 ^[e]	2k (2.0)	3d (1.5)	TMSOTf (1.5)	27
23 ^[e]	2k (3.0)	3d (1.5)	TMSOTf (1.5)	81
24 ^[e]	2k (4.0)	3d (1.5)	TMSOTf (1.5)	85
25 ^[e]	NaCN (5.5)	3d (1.5)	TMSOTf (1.5)	—
26 ^[e]	KCN (5.5)	3d (1.5)	TMSOTf (1.5)	—
27 ^[e]	Bu ₄ N ⁺ CN ⁻ (5.5)	3d (1.5)	TMSOTf (1.5)	—

[a] Reaction conditions: **1a** (0.20 mmol, 1.0 equiv), **2**, oxidant, additive, DCE (2 mL), 70 °C, 15 h. [b] Yield determined by ¹H NMR analysis using MeNO₂ as an internal standard. [c] Conducted at 40 °C. [d] Isolated in 87% yield. [e] Conducted at room temperature.

**Figure 1.** Various "CN" sources and oxidants tested. Ts = *p*-tolylsulfonyl.

efficiency (**4n**). Increasing the size of the α -alkyl substituent in the styrene substrate leads to diminished selectivity, as

Table 2: Substrate scope.^[a,b]

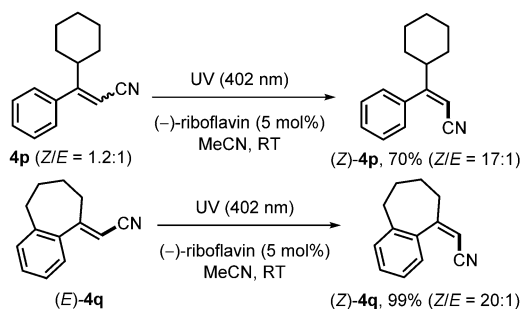
[a] Reaction conditions: **1** (0.20 mmol, 1.0 equiv), **2k** (1.1 mmol, 5.5 equiv), **3d** (0.30 mmol, 1.5 equiv), TMSOTf (0.30 mmol, 1.5 equiv), DCE (2 mL), 40 °C, 15 h. [b] Yields refer to the yield of the isolated major isomer if not otherwise noted. [c] Conducted at 70 °C. [d] These yields are based on ¹H NMR analysis with MeNO₂ as an internal standard. [e] Combined yield of both isomers. [f] **2k** (1.4 mmol, 7.0 equiv), **3d** (0.30 mmol, 1.5 equiv), TMSOTf (0.30 mmol, 1.5 equiv). [g] **2k** (0.30 mmol, 1.5 equiv), **2h** (0.30 mmol, 1.5 equiv). [h] The ratio of the major isomer to other isomers is given within parentheses.

shown by switching from α -methylstyrene to the *n*-propyl derivative (**4o**), and reversed selectivity was obtained for the α -cyclohexyl styrene (**4p**).

A bicyclic styrene with an exocyclic double bond reacted with excellent selectivity (**4q**), and 1,3-enynes engage in this transformation, providing the *Z* product as major isomer (see

4r; Table 2). The reaction works on β -substituted styrenes and indene was converted into **4s** in a good yield. A *trans*- β -methylstyrene and *trans*-stilbene reacted with complete regioselectivity and good stereoselectivity (**4t**, **4u**). Both acyclic and cyclic trisubstituted styrenes could be converted (**4v–x**) and conjugated dienes were also competent reaction partners, affording the monocyanoated products with high regioselectivity (**4y–4aa**). To document the practicability, reaction of **1a** on gram scale gave **4a** in 91% yield. Unfortunately, styrene did not react to cinnamitrile.

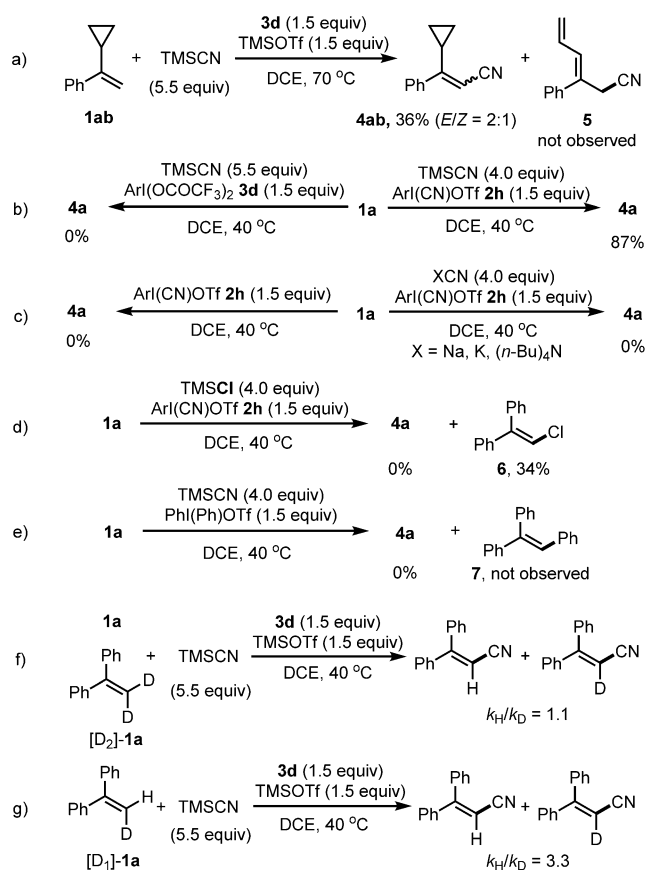
Notably, *Z* selectivity of **4p** could be improved from 1.2:1 to 17:1 upon *E*→*Z* isomerization under UV-irradiation (402 nm) following the Gilmour protocol in the presence of (–)-riboflavin (Scheme 2).^[13] This method was also applied to isomerize (*E*)-**4q** to its *Z* derivative, showing that both isomers are accessible using our approach.



Scheme 2. *E*→*Z* isomerization.

To elucidate the mechanism, control experiments were conducted. A radical pathway^[14] could be excluded based on the result obtained with the radical probe **1ab**, which reacted to give **4ab** without formation of any of the ring-opening product **5** (Scheme 3a). In the absence of Lewis acid, the cyanation did not occur, indicating that TMSOTf is essential for generating the active I^{III} species (Scheme 3b, left). ArI(CN)OTf (**2h**; 1.5 equiv) in combination with TMSCN (4 equiv) provided **4a** in comparable yield, showing that **2h** is a potentially active reagent that can be formed by reaction of **3d** with TMSCN and TMSOTf (Scheme 3b, right). However, we found that **2h** is not an active I^{III} species, since cyanation of **1a** with **2h** did not provide **4a**, and **1a** decomposed (Scheme 3c, left). Other nucleophilic CN reagents such as NaCN, KCN, and (*n*Bu)₄NCN did not work in combination with **2h**, showing the importance of the TMS moiety (Scheme 3c, right). Replacing TMSCN by TMSCl provided the chlorination product **6** in 34% yield, and **4a** was not formed (Scheme 3d). The analogue Ph₂IOTf was not a competent oxidant for cyanation of **1a** with TMSCN and the phenylated product **7** was also not identified (Scheme 3e). These results revealed that the active I^{III} reagent is likely the highly electrophilic [bis(cyano)iodo]arene^[15] formed in situ from **2h** and TMSCN.

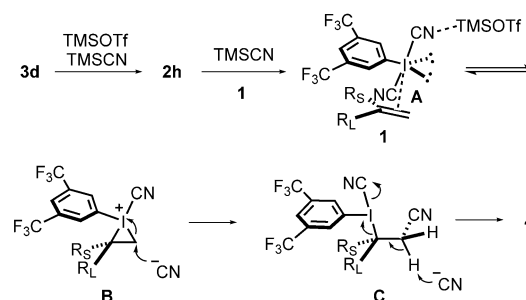
We also determined intermolecular and intramolecular kinetic isotope effects (KIEs). α -Phenylstyrene (**1a**) and [D₂]-**1a** (1:1) were subjected to the reaction conditions and a k_H/k_D value of 1.1 was measured for the intermolecular KIE



Scheme 3. Mechanistic studies.

(Scheme 3 f). A significant intramolecular KIE of 3.3 was determined for cyanation of [D₁]-**1a** (Scheme 3 g). These KIE experiments indicate that activation of the alkene by the I^{III} reagent is likely reversible and C–H bond cleavage is a slow step.^[16]

Based on these investigations, the following mechanism is suggested (Scheme 4). The aryl(cyano)iodonium triflate **2h**, generated from **3d** by ligand exchange, undergoes renewed ligand exchange with TMSCN to give the active species [bis(cyano)iodo]arene **A** and TMSOTf. The electrophilic activation of alkene **1** with **A**, which is additionally supported by interaction with TMSOTf, then reversibly leads to the cyclic iodonium intermediate **B**.^[17] Regioselective ring-opening of **B** by the cyanide anion provides the intermediate **C** and



Scheme 4. Suggested mechanism.

diastereoselective deprotonation of **C** in a conformation where the cyano group is positioned *anti* to the bulkier R_L substituent, and eventually provides **4**.

In summary, we have described a metal-free $C(sp^2)$ -H cyanation of various alkenes using TMSCN in combination with the [bis(trifluoroacetoxy)iodo]arene **3d**. Reactions proceed under mild reaction conditions and show broad substrate scope: 1,1-disubstituted, 1,2-disubstituted, and trisubstituted alkenes are smoothly converted into the corresponding cyanated products in high yields and good to excellent diastereoselectivities.

Acknowledgements

We thank the European Research Council (ERC Advanced Grant agreement No. 692640) for financial support.

Conflict of interest

The authors declare no conflict of interest.

Keywords: alkenes · C–H functionalization · cyanation · hypervalent compounds · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2018**, *57*, 11792–11796
Angew. Chem. **2018**, *130*, 11966–11970

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Manuscript received: June 25, 2018
Accepted manuscript online: July 11, 2018
Version of record online: August 6, 2018